# Lecture Notes on Thermodynamics and Statistical Mechanics
## (A Work in Progress)

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# Contents

## 0.1 Preface

This is a proto-preface. A more complete preface will be written after these notes are completed.

These lecture notes are intended to supplement a course in statistical physics at the upper division undergraduate or beginning graduate level.

I was fortunate to learn this subject from one of the great statistical physicists of our time, John Cardy.

I am grateful to my wife Joyce and to my children Ezra and Lily for putting up with all the outrageous lies I've told them about getting off the computer 'in just a few minutes' while working on these notes.

These notes are dedicated to the only two creatures I know who are never angry with me: my father and my dog.

Figure 1: My father (Louis) and my dog (Henry).

## 0.2 General references

- L. Peliti, *Statistical Mechanics in a Nutshell* (Princeton University Press, 2011)
  The best all-around book on the subject I've come across thus far. Appropriate for the graduate or advanced undergraduate level.

- J. P. Sethna, *Entropy, Order Parameters, and Complexity* (Oxford, 2006)
  An excellent introductory text with a very modern set of topics and exercises. Available online at http://www.physics.corn

- M. Kardar, *Statistical Physics of Particles* (Cambridge, 2007)
  A superb modern text, with many insightful presentations of key concepts.

- M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* ($3^{\text{rd}}$ edition, World Scientific, 2006)
  An excellent graduate level text. Less insightful than Kardar but still a good modern treatment of the subject. Good discussion of mean field theory.

- E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics* (part I, $3^{\text{rd}}$ edition, Pergamon, 1980)
  This is volume 5 in the famous Landau and Lifshitz *Course of Theoretical Physics*. Though dated, it still contains a wealth of information and physical insight.

- F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1987)
  This has been perhaps the most popular undergraduate text since it first appeared in 1967, and with good reason.

# Chapter 1

# Probability

## 1.1 References

- F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1987)
  This has been perhaps the most popular undergraduate text since it first appeared in 1967, and with good reason.
- E. T. Jaynes, *Probability Theory* (Cambridge, 2007)
  The bible on probability theory for physicists. A strongly Bayesian approach.
- C. Gardiner, *Stochastic Methods* (Springer-Verlag, 2010)
  Very clear and complete text on stochastic mathematics.

## 1.2 A Statistical View

### 1.2.1 Distributions for a random walk

Consider the mechanical system depicted in Fig. 1.1, a version of which is often sold in novelty shops. A ball is released from the top, which cascades consecutively through $N$ levels. The details of each ball's motion are governed by Newton's laws of motion. However, to predict where any given ball will end up in the bottom row is difficult, because the ball's trajectory depends sensitively on its initial conditions, and may even be influenced by random vibrations of the entire apparatus. We therefore abandon all hope of integrating the equations of motion and treat the system statistically. That is, we assume, at each level, that the ball moves to the right with probability $p$ and to the left with probability $q = 1 - p$. If there is no bias in the system, then $p = q = \frac{1}{2}$. The position $X_N$ after $N$ steps may be written

$$X = \sum_{j=1}^{N} \sigma_j \ , \tag{1.1}$$

where $\sigma_j = +1$ if the ball moves to the right at level $j$, and $\sigma_j = -1$ if the ball moves to the left at level $j$. At each level, the probability for these two outcomes is given by

$$P_\sigma = p\,\delta_{\sigma,+1} + q\,\delta_{\sigma,-1} = \begin{cases} p & \text{if } \sigma = +1 \\ q & \text{if } \sigma = -1 \ . \end{cases} \tag{1.2}$$

This is a normalized discrete probability distribution of the type discussed in section 1.4 below. The multivariate distribution for all the steps is then

$$\mathcal{P}(\sigma_1\,,\,\ldots\,,\sigma_N) = \prod_{j=1}^{N} P(\sigma_j) \ . \tag{1.3}$$

Our system is equivalent to a one-dimensional *random walk*. Imagine an inebriated pedestrian on a sidewalk taking steps to the right and left at random. After $N$ steps, the pedestrian's location is $X$.

Now let's compute the average of $X$:

$$\langle X \rangle = \Big\langle \sum_{j=1}^{N} \sigma_j \Big\rangle = N\langle \sigma \rangle = N \sum_{\sigma=\pm 1} \sigma\, P(\sigma) = N(p-q) = N(2p-1) \ . \tag{1.4}$$

This could be identified as an *equation of state* for our system, as it relates a measurable quantity $X$ to the number of steps $N$ and the local bias $p$. Next, let's compute the average of $X^2$:

$$\langle X^2 \rangle = \sum_{j=1}^{N} \sum_{j'=1}^{N} \langle \sigma_j \sigma_{j'} \rangle = N^2 (p-q)^2 + 4Npq \ . \tag{1.5}$$

Here we have used

$$\langle \sigma_j \sigma_{j'} \rangle = \delta_{jj'} + \big(1 - \delta_{jj'}\big)(p-q)^2 = \begin{cases} 1 & \text{if } j = j' \\ (p-q)^2 & \text{if } j \neq j' \ . \end{cases} \tag{1.6}$$

Note that $\langle X^2 \rangle \geq \langle X \rangle^2$, which must be so because

$$\text{Var}(X) = \langle (\Delta X)^2 \rangle \equiv \Big\langle \big(X - \langle X \rangle\big)^2 \Big\rangle = \langle X^2 \rangle - \langle X \rangle^2 \ . \tag{1.7}$$

This is called the *variance* of $X$. We have $\text{Var}(X) = 4Np\,q$. The *root mean square* deviation, $\Delta X_{\text{rms}}$, is the square root of the variance: $\Delta X_{\text{rms}} = \sqrt{\text{Var}(X)}$. Note that the mean value of $X$ is linearly proportional to $N$[1], but the RMS

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[1] The exception is the unbiased case $p = q = \frac{1}{2}$, where $\langle X \rangle = 0$.

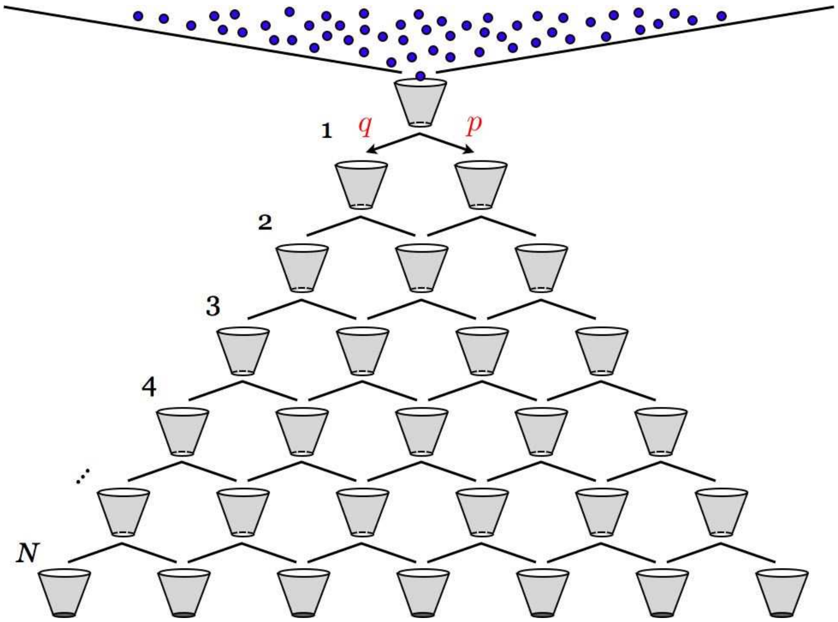

Figure 1.1: The falling ball system, which mimics a one-dimensional random walk.

fluctuations $\varDelta X_{\rm rms}$ are proportional to $N^{1/2}$. In the limit $N \to \infty$ then, the ratio $\varDelta X_{\rm rms}/\langle X\rangle$ vanishes as $N^{-1/2}$. This is a consequence of the central limit theorem (see §1.4.2 below), and we shall meet up with it again on several occasions.

We can do even better. We can find the complete probability distribution for $X$. It is given by

$$P_{N,X} = \binom{N}{N_{\rm R}} p^{N_{\rm R}}\, q^{N_{\rm L}} \ , \tag{1.8}$$

where $N_{\rm R/L}$ are the numbers of steps taken to the right/left, with $N = N_{\rm R} + N_{\rm L}$, and $X = N_{\rm R} - N_{\rm L}$. There are many independent ways to take $N_{\rm R}$ steps to the right. For example, our first $N_{\rm R}$ steps could all be to the right, and the remaining $N_{\rm L} = N - N_{\rm R}$ steps would then all be to the left. Or our final $N_{\rm R}$ steps could all be to the right. For each of these independent possibilities, the probability is $p^{N_{\rm R}}\, q^{N_{\rm L}}$. How many possibilities are there? Elementary combinatorics tells us this number is

$$\binom{N}{N_{\rm R}} = \frac{N!}{N_{\rm R}!\, N_{\rm L}!} \ . \tag{1.9}$$

Note that $N \pm X = 2N_{\rm R/L}$, so we can replace $N_{\rm R/L} = \frac{1}{2}(N \pm X)$. Thus,

$$P_{N,X} = \frac{N!}{\big(\frac{N+X}{2}\big)!\,\big(\frac{N-X}{2}\big)!}\, p^{(N+X)/2}\, q^{(N-X)/2} \ . \tag{1.10}$$

### 1.2.2 Thermodynamic limit

Consider the limit $N \to \infty$ but with $x \equiv X/N$ finite. This is analogous to what is called the *thermodynamic limit* in statistical mechanics. Since $N$ is large, $x$ may be considered a continuous variable. We evaluate $\ln P_{N,X}$ using Stirling's asymptotic expansion

$$\ln N! \simeq N \ln N - N + \mathcal{O}(\ln N) \ . \tag{1.11}$$

We then have

$$\begin{aligned}\ln P_{N,X} \simeq\; & N\ln N - N - \tfrac{1}{2}N(1+x)\ln\Big[\tfrac{1}{2}N(1+x)\Big] + \tfrac{1}{2}N(1+x)\\ & - \tfrac{1}{2}N(1-x)\ln\Big[\tfrac{1}{2}N(1-x)\Big] + \tfrac{1}{2}N(1-x) + \tfrac{1}{2}N(1+x)\,\ln p + \tfrac{1}{2}N(1-x)\,\ln q\\ =\; & -N\Big[\big(\tfrac{1+x}{2}\big)\ln\big(\tfrac{1+x}{2}\big) + \big(\tfrac{1-x}{2}\big)\ln\big(\tfrac{1-x}{2}\big)\Big] + N\Big[\big(\tfrac{1+x}{2}\big)\ln p + \big(\tfrac{1-x}{2}\big)\ln q\Big]\ . \end{aligned} \tag{1.12}$$

Notice that the terms proportional to $N\ln N$ have all cancelled, leaving us with a quantity which is linear in $N$. We may therefore write $\ln P_{N,X} = -N f(x) + \mathcal{O}(\ln N)$, where

$$f(x) = \Big[\big(\tfrac{1+x}{2}\big)\ln\big(\tfrac{1+x}{2}\big) + \big(\tfrac{1-x}{2}\big)\ln\big(\tfrac{1-x}{2}\big)\Big] - \Big[\big(\tfrac{1+x}{2}\big)\ln p + \big(\tfrac{1-x}{2}\big)\ln q\Big]\ . \tag{1.13}$$

We have just shown that in the large $N$ limit we may write

$$P_{N,X} = \mathcal{C}\, e^{-Nf(X/N)}\ , \tag{1.14}$$

where $\mathcal{C}$ is a normalization constant[2]. Since $N$ is by assumption large, the function $P_{N,X}$ is dominated by the minimum (or minima) of $f(x)$, where the probability is maximized. To find the minimum of $f(x)$, we set $f'(x)=0$, where

$$f'(x) = \tfrac{1}{2}\ln\left(\frac{q}{p}\cdot\frac{1+x}{1-x}\right)\ . \tag{1.15}$$

Setting $f'(x)=0$, we obtain

$$\frac{1+x}{1-x} = \frac{p}{q} \qquad \Rightarrow \qquad \bar{x} = p - q\ . \tag{1.16}$$

We also have

$$f''(x) = \frac{1}{1-x^2}\ , \tag{1.17}$$

so invoking Taylor's theorem,

$$f(x) = f(\bar{x}) + \tfrac{1}{2}f''(\bar{x})\,(x-\bar{x})^2 + \ldots\ . \tag{1.18}$$

Putting it all together, we have

$$P_{N,X} \approx \mathcal{C}\,\exp\left[-\frac{N(x-\bar{x})^2}{8pq}\right] = \mathcal{C}\,\exp\left[-\frac{(X-\bar{X})^2}{8Npq}\right]\ , \tag{1.19}$$

where $\bar{X} = \langle X\rangle = N(p-q) = N\bar{x}$. The constant $\mathcal{C}$ is determined by the normalization condition,

$$\sum_{X=-\infty}^{\infty} P_{N,X} \approx \tfrac{1}{2}\int\limits_{-\infty}^{\infty} dX\,\mathcal{C}\,\exp\left[-\frac{(X-\bar{X})^2}{8Npq}\right] = \sqrt{2\pi Npq}\,\mathcal{C}\ , \tag{1.20}$$

and thus $\mathcal{C} = 1/\sqrt{2\pi Npq}$. Why don't we go beyond second order in the Taylor expansion of $f(x)$? We will find out in §1.4.2 below.

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[2] The origin of $\mathcal{C}$ lies in the $\mathcal{O}(\ln N)$ and $\mathcal{O}(N^0)$ terms in the asymptotic expansion of $\ln N!$. We have ignored these terms here. Accounting for them carefully reproduces the correct value of $\mathcal{C}$ in eqn. 1.20.

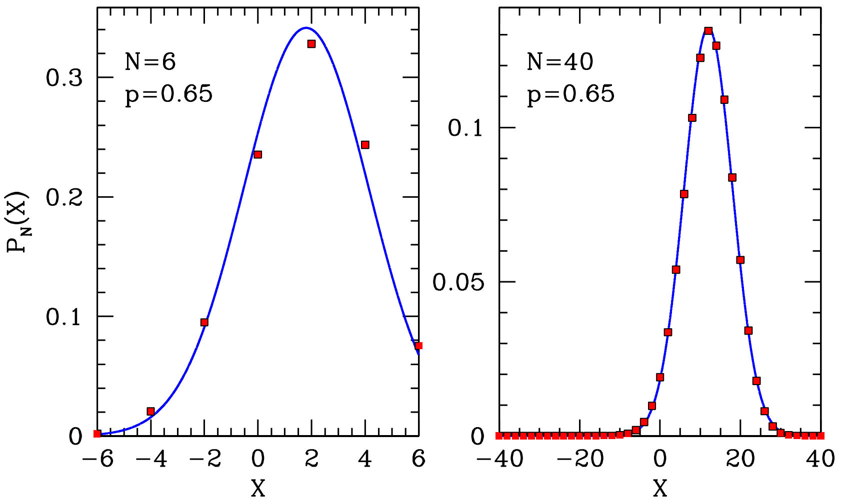

Figure 1.2: Comparison of exact distribution of eqn. 1.10 (red squares) with the Gaussian distribution of eqn. 1.19 (blue line).

### 1.2.3 Entropy and energy

The function $f(x)$ can be written as a sum of two contributions, $f(x) = e(x) - s(x)$, where

$$\begin{aligned} s(x) &= -\big(\tfrac{1+x}{2}\big)\ln\big(\tfrac{1+x}{2}\big) - \big(\tfrac{1-x}{2}\big)\ln\big(\tfrac{1-x}{2}\big) \\ e(x) &= -\tfrac{1}{2}\ln(pq) - \tfrac{1}{2}x\ln(p/q)\ . \end{aligned} \tag{1.21}$$

The function $S(N,x) \equiv N s(x)$ is analogous to the *statistical entropy* of our system[3]. We have

$$S(N,x) = N s(x) = \ln\binom{N}{N_{\rm R}} = \ln\binom{N}{\frac{1}{2}N(1+x)}\ . \tag{1.22}$$

Thus, *the statistical entropy is the logarithm of the number of ways the system can be configured so as to yield the same value of $X$ (at fixed $N$)*. The second contribution to $f(x)$ is the energy term. We write

$$E(N,x) = N e(x) = -\tfrac{1}{2}N\ln(pq) - \tfrac{1}{2}Nx\ln(p/q)\ . \tag{1.23}$$

The energy term biases the probability $P_{N,X} = \exp(S - E)$ so that *low energy configurations are more probable than high energy configurations*. For our system, we see that when $p < q$ (*i.e.* $p < \frac{1}{2}$), the energy is minimized by taking $x$ as small as possible (meaning as negative as possible). The smallest possible allowed value of $x = X/N$ is $x = -1$. Conversely, when $p > q$ (*i.e.* $p > \frac{1}{2}$), the energy is minimized by taking $x$ as large as possible, which means $x = 1$. The average value of $x$, as we have computed explicitly, is $\bar{x} = p - q = 2p - 1$, which falls somewhere in between these two extremes.

In actual thermodynamic systems, as we shall see, entropy and energy are not dimensionless. What we have called $S$ here is really $S/k_{\rm B}$, which is the entropy in units of Boltzmann's constant. And what we have called $E$ here is really $E/k_{\rm B}T$, which is energy in units of Boltzmann's constant times temperature.

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[3] The function $s(x)$ is the *specific entropy*.

### 1.2.4 Entropy and information theory

It was shown in the classic 1948 work of Claude Shannon that entropy is in fact a measure of *information*[4]. Suppose we observe that a particular event occurs with probability $p$. We associate with this observation an amount of information $I(p)$. The information $I(p)$ should satisfy certain desiderata:

1 Information is non-negative, *i.e.* $I(p) \geq 0$.

2 If two events occur independently so their joint probability is $p_1\, p_2$, then their information is additive, *i.e.* $I(p_1 p_2) = I(p_1) + I(p_2)$.

3 $I(p)$ is a continuous function of $p$.

4 There is no information content to an event which is always observed, *i.e.* $I(1) = 0$.

From these four properties, it is easy to show that the only possible function $I(p)$ is

$$I(p) = -A\, \ln p \ , \tag{1.24}$$

where $A$ is an arbitrary constant that can be absorbed into the base of the logarithm, since $\log_b x = \ln x / \ln b$. We will take $A = 1$ and use $e$ as the base, so $I(p) = -\ln p$. Another common choice is to take the base of the logarithm to be 2, so $I(p) = -\log_2 p$. In this latter case, the units of information are known as *bits*. Note that $I(0) = \infty$. This means that the observation of an extremely rare event carries a great deal of information.

Now suppose we have a set of events labeled by an integer $n$ which occur with probabilities $\{p_n\}$. What is the expected amount of information in $N$ observations? Since event $n$ occurs an average of $Np_n$ times, and the information content in $p_n$ is $-\ln p_n$, we have that the average information per observation is

$$S = \frac{\langle I_N \rangle}{N} = -\sum_n p_n \ln p_n \ , \tag{1.25}$$

which is known as the entropy of the distribution. Thus, maximizing $S$ is equivalent to maximizing the *information* content per observation.

Consider, for example, the information content of course grades. As we have seen, if the only constraint on the probability distribution is that of overall normalization, then $S$ is maximized when all the probabilities $p_n$ are equal. The binary entropy is then $S = \log_2 \varGamma$, since $p_n = 1/\varGamma$. Thus, for pass/fail grading, the maximum average information per grade is $-\log_2(\frac{1}{2}) = \log_2 2 = 1$ bit. If only A, B, C, D, and F grades are assigned, then the maximum average information per grade is $\log_2 5 = 2.32$ bits. If we expand the grade options to include {A+, A, A-, B+, B, B-, C+, C, C-, D, F}, then the maximum average information per grade is $\log_2 11 = 3.46$ bits.

Equivalently, consider, following the discussion in vol. 1 of Kardar, a random sequence $\{n_1, n_2, \ldots, n_N\}$ where each element $n_j$ takes one of $K$ possible values. There are then $K^N$ such possible sequences, and to specify one of them requires $\log_2(K^N) = N \log_2 K$ bits of information. However, if the value $n$ occurs with probability $p_n$, then on average it will occur $N_n = Np_n$ times in a sequence of length $N$, and the total number of such sequences will be

$$g(N) = \frac{N!}{\prod_{n=1}^K N_n!} \ . \tag{1.26}$$

In general, this is far less that the total possible number $K^N$, and the number of bits necessary to specify one from among these $g(N)$ possibilities is

$$\log_2 g(N) = \log_2(N!) - \sum_{n=1}^K \log_2(N_n!) \approx -N \sum_{n=1}^K p_n \log_2 p_n \ , \tag{1.27}$$

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[4] See 'An Introduction to Information Theory and Entropy' by T. Carter, Santa Fe Complex Systems Summer School, June 2011. Available online at http://astarte.csustan.edu/ tom/SFI-CSSS/info-theory/info-lec.pdf.

where we have invoked Stirling's approximation. If the distribution is uniform, then we have $p_n = \frac{1}{K}$ for all $n \in \{1, \ldots, K\}$, and $\log_2 g(N) = N \log_2 K$.

## 1.3 Probability Distributions from Maximum Entropy

We have shown how one can proceed from a probability distribution and compute various averages. We now seek to go in the other direction, and determine the full probability distribution based on a knowledge of certain averages.

At first, this seems impossible. Suppose we want to reproduce the full probability distribution for an $N$-step random walk from knowledge of the average $\langle X \rangle = (2p-1)N$. The problem seems ridiculously underdetermined, since there are $2^N$ possible configurations for an $N$-step random walk: $\sigma_j = \pm 1$ for $j = 1, \ldots, N$. Overall normalization requires

$$\sum_{\{\sigma_j\}} P(\sigma_1, \ldots, \sigma_N) = 1 \ , \tag{1.28}$$

but this just imposes one constraint on the $2^N$ probabilities $P(\sigma_1, \ldots, \sigma_N)$, leaving $2^N - 1$ overall parameters. What principle allows us to reconstruct the full probability distribution

$$P(\sigma_1, \ldots, \sigma_N) = \prod_{j=1}^{N} \big( p \, \delta_{\sigma_j, 1} + q \, \delta_{\sigma_j, -1} \big) = \prod_{j=1}^{N} p^{(1+\sigma_j)/2} \, q^{(1-\sigma_j)/2} \ , \tag{1.29}$$

corresponding to $N$ independent steps?

### 1.3.1 The principle of maximum entropy

The entropy of a discrete probability distribution $\{p_n\}$ is defined as

$$S = -\sum_n p_n \ln p_n \ , \tag{1.30}$$

where here we take $e$ as the base of the logarithm. The entropy may therefore be regarded as a function of the probability distribution: $S = S\big(\{p_n\}\big)$. One special property of the entropy is the following. Suppose we have two independent normalized distributions $\big\{p^{\mathsf{A}}_a\big\}$ and $\big\{p^{\mathsf{B}}_b\big\}$. The joint probability for events $a$ and $b$ is then $P_{a,b} = p^{\mathsf{A}}_a \, p^{\mathsf{B}}_b$. The entropy of the joint distribution is then

$$\begin{aligned} S &= -\sum_a \sum_b P_{a,b} \ln P_{a,b} = -\sum_a \sum_b p^{\mathsf{A}}_a \, p^{\mathsf{B}}_b \ln \big( p^{\mathsf{A}}_a \, p^{\mathsf{B}}_b \big) = -\sum_a \sum_b p^{\mathsf{A}}_a \, p^{\mathsf{B}}_b \big( \ln p^{\mathsf{A}}_a + \ln p^{\mathsf{B}}_b \big) \\ &= -\sum_a p^{\mathsf{A}}_a \ln p^{\mathsf{A}}_a \cdot \sum_b p^{\mathsf{B}}_b - \sum_b p^{\mathsf{B}}_b \ln p^{\mathsf{B}}_b \cdot \sum_a p^{\mathsf{A}}_a = -\sum_a p^{\mathsf{A}}_a \ln p^{\mathsf{A}}_a - \sum_b p^{\mathsf{B}}_b \ln p^{\mathsf{B}}_b \\ &= S^{\mathsf{A}} + S^{\mathsf{B}} \ . \end{aligned}$$

Thus, the entropy of a joint distribution formed from two independent distributions is additive.

Suppose all we knew about $\{p_n\}$ was that it was normalized. Then $\sum_n p_n = 1$. This is a constraint on the values $\{p_n\}$. Let us now extremize the entropy $S$ with respect to the distribution $\{p_n\}$, but subject to the normalization constraint. We do this using Lagrange's method of undetermined multipliers. We define

$$S^*\big(\{p_n\}, \lambda\big) = -\sum_n p_n \ln p_n - \lambda \Big( \sum_n p_n - 1 \Big) \tag{1.31}$$

and we freely extremize $S^*$ over all its arguments. Thus, for all $n$ we have

$$\frac{\partial S^*}{\partial p_n} = -\big(\ln p_n + 1 + \lambda\big) = 0 \tag{1.32}$$

as well as

$$\frac{\partial S^*}{\partial \lambda} = \sum_n p_n - 1 = 0 \,. \tag{1.33}$$

From the first of these equations, we obtain $p_n = e^{-(1+\lambda)}$, and from the second we obtain

$$\sum_n p_n = e^{-(1+\lambda)} \cdot \sum_n 1 = \varGamma \, e^{-(1+\lambda)} \,, \tag{1.34}$$

where $\varGamma \equiv \sum_n 1$ is the total number of possible events. Thus,

$$p_n = \frac{1}{\varGamma} \,, \tag{1.35}$$

which says that all events are equally probable.

Now suppose we know one other piece of information, which is the average value of some quantity $X = \sum_n X_n \, p_n$. We now extremize $S$ subject to two constraints, and so we define

$$S^*\big(\{p_n\},\lambda_0,\lambda_1\big) = -\sum_n p_n \ln p_n - \lambda_0 \Big(\sum_n p_n - 1\Big) - \lambda_1 \Big(\sum_n X_n \, p_n - X\Big) \,. \tag{1.36}$$

We then have

$$\frac{\partial S^*}{\partial p_n} = -\big(\ln p_n + 1 + \lambda_0 + \lambda_1 \, X_n\big) = 0 \,, \tag{1.37}$$

which yields the two-parameter distribution

$$p_n = e^{-(1+\lambda_0)} \, e^{-\lambda_1 X_n} \,. \tag{1.38}$$

To fully determine the distribution $\{p_n\}$ we need to invoke the two equations $\sum_n p_n = 1$ and $\sum_n X_n \, p_n = X$, which come from extremizing $S^*$ with respect to $\lambda_0$ and $\lambda_1$, respectively:

$$e^{-(1+\lambda_0)} \sum_n e^{-\lambda_1 X_n} = 1 \tag{1.39}$$

$$e^{-(1+\lambda_0)} \sum_n X_n \, e^{-\lambda_1 X_n} = X \,. \tag{1.40}$$

**General formulation**

The generalization to $K$ extra pieces of information (plus normalization) is immediately apparent. We have

$$X^a = \sum_n X^a_n \, p_n \,, \tag{1.41}$$

and therefore we define

$$S^*\big(\{p_n\},\{\lambda_a\}\big) = -\sum_n p_n \ln p_n - \sum_{a=0}^{K} \lambda_a \Big(\sum_n X^a_n \, p_n - X^a\Big) \,, \tag{1.42}$$

with $X_n^{(a=0)} \equiv X^{(a=0)} = 1$. Then the optimal distribution which extremizes $S$ subject to the $K+1$ constraints is

$$\begin{aligned} p_n &= \exp\left\{ -1 - \sum_{a=0}^{K} \lambda_a \, X_n^a \right\} \\ &= \frac{1}{Z} \exp\left\{ -\sum_{a=1}^{K} \lambda_a \, X_n^a \right\} , \end{aligned} \tag{1.43}$$

where $Z = e^{1+\lambda_0}$ is determined by normalization: $\sum_n p_n = 1$. This is a $(K+1)$-parameter distribution, with $\{\lambda_0, \lambda_1, \ldots, \lambda_K\}$ determined by the $K+1$ constraints in eqn. 1.41.

**Example**

As an example, consider the random walk problem. We have two pieces of information:

$$\sum_{\sigma_1} \cdots \sum_{\sigma_N} P(\sigma_1, \ldots, \sigma_N) = 1 \tag{1.44}$$

$$\sum_{\sigma_1} \cdots \sum_{\sigma_N} P(\sigma_1, \ldots, \sigma_N) \sum_{j=1}^{N} \sigma_j = X \, . \tag{1.45}$$

Here the discrete label $n$ from §1.3.1 ranges over $2^N$ possible values, and may be written as an $N$ digit binary number $r_N \cdots r_1$, where $r_j = \frac{1}{2}(1+\sigma_j)$ is 0 or 1. Extremizing $S$ subject to these constraints, we obtain

$$P(\sigma_1, \ldots, \sigma_N) = \mathcal{C} \, \exp\left\{ -\lambda \sum_j \sigma_j \right\} = \mathcal{C} \prod_{j=1}^{N} e^{-\lambda \, \sigma_j} \, , \tag{1.46}$$

where $\mathcal{C} \equiv e^{-(1+\lambda_0)}$ and $\lambda \equiv \lambda_2$. Normalization then requires

$$\mathsf{Tr}\, P \equiv \sum_{\{\sigma_j\}} = \mathcal{C} \left( e^{\lambda} + e^{-\lambda} \right)^N \, , \tag{1.47}$$

hence $\mathcal{C} = (\cosh \lambda)^{-N}$. We then have

$$P(\sigma_1, \ldots, \sigma_N) = \prod_{j=1}^{N} \frac{e^{-\lambda \sigma_j}}{e^{\lambda} + e^{-\lambda}} = \prod_{j=1}^{N} \left( p \, \delta_{\sigma_j,1} + q \, \delta_{\sigma_j,-1} \right) \, , \tag{1.48}$$

where

$$p = \frac{e^{-\lambda}}{e^{\lambda} + e^{-\lambda}} \quad , \quad q = 1 - p = \frac{e^{\lambda}}{e^{\lambda} + e^{-\lambda}} \, . \tag{1.49}$$

We then have $X = (2p-1)N$, which determines $p = \frac{1}{2}(N+X)$, and we have recovered the correct distribution.

### 1.3.2 Continuous probability distributions

Suppose we have a continuous probability density $P(\boldsymbol{\varphi})$ defined over some set $\Omega$. We have observables

$$X^a = \int_{\Omega} \! d\mu \; X^a(\boldsymbol{\varphi}) \, P(\boldsymbol{\varphi}) \, , \tag{1.50}$$

where $d\mu$ is the appropriate integration measure. We assume $d\mu = \prod_{j=1}^D d\varphi_j$, where $D$ is the dimension of $\Omega$. Then we extremize the functional

$$S^*\big[P(\boldsymbol{\varphi}),\{\lambda_a\}\big] = \int\limits_\Omega d\mu\, P(\boldsymbol{\varphi}) \ln P(\boldsymbol{\varphi}) - \sum_{a=0}^K \lambda_a \Bigg( \int\limits_\Omega d\mu\, P(\boldsymbol{\varphi})\, X^a(\boldsymbol{\varphi}) - X^a \Bigg) \tag{1.51}$$

with respect to $P(\boldsymbol{\varphi})$ and with respect to $\{\lambda_a\}$. Again, $X^0(\boldsymbol{\varphi}) \equiv X^0 \equiv 1$. This yields the following result:

$$\ln P(\boldsymbol{\varphi}) = -1 - \sum_{a=0}^K \lambda_a\, X^a(\boldsymbol{\varphi}) \ . \tag{1.52}$$

The $K+1$ Lagrange multipliers $\{\lambda_a\}$ are then determined from the $K+1$ constraint equations in eqn. 1.50.

As an example, consider a distribution $P(x)$ over the real numbers $\mathbb{R}$. We constrain

$$\int\limits_{-\infty}^{\infty} dx\, P(x) = 1 \quad , \quad \int\limits_{-\infty}^{\infty} dx\, x\, P(x) = \mu \quad , \quad \int\limits_{-\infty}^{\infty} dx\, x^2\, P(x) = \mu^2 + \sigma^2 \ . \tag{1.53}$$

Extremizing the entropy, we then obtain

$$P(x) = \mathcal{C}\, e^{-\lambda_1 x - \lambda_2 x^2} \ , \tag{1.54}$$

where $\mathcal{C} = e^{-(1+\lambda_0)}$. We already know the answer:

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-(x-\mu)^2/2\sigma^2} \ . \tag{1.55}$$

In other words, $\lambda_1 = -\mu/\sigma^2$ and $\lambda_2 = 1/2\sigma^2$, with $\mathcal{C} = e^{-\mu^2/2\sigma^2}/\sqrt{2\pi\sigma^2}$.

## 1.4 General Aspects of Probability Distributions

### 1.4.1 Discrete and continuous distributions

Consider a system whose possible configurations $|\, n \,\rangle$ can be labeled by a discrete variable $n \in \mathcal{C}$, where $\mathcal{C}$ is the set of possible configurations. The total number of possible configurations, which is to say the *order* of the set $\mathcal{C}$, may be finite or infinite. Next, consider an ensemble of such systems, and let $P_n$ denote the probability that a given random element from that ensemble is in the state (configuration) $|\, n \,\rangle$. The collection $\{P_n\}$ forms a *discrete probability distribution*. We assume that the distribution is *normalized*, meaning

$$\sum_{n \in \mathcal{C}} P_n = 1 \ . \tag{1.56}$$

Now let $A_n$ be a quantity which takes values depending on $n$. The average of $A$ is given by

$$\langle A \rangle = \sum_{n \in \mathcal{C}} P_n\, A_n \ . \tag{1.57}$$

Typically, $\mathcal{C}$ is the set of integers ($\mathbb{Z}$) or some subset thereof, but it could be any countable set. As an example, consider the throw of a single six-sided die. Then $P_n = \frac{1}{6}$ for each $n \in \{1, \ldots, 6\}$. Let $A_n = 0$ if $n$ is even and $1$ if $n$ is odd. Then find $\langle A \rangle = \frac{1}{2}$, *i.e.* on average half the throws of the die will result in an even number.

It may be that the system's configurations are described by several discrete variables $\{n_1, n_2, n_3, \ldots\}$. We can combine these into a vector $\boldsymbol{n}$ and then we write $P_{\boldsymbol{n}}$ for the discrete distribution, with $\sum_{\boldsymbol{n}} P_{\boldsymbol{n}} = 1$.

Another possibility is that the system's configurations are parameterized by a collection of continuous variables, $\boldsymbol{\varphi} = \{\varphi_1, \ldots, \varphi_n\}$. We write $\boldsymbol{\varphi} \in \Omega$, where $\Omega$ is the phase space (or configuration space) of the system. Let $d\mu$ be a *measure* on this space. In general, we can write

$$d\mu = W(\varphi_1, \ldots, \varphi_n)\, d\varphi_1\, d\varphi_2 \cdots d\varphi_n\ . \tag{1.58}$$

The phase space measure used in classical statistical mechanics gives equal weight $W$ to equal phase space volumes:

$$d\mu = \mathcal{C} \prod_{\sigma=1}^{r} dq_\sigma\, dp_\sigma\ , \tag{1.59}$$

where $\mathcal{C}$ is a constant we shall discuss later on below[5].

Any continuous probability distribution $P(\boldsymbol{\varphi})$ is normalized according to

$$\int_\Omega d\mu\, P(\boldsymbol{\varphi}) = 1\ . \tag{1.60}$$

The average of a function $A(\boldsymbol{\varphi})$ on configuration space is then

$$\langle A \rangle = \int_\Omega d\mu\, P(\boldsymbol{\varphi})\, A(\boldsymbol{\varphi})\ . \tag{1.61}$$

For example, consider the Gaussian distribution

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-(x-\mu)^2/2\sigma^2}\ . \tag{1.62}$$

From the result[6]

$$\int_{-\infty}^{\infty} dx\, e^{-\alpha x^2}\, e^{-\beta x} = \sqrt{\frac{\pi}{\alpha}}\, e^{\beta^2/4\alpha}\ , \tag{1.63}$$

we see that $P(x)$ is normalized. One can then compute

$$\begin{aligned} \langle x \rangle &= \mu \\ \langle x^2 \rangle - \langle x \rangle^2 &= \sigma^2\ . \end{aligned} \tag{1.64}$$

We call $\mu$ the *mean* and $\sigma$ the *standard deviation* of the distribution, eqn. 1.62.

The quantity $P(\boldsymbol{\varphi})$ is called the *distribution* or *probability density*. One has

$$P(\boldsymbol{\varphi})\, d\mu = \text{probability that configuration lies within volume } d\mu \text{ centered at } \boldsymbol{\varphi}$$

For example, consider the probability density $P = 1$ normalized on the interval $x \in \big[0, 1\big]$. The probability that some $x$ chosen at random will be *exactly* $\frac{1}{2}$, say, is infinitesimal – one would have to specify each of the infinitely many digits of $x$. However, we can say that $x \in \big[0.45\ ,\ 0.55\big]$ with probability $\frac{1}{10}$.

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[5] Such a measure is invariant with respect to canonical transformations, which are the broad class of transformations among coordinates and momenta which leave Hamilton's equations of motion invariant, and which preserve phase space volumes under Hamiltonian evolution. For this reason $d\mu$ is called an *invariant phase space measure*. See the discussion in appendix II of chapter 4.

[6] Memorize this!

If $x$ is distributed according to $P_1(x)$, then the probability distribution on the product space $(x_1\,,\,x_2)$ is simply the product of the distributions:

$$P_2(x_1,x_2) = P_1(x_1)\,P_1(x_2)\ . \tag{1.65}$$

Suppose we have a function $\phi(x_1,\ldots,x_N)$. How is it distributed? Let $Q(\phi)$ be the distribution for $\phi$. We then have

$$\begin{aligned}\mathcal{P}(\phi) &= \int\limits_{-\infty}^{\infty}\!dx_1 \cdots \int\limits_{-\infty}^{\infty}\!dx_N\; P_N(x_1,\ldots,x_N)\,\delta\Big(\phi(x_1,\ldots,x_N)-\phi\Big)\\ &= \int\limits_{-\infty}^{\infty}\!dx_1 \cdots \int\limits_{-\infty}^{\infty}\!x_N\; P_1(x_1)\cdots P_1(x_N)\,\delta\Big(\phi(x_1,\ldots,x_N)-\phi\Big)\ ,\end{aligned} \tag{1.66}$$

where the second line is appropriate if the $\{x_j\}$ are themselves distributed independently. Note that

$$\int\limits_{-\infty}^{\infty}\!d\phi\;\mathcal{P}(\phi) = 1\ , \tag{1.67}$$

so $\mathcal{P}(\phi)$ is itself normalized.

### 1.4.2 Central limit theorem

In particular, consider the distribution function of the sum

$$X = \sum_{i=1}^N x_i\ . \tag{1.68}$$

We will be particularly interested in the case where $N$ is large. For general $N$, though, we have

$$\mathcal{P}_N(X) = \int\limits_{-\infty}^{\infty}\!dx_1 \cdots \int\limits_{-\infty}^{\infty}\!dx_N\; P_1(x_1)\cdots P_1(x_N)\,\delta\big(x_1+x_2+\ldots+x_N-X\big)\ . \tag{1.69}$$

It is convenient to compute the Fourier transform[7] of $\mathcal{P}(X)$:

$$\begin{aligned}\hat{\mathcal{P}}_N(k) &= \int\limits_{-\infty}^{\infty} dX\, \mathcal{P}_N(X)\, e^{-ikX} \\ &= \int\limits_{-\infty}^{\infty} dX \int\limits_{-\infty}^{\infty} dx_1 \cdots \int\limits_{-\infty}^{\infty} x_N\, P_1(x_1) \cdots P_1(x_N)\, \delta\big(x_1 + \ldots + x_N - X\big)\, e^{-ikX} \\ &= \big[\hat{P}_1(k)\big]^N\ ,\end{aligned} \tag{1.70}$$

where

$$\hat{P}_1(k) = \int\limits_{-\infty}^{\infty} dx\, P_1(x)\, e^{-ikx} \tag{1.71}$$

is the Fourier transform of the single variable distribution $P_1(x)$. The distribution $\mathcal{P}_N(X)$ is a *convolution* of the individual $P_1(x_i)$ distributions. We have therefore proven that *the Fourier transform of a convolution is the product of the Fourier transforms*.

OK, now we can write for $\hat{P}_1(k)$

$$\begin{aligned}\hat{P}_1(k) &= \int\limits_{-\infty}^{\infty} dx\, P_1(x)\, \big(1 - ikx - \tfrac{1}{2}\, k^2 x^2 + \tfrac{1}{6}\, i\, k^3\, x^3 + \ldots\big) \\ &= 1 - ik\langle x\rangle - \tfrac{1}{2}\, k^2 \langle x^2\rangle + \tfrac{1}{6}\, i\, k^3 \langle x^3\rangle + \ldots\ .\end{aligned} \tag{1.72}$$

Thus,

$$\ln \hat{P}_1(k) = -i\mu k - \tfrac{1}{2}\sigma^2 k^2 + \tfrac{1}{6}\, i\, \gamma^3\, k^3 + \ldots\ , \tag{1.73}$$

where

$$\begin{aligned}\mu &= \langle x\rangle \\ \sigma^2 &= \langle x^2\rangle - \langle x\rangle^2 \\ \gamma^3 &= \langle x^3\rangle - 3\,\langle x^2\rangle\,\langle x\rangle + 2\,\langle x\rangle^3\end{aligned} \tag{1.74}$$

We can now write

$$\big[\hat{P}_1(k)\big]^N = e^{-iN\mu k}\, e^{-N\sigma^2 k^2/2}\, e^{iN\gamma^3 k^3/6} \cdots \tag{1.75}$$

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[7] Jean Baptiste Joseph Fourier (1768-1830) had an illustrious career. The son of a tailor, and orphaned at age eight, Fourier's ignoble status rendered him ineligible to receive a commission in the scientific corps of the French army. A Benedictine minister at the École Royale Militaire of Auxerre remarked, *"Fourier, not being noble, could not enter the artillery, although he were a second Newton."* Fourier prepared for the priesthood, but his affinity for mathematics proved overwhelming, and so he left the abbey and soon thereafter accepted a military lectureship position. Despite his initial support for revolution in France, in 1794 Fourier ran afoul of a rival sect while on a trip to Orléans and was arrested and very nearly guillotined. Fortunately the Reign of Terror ended soon after the death of Robespierre, and Fourier was released. He went on Napoleon Bonaparte's 1798 expedition to Egypt, where he was appointed governor of Lower Egypt. His organizational skills impressed Napoleon, and upon return to France he was appointed to a position of prefect in Grenoble. It was in Grenoble that Fourier performed his landmark studies of heat, and his famous work on partial differential equations and Fourier series. It seems that Fourier's fascination with heat began in Egypt, where he developed an appreciation of desert climate. His fascination developed into an obsession, and he became convinced that heat could promote a healthy body. He would cover himself in blankets, like a mummy, in his heated apartment, even during the middle of summer. On May 4, 1830, Fourier, so arrayed, tripped and fell down a flight of stairs. This aggravated a developing heart condition, which he refused to treat with anything other than more heat. Two weeks later, he died. Fourier's is one of the 72 names of scientists, engineers and other luminaries which are engraved on the Eiffel Tower. Source: http://www.robertnowlan.com/pdfs/Fourier,%20Joseph.pdf

Now for the inverse transform. In computing $\mathcal{P}_N(X)$, we will expand the term $e^{iN\gamma^3k^3/6}$ and all subsequent terms in the above product as a power series in $k$. We then have

$$\begin{aligned}\mathcal{P}_N(X) &= \int\limits_{-\infty}^{\infty}\frac{dk}{2\pi}\, e^{ik(X-N\mu)}\, e^{-N\sigma^2k^2/2}\left\{1+\tfrac{1}{6}\,i\,N\gamma^3k^3+\ldots\right\} \\ &= \left(1-\tfrac{1}{6}N\gamma^3\,\frac{\partial^3}{\partial X^3}+\ldots\right)\frac{1}{\sqrt{2\pi N\sigma^2}}\,e^{-(X-N\mu)^2/2N\sigma^2} \\ &= \frac{1}{\sqrt{2\pi N\sigma^2}}\,e^{-(X-N\mu)^2/2N\sigma^2}\qquad (N\to\infty)\ .\end{aligned} \tag{1.76}$$

In going from the second line to the third, we have written $X=\sqrt{N}\,\xi$, in which case $N\frac{\partial^3}{\partial X^3}=N^{-1/2}\,\frac{\partial^3}{\partial\xi^3}$, which gives a subleading contribution which vanishes in the $N\to\infty$ limit. We have just proven the *central limit theorem*: in the limit $N\to\infty$, the distribution of a sum of $N$ independent random variables $x_i$ is a Gaussian with mean $N\mu$ and standard deviation $\sqrt{N}\,\sigma$. Our only assumptions are that the mean $\mu$ and standard deviation $\sigma$ exist for the distribution $P_1(x)$. Note that $P_1(x)$ itself need not be a Gaussian – it could be a very peculiar distribution indeed, but so long as its first and second moment exist, where the $k^{\text{th}}$ moment is simply $\langle x^k\rangle$, the distribution of the sum $X=\sum_{i=1}^N x_i$ is a Gaussian.

### 1.4.3 Multidimensional Gaussian integral

Consider the multivariable Gaussian distribution,

$$P(\boldsymbol{x})\equiv\left(\frac{\det A}{(2\pi)^n}\right)^{1/2}\exp\Big(-\tfrac{1}{2}\,x_i\,A_{ij}\,x_j\Big)\ , \tag{1.77}$$

where $A$ is a positive definite matrix of rank $n$. A mathematical result which is extremely important throughout physics is the following:

$$Z(\boldsymbol{b})=\left(\frac{\det A}{(2\pi)^n}\right)^{1/2}\int\limits_{-\infty}^{\infty}\!dx_1\cdots\int\limits_{-\infty}^{\infty}\!dx_n\ \exp\Big(-\tfrac{1}{2}\,x_i\,A_{ij}\,x_j+b_i\,x_i\Big)=\exp\Big(\tfrac{1}{2}\,b_i\,A^{-1}_{ij}\,b_j\Big)\ . \tag{1.78}$$

Here, the vector $\boldsymbol{b}=(b_1\,,\,\ldots\,,\,b_n)$ is identified as a *source*. Since $Z(0)=1$, we have that the distribution $P(\boldsymbol{x})$ is normalized. Now consider averages of the form

$$\begin{aligned}\langle\, x_{j_1}\cdots x_{j_{2k}}\,\rangle &= \int\! d^n\!x\ P(\boldsymbol{x})\,x_{j_1}\cdots\,x_{j_{2k}} \\ &= \frac{\partial^n Z(\boldsymbol{b})}{\partial b_{j_1}\cdots\,\partial b_{j_{2k}}}\bigg|_{\boldsymbol{b}=0} \\ &= \sum_{\text{contractions}} A^{-1}_{j_{\sigma(1)}j_{\sigma(2)}}\cdots A^{-1}_{j_{\sigma(2k-1)}j_{\sigma(2k)}}\ .\end{aligned} \tag{1.79}$$

The sum in the last term is over all *contractions* of the indices $\{j_1\,,\,\ldots\,,\,j_{2k}\}$. A contraction is an arrangement of the $2k$ indices into $k$ pairs. There are $C_{2k}=(2k)!/2^k k!$ possible such contractions. To obtain this result for $C_k$, we start with the first index and then find a mate among the remaining $2k-1$ indices. Then we choose the next unpaired index and find a mate among the remaining $2k-3$ indices. Proceeding in this manner, we have

$$C_{2k}=(2k-1)\cdot(2k-3)\cdots 3\cdot 1=\frac{(2k)!}{2^k k!}\ . \tag{1.80}$$

Equivalently, we can take all possible permutations of the $2k$ indices, and then divide by $2^k k!$ since permutation within a given pair results in the same contraction and permutation among the $k$ pairs results in the same contraction. For example, for $k = 2$, we have $C_4 = 3$, and

$$\langle\, x_{j_1} x_{j_2} x_{j_3} x_{j_4} \,\rangle = A^{-1}_{j_1 j_2} A^{-1}_{j_3 j_4} + A^{-1}_{j_1 j_3} A^{-1}_{j_2 j_4} + A^{-1}_{j_1 j_4} A^{-1}_{j_2 j_3} \ . \tag{1.81}$$

## 1.5 Appendix : Bayesian Statistics

Let the probability of a discrete event $A$ be $P(A)$. We now introduce two additional probabilities. The *joint probability* for events $A$ and $B$ together is written $P(A \cap B)$. The *conditional probability* of $B$ given $A$ is $P(B|A)$. We can compute the joint probability $P(A \cap B) = P(B \cap A)$ in two ways:

$$P(A \cap B) = P(A|B) \cdot P(B) = P(B|A) \cdot P(A) \ . \tag{1.82}$$

Thus,

$$P(A|B) = \frac{P(B|A) \cdot P(A)}{P(B)} \ , \tag{1.83}$$

a result known as *Bayes' theorem*. Now suppose the 'event space' is partitioned as $\{A_i\}$. Then

$$P(B) = \sum_i P(B|A_i) \cdot P(A_i) \ . \tag{1.84}$$

We then have

$$P(A_i|B) = \frac{P(B|A_i) \cdot P(A_i)}{\sum_j P(B|A_j) \cdot P(A_j)} \ , \tag{1.85}$$

a result sometimes known as the *extended form of Bayes' theorem*. When the event space is a 'binary partition' $\{A, \neg A\}$, we have

$$P(A|B) = \frac{P(B|A) \cdot P(A)}{P(B|A) \cdot P(A) + P(B|\neg A) \cdot P(\neg A)} \ . \tag{1.86}$$

Note that $P(A|B) + P(\neg A|B) = 1$ (which follows from $\neg\neg A = A$).

As an example, consider the following problem in epidemiology. Suppose there is a rare but highly contagious disease $A$ which occurs in $0.01\%$ of the general population. Suppose further that there is a simple test for the disease which is accurate $99.99\%$ of the time. That is, out of every 10,000 tests, the correct answer is returned 9,999 times, and the incorrect answer is returned only once[8]. Now let us administer the test to a large group of people from the general population. Those who test positive are quarantined. Question: what is the probability that someone chosen at random from the quarantine group actually has the disease? We use Bayes' theorem with the binary partition $\{A, \neg A\}$. Let $B$ denote the event that an individual tests positive. Anyone from the quarantine group has tested positive. Given this datum, we want to know the probability that that person has the disease. That is, we want $P(A|B)$. Applying eqn. 1.86 with

$$P(A) = 0.0001 \quad , \quad P(\neg A) = 0.9999 \quad , \quad P(B|A) = 0.9999 \quad , \quad P(B|\neg A) = 0.0001 \ ,$$

we find $P(A|B) = \frac{1}{2}$. That is, there is only a $50\%$ chance that someone who tested positive actually has the disease, despite the test being $99.99\%$ accurate! The reason is that, given the rarity of the disease in the general population, the number of false positives is statistically equal to the number of true positives.

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[8] Epidemiologists define the *sensitivity* of a binary classification test as the fraction of actual positives which are correctly identified, and the *specificity* as the fraction of actual negatives that are correctly identified. In our example in the text, the sensitivity and specificity are both 0.9999.

For continuous distributions, we speak of a probability density. We then have

$$P(y) = \int dx\, P(y|x) \cdot P(x) \tag{1.87}$$

and

$$P(x|y) = \frac{P(y|x) \cdot P(x)}{\int dx'\, P(y|x') \cdot P(x')} \ . \tag{1.88}$$

The range of integration may depend on the specific application.

The quantities $P(A_i)$ are called the *prior distribution*. Clearly in order to compute $P(B)$ or $P(A_i|B)$ we must know the priors, and this is usually the weakest link in the Bayesian chain of reasoning. If our prior distribution is not accurate, Bayes' theorem will generate incorrect results. One approach to obtaining the prior probabilities $P(A_i)$ is to obtain them from a maximum entropy construction.

# Chapter 2

# Thermodynamics

## 2.1 References

- E. Fermi, *Thermodynamics* (Dover, 1956)
  This outstanding and inexpensive little book is a model of clarity.
- A. H. Carter, *Classical and Statistical Thermodynamics*
  (Benjamin Cummings, 2000)
  A very relaxed treatment appropriate for undergraduate physics majors.
- H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*
  (2nd edition, Wiley, 1985)
  A comprehensive text appropriate for an extended course on thermodynamics.
- D. V. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley, 2000)
  An excellent thermodynamics text appropriate for upper division undergraduates. Contains many illustrative practical applications.
- D. Kondepudi and I. Prigogine, *Modern Thermodynamics: From Heat Engines to Dissipative Structures*
  (Wiley, 1998)
  Lively modern text with excellent choice of topics and good historical content. More focus on chemical and materials applications than in Callen.
- L. E. Reichl, *A Modern Course in Statistical Physics* (2nd edition, Wiley, 1998)
  A graduate level text with an excellent and crisp section on thermodynamics.

## 2.2 What is Thermodynamics?

Thermodynamics is the study of relations among the *state variables* describing a thermodynamic system, and of transformations of heat into work and *vice versa*.

### 2.2.1 Thermodynamic systems and state variables

Thermodynamic systems contain large numbers of constituent particles, and are described by a set of *state variables* which describe the system's properties in an average sense. State variables are classified as being either *extensive* or *intensive*.

Extensive variables, such as volume $V$, particle number $N$, total internal energy $E$, magnetization $M$, *etc.*, scale linearly with the system size, *i.e.* as the first power of the system volume. If we take two identical thermodynamic systems, place them next to each other, and remove any barriers between them, then all the extensive variables will double in size.

Intensive variables, such as the pressure $p$, the temperature $T$, the chemical potential $\mu$, the electric field $\boldsymbol{E}$, *etc.*, are independent of system size, scaling as the zeroth power of the volume. They are the same throughout the system, if that system is in an appropriate state of *equilibrium*. The ratio of any two extensive variables is an intensive variable. For example, we write $n = N/V$ for the number density, which scales as $V^0$. Intensive variables may also be *inhomogeneous*. For example, $n(\boldsymbol{r})$ is the number density at position $\boldsymbol{r}$, and is defined as the limit of $\Delta N/\Delta V$ of the number of particles $\Delta N$ inside a volume $\Delta V$ which contains the point $\boldsymbol{r}$, in the limit $V \gg \Delta V \gg V/N$.

Classically, the full motion of a system of $N$ point particles requires $6N$ variables to fully describe it ($3N$ positions and $3N$ velocities or momenta, in three space dimensions)[1]. Since the constituents are very small, $N$ is typically very large. A typical solid or liquid, for example, has a mass density on the order of $\varrho \sim 1\,\mathrm{g/cm^3}$; for gases, $\varrho \sim 10^{-3}\,\mathrm{g/cm^3}$. The constituent atoms have masses of $10^0$ to $10^2$ grams per mole, where one mole of $X$ contains $N_{\mathrm{A}}$ of $X$, and $N_{\mathrm{A}} = 6.0221415 \times 10^{23}$ is Avogadro's number. Thus, for solids and liquids we roughly expect number densities $n$ of $10^{-2} - 10^{0}\,\mathrm{mol/cm^3}$ for solids and liquids, and $10^{-5} - 10^{-3}\,\mathrm{mol/cm^3}$ for gases. Clearly we are dealing with fantastically large numbers of constituent particles in a typical thermodynamic system. The underlying theoretical basis for thermodynamics, where we use a small number of state variables to describe a system, is provided by the microscopic theory of statistical mechanics, which we shall study in the weeks ahead.

Intensive quantities such as $p$, $T$, and $n$ ultimately involve averages over both space and time. Consider for example the case of a gas enclosed in a container. We can measure the pressure (relative to atmospheric pressure) by attaching a spring to a moveable wall, as shown in Fig. 2.2. From the displacement of the spring and the value of its spring constant $k$ we determine the force $F$. This force is due to the difference in pressures, so $p = p_0 + F/A$. Microscopically, the gas consists of constituent atoms or molecules, which are constantly undergoing collisions with each other and with the walls of the container. When a particle bounces off a wall, it imparts an impulse $2\hat{\boldsymbol{n}}(\hat{\boldsymbol{n}} \cdot \boldsymbol{p})$, where $\boldsymbol{p}$ is the particle's momentum and $\hat{\boldsymbol{n}}$ is the unit vector normal to the wall. (Only particles with $\boldsymbol{p} \cdot \hat{\boldsymbol{n}} > 0$ will hit the wall.) Multiply this by the number of particles colliding with the wall per unit time, and one finds the net force on the wall; dividing by the area gives the pressure $p$. Within the gas, each particle travels for a distance $\ell$, called the *mean free path*, before it undergoes a collision. We can write $\ell = \bar{v}\tau$, where $\bar{v}$ is the average particle speed and $\tau$ is the *mean free time*. When we study the kinetic theory of gases, we will derive formulas for $\ell$ and $\bar{v}$ (and hence $\tau$). For now it is helpful to quote some numbers to get an idea of the relevant distance and time scales. For $O_2$ gas at standard temperature and pressure ($T = 0°\,\mathrm{C}$, $p = 1\,\mathrm{atm}$), the mean free path is $\ell \approx 1.1 \times 10^{-5}$ cm, the average speed is $\bar{v} \approx 480\,\mathrm{m/s}$, and the mean free time is $\tau \approx 2.5 \times 10^{-10}$ s. Thus, particles in the gas undergo collisions at a rate $\tau^{-1} \approx 4.0 \times 10^{9}\,\mathrm{s^{-1}}$. A measuring device, such as our spring, or a thermometer,

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[1] For a system of $N$ molecules which can freely rotate, we must then specify $3N$ additional orientational variables – the Euler angles – and their $3N$ conjugate momenta. The dimension of phase space is then $12N$.

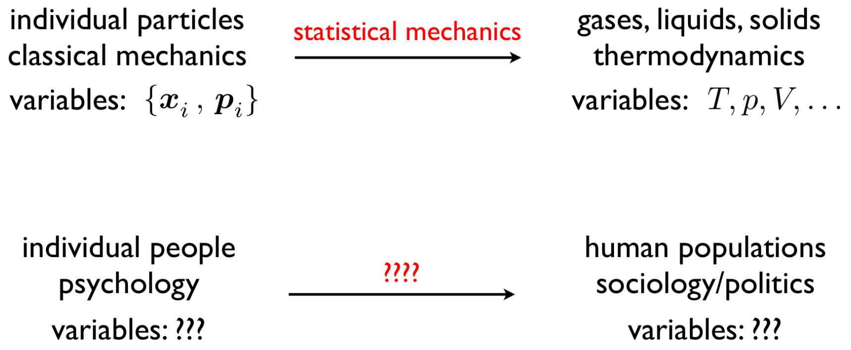

Figure 2.1: From microscale to macroscale : physical *versus* social sciences.

effectively performs time and space averages. If there are $N_{\text{c}}$ collisions with a particular patch of wall during some time interval on which our measurement device responds, then the root mean square relative fluctuations in the local pressure will be on the order of $N_{\text{c}}^{-1/2}$ times the average. Since $N_{\text{c}}$ is a very large number, the fluctuations are negligible.

If the system is in *steady state*, the state variables do not change with time. If furthermore there are no macroscopic currents of energy or particle number flowing through the system, the system is said to be in *equilibrium*. A continuous succession of equilibrium states is known as a *thermodynamic path*, which can be represented as a smooth curve in a multidimensional space whose axes are labeled by state variables. A thermodynamic *process* is any change or succession of changes which results in a change of the state variables. In a *cyclic* process, the initial and final states are the same. In a *quasistatic* process, the system passes through a continuous succession of equilibria. A *reversible* process is one where the external conditions and the thermodynamic path of the system can be reversed (at first this seems to be a tautology). All reversible processes are quasistatic, but not all quasistatic processes are reversible. For example, the slow expansion of a gas against a piston head, whose counter-force is always infinitesimally less than the force $pA$ exerted by the gas, is reversible. To reverse this process, we simply add infinitesimally more force to $pA$ and the gas compresses. A quasistatic process which is not reversible: slowly dragging a block across the floor, or the slow leak of air from a tire. Irreversible processes, as a rule, are dissipative. Other special processes include isothermal ($dT = 0$) isobaric ($dp = 0$), isochoric ($dV = 0$), and adiabatic ($\text{đ}Q = 0$, *i.e.* no heat exchange):

$$\begin{aligned} &\textit{reversible: } \text{đ}Q = T\,dS && \textit{isothermal: } dT = 0 \\ &\textit{spontaneous: } \text{đ}Q < T\,dS && \textit{isochoric: } dV = 0 \\ &\textit{adiabatic: } \text{đ}Q = 0 && \textit{isobaric: } dp = 0 \\ &\textit{quasistatic: } \text{infinitely slowly} && \end{aligned}$$

We shall discuss later the entropy $S$ and its connection with irreversibility.

How many state variables are necessary to fully specify the equilibrium state of a thermodynamic system? For a single component system, such as water which is composed of one constituent molecule, the answer is three. These can be taken to be $T$, $p$, and $V$. One always must specify at least one extensive variable, else we cannot determine the overall size of the system. For a multicomponent system with $g$ different species, we must specify $g + 2$ state variables, which may be $\{T, p, N_1, \ldots, N_g\}$, where $N_a$ is the number of particles of species $a$. Another possibility is the set $(T, p, V, x_1, \ldots, x_{g-1}\}$, where the *concentration* of species $a$ is $x_a = N_a/N$. Here, $N = \sum_{a=1}^{g} N_a$ is the total number of particles. Note that $\sum_{a=1}^{g} x_a = 1$.

If then follows that if we specify more than $g + 2$ state variables, there must exist a relation among them. Such relations are known as *equations of state*. The most famous example is the ideal gas law,

$$pV = Nk_{\text{B}}T\ , \tag{2.1}$$

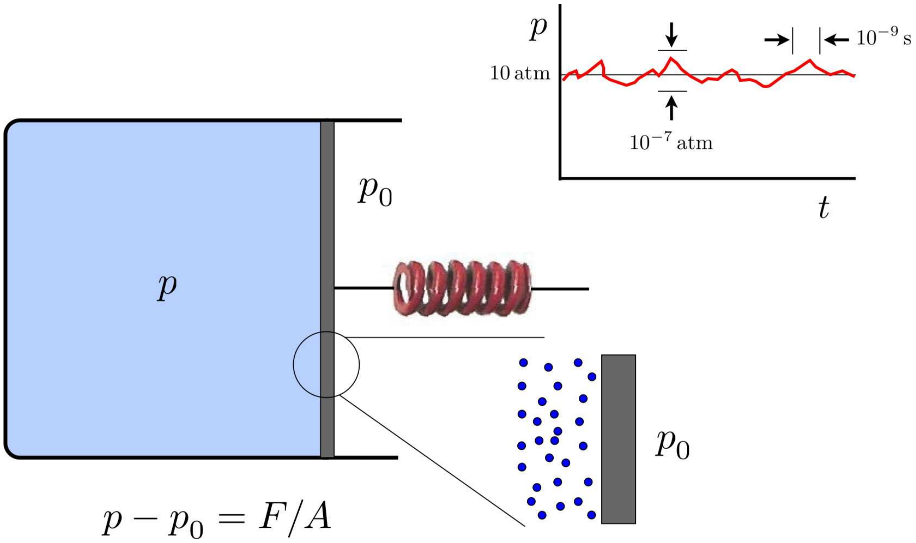

Figure 2.2: The pressure $p$ of a gas is due to an average over space and time of the impulses due to the constituent particles.

relating the four state variables $T$, $p$, $V$, and $N$. Here $k_B = 1.3806503 \times 10^{-16}\,\mathrm{erg/K}$ is Boltzmann's constant. Another example is the van der Waals equation,

$$\left(p + \frac{aN^2}{V^2}\right)(V - bN) = Nk_B T \ , \tag{2.2}$$

where $a$ and $b$ are constants which depend on the molecule which forms the gas. For a third example, consider a paramagnet, where

$$\frac{M}{V} = \frac{CH}{T} \ , \tag{2.3}$$

where $M$ is the magnetization, $H$ the magnetic field, and $C$ the Curie constant.

Any quantity which, in equilibrium, depends only on the state variables is called a *state function*. For example, the total internal energy $E$ of a thermodynamics system is a state function, and we may write $E = E(T, p, V)$. State functions can also serve as state variables, although the most natural state variables are those which can be directly measured.

### 2.2.2 Heat

Once thought to be a type of fluid, heat is now understood in terms of the kinetic theory of gases, liquids, and solids as a form of energy stored in the disordered motion of constituent particles. The units of heat are therefore units of energy, and it is appropriate to speak of *heat energy*, which we shall simply abbreviate as *heat*:[2]

$$1\,\mathrm{J} = 10^7\,\mathrm{erg} = 6.242 \times 10^{18}\,\mathrm{eV} = 2.390 \times 10^{-4}\,\mathrm{kcal} = 9.478 \times 10^{-4}\,\mathrm{BTU} \ . \tag{2.4}$$

We will use the symbol $Q$ to denote the amount of heat energy absorbed by a system during some given thermodynamic process, and $đQ$ to denote a differential amount of heat energy. The symbol $đ$ indicates an 'inexact differential', about which we shall have more to say presently. This means that heat is not a state function: there is no 'heat function' $Q(T, p, V)$.

---

[2] One calorie (cal) is the amount of heat needed to raise 1 g of $H_2O$ from $T_0 = 14.5°$ C to $T_1 = 15.5°$ C at a pressure of $p_0 = 1$ atm. One British Thermal Unit (BTU) is the amount of heat needed to raise 1 lb. of $H_2O$ from $T_0 = 63°$ F to $T_1 = 64°$ F at a pressure of $p_0 = 1$ atm.

### 2.2.3 Work

In general we will write the differential element of work $đW$ done *by* the system as

$$đW = \sum_i F_i \, dX_i \; , \tag{2.5}$$

where $F_i$ is a *generalized force* and $dX_i$ a *generalized displacement*[3]. The generalized forces and displacements are themselves state variables, and by convention we will take the generalized forces to be *intensive* and the generalized displacements to be *extensive*. As an example, in a simple one-component system, we have $đW = p \, dV$. More generally, we write

$$đW = \overbrace{\big(p \, dV - \boldsymbol{H} \cdot d\boldsymbol{M} - \boldsymbol{E} \cdot d\boldsymbol{P} - \sigma \, dA + \ldots\big)}^{-\sum_j y_j \, dX_j} - \overbrace{\big(\mu_1 \, dN_1 + \mu_2 \, dN_2 + \ldots\big)}^{\sum_a \mu_a \, dN_a} \tag{2.6}$$

Here we distinguish between two types of work. The first involves changes in quantities such as volume, magnetization, electric polarization, area, *etc.* The conjugate forces $y_i$ applied *to* the system are then $-p$, the magnetic field $\boldsymbol{H}$, the electric field $\boldsymbol{E}$, the surface tension $\sigma$, respectively. The second type of work involves changes in the number of constituents of a given species. For example, energy is required in order to dissociate two hydrogen atoms in an $H_2$ molecule. The effect of such a process is $dN_{\mathrm{H}_2} = -1$ and $dN_{\mathrm{H}} = +2$.

As with heat, $đW$ is an inexact differential, and work $W$ is not a state variable, since it is path-dependent. There is no 'work function' $W(T, p, V)$.

### 2.2.4 Pressure and Temperature

The units of pressure ($p$) are force per unit area. The SI unit is the Pascal (Pa): $1 \, \mathrm{Pa} = 1 \, \mathrm{N/m^2} = 1 \, \mathrm{kg/m \, s^2}$. Other units of pressure we will encounter:

$$\begin{aligned} 1 \, \mathrm{bar} &\equiv 10^5 \, \mathrm{Pa} \\ 1 \, \mathrm{atm} &\equiv 1.01325 \times 10^5 \, \mathrm{Pa} \\ 1 \, \mathrm{torr} &\equiv 133.3 \, \mathrm{Pa} \, . \end{aligned}$$

Temperature ($T$) has a very precise definition from the point of view of statistical mechanics, as we shall see. Many physical properties depend on the temperature – such properties are called *thermometric properties*. For example, the resistivity of a metal $\rho(T, p)$ or the number density of a gas $n(T, p)$ are both thermometric properties, and can be used to define a temperature scale. Consider the device known as the 'constant volume gas thermometer' depicted in Fig. 2.3, in which the volume or pressure of a gas may be used to measure temperature. The gas is assumed to be in equilibrium at some pressure $p$, volume $V$, and temperature $T$. An incompressible fluid of density $\varrho$ is used to measure the pressure difference $\Delta p = p - p_0$, where $p_0$ is the ambient pressure at the top of the reservoir:

$$p - p_0 = \varrho g (h_2 - h_1) \; , \tag{2.7}$$

where $g$ is the acceleration due to gravity. The height $h_1$ of the left column of fluid in the U-tube provides a measure of the change in the volume of the gas:

$$V(h_1) = V(0) - A h_1 \; , \tag{2.8}$$

where $A$ is the (assumed constant) cross-sectional area of the left arm of the U-tube. The device can operate in two modes:

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[3] We use the symbol $đ$ in the differential $đW$ to indicate that this is not an exact differential. More on this in section 2.4 below.

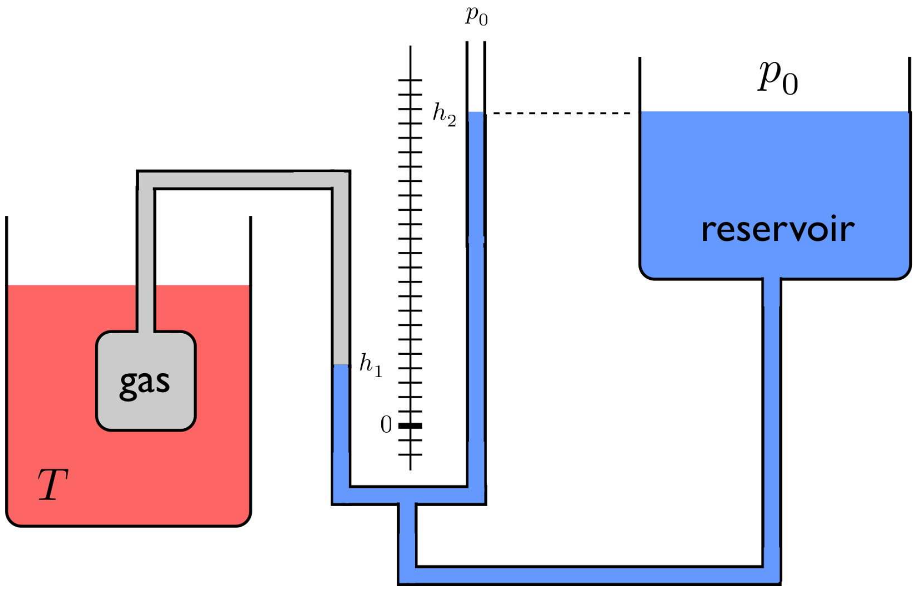

Figure 2.3: The constant volume gas thermometer. The gas is placed in thermal contact with an object of temperature $T$. An incompressible fluid of density $\varrho$ is used to measure the pressure difference $\Delta p = p_{\text{gas}} - p_0$.

- Constant pressure mode : The height of the reservoir is adjusted so that the height difference $h_2 - h_1$ is held constant. This fixes the pressure $p$ of the gas. The gas volume still varies with temperature $T$, and we can define

  $$\frac{T}{T_{\text{ref}}} = \frac{V}{V_{\text{ref}}} \ , \tag{2.9}$$

  where $T_{\text{ref}}$ and $V_{\text{ref}}$ are the reference temperature and volume, respectively.

- Constant volume mode : The height of the reservoir is adjusted so that $h_1 = 0$, hence the volume of the gas is held fixed, and the pressure varies with temperature. We then define

  $$\frac{T}{T_{\text{ref}}} = \frac{p}{p_{\text{ref}}} \ , \tag{2.10}$$

  where $T_{\text{ref}}$ and $p_{\text{ref}}$ are the reference temperature and pressure, respectively.

What should we use for a reference? One might think that a pot of boiling water will do, but anyone who has gone camping in the mountains knows that water boils at lower temperatures at high altitude (lower pressure). This phenomenon is reflected in the *phase diagram* for $H_2O$, depicted in Fig. 2.4. There are two special points in the phase diagram, however. One is the *triple point*, where the solid, liquid, and vapor (gas) phases all coexist. The second is the *critical point*, which is the terminus of the curve separating liquid from gas. At the critical point, the *latent heat of transition* between liquid and gas phases vanishes (more on this later on). The triple point temperature $T_{\text{t}}$ at thus *unique* and is *by definition* $T_{\text{t}} = 273.16\,\text{K}$. The pressure at the triple point is $611.7\,\text{Pa} = 6.056 \times 10^{-3}\,\text{atm}$.

A question remains: are the two modes of the thermometer compatible? *E.g.* it we boil water at $p = p_0 = 1\,\text{atm}$, do they yield the same value for $T$? And what if we use a different gas in our measurements? In fact, all these measurements will in general be *incompatible*, yielding different results for the temperature $T$. However, in the limit that we use a very low density gas, all the results converge. This is because all low density gases behave as *ideal gases*, and obey the ideal gas equation of state $pV = Nk_{\text{B}}T$.

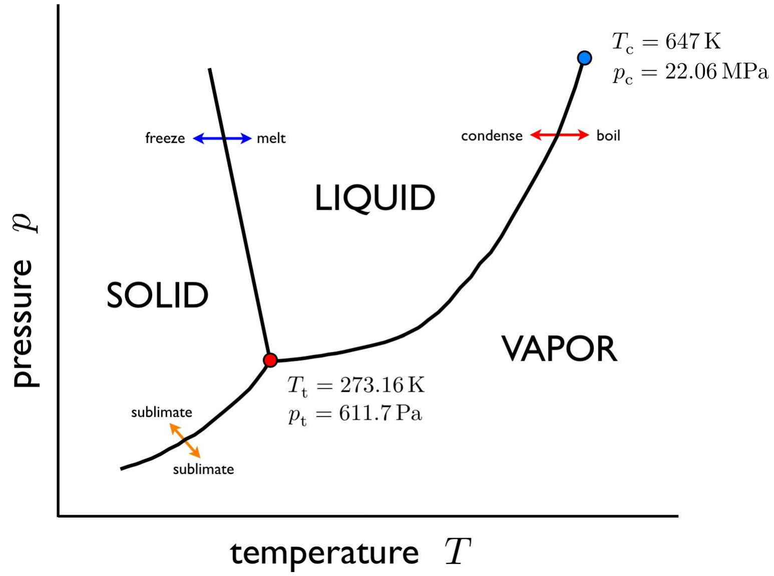

Figure 2.4: A sketch of the phase diagram of $H_2O$ (water). Two special points are identified: the triple point $(T_t, p_t)$ at which there is three phase coexistence, and the critical point $(T_c, p_c)$, where the latent heat of transformation from liquid to gas vanishes. Not shown are transitions between several different solid phases.

### 2.2.5 Standard temperature and pressure

It is customary in the physical sciences to define certain standard conditions with respect to which any arbitrary conditions may be compared. In thermodynamics, there is a notion of *standard temperature and pressure*, abbreviated STP. Unfortunately, there are two *different* definitions of STP currently in use, one from the International Union of Pure and Applied Chemistry (IUPAC), and the other from the U.S. National Institute of Standards and Technology (NIST). The two standards are:

$$\begin{aligned}\text{IUPAC} &: T_0 = 0^\circ\,\mathrm{C} = 273.15\,\mathrm{K} \quad , \quad p_0 = 10^5\,\mathrm{Pa}\\ \text{NIST} &: T_0 = 20^\circ\,\mathrm{C} = 293.15\,\mathrm{K} \quad , \quad p_0 = 1\,\mathrm{atm} = 1.01325 \times 10^5\,\mathrm{Pa}\end{aligned}$$

To make matters worse, in the past it was customary to define STP as $T_0 = 0^\circ\,\mathrm{C}$ and $p_0 = 1\,\mathrm{atm}$. We will use the NIST definition in this course. Unless I slip and use the IUPAC definition. Figuring out what I mean by STP will keep you on your toes.

The volume of one mole of ideal gas at STP is then

$$V = \frac{N_{\mathrm{A}} k_{\mathrm{B}} T_0}{p_0} = \begin{cases} 22.711\,\ell & \text{(IUPAC)} \\ 24.219\,\ell & \text{(NIST)}\ , \end{cases} \tag{2.11}$$

where $1\,\ell = 10^6\,\mathrm{cm}^3 = 10^{-3}\,\mathrm{m}^3$ is one liter. Under the old definition of STP as $T_0 = 0^\circ\,\mathrm{C}$ and $p_0 = 1\,\mathrm{atm}$, the volume of one mole of gas at STP is $22.414\,\ell$, which is a figure I remember from my 10th grade chemistry class with Mr. Lawrence.

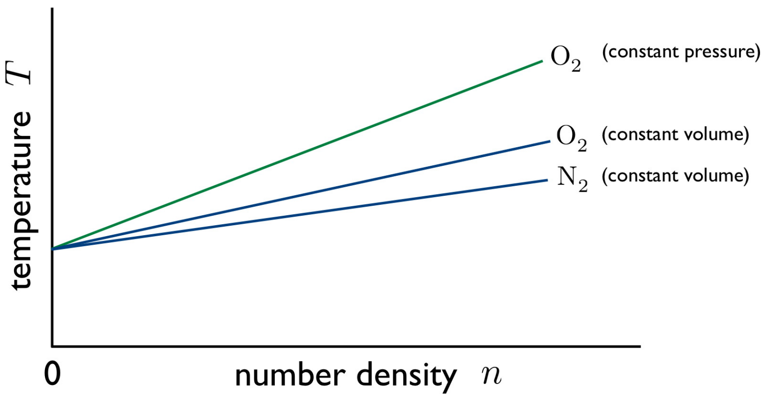

Figure 2.5: As the gas density tends to zero, the readings of the constant volume gas thermometer converge.

## 2.3 The Zeroth Law of Thermodynamics

Equilibrium is established by the exchange of energy, volume, or particle number between different systems or subsystems:

$$\begin{aligned} &\text{energy exchange} && \Longrightarrow && T = \text{ constant} && \Longrightarrow && \text{thermal equilibrium} \\ &\text{volume exchange} && \Longrightarrow && p = \text{ constant} && \Longrightarrow && \text{mechanical equilibrium} \\ &\text{particle exchange} && \Longrightarrow && \mu = \text{ constant} && \Longrightarrow && \text{chemical equilibrium} \end{aligned}$$

Equilibrium is transitive, so

> If A is in equilibrium with B, and B is in equilibrium with C, then A is in equilibrium with C.

This known as the Zeroth Law of Thermodynamics[4].

## 2.4 Mathematical Interlude : Exact and Inexact Differentials

The differential

$$dF = \sum_{i=1}^{k} A_i \, dx_i \tag{2.12}$$

is called *exact* if there is a function $F(x_1, \ldots, x_k)$ whose differential gives the right hand side of eqn. 2.12. In this case, we have

$$A_i = \frac{\partial F}{\partial x_i} \qquad \Longleftrightarrow \qquad \frac{\partial A_i}{\partial x_j} = \frac{\partial A_j}{\partial x_i} \quad \forall \, i, j \; . \tag{2.13}$$

---

[4] As we shall see further below, thermomechanical equilibrium in fact leads to constant $p/T$, and thermochemical equilibrium to constant $\mu/T$. If there is thermal equilibrium, then $T$ is already constant, and so thermomechanical and thermochemical equilibria then guarantee the constancy of $p$ and $\mu$.

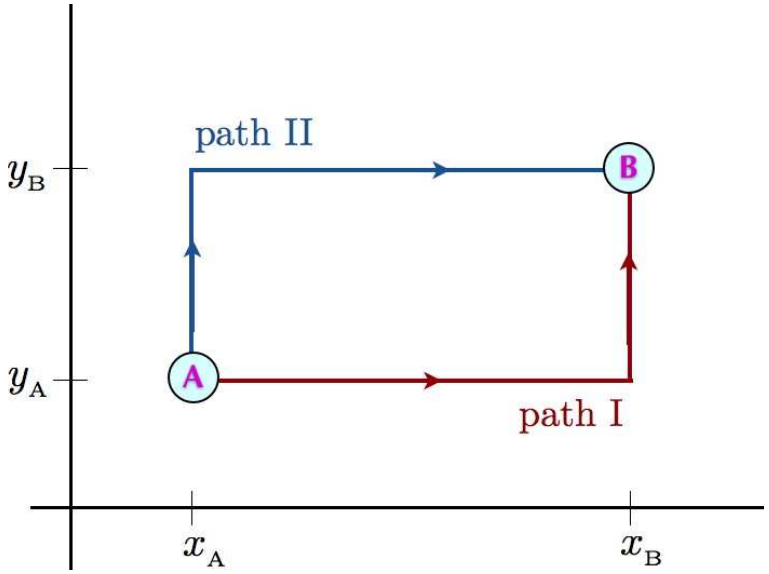

Figure 2.6: Two distinct paths with identical endpoints.

For exact differentials, the integral between fixed endpoints is path-independent:

$$\int_A^B dF = F(x_1^B, \ldots, x_k^B) - F(x_1^A, \ldots, x_k^A) \ , \tag{2.14}$$

from which it follows that the integral of $dF$ around any closed path must vanish:

$$\oint dF = 0 \ . \tag{2.15}$$

When the cross derivatives are not identical, *i.e.* when $\partial A_i / \partial x_j \neq \partial A_j / \partial x_i$, the differential is *inexact*. In this case, the integral of $dF$ is path dependent, and does not depend solely on the endpoints.

As an example, consider the differential

$$dF = K_1 \, y \, dx + K_2 \, x \, dy \ . \tag{2.16}$$

Let's evaluate the integral of $dF$, which is the work done, along each of the two paths in Fig. 2.6:

$$W^{(\mathrm{I})} = K_1 \int_{x_A}^{x_B} dx \, y_A + K_2 \int_{y_A}^{y_B} dy \, x_B = K_1 \, y_A \, (x_B - x_A) + K_2 \, x_B \, (y_B - y_A) \tag{2.17}$$

$$W^{(\mathrm{II})} = K_1 \int_{x_A}^{x_B} dx \, y_B + K_2 \int_{y_A}^{y_B} dy \, x_A = K_1 \, y_B \, (x_B - x_A) + K_2 \, x_A \, (y_B - y_A) \ . \tag{2.18}$$

Note that in general $W^{(\mathrm{I})} \neq W^{(\mathrm{II})}$. Thus, if we start at point A, the kinetic energy at point B will depend on the path taken, since the work done is path-dependent.

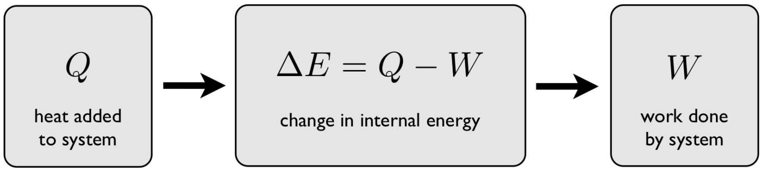

Figure 2.7: The first law of thermodynamics is a statement of energy conservation.

The difference between the work done along the two paths is

$$W^{(\mathrm{I})} - W^{(\mathrm{II})} = \oint dF = (K_2 - K_1)\,(x_{\mathrm{B}} - x_{\mathrm{A}})\,(y_{\mathrm{B}} - y_{\mathrm{A}}) \ . \tag{2.19}$$

Thus, we see that if $K_1 = K_2$, the work is the same for the two paths. In fact, if $K_1 = K_2$, the work would be path-independent, and would depend only on the endpoints. This is true for *any* path, and not just piecewise linear paths of the type depicted in Fig. 2.6. Thus, if $K_1 = K_2$, we are justified in using the notation $dF$ for the differential in eqn. 2.16; explicitly, we then have $F = K_1\, xy$. However, if $K_1 \neq K_2$, the differential is inexact, and we will henceforth write $\text{đ}F$ in such cases.

## 2.5 The First Law of Thermodynamics

### 2.5.1 Conservation of energy

The first law is a statement of energy conservation, and is depicted in Fig. 2.7. It says, quite simply, that during a thermodynamic process, the change in a system's internal energy $E$ is given by the heat energy $Q$ added *to* the system, minus the work $W$ done *by* the system:

$$\Delta E = Q - W \ . \tag{2.20}$$

The differential form of this, the First Law of Thermodynamics, is

$$dE = \text{đ}Q - \text{đ}W \ . \tag{2.21}$$

We use the symbol $\text{đ}$ in the differentials $\text{đ}Q$ and $\text{đ}W$ to remind us that these are inexact differentials. The energy $E$, however, is a state function, hence $dE$ is an exact differential.

Consider a volume $V$ of fluid held in a flask, initially at temperature $T_0$, and held at atmospheric pressure. The internal energy is then $E_0 = E(T_0, p, V)$. Now let us contemplate changing the temperature in two different ways. The first method (A) is to place the flask on a hot plate until the temperature of the fluid rises to a value $T_1$. The second method (B) is to stir the fluid vigorously. In the first case, we add heat $Q_{\mathrm{A}} > 0$ but no work is done, so $W_{\mathrm{A}} = 0$. In the second case, if we thermally insulate the flask and use a stirrer of very low thermal conductivity, then no heat is added, *i.e.* $Q_{\mathrm{B}} = 0$. However, the stirrer does work $-W_{\mathrm{B}} > 0$ on the fluid (remember $W$ is the work done by the system). If we end up at the same temperature $T_1$, then the final energy is $E_1 = E(T_1, p, V)$ in both cases. We then have

$$\Delta E = E_1 - E_0 = Q_{\mathrm{A}} = -W_{\mathrm{B}} \ . \tag{2.22}$$

It also follows that for any cyclic transformation, where the state variables are the same at the beginning and the end, we have

$$\Delta E_{\mathrm{cyclic}} = Q - W = 0 \quad \Longrightarrow \quad Q = W \quad \text{(cyclic)} \ . \tag{2.23}$$

### 2.5.2 Single component systems

A single component system is specified by three state variables. In many applications, the total number of particles $N$ is conserved, so it is useful to take $N$ as one of the state variables. The remaining two can be $(T, V)$ or $(T, p)$ or $(p, V)$. The differential form of the first law says

$$\begin{aligned} dE &= đQ - đW \\ &= đQ - p\,dV + \mu\,dN \ . \end{aligned} \tag{2.24}$$

The quantity $\mu$ is called the *chemical potential*. Here we shall be interested in the case $dN = 0$ so the last term will not enter into our considerations. We ask: how much heat is required in order to make an infinitesimal change in temperature, pressure, or volume? We start by rewriting eqn. 2.24 as

$$đQ = dE + p\,dV - \mu\,dN \ . \tag{2.25}$$

We now must roll up our sleeves and do some work with partial derivatives.

• $(T, V, N)$ systems : If the state variables are $(T, V, N)$, we write

$$dE = \left(\frac{\partial E}{\partial T}\right)_{V,N} dT + \left(\frac{\partial E}{\partial V}\right)_{T,N} dV + \left(\frac{\partial E}{\partial N}\right)_{T,V} dN \ . \tag{2.26}$$

Then

$$đQ = \left(\frac{\partial E}{\partial T}\right)_{V,N} dT + \left[\left(\frac{\partial E}{\partial V}\right)_{T,N} + p\right] dV + \left[\left(\frac{\partial E}{\partial N}\right)_{T,V} - \mu\right] dN \ . \tag{2.27}$$

• $(T, p, N)$ systems : If the state variables are $(T, p, N)$, we write

$$dE = \left(\frac{\partial E}{\partial T}\right)_{p,N} dT + \left(\frac{\partial E}{\partial p}\right)_{T,N} dp + \left(\frac{\partial E}{\partial N}\right)_{T,p} dN \ . \tag{2.28}$$

We also write

$$dV = \left(\frac{\partial V}{\partial T}\right)_{p,N} dT + \left(\frac{\partial V}{\partial p}\right)_{T,N} dp + \left(\frac{\partial V}{\partial N}\right)_{T,p} dN \ . \tag{2.29}$$

Then

$$\begin{aligned} đQ = &\left[\left(\frac{\partial E}{\partial T}\right)_{p,N} + p\left(\frac{\partial V}{\partial T}\right)_{p,N}\right] dT + \left[\left(\frac{\partial E}{\partial p}\right)_{T,N} + p\left(\frac{\partial V}{\partial p}\right)_{T,N}\right] dp \\ &+ \left[\left(\frac{\partial E}{\partial N}\right)_{T,p} + p\left(\frac{\partial V}{\partial N}\right)_{T,p} - \mu\right] dN \ . \end{aligned} \tag{2.30}$$

• $(p, V, N)$ systems : If the state variables are $(p, V, N)$, we write

$$dE = \left(\frac{\partial E}{\partial p}\right)_{V,N} dp + \left(\frac{\partial E}{\partial V}\right)_{p,N} dV + \left(\frac{\partial E}{\partial N}\right)_{p,V} dN \ . \tag{2.31}$$

Then

$$đQ = \left(\frac{\partial E}{\partial p}\right)_{V,N} dp + \left[\left(\frac{\partial E}{\partial V}\right)_{p,N} + p\right] dV + \left[\left(\frac{\partial E}{\partial N}\right)_{p,V} - \mu\right] dN \ . \tag{2.32}$$

| SUBSTANCE | $c_p$ (J/mol K) | $\tilde{c}_p$ (J/g K) | SUBSTANCE | $c_p$ (J/mol K) | $\tilde{c}_p$ (J/g K) |
|---|---|---|---|---|---|
| Air | 29.07 | 1.01 | $H_2O$ (25° C) | 75.34 | 4.181 |
| Aluminum | 24.2 | 0.897 | $H_2O$ ($100^\circ_+$ C) | 37.47 | 2.08 |
| Copper | 24.47 | 0.385 | Iron | 25.1 | 0.450 |
| $CO_2$ | 36.94 | 0.839 | Lead | 26.4 | 0.127 |
| Diamond | 6.115 | 0.509 | Lithium | 24.8 | 3.58 |
| Ethanol | 112 | 2.44 | Neon | 20.786 | 1.03 |
| Gold | 25.42 | 0.129 | Oxygen | 29.38 | 0.918 |
| Helium | 20.786 | 5.193 | Paraffin (wax) | 900 | 2.5 |
| Hydrogen | 28.82 | 5.19 | Uranium | 27.7 | 0.116 |
| $H_2O$ ($-10^\circ$ C) | 38.09 | 2.05 | Zinc | 25.3 | 0.387 |

Table 2.1: Specific heat (at $25^\circ$ C, unless otherwise noted) of some common substances. (*Source: Wikipedia*.)

The *heat capacity* of a body, $C$, is by definition the ratio $\text{đ}Q/dT$ of the amount of heat absorbed by the body to the associated infinitesimal change in temperature $dT$. The heat capacity will in general be different if the body is heated at constant volume or at constant pressure. Setting $dV = 0$ gives, from eqn. 2.27,

$$C_{V,N} = \left(\frac{\text{đ}Q}{dT}\right)_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N} \ . \tag{2.33}$$

Similarly, if we set $dp = 0$, then eqn. 2.30 yields

$$C_{p,N} = \left(\frac{\text{đ}Q}{dT}\right)_{p,N} = \left(\frac{\partial E}{\partial T}\right)_{p,N} + p\left(\frac{\partial V}{\partial T}\right)_{p,N} \ . \tag{2.34}$$

Unless explicitly stated as otherwise, we shall assume that $N$ is fixed, and will write $C_V$ for $C_{V,N}$ and $C_p$ for $C_{p,N}$.

The units of heat capacity are energy divided by temperature, *e.g.* J/K. The heat capacity is an extensive quantity, scaling with the size of the system. If we divide by the number of moles $N/N_{\text{A}}$, we obtain the *molar heat capacity*, sometimes called the *molar specific heat*: $c = C/\nu$, where $\nu = N/N_{\text{A}}$ is the number of moles of substance. Specific heat is also sometimes quoted in units of heat capacity per gram of substance. We shall define

$$\tilde{c} = \frac{C}{mN} = \frac{c}{M} = \frac{\text{heat capacity per mole}}{\text{mass per mole}} \ . \tag{2.35}$$

Here $m$ is the mass per particle and $M$ is the mass per mole: $M = N_{\text{A}}\, m$.

Suppose we raise the temperature of a body from $T = T_{\text{A}}$ to $T = T_{\text{B}}$. How much heat is required? We have

$$Q = \int\limits_{T_{\text{A}}}^{T_{\text{B}}} dT\, C(T) \ , \tag{2.36}$$

where $C = C_V$ or $C = C_p$ depending on whether volume or pressure is held constant. For ideal gases, as we shall discuss below, $C(T)$ is constant, and thus

$$Q = C(T_{\text{B}} - T_{\text{A}}) \quad \Longrightarrow \quad T_{\text{B}} = T_{\text{A}} + \frac{Q}{C} \ . \tag{2.37}$$

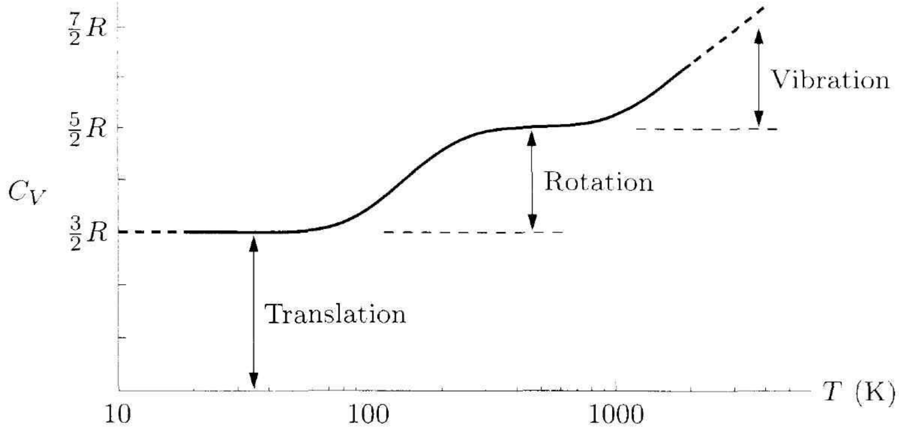

Figure 2.8: Heat capacity $C_V$ for one mole of hydrogen ($H_2$) gas. At the lowest temperatures, only translational degrees of freedom are relevant, and $f = 3$. At around 200 K, two rotational modes are excitable and $f = 5$. Above 1000 K, the vibrational excitations begin to contribute. Note the logarithmic temperature scale. (Data from H. W. Wooley *et al.*, *Jour. Natl. Bureau of Standards*, **41**, 379 (1948).)

In metals at very low temperatures one finds $C = \gamma T$, where $\gamma$ is a constant[5]. We then have

$$Q = \int_{T_A}^{T_B} dT\, C(T) = \tfrac{1}{2}\gamma\big(T_B^2 - T_A^2\big) \tag{2.38}$$

$$T_B = \sqrt{T_A^2 + 2\gamma^{-1}Q}\ . \tag{2.39}$$

### 2.5.3 Ideal gases

The ideal gas equation of state is $pV = Nk_BT$. In order to invoke the formulae in eqns. 2.27, 2.30, and 2.32, we need to know the state function $E(T,V,N)$. A landmark experiment by Joule in the mid-19th century established that the energy of a low density gas is independent of its volume[6]. Essentially, a gas at temperature $T$ was allowed to freely expand from one volume $V$ to a larger volume $V' > V$, with no added heat $Q$ and no work $W$ done. Therefore the energy cannot change. What Joule found was that the temperature also did not change. This means that $E(T,V,N) = E(T,N)$ cannot be a function of the volume.

Since $E$ is extensive, we conclude that

$$E(T,V,N) = \nu\,\varepsilon(T)\ , \tag{2.40}$$

where $\nu = N/N_A$ is the number of moles of substance. Note that $\nu$ is an extensive variable. From eqns. 2.33 and 2.34, we conclude

$$C_V(T) = \nu\,\varepsilon'(T) \qquad , \qquad C_p(T) = C_V(T) + \nu R\ , \tag{2.41}$$

where we invoke the ideal gas law to obtain the second of these. Empirically it is found that $C_V(T)$ is temperature independent over a wide range of $T$, far enough from boiling point. We can then write $C_V = \nu\, c_V$, where $\nu \equiv N/N_A$ is the number of moles, and where $c_V$ is the molar heat capacity. We then have

$$c_p = c_V + R\ , \tag{2.42}$$

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[5] In most metals, the difference between $C_V$ and $C_p$ is negligible.

[6] See the description in E. Fermi, *Thermodynamics*, pp. 22-23.

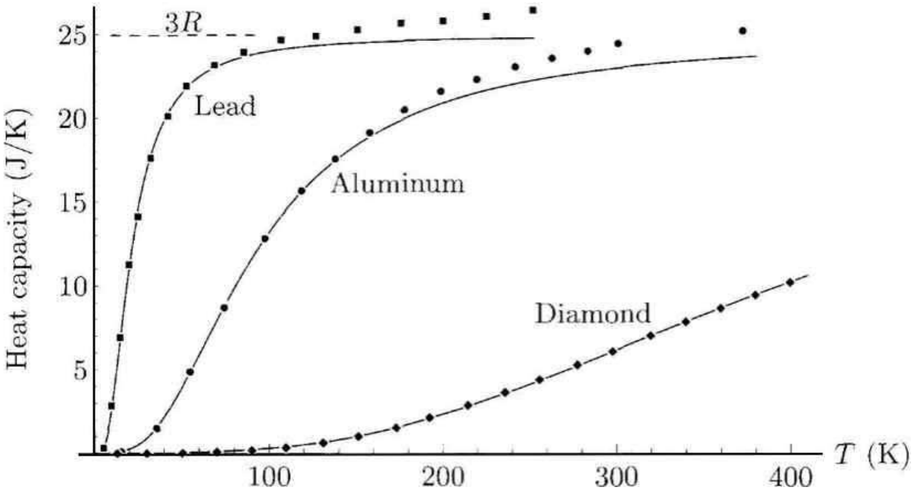


Figure 2.9: Molar heat capacities $c_V$ for three solids. The solid curves correspond to the predictions of the Debye model, which we shall discuss later.

where $R = N_{\rm A} k_{\rm B} = 8.31457\,{\rm J/mol\,K}$ is the *gas constant*. We denote by $\gamma = c_p/c_V$ the ratio of specific heat at constant pressure and at constant volume.

From the kinetic theory of gases, one can show that

$$\begin{aligned}
\text{monatomic gases:}\quad & c_V = \tfrac{3}{2}R \quad , \quad c_p = \tfrac{5}{2}R \quad , \quad \gamma = \tfrac{5}{3}\\
\text{diatomic gases:}\quad & c_V = \tfrac{5}{2}R \quad , \quad c_p = \tfrac{7}{2}R \quad , \quad \gamma = \tfrac{7}{5}\\
\text{polyatomic gases:}\quad & c_V = 3R \quad , \quad c_p = 4R \quad , \quad \gamma = \tfrac{4}{3}\ .
\end{aligned}$$

**Digression : kinetic theory of gases**

We will conclude in general from noninteracting classical statistical mechanics that the specific heat of a substance is $c_v = \frac{1}{2} f R$, where $f$ is the number of phase space coordinates, per particle, for which there is a quadratic kinetic or potential energy function. For example, a point particle has three translational degrees of freedom, and the kinetic energy is a quadratic function of their conjugate momenta: $H_0 = (p_x^2 + p_y^2 + p_z^2)/2m$. Thus, $f = 3$. Diatomic molecules have two additional rotational degrees of freedom – we don't count rotations about the symmetry axis – and their conjugate momenta also appear quadratically in the kinetic energy, leading to $f = 5$. For polyatomic molecules, all three Euler angles and their conjugate momenta are in play, and $f = 6$.

The reason that $f = 5$ for diatomic molecules rather than $f = 6$ is due to quantum mechanics. While translational eigenstates form a continuum, or are quantized in a box with $\Delta k_\alpha = 2\pi/L_\alpha$ being very small, since the dimensions $L_\alpha$ are macroscopic, angular momentum, and hence rotational kinetic energy, is quantized. For rotations about a principal axis with very low moment of inertia $I$, the corresponding energy scale $\hbar^2/2I$ is very large, and a high temperature is required in order to thermally populate these states. Thus, degrees of freedom with a quantization energy on the order or greater than $\varepsilon_0$ are 'frozen out' for temperatures $T \lesssim \varepsilon_0/k_{\rm B}$.

In solids, each atom is effectively connected to its neighbors by springs; such a potential arises from quantum mechanical and electrostatic consideration of the interacting atoms. Thus, each degree of freedom contributes to the potential energy, and its conjugate momentum contributes to the kinetic energy. This results in $f = 6$. Assuming only lattice vibrations, then, the high temperature limit for $c_V(T)$ for any solid is predicted to be $3R = 24.944\,{\rm J/mol\,K}$. This is called the *Dulong-Petit law*. The high temperature limit is reached above the so-called *Debye* *temperature*, which is roughly proportional to the melting temperature of the solid.

In table 2.1, we list $c_p$ and $\tilde{c}_p$ for some common substances at $T = 25^\circ\,\mathrm{C}$ (unless otherwise noted). Note that $c_p$ for the monatomic gases He and Ne is to high accuracy given by the value from kinetic theory, $c_p = \frac{5}{2}R = 20.7864\,\mathrm{J/mol\,K}$. For the diatomic gases oxygen ($O_2$) and air (mostly $N_2$ and $O_2$), kinetic theory predicts $c_p = \frac{7}{2}R = 29.10$, which is close to the measured values. Kinetic theory predicts $c_p = 4R = 33.258$ for polyatomic gases; the measured values for $CO_2$ and $H_2O$ are both about 10% higher.

### 2.5.4 Adiabatic transformations of ideal gases

Assuming $dN = 0$ and $E = \nu\,\varepsilon(T)$, eqn. 2.27 tells us that

$$đQ = C_V\,dT + p\,dV \ . \tag{2.43}$$

Invoking the ideal gas law to write $p = \nu RT/V$, and remembering $C_V = \nu\,c_V$, we have, setting $đQ = 0$,

$$\frac{dT}{T} + \frac{R}{c_V}\,\frac{dV}{V} = 0 \ . \tag{2.44}$$

We can immediately integrate to obtain

$$đQ = 0 \quad \Longrightarrow \quad \begin{cases} TV^{\gamma-1} = \text{constant} \\ pV^{\gamma} = \text{constant} \\ T^{\gamma}p^{1-\gamma} = \text{constant} \end{cases} \tag{2.45}$$

where the second two equations are obtained from the first by invoking the ideal gas law. These are all *adiabatic equations of state*. Note the difference between the adiabatic equation of state $d(pV^\gamma) = 0$ and the isothermal equation of state $d(pV) = 0$. Equivalently, we can write these three conditions as

$$V^2\,T^f = V_0^2\,T_0^f \qquad , \qquad p^f\,V^{f+2} = p_0^f\,V_0^{f+2} \qquad , \qquad T^{f+2}\,p^{-2} = T_0^{f+2}\,p_0^{-2} \ . \tag{2.46}$$

It turns out that air is a rather poor conductor of heat. This suggests the following model for an *adiabatic atmosphere*. The hydrostatic pressure decrease associated with an increase $dz$ in height is $dp = -\varrho g\,dz$, where $\varrho$ is the density and $g$ the acceleration due to gravity. Assuming the gas is ideal, the density can be written as $\varrho = Mp/RT$, where $M$ is the molar mass. Thus,

$$\frac{dp}{p} = -\frac{Mg}{RT}\,dz \ . \tag{2.47}$$

If the height changes are adiabatic, then, from $d(T^\gamma p^{1-\gamma}) = 0$, we have

$$dT = \frac{\gamma-1}{\gamma}\,\frac{T dp}{p} = -\frac{\gamma-1}{\gamma}\,\frac{Mg}{R}\,dz \ , \tag{2.48}$$

with the solution

$$T(z) = T_0 - \frac{\gamma-1}{\gamma}\,\frac{Mg}{R}\,z = \left(1 - \frac{\gamma-1}{\gamma}\,\frac{z}{\lambda}\right) T_0 \ , \tag{2.49}$$

where $T_0 = T(0)$ is the temperature at the earth's surface, and

$$\lambda = \frac{RT_0}{Mg} \ . \tag{2.50}$$

With $M = 28.88\,\mathrm{g}$ and $\gamma = \frac{7}{5}$ for air, and assuming $T_0 = 293\,\mathrm{K}$, we find $\lambda = 8.6\,\mathrm{km}$, and $dT/dz = -(1-\gamma^{-1})\,T_0/\lambda = -9.7\,\mathrm{K/km}$. Note that in this model the atmosphere ends at a height $z_{\mathrm{max}} = \gamma\lambda/(\gamma-1) = 30\,\mathrm{km}$.

Again invoking the adiabatic equation of state, we can find $p(z)$:

$$\frac{p(z)}{p_0} = \left(\frac{T}{T_0}\right)^{\frac{\gamma}{\gamma-1}} = \left(1 - \frac{\gamma-1}{\gamma}\,\frac{z}{\lambda}\right)^{\frac{\gamma}{\gamma-1}} \tag{2.51}$$

Recall that

$$e^x = \lim_{k\to\infty}\left(1 + \frac{x}{k}\right)^k . \tag{2.52}$$

Thus, in the limit $\gamma \to 1$, where $k = \gamma/(\gamma-1) \to \infty$, we have $p(z) = p_0\,\exp(-z/\lambda)$. Finally, since $\varrho \propto p/T$ from the ideal gas law, we have

$$\frac{\varrho(z)}{\varrho_0} = \left(1 - \frac{\gamma-1}{\gamma}\,\frac{z}{\lambda}\right)^{\frac{1}{\gamma-1}} . \tag{2.53}$$

### 2.5.5 Adiabatic free expansion

Consider the situation depicted in Fig. 2.10. A quantity ($\nu$ moles) of gas in equilibrium at temperature $T$ and volume $V_1$ is allowed to expand freely into an evacuated chamber of volume $V_2$ by the removal of a barrier. Clearly no work is done on or by the gas during this process, hence $W = 0$. If the walls are everywhere insulating, so that no heat can pass through them, then $Q = 0$ as well. The First Law then gives $\Delta E = Q - W = 0$, and there is no change in energy.

If the gas is ideal, then since $E(T,V,N) = Nc_V T$, then $\Delta E = 0$ gives $\Delta T = 0$, and there is no change in temperature. (If the walls are insulating against the passage of heat, they must also prevent the passage of particles, so $\Delta N = 0$.) There is of course a change in volume: $\Delta V = V_2$, hence there is a change in pressure. The initial pressure is $p = Nk_B T/V_1$ and the final pressure is $p' = Nk_B T/(V_1 + V_2)$.

If the gas is nonideal, then the temperature will in general change. Suppose, for example, that $E(T,V,N) = \alpha\, V^x\, N^{1-x}\, T^y$, where $\alpha$, $x$, and $y$ are constants. This form is properly extensive: if $V$ and $N$ double, then $E$ doubles. If the volume changes from $V$ to $V'$ under an adiabatic free expansion, then we must have, from $\Delta E = 0$,

$$\left(\frac{V}{V'}\right)^x = \left(\frac{T'}{T}\right)^y \qquad \Longrightarrow \qquad T' = T \cdot \left(\frac{V}{V'}\right)^{x/y} . \tag{2.54}$$

If $x/y > 0$, the temperature decreases upon the expansion. If $x/y < 0$, the temperature increases. Without an equation of state, we can't say what happens to the pressure.

Adiabatic free expansion of a gas is a *spontaneous process*, arising due to the natural internal dynamics of the system. It is also *irreversible*. If we wish to take the gas back to its original state, we must do work on it to compress it. If the gas is ideal, then the initial and final temperatures are identical, so we can place the system in thermal contact with a reservoir at temperature $T$ and follow a thermodynamic path along an isotherm. The work done *on the gas* during compression is then

$$\mathcal{W} = -Nk_B T \int\limits_{V_f}^{V_i} \frac{dV}{V} = Nk_B T\,\ln\!\left(\frac{V_f}{V_i}\right) = Nk_B T\,\ln\!\left(1 + \frac{V_2}{V_1}\right) \tag{2.55}$$

The work done *by the gas* is $W = \int p\,dV = -\mathcal{W}$. During the compression, heat energy $Q = W < 0$ is transferred to the gas from the reservoir. Thus, $\mathcal{Q} = \mathcal{W} > 0$ is given off by the gas to its environment.

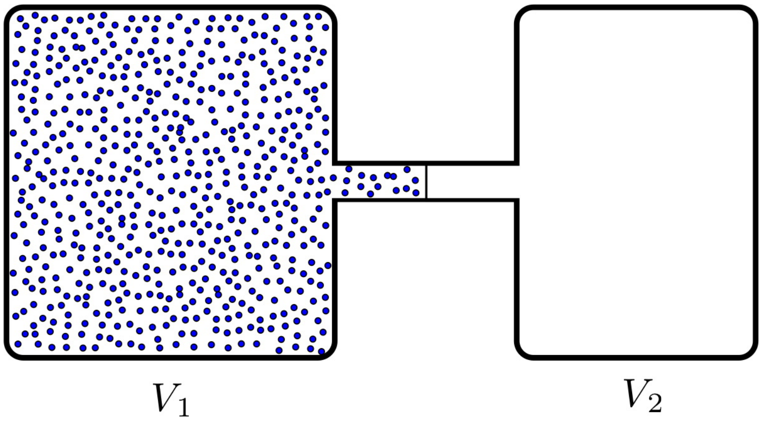


Figure 2.10: In the adiabatic free expansion of a gas, there is volume expansion with no work or heat exchange with the environment: $\Delta E = Q = W = 0$.

## 2.6 Heat Engines and the Second Law of Thermodynamics

### 2.6.1 There's no free lunch so quit asking

A *heat engine* is a device which takes a thermodynamic system through a repeated cycle which can be represented as a succession of equilibrium states: $\mathrm{A} \to \mathrm{B} \to \mathrm{C} \cdots \to \mathrm{A}$. The net result of such a cyclic process is to convert heat into mechanical work, or *vice versa*.

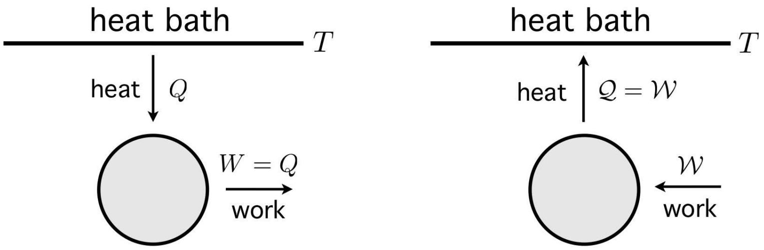
For a system in equilibrium at temperature $T$, there is a thermodynamically large amount of internal energy stored in the random internal motion of its constituent particles. Later, when we study statistical mechanics, we will see how each 'quadratic' degree of freedom in the Hamiltonian contributes $\frac{1}{2}k_{\mathrm{B}}T$ to the total internal energy. An immense body in equilibrium at temperature $T$ has an enormous heat capacity $C$, hence extracting a finite quantity of heat $Q$ from it results in a temperature change $\Delta T = -Q/C$ which is utterly negligible. Such a body is called a *heat bath*, or *thermal reservoir*. A *perfect engine* would, in each cycle, extract an amount of heat $Q$ from the bath and convert it into work. Since $\Delta E = 0$ for a cyclic process, the First Law then gives $W = Q$. This situation is depicted schematically in Fig. 2.11. One could imagine running this process virtually indefinitely, slowly sucking energy out of an immense heat bath, converting the random thermal motion of its constituent molecules into useful mechanical work. Sadly, this is not possible:

> *A transformation whose only final result is to extract heat from a source at fixed temperature and transform that heat into work is impossible.*

This is known as the *Postulate of Lord Kelvin*. It is equivalent to the *postulate of Clausius*,

> *A transformation whose only result is to transfer heat from a body at a given temperature to a body at higher temperature is impossible.*

These postulates which have been repeatedly validated by empirical observations, constitute the Second Law of Thermodynamics.



(a) a perfect engine (b) a perfect waste of time

Figure 2.11: A *perfect engine* would extract heat $Q$ from a thermal reservoir at some temperature $T$ and convert it into useful mechanical work $W$. This process is alas impossible, according to the Second Law of thermodynamics. The inverse process, where work $\mathcal{W}$ is converted into heat $\mathcal{Q}$, is always possible.

### 2.6.2 Engines and refrigerators

While it is not possible to convert heat into work with 100% efficiency, it is possible to transfer heat from one thermal reservoir to another one, at lower temperature, and to convert some of that heat into work. This is what an engine does. The energy accounting for one cycle of the engine is depicted in the left hand panel of Fig. 2.12. An amount of heat $Q_2 > 0$ is extracted- from the reservoir at temperature $T_2$. Since the reservoir is assumed to be enormous, its temperature change $\Delta T_2 = -Q_2/C_2$ is negligible, and its temperature remains constant – this is what it means for an object to be a reservoir. A lesser amount of heat, $\mathcal{Q}_1$, with $0 < \mathcal{Q}_1 < Q_2$, is deposited in a second reservoir at a lower temperature $T_1$. Its temperature change $\Delta T_1 = +\mathcal{Q}_1/C_1$ is also negligible. The difference $W = Q_2 - \mathcal{Q}_1$ is extracted as useful work. We define the *efficiency*, $\eta$, of the engine as the ratio of the work done to the heat extracted from the upper reservoir, per cycle:

$$\eta = \frac{W}{Q_2} = 1 - \frac{\mathcal{Q}_1}{Q_2} \ . \tag{2.56}$$

This is a natural definition of efficiency, since it will cost us fuel to maintain the temperature of the upper reservoir over many cycles of the engine. Thus, the efficiency is proportional to the ratio of the work done to the cost of the fuel.

A refrigerator works according to the same principles, but the process runs in reverse. An amount of heat $Q_1$ is extracted from the lower reservoir – the inside of our refrigerator – and is pumped into the upper reservoir. As Clausius' form of the Second Law asserts, it is impossible for this to be the only result of our cycle. Some amount of work $\mathcal{W}$ must be performed on the refrigerator in order for it to extract the heat $Q_1$. Since $\Delta E = 0$ for the cycle, a heat $\mathcal{Q}_2 = \mathcal{W} + Q_1$ must be deposited into the upper reservoir during each cycle. The analog of efficiency here is called the *coefficient of refrigeration*, $\kappa$, defined as

$$\kappa = \frac{Q_1}{\mathcal{W}} = \frac{Q_1}{\mathcal{Q}_2 - Q_1} \ . \tag{2.57}$$

Thus, $\kappa$ is proportional to the ratio of the heat extracted to the cost of electricity, per cycle.

Please note the deliberate notation here. I am using symbols $Q$ and $W$ to denote the heat supplied *to* the engine (or refrigerator) and the work done *by* the engine, respectively, and $\mathcal{Q}$ and $\mathcal{W}$ to denote the heat taken *from* the engine and the work done *on* the engine.

A perfect engine has $\mathcal{Q}_1 = 0$ and $\eta = 1$; a perfect refrigerator has $Q_1 = \mathcal{Q}_2$ and $\kappa = \infty$. Both violate the Second Law. Sadi Carnot[7] (1796 – 1832) realized that a *reversible* cyclic engine operating between two thermal reservoirs

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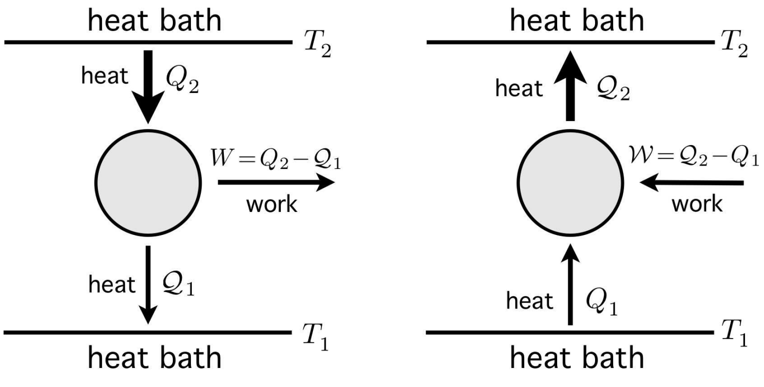
[7] Carnot died during cholera epidemic of 1832. His is one of the 72 names engraved on the Eiffel Tower.



(a) engine (b) refrigerator

Figure 2.12: An engine (left) extracts heat $Q_2$ from a reservoir at temperature $T_2$ and deposits a smaller amount of heat $\mathcal{Q}_1$ into a reservoir at a lower temperature $T_1$, during each cycle. The difference $W = Q_2 - \mathcal{Q}_1$ is transformed into mechanical work. A refrigerator (right) performs the inverse process, drawing heat $Q_1$ from a low temperature reservoir and depositing heat $\mathcal{Q}_2 = Q_1 + \mathcal{W}$ into a high temperature reservoir, where $\mathcal{W}$ is the mechanical (or electrical) work done per cycle.

must produce the maximum amount of work $W$, and that the amount of work produced is *independent of the material properties of the engine*. We call any such engine a *Carnot engine*.

The efficiency of a Carnot engine may be used to define a temperature scale. We know from Carnot's observations that the efficiency $\eta_{\rm C}$ can only be a function of the temperatures $T_1$ and $T_2$: $\eta_{\rm C} = \eta_{\rm C}(T_1, T_2)$. We can then define

$$\frac{T_1}{T_2} \equiv 1 - \eta_{\rm C}(T_1, T_2) \ . \tag{2.58}$$

Below, in §2.6.4, we will see that how, using an ideal gas as the 'working substance' of the Carnot engine, this temperature scale coincides precisely with the ideal gas temperature scale from §2.2.4.

### 2.6.3 Nothing beats a Carnot engine

The Carnot engine is the most efficient engine possible operating between two thermal reservoirs. To see this, let's suppose that an amazing wonder engine has an efficiency even greater than that of the Carnot engine. A key feature of the Carnot engine is its reversibility – we can just go around its cycle in the opposite direction, creating a Carnot refrigerator. Let's use our notional wonder engine to drive a Carnot refrigerator, as depicted in Fig. 2.13.

We assume that

$$\frac{W}{Q_2} = \eta_{\rm wonder} > \eta_{\rm Carnot} = \frac{\mathcal{W}'}{\mathcal{Q}_2'} \ . \tag{2.59}$$

But from the figure, we have $W = \mathcal{W}'$, and therefore the heat energy $\mathcal{Q}_2' - Q_2$ transferred *to* the upper reservoir is positive. From

$$W = Q_2 - \mathcal{Q}_1 = \mathcal{Q}_2' - Q_1' = \mathcal{W}' \ , \tag{2.60}$$

we see that this is equal to the heat energy extracted *from* the lower reservoir, since no external work is done on the system:

$$\mathcal{Q}_2' - Q_2 = Q_1' - \mathcal{Q}_1 > 0 \ . \tag{2.61}$$

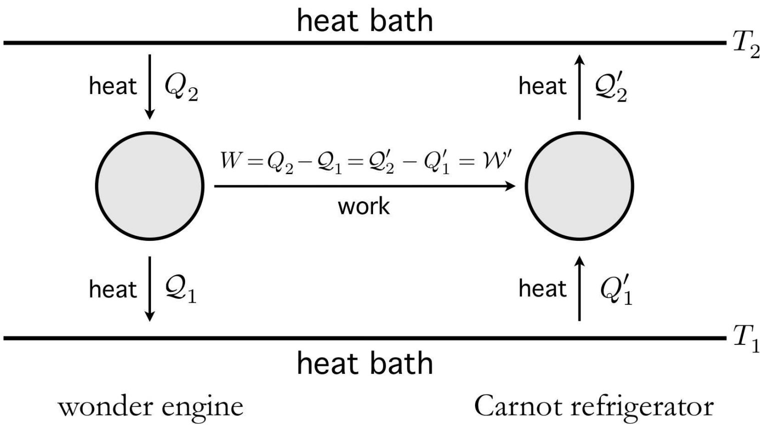


Figure 2.13: A wonder engine driving a Carnot refrigerator.

Therefore, the existence of the wonder engine entails a violation of the Second Law. Since the Second Law is correct – *Lord* Kelvin articulated it, and who are we to argue with a *Lord*? – the wonder engine cannot exist.

We further conclude that *all reversible engines running between two thermal reservoirs have the same efficiency, which is the efficiency of a Carnot engine.* For an irreversible engine, we must have

$$\eta = \frac{W}{Q_2} = 1 - \frac{\mathcal{Q}_1}{Q_2} \leq 1 - \frac{T_1}{T_2} = \eta_{\rm C} \ . \tag{2.62}$$

Thus,

$$\frac{Q_2}{T_2} - \frac{\mathcal{Q}_1}{T_1} \leq 0 \ . \tag{2.63}$$

### 2.6.4 The Carnot cycle

Let us now consider a specific cycle, known as the Carnot cycle, depicted in Fig. 2.14. The cycle consists of two adiabats and two isotherms. The work done per cycle is simply the area inside the curve on our $p - V$ diagram:

$$W = \oint p\, dV \ . \tag{2.64}$$

The gas inside our Carnot engine is called the 'working substance'. Whatever it may be, the system obeys the First Law,

$$dE = \text{đ}Q - \text{đ}W = \text{đ}Q - p\, dV \ . \tag{2.65}$$

We will now assume that the working material is an ideal gas, and we compute $W$ as well as $\mathcal{Q}_1$ and $Q_2$ to find the efficiency of this cycle. In order to do this, we will rely upon the ideal gas equations,

$$E = \frac{\nu RT}{\gamma - 1} \qquad , \qquad pV = \nu RT \ , \tag{2.66}$$

where $\gamma = c_p/c_v = 1 + \frac{2}{f}$, where $f$ is the effective number of molecular degrees of freedom contributing to the internal energy. Recall $f = 3$ for monatomic gases, $f = 5$ for diatomic gases, and $f = 6$ for polyatomic gases. The finite difference form of the first law is

$$\Delta E = E_{\rm f} - E_{\rm i} = Q_{\sf if} - W_{\sf if} \ , \tag{2.67}$$

where $\rm i$ denotes the initial state and $\rm f$ the final state.

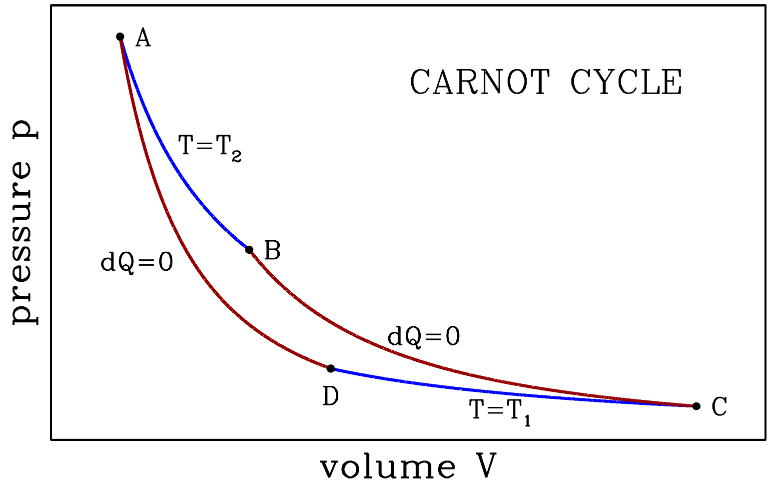


Figure 2.14: The Carnot cycle consists of two adiabats (dark red) and two isotherms (blue).

AB: This stage is an isothermal expansion at temperature $T_2$. It is the 'power stroke' of the engine. We have

$$W_{\rm AB} = \int\limits_{V_{\rm A}}^{V_{\rm B}} dV\,\frac{\nu RT_2}{V} = \nu RT_2\,\ln\left(\frac{V_{\rm B}}{V_{\rm A}}\right) \tag{2.68}$$

$$E_{\rm A} = E_{\rm B} = \frac{\nu RT_2}{\gamma-1}\ , \tag{2.69}$$

hence

$$Q_{\rm AB} = \Delta E_{\rm AB} + W_{\rm AB} = \nu RT_2\,\ln\left(\frac{V_{\rm B}}{V_{\rm A}}\right)\ . \tag{2.70}$$

BC: This stage is an adiabatic expansion. We have

$$Q_{\rm BC} = 0 \tag{2.71}$$

$$\Delta E_{\rm BC} = E_{\rm C} - E_{\rm B} = \frac{\nu R}{\gamma-1}\,(T_1 - T_2)\ . \tag{2.72}$$

The energy change is negative, and the heat exchange is zero, so the engine still does some work during this stage:

$$W_{\rm BC} = Q_{\rm BC} - \Delta E_{\rm BC} = \frac{\nu R}{\gamma-1}\,(T_2 - T_1)\ . \tag{2.73}$$

CD: This stage is an isothermal compression, and we may apply the analysis of the isothermal expansion, *mutatis mutandis*:

$$W_{\rm CD} = \int\limits_{V_{\rm C}}^{V_{\rm D}} dV\,\frac{\nu RT_2}{V} = \nu RT_1\,\ln\left(\frac{V_{\rm D}}{V_{\rm C}}\right) \tag{2.74}$$

$$E_{\rm C} = E_{\rm D} = \frac{\nu RT_1}{\gamma-1}\ , \tag{2.75}$$

hence

$$Q_{\rm CD} = \Delta E_{\rm CD} + W_{\rm CD} = \nu RT_1\,\ln\left(\frac{V_{\rm D}}{V_{\rm C}}\right)\ . \tag{2.76}$$

DA: This last stage is an adiabatic compression, and we may draw on the results from the adiabatic expansion in BC:

$$Q_{\rm DA} = 0 \tag{2.77}$$

$$\Delta E_{\rm DA} = E_{\rm D} - E_{\rm A} = \frac{\nu R}{\gamma - 1}\,(T_2 - T_1)\,. \tag{2.78}$$

The energy change is positive, and the heat exchange is zero, so work is done on the engine:

$$W_{\rm DA} = Q_{\rm DA} - \Delta E_{\rm DA} = \frac{\nu R}{\gamma - 1}\,(T_1 - T_2)\,. \tag{2.79}$$

We now add up all the work values from the individual stages to get for the cycle

$$\begin{aligned} W &= W_{\rm AB} + W_{\rm BC} + W_{\rm CD} + W_{\rm DA} \\ &= \nu R T_2 \,\ln\!\left(\frac{V_{\rm B}}{V_{\rm A}}\right) + \nu R T_1 \,\ln\!\left(\frac{V_{\rm D}}{V_{\rm C}}\right)\,. \end{aligned} \tag{2.80}$$

Since we are analyzing a cyclic process, we must have $\Delta E = 0$, we must have $Q = W$, which can of course be verified explicitly, by computing $Q = Q_{\rm AB} + Q_{\rm BC} + Q_{\rm CD} + Q_{\rm DA}$. To finish up, recall the adiabatic ideal gas equation of state, $d(TV^{\gamma-1}) = 0$. This tells us that

$$T_2\, V_{\rm B}^{\gamma-1} = T_1\, V_{\rm C}^{\gamma-1} \tag{2.81}$$

$$T_2\, V_{\rm A}^{\gamma-1} = T_1\, V_{\rm D}^{\gamma-1}\,. \tag{2.82}$$

Dividing these two equations, we find

$$\frac{V_{\rm B}}{V_{\rm A}} = \frac{V_{\rm C}}{V_{\rm D}}\,, \tag{2.83}$$

and therefore

$$W = \nu R (T_2 - T_1)\,\ln\!\left(\frac{V_{\rm B}}{V_{\rm A}}\right) \tag{2.84}$$

$$Q_{\rm AB} = \nu R T_2 \,\ln\!\left(\frac{V_{\rm B}}{V_{\rm A}}\right)\,. \tag{2.85}$$

Finally, the efficiency is given by the ratio of these two quantities:

$$\eta = \frac{W}{Q_{\rm AB}} = 1 - \frac{T_1}{T_2}\,. \tag{2.86}$$

### 2.6.5 The Stirling cycle

Many other engine cycles are possible. The Stirling cycle, depicted in Fig. 2.15, consists of two isotherms and two isochores. Recall the isothermal ideal gas equation of state, $d(pV) = 0$. Thus, for an ideal gas Stirling cycle, we have

$$p_{\rm A} V_1 = p_{\rm B} V_2 \qquad , \qquad p_{\rm D} V_1 = p_{\rm C} V_2\,, \tag{2.87}$$

which says

$$\frac{p_{\rm B}}{p_{\rm A}} = \frac{p_{\rm C}}{p_{\rm D}} = \frac{V_1}{V_2}\,. \tag{2.88}$$

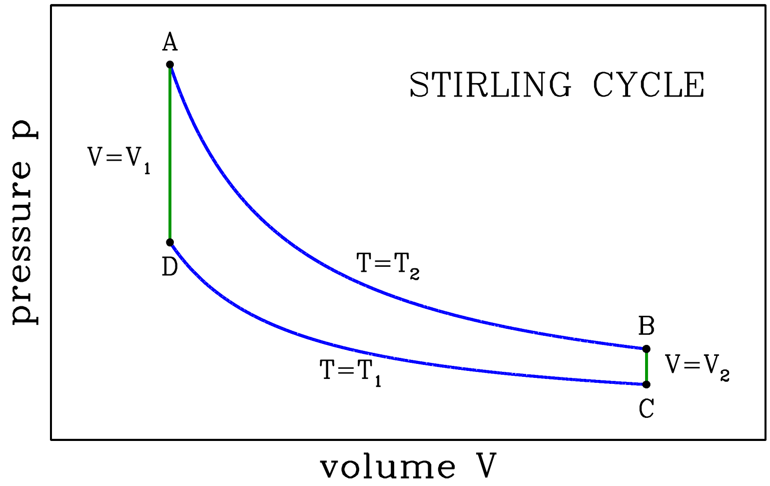


Figure 2.15: A Stirling cycle consists of two isotherms (blue) and two isochores (green).

AB: This isothermal expansion is the power stroke. Assuming $\nu$ moles of ideal gas throughout, we have $pV = \nu RT_2 = p_1 V_1$, hence

$$W_{AB} = \int\limits_{V_1}^{V_2} dV \, \frac{\nu RT_2}{V} = \nu RT_2 \, \ln\left(\frac{V_2}{V_1}\right) . \tag{2.89}$$

Since AB is an isotherm, we have $E_A = E_B$, and from $\Delta E_{AB} = 0$ we conclude $Q_{AB} = W_{AB}$.

BC: Isochoric cooling. Since $dV = 0$ we have $W_{BC} = 0$. The energy change is given by

$$\Delta E_{BC} = E_C - E_B = \frac{\nu R(T_1 - T_2)}{\gamma - 1} , \tag{2.90}$$

which is negative. Since $W_{BC} = 0$, we have $Q_{BC} = \Delta E_{BC}$.

CD: Isothermal compression. Clearly

$$W_{CD} = \int\limits_{V_2}^{V_1} dV \, \frac{\nu RT_1}{V} = -\nu RT_1 \, \ln\left(\frac{V_2}{V_1}\right) . \tag{2.91}$$

Since CD is an isotherm, we have $E_C = E_D$, and from $\Delta E_{CD} = 0$ we conclude $Q_{CD} = W_{CD}$.

DA: Isochoric heating. Since $dV = 0$ we have $W_{DA} = 0$. The energy change is given by

$$\Delta E_{DA} = E_A - E_D = \frac{\nu R(T_2 - T_1)}{\gamma - 1} , \tag{2.92}$$

which is positive, and opposite to $\Delta E_{BC}$. Since $W_{DA} = 0$, we have $Q_{DA} = \Delta E_{DA}$.

We now add up all the work contributions to obtain

$$\begin{aligned} W &= W_{AB} + W_{BC} + W_{CD} + W_{DA} \\ &= \nu R(T_2 - T_1) \, \ln\left(\frac{V_2}{V_1}\right) . \end{aligned} \tag{2.93}$$

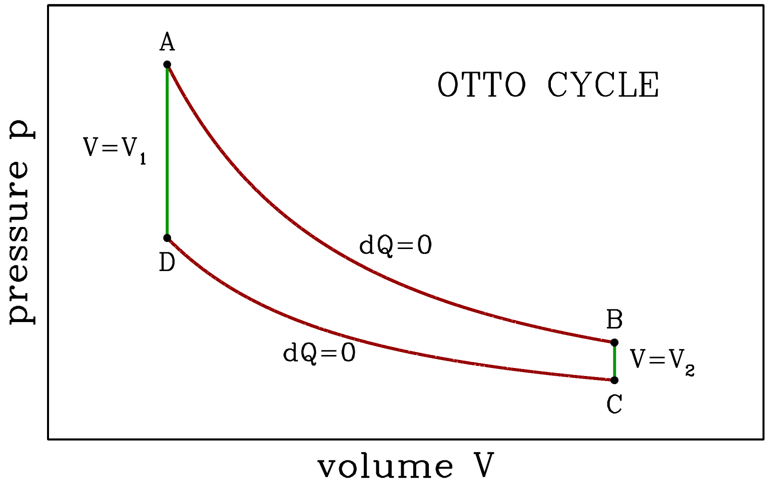


Figure 2.16: An Otto cycle consists of two adiabats (dark red) and two isochores (green).

The cycle efficiency is once again

$$\eta = \frac{W}{Q_{\rm AB}} = 1 - \frac{T_1}{T_2} \ . \tag{2.94}$$

### 2.6.6 The Otto and Diesel cycles

The Otto cycle is a rough approximation to the physics of a gasoline engine. It consists of two adiabats and two isochores, and is depicted in Fig. 2.16. Assuming an ideal gas, along the adiabats we have $d(pV^\gamma)=0$. Thus,

$$p_{\rm A}\, V_1^\gamma = p_{\rm B}\, V_2^\gamma \qquad , \qquad p_{\rm D}\, V_1^\gamma = p_{\rm C}\, V_2^\gamma \ , \tag{2.95}$$

which says

$$\frac{p_{\rm B}}{p_{\rm A}} = \frac{p_{\rm C}}{p_{\rm D}} = \left(\frac{V_1}{V_2}\right)^\gamma \ . \tag{2.96}$$

AB: Adiabatic expansion, the power stroke. The heat transfer is $Q_{\rm AB}=0$, so from the First Law we have $W_{\rm AB} = -\Delta E_{\rm AB} = E_{\rm A} - E_{\rm B}$, thus

$$W_{\rm AB} = \frac{p_{\rm A}V_1 - p_{\rm B}V_2}{\gamma-1} = \frac{p_{\rm A}V_1}{\gamma-1}\left[1-\left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] \ . \tag{2.97}$$

Note that this result can also be obtained from the adiabatic equation of state $pV^\gamma = p_{\rm A}V_1^\gamma$:

$$W_{\rm AB} = \int\limits_{V_1}^{V_2}\! p\, dV = p_{\rm A}V_1^\gamma \int\limits_{V_1}^{V_2}\! dV\, V^{-\gamma} = \frac{p_{\rm A}V_1}{\gamma-1}\left[1-\left(\frac{V_1}{V_2}\right)^{\gamma-1}\right] \ . \tag{2.98}$$

BC: Isochoric cooling (exhaust); $dV=0$ hence $W_{\rm BC}=0$. The heat $Q_{\rm BC}$ absorbed is then

$$Q_{\rm BC} = E_{\rm C} - E_{\rm B} = \frac{V_2}{\gamma-1}\,(p_{\rm C} - p_{\rm B}) \ . \tag{2.99}$$

In a realistic engine, this is the stage in which the old burned gas is ejected and new gas is inserted.

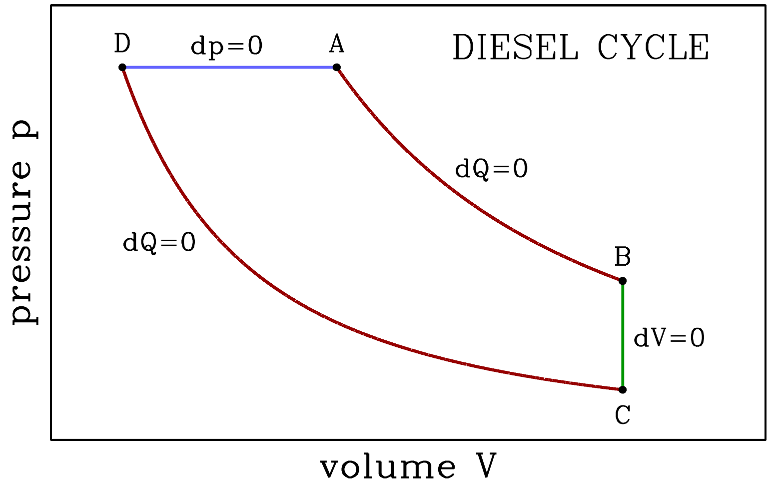


Figure 2.17: A Diesel cycle consists of two adiabats (dark red), one isobar (light blue), and one isochore (green).

CD: Adiabatic compression; $Q_{\text{CD}} = 0$ and $W_{\text{CD}} = E_{\text{C}} - E_{\text{D}}$:

$$W_{\text{CD}} = \frac{p_{\text{C}} V_2 - p_{\text{D}} V_1}{\gamma - 1} = -\frac{p_{\text{D}} V_1}{\gamma - 1} \left[ 1 - \left( \frac{V_1}{V_2} \right)^{\gamma - 1} \right] . \tag{2.100}$$

DA: Isochoric heating, *i.e.* the combustion of the gas. As with BC we have $dV = 0$, and thus $W_{\text{DA}} = 0$. The heat $Q_{\text{DA}}$ absorbed by the gas is then

$$Q_{\text{DA}} = E_{\text{A}} - E_{\text{D}} = \frac{V_1}{\gamma - 1} \left( p_{\text{A}} - p_{\text{D}} \right) . \tag{2.101}$$

The total work done per cycle is then

$$\begin{aligned} W &= W_{\text{AB}} + W_{\text{BC}} + W_{\text{CD}} + W_{\text{DA}} \\ &= \frac{(p_{\text{A}} - p_{\text{D}}) V_1}{\gamma - 1} \left[ 1 - \left( \frac{V_1}{V_2} \right)^{\gamma - 1} \right] , \end{aligned} \tag{2.102}$$

and the efficiency is defined to be

$$\eta \equiv \frac{W}{Q_{\text{DA}}} = 1 - \left( \frac{V_1}{V_2} \right)^{\gamma - 1} . \tag{2.103}$$

The ratio $V_2/V_1$ is called the *compression ratio*. We can make our Otto cycle more efficient simply by increasing the compression ratio. The problem with this scheme is that if the fuel mixture becomes too hot, it will spontaneously ‘preignite’, and the pressure will jump up before point D in the cycle is reached. A Diesel engine avoids preignition by compressing the air only, and then later spraying the fuel into the cylinder when the air temperature is sufficient for fuel ignition. The rate at which fuel is injected is adjusted so that the ignition process takes place at constant pressure. Thus, in a Diesel engine, step DA is an isobar. The compression ratio is $r \equiv V_{\text{B}}/V_{\text{D}}$, and the *cutoff ratio* is $s \equiv V_{\text{A}}/V_{\text{D}}$. This refinement of the Otto cycle allows for higher compression ratios (of about 20) in practice, and greater engine efficiency.

For the Diesel cycle, we have, briefly,

$$\begin{aligned} W &= p_{\rm A}(V_{\rm A}-V_{\rm D}) + \frac{p_{\rm A}V_{\rm A}-p_{\rm B}V_{\rm B}}{\gamma-1} + \frac{p_{\rm C}V_{\rm C}-p_{\rm D}V_{\rm D}}{\gamma-1} \\ &= \frac{\gamma\, p_{\rm A}(V_{\rm A}-V_{\rm D})}{\gamma-1} - \frac{(p_{\rm B}-p_{\rm C})V_{\rm B}}{\gamma-1} \end{aligned} \tag{2.104}$$

and

$$Q_{\rm DA} = \frac{\gamma\, p_{\rm A}(V_{\rm A}-V_{\rm D})}{\gamma-1} \ . \tag{2.105}$$

To find the efficiency, we will need to eliminate $p_{\rm B}$ and $p_{\rm C}$ in favor of $p_{\rm A}$ using the adiabatic equation of state $d(pV^\gamma)=0$. Thus,

$$p_{\rm B} = p_{\rm A}\cdot\left(\frac{V_{\rm A}}{V_{\rm B}}\right)^{\gamma} \qquad , \qquad p_{\rm C} = p_{\rm A}\cdot\left(\frac{V_{\rm D}}{V_{\rm B}}\right)^{\gamma} , \tag{2.106}$$

where we've used $p_{\rm D}=p_{\rm A}$ and $V_{\rm C}=V_{\rm B}$. Putting it all together, the efficiency of the Diesel cycle is

$$\eta = \frac{W}{Q_{\rm DA}} = 1 - \frac{1}{\gamma}\,\frac{r^{1-\gamma}(s^\gamma-1)}{s-1} \ . \tag{2.107}$$

### 2.6.7 The Joule-Brayton cycle

Our final example is the Joule-Brayton cycle, depicted in Fig. 2.18, consisting of two adiabats and two isobars. Along the adiabats we have Thus,

$$p_2\, V_{\rm A}^\gamma = p_1\, V_{\rm D}^\gamma \qquad , \qquad p_2\, V_{\rm B}^\gamma = p_1\, V_{\rm C}^\gamma \ , \tag{2.108}$$

which says

$$\frac{V_{\rm D}}{V_{\rm A}} = \frac{V_{\rm C}}{V_{\rm B}} = \left(\frac{p_2}{p_1}\right)^{\gamma^{-1}} \ . \tag{2.109}$$

AB: This isobaric expansion at $p=p_2$ is the power stroke. We have

$$W_{\rm AB} = \int\limits_{V_{\rm A}}^{V_{\rm B}} dV\, p_2 = p_2\,(V_{\rm B}-V_{\rm A}) \tag{2.110}$$

$$\Delta E_{\rm AB} = E_{\rm B} - E_{\rm A} = \frac{p_2\,(V_{\rm B}-V_{\rm A})}{\gamma-1} \tag{2.111}$$

$$Q_{\rm AB} = \Delta E_{\rm AB} + W_{\rm AB} = \frac{\gamma\, p_2\,(V_{\rm B}-V_{\rm A})}{\gamma-1} \ . \tag{2.112}$$

BC: Adiabatic expansion; $Q_{\rm BC}=0$ and $W_{\rm BC}=E_{\rm B}-E_{\rm C}$. The work done by the gas is

$$\begin{aligned} W_{\rm BC} &= \frac{p_2V_{\rm B}-p_1V_{\rm C}}{\gamma-1} = \frac{p_2V_{\rm B}}{\gamma-1}\left(1-\frac{p_1}{p_2}\cdot\frac{V_{\rm C}}{V_{\rm B}}\right) \\ &= \frac{p_2\,V_{\rm B}}{\gamma-1}\left[1-\left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}}\right] \ . \end{aligned} \tag{2.113}$$

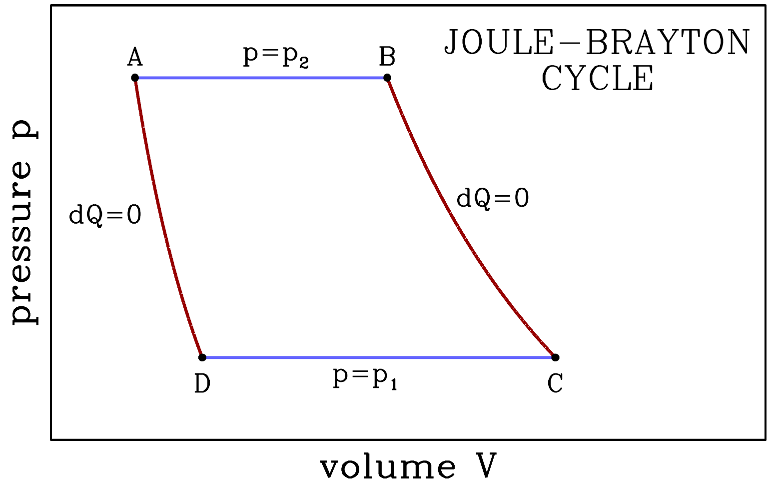


Figure 2.18: A Joule-Brayton cycle consists of two adiabats (dark red) and two isobars (light blue).

CD: Isobaric compression at $p = p_1$.

$$W_{\rm CD} = \int\limits_{V_{\rm C}}^{V_{\rm D}} dV\, p_1 = p_1\,(V_{\rm D} - V_{\rm C}) = -p_2\,(V_{\rm B} - V_{\rm A}) \left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}} \tag{2.114}$$

$$\Delta E_{\rm CD} = E_{\rm D} - E_{\rm C} = \frac{p_1\,(V_{\rm D} - V_{\rm C})}{\gamma - 1} \tag{2.115}$$

$$Q_{\rm CD} = \Delta E_{\rm CD} + W_{\rm CD} = -\frac{\gamma\, p_2}{\gamma - 1}\,(V_{\rm B} - V_{\rm A}) \left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}} . \tag{2.116}$$

BC: Adiabatic expansion; $Q_{\rm DA} = 0$ and $W_{\rm DA} = E_{\rm D} - E_{\rm A}$. The work done by the gas is

$$\begin{aligned} W_{\rm DA} &= \frac{p_1 V_{\rm D} - p_2 V_{\rm A}}{\gamma - 1} = -\frac{p_2 V_{\rm A}}{\gamma - 1}\left(1 - \frac{p_1}{p_2} \cdot \frac{V_{\rm D}}{V_{\rm A}}\right) \\ &= -\frac{p_2\, V_{\rm A}}{\gamma - 1}\left[1 - \left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}}\right] . \end{aligned} \tag{2.117}$$

The total work done per cycle is then

$$\begin{aligned} W &= W_{\rm AB} + W_{\rm BC} + W_{\rm CD} + W_{\rm DA} \\ &= \frac{\gamma\, p_2\,(V_{\rm B} - V_{\rm A})}{\gamma - 1}\left[1 - \left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}}\right] \end{aligned} \tag{2.118}$$

and the efficiency is defined to be

$$\eta \equiv \frac{W}{Q_{\rm AB}} = 1 - \left(\frac{p_1}{p_2}\right)^{1-\gamma^{-1}} . \tag{2.119}$$

### 2.6.8 Carnot engine at maximum power output

While the Carnot engine described above in §2.6.4 has maximum efficiency, it is practically useless, because the isothermal processes must take place infinitely slowly in order for the working material to remain in thermal equilibrium with each reservoir. Thus, while the work done per cycle is finite, the cycle period is infinite, and the engine *power* is zero.

A modification of the ideal Carnot cycle is necessary to create a practical engine. The idea[8] is as follows. During the isothermal expansion stage, the working material is maintained at a temperature $T_{2\mathrm{w}} < T_2$. The temperature difference between the working material and the hot reservoir drives a thermal current,

$$\frac{đQ_2}{dt} = \kappa_2 \, (T_2 - T_{2\mathrm{w}}) \, . \tag{2.120}$$

Here, $\kappa_2$ is a *transport coefficient* which describes the *thermal conductivity* of the chamber walls, multiplied by a geometric parameter (which is the ratio of the total wall area to its thickness). Similarly, during the isothermal compression, the working material is maintained at a temperature $T_{1\mathrm{w}} > T_1$, which drives a thermal current to the cold reservoir,

$$\frac{đ\mathcal{Q}_1}{dt} = \kappa_1 \, (T_{1\mathrm{w}} - T_1) \, . \tag{2.121}$$

Now let us assume that the upper isothermal stage requires a duration $\Delta t_2$ and the lower isotherm a duration $\Delta t_1$. Then

$$Q_2 = \kappa_2 \, \Delta t_2 \, (T_2 - T_{2\mathrm{w}}) \tag{2.122}$$

$$\mathcal{Q}_1 = \kappa_1 \, \Delta t_1 \, (T_{1\mathrm{w}} - T_1) \, . \tag{2.123}$$

Since the engine is reversible, we must have

$$\frac{\mathcal{Q}_1}{T_{1\mathrm{w}}} = \frac{Q_2}{T_{2\mathrm{w}}} \, , \tag{2.124}$$

which says

$$\frac{\Delta t_1}{\Delta t_2} = \frac{\kappa_2 \, T_{2\mathrm{w}} \, (T_{1\mathrm{w}} - T_1)}{\kappa_1 \, T_{1\mathrm{w}} \, (T_2 - T_{2\mathrm{w}})} \, . \tag{2.125}$$

The power is

$$P = \frac{Q_2 - \mathcal{Q}_1}{(1+\alpha) \, (\Delta t_1 + \Delta t_2)} \, , \tag{2.126}$$

where we assume that the adiabatic stages require a combined time of $\alpha \, (\Delta t_1 + \Delta t_2)$. Thus, we find

$$P = \frac{\kappa_1 \, \kappa_2 \, (T_{2\mathrm{w}} - T_{1\mathrm{w}}) \, (T_{1\mathrm{w}} - T_1) \, (T_2 - T_{2\mathrm{w}})}{(1+\alpha) \, \big[ \kappa_1 \, T_2 \, (T_{1\mathrm{w}} - T_1) + \kappa_2 \, T_1 \, (T_2 - T_{2\mathrm{w}}) + (\kappa_2 - \kappa_1) \, (T_{1\mathrm{w}} - T_1) \, (T_2 - T_{2\mathrm{w}}) \big]} \tag{2.127}$$

We optimize the engine by maximizing $P$ with respect to the temperatures $T_{1\mathrm{w}}$ and $T_{2\mathrm{w}}$. This yields

$$T_{2\mathrm{w}} = T_2 - \frac{T_2 - \sqrt{T_1 T_2}}{1 + \sqrt{\kappa_2/\kappa_1}} \tag{2.128}$$

$$T_{1\mathrm{w}} = T_1 + \frac{\sqrt{T_1 T_2} - T_1}{1 + \sqrt{\kappa_1/\kappa_2}} \, . \tag{2.129}$$

---

[8] See F. L. Curzon and B. Ahlborn, *Am. J. Phys.* **43**, 22 (1975).

| Power source | $T_1$ (°C) | $T_2$ (°C) | $\eta_{\rm Carnot}$ | $\eta$ (theor.) | $\eta$ (obs.) |
|---|---|---|---|---|---|
| West Thurrock (UK)<br>Coal Fired Steam Plant | $\sim 25$ | 565 | 0.641 | 0.40 | 0.36 |
| CANDU (Canada)<br>PHW Nuclear Reactor | $\sim 25$ | 300 | 0.480 | 0.28 | 0.30 |
| Larderello (Italy)<br>Geothermal Steam Plant | $\sim 80$ | 250 | 0.323 | 0.175 | 0.16 |

Table 2.2: Observed performances of real heat engines, taken from table 1 from Curzon and Albhorn (1975).

The efficiency at maximum power is then

$$\eta = \frac{Q_2 - \mathcal{Q}_1}{Q_2} = 1 - \frac{T_{1\rm w}}{T_{2\rm w}} = 1 - \sqrt{\frac{T_1}{T_2}}\ . \tag{2.130}$$

One also finds at maximum power

$$\frac{\Delta t_2}{\Delta t_1} = \sqrt{\frac{\kappa_1}{\kappa_2}}\ . \tag{2.131}$$

Finally, the maximized power is

$$P_{\rm max} = \frac{\kappa_1 \kappa_2}{1+\alpha}\left(\frac{\sqrt{T_2} - \sqrt{T_1}}{\sqrt{\kappa_1} + \sqrt{\kappa_2}}\right)^2 . \tag{2.132}$$

Table 2.2, taken from the article of Curzon and Albhorn (1975), shows how the efficiency of this practical Carnot cycle, given by eqn. 2.130, rather accurately predicts the efficiencies of functioning power plants.

## 2.7 The Entropy

### 2.7.1 Entropy and heat

The Second Law guarantees us that an engine operating between two heat baths at temperatures $T_1$ and $T_2$ must satisfy

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \le 0\ , \tag{2.133}$$

with the equality holding for reversible processes. This is a restatement of eqn. 2.63, after writing $Q_1 = -\mathcal{Q}_1$ for the heat transferred *to* the engine from reservoir #1. Consider now an arbitrary curve in the $p - V$ plane. We can describe such a curve, to arbitrary accuracy, as a combination of Carnot cycles, as shown in Fig. 2.19. Each little Carnot cycle consists of two adiabats and two isotherms. We then conclude

$$\sum_i \frac{Q_i}{T_i} \longrightarrow \oint\limits_{\mathcal{C}} \frac{đQ}{T} \le 0\ , \tag{2.134}$$

with equality holding if all the cycles are reversible. Rudolf Clausius, in 1865, realized that one could then define a new state function, which he called the *entropy*, $S$, that depended only on the initial and final states of a reversible

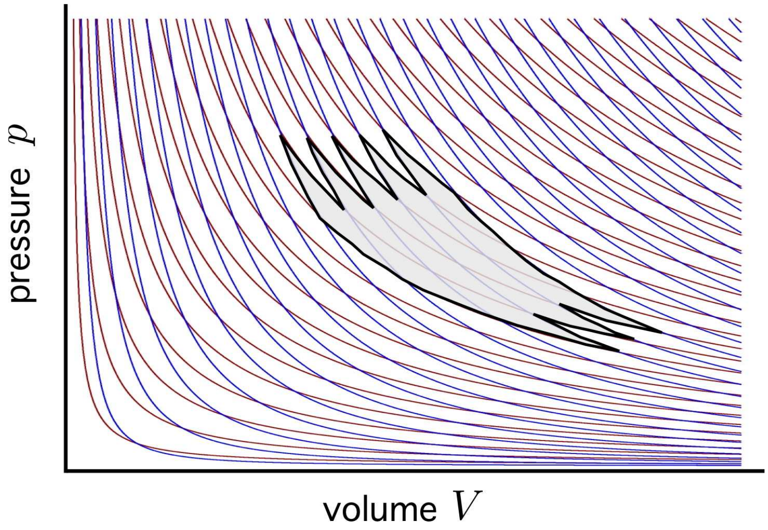


Figure 2.19: An arbitrarily shaped cycle in the $p - V$ plane can be decomposed into a number of smaller Carnot cycles. Red curves indicate isotherms and blue curves adiabats, with $\gamma = \frac{5}{3}$.

process:

$$dS = \frac{đQ}{T} \quad \Longrightarrow \quad S_{\rm B} - S_{\rm A} = \int\limits_{\rm A}^{\rm B} \frac{đQ}{T} \ . \tag{2.135}$$

Since $Q$ is extensive, so is $S$; the units of entropy are $[S] = {\rm J/K}$.

### 2.7.2 The Third Law of Thermodynamics

Eqn. 2.135 determines the entropy up to a constant. By choosing a standard state $\Upsilon$, we can define $S_\Upsilon = 0$, and then by taking ${\rm A} = \Upsilon$ in the above equation, we can define the absolute entropy $S$ for any state. However, it turns out that this seemingly arbitrary constant $S_\Upsilon$ in the entropy does have consequences, for example in the theory of gaseous equilibrium. The proper definition of entropy, from the point of view of statistical mechanics, will lead us to understand how the zero temperature entropy of a system is related to its quantum mechanical ground state degeneracy. Walther Nernst, in 1906, articulated a principle which is sometimes called the Third Law of Thermodynamics,

> *The entropy of every system at absolute zero temperature always vanishes.*

Again, this is not quite correct, and quantum mechanics tells us that $S(T = 0) = k_{\rm B} \ln g$, where $g$ is the ground state degeneracy. Nernst's law holds when $g = 1$.

We can combine the First and Second laws to write

$$dE + đW = đQ \leq T\,dS \ , \tag{2.136}$$

where the equality holds for reversible processes.

### 2.7.3 Entropy changes in cyclic processes

For a cyclic process, whether reversible or not, the change in entropy around a cycle is zero: $\Delta S_{\text{CYC}} = 0$. This is because the entropy $S$ is a state function, with a unique value for every equilibrium state. A cyclical process returns to the same equilibrium state, hence $S$ must return as well to its corresponding value from the previous cycle.

Consider now a general engine, as in Fig. 2.12. Let us compute the total entropy change in the entire Universe over one cycle. We have

$$(\Delta S)_{\text{TOTAL}} = (\Delta S)_{\text{ENGINE}} + (\Delta S)_{\text{HOT}} + (\Delta S)_{\text{COLD}} \ , \tag{2.137}$$

written as a sum over entropy changes of the engine itself, the hot reservoir, and the cold reservoir[9]. Clearly $(\Delta S)_{\text{ENGINE}} = 0$. The changes in the reservoir entropies are

$$(\Delta S)_{\text{HOT}} = \int\limits_{T=T_2} \frac{\text{đ}Q_{\text{HOT}}}{T} = -\frac{Q_2}{T_2} \ < \ 0 \tag{2.138}$$

$$(\Delta S)_{\text{COLD}} = \int\limits_{T=T_1} \frac{\text{đ}Q_{\text{COLD}}}{T} = \frac{\mathcal{Q}_1}{T_1} = -\frac{Q_1}{T_1} \ > \ 0 \ , \tag{2.139}$$

because the hot reservoir loses heat $Q_2 > 0$ to the engine, and the cold reservoir gains heat $\mathcal{Q}_1 = -Q_1 > 0$ from the engine. Therefore,

$$(\Delta S)_{\text{TOTAL}} = -\bigg(\frac{Q_1}{T_1} + \frac{Q_2}{T_2}\bigg) \geq 0 \ . \tag{2.140}$$

Thus, for a reversible cycle, the net change in the total entropy of the engine plus reservoirs is zero. For an irreversible cycle, there is an increase in total entropy, due to spontaneous processes.

### 2.7.4 Gibbs-Duhem relation

Recall eqn. 2.6:

$$\text{đ}W = -\sum_j y_j \, dX_j - \sum_a \mu_a \, dN_a \ . \tag{2.141}$$

For reversible systems, we can therefore write

$$dE = T\,dS + \sum_j y_j \, dX_j + \sum_a \mu_a \, dN_a \ . \tag{2.142}$$

This says that the energy $E$ is a function of the entropy $S$, the generalized displacements $\{X_j\}$, and the particle numbers $\{N_a\}$:

$$E = E\big(S, \{X_j\}, \{N_a\}\big) \ . \tag{2.143}$$

Furthermore, we have

$$T = \bigg(\frac{\partial E}{\partial S}\bigg)_{\{X_j, N_a\}} \quad , \quad y_j = \bigg(\frac{\partial E}{\partial X_j}\bigg)_{S, \{X_{i(\neq j)}, N_a\}} \quad , \quad \mu_a = \bigg(\frac{\partial E}{\partial N_a}\bigg)_{S, \{X_j, N_{b(\neq a)}\}} \tag{2.144}$$

Since $E$ and all its arguments are extensive, we have

$$\lambda E = E\big(\lambda S, \{\lambda X_j\}, \{\lambda N_a\}\big) \ . \tag{2.145}$$

---

[9] We neglect any interfacial contributions to the entropy change, which will be small compared with the bulk entropy change in the thermodynamic limit of large system size.

We now differentiate the LHS and RHS above with respect to $\lambda$, setting $\lambda = 1$ afterward. The result is

$$\begin{aligned} E &= S\,\frac{\partial E}{\partial S} + \sum_j X_j\,\frac{\partial E}{\partial X_j} + \sum_a N_a\,\frac{\partial E}{\partial N_a} \\ &= TS + \sum_j y_j\,X_j + \sum_a \mu_a\,N_a\ . \end{aligned} \tag{2.146}$$

Mathematically astute readers will recognize this result as an example of Euler's theorem for homogeneous functions. Taking the differential of eqn. 2.146, and then subtracting eqn. 2.142, we obtain

$$S\,dT + \sum_j X_j\,dy_j + \sum_a N_a\,d\mu_a = 0\ . \tag{2.147}$$

This is called the *Gibbs-Duhem relation*. It says that there is one equation of state which may be written in terms of all the intensive quantities alone. For example, for a single component system, we must have $p = p(T,\mu)$, which follows from

$$S\,dT - V\,dp + N\,d\mu = 0\ . \tag{2.148}$$

### 2.7.5 Entropy for an ideal gas

For an ideal gas, we have $E = \frac{1}{2}fNk_BT$, and

$$\begin{aligned} dS &= \frac{1}{T}\,dE + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN \\ &= \tfrac{1}{2}fNk_B\,\frac{dT}{T} + \frac{p}{T}\,dV + \bigg(\tfrac{1}{2}fk_B - \frac{\mu}{T}\bigg)\,dN\ . \end{aligned} \tag{2.149}$$

Invoking the ideal gas equation of state $pV = Nk_BT$, we have

$$dS\big|_N = \tfrac{1}{2}fNk_B\,d\ln T + Nk_B d\ln V\ . \tag{2.150}$$

Integrating, we obtain

$$S(T,V,N) = \tfrac{1}{2}fNk_B\,\ln T + Nk_B\,\ln V + \varphi(N)\ , \tag{2.151}$$

where $\varphi(N)$ is an arbitrary function. Extensivity of $S$ places restrictions on $\varphi(N)$, so that the most general case is

$$S(T,V,N) = \tfrac{1}{2}fNk_B\,\ln T + Nk_B\,\ln\bigg(\frac{V}{N}\bigg) + Na\ , \tag{2.152}$$

where $a$ is a constant. Equivalently, we could write

$$S(E,V,N) = \tfrac{1}{2}fNk_B\,\ln\bigg(\frac{E}{N}\bigg) + Nk_B\,\ln\bigg(\frac{V}{N}\bigg) + Nb\ , \tag{2.153}$$

where $b = a - \frac{1}{2}fk_B\ln(\frac{1}{2}fk_B)$ is another constant. When we study statistical mechanics, we will find that for the monatomic ideal gas the entropy is

$$S(T,V,N) = Nk_B\bigg[\tfrac{5}{2} + \ln\bigg(\frac{V}{N\lambda_T^3}\bigg)\bigg]\ , \tag{2.154}$$

where $\lambda_T = \sqrt{2\pi\hbar^2/mk_BT}$ is the *thermal wavelength*, which involved Planck's constant. Let's now contrast two illustrative cases.

- *Adiabatic free expansion* – Suppose the volume freely expands from $V_{\rm i}$ to $V_{\rm f} = r\,V_{\rm i}$, with $r > 1$. Such an expansion can be effected by a removal of a partition between two chambers that are otherwise thermally insulated (see Fig. 2.10). We have already seen how this process entails

  $$\Delta E = Q = W = 0\ . \tag{2.155}$$

  But the entropy changes! According to eqn. 2.153, we have

  $$\Delta S = S_{\rm f} - S_{\rm i} = N k_{\rm B} \ln r\ . \tag{2.156}$$

- *Reversible adiabatic expansion* – If the gas expands quasistatically and reversibly, then $S = S(E,V,N)$ holds everywhere along the thermodynamic path. We then have, assuming $dN = 0$,

  $$\begin{aligned} 0 = dS &= \tfrac{1}{2} f N k_{\rm B} \, \frac{dE}{E} + N k_{\rm B} \, \frac{dV}{V} \\ &= N k_{\rm B} \, d \ln\big(V E^{f/2}\big)\ . \end{aligned} \tag{2.157}$$

  Integrating, we find

  $$\frac{E}{E_0} = \bigg(\frac{V_0}{V}\bigg)^{2/f}\ . \tag{2.158}$$

  Thus,

  $$E_{\rm f} = r^{-2/f}\, E_{\rm i} \quad \Longleftrightarrow \quad T_{\rm f} = r^{-2/f}\, T_{\rm i}\ . \tag{2.159}$$

### 2.7.6 Example system

Consider a model thermodynamic system for which

$$E(S,V,N) = \frac{aS^3}{NV}\ , \tag{2.160}$$

where $a$ is a constant. We have

$$dE = T\,dS - p\,dV + \mu\,dN\ , \tag{2.161}$$

and therefore

$$T = \bigg(\frac{\partial E}{\partial S}\bigg)_{V,N} = \frac{3aS^2}{NV} \tag{2.162}$$

$$p = -\bigg(\frac{\partial E}{\partial V}\bigg)_{S,N} = \frac{aS^3}{NV^2} \tag{2.163}$$

$$\mu = \bigg(\frac{\partial E}{\partial N}\bigg)_{S,V} = -\frac{aS^3}{N^2 V}\ . \tag{2.164}$$

Choosing any two of these equations, we can eliminate $S$, which is inconvenient for experimental purposes. This yields three equations of state,

$$\frac{T^3}{p^2} = 27a\,\frac{V}{N} \quad , \quad \frac{T^3}{\mu^2} = 27a\,\frac{N}{V} \quad , \quad \frac{p}{\mu} = -\frac{N}{V}\ , \tag{2.165}$$

only two of which are independent.

What about $C_V$ and $C_p$? To find $C_V$, we recast eqn. 2.162 as

$$S = \left(\frac{NVT}{3a}\right)^{1/2} . \tag{2.166}$$

We then have

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \frac{1}{2}\left(\frac{NVT}{3a}\right)^{1/2} = \frac{N}{18a}\,\frac{T^2}{p} , \tag{2.167}$$

where the last equality on the RHS follows upon invoking the first of the equations of state in eqn. 2.165. To find $C_p$, we eliminate $V$ from eqns. 2.162 and 2.163, obtaining $T^2/p = 9aS/N$. From this we obtain

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = \frac{2N}{9a}\,\frac{T^2}{p} . \tag{2.168}$$

Thus, $C_p/C_V = 4$.

We can derive still more. To find the isothermal compressibility $\kappa_T = -\frac{1}{V}\big(\frac{\partial V}{\partial p}\big)_{T,N}$, use the first of the equations of state in eqn. 2.165. To derive the adiabatic compressibility $\kappa_S = -\frac{1}{V}\big(\frac{\partial V}{\partial p}\big)_{S,N}$, use eqn. 2.163, and then eliminate the inconvenient variable $S$.

Suppose we use this system as the working substance for a Carnot engine. Let's compute the work done and the engine efficiency. To do this, it is helpful to eliminate $S$ in the expression for the energy, and to rewrite the equation of state:

$$E = pV = \sqrt{\frac{N}{27a}}\,V^{1/2}\,T^{3/2} \qquad , \qquad p = \sqrt{\frac{N}{27a}}\,\frac{T^{3/2}}{V^{1/2}} . \tag{2.169}$$

We assume $dN = 0$ throughout. We now see that for isotherms,

$$dT = 0 \ : \ \frac{E}{\sqrt{V}} = \text{constant} \tag{2.170}$$

Furthermore, since

$$đW\big|_T = \sqrt{\frac{N}{27a}}\,T^{3/2}\,\frac{dV}{V^{1/2}} = 2\,dE\big|_T , \tag{2.171}$$

we conclude that

$$dT = 0 \ : \ W_{\rm if} = 2(E_{\rm f} - E_{\rm i}) \quad , \quad Q_{\rm if} = E_{\rm f} - E_{\rm i} + W_{\rm if} = 3(E_{\rm f} - E_{\rm i}) . \tag{2.172}$$

For adiabats, eqn. 2.162 says $d(TV) = 0$, and therefore

$$đQ = 0 \ : \ TV = \text{constant} \quad , \quad \frac{E}{T} = \text{constant} \quad , \quad EV = \text{constant} \tag{2.173}$$

as well as $W_{\rm if} = E_{\rm i} - E_{\rm f}$. We can use these relations to derive the following:

$$E_{\rm B} = \sqrt{\frac{V_{\rm B}}{V_{\rm A}}}\,E_{\rm A} \quad , \quad E_{\rm C} = \frac{T_1}{T_2}\sqrt{\frac{V_{\rm B}}{V_{\rm A}}}\,E_{\rm A} \quad , \quad E_{\rm D} = \frac{T_1}{T_2}\,E_{\rm A} . \tag{2.174}$$

Now we can write

$$W_{\rm AB} = 2(E_{\rm B} - E_{\rm A}) = 2\left(\sqrt{\frac{V_{\rm B}}{V_{\rm A}}} - 1\right) E_{\rm A} \tag{2.175}$$

$$W_{\rm BC} = (E_{\rm B} - E_{\rm C}) = \sqrt{\frac{V_{\rm B}}{V_{\rm A}}}\left(1 - \frac{T_1}{T_2}\right) E_{\rm A} \tag{2.176}$$

$$W_{\rm CD} = 2(E_{\rm D} - E_{\rm C}) = 2\frac{T_1}{T_2}\left(1 - \sqrt{\frac{V_{\rm B}}{V_{\rm A}}}\right) E_{\rm A} \tag{2.177}$$

$$W_{\rm DA} = (E_{\rm D} - E_{\rm A}) = \left(\frac{T_1}{T_2} - 1\right) E_{\rm A} \tag{2.178}$$

Adding up all the work, we obtain

$$\begin{aligned} W &= W_{\rm AB} + W_{\rm BC} + W_{\rm CD} + W_{\rm DA} \\ &= 3\left(\sqrt{\frac{V_{\rm B}}{V_{\rm A}}} - 1\right)\left(1 - \frac{T_1}{T_2}\right) E_{\rm A} \ . \end{aligned} \tag{2.179}$$

Since

$$Q_{\rm AB} = 3(E_{\rm B} - E_{\rm A}) = \tfrac{3}{2} W_{\rm AB} = 3\left(\sqrt{\frac{V_{\rm B}}{V_{\rm A}}} - 1\right) E_{\rm A} \ , \tag{2.180}$$

we find once again

$$\eta = \frac{W}{Q_{\rm AB}} = 1 - \frac{T_1}{T_2} \ . \tag{2.181}$$

### 2.7.7 Measuring the entropy of a substance

If we can measure the heat capacity $C_V(T)$ or $C_p(T)$ of a substance as a function of temperature down to the lowest temperatures, then we can measure the entropy. At constant pressure, for example, we have $T\,dS = C_p\,dT$, hence

$$S(p,T) = S(p,T=0) + \int\limits_0^T \! dT' \, \frac{C_p(T')}{T'} \ . \tag{2.182}$$

The zero temperature entropy is $S(p,T=0) = k_{\rm B} \ln g$ where $g$ is the quantum ground state degeneracy at pressure $p$. In all but highly unusual cases, $g = 1$ and $S(p,T=0) = 0$.

## 2.8 Thermodynamic Potentials

Thermodynamic systems may do work on their environments. Under certain constraints, the work done may be bounded from above by the change in an appropriately defined *thermodynamic potential*.

### 2.8.1 Energy $E$

Suppose we wish to create a thermodynamic system from scratch. Let's imagine that we create it from scratch in a thermally insulated box of volume $V$. The work we must to to assemble the system is then

$$\mathcal{W} = E\ . \tag{2.183}$$

After we bring all the constituent particles together, pulling them in from infinity (say), the system will have total energy $E$. After we finish, the system may not be in thermal equilibrium. Spontaneous processes will then occur so as to maximize the system's entropy, but the internal energy remains at $E$.

We have, from the First Law, $dE = đQ - đW$. For equilibrium systems, we have

$$dE = T\,dS - p\,dV + \mu\,dN\ , \tag{2.184}$$

which says that $E = E(S,V,N)$, and

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \qquad , \qquad -p = \left(\frac{\partial E}{\partial V}\right)_{S,N} \qquad , \qquad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}\ . \tag{2.185}$$

The Second Law, in the form $đQ \le T\,dS$, then yields

$$dE \le T\,dS - p\,dV + \mu\,dN\ . \tag{2.186}$$

This form is valid for single component systems and is easily generalized to multicomponent systems, or magnetic systems, *etc.* Now consider a process at fixed $(S,V,N)$. We then have $dE \le 0$. This says that spontaneous processes in a system with $dS = dV = dN = 0$ always lead to a reduction in the internal energy $E$. Therefore, *spontaneous processes drive the internal energy $E$ to a minimum in systems at fixed $(S,V,N)$.*

Allowing for other work processes, we have

$$đW \le T\,dS - dE\ . \tag{2.187}$$

Hence, *the work done by a thermodynamic system under conditions of constant entropy is bounded above by $-dE$, and the maximum $đW$ is achieved for a reversible process.*

It is useful to define the quantity

$$đW_{\text{free}} = đW - p\,dV\ , \tag{2.188}$$

which is the differential work done by the system other than that required to change its volume. Then

$$đW_{\text{free}} \le T\,dS - p\,dV - dE\ , \tag{2.189}$$

and we conclude that for systems at fixed $(S,V)$ that $đW_{\text{free}} \le -dE$.

### 2.8.2 Helmholtz free energy $F$

Suppose that when we spontaneously create our system while it is in constant contact with a thermal reservoir at temperature $T$. Then as we create our system, it will absorb heat from the reservoir. Therefore, we don't have to supply the full internal energy $E$, but rather only $E - Q$, since the system receives heat energy $Q$ from the reservoir. In other words, we must perform work

$$\mathcal{W} = E - TS \tag{2.190}$$

to create our system, if it is constantly in equilibrium at temperature $T$. The quantity $E - TS$ is known as the *Helmholtz free energy*, $F$, which is related to the energy $E$ by a *Legendre transformation*,

$$F = E - TS \, . \tag{2.191}$$

The general properties of Legendre transformations are discussed in Appendix II, §2.16.

Under equilibrium conditions, we have

$$dF = -S\,dT - p\,dV + \mu\,dN \, . \tag{2.192}$$

Thus, $F = F(T, V, N)$, whereas $E = E(S, V, N)$, and

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \quad , \quad -p = \left(\frac{\partial F}{\partial V}\right)_{T,N} \quad , \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \, . \tag{2.193}$$

In general, the Second Law tells us that

$$dF \le -S\,dT - p\,dV + \mu\,dN \, . \tag{2.194}$$

The equality holds for reversible processes, and the inequality for spontaneous processes. Therefore, *spontaneous processes drive the Helmholtz free energy $F$ to a minimum in systems at fixed $(T, V, N)$.*

We may also write

$$đW \le -S\,dT - dF \, , \tag{2.195}$$

In other words, *the work done by a thermodynamic system under conditions of constant temperature is bounded above by $-dF$, and the maximum $đW$ is achieved for a reversible process.* We also have

$$đW_{\text{free}} \le -S\,dT - p\,dV - dF \, , \tag{2.196}$$

and we conclude, for systems at fixed $(T, V)$, that $đW_{\text{free}} \le -dF$.

### 2.8.3 Enthalpy $\mathsf{H}$

Suppose that when we spontaneously create our system while it is thermally insulated, but in constant mechanical contact with a 'volume bath' at pressure $p$. For example, we could create our system inside a thermally insulated chamber with one movable wall where the external pressure is fixed at $p$. Thus, when creating the system, in addition to the system's internal energy $E$, we must also perform work $pV$ in order to make room for the it. In other words, we must perform work

$$\mathcal{W} = E + pV \, . \tag{2.197}$$

The quantity $E + pV$ is known as the *enthalpy*, $\mathsf{H}$. (We use the sans-serif symbol $\mathsf{H}$ for enthalpy to avoid confusing it with magnetic field, $H$.)

The enthalpy is obtained from the energy via a different Legendre transformation:

$$\mathsf{H} = E + pV \, . \tag{2.198}$$

In equilibrium, then,

$$d\mathsf{H} = T\,dS + V\,dp + \mu\,dN \, , \tag{2.199}$$

which says $\mathsf{H} = \mathsf{H}(S, p, N)$, with

$$T = \left(\frac{\partial \mathsf{H}}{\partial S}\right)_{p,N} \quad , \quad V = \left(\frac{\partial \mathsf{H}}{\partial p}\right)_{S,N} \quad , \quad \mu = \left(\frac{\partial \mathsf{H}}{\partial N}\right)_{S,p} \, . \tag{2.200}$$

In general, we have

$$d\mathsf{H} \leq T\,dS + V\,dp + \mu\,dN\ , \tag{2.201}$$

hence *spontaneous processes drive the enthalpy* $\mathsf{H}$ *to a minimum in systems at fixed* $(S, p, N)$.

For general systems,

$$d\mathsf{H} \leq T\,dS - đW + p\,dV + V\,dp\ , \tag{2.202}$$

hence

$$đW_{\text{free}} \leq T\,dS + V\,dp - d\mathsf{H}\ , \tag{2.203}$$

and we conclude, for systems at fixed $(S, p)$, that $đW_{\text{free}} \leq -d\mathsf{H}$.

### 2.8.4 Gibbs free energy $G$

If we create a thermodynamic system at conditions of constant temperature $T$ and constant pressure $p$, then it absorbs heat energy $Q = TS$ from the reservoir and we must expend work energy $pV$ in order to make room for it. Thus, the total amount of work we must do in assembling our system is

$$\mathcal{W} = E - TS + pV\ . \tag{2.204}$$

This is the *Gibbs free energy*, $G$.

The Gibbs free energy is obtained by a second Legendre transformation:

$$G = E - TS + pV \tag{2.205}$$

Note that $G = F + pV = \mathsf{H} - TS$. For equilibrium systems, the differential of $G$ is

$$dG = -S\,dT + V\,dp + \mu\,dN\ , \tag{2.206}$$

therefore $G = G(T, p, N)$, with

$$-S = \left(\frac{\partial G}{\partial T}\right)_{p,N} \quad , \quad V = \left(\frac{\partial G}{\partial p}\right)_{T,N} \quad , \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p}\ . \tag{2.207}$$

From eqn. 2.146, we have

$$E = TS - pV + \mu N\ , \tag{2.208}$$

therefore

$$G = \mu N\ . \tag{2.209}$$

The Second Law says that

$$dG \leq -S\,dT + V\,dp + \mu\,dN\ , \tag{2.210}$$

hence *spontaneous processes drive the Gibbs free energy* $G$ *to a minimum in systems at fixed* $(T, p, N)$. For general systems,

$$đW_{\text{free}} \leq -S\,dT + V\,dp - dG\ . \tag{2.211}$$

Accordingly, we conclude, for systems at fixed $(T, p)$, that $đW_{\text{free}} \leq -dG$.

### 2.8.5 Grand potential $\Omega$

The grand potential, sometimes called the Landau free energy, is defined by

$$\Omega = E - TS - \mu N \ . \tag{2.212}$$

Its differential is

$$d\Omega = -S\,dT - p\,dV - N\,d\mu \ , \tag{2.213}$$

hence

$$-S = \left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu} \quad , \quad -p = \left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} \quad , \quad -N = \left(\frac{\partial\Omega}{\partial \mu}\right)_{T,V} \ . \tag{2.214}$$

Again invoking eqn. 2.146, we find

$$\Omega = -pV \ . \tag{2.215}$$

The Second Law tells us

$$d\Omega \le -đW - S\,dT - \mu\,dN - N\,d\mu \ , \tag{2.216}$$

hence

$$đ\widetilde{W}_{\rm free} \equiv đW_{\rm free} + \mu\,dN \le -S\,dT - p\,dV - N\,d\mu - d\Omega \ . \tag{2.217}$$

We conclude, for systems at fixed $(T, V, \mu)$, that $đ\widetilde{W}_{\rm free} \le -d\Omega$.

## 2.9 Maxwell Relations

Maxwell relations are conditions equating certain derivatives of state variables which follow from the exactness of the differentials of the various state functions.

### 2.9.1 Relations deriving from $E(S, V, N)$

The energy $E(S, V, N)$ is a state function, with

$$dE = T\,dS - p\,dV + \mu\,dN \ , \tag{2.218}$$

and therefore

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \quad , \quad -p = \left(\frac{\partial E}{\partial V}\right)_{S,N} \quad , \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \ . \tag{2.219}$$

Taking the mixed second derivatives, we find

$$\frac{\partial^2 E}{\partial S\,\partial V} = \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N} \tag{2.220}$$

$$\frac{\partial^2 E}{\partial S\,\partial N} = \left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \tag{2.221}$$

$$\frac{\partial^2 E}{\partial V\,\partial N} = -\left(\frac{\partial p}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N} \ . \tag{2.222}$$

### 2.9.2 Relations deriving from $F(T,V,N)$

The energy $F(T,V,N)$ is a state function, with

$$dF = -S\,dT - p\,dV + \mu\,dN \ , \tag{2.223}$$

and therefore

$$-S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \quad , \quad -p = \left(\frac{\partial F}{\partial V}\right)_{T,N} \quad , \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \ . \tag{2.224}$$

Taking the mixed second derivatives, we find

$$\frac{\partial^2 F}{\partial T\,\partial V} = -\left(\frac{\partial S}{\partial V}\right)_{T,N} = -\left(\frac{\partial p}{\partial T}\right)_{V,N} \tag{2.225}$$

$$\frac{\partial^2 F}{\partial T\,\partial N} = -\left(\frac{\partial S}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial T}\right)_{V,N} \tag{2.226}$$

$$\frac{\partial^2 F}{\partial V\,\partial N} = -\left(\frac{\partial p}{\partial N}\right)_{T,V} = \left(\frac{\partial \mu}{\partial V}\right)_{T,N} \ . \tag{2.227}$$

### 2.9.3 Relations deriving from $\mathsf{H}(S,p,N)$

The enthalpy $\mathsf{H}(S,p,N)$ satisfies

$$d\mathsf{H} = T\,dS + V\,dp + \mu\,dN \ , \tag{2.228}$$

which says $\mathsf{H} = \mathsf{H}(S,p,N)$, with

$$T = \left(\frac{\partial \mathsf{H}}{\partial S}\right)_{p,N} \quad , \quad V = \left(\frac{\partial \mathsf{H}}{\partial p}\right)_{S,N} \quad , \quad \mu = \left(\frac{\partial \mathsf{H}}{\partial N}\right)_{S,p} \ . \tag{2.229}$$

Taking the mixed second derivatives, we find

$$\frac{\partial^2 \mathsf{H}}{\partial S\,\partial p} = \left(\frac{\partial T}{\partial p}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{p,N} \tag{2.230}$$

$$\frac{\partial^2 \mathsf{H}}{\partial S\,\partial N} = \left(\frac{\partial T}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial S}\right)_{p,N} \tag{2.231}$$

$$\frac{\partial^2 \mathsf{H}}{\partial p\,\partial N} = \left(\frac{\partial V}{\partial N}\right)_{S,p} = \left(\frac{\partial \mu}{\partial p}\right)_{S,N} \ . \tag{2.232}$$

### 2.9.4 Relations deriving from $G(T,p,N)$

The Gibbs free energy $G(T,p,N)$ satisfies

$$dG = -S\,dT + V\,dp + \mu\,dN \ , \tag{2.233}$$

therefore $G = G(T,p,N)$, with

$$-S = \left(\frac{\partial G}{\partial T}\right)_{p,N} \quad , \quad V = \left(\frac{\partial G}{\partial p}\right)_{T,N} \quad , \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,p} \ . \tag{2.234}$$

Taking the mixed second derivatives, we find

$$\frac{\partial^2 G}{\partial T\,\partial p} = -\left(\frac{\partial S}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial T}\right)_{p,N} \tag{2.235}$$

$$\frac{\partial^2 G}{\partial T\,\partial N} = -\left(\frac{\partial S}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial T}\right)_{p,N} \tag{2.236}$$

$$\frac{\partial^2 G}{\partial p\,\partial N} = \left(\frac{\partial V}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial p}\right)_{T,N} . \tag{2.237}$$

### 2.9.5 Relations deriving from $\Omega(T,V,\mu)$

The grand potential $\Omega(T,V,\mu)$ satisfied

$$d\Omega = -S\,dT - p\,dV - N\,d\mu \ , \tag{2.238}$$

hence

$$-S = \left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu} \quad , \quad -p = \left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \quad , \quad -N = \left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} . \tag{2.239}$$

Taking the mixed second derivatives, we find

$$\frac{\partial^2 \Omega}{\partial T\,\partial V} = -\left(\frac{\partial S}{\partial V}\right)_{T,\mu} = -\left(\frac{\partial p}{\partial T}\right)_{V,\mu} \tag{2.240}$$

$$\frac{\partial^2 \Omega}{\partial T\,\partial \mu} = -\left(\frac{\partial S}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial N}{\partial T}\right)_{V,\mu} \tag{2.241}$$

$$\frac{\partial^2 \Omega}{\partial V\,\partial \mu} = -\left(\frac{\partial p}{\partial \mu}\right)_{T,V} = -\left(\frac{\partial N}{\partial V}\right)_{T,\mu} . \tag{2.242}$$

**Relations deriving from $S(E,V,N)$**

We can also derive Maxwell relations based on the entropy $S(E,V,N)$ itself. For example, we have

$$dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN \ . \tag{2.243}$$

Therefore $S = S(E,V,N)$ and

$$\frac{\partial^2 S}{\partial E\,\partial V} = \left(\frac{\partial (T^{-1})}{\partial V}\right)_{E,N} = \left(\frac{\partial (pT^{-1})}{\partial E}\right)_{V,N} , \tag{2.244}$$

*et cetera*.

### 2.9.6 Generalized thermodynamic potentials

We have up until now assumed a generalized force-displacement pair $(y, X) = (-p, V)$. But the above results also generalize to *e.g.* magnetic systems, where $(y, X) = (H, M)$. In general, we have

$$\texttt{THIS SPACE AVAILABLE} \qquad dE = T\,dS + y\,dX + \mu\,dN \tag{2.245}$$

$$F = E - TS \qquad dF = -S\,dT + y\,dX + \mu\,dN \tag{2.246}$$

$$\mathsf{H} = E - yX \qquad d\mathsf{H} = T\,dS - X\,dy + \mu\,dN \tag{2.247}$$

$$G = E - TS - yX \qquad dG = -S\,dT - X\,dy + \mu\,dN \tag{2.248}$$

$$\Omega = E - TS - \mu N \qquad d\Omega = -S\,dT + y\,dX - N\,d\mu\ . \tag{2.249}$$

Generalizing $(-p, V) \to (y, X)$, we also obtain, *mutatis mutandis*, the following Maxwell relations:

$$\begin{array}{lll}
\left(\frac{\partial T}{\partial X}\right)_{S,N} = \left(\frac{\partial y}{\partial S}\right)_{X,N} & \left(\frac{\partial T}{\partial N}\right)_{S,X} = \left(\frac{\partial \mu}{\partial S}\right)_{X,N} & \left(\frac{\partial y}{\partial N}\right)_{S,X} = \left(\frac{\partial \mu}{\partial X}\right)_{S,N} \\
\left(\frac{\partial T}{\partial y}\right)_{S,N} = -\left(\frac{\partial X}{\partial S}\right)_{y,N} & \left(\frac{\partial T}{\partial N}\right)_{S,y} = \left(\frac{\partial \mu}{\partial S}\right)_{y,N} & \left(\frac{\partial X}{\partial N}\right)_{S,y} = -\left(\frac{\partial \mu}{\partial y}\right)_{S,N} \\
\left(\frac{\partial S}{\partial X}\right)_{T,N} = -\left(\frac{\partial y}{\partial T}\right)_{X,N} & \left(\frac{\partial S}{\partial N}\right)_{T,X} = -\left(\frac{\partial \mu}{\partial T}\right)_{X,N} & \left(\frac{\partial y}{\partial N}\right)_{T,X} = \left(\frac{\partial \mu}{\partial X}\right)_{T,N} \\
\left(\frac{\partial S}{\partial y}\right)_{T,N} = \left(\frac{\partial X}{\partial T}\right)_{y,N} & \left(\frac{\partial S}{\partial N}\right)_{T,y} = -\left(\frac{\partial \mu}{\partial T}\right)_{y,N} & \left(\frac{\partial X}{\partial N}\right)_{T,y} = -\left(\frac{\partial \mu}{\partial y}\right)_{T,N} \\
\left(\frac{\partial S}{\partial X}\right)_{T,\mu} = -\left(\frac{\partial y}{\partial T}\right)_{X,\mu} & \left(\frac{\partial S}{\partial \mu}\right)_{T,X} = \left(\frac{\partial N}{\partial T}\right)_{X,\mu} & \left(\frac{\partial y}{\partial \mu}\right)_{T,X} = -\left(\frac{\partial N}{\partial X}\right)_{T,\mu}\ .
\end{array}$$

## 2.10 Equilibrium and Stability

Suppose we have two systems, A and B, which are free to exchange energy, volume, and particle number, subject to overall conservation rules

$$E_{\mathrm{A}} + E_{\mathrm{B}} = E \quad , \quad V_{\mathrm{A}} + V_{\mathrm{B}} = V \quad , \quad N_{\mathrm{A}} + N_{\mathrm{B}} = N\ , \tag{2.250}$$

where $E$, $V$, and $N$ are fixed. Now let us compute the change in the total entropy of the combined systems when they are allowed to exchange energy, volume, or particle number. We assume that the entropy is additive, *i.e.*

$$\begin{aligned}
dS = \Bigg[\left(\frac{\partial S_{\mathrm{A}}}{\partial E_{\mathrm{A}}}\right)_{V_{\mathrm{A}},N_{\mathrm{A}}} - \left(\frac{\partial S_{\mathrm{B}}}{\partial E_{\mathrm{B}}}\right)_{V_{\mathrm{B}},N_{\mathrm{B}}}\Bigg]\, dE_{\mathrm{A}} + \Bigg[\left(\frac{\partial S_{\mathrm{A}}}{\partial V_{\mathrm{A}}}\right)_{E_{\mathrm{A}},N_{\mathrm{A}}} - \left(\frac{\partial S_{\mathrm{B}}}{\partial V_{\mathrm{B}}}\right)_{E_{\mathrm{B}},N_{\mathrm{B}}}\Bigg]\, dV_{\mathrm{A}} \\
+ \Bigg[\left(\frac{\partial S_{\mathrm{A}}}{\partial N_{\mathrm{A}}}\right)_{E_{\mathrm{A}},V_{\mathrm{A}}} - \left(\frac{\partial S_{\mathrm{B}}}{\partial N_{\mathrm{B}}}\right)_{E_{\mathrm{B}},V_{\mathrm{B}}}\Bigg]\, dN_{\mathrm{A}}\ .
\end{aligned} \tag{2.251}$$

Note that we have used $dE_{\mathrm{B}} = -dE_{\mathrm{A}}$, $dV_{\mathrm{B}} = -dV_{\mathrm{A}}$, and $dN_{\mathrm{B}} = -dN_{\mathrm{A}}$. Now we know from the Second Law that spontaneous processes result in $T\,dS > 0$, which means that $S$ tends to a maximum. If $S$ is a maximum, it must

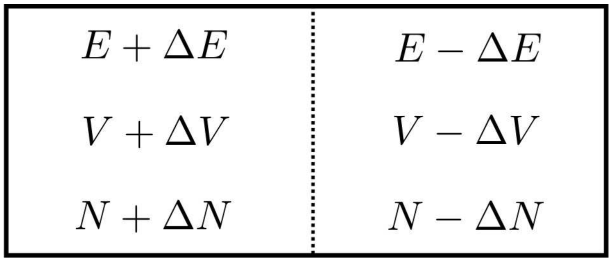


Figure 2.20: To check for an instability, we compare the energy of a system to its total energy when we reapportion its energy, volume, and particle number slightly unequally.

be that the coefficients of $dE_\mathrm{A}$, $dV_\mathrm{A}$, and $dN_\mathrm{A}$ all vanish, else we could increase the total entropy of the system by a judicious choice of these three differentials. From $T\,dS = dE + p\,dV - \mu, dN$, we have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \quad , \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \quad , \quad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V} \quad . \tag{2.252}$$

Thus, we conclude that in order for the system to be in equilibrium, so that $S$ is maximized and can increase no further under spontaneous processes, we must have

$$T_\mathrm{A} = T_\mathrm{B} \qquad \text{(thermal equilibrium)} \tag{2.253}$$

$$\frac{p_\mathrm{A}}{T_\mathrm{A}} = \frac{p_\mathrm{B}}{T_\mathrm{B}} \qquad \text{(mechanical equilibrium)} \tag{2.254}$$

$$\frac{\mu_\mathrm{A}}{T_\mathrm{A}} = \frac{\mu_\mathrm{B}}{T_\mathrm{B}} \qquad \text{(chemical equilibrium)} \tag{2.255}$$

Now consider a uniform system with energy $E' = 2E$, volume $V' = 2V$, and particle number $N' = 2N$. We wish to check that this system is not unstable with respect to spontaneously becoming inhomogeneous. To that end, we imagine dividing the system in half. Each half would have energy $E$, volume $V$, and particle number $N$. But suppose we divided up these quantities differently, so that the left half had slightly different energy, volume, and particle number than the right, as depicted in Fig. 2.20. Does the entropy increase or decrease? We have

$$\begin{aligned}
\Delta S &= S(E + \Delta E, V + \Delta V, N + \Delta N) + S(E - \Delta E, V - \Delta V, N - \Delta N) - S(2E, 2V, 2N) \\
&= \frac{\partial^2 S}{\partial E^2}\,(\Delta E)^2 + \frac{\partial^2 S}{\partial V^2}\,(\Delta V)^2 + \frac{\partial^2 S}{\partial N^2}\,(\Delta N)^2 \\
&\qquad + 2\,\frac{\partial^2 S}{\partial E\,\partial V}\,\Delta E\,\Delta V + 2\,\frac{\partial^2 S}{\partial E\,\partial N}\,\Delta E\,\Delta N + 2\,\frac{\partial^2 S}{\partial V\,\partial N}\,\Delta V\,\Delta N \ .
\end{aligned} \tag{2.256}$$

Thus, we can write

$$\Delta S = \sum_{i,j} Q_{ij}\,\Psi_i\,\Psi_j \ , \tag{2.257}$$

where

$$Q = \begin{pmatrix} \frac{\partial^2 S}{\partial E^2} & \frac{\partial^2 S}{\partial E\,\partial V} & \frac{\partial^2 S}{\partial E\,\partial N} \\ \frac{\partial^2 S}{\partial E\,\partial V} & \frac{\partial^2 S}{\partial V^2} & \frac{\partial^2 S}{\partial V\,\partial N} \\ \frac{\partial^2 S}{\partial E\,\partial N} & \frac{\partial^2 S}{\partial V\,\partial N} & \frac{\partial^2 S}{\partial N^2} \end{pmatrix} \tag{2.258}$$

is the matrix of second derivatives, known in mathematical parlance as the *Hessian*, and $\boldsymbol{\Psi} = (\Delta E, \Delta V, \Delta N)$. Note that $Q$ is a symmetric matrix.

Since $S$ must be a maximum in order for the system to be in equilibrium, we are tempted to conclude that the homogeneous system is stable if and only if all three eigenvalues of $Q$ are negative. If one or more of the eigenvalues is positive, then it is possible to choose a set of variations $\boldsymbol{\Psi}$ such that $\Delta S > 0$, which would contradict the assumption that the homogeneous state is one of maximum entropy. A matrix with this restriction is said to be *negative definite*. While it is true that $Q$ can have no positive eigenvalues, it is clear from homogeneity of $S(E,V,N)$ that one of the three eigenvalues must be zero, corresponding to the eigenvector $\boldsymbol{\Psi} = (E,V,N)$. Homogeneity means $S(\lambda E, \lambda V, \lambda N) = \lambda S(E,V,N)$. Now let us take $\lambda = 1 + \eta$, where $\eta$ is infinitesimal. Then $\Delta E = \eta E$, $\Delta V = \eta V$, and $\Delta N = \eta N$, and homogeneity says $S(E \pm \Delta E, V \pm \Delta V, N \pm \Delta N) = (1 \pm \eta)\, S(E,V,N)$ and $\Delta S = (1+\eta)S + (1-\eta)S - 2S = 0$. We then have a slightly weaker characterization of $Q$ as *negative semidefinite*.

However, if we fix one of the components of $(\Delta E, \Delta V, \Delta N)$ to be zero, then $\boldsymbol{\Psi}$ must have some component orthogonal to the zero eigenvector, in which case $\Delta S > 0$. Suppose we set $\Delta N = 0$ and we just examine the stability with respect to inhomogeneities in energy and volume. We then restrict our attention to the upper left $2 \times 2$ submatrix of $Q$. A general symmetric $2 \times 2$ matrix may be written

$$Q = \begin{pmatrix} a & b \\ b & c \end{pmatrix} \tag{2.259}$$

It is easy to solve for the eigenvalues of $Q$. One finds

$$\lambda_\pm = \left(\frac{a+c}{2}\right) \pm \sqrt{\left(\frac{a-c}{2}\right)^2 + b^2} \ . \tag{2.260}$$

In order for $Q$ to be negative definite, we require $\lambda_+ < 0$ and $\lambda_- < 0$. Clearly we must have $a + c < 0$, or else $\lambda_+ > 0$ for sure. If $a + c < 0$ then clearly $\lambda_- < 0$, but there still is a possibility that $\lambda_+ > 0$, if the radical is larger than $-\frac{1}{2}(a+c)$. Demanding that $\lambda_+ < 0$ therefore yields two conditions:

$$a + c < 0 \qquad \text{and} \qquad ac > b^2 \ . \tag{2.261}$$

Clearly both $a$ and $c$ must be negative, else one of the above two conditions is violated. So in the end we have three conditions which are necessary and sufficient in order that $Q$ be negative definite:

$$a < 0 \quad , \quad c < 0 \quad , \quad ac > b^2 \ . \tag{2.262}$$

Going back to thermodynamic variables, this requires

$$\frac{\partial^2 S}{\partial E^2} < 0 \quad , \quad \frac{\partial^2 S}{\partial V^2} < 0 \quad , \quad \frac{\partial^2 S}{\partial E^2} \cdot \frac{\partial^2 S}{\partial V^2} > \left(\frac{\partial^2 S}{\partial E\, \partial V}\right)^2 \ . \tag{2.263}$$

Another way to say it: *the entropy is a concave function of* $(E,V)$ *at fixed* $N$. Had we set $\Delta E = 0$ and considered the lower right $2 \times 2$ submatrix of $Q$, we'd have concluded that $S(V,N)$ is concave at fixed $E$.

Many thermodynamic systems are held at fixed $(T,p,N)$, which suggests we examine the stability criteria for $G(T,p,N)$. Suppose our system is in equilibrium with a reservoir at temperature $T_0$ and pressure $p_0$. Then, suppressing $N$ (which is assumed constant), we have

$$G(T_0, p_0) = E - T_0\, S + p_0\, V \ . \tag{2.264}$$

Now suppose there is a fluctuation in the entropy and the volume of our system. Going to second order in $\Delta S$ and $\Delta V$, we have

$$\begin{aligned} \Delta G = &\left[\left(\frac{\partial E}{\partial S}\right)_{\!V} - T_0\right] \Delta S + \left[\left(\frac{\partial E}{\partial V}\right)_{\!S} + p_0\right] \Delta V \\ &+ \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}\,(\Delta S)^2 + 2\,\frac{\partial^2 E}{\partial S\,\partial V}\,\Delta S\,\Delta V + \frac{\partial^2 E}{\partial V^2}\,(\Delta V)^2\right] + \ldots \ . \end{aligned} \tag{2.265}$$

The condition for equilibrium is that $\Delta G > 0$ for all $(\Delta S, \Delta V)$. The linear terms vanish by the definition since $T = T_0$ and $p = p_0$. Stability then requires that the Hessian matrix $Q$ be positive definite, with

$$Q = \begin{pmatrix} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S\,\partial V} \\ \frac{\partial^2 E}{\partial S\,\partial V} & \frac{\partial^2 E}{\partial V^2} \end{pmatrix} . \tag{2.266}$$

Thus, we have the following three conditions:

$$\frac{\partial^2 E}{\partial S^2} = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0 \tag{2.267}$$

$$\frac{\partial^2 E}{\partial V^2} = -\left(\frac{\partial p}{\partial V}\right)_S = \frac{1}{V\kappa_S} > 0 \tag{2.268}$$

$$\frac{\partial^2 E}{\partial S^2} \cdot \frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S\,\partial V}\right)^2 = \frac{T}{V\kappa_S\,C_V} - \left(\frac{\partial T}{\partial V}\right)_S^2 > 0\,. \tag{2.269}$$

## 2.11 Applications of Thermodynamics

A discussion of various useful mathematical relations among partial derivatives may be found in the appendix in §2.17. Some facility with the differential multivariable calculus is extremely useful in the analysis of thermodynamics problems.

### 2.11.1 Adiabatic free expansion revisited

Consider once again the adiabatic free expansion of a gas from initial volume $V_\mathrm{i}$ to final volume $V_\mathrm{f} = rV_\mathrm{i}$. Since the system is not in equilibrium during the free expansion process, the initial and final states do not lie along an adiabat, *i.e.* they do not have the same entropy. Rather, as we found, from $Q = W = 0$, we have that $E_\mathrm{i} = E_\mathrm{f}$, which means they have the same *energy*, and, in the case of an ideal gas, the same temperature (assuming $N$ is constant). Thus, the initial and final states lie along an *isotherm*. The situation is depicted in Fig. 2.21. Now let us compute the change in entropy $\Delta S = S_\mathrm{f} - S_\mathrm{i}$ by integrating along this isotherm. Note that the actual dynamics are *irreversible* and *do not* quasistatically follow any continuous thermodynamic path. However, we can use what is a fictitious thermodynamic path as a means of comparing $S$ in the initial and final states.

We have

$$\Delta S = S_\mathrm{f} - S_\mathrm{i} = \int\limits_{V_\mathrm{i}}^{V_\mathrm{f}} dV \left(\frac{\partial S}{\partial V}\right)_{T,N} . \tag{2.270}$$

But from a Maxwell equation deriving from $F$, we have

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N} , \tag{2.271}$$

hence

$$\Delta S = \int\limits_{V_\mathrm{i}}^{V_\mathrm{f}} dV \left(\frac{\partial p}{\partial T}\right)_{V,N} . \tag{2.272}$$

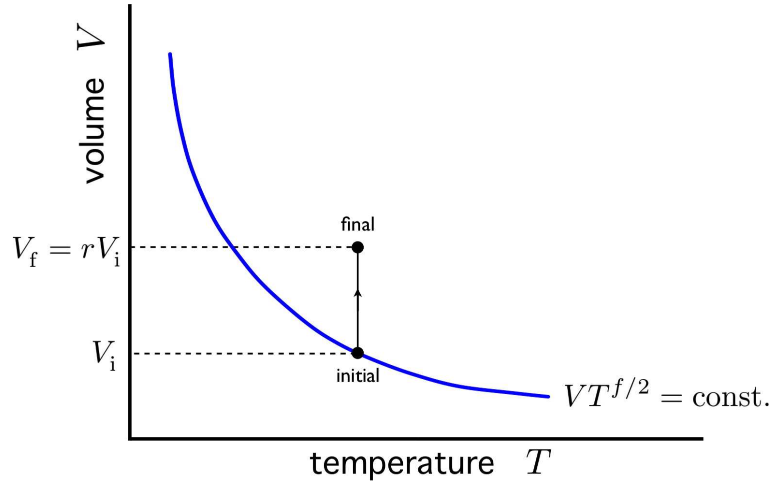


Figure 2.21: Adiabatic free expansion via a thermal path. The initial and final states do not lie along an adabat! Rather, for an ideal gas, the initial and final states lie along an isotherm.

For an ideal gas, we can use the equation of state $pV = Nk_{\rm B}T$ to obtain

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{Nk_{\rm B}}{V} \ . \tag{2.273}$$

The integral can now be computed:

$$\Delta S = \int\limits_{V_{\rm i}}^{rV_{\rm i}} \! dV \, \frac{Nk_{\rm B}}{V} = Nk_{\rm B} \, \ln r \ , \tag{2.274}$$

as we found before, in eqn. 2.156 What is different about this derivation? Previously, we derived the entropy change from the explicit formula for $S(E, V, N)$. Here, we did not need to know this function. The Maxwell relation allowed us to compute the entropy change using only the equation of state.

### 2.11.2 Energy and volume

We saw how $E(T, V, N) = \frac{1}{2} f Nk_{\rm B}T$ for an ideal gas, independent of the volume. In general we should have

$$E(T, V, N) = N \, \phi\big(T, \tfrac{V}{N}\big) \ . \tag{2.275}$$

For the ideal gas, $\phi\big(T, \frac{V}{N}\big) = \frac{1}{2} f k_{\rm B}T$ is a function of $T$ alone and is independent on the other intensive quantity $V/N$. How does energy vary with volume? At fixed temperature and particle number, we have, from $E = F + TS$,

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = \left(\frac{\partial F}{\partial V}\right)_{T,N} + T\left(\frac{\partial S}{\partial V}\right)_{T,N} = -p + T\left(\frac{\partial p}{\partial T}\right)_{V,N} \ , \tag{2.276}$$

where we have used the Maxwell relation $\big(\frac{\partial S}{\partial V}\big)_{T,N} = \big(\frac{\partial p}{\partial T}\big)_{V,N}$, derived from the mixed second derivative $\frac{\partial^2 F}{\partial T \, \partial V}$. Another way to derive this result is as follows. Write $dE = T\,dS - p\,dV + \mu\,dN$ and then express $dS$ in terms of $dT$, $dV$, and $dN$, resulting in

$$dE = T\left(\frac{\partial S}{\partial T}\right)_{V,N} dT + \left[T\left(\frac{\partial S}{\partial V}\right)_{T,N} - p\right] dV - \left[T\left(\frac{\partial \mu}{\partial T}\right)_{V,N} + \mu\right] dN \ . \tag{2.277}$$

Now read off $\big(\frac{\partial E}{\partial V}\big)_{V,N}$ and use the same Maxwell relation as before to recover eqn. 2.276. Applying this result to the ideal gas law $pV = Nk_{\rm B}T$ results in the vanishing of the RHS, hence for any substance obeying the ideal gas law we must have

$$E(T,V,N) = \nu\,\varepsilon(T) = N\varepsilon(T)/N_{\rm A}\ . \tag{2.278}$$

### 2.11.3 van der Waals equation of state

It is clear that the same conclusion follows for any equation of state of the form $p(T,V,N) = T \cdot f(V/N)$, where $f(V/N)$ is an arbitrary function of its argument: the ideal gas law remains valid[10]. This is not true, however, for the van der Waals equation of state,

$$\bigg(p + \frac{a}{v^2}\bigg)(v-b) = RT\ , \tag{2.279}$$

where $v = N_{\rm A}V/N$ is the molar volume. We then find (always assuming constant $N$),

$$\bigg(\frac{\partial E}{\partial V}\bigg)_T = \bigg(\frac{\partial \varepsilon}{\partial v}\bigg)_T = T\bigg(\frac{\partial p}{\partial T}\bigg)_V - p = \frac{a}{v^2}\ , \tag{2.280}$$

where $E(T,V,N) \equiv \nu\,\varepsilon(T,v)$. We can integrate this to obtain

$$\varepsilon(T,v) = \omega(T) - \frac{a}{v}\ , \tag{2.281}$$

where $\omega(T)$ is arbitrary. From eqn. 2.33, we immediately have

$$c_V = \bigg(\frac{\partial \varepsilon}{\partial T}\bigg)_v = \omega'(T)\ . \tag{2.282}$$

What about $c_p$? This requires a bit of work. We start with eqn. 2.34,

$$\begin{aligned} c_p &= \bigg(\frac{\partial \varepsilon}{\partial T}\bigg)_p + p\,\bigg(\frac{\partial v}{\partial T}\bigg)_p \\ &= \omega'(T) + \bigg(p + \frac{a}{v^2}\bigg)\bigg(\frac{\partial v}{\partial T}\bigg)_p \end{aligned} \tag{2.283}$$

We next take the differential of the equation of state (at constant $N$):

$$\begin{aligned} R\,dT &= \bigg(p + \frac{a}{v^2}\bigg)\,dv + \big(v-b\big)\bigg(dp - \frac{2a}{v}\,dv\bigg) \\ &= \bigg(p - \frac{a}{v^2} + \frac{2ab}{v^3}\bigg)\,dv + \big(v-b\big)\,dp\ . \end{aligned} \tag{2.284}$$

We can now read off the result for the volume expansion coefficient,

$$\alpha_p = \frac{1}{v}\bigg(\frac{\partial v}{\partial T}\bigg)_p = \frac{1}{v}\cdot\frac{R}{p - \frac{a}{v^2} + \frac{2ab}{v^3}}\ . \tag{2.285}$$

---

[10] Note $V/N = v/N_{\rm A}$.

We now have for $c_p$,

$$\begin{aligned} c_p &= \omega'(T) + \frac{\big(p + \frac{a}{v^2}\big)\,R}{p - \frac{a}{v^2} + \frac{2ab}{v^3}} \\ &= \omega'(T) + \frac{R^2 T v^3}{RTv^3 - 2a(v-b)^2} \ . \end{aligned} \tag{2.286}$$

where $v = VN_{\rm A}/N$ is the molar volume.

To fix $\omega(T)$, we consider the $v \to \infty$ limit, where the density of the gas vanishes. In this limit, the gas must be ideal, hence eqn. 2.281 says that $\omega(T) = \frac{1}{2} f RT$. Therefore $c_V(T,v) = \frac{1}{2} f R$, just as in the case of an ideal gas. However, rather than $c_p = c_V + R$, which holds for ideal gases, $c_p(T,v)$ is given by eqn. 2.286. Thus,

$$c_V^{\rm VDW} = \tfrac{1}{2} f R \tag{2.287}$$

$$c_p^{\rm VDW} = \tfrac{1}{2} f R + \frac{R^2 T v^3}{RTv^3 - 2a(v-b)^2} \ . \tag{2.288}$$

Note that $c_p(a \to 0) = c_V + R$, which is the ideal gas result.

### 2.11.4 Thermodynamic response functions

Consider the entropy $S$ expressed as a function of $T$, $V$, and $N$:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{V,N} dT + \left(\frac{\partial S}{\partial V}\right)_{T,N} dV + \left(\frac{\partial S}{\partial N}\right)_{T,V} dN \ . \tag{2.289}$$

Dividing by $dT$, multiplying by $T$, and assuming $dN = 0$ throughout, we have

$$C_p - C_V = T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \ . \tag{2.290}$$

Appealing to a Maxwell relation derived from $F(T,V,N)$, and then appealing to eqn. 2.492, we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \ . \tag{2.291}$$

This allows us to write

$$C_p - C_V = -T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p^2 \ . \tag{2.292}$$

We define the *response functions*,

$$\text{isothermal compressibility:}\quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\frac{\partial^2 G}{\partial p^2} \tag{2.293}$$

$$\text{adiabatic compressibility:}\quad \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = -\frac{1}{V}\frac{\partial^2 \mathsf{H}}{\partial p^2} \tag{2.294}$$

$$\text{thermal expansivity:}\quad \alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \ . \tag{2.295}$$

Thus,

$$C_p - C_V = V\,\frac{T\alpha_p^2}{\kappa_T}\ , \tag{2.296}$$

or, in terms of intensive quantities,

$$c_p - c_V = \frac{v\,T\alpha_p^2}{\kappa_T}\ , \tag{2.297}$$

where, as always, $v = VN_{\rm A}/N$ is the molar volume.

This above relation generalizes to any conjugate force-displacement pair $(-p,V) \to (y,X)$:

$$\begin{aligned} C_y - C_X &= -T\left(\frac{\partial y}{\partial T}\right)_X \left(\frac{\partial X}{\partial T}\right)_y \\ &= T\left(\frac{\partial y}{\partial X}\right)_T \left(\frac{\partial X}{\partial T}\right)_y^2 . \end{aligned} \tag{2.298}$$

For example, we could have $(y,X) = (H^\alpha, M^\alpha)$.

A similar relationship can be derived between the compressibilities $\kappa_T$ and $\kappa_S$. We then clearly must start with the volume, writing

$$dV = \left(\frac{\partial V}{\partial p}\right)_{S,N} dp + \left(\frac{\partial V}{\partial S}\right)_{p,N} dS + \left(\frac{\partial V}{\partial p}\right)_{S,p} dN\ . \tag{2.299}$$

Dividing by $dp$, multiplying by $-V^{-1}$, and keeping $N$ constant, we have

$$\kappa_T - \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T\ . \tag{2.300}$$

Again we appeal to a Maxwell relation, writing

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p\ , \tag{2.301}$$

and after invoking the chain rule,

$$\left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p\ , \tag{2.302}$$

we obtain

$$\kappa_T - \kappa_S = \frac{v\,T\alpha_p^2}{c_p}\ . \tag{2.303}$$

Comparing eqns. 2.297 and 2.303, we find

$$(c_p - c_V)\,\kappa_T = (\kappa_T - \kappa_S)\,c_p = v\,T\alpha_p^2\ . \tag{2.304}$$

This result entails

$$\frac{c_p}{c_V} = \frac{\kappa_T}{\kappa_S}\ . \tag{2.305}$$

The corresponding result for magnetic systems is

$$(c_H - c_M)\,\chi_T = (\chi_T - \chi_S)\,c_H = T\left(\frac{\partial m}{\partial T}\right)_H^2\ , \tag{2.306}$$

where $m = M/\nu$ is the magnetization per mole of substance, and

$$\text{isothermal susceptibility:} \quad \chi_T = \left(\frac{\partial M}{\partial H}\right)_T = -\frac{1}{\nu}\,\frac{\partial^2 G}{\partial H^2} \tag{2.307}$$

$$\text{adiabatic susceptibility:} \quad \chi_S = \left(\frac{\partial M}{\partial H}\right)_S = -\frac{1}{\nu}\,\frac{\partial^2 \mathsf{H}}{\partial H^2} \ . \tag{2.308}$$

Here the enthalpy and Gibbs free energy are

$$\mathsf{H} = E - HM \qquad\qquad d\mathsf{H} = T\,dS - M\,dH \tag{2.309}$$

$$G = E - TS - HM \qquad\qquad dG = -S\,dT - M\,dH \ . \tag{2.310}$$

*Remark:* The previous discussion has assumed an isotropic magnetic system where $\boldsymbol{M}$ and $\boldsymbol{H}$ are collinear, hence $\boldsymbol{H}\cdot\boldsymbol{M} = HM$.

$$\chi_T^{\alpha\beta} = \left(\frac{\partial M^\alpha}{\partial H^\beta}\right)_T = -\frac{1}{\nu}\,\frac{\partial^2 G}{\partial H^\alpha\,\partial H^\beta} \tag{2.311}$$

$$\chi_S^{\alpha\beta} = \left(\frac{\partial M^\alpha}{\partial H^\beta}\right)_S = -\frac{1}{\nu}\,\frac{\partial^2 \mathsf{H}}{\partial H^\alpha\,\partial H^\beta} \ . \tag{2.312}$$

In this case, the enthalpy and Gibbs free energy are

$$\mathsf{H} = E - \boldsymbol{H}\cdot\boldsymbol{M} \qquad\qquad d\mathsf{H} = T\,dS - \boldsymbol{M}\cdot d\boldsymbol{H} \tag{2.313}$$

$$G = E - TS - \boldsymbol{H}\cdot\boldsymbol{M} \qquad\qquad dG = -S\,dT - \boldsymbol{M}\cdot d\boldsymbol{H} \ . \tag{2.314}$$

### 2.11.5 Joule effect: free expansion of a gas

Previously we considered the adiabatic free expansion of an ideal gas. We found that $Q = W = 0$ hence $\Delta E = 0$, which means the process is isothermal, since $E = \nu\varepsilon(T)$ is volume-independent. The entropy changes, however, since $S(E,V,N) = Nk_{\rm B}\ln(V/N) + \frac{1}{2}fNk_{\rm B}\ln(E/N) + Ns_0$. Thus,

$$S_{\rm f} = S_{\rm i} + Nk_{\rm B}\ln\!\left(\frac{V_{\rm f}}{V_{\rm i}}\right) . \tag{2.315}$$

What happens if the gas is nonideal?

We integrate along a fictitious thermodynamic path connecting initial and final states, where $dE = 0$ along the path. We have

$$0 = dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT \tag{2.316}$$

hence

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} = -\frac{1}{C_V}\left(\frac{\partial E}{\partial V}\right)_T \ . \tag{2.317}$$

We also have

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p \ . \tag{2.318}$$

Thus,

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] . \tag{2.319}$$

| gas | $a$ $\left(\frac{\mathrm{L}^2\cdot\mathrm{bar}}{\mathrm{mol}^2}\right)$ | $b$ $\left(\frac{\mathrm{L}}{\mathrm{mol}}\right)$ | $p_c$ (bar) | $T_c$ (K) | $v_c$ (L/mol) |
|---|---|---|---|---|---|
| Acetone | 14.09 | 0.0994 | 52.82 | 505.1 | 0.2982 |
| Argon | 1.363 | 0.03219 | 48.72 | 150.9 | 0.0966 |
| Carbon dioxide | 3.640 | 0.04267 | 7404 | 304.0 | 0.1280 |
| Ethanol | 12.18 | 0.08407 | 63.83 | 516.3 | 0.2522 |
| Freon | 10.78 | 0.0998 | 40.09 | 384.9 | 0.2994 |
| Helium | 0.03457 | 0.0237 | 2.279 | 5.198 | 0.0711 |
| Hydrogen | 0.2476 | 0.02661 | 12.95 | 33.16 | 0.0798 |
| Mercury | 8.200 | 0.01696 | 1055 | 1723 | 0.0509 |
| Methane | 2.283 | 0.04278 | 46.20 | 190.2 | 0.1283 |
| Nitrogen | 1.408 | 0.03913 | 34.06 | 128.2 | 0.1174 |
| Oxygen | 1.378 | 0.03183 | 50.37 | 154.3 | 0.0955 |
| Water | 5.536 | 0.03049 | 220.6 | 647.0 | 0.0915 |

Table 2.3: Van der Waals parameters for some common gases. (*Source: Wikipedia.*)

Note that the term in square brackets vanishes for any system obeying the ideal gas law. For a nonideal gas,

$$\Delta T = \int\limits_{V_\mathrm{i}}^{V_\mathrm{f}} dV \left(\frac{\partial T}{\partial V}\right)_{\!E} \ , \tag{2.320}$$

which is in general nonzero.

Now consider a van der Waals gas, for which

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT \ .$$

We then have

$$p - T\left(\frac{\partial p}{\partial T}\right)_{\!V} = -\frac{a}{v^2} = -\frac{a\nu^2}{V^2} \ . \tag{2.321}$$

In §2.11.3 we concluded that $C_V = \frac{1}{2} f \nu R$ for the van der Waals gas, hence

$$\Delta T = -\frac{2a\nu}{fR} \int\limits_{V_\mathrm{i}}^{V_\mathrm{f}} \frac{dV}{V^2} = \frac{2a}{fR}\left(\frac{1}{v_\mathrm{f}} - \frac{1}{v_\mathrm{i}}\right) \ . \tag{2.322}$$

Thus, if $V_\mathrm{f} > V_\mathrm{i}$, we have $T_\mathrm{f} < T_\mathrm{i}$ and the gas cools upon expansion.

Consider $O_2$ gas with an initial specific volume of $v_\mathrm{i} = 22.4\,\mathrm{L/mol}$, which is the STP value for an ideal gas, freely expanding to a volume $v_\mathrm{f} = \infty$ for maximum cooling. According to table 2.3, $a = 1.378\,\mathrm{L}^2 \cdot \mathrm{bar/mol}^2$, and we have $\Delta T = -2a/fRv_i = -0.296\,\mathrm{K}$, which is a pitifully small amount of cooling. Adiabatic free expansion is a very inefficient way to cool a gas.

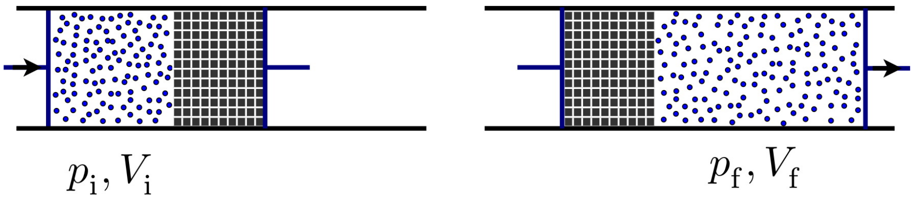


Figure 2.22: In a throttle, a gas is pushed through a porous plug separating regions of different pressure. The change in energy is the work done, hence enthalpy is conserved during the throttling process.

### 2.11.6 Throttling: the Joule-Thompson effect

In a throttle, depicted in Fig. 2.22, a gas is forced through a porous plug which separates regions of different pressures. According to the figure, the work done on a given element of gas is

$$W = \int\limits_0^{V_{\rm f}} dV\, p_{\rm f} \; - \int\limits_0^{V_{\rm i}} dV\, p_{\rm i} = p_{\rm f} V_{\rm f} - p_{\rm i} V_{\rm i} \ . \tag{2.323}$$

Now we assume that the system is thermally isolated so that the gas exchanges no heat with its environment, nor with the plug. Then $Q = 0$ so $\Delta E = -W$, and

$$E_{\rm i} + p_{\rm i} V_{\rm i} = E_{\rm f} + p_{\rm f} V_{\rm f} \tag{2.324}$$

$$\mathsf{H}_{\rm i} = \mathsf{H}_{\rm f} \ , \tag{2.325}$$

where $\mathsf{H}$ is enthalpy. Thus, the throttling process is *isenthalpic*. We can therefore study it by defining a fictitious thermodynamic path along which $d\mathsf{H} = 0$. The, choosing $T$ and $p$ as state variables,

$$0 = d\mathsf{H} = \left(\frac{\partial \mathsf{H}}{\partial T}\right)_{\!p} dp \; + \left(\frac{\partial \mathsf{H}}{\partial p}\right)_{\!T} dT \tag{2.326}$$

hence

$$\left(\frac{\partial T}{\partial p}\right)_{\!\mathsf{H}} = -\frac{(\partial \mathsf{H}/\partial p)_T}{(\partial \mathsf{H}/\partial T)_p} \ . \tag{2.327}$$

The numerator on the RHS is computed by writing $d\mathsf{H} = T\,dS + V\,dp$ and then dividing by $dp$, to obtain

$$\left(\frac{\partial \mathsf{H}}{\partial p}\right)_{\!T} = V + T\left(\frac{\partial S}{\partial p}\right)_{\!T} = V - T\left(\frac{\partial V}{\partial T}\right)_{\!p} \ . \tag{2.328}$$

The denominator is

$$\begin{aligned} \left(\frac{\partial \mathsf{H}}{\partial T}\right)_{\!p} &= \left(\frac{\partial \mathsf{H}}{\partial S}\right)_{\!p} \left(\frac{\partial S}{\partial T}\right)_{\!p} \\ &= T\left(\frac{\partial S}{\partial T}\right)_{\!p} = C_p \ . \end{aligned} \tag{2.329}$$

Thus,

$$\begin{aligned} \left(\frac{\partial T}{\partial p}\right)_{\!\mathsf{H}} &= \frac{1}{c_p}\left[ T\left(\frac{\partial v}{\partial T}\right)_{\!p} - v \right] \\ &= \frac{v}{c_p}\big(T\alpha_p - 1\big) \ , \end{aligned} \tag{2.330}$$

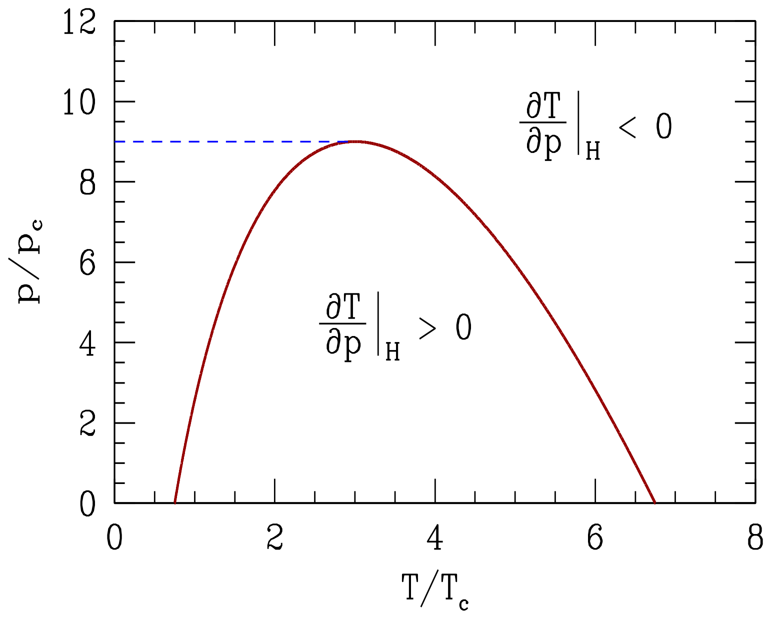


Figure 2.23: Inversion temperature $T^*(p)$ for the van der Waals gas. Pressure and temperature are given in terms of $p_c = a/27b^2$ and $T_c = 8a/27bR$, respectively.

where $\alpha_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ is the volume expansion coefficient.

From the van der Waals equation of state, we obtain, from eqn. 2.285,

$$T\alpha_p = \frac{T}{v}\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT/v}{p - \frac{a}{v^2} + \frac{2ab}{v^3}} = \frac{v-b}{v - \frac{2a}{RT}\left(\frac{v-b}{v}\right)^2} . \tag{2.331}$$

Assuming $v \gg \frac{a}{RT}, b$, we have

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{c_p}\left(\frac{2a}{RT} - b\right) . \tag{2.332}$$

Thus, for $T > T^* = \frac{2a}{Rb}$, we have $\left(\frac{\partial T}{\partial p}\right)_H < 0$ and the gas heats up upon an isenthalpic pressure decrease. For $T < T^*$, the gas cools under such conditions.

In fact, there are two inversion temperatures $T^*_{1,2}$ for the van der Waals gas. To see this, we set $T\alpha_p = 1$, which is the criterion for inversion. From eqn. 2.331 it is easy to derive

$$\frac{b}{v} = 1 - \sqrt{\frac{bRT}{2a}} . \tag{2.333}$$

We insert this into the van der Waals equation of state to derive a relationship $T = T^*(p)$ at which $T\alpha_p = 1$ holds. After a little work, we find

$$p = -\frac{3RT}{2b} + \sqrt{\frac{8aRT}{b^3}} - \frac{a}{b^2} . \tag{2.334}$$

This is a quadratic equation for $T$, the solution of which is

$$T^*(p) = \frac{2a}{9\,bR}\left(2 \pm \sqrt{1 - \frac{3b^2p}{a}}\right)^2 . \tag{2.335}$$

In Fig. 2.23 we plot pressure *versus* temperature in scaled units, showing the curve along which $\left(\frac{\partial T}{\partial p}\right)_{\mathsf{H}} = 0$. The volume, pressure, and temperature scales defined are

$$v_{\mathrm{c}} = 3b \qquad , \qquad p_{\mathrm{c}} = \frac{a}{27\,b^2} \qquad , \qquad T_{\mathrm{c}} = \frac{8a}{27\,bR} \ . \tag{2.336}$$

Values for $p_{\mathrm{c}}$, $T_{\mathrm{c}}$, and $v_{\mathrm{c}}$ are provided in table 2.3. If we define $v = v/v_{\mathrm{c}}$, $p = p/p_{\mathrm{c}}$, and $T = T/T_{\mathrm{c}}$, then the van der Waals equation of state may be written in dimensionless form:

$$\left(p + \frac{3}{v^2}\right)(3v - 1) = 8T \ . \tag{2.337}$$

In terms of the scaled parameters, the equation for the inversion curve $\left(\frac{\partial T}{\partial p}\right)_{\mathsf{H}} = 0$ becomes

$$p = 9 - 36\left(1 - \sqrt{\tfrac{1}{3}T}\,\right)^2 \qquad \Longleftrightarrow \qquad T = 3\Big(1 \pm \sqrt{1 - \tfrac{1}{9}\,p}\,\Big)^2 \ . \tag{2.338}$$

Thus, there is no inversion for $p > 9\,p_{\mathrm{c}}$. We are usually interested in the upper inversion temperature, $T_2^*$, corresponding to the upper sign in eqn. 2.335. The maximum inversion temperature occurs for $p = 0$, where $T^*_{\mathrm{max}} = \frac{2a}{bR} = \frac{27}{4}\,T_{\mathrm{c}}$. For $H_2$, from the data in table 2.3, we find $T^*_{\mathrm{max}}(H_2) = 224\,\mathrm{K}$, which is within 10% of the experimentally measured value of $205\,\mathrm{K}$.

What happens when $H_2$ gas leaks from a container with $T > T_2^*$? Since $\left(\frac{\partial T}{\partial p}\right)_{\mathsf{H}} < 0$ and $\Delta p < 0$, we have $\Delta T > 0$. The gas warms up, and the heat facilitates the reaction $2\,H_2 + O_2 \longrightarrow 2\,H_2O$, which releases energy, and we have a nice explosion.

## 2.12 Phase Transitions and Phase Equilibria

A typical phase diagram of a $p$-$V$-$T$ system is shown in the Fig. 2.24(a). The solid lines delineate boundaries between distinct thermodynamic phases. These lines are called *coexistence curves*. Along these curves, we can have coexistence of two phases, and the thermodynamic potentials are singular. The order of the singularity is often taken as a classification of the phase transition. *I.e.* if the thermodynamic potentials $E$, $F$, $G$, and $\mathsf{H}$ have discontinuous or divergent $m^{\mathrm{th}}$ derivatives, the transition between the respective phases is said to be $m^{\mathrm{th}}$ *order*. Modern theories of phase transitions generally only recognize two possibilities: *first order transitions*, where the *order parameter* changes *discontinuously* through the transition, and *second order transitions*, where the order parameter vanishes continuously at the boundary from ordered to disordered phases[11]. We'll discuss order parameters during Physics 140B.

For a more interesting phase diagram, see Fig. 2.24(b,c), which displays the phase diagrams for $^3$He and $^4$He. The only difference between these two atoms is that the former has one fewer neutron: (2p + 1n + 2e) in $^3$He *versus* (2p + 2n + 2e) in $^4$He. As we shall learn when we study quantum statistics, this extra neutron makes all the difference, because $^3$He is a fermion while $^4$He is a boson.

### 2.12.1 $p$-$v$-$T$ surfaces

The equation of state for a single component system may be written as

$$f(p, v, T) = 0 \ . \tag{2.339}$$

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[11] Some exotic phase transitions in quantum matter, which do not quite fit the usual classification schemes, have recently been proposed.

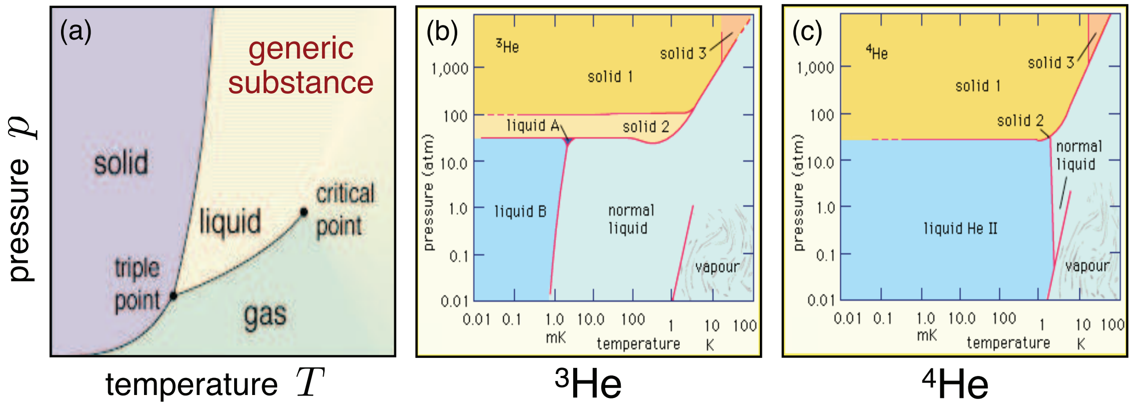

Figure 2.24: (a) Typical thermodynamic phase diagram of a single component $p$-$V$-$T$ system, showing triple point (three phase coexistence) and critical point. (*Source: Univ. of Helsinki.*) Also shown: phase diagrams for $^3$He (b) and $^4$He (c). What a difference a neutron makes! (*Source: Brittanica.*)

This may in principle be inverted to yield $p = p(v, T)$ or $v = v(T, p)$ or $T = T(p, v)$. The single constraint $f(p, v, T)$ on the three state variables defines a *surface* in $\{p, v, T\}$ space. An example of such a surface is shown in Fig. 2.25, for the ideal gas.

Real $p$-$v$-$T$ surfaces are much richer than that for the ideal gas, because real systems undergo *phase transitions* in which thermodynamic properties are singular or discontinuous along certain curves on the $p$-$v$-$T$ surface. An example is shown in Fig. 2.26. The high temperature isotherms resemble those of the ideal gas, but as one cools below the *critical temperature* $T_c$, the isotherms become singular. Precisely at $T = T_c$, the isotherm $p = p(v, T_c)$ becomes perfectly horizontal at $v = v_c$, which is the *critical molar volume*. This means that the isothermal compressibility, $\kappa_T = -\frac{1}{v}\big(\frac{\partial v}{\partial p}\big)_T$ *diverges* at $T = T_c$. Below $T_c$, the isotherms have a flat portion, as shown in Fig. 2.28, corresponding to a *two-phase region* where liquid and vapor coexist. In the $(p, T)$ plane, sketched for $H_2O$ in Fig. 2.4 and shown for $CO_2$ in Fig. 2.29, this liquid-vapor phase coexistence occurs along a curve, called the vaporization (or boiling) curve. The density changes discontinuously across this curve; for $H_2O$, the liquid is approximately 1000 times denser than the vapor at atmospheric pressure. The density discontinuity vanishes at the critical point. Note that one can continuously transform between liquid and vapor phases, without encountering any phase transitions, by going around the critical point and avoiding the two-phase region.

In addition to liquid-vapor coexistence, solid-liquid and solid-vapor coexistence also occur, as shown in Fig. 2.26. The *triple point* $(\mathrm{T_t}, p_t)$ lies at the confluence of these three coexistence regions. For $H_2O$, the location of the triple point and critical point are given by

$$\begin{aligned} \mathrm{T_t} &= 273.16\,\mathrm{K} & \qquad\qquad T_c &= 647\,\mathrm{K} \\ \mathrm{p_t} &= 611.7\,\mathrm{Pa} = 6.037\times 10^{-3}\,\mathrm{atm} & \qquad\qquad \mathrm{p_c} &= 22.06\,\mathrm{MPa} = 217.7\,\mathrm{atm} \end{aligned}$$

### 2.12.2 The Clausius-Clapeyron relation

Recall that the homogeneity of $E(S, V, N)$ guaranteed $E = TS - pV + \mu N$, from Euler's theorem. It also guarantees a relation between the intensive variables $T$, $p$, and $\mu$, according to eqn. 2.148. Let us define $g \equiv G/\nu = N_A\mu$, the Gibbs free energy per mole. Then

$$dg = -s\,dT + v\,dp\;, \tag{2.340}$$

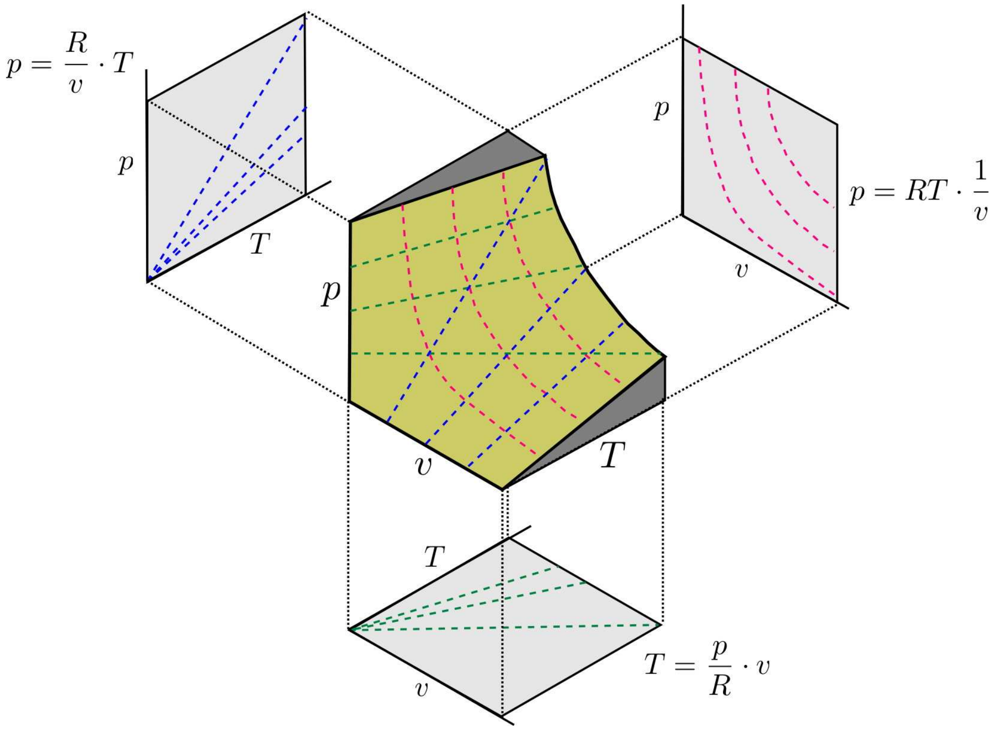

Figure 2.25: The surface $p(v,T) = RT/v$ corresponding to the ideal gas equation of state, and its projections onto the $(p,T)$, $(p,v)$, and $(T,v)$ planes.

where $s = S/\nu$ and $v = V/\nu$ are the molar entropy and molar volume, respectively. Along a coexistence curve between phase #1 and phase #2, we must have $g_1 = g_2$, since the phases are free to exchange energy and particle number, *i.e.* they are in thermal and chemical equilibrium. This means

$$dg_1 = -s_1\, dT + v_1\, dp = -s_2\, dT + v_2\, dp = dg_2 \ . \tag{2.341}$$

Therefore, along the coexistence curve we must have

$$\bigg(\frac{dp}{dT}\bigg)_{\rm coex} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T\,\Delta v} \ , \tag{2.342}$$

where

$$\ell \equiv T\,\Delta s = T\,(s_2 - s_1) \tag{2.343}$$

is the *molar latent heat of transition*. A heat $\ell$ must be supplied in order to change from phase #1 to phase #2, even without changing $p$ or $T$. If $\ell$ is the latent heat per mole, then we write $\tilde\ell$ as the latent heat per gram: $\tilde\ell = \ell/M$, where $M$ is the molar mass.

Along the liquid-gas coexistence curve, we typically have $v_{\rm gas} \gg v_{\rm liquid}$, and assuming the vapor is ideal, we may write $\Delta v \approx v_{\rm gas} \approx RT/p$. Thus,

$$\bigg(\frac{dp}{dT}\bigg)_{\rm liq-gas} = \frac{\ell}{T\,\Delta v} \approx \frac{p\,\ell}{RT^2} \ . \tag{2.344}$$

If $\ell$ remains constant throughout a section of the liquid-gas coexistence curve, we may integrate the above equation to get

$$\frac{dp}{p} = \frac{\ell}{R}\,\frac{dT}{T^2} \qquad \Longrightarrow \qquad p(T) = p(T_0)\, e^{\ell/RT_0}\, e^{-\ell/RT} \ . \tag{2.345}$$

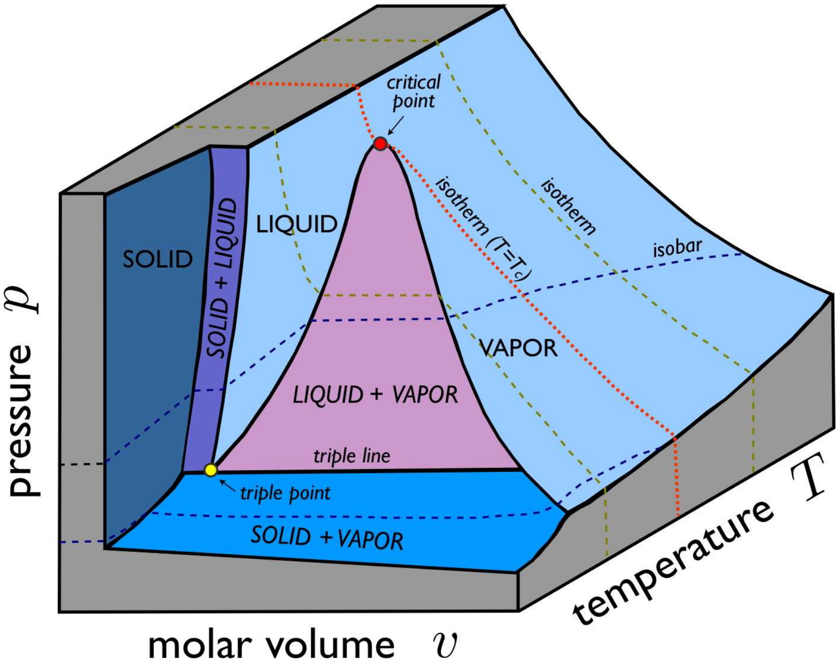

Figure 2.26: A $p$-$v$-$T$ surface for a substance which contracts upon freezing. The red dot is the *critical point* and the red dashed line is the *critical isotherm*. The yellow dot is the *triple point* at which there is three phase coexistence of solid, liquid, and vapor.

### 2.12.3 Liquid-solid line in $H_2O$

Life on planet earth owes much of its existence to a peculiar property of water: the solid is less dense than the liquid along the coexistence curve. For example at $T = 273.1\,\text{K}$ and $p = 1\,\text{atm}$,

$$\tilde{v}_{\text{water}} = 1.00013\,\text{cm}^3/\text{g} \qquad , \qquad \tilde{v}_{\text{ice}} = 1.0907\,\text{cm}^3/\text{g}\,. \tag{2.346}$$

The latent heat of the transition is $\tilde{\ell} = 333\,\text{J/g} = 79.5\,\text{cal/g}$. Thus,

$$\begin{aligned}\left(\frac{dp}{dT}\right)_{\text{liq}-\text{sol}} &= \frac{\tilde{\ell}}{T\,\Delta\tilde{v}} = \frac{333\,\text{J/g}}{(273.1\,\text{K})\,(-9.05\times10^{-2}\,\text{cm}^3/\text{g})}\\ &= -1.35\times10^{8}\,\frac{\text{dyn}}{\text{cm}^2\,\text{K}} = -134\,\frac{\text{atm}}{{}^\circ\text{C}}\,.\end{aligned} \tag{2.347}$$

The negative slope of the melting curve is invoked to explain the movement of glaciers: as glaciers slide down a rocky slope, they generate enormous pressure at obstacles[12] Due to this pressure, the story goes, the melting temperature decreases, and the glacier melts around the obstacle, so it can flow past it, after which it refreezes. But it is not the case that the bottom of the glacier melts under the pressure, for consider a glacier of height $h = 1\,\text{km}$. The pressure at the bottom is $p \sim gh/\tilde{v} \sim 10^7\,\text{Pa}$, which is only about 100 atmospheres. Such a pressure can produce only a small shift in the melting temperature of about $\Delta T_{\text{melt}} = -0.75^\circ\,\text{C}$.

Does the Clausius-Clapeyron relation explain how we can skate on ice? My seven year old daughter has a mass of about $M = 20\,\text{kg}$. Her ice skates have blades of width about $5\,\text{mm}$ and length about $10\,\text{cm}$. Thus, even on one

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[12] The melting curve has a negative slope at relatively low pressures, where the solid has the so-called Ih hexagonal crystal structure. At pressures above about 2500 atmospheres, the crystal structure changes, and the slope of the melting curve becomes positive.

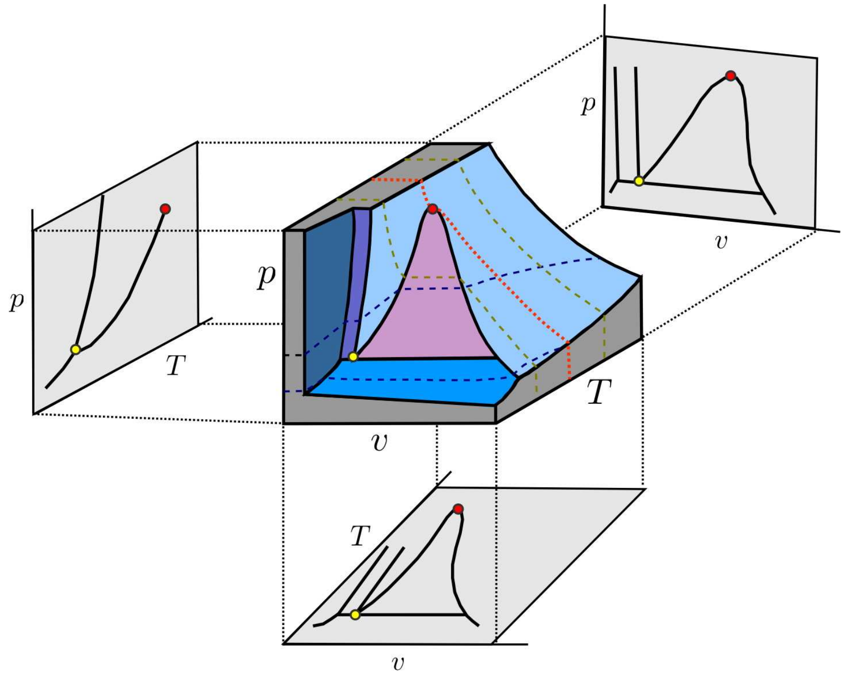

Figure 2.27: Equation of state for a substance which expands upon freezing, projected to the $(v, T)$ and $(v, p)$ and $(T, p)$ planes.

foot, she only imparts an additional pressure of

$$\Delta p = \frac{Mg}{A} \approx \frac{20\,\mathrm{kg} \times 9.8\,\mathrm{m/s^2}}{(5 \times 10^{-3}\,\mathrm{m}) \times (10^{-1}\,\mathrm{m})} = 3.9 \times 10^5\,\mathrm{Pa} = 3.9\,\mathrm{atm}\ . \tag{2.348}$$

The change in the melting temperature is thus minuscule: $\Delta T_{\mathrm{melt}} \approx -0.03^\circ\,\mathrm{C}$.

So why can my daughter skate so nicely? The answer isn't so clear![13] There seem to be two relevant issues in play. First, friction generates heat which can locally melt the surface of the ice. Second, the surface of ice, and of many solids, is naturally slippery. Indeed, this is the case for ice even if one is standing still, generating no frictional forces. Why is this so? It turns out that the Gibbs free energy of the ice-air interface is larger than the sum of free energies of ice-water and water-air interfaces. That is to say, ice, as well as many simple solids, prefers to have a thin layer of liquid on its surface, even at temperatures well below its bulk melting point. If the intermolecular interactions are not short-ranged[14], theory predicts a surface melt thickness $d \propto (T_{\mathrm{m}} - T)^{-1/3}$. In Fig. 2.30 we show measurements by Gilpin (1980) of the surface melt on ice, down to about $-50^\circ$ C. Near $0^\circ$ C the melt layer thickness is about $40\,\mathrm{nm}$, but this decreases to $\sim 1\,\mathrm{nm}$ at $T = -35^\circ\,\mathrm{C}$. At very low temperatures, skates stick rather than glide. Of course, the skate material is also important, since that will affect the energetics of the second interface. The 19th century novel, *Hans Brinker, or The Silver Skates* by Mary Mapes Dodge tells the story of the poor but stereotypically decent and hardworking Dutch boy Hans Brinker, who dreams of winning an upcoming ice skating race, along with the top prize: a pair of silver skates. All he has are some lousy wooden skates, which won't do him any good in the race. He has money saved to buy steel skates, but of course his father desperately needs an operation because – I am not making this up – he fell off a dike and lost his mind. The family has no other way to pay for the doctor. What a story! At this point, I imagine the suspense must be too much for you to bear, but this isn't an American Literature class, so you can use Google to find out what happens (or rent the 1958

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[13] For a recent discussion, see R. Rosenberg, *Physics Today* **58**, 50 (2005).

[14] For example, they could be of the van der Waals form, due to virtual dipole fluctuations, with an attractive $1/r^6$ tail.

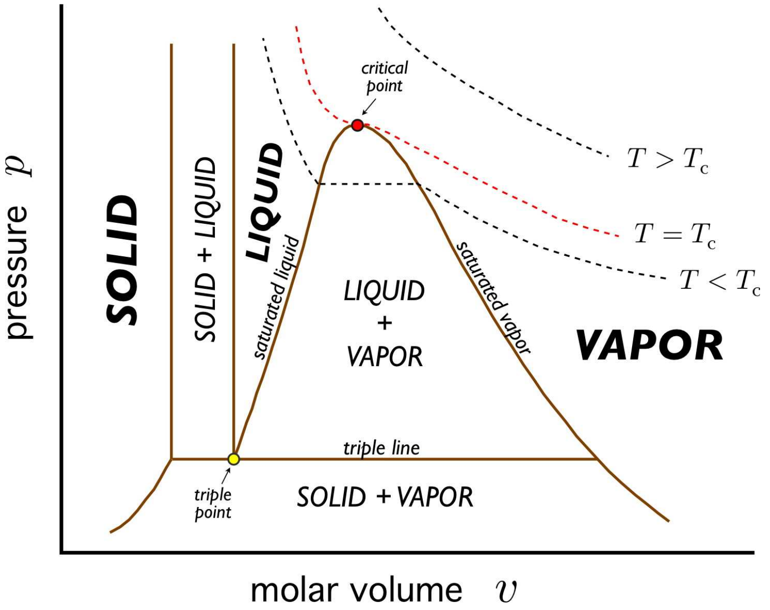

Figure 2.28: Projection of the $p$-$v$-$T$ surface of Fig. 2.26 onto the $(v, p)$ plane.

movie, directed by Sidney Lumet). My point here is that Hans' crappy wooden skates can't compare to the metal ones, even though the surface melt between the ice and the air is the same. The skate blade material also makes a difference, both for the interface energy and, perhaps more importantly, for the generation of friction as well.

### 2.12.4 Slow melting of ice : a quasistatic but irreversible process

Suppose we have an ice cube initially at temperature $T_0 < \Theta \equiv 273.15\,\mathrm{K}$ (*i.e.* $\Theta = 0^\circ$ C) and we toss it into a pond of water. We regard the pond as a heat bath at some temperature $T_1 > \Theta$. Let the mass of the ice be $M$. How much heat $Q$ is absorbed by the ice in order to raise its temperature to $T_1$? Clearly

$$Q = M\tilde{c}_{\mathrm{S}}(\Theta - T_0) + M\tilde{\ell} + M\tilde{c}_{\mathrm{L}}(T_1 - \Theta) \; , \tag{2.349}$$

where $\tilde{c}_{\mathrm{S}}$ and $\tilde{c}_{\mathrm{L}}$ are the specific heats of ice (solid) and water (liquid), respectively[15], and $\tilde{\ell}$ is the latent heat of melting per unit mass. The pond must give up this much heat to the ice, hence the entropy of the pond, discounting the new water which will come from the melted ice, must decrease:

$$\Delta S_{\mathrm{pond}} = -\frac{Q}{T_1} \; . \tag{2.350}$$

Now we ask what is the entropy change of the $H_2O$ in the ice. We have

$$\begin{aligned} \Delta S_{\mathrm{ice}} &= \int \frac{đQ}{T} = \int\limits_{T_0}^{\Theta} dT\,\frac{M\tilde{c}_{\mathrm{S}}}{T} + \frac{M\tilde{\ell}}{\Theta} + \int\limits_{\Theta}^{T_1} dT\,\frac{M\tilde{c}_{\mathrm{L}}}{T} \\ &= M\tilde{c}_{\mathrm{S}} \ln\!\bigg(\frac{\Theta}{T_0}\bigg) + \frac{M\tilde{\ell}}{\Theta} + M\tilde{c}_{\mathrm{L}} \ln\!\bigg(\frac{T_1}{\Theta}\bigg) \; . \end{aligned} \tag{2.351}$$

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[15] We assume $\tilde{c}_{\mathrm{S}}(T)$ and $\tilde{c}_{\mathrm{L}}(T)$ have no appreciable temperature dependence, and we regard them both as constants.

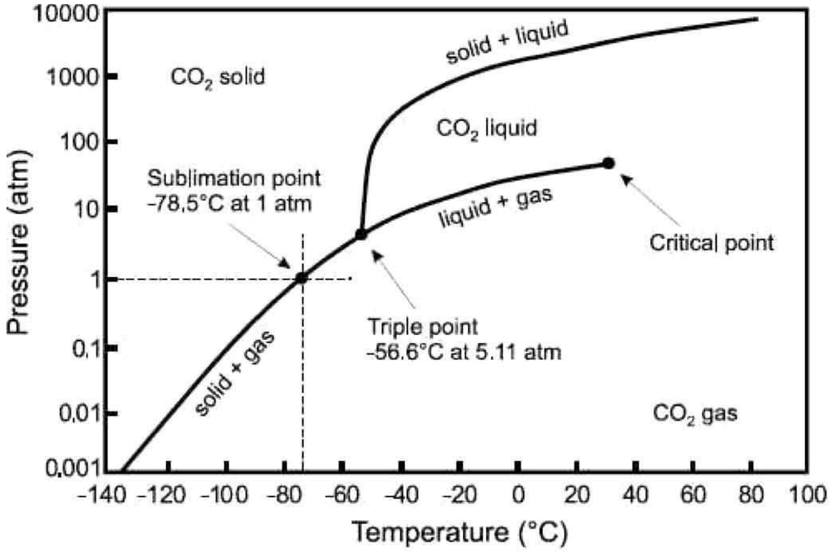

Figure 2.29: Phase diagram for $\mathrm{CO_2}$ in the $(p,T)$ plane. (*Source: www.scifun.org.*)

The total entropy change of the system is then

$$\begin{aligned}\Delta S_{\rm total} &= \Delta S_{\rm pond} + \Delta S_{\rm ice}\\ &= M\tilde c_{\rm S}\ln\!\bigg(\frac{\Theta}{T_0}\bigg) - M\tilde c_{\rm S}\bigg(\frac{\Theta-T_0}{T_1}\bigg) + M\tilde\ell\,\bigg(\frac{1}{\Theta}-\frac{1}{T_1}\bigg) + M\tilde c_{\rm L}\ln\!\bigg(\frac{T_1}{\Theta}\bigg) - M\tilde c_{\rm L}\bigg(\frac{T_1-\Theta}{T_1}\bigg)\end{aligned} \tag{2.352}$$

Now since $T_0 < \Theta < T_1$, we have

$$M\tilde c_{\rm S}\bigg(\frac{\Theta-T_0}{T_1}\bigg) < M\tilde c_{\rm S}\bigg(\frac{\Theta-T_0}{\Theta}\bigg) . \tag{2.353}$$

Therefore,

$$\Delta S > M\tilde\ell\,\bigg(\frac{1}{\Theta}-\frac{1}{T_1}\bigg) + M\tilde c_{\rm S}\, f\big(T_0/\Theta\big) + M\tilde c_{\rm L}\, f\big(\Theta/T_1\big) , \tag{2.354}$$

where $f(x) = x-1-\ln x$. Clearly $f'(x) = 1-x^{-1}$ is negative on the interval $(0,1)$, which means that the maximum of $f(x)$ occurs at $x=0$ and the minimum at $x=1$. But $f(0)=\infty$ and $f(1)=0$, which means that $f(x)\ge 0$ for $x\in[0,1]$. Since $T_0 < \Theta < T_1$, we conclude $\Delta S_{\rm total} > 0$.

### 2.12.5 Gibbs phase rule

Equilibrium between two phases means that $p$, $T$, and $\mu(p,T)$ are identical. From

$$\mu_1(p,T) = \mu_2(p,T) , \tag{2.355}$$

we derive an equation for the slope of the coexistence curve, the Clausius-Clapeyron relation. Note that we have one equation in two unknowns $(T,p)$, so the solution set is a curve. For three phase coexistence, we have

$$\mu_1(p,T) = \mu_2(p,T) = \mu_3(p,T) , \tag{2.356}$$

which gives us two equations in two unknowns. The solution is then a point (or a set of points). A *critical point* also is a solution of two simultaneous equations:

$$\text{critical point} \quad\Longrightarrow\quad v_1(p,T) = v_2(p,T) \quad , \quad \mu_1(p,T) = \mu_2(p,T) . \tag{2.357}$$

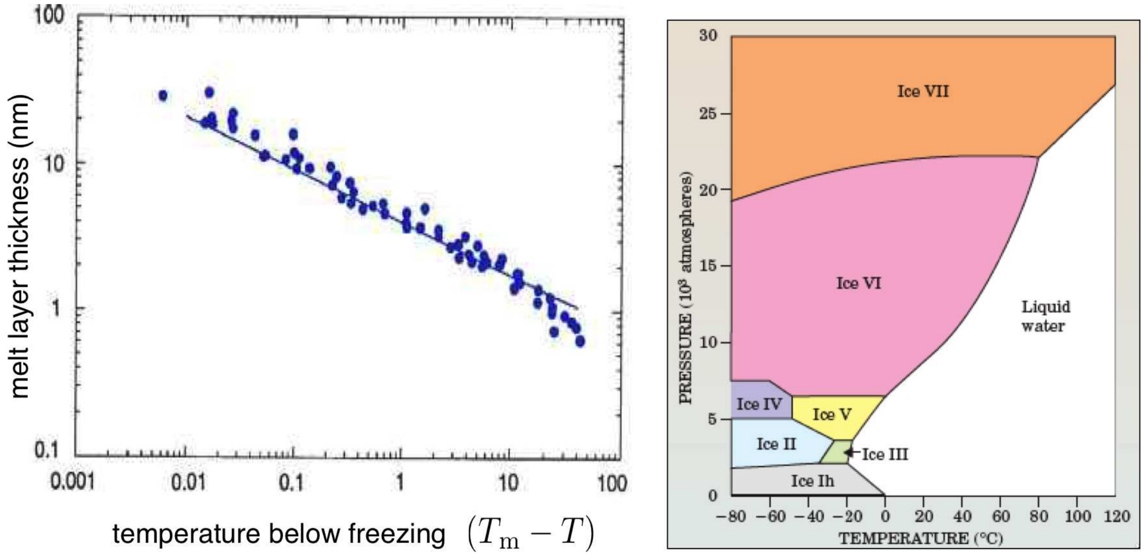

Figure 2.30: Left panel: data from R. R. Gilpin, *J. Colloid Interface Sci.* **77**, 435 (1980) showing measured thickness of the surface melt on ice at temperatures below 0°C. The straight line has slope $-\frac{1}{3}$, as predicted by theory. Right panel: phase diagram of $H_2O$, showing various high pressure solid phases. (*Source* : *Physics Today*, December 2005).

Recall $v = N_\mathrm{A} \big(\frac{\partial\mu}{\partial p}\big)_T$. Note that there can be no four phase coexistence for a simple $p$-$V$-$T$ system.

Now for the general result. Suppose we have $\sigma$ species, with particle numbers $N_a$, where $a = 1, \ldots, \sigma$. It is useful to briefly recapitulate the derivation of the Gibbs-Duhem relation. The energy $E(S, V, N_1, \ldots, N_\sigma)$ is a homogeneous function of degree one:

$$E(\lambda S, \lambda V, \lambda N_1, \ldots, \lambda N_\sigma) = \lambda E(S, V, N_1, \ldots, N_\sigma) \ . \tag{2.358}$$

From Euler's theorem for homogeneous functions (just differentiate with respect to $\lambda$ and then set $\lambda = 1$), we have

$$E = TS - p\,V + \sum_{a=1}^{\sigma} \mu_a\, N_a \ . \tag{2.359}$$

Taking the differential, and invoking the First Law,

$$dE = T\,dS - p\,dV + \sum_{a=1}^{\sigma} \mu_a\, dN_a \ , \tag{2.360}$$

we arrive at the relation

$$S\,dT - V\,dp + \sum_{a=1}^{\sigma} N_a\, d\mu_a = 0 \ , \tag{2.361}$$

of which eqn. 2.147 is a generalization to additional internal 'work' variables. This says that the $\sigma + 2$ quantities $(T, p, \mu_1, \ldots, \mu_\sigma)$ are not all independent. We can therefore write

$$\mu_\sigma = \mu_\sigma\big(T, p, \mu_1, \ldots, \mu_{\sigma-1}\big) \ . \tag{2.362}$$

If there are $\varphi$ different phases, then in each phase $j$, with $j = 1, \ldots, \varphi$, there is a chemical potential $\mu_a^{(j)}$ for each species $a$. We then have

$$\mu_\sigma^{(j)} = \mu_\sigma^{(j)}\Big(T, p, \mu_1^{(j)}, \ldots, \mu_{\sigma-1}^{(j)}\Big) \ . \tag{2.363}$$

Here $\mu_a^{(j)}$ is the chemical potential of the $a^{\rm th}$ species in the $j^{\rm th}$ phase. Thus, there are $\varphi$ such equations relating the $2+\varphi\,\sigma$ variables $\big(T, p, \{\mu_a^{(j)}\}\big)$, meaning that only $2+\varphi\,(\sigma-1)$ of them may be chosen as independent. This, then, is the dimension of 'thermodynamic space' containing a maximal number of intensive variables:

$$d_{\rm TD}(\sigma,\varphi) = 2 + \varphi\,(\sigma-1)\ . \tag{2.364}$$

To completely specify the state of our system, we of course introduce a single extensive variable, such as the total volume $V$. Note that the total particle number $N = \sum_{a=1}^{\sigma} N_a$ may not be conserved in the presence of chemical reactions!

Now suppose we have equilibrium among $\varphi$ phases. We have implicitly assumed thermal and mechanical equilibrium among all the phases, meaning that $p$ and $T$ are constant. Chemical equilibrium applies on a species-by-species basis. This means

$$\mu_a^{(j)} = \mu_a^{(j')} \tag{2.365}$$

where $j, j' \in \{1, \ldots, \varphi\}$. This gives $\sigma(\varphi-1)$ independent equations equations[16]. Thus, we can have *phase equilibrium* among the $\varphi$ phases of $\sigma$ species over a region of dimension

$$\begin{aligned} d_{\rm PE}(\sigma,\varphi) &= 2 + \varphi\,(\sigma-1) - \sigma\,(\varphi-1) \\ &= 2 + \sigma - \varphi\ . \end{aligned} \tag{2.366}$$

Since $d_{\rm PE} \geq 0$, we must have $\varphi \leq \sigma + 2$. Thus, with two species ($\sigma = 2$), we could have at most four phase coexistence.

If the various species can undergo $\rho$ distinct chemical reactions of the form

$$\zeta_1^{(r)}\,{\rm A}_1 + \zeta_2^{(r)}\,{\rm A}_2 + \cdots + \zeta_\sigma^{(r)}\,{\rm A}_\sigma = 0\ , \tag{2.367}$$

where ${\rm A}_a$ is the chemical formula for species $a$, and $\zeta_a^{(r)}$ is the stoichiometric coefficient for the $a^{\rm th}$ species in the $r^{\rm th}$ reaction, with $r = 1, \ldots, \rho$, then we have an additional $\rho$ constraints of the form

$$\sum_{a=1}^{\sigma} \zeta_a^{(r)}\,\mu_a^{(j)} = 0\ . \tag{2.368}$$

Therefore,

$$d_{\rm PE}(\sigma,\varphi,\rho) = 2 + \sigma - \varphi - \rho\ . \tag{2.369}$$

One might ask what value of $j$ are we to use in eqn. 2.368, or do we in fact have $\varphi$ such equations for each $r$? The answer is that eqn. 2.365 guarantees that the chemical potential of species $a$ is the same in all the phases, hence it doesn't matter what value one chooses for $j$ in eqn. 2.368.

Let us assume that no reactions take place, *i.e.* $\rho = 0$, so the total number of particles $\sum_{b=1}^{\sigma} N_b$ is conserved. Instead of choosing $(T, p, \mu_1, \ldots, \mu_{\sigma-1}^{(j)})$ as $d_{\rm TD}$ intensive variables, we could have chosen $(T, p, \mu_1, \ldots, x_{\sigma-1}^{(j)})$, where $x_a = N_a/N$ is the concentration of species $a$.

Why do phase diagrams in the $(p, v)$ and $(T, v)$ plane look different than those in the $(p, T)$ plane?[17] For example, Fig. 2.27 shows projections of the $p$-$v$-$T$ surface of a typical single component substance onto the $(T, v)$, $(p, v)$, and $(p, T)$ planes. Coexistence takes place along *curves* in the $(p, T)$ plane, but in extended two-dimensional regions in the $(T, v)$ and $(p, v)$ planes. The reason that $p$ and $T$ are special is that temperature, pressure, and chemical potential must be equal throughout an equilibrium phase if it is truly in thermal, mechanical, and chemical equilibrium. This is not the case for an intensive variable such as specific volume $v = N_{\rm A} V/N$ or chemical concentration $x_a = N_a/N$.

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[16] Set $j = 1$ and let $j'$ range over the $\varphi - 1$ values $2, \ldots, \varphi$.

[17] The same can be said for multicomponent systems: the phase diagram in the $(T, x)$ plane at constant $p$ looks different than the phase diagram in the $(T, \mu)$ plane at constant $p$.

## 2.13 Entropy of Mixing and the Gibbs Paradox

### 2.13.1 Computing the entropy of mixing

Entropy is widely understood as a measure of disorder. Of course, such a definition should be supplemented by a more precise definition of disorder – after all, one man's trash is another man's treasure. To gain some intuition about entropy, let us explore the mixing of a multicomponent ideal gas. Let $N = \sum_a N_a$ be the total number of particles of all species, and let $x_a = N_a/N$ be the concentration of species $a$. Note that $\sum_a x_a = 1$.

For any substance obeying the ideal gas law $pV = Nk_{\rm B}T$, the entropy is

$$S(T,V,N) = Nk_{\rm B}\ln(V/N) + N\phi(T) \ , \tag{2.370}$$

since $\big(\frac{\partial S}{\partial V}\big)_{T,N} = \big(\frac{\partial p}{\partial T}\big)_{V,N} = \frac{Nk_{\rm B}}{V}$. Note that in eqn. 2.370 we have divided $V$ by $N$ before taking the logarithm. This is essential if the entropy is to be an extensive function (see §2.7.5). One might think that the configurational entropy of an ideal gas should scale as $\ln(V^N) = N\ln V$, since each particle can be anywhere in the volume $V$. However, if the particles are *indistinguishable*, then permuting the particle labels does not result in a distinct configuration, and so the configurational entropy is proportional to $\ln(V^N/N!) \sim N\ln(V/N) - N$. The origin of this indistinguishability factor will become clear when we discuss the quantum mechanical formulation of statistical mechanics. For now, note that such a correction is necessary in order that the entropy be an extensive function.

If we did not include this factor and instead wrote $S^*(T,V,N) = Nk_{\rm B}\ln V + N\phi(T)$, then we would find $S^*(T,V,N) - 2S^*(T,\frac{1}{2}V,\frac{1}{2}N) = Nk_{\rm B}\ln 2$, *i.e.* the total entropy of two identical systems of particles separated by a barrier will increase if the barrier is removed and they are allowed to mix. This seems absurd, though, because we could just as well regard the barriers as invisible. This is known as the *Gibbs paradox*. The resolution of the Gibbs paradox is to include the indistinguishability correction, which renders $S$ extensive, in which case $S(T,V,N) = 2S(T,\frac{1}{2}V,\frac{1}{2}N)$.

Consider now the situation in Fig. 2.31, where we have separated the different components into their own volumes $V_a$. Let the pressure and temperature be the same everywhere, so $pV_a = N_a k_{\rm B}T$. The entropy of the unmixed system is then

$$S_{\rm unmixed} = \sum_a S_a = \sum_a \Big[N_a\,k_{\rm B}\ln(V_a/N_a) + N_a\,\phi_a(T)\Big] \ . \tag{2.371}$$

Now let us imagine removing all the barriers separating the different gases and letting the particles mix thoroughly. The result is that each component gas occupies the full volume $V$, so the entropy is

$$S_{\rm mixed} = \sum_a S_a = \sum_a \Big[N_a\,k_{\rm B}\ln(V/N_a) + N_a\,\phi_a(T)\Big] \ . \tag{2.372}$$

Thus, the *entropy of mixing* is

$$\begin{aligned} \Delta S_{\rm mix} &= S_{\rm mixed} - S_{\rm unmixed} \\ &= \sum_a N_a\,k_{\rm B}\,\ln(V/V_a) = -Nk_{\rm B}\sum_a x_a\ln x_a \ , \end{aligned} \tag{2.373}$$

where $x_a = \frac{N_a}{N} = \frac{V_a}{V}$ is the fraction of species $a$. Note that $\Delta S_{\rm mix} = 0$.

What if all the components were initially identical? It seems absurd that the entropy should increase simply by removing some invisible barriers. This is again the Gibbs paradox. In this case, the resolution of the paradox is to note that the sum in the expression for $S_{\rm mixed}$ is a sum over distinct species. Hence if the particles are all identical, we have $S_{\rm mixed} = Nk_{\rm B}\ln(V/N) + N\phi(T) = S_{\rm unmixed}$, hence $\Delta S_{\rm mix} = 0$.

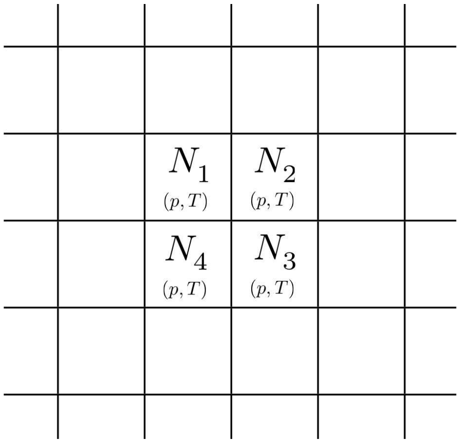

Figure 2.31: A multicomponent system consisting of isolated gases, each at temperature $T$ and pressure $p$. Then system entropy increases when all the walls between the different subsystems are removed.

### 2.13.2 Entropy and combinatorics

As we shall learn when we study statistical mechanics, the entropy may be interpreted in terms of the number of ways $W(E,V,N)$ a system at fixed energy and volume can arrange itself. One has

$$S(E,V,N)=k_{\mathrm{B}}\ln W(E,V,N)\ . \tag{2.374}$$

Consider a system consisting of $\sigma$ different species of particles. Now let it be that for each species label $a$, $N_a$ particles of that species are confined among $Q_a$ little boxes such that at most one particle can fit in a box (see Fig. 2.32). How many ways $W$ are there to configure $N$ identical particles among $Q$ boxes? Clearly

$$W=\binom{Q}{N}=\frac{Q!}{N!\,(Q-N)!}\ . \tag{2.375}$$

Were the particles distinct, we'd have $W_{\mathrm{distinct}}=\frac{Q!}{(Q-N)!}$, which is $N!$ times greater. This is because permuting distinct particles results in a different configuration, and there are $N!$ ways to permute $N$ particles.

The entropy for species $a$ is then $S_a=k_{\mathrm{B}}\ln W_a=k_{\mathrm{B}}\ln\binom{Q_a}{N_a}$. We then use Stirling's approximation,

$$\ln(K!)=K\ln K-K+\tfrac{1}{2}\ln K+\tfrac{1}{2}\ln(2\pi)+\mathcal{O}(K^{-1})\ , \tag{2.376}$$

which is an asymptotic expansion valid for $K\gg 1$. One then finds for $Q,N\gg 1$, with $x=N/Q\in[0,1]$,

$$\begin{aligned}\ln\binom{Q}{N}&=\Big(Q\ln Q-Q\Big)-\Big(xQ\ln(xQ)-xQ\Big)-\Big((1-x)Q\ln\big((1-x)Q\big)-(1-x)Q\Big)\\&=-Q\Big[x\ln x+(1-x)\ln(1-x)\Big]\ .\end{aligned} \tag{2.377}$$

This is valid up to terms of order $Q$ in Stirling's expansion. Since $\ln Q\ll Q$, the next term is small and we are safe to stop here. Summing up the contributions from all the species, we get

$$S_{\mathrm{unmixed}}=k_{\mathrm{B}}\sum_{a=1}^{\sigma}\ln W_a=-k_{\mathrm{B}}\sum_{a=1}^{\sigma}Q_a\Big[x_a\ln x_a+(1-x_a)\ln(1-x_a)\Big]\ , \tag{2.378}$$

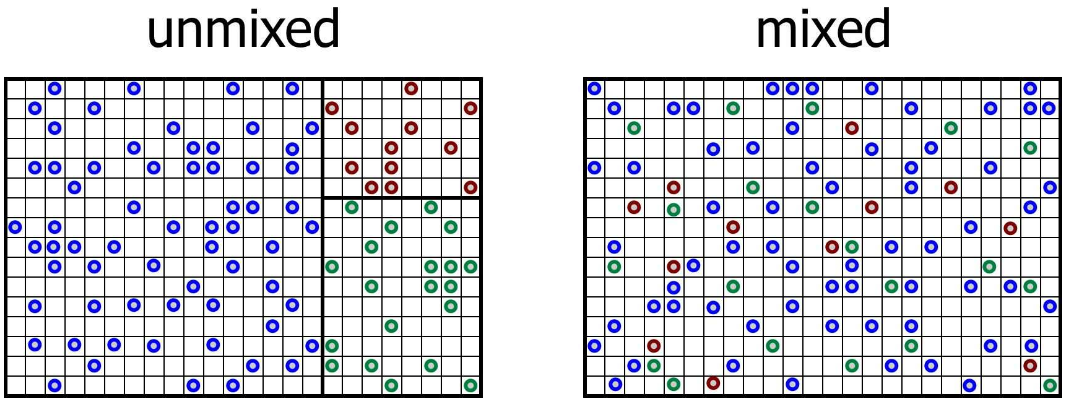

Figure 2.32: Mixing among three different species of particles. The mixed configuration has an additional entropy, $\Delta S_{\rm mix}$.

where $x_a = N_a/Q_a$ is the initial dimensionless density of species $a$.

Now let's remove all the partitions between the different species so that each of the particles is free to explore all of the boxes. There are $Q = \sum_a Q_a$ boxes in all. The total number of ways of placing $N_1$ particles of species $a = 1$ through $N_\sigma$ particles of species $\sigma$ is

$$W_{\rm mixed} = \frac{Q!}{N_0!\,N_1!\cdots N_\sigma!} \ , \tag{2.379}$$

where $N_0 = Q - \sum_{a=1}^\sigma N_a$ is the number of vacant boxes. Again using Stirling's rule, we find

$$S_{\rm mixed} = -k_{\rm B}\,Q \sum_{a=0}^\sigma \widetilde{x}_a \ln \widetilde{x}_a \ , \tag{2.380}$$

where $\widetilde{x}_a = N_a/Q$ is the fraction of *all* boxes containing a particle of species $a$, and $N_0$ is the number of empty boxes. Note that

$$\widetilde{x}_a = \frac{N_a}{Q} = \frac{N_a}{Q_a} \cdot \frac{Q_a}{Q} = x_a\, f_a \ , \tag{2.381}$$

where $f_a \equiv Q_a/Q$. Note that $\sum_{a=1}^\sigma f_a = 1$.

Let's assume all the densities are initially the same, so $x_a = x \forall a$, so $\widetilde{x}_a = x\, f_a$. In this case, $f_a = \frac{Q_a}{Q} = \frac{N_a}{N}$ is the fraction of species $a$ among all the particles. We then have $\widetilde{x}_0 = 1 - x$, and

$$\begin{aligned} S_{\rm mixed} &= -k_{\rm B}\,Q \sum_{a=1}^\sigma x f_a \ln(x f_a) - k_{\rm B}\,Q\,\widetilde{x}_0 \ln \widetilde{x}_0 \\ &= -k_{\rm B}\,Q\Big[x\ln x + (1-x)\ln(1-x)\Big] - k_{\rm B}\,x\,Q \sum_{a=1}^\sigma f_a \ln f_a \ . \end{aligned} \tag{2.382}$$

Thus, the entropy of mixing is

$$\Delta S_{\rm mix} = -N k_{\rm B} \sum_{a=1}^\sigma f_a \ln f_a \ , \tag{2.383}$$

where $N = \sum_{a=1}^\sigma N_a$ is the total number of particles among all species (excluding vacancies) and $f_a = N_a/(N + N_0)$is the fraction of all boxes occupied by species $a$.

### 2.13.3 Weak solutions and osmotic pressure

Suppose one of the species is much more plentiful than all the others, and label it with $a = 0$. We will call this the *solvent*. The entropy of mixing is then

$$\Delta S_{\text{mix}} = -k_{\text{B}}\left[N_0 \ln\!\left(\frac{N_0}{N_0 + N'}\right) + \sum_{a=1}^{\sigma} N_a \ln\!\left(\frac{N_a}{N_0 + N'}\right)\right] , \tag{2.384}$$

where $N' = \sum_{a=1}^{\sigma} N_a$ is the total number of solvent molecules, summed over all species. We assume the solution is *weak*, which means $N_a \le N' \ll N_0$. Expanding in powers of $N'/N_0$ and $N_a/N_0$, we find

$$\Delta S_{\text{mix}} = -k_{\text{B}} \sum_{a=1}^{\sigma} \left[N_a \ln\!\left(\frac{N_a}{N_0}\right) - N_a\right] + \mathcal{O}\big(N'^2/N_0\big) . \tag{2.385}$$

Consider now a solution consisting of $N_0$ molecules of a solvent and $N_a$ molecules of species $a$ of solute, where $a = 1, \ldots, \sigma$. We begin by expanding the Gibbs free energy $G(T, p, N_0, N_1, \ldots, N_\sigma)$, where there are $\sigma$ species of solutes, as a power series in the small quantities $N_a$. We have

$$\begin{aligned} G\big(T, p, N_0, \{N_a\}\big) &= N_0\, g_0(T, p) + k_{\text{B}} T \sum_a N_a \ln\!\left(\frac{N_a}{eN_0}\right) \\ &\qquad + \sum_a N_a\, \psi_a(T, p) + \frac{1}{2N_0} \sum_{a,b} A_{ab}(T, p)\, N_a\, N_b . \end{aligned} \tag{2.386}$$

The first term on the RHS corresponds to the Gibbs free energy of the solvent. The second term is due to the entropy of mixing. The third term is the contribution to the total free energy from the individual species. Note the factor of $e$ in the denominator inside the logarithm, which accounts for the second term in the brackets on the RHS of eqn. 2.385. The last term is due to interactions between the species; it is truncated at second order in the solute numbers.

The chemical potential for the solvent is

$$\mu_0(T, p) = \frac{\partial G}{\partial N_0} = g_0(T, p) - k_{\text{B}} T \sum_a x_a - \tfrac{1}{2} \sum_{a,b} A_{ab}(T, p)\, x_a\, x_b , \tag{2.387}$$

and the chemical potential for species $a$ is

$$\mu_a(T, p) = \frac{\partial G}{\partial N_a} = k_{\text{B}} T \ln x_a + \psi_a(T, p) + \sum_b A_{ab}(T, p)\, x_b , \tag{2.388}$$

where $x_a = N_a/N_0$ is the concentrations of solute species $a$. By assumption, the last term on the RHS of each of these equations is small, since $N_{\text{solute}} \ll N_0$, where $N_{\text{solute}} = \sum_{a=1}^{\sigma} N_a$ is the total number of solute molecules. To lowest order, then, we have

$$\mu_0(T, p) = g_0(T, p) - x\, k_{\text{B}} T \tag{2.389}$$

$$\mu_a(T, p) = k_{\text{B}} T \ln x_a + \psi_a(T, p) , \tag{2.390}$$

where $x = \sum_a x_a$ is the total solute concentration.

If we add sugar to a solution confined by a semipermeable membrane[18], the pressure increases! To see why, consider a situation where a rigid semipermeable membrane separates a solution (solvent plus solutes) from a

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[18] 'Semipermeable' in this context means permeable to the solvent but not the solute(s).

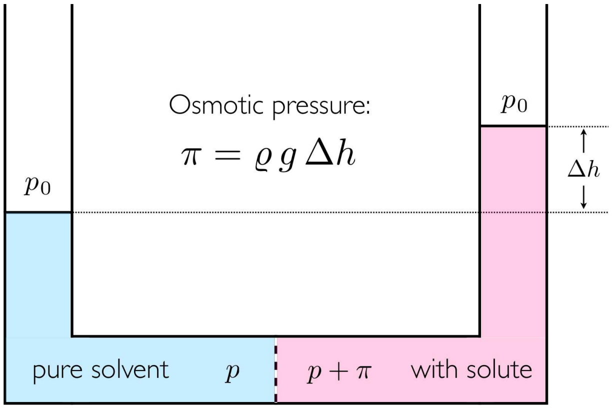

Figure 2.33: Osmotic pressure causes the column on the right side of the U-tube to rise higher than the column on the left by an amount $\Delta h = \pi/\varrho\, g$.

pure solvent. There is energy exchange through the membrane, so the temperature is $T$ throughout. There is no volume exchange, however: $dV = dV' = 0$, hence the pressure need not be the same. Since the membrane is permeable to the solvent, we have that the chemical potential $\mu_0$ is the same on each side. This means

$$g_0(T, p_{\rm R}) - x k_{\rm B} T = g_0(T, p_{\rm L}) \ , \tag{2.391}$$

where $p_{\rm L,R}$ is the pressure on the left and right sides of the membrane, and $x = N/N_0$ is again the total solute concentration. This equation once again tells us that the pressure $p$ cannot be the same on both sides of the membrane. If the pressure difference is small, we can expand in powers of the *osmotic pressure*, $\pi \equiv p_{\rm R} - p_{\rm L}$ , and we find

$$\pi = x\, k_{\rm B} T \bigg/ \bigg(\frac{\partial \mu_0}{\partial p}\bigg)_{\!T} \ . \tag{2.392}$$

But a Maxwell relation (§2.9) guarantees

$$\bigg(\frac{\partial \mu}{\partial p}\bigg)_{\!T,N} = \bigg(\frac{\partial V}{\partial N}\bigg)_{\!T,p} = v(T,p)/N_{\rm A} \ , \tag{2.393}$$

where $v(T,p)$ is the molar volume of the solvent.

$$\pi v = xRT \ , \tag{2.394}$$

which looks very much like the ideal gas law, even though we are talking about dense (but 'weak') solutions! The resulting pressure has a demonstrable effect, as sketched in Fig. 2.33. Consider a solution containing $\nu$ moles of sucrose ($C_{12}H_{22}O_{11}$) per kilogram ($55.52\,{\rm mol}$) of water at 30° C. We find $\pi = 2.5\,{\rm atm}$ when $\nu = 0.1$.

One might worry about the expansion in powers of $\pi$ when $\pi$ is much larger than the ambient pressure. But in fact the next term in the expansion is smaller than the first term by a factor of $\pi\kappa_T$, where $\kappa_T$ is the isothermal compressibility. For water one has $\kappa_T \approx 4.4 \times 10^{-5}\,({\rm atm})^{-1}$, hence we can safely ignore the higher order terms in the Taylor expansion.

### 2.13.4 Effect of impurities on boiling and freezing points

Along the coexistence curve separating liquid and vapor phases, the chemical potentials of the two phases are identical:

$$\mu^0_{\rm L}(T,p) = \mu^0_{\rm V}(T,p) \ . \tag{2.395}$$

| Substance | Latent Heat of Fusion $\tilde{\ell}_\mathrm{f}$ J/g | Melting Point °C | Latent Heat of Vaporization $\tilde{\ell}_\mathrm{v}$ J/g | Boiling Point °C |
|---|---|---|---|---|
| $C_2H_5OH$ | 108 | -114 | 855 | 78.3 |
| $NH_3$ | 339 | -75 | 1369 | -33.34 |
| $CO_2$ | 184 | -57 | 574 | -78 |
| He | – | – | 21 | -268.93 |
| H | 58 | -259 | 455 | -253 |
| Pb | 24.5 | 372.3 | 871 | 1750 |
| $N_2$ | 25.7 | -210 | 200 | -196 |
| $O_2$ | 13.9 | -219 | 213 | -183 |
| $H_2O$ | 334 | 0 | 2270 | 100 |

Table 2.4: Latent heats of fusion and vaporization at $p = 1$ atm.

Here we write $\mu^0$ for $\mu$ to emphasize that we are talking about a phase with no impurities present. This equation provides a single constraint on the two variables $T$ and $p$, hence one can, in principle, solve to obtain $T = T_0^*(p)$, which is the equation of the liquid-vapor coexistence curve in the $(T,p)$ plane. Now suppose there is a solute present in the liquid. We then have

$$\mu_\mathrm{L}(T,p,x) = \mu^0_\mathrm{L}(T,p) - x k_\mathrm{B} T \ , \tag{2.396}$$

where $x$ is the dimensionless solute concentration, summed over all species. The condition for liquid-vapor coexistence now becomes

$$\mu^0_\mathrm{L}(T,p) - x k_\mathrm{B} T = \mu^0_\mathrm{V}(T,p) \ . \tag{2.397}$$

This will lead to a shift in the boiling temperature at fixed $p$. Assuming this shift is small, let us expand to lowest order in $\big(T - T_0^*(p)\big)$, writing

$$\mu^0_\mathrm{L}(T_0^*,p) + \left(\frac{\partial \mu^0_\mathrm{L}}{\partial T}\right)_{\!p} \big(T - T_0^*\big) - x k_\mathrm{B} T = \mu^0_\mathrm{V}(T_0^*,p) + \left(\frac{\partial \mu^0_\mathrm{V}}{\partial T}\right)_{\!p} \big(T - T_0^*\big) \ . \tag{2.398}$$

Note that

$$\left(\frac{\partial \mu}{\partial T}\right)_{\!p,N} = -\left(\frac{\partial S}{\partial N}\right)_{\!T,p} \tag{2.399}$$

from a Maxwell relation deriving from exactness of $dG$. Since $S$ is extensive, we can write $S = (N/N_\mathrm{A})\, s(T,p)$, where $s(T,p)$ is the molar entropy. Solving for $T$, we obtain

$$T^*(p,x) = T_0^*(p) + \frac{xR\big[T_0^*(p)\big]^2}{\ell_\mathrm{v}(p)} \ , \tag{2.400}$$

where $\ell_\mathrm{v} = T_0^* \cdot (s_\mathrm{V} - s_\mathrm{L})$ is the *latent heat* of the liquid-vapor transition[19]. The shift $\Delta T^* = T^* - T_0^*$ is called the *boiling point elevation*.

As an example, consider seawater, which contains approximately $35\,\mathrm{g}$ of dissolved $\mathrm{Na^+Cl^-}$ per kilogram of $H_2O$. The atomic masses of Na and Cl are $23.0$ and $35.4$, respectively, hence the total ionic concentration in seawater (neglecting everything but sodium and chlorine) is given by

$$x = \frac{2 \cdot 35}{23.0 + 35.4} \bigg/ \frac{1000}{18} \approx 0.022 \ . \tag{2.401}$$

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[19] We shall discuss latent heat again in §2.12.2 below.

The latent heat of vaporization of $H_2O$ at atmospheric pressure is $\ell = 40.7\,\text{kJ/mol}$, hence

$$\Delta T^* = \frac{(0.022)(8.3\,\text{J/mol K})(373\,\text{K})^2}{4.1\times 10^4\,\text{J/mol}} \approx 0.6\,\text{K} . \tag{2.402}$$

Put another way, the boiling point elevation of $H_2O$ at atmospheric pressure is about $0.28°\text{C}$ per percent solute. We can express this as $\Delta T^* = Km$, where the *molality* $m$ is the number of moles of solute per kilogram of solvent. For $H_2O$, we find $K = 0.51°\text{C kg/mol}$.

Similar considerations apply at the freezing point, when we equate the chemical potential of the solvent plus solute to that of the pure solid. The *latent heat of fusion* for $H_2O$ is about $\ell_f = T_f^0 \cdot (s_{\text{LIQUID}} - s_{\text{SOLID}}) = 6.01\,\text{kJ/mol}$[20] We thus predict a *freezing point depression* of $\Delta T^* = -xR\big[T_0^*\big]^2/\ell_f = 1.03°\text{C}\cdot x[\%]$. This can be expressed once again as $\Delta T^* = -Km$, with $K = 1.86°\text{C kg/mol}$[21].

### 2.13.5 Binary solutions

Consider a binary solution, and write the Gibbs free energy $G(T,p,N_{\mathsf{A}},N_{\mathsf{B}})$ as

$$\begin{aligned} G(T,p,N_{\mathsf{A}},N_{\mathsf{B}}) = N_{\mathsf{A}}\,\mu^0_{\mathsf{A}}(T,p) + N_{\mathsf{B}}\,\mu^0_{\mathsf{B}}(T,p) + N_{\mathsf{A}} k_{\rm B}T\,\ln\!\left(\frac{N_{\mathsf{A}}}{N_{\mathsf{A}}+N_{\mathsf{B}}}\right) \\ + N_{\mathsf{B}}\,k_{\rm B}T\,\ln\!\left(\frac{N_{\mathsf{B}}}{N_{\mathsf{A}}+N_{\mathsf{B}}}\right) + \lambda\,\frac{N_{\mathsf{A}}N_{\mathsf{B}}}{N_{\mathsf{A}}+N_{\mathsf{B}}} . \end{aligned} \tag{2.403}$$

The first four terms on the RHS represent the free energy of the individual component fluids and the entropy of mixing. The last term is an interaction contribution. With $\lambda > 0$, the interaction term prefers that the system be either fully A or fully B. The entropy contribution prefers a mixture, so there is a competition. What is the stable thermodynamic state?

It is useful to write the Gibbs free energy per particle, $g(T,p,x) = G/(N_{\mathsf{A}}+N_{\mathsf{B}})$, in terms of $T$, $p$, and the concentration $x \equiv x_{\mathsf{B}} = N_{\mathsf{B}}/(N_{\mathsf{A}}+N_{\mathsf{B}})$ of species B (hence $x_{\mathsf{A}} = 1-x$ is the concentration of species A). Then

$$g(T,p,x) = (1-x)\,\mu^0_{\mathsf{A}} + x\,\mu^0_{\mathsf{B}} + k_{\rm B}T\Big[x\ln x + (1-x)\ln(1-x)\Big] + \lambda\,x\,(1-x) . \tag{2.404}$$

In order for the system to be stable against phase separation into relatively A-rich and B-rich regions, we must have that $g(T,p,x)$ be a convex function of $x$. Our first check should be for a local instability, *i.e.* spinodal decomposition. We have

$$\frac{\partial g}{\partial x} = \mu^0_{\mathsf{B}} - \mu^0_{\mathsf{A}} + k_{\rm B}T\,\ln\!\left(\frac{x}{1-x}\right) + \lambda\,(1-2x) \tag{2.405}$$

and

$$\frac{\partial^2 g}{\partial x^2} = \frac{k_{\rm B}T}{x} + \frac{k_{\rm B}T}{1-x} - 2\lambda . \tag{2.406}$$

The spinodal is given by the solution to the equation $\frac{\partial^2 g}{\partial x^2} = 0$, which is

$$T^*(x) = \frac{2\lambda}{k_{\rm B}}\,x\,(1-x) . \tag{2.407}$$

Since $x\,(1-x)$ achieves its maximum value of $\frac{1}{4}$ at $x = \frac{1}{2}$, we have $T^* \le k_{\rm B}/2\lambda$.

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[20] See table 2.4, and recall $M = 18\,\text{g}$ is the molar mass of $H_2O$.

[21] It is more customary to write $\Delta T^* = T^*_{\text{pure solvent}} - T^*_{\text{solution}}$ in the case of the freezing point depression, in which case $\Delta T^*$ is positive.

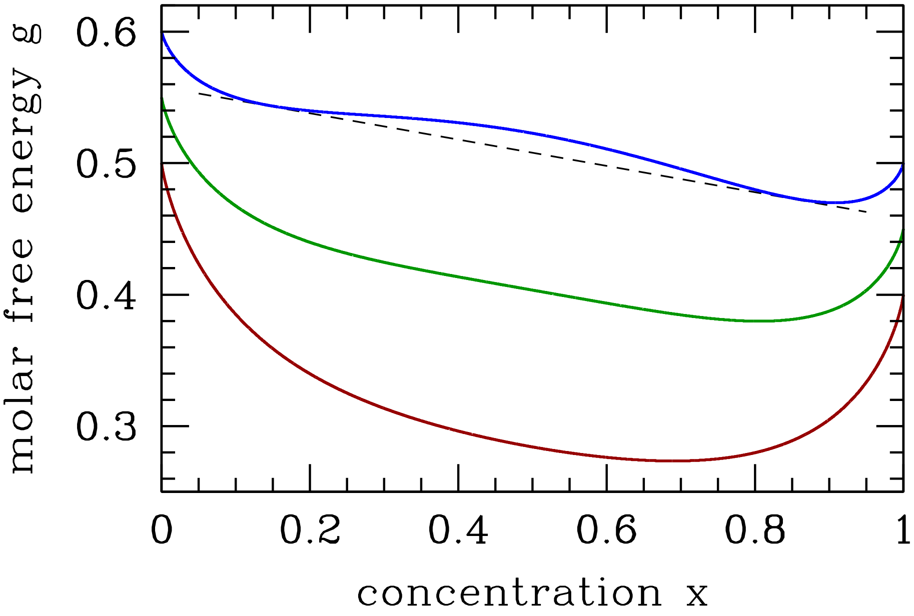

Figure 2.34: Gibbs free energy per particle for a binary solution as a function of concentration $x = x_{\mathsf{B}}$ of the B species (pure A at the left end $x = 0$ ; pure B at the right end $x = 1$), in units of the interaction parameter $\lambda$. Dark red curve: $T = 0.65\,\lambda/k_{\rm B} > T_{\rm c}$ ; green curve: $T = \lambda/2k_{\rm B} = T_{\rm c}$ ; blue curve: $T = 0.40\,\lambda/k_{\rm B} < T_{\rm c}$. We have chosen $\mu^0_{\mathsf{A}} = 0.60\,\lambda - 0.50\,k_{\rm B}T$ and $\mu^0_{\mathsf{B}} = 0.50\,\lambda - 0.\,50\,k_{\rm B}T$. Note that the free energy $g(T,p,x)$ is not convex in $x$ for $T < T_{\rm c}$, indicating an instability and necessitating a Maxwell construction.

In Fig. 2.34 we sketch the free energy $g(T,p,x)$ *versus* $x$ for three representative temperatures. For $T > \lambda/2k_{\rm B}$, the free energy is everywhere convex in $\lambda$. When $T < \lambda/2k_{\rm B}$, there free energy resembles the blue curve in Fig. 2.34, and the system is unstable to phase separation. The two phases are said to be *immiscible*, or, equivalently, there exists a *solubility gap*. To determine the coexistence curve, we perform a Maxwell construction, writing

$$\frac{g(x_2) - g(x_1)}{x_2 - x_1} = \frac{\partial g}{\partial x}\bigg|_{x_1} = \frac{\partial g}{\partial x}\bigg|_{x_2} \ . \tag{2.408}$$

Here, $x_1$ and $x_2$ are the boundaries of the two phase region. These equations admit a symmetry of $x \leftrightarrow 1 - x$, hence we can set $x = x_1$ and $x_2 = 1 - x$. We find

$$g(1-x) - g(x) = (1-2x)\left(\mu^0_{\mathsf{B}} - \mu^0_{\mathsf{A}}\right) \ , \tag{2.409}$$

and invoking eqns. 2.408 and 2.405 we obtain the solution

$$T_{\rm coex}(x) = \frac{\lambda}{k_{\rm B}} \cdot \frac{1-2x}{\ln\left(\frac{1-x}{x}\right)} \ . \tag{2.410}$$

The phase diagram for the binary system is shown in Fig. 2.36. For $T < T^*(x)$, the system is unstable, and spinodal decomposition occurs. For $T^*(x) < T < T_{\rm coex}(x)$, the system is *metastable*, just like the van der Waals gas in its corresponding regime. Real binary solutions behave qualitatively like the model discussed here, although the coexistence curve is generally not symmetric under $x \leftrightarrow 1 - x$, and the single phase region extends down to low temperatures for $x \approx 0$ and $x \approx 1$. If $\lambda$ itself is temperature-dependent, there can be multiple solutions to eqns. 2.407 and 2.410. For example, one could take

$$\lambda(T) = \frac{\lambda_0\,T^2}{T^2 + T_0^2} \ . \tag{2.411}$$

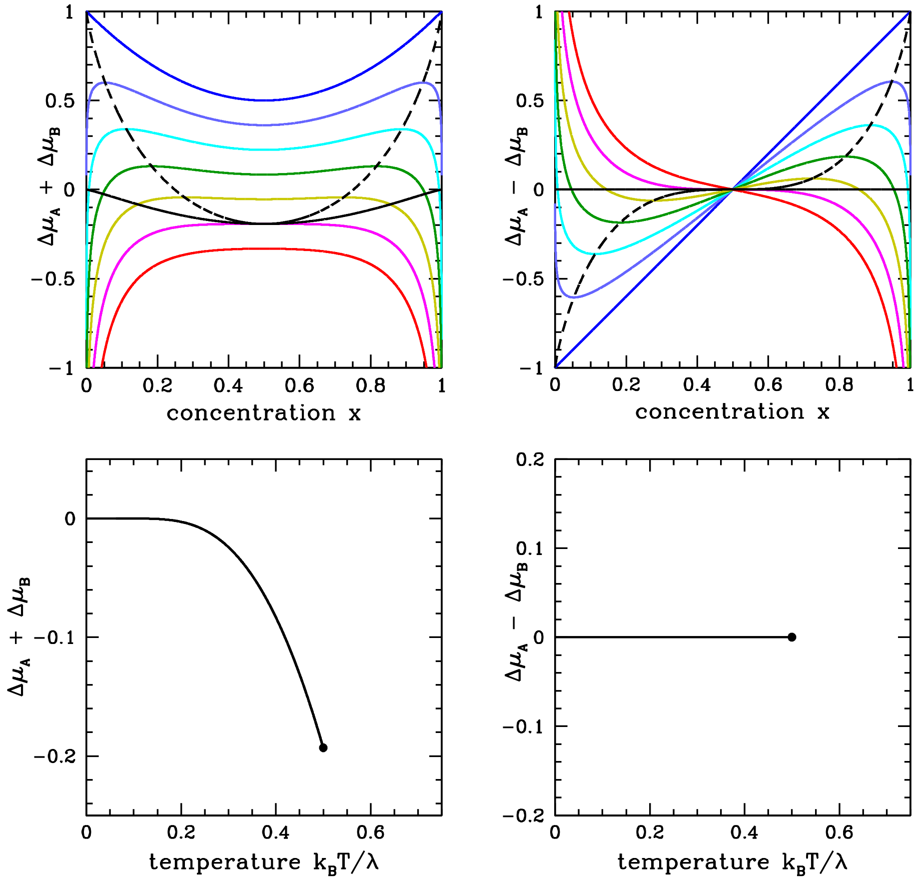

Figure 2.35: Upper panels: chemical potential shifts $\Delta\mu_{\pm} = \Delta\mu_{\mathsf{A}} \pm \Delta\mu_{\mathsf{B}}$ *versus* concentration $x = x_{\mathsf{B}}$. The dashed black line is the spinodal, and the solid black line the coexistence boundary. Temperatures range from $T = 0$ (dark blue) to $T = 0.6\,\lambda/k_{\mathrm{B}}$ (red) in units of $0.1\,\lambda/k_{\mathrm{B}}$. Lower panels: phase diagram in the $(T, \Delta\mu_{\pm})$ planes. The black dot is the critical point.

In this case, $k_{\mathrm{B}}T > \lambda$ at both high and low temperatures, and we expect the single phase region to be *reentrant*. Such a phenomenon occurs in water-nicotine mixtures, for example.

It is instructive to consider the phase diagram in the $(T, \mu)$ plane. We define the chemical potential shifts,

$$\Delta\mu_{\mathsf{A}} \equiv \mu_{\mathsf{A}} - \mu^0_{\mathsf{A}} = k_{\mathrm{B}}T\ln(1-x) + \lambda\, x^2 \tag{2.412}$$

$$\Delta\mu_{\mathsf{B}} \equiv \mu_{\mathsf{B}} - \mu^0_{\mathsf{B}} = k_{\mathrm{B}}T\ln x + \lambda\,(1-x)^2 \ , \tag{2.413}$$

and their sum and difference, $\Delta\mu_{\pm} \equiv \Delta\mu_{\mathsf{A}} \pm \Delta\mu_{\mathsf{B}}$. From the Gibbs-Duhem relation, we know that we can write $\mu_{\mathsf{B}}$ as a function of $T$, $p$, and $\mu_{\mathsf{A}}$. Alternately, we could write $\Delta\mu_{\pm}$ in terms of $T$, $p$, and $\Delta\mu_{\mp}$, so we can choose which among $\Delta\mu_{+}$ and $\Delta\mu_{-}$ we wish to use in our phase diagram. The results are plotted in Fig. 2.35. It is perhaps easiest to understand the phase diagram in the $(T, \Delta\mu_{-})$ plane. At low temperatures, below $T = T_{\mathrm{c}} = \lambda/2k_{\mathrm{B}}$, there is a first order phase transition at $\Delta\mu_{-} = 0$. For $T < T_{\mathrm{c}} = \lambda/2k_{\mathrm{B}}$ and $\Delta\mu_{-} = 0^{+}$, *i.e.* infinitesimally positive, the system is in the A-rich phase, but for $\Delta\mu_{-} = 0^{-}$, *i.e.* infinitesimally negative, it is B-rich. The concentration $x = x_{\mathsf{B}}$ changes discontinuously across the phase boundary. The critical point lies at $(T, \Delta\mu_{-}) = (\lambda/2k_{\mathrm{B}}\,,\,0)$.

If we choose $N = N_{\mathsf{A}} + N_{\mathsf{B}}$ to be the extensive variable, then fixing $N$ means $dN_{\mathsf{A}} + dN_{\mathsf{B}} = 0$. So st fixed $T$ and $p$,

$$dG\big|_{T,p} = \mu_{\mathsf{A}}\, dN_{\mathsf{A}} + \mu_{\mathsf{B}}\, dN_{\mathsf{B}} \qquad \Rightarrow \qquad dg\big|_{T,p} = -\Delta\mu_{-}\, dx \ . \tag{2.414}$$

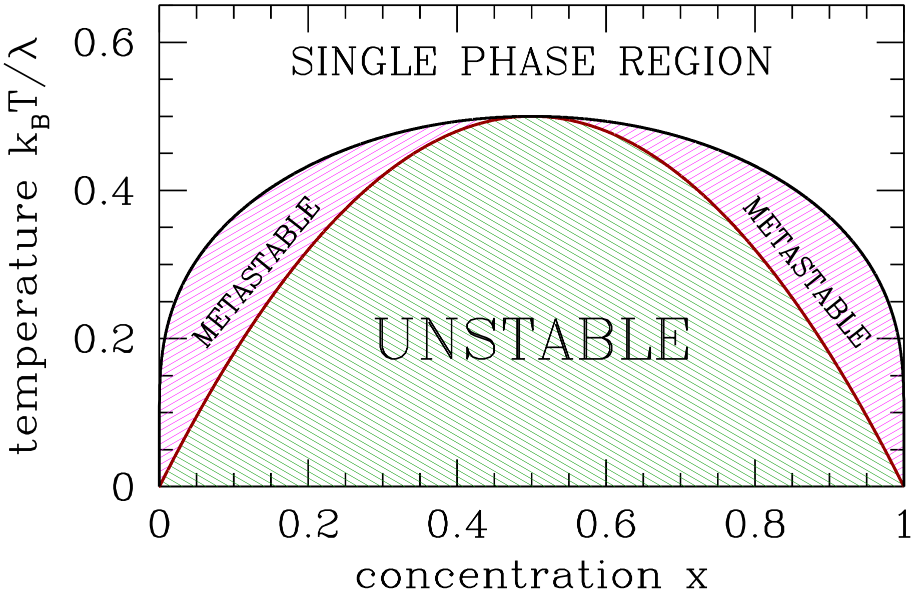

Figure 2.36: Phase diagram for the binary system. The black curve is the coexistence curve, and the dark red curve is the spinodal. A-rich material is to the left and B-rich to the right.

Since $\Delta\mu_-(x,T) = \varphi(x,T) - \varphi(1-x,T) = -\Delta\mu_-(1-x,T)$, where $\varphi(x,T) = \lambda x - k_{\rm B}T\ln x$, we have that the coexistence boundary in the $(x, \Delta_-)$ plane is simply the line $\Delta\mu_- = 0$, because $\int\limits_x^{1-x} dx'\, \Delta\mu_-(x',T) = 0$.

Note also that there is no two-phase region in the $(T, \Delta\mu)$ plane; the phase boundary in this plane is a curve which terminates at a critical point. As we saw in §2.12, the same situation pertains in single component $(p, v, T)$ systems. That is, the phase diagram in the $(p, v)$ or $(T, v)$ plane contains two-phase regions, but in the $(p, T)$ plane the boundaries between phases are one-dimensional curves. Any two-phase behavior is confined to these curves, where the thermodynamic potentials are singular.

The phase separation can be seen in a number of systems. A popular example involves mixtures of water and ouzo or other anise-based liqueurs, such as arak and absinthe. Starting with the pure liqueur ($x = 1$), and at a temperature below the coexistence curve maximum, the concentration is diluted by adding water. Follow along on Fig. 2.36 by starting at the point ($x = 1$ , $k_{\rm B}T/\lambda = 0.4$) and move to the left. Eventually, one hits the boundary of the two-phase region. At this point, the mixture turns milky, due to the formation of large droplets of the pure phases on either side of coexistence region which scatter light, a process known as *spontaneous emulsification*[22]. As one continues to dilute the solution with more water, eventually one passes all the way through the coexistence region, at which point the solution becomes clear once again, and described as a single phase.

What happens if $\lambda < 0$? In this case, both the entropy and the interaction energy prefer a mixed phase, and there is no instability to phase separation. The two fluids are said to be *completely miscible*. An example would be benzene, $C_6H_6$, and toluene, $C_7H_8$ (*i.e.* $C_6H_5CH_3$). The phase diagram would be blank, with no phase boundaries below the boiling transition, because the fluid could exist as a mixture in any proportion.

Any fluid will eventually boil if the temperature is raised sufficiently high. Let us assume that the boiling points of our A and B fluids are $T^*_{\rm A,B}$, and without loss of generality let us take $T^*_{\sf A} < T^*_{\sf B}$ at some given fixed pressure[23]. This means $\mu^{\rm L}_{\sf A}(T^*_{\sf A}, p) = \mu^{\rm V}_{\sf A}(T^*_{\sf A}, p)$ and $\mu^{\rm L}_{\sf B}(T^*_{\sf B}, p) = \mu^{\rm V}_{\sf B}(T^*_{\sf B}, p)$. What happens to the mixture? We begin by writing

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[22] An emulsion is a mixture of two or more immiscible liquids.

[23] We assume the boiling temperatures are not exactly equal!

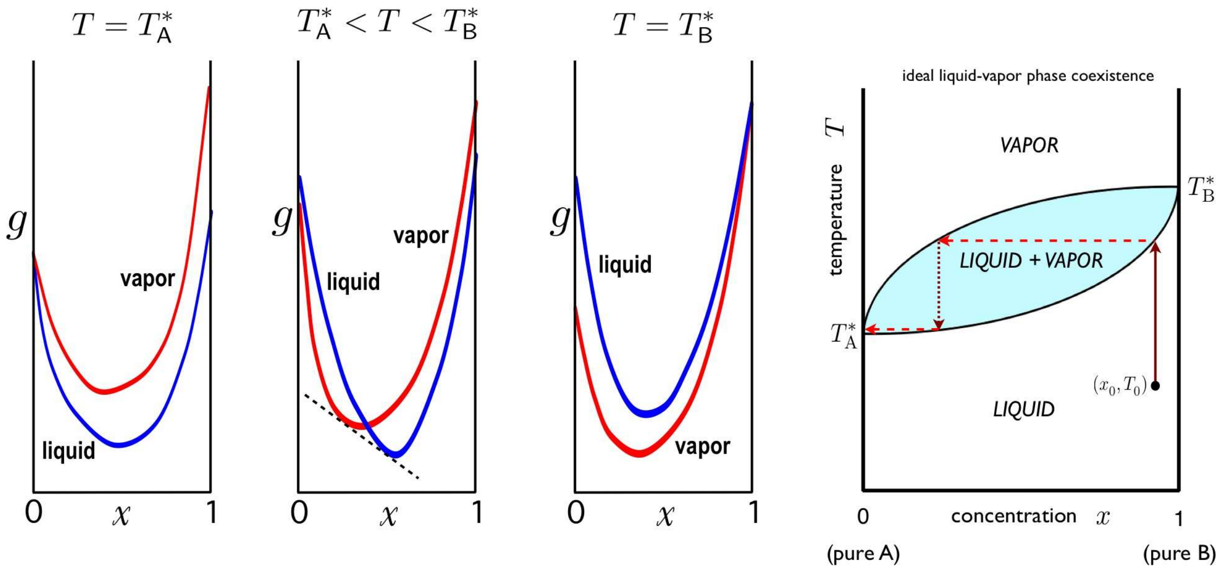

Figure 2.37: Gibbs free energy per particle $g$ for an ideal binary solution for temperatures $T \in [T^*_{\mathsf{A}}, T^*_{\mathsf{B}}]$. The Maxwell construction is shown for the case $T^*_{\mathsf{A}} < T < T^*_{\mathsf{B}}$. Right: phase diagram, showing two-phase region and distillation sequence in $(x, T)$ space.

the free energies of the mixed liquid and mixed vapor phases as

$$g_{\mathrm{L}}(T,p,x) = (1-x)\,\mu^{\mathrm{L}}_{\mathsf{A}}(T,p) + x\,\mu^{\mathrm{L}}_{\mathsf{B}}(T,p) + k_{\mathrm{B}}T\Big[x\ln x + (1-x)\ln(1-x)\Big] + \lambda_{\mathrm{L}}\,x(1-x) \tag{2.415}$$

$$g_{\mathrm{V}}(T,p,x) = (1-x)\,\mu^{\mathrm{V}}_{\mathsf{A}}(T,p) + x\,\mu^{\mathrm{V}}_{\mathsf{B}}(T,p) + k_{\mathrm{B}}T\Big[x\ln x + (1-x)\ln(1-x)\Big] + \lambda_{\mathrm{V}}\,x(1-x)\ . \tag{2.416}$$

Typically $\lambda_{\mathrm{V}} \approx 0$. Consider these two free energies as functions of the concentration $x$, at fixed $T$ and $p$. If the curves never cross, and $g_{\mathrm{L}}(x) < g_{\mathrm{V}}(x)$ for all $x \in [0,1]$, then the liquid is always the state of lowest free energy. This is the situation in the first panel of Fig. 2.37. Similarly, if $g_{\mathrm{V}}(x) < g_{\mathrm{L}}(x)$ over this range, then the mixture is in the vapor phase throughout. What happens if the two curves cross at some value of $x$? This situation is depicted in the second panel of Fig. 2.37. In this case, there is always a Maxwell construction which lowers the free energy throughout some range of concentration, *i.e.* the system undergoes phase separation.

In an *ideal fluid*, we have $\lambda_{\mathrm{L}} = \lambda_{\mathrm{V}} = 0$, and setting $g_{\mathrm{L}} = g_{\mathrm{V}}$ requires

$$(1-x)\,\Delta\mu_{\mathsf{A}}(T,p) + x\,\Delta\mu_{\mathsf{B}}(T,p) = 0\ , \tag{2.417}$$

where $\Delta\mu_{\mathsf{A/B}}(T,p) = \mu^{\mathrm{L}}_{\mathsf{A/B}}(T,p) - \mu^{\mathrm{V}}_{\mathsf{A/B}}(T,p)$. Expanding the chemical potential about a given temperature $T^*$,

$$\mu(T,p) = \mu(T^*,p) - s(T^*,p)\,(T-T^*) - \frac{c_p(T^*,p)}{2T}\,(T-T^*)^2 + \ldots\ , \tag{2.418}$$

where we have used $\big(\frac{\partial\mu}{\partial T}\big)_{p,N} = -\big(\frac{\partial S}{\partial N}\big)_{T,p} = -s(T,p)$, the entropy per particle, and $\big(\frac{\partial s}{\partial T}\big)_{p,N} = c_p/T$. Thus, expanding $\Delta\mu_{\mathsf{A/B}}$ about $T^*_{\mathsf{A/B}}$, we have

$$\begin{aligned}\Delta\mu_{\mathsf{A}} &\equiv \mu^{\mathrm{L}}_{\mathsf{A}} - \mu^{\mathrm{V}}_{\mathsf{A}} = (s^{\mathrm{V}}_{\mathsf{A}} - s^{\mathrm{L}}_{\mathsf{A}})(T - T^*_{\mathsf{A}}) + \frac{c^{\mathrm{V}}_{p\mathsf{A}} - c^{\mathrm{L}}_{p\mathsf{A}}}{2T^*_{\mathsf{A}}}\,(T-T^*_{\mathsf{A}})^2 + \ldots \\ \Delta\mu_{\mathsf{B}} &\equiv \mu^{\mathrm{L}}_{\mathsf{B}} - \mu^{\mathrm{V}}_{\mathsf{B}} = (s^{\mathrm{V}}_{\mathsf{B}} - s^{\mathrm{L}}_{\mathsf{B}})(T - T^*_{\mathsf{B}}) + \frac{c^{\mathrm{V}}_{p\mathsf{B}} - c^{\mathrm{L}}_{p\mathsf{B}}}{2T^*_{\mathsf{B}}}\,(T-T^*_{\mathsf{B}})^2 + \ldots\end{aligned} \tag{2.419}$$

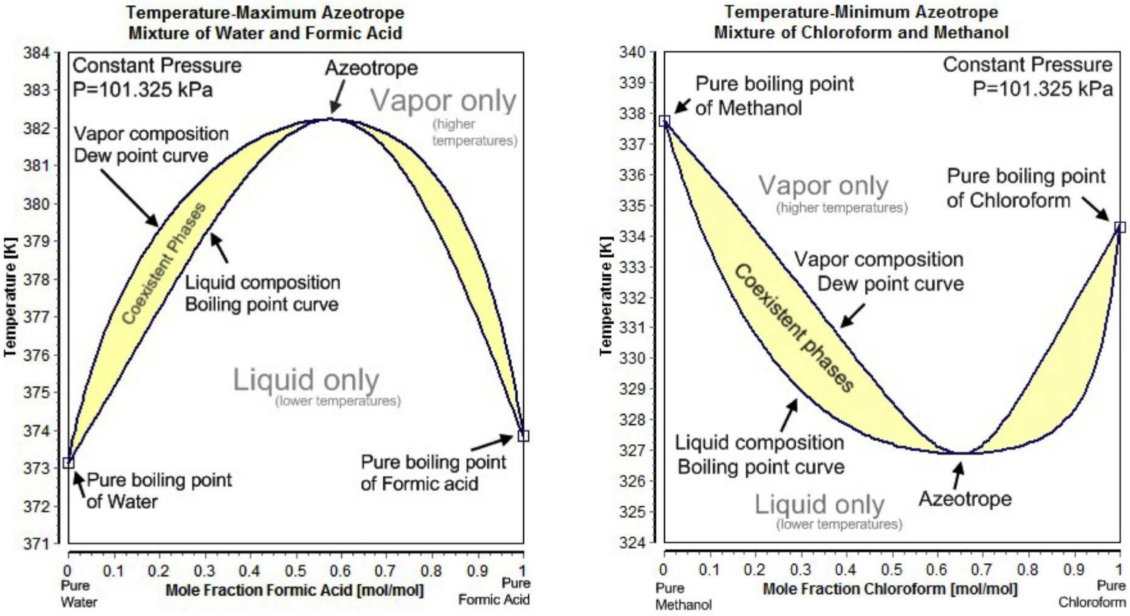

Figure 2.38: Negative (left) and positive (right) azeotrope phase diagrams. From *Wikipedia*.

We assume $s^{\mathrm{V}}_{\mathsf{A/B}} > s^{\mathrm{L}}_{\mathsf{A/B}}$, *i.e.* the vapor phase has greater entropy per particle. Thus, $\Delta\mu_{\mathsf{A/B}}(T)$ changes sign from negative to positive as $T$ rises through $T^*_{\mathsf{A/B}}$. If we assume that these are the *only* sign changes for $\Delta\mu_{\mathsf{A/B}}(T)$ at fixed $p$, then eqn. 2.417 can only be solved for $T \in [T^*_{\mathsf{A}}, T^*_{\mathsf{B}}]$. This immediately leads to the phase diagram in the rightmost panel of Fig. 2.37.

According to the Gibbs phase rule, with $\sigma = 2$, two-phase equilibrium ($\varphi = 2$) occurs along a subspace of dimension $d_{\mathrm{PE}} = 2 + \sigma - \varphi = 2$. Thus, if we fix the pressure $p$ and the concentration $x = x_{\mathrm{B}}$, liquid-gas equilibrium occurs at a particular temperature $T^*$, known as the boiling point. Since the liquid and the vapor with which it is in equilibrium at $T^*$ may have different composition, *i.e.* different values of $x$, one may *distill* the mixture to separate the two pure substances, as follows. First, given a liquid mixture of A and B, we bring it to boiling, as shown in the rightmost panel of Fig. 2.37. The vapor is at a different concentration $x$ than the liquid (a lower value of $x$ if the boiling point of pure A is less than that of pure B, as shown). If we collect the vapor, the remaining fluid is at a higher value of $x$. The collected vapor is then captured and then condensed, forming a liquid at the lower $x$ value. This is then brought to a boil, and the resulting vapor is drawn off and condensed, etc The result is a purified A state. The remaining liquid is then at a higher B concentration. By repeated boiling and condensation, A and B can be separated. For liquid-vapor transitions, the upper curve, representing the lowest temperature at a given concentration for which the mixture is a homogeneous vapor, is called the *dew point curve*. The lower curve, representing the highest temperature at a given concentration for which the mixture is a homogeneous liquid, is called the *bubble point curve*. The same phase diagram applies to liquid-solid mixtures where both phases are completely miscible. In that case, the upper curve is called the *liquidus*, and the lower curve the *solidus*.

When a homogeneous liquid or vapor at concentration $x$ is heated or cooled to a temperature $T$ such that $(x, T)$ lies within the two-phase region, the mixture phase separates into the the two end components $(x^*_{\mathrm{L}}, T)$ and $(x^*_{\mathrm{V}}, T)$, which lie on opposite sides of the boundary of the two-phase region, at the same temperature. The locus of points at constant $T$ joining these two points is called the *tie line*. To determine how much of each of these two homogeneous phases separates out, we use particle number conservation. If $\eta_{\mathrm{L,V}}$ is the fraction of the homogeneous liquid and homogeneous vapor phases present, then $\eta_{\mathrm{L}} x^*_{\mathrm{L}} + \eta_{\mathrm{V}} x^*_{\mathrm{V}} = x$, which says $\eta_{\mathrm{L}} = (x - x^*_{\mathrm{V}})/(x^*_{\mathrm{L}} - x^*_{\mathrm{V}})$ and $\eta_{\mathrm{V}} = (x - x^*_{\mathrm{L}})/(x^*_{\mathrm{V}} - x^*_{\mathrm{L}})$. This is known as the *lever rule*.

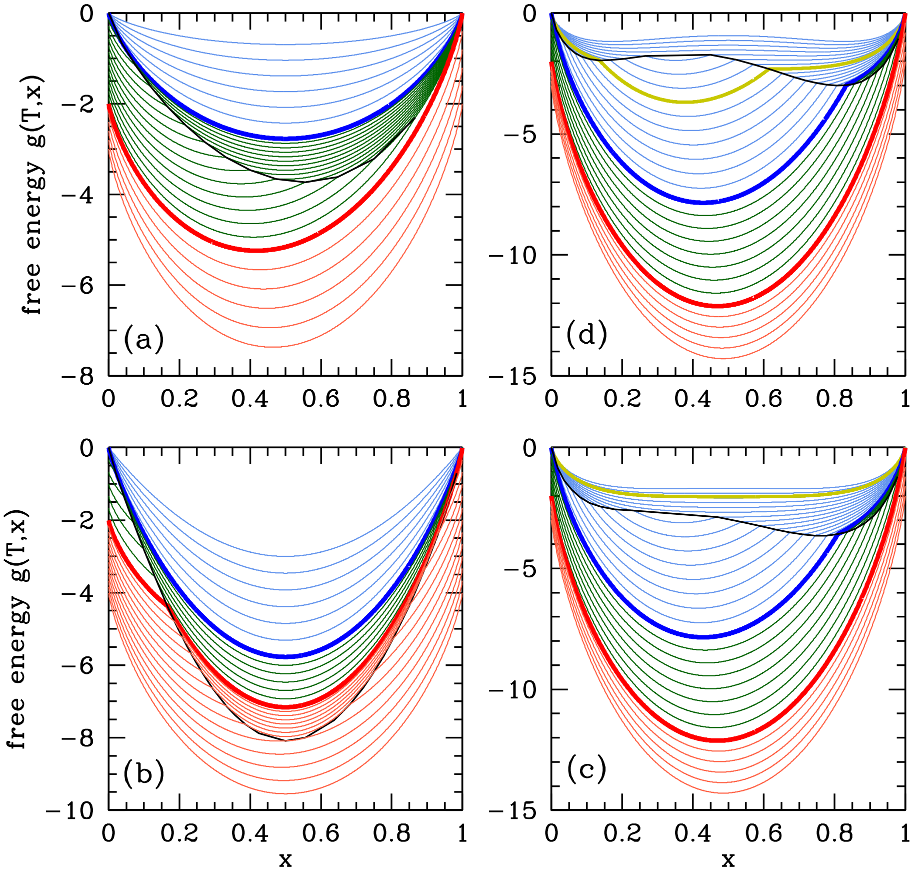

Figure 2.39: Free energies *before Maxwell constructions* for a binary fluid mixture in equilibrium with a vapor ($\lambda_{\mathrm{V}} = 0$). Panels show (a) $\lambda_{\mathrm{L}} = 0$ (ideal fluid), (b) $\lambda_{\mathrm{L}} < 0$ (miscible fluid; negative azeotrope), (c) $\lambda^{\mathrm{L}}_{\mathrm{AB}} > 0$ (positive azeotrope), (d) $\lambda^{\mathrm{L}}_{\mathrm{AB}} > 0$ (heteroazeotrope). Thick blue and red lines correspond to temperatures $T^*_{\mathsf{A}}$ and $T^*_{\mathsf{B}}$, respectively, with $T^*_{\mathsf{A}} < T^*_{\mathsf{B}}$. Thin blue and red curves are for temperatures outside the range $[T^*_{\mathsf{A}}, T^*_{\mathsf{B}}]$. The black curves show the locus of points where $g$ is discontinuous, *i.e.* where the liquid and vapor free energy curves cross. The yellow curve in (d) corresponds to the coexistence temperature for the fluid mixture. In this case the azeotrope forms within the coexistence region.

For many binary mixtures, the boiling point curve is as shown in Fig. 2.38. Such cases are called *azeotropes*. For *negative azeotropes*, the maximum of the boiling curve lies above both $T^*_{\mathsf{A,B}}$. The free energy curves for this case are shown in panel (b) of Fig. 2.39. For $x < x^*$, where $x^*$ is the azeotropic composition, one can distill A but not B. Similarly, for $x > x^*$ one can distill B but not A. The situation is different for *positive azeotropes*, where the minimum of the boiling curve lies below both $T^*_{\mathsf{A,B}}$, corresponding to the free energy curves in panel (c) of Fig. 2.39. In this case, distillation (*i.e.* condensing and reboiling the collected vapor) from either side of $x^*$ results in the azeotrope. One can of course collect the fluid instead of the vapor. In general, for both positive and negative azeotropes, starting from a given concentration $x$, one can only arrive at pure A plus azeotrope (if $x < x^*$) or pure B plus azeotrope (if $x > x^*$). Ethanol ($C_2H_5OH$) and water ($H_2O$) form a positive azeotrope which is 95.6% ethanol and 4.4% water by weight. The individual boiling points are $T^*_{\mathrm{C_2H_5OH}} = 78.4°\mathrm{C}$, $T^*_{\mathrm{H_2O}} = 100°\mathrm{C}$, while the azeotrope boils at $T^*_{\mathrm{AZ}} = 78.2°\mathrm{C}$. No amount of distillation of this mixture can purify ethanol beyond the 95.6% level. To go beyond this level of purity, one must resort to *azeotropic distillation*, which involved introducing another component, such as benzene (or a less carcinogenic additive), which alters the molecular interactions.

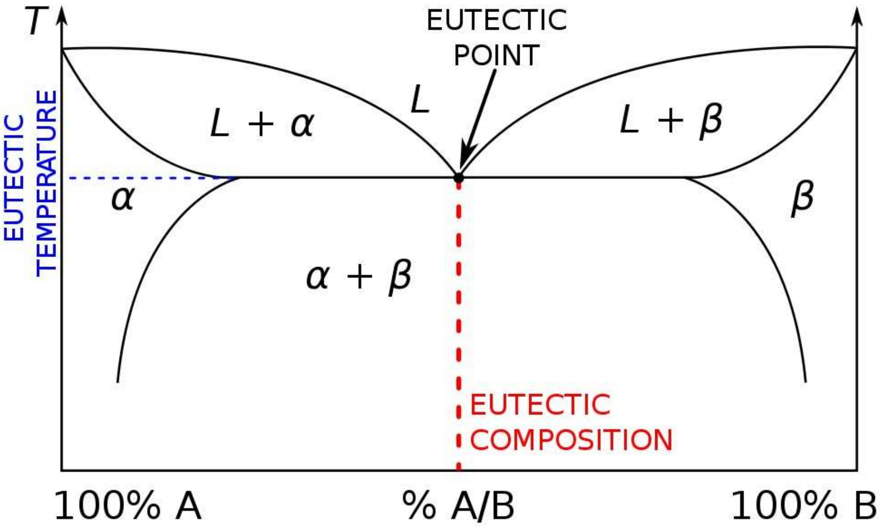

Figure 2.40: Phase diagram for a eutectic mixture in which a liquid $L$ is in equilibrium with two solid phases $\alpha$ and $\beta$. The same phase diagram holds for heteroazeotropes, where a vapor is in equilibrium with two liquid phases.

To model the azeotrope system, we need to take $\lambda_{\rm L} \neq 0$, in which case one can find *two* solutions to the energy crossing condition $g_{\rm V}(x) = g_{\rm L}(x)$. With two such crossings come two Maxwell constructions, hence the phase diagrams in Fig. 2.38. *Generally*, negative azeotropes are found in systems with $\lambda_{\rm L} < 0$, whereas positive azeotropes are found when $\lambda_{\rm L} > 0$. As we've seen, such repulsive interactions between the A and B components in general lead to a phase separation below a coexistence temperature $T_{\rm COEX}(x)$ given by eqn. 2.410. What happens if the minimum boiling point lies within the coexistence region? This is the situation depicted in panel (d) of Fig. 2.39. The system is then a liquid/vapor version of the solid/liquid *eutectic* (see Fig. 2.40), and the minimum boiling point mixture is called a *heteroazeotrope*.

## 2.14 Some Concepts in Thermochemistry

### 2.14.1 Chemical reactions and the law of mass action

Suppose we have a chemical reaction among $\sigma$ species, written as

$$\zeta_1 \, {\rm A}_1 + \zeta_2 \, {\rm A}_2 + \cdots + \zeta_\sigma \, {\rm A}_\sigma = 0 \, , \tag{2.420}$$

where

$$\begin{aligned} {\rm A}_a &= \text{chemical formula} \\ \zeta_a &= \text{stoichiometric coefficient} \, . \end{aligned}$$

For example, we could have

$$-3 \, {\rm H}_2 - {\rm N}_2 + 2 \, {\rm NH}_3 = 0 \qquad (3 \, {\rm H}_2 + {\rm N}_2 \rightleftharpoons 2 \, {\rm NH}_3) \tag{2.421}$$

for which

$$\zeta({\rm H}_2) = -3 \quad , \quad \zeta({\rm N}_2) = -1 \quad , \quad \zeta({\rm NH}_3) = 2 \, . \tag{2.422}$$

When $\zeta_a > 0$, the corresponding $\mathrm{A}_a$ is a *product*; when $\zeta_a < 0$, the corresponding $\mathrm{A}_a$ is a *reactant*. The bookkeeping of the coefficients $\zeta_a$ which ensures conservation of each individual species of atom in the reaction(s) is known as *stoichiometry*[24]

Now we ask: what are the conditions for equilibrium? At constant $T$ and $p$, which is typical for many chemical reactions, the conditions are that $G\big(T,p,\{N_a\}\big)$ be a minimum. Now

$$dG = -S\,dT + V\,dp + \sum_i \mu_a\,dN_a \ , \tag{2.423}$$

so if we let the reaction go forward, we have $dN_a = \zeta_a$, and if it runs in reverse we have $dN_a = -\zeta_a$. Thus, setting $dT = dp = 0$, we have the equilibrium condition

$$\sum_{a=1}^{\sigma} \zeta_a\,\mu_a = 0 \ . \tag{2.424}$$

Let us investigate the consequences of this relation for ideal gases. The chemical potential of the $a^{\rm th}$ species is

$$\mu_a(T,p) = k_{\rm B}T\,\phi_a(T) + k_{\rm B}T\ln p_a \ . \tag{2.425}$$

Here $p_a = p\,x_a$ is the partial pressure of species $a$, where $x_a = N_a/\sum_b N_b$ the dimensionless concentration of species $a$. Chemists sometimes write $x_a = [\mathrm{A}_a]$ for the concentration of species $a$. In equilibrium we must have

$$\sum_a \zeta_a \Big[\ln p + \ln x_a + \phi_a(T)\Big] = 0 \ , \tag{2.426}$$

which says

$$\sum_a \zeta_a\,\ln x_a = -\sum_a \zeta_a\,\ln p - \sum_a \zeta_a\,\phi_a(T) \ . \tag{2.427}$$

Exponentiating, we obtain the *law of mass action*:

$$\prod_a x_a^{\zeta_a} = p^{-\sum_a \zeta_a}\,\exp\Big(-\sum_a \zeta_a\,\phi_a(T)\Big) \equiv \kappa(p,T) \ . \tag{2.428}$$

The quantity $\kappa(p,T)$ is called the *equilibrium constant*. When $\kappa$ is large, the LHS of the above equation is large. This favors maximal concentration $x_a$ for the products ($\zeta_a > 0$) and minimal concentration $x_a$ for the reactants ($\zeta_a < 0$). This means that the equation $\mathsf{REACTANTS} \rightleftharpoons \mathsf{PRODUCTS}$ is shifted to the right, *i.e.* the products are plentiful and the reactants are scarce. When $\kappa$ is small, the LHS is small and the reaction is shifted to the left, *i.e.* the reactants are plentiful and the products are scarce. Remember we are describing *equilibrium conditions* here. Now we observe that reactions for which $\sum_a \zeta_a > 0$ shift to the left with increasing pressure and shift to the right

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[24] Antoine Lavoisier, the "father of modern chemistry", made pioneering contributions in both chemistry and biology. In particular, he is often credited as the progenitor of stoichiometry. An aristocrat by birth, Lavoisier was an administrator of the *Ferme générale*, an organization in pre-revolutionary France which collected taxes on behalf of the king. At the age of 28, Lavoisier married Marie-Anne Pierette Paulze, the 13-year-old daughter of one of his business partners. She would later join her husband in his research, and she played a role in his disproof of the phlogiston theory of combustion. The phlogiston theory was superseded by Lavoisier's work, where, based on contemporary experiments by Joseph Priestley, he correctly identified the pivotal role played by oxygen in both chemical and biological processes (*i.e.* respiration). Despite his fame as a scientist, Lavoisier succumbed to the Reign of Terror. His association with the *Ferme générale*, which collected taxes from the poor and the downtrodden, was a significant liability in revolutionary France (think Mitt Romney *vis-a-vis* Bain Capital). Furthermore – and let this be a lesson to all of us – Lavoisier had unwisely ridiculed a worthless pseudoscientific pamphlet, ostensibly on the physics of fire, and its author, Jean-Paul Marat. Marat was a journalist with scientific pretensions, but apparently little in the way of scientific talent or acumen. Lavoisier effectively blackballed Marat's candidacy to the French Academy of Sciences, and the time came when Marat sought revenge. Marat was instrumental in getting Lavoisier and other members of the *Ferme générale* arrested on charges of counterrevolutionary activities, and on May 8, 1794, after a trial lasting less than a day, Lavoisier was guillotined. Along with Fourier and Carnot, Lavoisier's name is one of the 72 engraved on the Eiffel Tower. *Source: http://www.vigyanprasar.gov.in/scientists/ALLavoisier.htm.*

with decreasing pressure, while reactions for which $\sum_a \zeta_a > 0$ the situation is reversed: they shift to the right with increasing pressure and to the left with decreasing pressure. When $\sum_a \zeta_a = 0$ there is no shift upon increasing or decreasing pressure.

The rate at which the equilibrium constant changes with temperature is given by

$$\left(\frac{\partial \ln \kappa}{\partial T}\right)_p = -\sum_a \zeta_a \, \phi'_a(T) \, . \tag{2.429}$$

Now from eqn. 2.425 we have that the enthalpy per particle for species $i$ is

$$\mathsf{h}_a = \mu_a - T\left(\frac{\partial \mu_a}{\partial T}\right)_p \, , \tag{2.430}$$

since $\mathsf{H} = G + TS$ and $S = -\left(\frac{\partial G}{\partial T}\right)_p$. We find

$$\mathsf{h}_a = -k_{\rm B} T^2 \, \phi'_a(T) \, , \tag{2.431}$$

and thus

$$\left(\frac{\partial \ln \kappa}{\partial T}\right)_p = \frac{\sum_i \zeta_a \, \mathsf{h}_a}{k_{\rm B} T^2} = \frac{\Delta \mathsf{h}}{k_{\rm B} T^2} \, , \tag{2.432}$$

where $\Delta\mathsf{h}$ is the enthalpy of the reaction, which is the heat absorbed or emitted as a result of the reaction.

When $\Delta\mathsf{h} > 0$ the reaction is *endothermic* and the yield increases with increasing $T$. When $\Delta\mathsf{h} < 0$ the reaction is *exothermic* and the yield decreases with increasing $T$.

As an example, consider the reaction $H_2 + I_2 \rightleftharpoons 2\,HI$. We have

$$\zeta(H_2) = -1 \quad , \quad \zeta(I_2) = -1 \qquad \zeta(HI) = 2 \, . \tag{2.433}$$

Suppose our initial system consists of $\nu_1^0$ moles of $H_2$, $\nu_2^0 = 0$ moles of $I_2$, and $\nu_3^0$ moles of undissociated HI . These mole numbers determine the initial concentrations $x_a^0$, where $x_a = \nu_a / \sum_b \nu_b$. Define

$$\alpha \equiv \frac{x_3^0 - x_3}{x_3} \, , \tag{2.434}$$

in which case we have

$$x_1 = x_1^0 + \tfrac{1}{2}\alpha x_3^0 \qquad , \qquad x_2 = \tfrac{1}{2}\alpha x_3^0 \qquad , \qquad x_3 = (1-\alpha)\, x_3^0 \, . \tag{2.435}$$

Then the law of mass action gives

$$\frac{4\,(1-\alpha)^2}{\alpha(\alpha + 2r)} = \kappa \, . \tag{2.436}$$

where $r \equiv x_1^0 / x_3^0 = \nu_1^0 / \nu_3^0$. This yields a quadratic equation, which can be solved to find $\alpha(\kappa, r)$. Note that $\kappa = \kappa(T)$ for this reaction since $\sum_a \zeta_a = 0$. The enthalpy of this reaction is positive: $\Delta\mathsf{h} > 0$.

### 2.14.2 Enthalpy of formation

Most chemical reactions take place under constant pressure. The heat $Q_{\rm if}$ associated with a given isobaric process is

$$Q_{\rm if} = \int_{\rm i}^{\rm f} dE + \int_{\rm i}^{\rm f} p \, dV = (E_{\rm f} - E_{\rm i}) + p\,(V_{\rm f} - V_{\rm i}) = \mathsf{H}_{\rm f} - \mathsf{H}_{\rm i} \, , \tag{2.437}$$

| Formula | Name | State | $\Delta H_f^0$ kJ/mol | Formula | Name | State | $\Delta H_f^0$ kJ/mol |
|---|---|---|---|---|---|---|---|
| Ag | Silver | crystal | 0.0 | $NiSO_4$ | Nickel sulfate | crystal | -872.9 |
| C | Graphite | crystal | 0.0 | $Al_2O_3$ | Aluminum oxide | crystal | -1657.7 |
| C | Diamond | crystal | 1.9 | $Ca_3P_2O_8$ | Calcium phosphate | gas | -4120.8 |
| $O_3$ | Ozone | gas | 142.7 | HCN | Hydrogen cyanide | liquid | 108.9 |
| $H_2O$ | Water | liquid | -285.8 | $SF_6$ | Sulfur hexafluoride | gas | -1220.5 |
| $H_3BO_3$ | Boric acid | crystal | -1094.3 | $CaF_2$ | Calcium fluoride | crystal | -1228.0 |
| $ZnSO_4$ | Zinc sulfate | crystal | -982.8 | $CaCl_2$ | Calcium chloride | crystal | -795.4 |

Table 2.5: Enthalpies of formation of some common substances.

where $\mathsf{H}$ is the *enthalpy*,

$$\mathsf{H} = E + pV \ . \tag{2.438}$$

Note that the enthalpy $\mathsf{H}$ is a state function, since $E$ is a state function and $p$ and $V$ are state variables. Hence, we can meaningfully speak of changes in enthalpy: $\Delta\mathsf{H} = \mathsf{H}_f - \mathsf{H}_i$. If $\Delta\mathsf{H} < 0$ for a given reaction, we call it *exothermic* – this is the case when $Q_{if} < 0$ and thus heat is transferred to the surroundings. Such reactions can occur spontaneously, and, in really fun cases, can produce explosions. The combustion of fuels is always exothermic. If $\Delta\mathsf{H} > 0$, the reaction is called *endothermic*. Endothermic reactions require that heat be supplied in order for the reaction to proceed. Photosynthesis is an example of an endothermic reaction.

Suppose we have two reactions

$$A + B \xrightarrow{(\Delta\mathsf{H})_1} C \tag{2.439}$$

and

$$C + D \xrightarrow{(\Delta\mathsf{H})_2} E \ . \tag{2.440}$$

Then we may write

$$A + B + D \xrightarrow{(\Delta\mathsf{H})_3} E \ , \tag{2.441}$$

with

$$(\Delta\mathsf{H})_1 + (\Delta\mathsf{H})_2 = (\Delta\mathsf{H})_3 \ . \tag{2.442}$$

We can use this additivity of reaction enthalpies to define a *standard molar enthalpy of formation*. We first define the *standard state* of a pure substance at a given temperature to be its state (gas, liquid, or solid) at a pressure $p = 1\,$bar. The *standard reaction enthalpies* at a given temperature are then defined to be the reaction enthalpies when the reactants and products are all in their standard states. Finally, we define the *standard molar enthalpy of formation* $\Delta\mathsf{H}_f^0(X)$ of a compound $X$ at temperature $T$ as the reaction enthalpy for the compound $X$ to be produced by its constituents when they are in their standard state. For example, if $X = \mathrm{SO_2}$, then we write

$$\mathrm{S} + \mathrm{O_2} \xrightarrow{\Delta\mathsf{H}_f^0[\mathrm{SO_2}]} \mathrm{SO_2} \ . \tag{2.443}$$

The enthalpy of formation of any substance in its standard state is zero at all temperatures, by definition: $\Delta\mathsf{H}_f^0[\mathrm{O_2}] = \Delta\mathsf{H}_f^0[\mathrm{He}] = \Delta\mathsf{H}_f^0[\mathrm{K}] = \Delta\mathsf{H}_f^0[\mathrm{Mn}] = 0$, *etc.*

Suppose now we have a reaction

$$a\,A + b\,B \xrightarrow{\Delta\mathsf{H}} c\,C + d\,D \ . \tag{2.444}$$

To compute the reaction enthalpy $\Delta\mathsf{H}$, we can imagine forming the components $A$ and $B$ from their standard state constituents. Similarly, we can imagine doing the same for $C$ and $D$. Since the number of atoms of a given kind is conserved in the process, the constituents of the reactants must be the same as those of the products, we have

$$\Delta\mathsf{H} = -a\,\Delta\mathsf{H}_f^0(A) - b\,\Delta\mathsf{H}_f^0(B) + c\,\Delta\mathsf{H}_f^0(C) + d\,\Delta\mathsf{H}_f^0(D) \ . \tag{2.445}$$

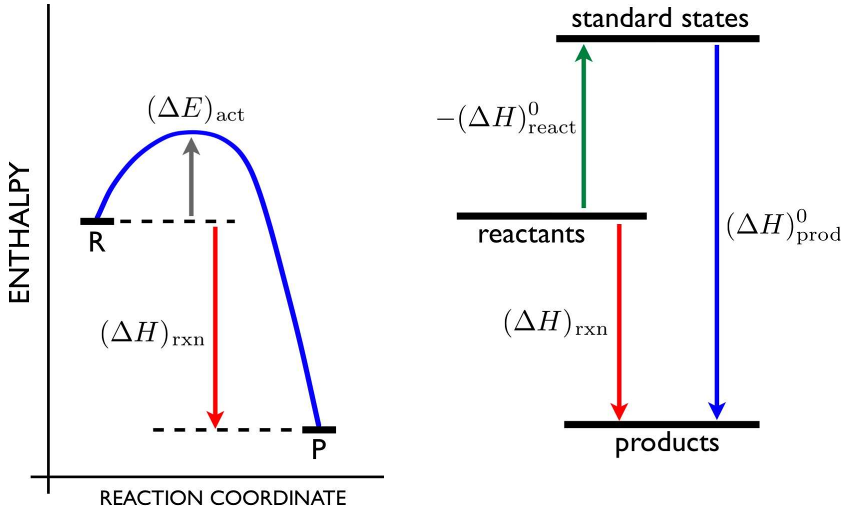


Figure 2.41: Left panel: reaction enthalpy and activation energy (exothermic case shown). Right panel: reaction enthalpy as a difference between enthalpy of formation of reactants and products.

A list of a few enthalpies of formation is provided in table 2.5. Note that the reaction enthalpy is independent of the actual reaction path. That is, the difference in enthalpy between $A$ and $B$ is the same whether the reaction is $A \longrightarrow B$ or $A \longrightarrow X \longrightarrow (Y+Z) \longrightarrow B$. This statement is known as *Hess's Law*.

Note that

$$d\mathsf{H} = dE + p\,dV + V\,dp = đQ + V\,dp \;, \tag{2.446}$$

hence

$$C_p = \left(\frac{đQ}{dT}\right)_p = \left(\frac{\partial \mathsf{H}}{\partial T}\right)_p \,. \tag{2.447}$$

We therefore have

$$\mathsf{H}(T,p,\nu) = \mathsf{H}(T_0,p,\nu) + \nu \int\limits_{T_0}^{T} \! dT'\,c_p(T') \;. \tag{2.448}$$

For ideal gases, we have $c_p(T) = (1+\frac{1}{2}f)\,R$. For real gases, over a range of temperatures, there are small variations:

$$c_p(T) = \alpha + \beta\,T + \gamma\,T^2 \;. \tag{2.449}$$

Two examples ($300\,{\rm K} < T < 1500\,{\rm K}, p = 1\,$atm):

$$\begin{array}{llll}
{\rm O}_2: & \alpha = 25.503\,\frac{\rm J}{\rm mol\,K} \;, & \beta = 13.612\times 10^{-3}\,\frac{\rm J}{\rm mol\,K^2} \;, & \gamma = -42.553\times 10^{-7}\,\frac{\rm J}{\rm mol\,K^3} \\
{\rm H_2O}: & \alpha = 30.206\,\frac{\rm J}{\rm mol\,K} \;, & \beta = 9.936\times 10^{-3}\,\frac{\rm J}{\rm mol\,K^2} \;, & \gamma = 11.14\times 10^{-7}\,\frac{\rm J}{\rm mol\,K^3}
\end{array}$$

If all the gaseous components in a reaction can be approximated as ideal, then we may write

$$(\Delta \mathsf{H})_{\rm rxn} = (\Delta E)_{\rm rxn} + \sum_a \zeta_a\,RT \;, \tag{2.450}$$

where the subscript 'rxn' stands for 'reaction'. Here $(\Delta E)_{\rm rxn}$ is the change in energy from reactants to products.

| bond | enthalpy (kJ/mol) | bond | enthalpy (kJ/mol) | bond | enthalpy (kJ/mol) | bond | enthalpy (kJ/mol) |
|---|---|---|---|---|---|---|---|
| H – H | 436 | C – C | 348 | C – S | 259 | F – F | 155 |
| H – C | 412 | C = C | 612 | N – N | 163 | F – Cl | 254 |
| H – N | 388 | C ≡ C | 811 | N = N | 409 | Cl – Br | 219 |
| H – O | 463 | C – N | 305 | N ≡ N | 945 | Cl – I | 210 |
| H – F | 565 | C = N | 613 | N – O | 157 | Cl – S | 250 |
| H – Cl | 431 | C ≡ N | 890 | N – F | 270 | Br – Br | 193 |
| H – Br | 366 | C – O | 360 | N – Cl | 200 | Br – I | 178 |
| H – I | 299 | C = O | 743 | N – Si | 374 | Br – S | 212 |
| H – S | 338 | C – F | 484 | O – O | 146 | I – I | 151 |
| H – P | 322 | C – Cl | 338 | O = O | 497 | S – S | 264 |
| H – Si | 318 | C – Br | 276 | O – F | 185 | P – P | 172 |
| | | C – I | 238 | O – Cl | 203 | Si – Si | 176 |

Table 2.6: Average bond enthalpies for some common bonds. (*Source:* L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, NY, 1960).)

### 2.14.3 Bond enthalpies

The enthalpy needed to break a chemical bond is called the *bond enthalpy*, $\mathsf{h}[\,\bullet\,]$. The bond enthalpy is the energy required to dissociate one mole of gaseous bonds to form gaseous atoms. A table of bond enthalpies is given in Tab. 2.6. Bond enthalpies are endothermic, since energy is required to break chemical bonds. Of course, the actual bond energies can depend on the location of a bond in a given molecule, and the values listed in the table reflect averages over the possible bond environment.

The bond enthalpies in Tab. 2.6 may be used to compute reaction enthalpies. Consider, for example, the reaction $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(\mathsf{l})$. We then have, from the table,

$$\begin{aligned}(\Delta\mathsf{H})_{\rm rxn} &= 2\,\mathsf{h}[\mathrm{H{-}H}] + \mathsf{h}[\mathrm{O{=}O}] - 4\,\mathsf{h}[\mathrm{H{-}O}] \\ &= -483\,\mathrm{kJ/mol\ O_2}\ .\end{aligned} \tag{2.451}$$

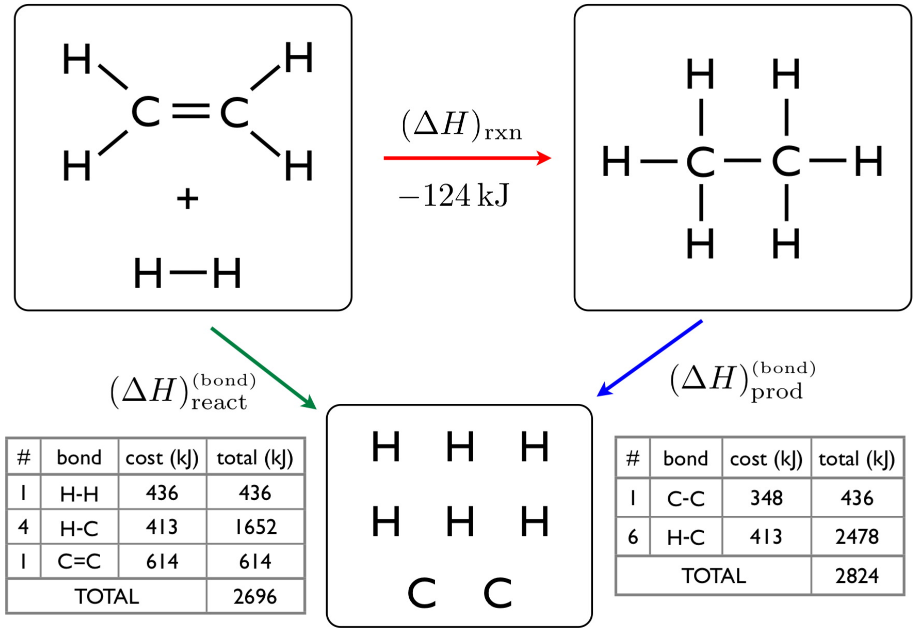
Thus, 483 kJ of heat would be released for every two moles of $H_2O$ produced, if the $H_2O$ were in the gaseous phase. Since $H_2O$ is liquid at STP, we should also include the condensation energy of the gaseous water vapor into liquid water. At $T = 100°\mathrm{C}$ the latent heat of vaporization is $\tilde{\ell} = 2270\,\mathrm{J/g}$, but at $T = 20°\mathrm{C}$, one has $\tilde{\ell} = 2450\,\mathrm{J/g}$, hence with $M = 18$ we have $\ell = 44.1\,\mathrm{kJ/mol}$. Therefore, the heat produced by the reaction $2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(\mathsf{l})$ is $(\Delta\mathsf{H})_{\rm rxn} = -571.2\,\mathrm{kJ\,/\,mol\ O_2}$. Since the reaction produces two moles of water, we conclude that the enthalpy of formation of liquid water at STP is half this value: $\Delta\mathsf{H}^0_{\rm f}[H_2O] = 285.6\,\mathrm{kJ/mol}$.

Consider next the hydrogenation of ethene (ethylene): $C_2H_4 + H_2 \rightleftharpoons C_2H_6$. The product is known as ethane. The energy accounting is shown in Fig. 2.42. To compute the enthalpies of formation of ethene and ethane from the bond enthalpies, we need one more bit of information, which is the standard enthalpy of formation of C(g) from C(s), since the solid is the standard state at STP. This value is $\Delta\mathsf{H}^0_{\rm f}[C(g)] = 718\,\mathrm{kJ/mol}$. We may now write

$$\begin{aligned}2\,C(g) + 4\,H(g) &\xrightarrow{-2260\,\mathrm{kJ}} C_2H_4(g) \\ 2\,C(s) &\xrightarrow{1436\,\mathrm{kJ}} 2\,C(g) \\ 2\,H_2(g) &\xrightarrow{872\,\mathrm{kJ}} 4\,H(g)\ .\end{aligned}$$

Thus, using Hess's law, *i.e.* adding up these reaction equations, we have

$$2\,C(s) + 2\,H_2(g) \xrightarrow{48\,\mathrm{kJ}} C_2H_4(g)\ .$$



| # | bond | cost (kJ) | total (kJ) |
|---|---|---|---|
| 1 | H-H | 436 | 436 |
| 4 | H-C | 413 | 1652 |
| 1 | C=C | 614 | 614 |
| TOTAL | | | 2696 |

| # | bond | cost (kJ) | total (kJ) |
|---|---|---|---|
| 1 | C-C | 348 | 436 |
| 6 | H-C | 413 | 2478 |
| TOTAL | | | 2824 |

Figure 2.42: Calculation of reaction enthalpy for the hydrogenation of ethene (ethylene), $C_2H_4$.

Thus, the formation of ethene is endothermic. For ethane,

$$\begin{aligned} 2\,{\rm C(g)} + 6\,{\rm H(g)} &\xrightarrow{-2820\,{\rm kJ}} {\rm C_2H_6(g)} \\ 2\,{\rm C(s)} &\xrightarrow{1436\,{\rm kJ}} 2\,{\rm C(g)} \\ 3\,{\rm H_2(g)} &\xrightarrow{1306\,{\rm kJ}} 6\,{\rm H(g)} \end{aligned}$$

For ethane,

$$2\,{\rm C(s)} + 3\,{\rm H_2(g)} \xrightarrow{-76\,{\rm kJ}} {\rm C_2H_6(g)}\ ,$$

which is exothermic.

## 2.15 Appendix I : Integrating factors

Suppose we have an inexact differential

$$đW = A_i\,dx_i\ . \tag{2.452}$$

Here I am adopting the 'Einstein convention' where we sum over repeated indices unless otherwise explicitly stated; $A_i\,dx_i = \sum_i A_i\,dx_i$. An *integrating factor* $e^{L(\vec{x})}$ is a function which, when divided into $đF$, yields an exact differential:

$$dU = e^{-L}\,đW = \frac{\partial U}{\partial x_i}\,dx_i\ . \tag{2.453}$$

Clearly we must have

$$\frac{\partial^2 U}{\partial x_i\,\partial x_j} = \frac{\partial}{\partial x_i}\big(e^{-L}\,A_j\big) = \frac{\partial}{\partial x_j}\big(e^{-L}\,A_i\big)\ . \tag{2.454}$$

Applying the Leibniz rule and then multiplying by $e^L$ yields

$$\frac{\partial A_j}{\partial x_i} - A_j\,\frac{\partial L}{\partial x_i} = \frac{\partial A_i}{\partial x_j} - A_i\,\frac{\partial L}{\partial x_j}\ . \tag{2.455}$$

If there are $K$ independent variables $\{x_1, \ldots, x_K\}$, then there are $\frac{1}{2}K(K-1)$ independent equations of the above form – one for each distinct $(i, j)$ pair. These equations can be written compactly as

$$\Omega_{ijk} \, \frac{\partial L}{\partial x_k} = F_{ij} \; , \tag{2.456}$$

where

$$\Omega_{ijk} = A_j \, \delta_{ik} - A_i \, \delta_{jk} \tag{2.457}$$

$$F_{ij} = \frac{\partial A_j}{\partial x_i} - \frac{\partial A_i}{\partial x_j} \; . \tag{2.458}$$

Note that $F_{ij}$ is antisymmetric, and resembles a field strength tensor, and that $\Omega_{ijk} = -\Omega_{jik}$ is antisymmetric in the first two indices (but is not totally antisymmetric in all three).

Can we solve these $\frac{1}{2}K(K-1)$ coupled equations to find an integrating factor $L$? In general the answer is *no*. However, when $K = 2$ we can always find an integrating factor. To see why, let's call $x \equiv x_1$ and $y \equiv x_2$. Consider now the ODE

$$\frac{dy}{dx} = -\frac{A_x(x,y)}{A_y(x,y)} \; . \tag{2.459}$$

This equation can be integrated to yield a one-parameter set of integral curves, indexed by an initial condition. The equation for these curves may be written as $U_c(x, y) = 0$, where $c$ labels the curves. Then along each curve we have

$$\begin{aligned} 0 = \frac{dU_c}{dx} &= \frac{\partial U_x}{\partial x} + \frac{\partial U_c}{\partial y} \, \frac{dy}{dx} \\ &= \frac{\partial U_c}{\partial x} - \frac{A_x}{A_y} \, \frac{\partial U_c}{\partial y} \; . \end{aligned} \tag{2.460}$$

Thus,

$$\frac{\partial U_c}{\partial x} \, A_y = \frac{\partial U_c}{\partial y} \, A_x \equiv e^{-L} A_x \, A_y \; . \tag{2.461}$$

This equation defines the integrating factor $L$ :

$$L = -\ln\!\bigg(\frac{1}{A_x} \, \frac{\partial U_c}{\partial x}\bigg) = -\ln\!\bigg(\frac{1}{A_y} \, \frac{\partial U_c}{\partial y}\bigg) \; . \tag{2.462}$$

We now have that

$$A_x = e^L \, \frac{\partial U_c}{\partial x} \qquad , \qquad A_y = e^L \, \frac{\partial U_c}{\partial y} \; , \tag{2.463}$$

and hence

$$e^{-L} \, {\mathchar'26\mkern-12mu d}W = \frac{\partial U_c}{\partial x} \, dx + \frac{\partial U_c}{\partial y} \, dy = dU_c \; . \tag{2.464}$$

## 2.16 Appendix II : Legendre Transformations

A *convex function* of a single variable $f(x)$ is one for which $f''(x) > 0$ everywhere. The *Legendre transform* of a convex function $f(x)$ is a function $g(p)$ defined as follows. Let $p$ be a real number, and consider the line $y = px$, as shown in Fig. 2.43. We define the point $x(p)$ as the value of $x$ for which the difference $F(x, p) = px - f(x)$ is

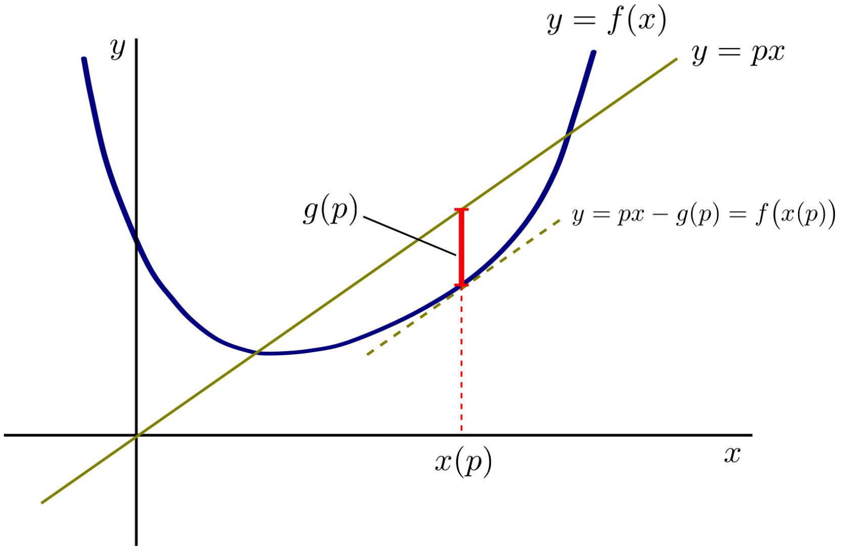


Figure 2.43: Construction for the Legendre transformation of a function $f(x)$.

greatest. Then define $g(p) = F\big(x(p), p\big)$.[25] The value $x(p)$ is unique if $f(x)$ is convex, since $x(p)$ is determined by the equation

$$f'\big(x(p)\big) = p\ . \tag{2.465}$$

Note that from $p = f'\big(x(p)\big)$ we have, according to the chain rule,

$$\frac{d}{dp}\, f'\big(x(p)\big) = f''\big(x(p)\big)\, x'(p) \qquad \Longrightarrow \qquad x'(p) = \Big[f''\big(x(p)\big)\Big]^{-1}\ . \tag{2.466}$$

From this, we can prove that $g(p)$ is itself convex:

$$\begin{aligned} g'(p) &= \frac{d}{dp}\Big[p\, x(p) - f\big(x(p)\big)\Big] \\ &= p\, x'(p) + x(p) - f'\big(x(p)\big)\, x'(p) = x(p)\ , \end{aligned} \tag{2.467}$$

hence

$$g''(p) = x'(p) = \Big[f''\big(x(p)\big)\Big]^{-1} > 0\ . \tag{2.468}$$

In higher dimensions, the generalization of the definition $f''(x) > 0$ is that a function $F(x_1, \ldots, x_n)$ is convex if the matrix of second derivatives, called the *Hessian*,

$$H_{ij}(\boldsymbol{x}) = \frac{\partial^2 F}{\partial x_i\, \partial x_j} \tag{2.469}$$

is positive definite. That is, all the eigenvalues of $H_{ij}(\boldsymbol{x})$ must be positive for every $\boldsymbol{x}$. We then define the Legendre transform $\boldsymbol{G}(\boldsymbol{p})$ as

$$\boldsymbol{G}(\boldsymbol{p}) = \boldsymbol{p} \cdot \boldsymbol{x} - F(\boldsymbol{x}) \tag{2.470}$$

where

$$\boldsymbol{p} = \boldsymbol{\nabla} F\ . \tag{2.471}$$

---

[25] Note that $g(p)$ may be a negative number, if the line $y = px$ lies everywhere below $f(x)$.

Note that

$$dG = \boldsymbol{x} \cdot d\boldsymbol{p} + \boldsymbol{p} \cdot d\boldsymbol{x} - \boldsymbol{\nabla} F \cdot d\boldsymbol{x} = \boldsymbol{x} \cdot d\boldsymbol{p} \ , \tag{2.472}$$

which establishes that $G$ is a function of $\boldsymbol{p}$ and that

$$\frac{\partial G}{\partial p_j} = x_j \ . \tag{2.473}$$

Note also that the Legendre transformation is *self dual*, which is to say that the Legendre transform of $G(\boldsymbol{p})$ is $F(\boldsymbol{x})$: $F \to G \to F$ under successive Legendre transformations.

We can also define a *partial Legendre transformation* as follows. Consider a function of $q$ variables $F(\boldsymbol{x}, \boldsymbol{y})$, where $\boldsymbol{x} = \{x_1, \ldots, x_m\}$ and $\boldsymbol{y} = \{y_1, \ldots, y_n\}$, with $q = m + n$. Define $\boldsymbol{p} = \{p_1, \ldots, p_m\}$, and

$$G(\boldsymbol{p}, \boldsymbol{y}) = \boldsymbol{p} \cdot \boldsymbol{x} - F(\boldsymbol{x}, \boldsymbol{y}) \ , \tag{2.474}$$

where

$$p_a = \frac{\partial F}{\partial x_a} \qquad (a = 1, \ldots, m) \ . \tag{2.475}$$

These equations are then to be inverted to yield

$$x_a = x_a(\boldsymbol{p}, \boldsymbol{y}) = \frac{\partial G}{\partial p_a} \ . \tag{2.476}$$

Note that

$$p_a = \frac{\partial F}{\partial x_a} \big( \boldsymbol{x}(\boldsymbol{p}, \boldsymbol{y}), \boldsymbol{y} \big) \ . \tag{2.477}$$

Thus, from the chain rule,

$$\delta_{ab} = \frac{\partial p_a}{\partial p_b} = \frac{\partial^2 F}{\partial x_a \, \partial x_c} \, \frac{\partial x_c}{\partial p_b} = \frac{\partial^2 F}{\partial x_a \, \partial x_c} \, \frac{\partial^2 G}{\partial p_c \, \partial p_b} \ , \tag{2.478}$$

which says

$$\frac{\partial^2 G}{\partial p_a \, \partial p_b} = \frac{\partial x_a}{\partial p_b} = \mathsf{K}^{-1}_{ab} \ , \tag{2.479}$$

where the $m \times m$ partial Hessian is

$$\frac{\partial^2 F}{\partial x_a \, \partial x_b} = \frac{\partial p_a}{\partial x_b} = \mathsf{K}_{ab} \ . \tag{2.480}$$

Note that $\mathsf{K}_{ab} = \mathsf{K}_{ba}$ is symmetric. And with respect to the $\boldsymbol{y}$ coordinates,

$$\frac{\partial^2 G}{\partial y_\mu \, \partial y_\nu} = -\frac{\partial^2 F}{\partial y_\mu \, \partial y_\nu} = -\mathsf{L}_{\mu\nu} \ , \tag{2.481}$$

where

$$\mathsf{L}_{\mu\nu} = \frac{\partial^2 F}{\partial y_\mu \, \partial y_\nu} \tag{2.482}$$

is the partial Hessian in the $\boldsymbol{y}$ coordinates. Now it is easy to see that if the full $q \times q$ Hessian matrix $H_{ij}$ is positive definite, then any submatrix such as $\mathsf{K}_{ab}$ or $\mathsf{L}_{\mu\nu}$ must also be positive definite. In this case, the partial Legendre transform is convex in $\{p_1, \ldots, p_m\}$ and concave in $\{y_1, \ldots, y_n\}$.

## 2.17 Appendix III : Useful Mathematical Relations

Consider a set of $n$ independent variables $\{x_1,\ldots,x_n\}$, which can be thought of as a point in $n$-dimensional space. Let $\{y_1,\ldots,y_n\}$ and $\{z_1,\ldots,z_n\}$ be other choices of coordinates. Then

$$\frac{\partial x_i}{\partial z_k} = \frac{\partial x_i}{\partial y_j}\,\frac{\partial y_j}{\partial z_k} \ . \tag{2.483}$$

Note that this entails a matrix multiplication: $A_{ik} = B_{ij}\,C_{jk}$, where $A_{ik} = \partial x_i/\partial z_k$, $B_{ij} = \partial x_i/\partial y_j$, and $C_{jk} = \partial y_j/\partial z_k$. We define the determinant

$$\det\bigg(\frac{\partial x_i}{\partial z_k}\bigg) \equiv \frac{\partial(x_1,\ldots,x_n)}{\partial(z_1,\ldots,z_n)} \ . \tag{2.484}$$

Such a determinant is called a Jacobean. Now if $A = BC$, then $\det(A) = \det(B)\cdot\det(C)$. Thus,

$$\frac{\partial(x_1,\ldots,x_n)}{\partial(z_1,\ldots,z_n)} = \frac{\partial(x_1,\ldots,x_n)}{\partial(y_1,\ldots,y_n)}\cdot\frac{\partial(y_1,\ldots,y_n)}{\partial(z_1,\ldots,z_n)} \ . \tag{2.485}$$

Recall also that

$$\frac{\partial x_i}{\partial x_k} = \delta_{ik} \ . \tag{2.486}$$

Consider the case $n = 2$. We have

$$\frac{\partial(x,y)}{\partial(u,v)} = \det\begin{pmatrix} \big(\frac{\partial x}{\partial u}\big)_v & \big(\frac{\partial x}{\partial v}\big)_u \\ \\ \big(\frac{\partial y}{\partial u}\big)_v & \big(\frac{\partial y}{\partial v}\big)_u \end{pmatrix} = \bigg(\frac{\partial x}{\partial u}\bigg)_{\!v}\bigg(\frac{\partial y}{\partial v}\bigg)_{\!u} - \bigg(\frac{\partial x}{\partial v}\bigg)_{\!u}\bigg(\frac{\partial y}{\partial u}\bigg)_{\!v} \ . \tag{2.487}$$

We also have

$$\frac{\partial(x,y)}{\partial(u,v)}\cdot\frac{\partial(u,v)}{\partial(r,s)} = \frac{\partial(x,y)}{\partial(r,s)} \ . \tag{2.488}$$

From this simple mathematics follows several very useful results.

1) First, write

$$\frac{\partial(x,y)}{\partial(u,v)} = \Bigg[\frac{\partial(u,v)}{\partial(x,y)}\Bigg]^{-1} \ . \tag{2.489}$$

Now let $y = v$:

$$\frac{\partial(x,y)}{\partial(u,y)} = \bigg(\frac{\partial x}{\partial u}\bigg)_{\!y} = \frac{1}{\big(\frac{\partial u}{\partial x}\big)_y} \ . \tag{2.490}$$

Thus,

$$\bigg(\frac{\partial x}{\partial u}\bigg)_{\!y} = 1\Big/\bigg(\frac{\partial u}{\partial x}\bigg)_{\!y} \tag{2.491}$$

2) Second, we have

$$\frac{\partial(x,y)}{\partial(u,y)} = \bigg(\frac{\partial x}{\partial u}\bigg)_{\!y} = \frac{\partial(x,y)}{\partial(x,u)}\cdot\frac{\partial(x,u)}{\partial(u,y)} = -\bigg(\frac{\partial y}{\partial u}\bigg)_{\!x}\bigg(\frac{\partial x}{\partial y}\bigg)_{\!u} \ ,$$

which is to say

$$\bigg(\frac{\partial x}{\partial y}\bigg)_{\!u}\bigg(\frac{\partial y}{\partial u}\bigg)_{\!x} = -\bigg(\frac{\partial x}{\partial u}\bigg)_{\!y} \ . \tag{2.492}$$

Invoking eqn. 2.491, we conclude that

$$\left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial u}\right)_x \left(\frac{\partial u}{\partial x}\right)_y = -1 \; . \tag{2.493}$$

3) Third, we have

$$\frac{\partial(x,v)}{\partial(u,v)} = \frac{\partial(x,v)}{\partial(y,v)} \cdot \frac{\partial(y,v)}{\partial(u,v)} \; , \tag{2.494}$$

which says

$$\left(\frac{\partial x}{\partial u}\right)_v = \left(\frac{\partial x}{\partial y}\right)_v \left(\frac{\partial y}{\partial u}\right)_v \tag{2.495}$$

This is simply the chain rule of partial differentiation.

4) Fourth, we have

$$\begin{aligned}\frac{(\partial x,\partial y)}{(\partial u,\partial y)} &= \frac{(\partial x,\partial y)}{(\partial u,\partial v)} \cdot \frac{(\partial u,\partial v)}{(\partial u,\partial y)} \\ &= \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u \left(\frac{\partial v}{\partial y}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \left(\frac{\partial v}{\partial y}\right)_u \; ,\end{aligned} \tag{2.496}$$

which says

$$\left(\frac{\partial x}{\partial u}\right)_y = \left(\frac{\partial x}{\partial u}\right)_v - \left(\frac{\partial x}{\partial y}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \tag{2.497}$$

5) Fifth, whenever we differentiate one extensive quantity with respect to another, holding only intensive quantities constant, the result is simply the ratio of those extensive quantities. For example,

$$\left(\frac{\partial S}{\partial V}\right)_{p,T} = \frac{S}{V} \; . \tag{2.498}$$

The reason should be obvious. In the above example, $S(p,V,T) = V\phi(p,T)$, where $\phi$ is a function of the two intensive quantities $p$ and $T$. Hence differentiating $S$ with respect to $V$ holding $p$ and $T$ constant is the same as dividing $S$ by $V$. Note that this implies

$$\left(\frac{\partial S}{\partial V}\right)_{p,T} = \left(\frac{\partial S}{\partial V}\right)_{p,\mu} = \left(\frac{\partial S}{\partial V}\right)_{n,T} = \frac{S}{V} \; , \tag{2.499}$$

where $n = N/V$ is the particle density.

6) Sixth, suppose we have a function $E(y,v)$ and we write

$$dE = x\,dy + u\,dv \; . \tag{2.500}$$

That is,

$$x = \left(\frac{\partial E}{\partial y}\right)_v \equiv E_y \qquad , \qquad u = \left(\frac{\partial E}{\partial v}\right)_y \equiv E_v \; . \tag{2.501}$$

Writing

$$dx = E_{yy}\,dy + E_{yv}\,dv \tag{2.502}$$

$$du = E_{vy}\,dy + E_{vv}\,dv \; , \tag{2.503}$$

and demanding $du = 0$ yields

$$\left(\frac{\partial x}{\partial u}\right)_{v} = \frac{E_{yy}}{E_{vy}} \,. \tag{2.504}$$

Note that $E_{vy} = E_{vy}$. From the equation $du = 0$ we also derive

$$\left(\frac{\partial y}{\partial v}\right)_{u} = -\frac{E_{vv}}{E_{vy}} \,. \tag{2.505}$$

Next, we use eqn. 2.503 with $du = 0$ to eliminate $dy$ in favor of $dv$, and then substitute into eqn. 2.502. This yields

$$\left(\frac{\partial x}{\partial v}\right)_{u} = E_{yv} - \frac{E_{yy}\,E_{vv}}{E_{vy}} \,. \tag{2.506}$$

Finally, eqn. 2.503 with $dv = 0$ yields

$$\left(\frac{\partial y}{\partial u}\right)_{v} = \frac{1}{E_{vy}} \,. \tag{2.507}$$

Combining the results of eqns. 2.504, 2.505, 2.506, and 2.507, we have

$$\begin{aligned} \frac{\partial(x,y)}{\partial(u,v)} &= \left(\frac{\partial x}{\partial u}\right)_{v} \left(\frac{\partial y}{\partial v}\right)_{u} - \left(\frac{\partial x}{\partial v}\right)_{u} \left(\frac{\partial y}{\partial u}\right)_{v} \\ &= \left(\frac{E_{yy}}{E_{vy}}\right)\left(-\frac{E_{vv}}{E_{vy}}\right) - \left(E_{yv} - \frac{E_{yy}\,E_{vv}}{E_{vy}}\right)\left(\frac{1}{E_{vy}}\right) = -1 \,. \end{aligned} \tag{2.508}$$

Thus,

$$\frac{\partial(T,S)}{\partial(p,V)} = 1 \,. \tag{2.509}$$

*Nota bene:* It is important to understand what other quantities are kept constant, otherwise we can run into trouble. For example, it would seem that eqn. 2.508 would also yield

$$\frac{\partial(\mu,N)}{\partial(p,V)} = 1 \,. \tag{2.510}$$

But then we should have

$$\frac{\partial(T,S)}{\partial(\mu,N)} = \frac{\partial(T,S)}{\partial(p,V)} \cdot \frac{\partial(p,V)}{\partial(\mu,N)} = 1 \qquad \text{(WRONG!)}$$

when according to eqn. 2.508 it should be $-1$. What has gone wrong?

The problem is that we have not properly specified what else is being held constant. In eqn. 2.509 it is $N$ (or $\mu$) which is being held constant, while in eqn. 2.510 it is $S$ (or $T$) which is being held constant. Therefore a naive application of the chain rule for determinants yields the wrong result, as we have seen.

Let's be more careful. Applying the same derivation to $dE = x\,dy + u\,dv + r\,ds$ and holding $s$ constant, we conclude

$$\frac{\partial(x,y,s)}{\partial(u,v,s)} = \left(\frac{\partial x}{\partial u}\right)_{v,s} \left(\frac{\partial y}{\partial v}\right)_{u,s} - \left(\frac{\partial x}{\partial v}\right)_{u,s} \left(\frac{\partial y}{\partial u}\right)_{v,s} = -1 \,. \tag{2.511}$$

Thus, the appropriate thermodynamic relations are

$$\begin{aligned} \frac{\partial(T,S,N)}{\partial(y,X,N)} &= -1 & \qquad \frac{\partial(T,S,\mu)}{\partial(y,X,\mu)} &= -1 \\ \frac{\partial(T,S,X)}{\partial(\mu,N,X)} &= -1 & \qquad \frac{\partial(T,S,y)}{\partial(\mu,N,y)} &= -1 \\ \frac{\partial(y,X,S)}{\partial(\mu,N,S)} &= -1 & \qquad \frac{\partial(y,X,T)}{\partial(\mu,N,T)} &= -1 \end{aligned} \tag{2.512}$$

For example, if we add $(\mu, N)$ to the mix, we should write

$$\frac{\partial(T,S,N)}{\partial(-p,V,N)} = \frac{\partial(-p,V,S)}{\partial(\mu,N,S)} = \frac{\partial(\mu,N,V)}{\partial(T,S,V)} = -1 \; . \tag{2.513}$$

If we are careful, then the general result in eq. 2.512, where $(y,X) = (-p,V)$ or $(H^\alpha, M^\alpha)$ or $(E^\alpha, P^\alpha)$, can be quite handy, especially when used in conjunction with eqn. 2.485. For example, we have

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \frac{\partial(T,S,N)}{\partial(T,V,N)} = \overbrace{\frac{\partial(T,S,N)}{\partial(p,V,N)}}^{=1} \cdot \frac{\partial(p,V,N)}{\partial(T,V,N)} = \left(\frac{\partial p}{\partial T}\right)_{V,N} \; , \tag{2.514}$$

which is one of the Maxwell relations derived from the exactness of $dF$. Some other examples:

$$\left(\frac{\partial V}{\partial S}\right)_{p,N} = \frac{\partial(V,p,N)}{\partial(S,p,N)} = \frac{\partial(V,p,N)}{\partial(S,T,N)} \cdot \frac{\partial(S,T,N)}{\partial(S,p,N)} = \left(\frac{\partial T}{\partial p}\right)_{S,N} \tag{2.515}$$

$$\left(\frac{\partial S}{\partial N}\right)_{T,p} = \frac{\partial(S,T,p)}{\partial(N,T,p)} = \frac{\partial(S,T,p)}{\partial(\mu,N,p)} \cdot \frac{\partial(\mu,N,p)}{\partial(N,T,p)} = -\left(\frac{\partial \mu}{\partial T}\right)_{p,N} \; . \tag{2.516}$$

Note that due to the alternating nature of the determinant – it is antisymmetric under interchange of any two rows or columns – we have

$$\frac{\partial(x,y,z)}{\partial(u,v,w)} = -\frac{\partial(y,x,z)}{\partial(u,v,w)} = \frac{\partial(y,x,z)}{\partial(w,v,u)} = \ldots \; . \tag{2.517}$$

In general, it is usually advisable to eliminate $S$ from a Jacobean. If we have a Jacobean involving $T$, $S$, and $N$, we can write

$$\frac{\partial(T,S,N)}{\partial(\,\bullet\,,\,\bullet\,,N)} = \frac{\partial(T,S,N)}{\partial(p,V,N)}\,\frac{\partial(p,V,N)}{\partial(\,\bullet\,,\,\bullet\,,N)} = \frac{\partial(p,V,N)}{\partial(\,\bullet\,,\,\bullet\,,N)} \; , \tag{2.518}$$

where each $\bullet$ is a distinct arbitrary state variable other than $N$.

If our Jacobean involves the $S$, $V$, and $N$, we write

$$\frac{\partial(S,V,N)}{\partial(\,\bullet\,,\,\bullet\,,N)} = \frac{\partial(S,V,N)}{\partial(T,V,N)} \cdot \frac{\partial(T,V,N)}{\partial(\,\bullet\,,\,\bullet\,,N)} = \frac{C_V}{T} \cdot \frac{\partial(T,V,N)}{\partial(\,\bullet\,,\,\bullet\,,N)} \; . \tag{2.519}$$

If our Jacobean involves the $S$, $p$, and $N$, we write

$$\frac{\partial(S,p,N)}{\partial(\,\bullet\,,\,\bullet\,,N)} = \frac{\partial(S,p,N)}{\partial(T,p,N)} \cdot \frac{\partial(T,p,N)}{\partial(\,\bullet\,,\,\bullet\,,N)} = \frac{C_p}{T} \cdot \frac{\partial(T,p,N)}{\partial(\,\bullet\,,\,\bullet\,,N)} \; . \tag{2.520}$$

For example,

$$\left(\frac{\partial T}{\partial p}\right)_{S,N} = \frac{\partial(T,S,N)}{\partial(p,S,N)} = \frac{\partial(T,S,N)}{\partial(p,V,N)} \cdot \frac{\partial(p,V,N)}{\partial(p,T,N)} \cdot \frac{\partial(p,T,N)}{\partial(p,S,N)} = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_{p,N} \tag{2.521}$$

$$\left(\frac{\partial V}{\partial p}\right)_{S,N} = \frac{\partial(V,S,N)}{\partial(p,S,N)} = \frac{\partial(V,S,N)}{\partial(V,T,N)} \cdot \frac{\partial(V,T,N)}{\partial(p,T,N)} \cdot \frac{\partial(p,T,N)}{\partial(p,S,N)} = \frac{C_V}{C_p}\left(\frac{\partial V}{\partial p}\right)_{T,N} . \tag{2.522}$$

# Chapter 3

# Ergodicity and the Approach to Equilibrium

## 3.1 References

- R. Balescu, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, 1975)
  An advanced text with an emphasis on fluids and kinetics.
- R. Balian, *From Macrophysics to Microphysics* (2 vols., Springer-Verlag, 2006)
  A very detailed discussion of the fundamental postulates of statistical mechanics and their implications.)

## 3.2 Modeling the Approach to Equilibrium

### 3.2.1 Equilibrium

A thermodynamic system typically consists of an enormously large number of constituent particles, a typical 'large number' being Avogadro's number, $N_{\text{A}} = 6.02 \times 10^{23}$. Nevertheless, in *equilibrium*, such a system is characterized by a relatively small number of thermodynamic state variables. Thus, while a complete description of a (classical) system would require us to account for $\mathcal{O}\big(10^{23}\big)$ evolving degrees of freedom, with respect to the physical quantities in which we are interested, the details of the initial conditions are effectively forgotten over some microscopic time scale $\tau$, called the collision time, and over some microscopic distance scale, $\ell$, called the mean free path[1]. The equilibrium state is time-independent.

### 3.2.2 The Master Equation

Relaxation to equilibrium is often modeled with something called the *master equation*. Let $P_i(t)$ be the probability that the system is in a quantum or classical state $i$ at time $t$. Then write

$$\frac{dP_i}{dt} = \sum_j \big(W_{ij}\,P_j - W_{ji}\,P_i\big)\ . \tag{3.1}$$

Here, $W_{ij}$ is the rate at which $j$ makes a transition to $i$. Note that we can write this equation as

$$\frac{dP_i}{dt} = -\sum_j \varGamma_{ij}\,P_j\ , \tag{3.2}$$

where

$$\varGamma_{ij} = \begin{cases} -W_{ij} & \text{if } i \neq j \\ \sum'_k W_{kj} & \text{if } i = j\ , \end{cases} \tag{3.3}$$

where the prime on the sum indicates that $k = j$ is to be excluded. The constraints on the $W_{ij}$ are that $W_{ij} \geq 0$ for all $i, j$, and we may take $W_{ii} \equiv 0$ (no sum on $i$). Fermi's Golden Rule of quantum mechanics says that

$$W_{ij} = \frac{2\pi}{\hbar}\,\big|\langle\, i\,|\,\hat{V}\,|\,j\,\rangle\big|^2\,\rho(E_j)\ , \tag{3.4}$$

where $\hat{H}_0\,\big|\,i\,\big\rangle = E_i\,\big|\,i\,\big\rangle$, $\hat{V}$ is an additional potential which leads to transitions, and $\rho(E_i)$ is the density of final states at energy $E_i$. The fact that $W_{ij} \geq 0$ means that if each $P_i(t=0) \geq 0$, then $P_i(t) \geq 0$ for all $t \geq 0$. To see this, suppose that at some time $t > 0$ one of the probabilities $P_i$ is crossing zero and about to become negative. But then eqn. 3.1 says that $\dot{P}_i(t) = \sum_j W_{ij} P_j(t) \geq 0$. So $P_i(t)$ can never become negative.

### 3.2.3 Equilibrium distribution and detailed balance

If the transition rates $W_{ij}$ are themselves time-independent, then we may formally write

$$P_i(t) = \big(e^{-\varGamma t}\big)_{ij}\,P_j(0)\ . \tag{3.5}$$

---

[1] Exceptions involve quantities which are conserved by collisions, such as overall particle number, momentum, and energy. These quantities relax to equilibrium in a special way called *hydrodynamics*.

Here we have used the Einstein 'summation convention' in which repeated indices are summed over (in this case, the $j$ index). Note that

$$\sum_i \Gamma_{ij} = 0 \,, \tag{3.6}$$

which says that the total probability $\sum_i P_i$ is conserved:

$$\frac{d}{dt}\sum_i P_i = -\sum_{i,j} \Gamma_{ij}\, P_j = -\sum_j \bigg(P_j \sum_i \Gamma_{ij}\bigg) = 0 \,. \tag{3.7}$$

We conclude that $\vec{\phi} = (1, 1, \ldots, 1)$ is a left eigenvector of $\Gamma$ with eigenvalue $\lambda = 0$. The corresponding right eigenvector, which we write as $P_i^{\rm eq}$, satisfies $\Gamma_{ij} P_j^{\rm eq} = 0$, and is a stationary (*i.e.* time independent) solution to the master equation. Generally, there is only one right/left eigenvector pair corresponding to $\lambda = 0$, in which case any initial probability distribution $P_i(0)$ converges to $P_i^{\rm eq}$ as $t \to \infty$, as shown in Appendix I (§3.7).

In equilibrium, the net rate of transitions into a state $|\,i\,\rangle$ is equal to the rate of transitions out of $|\,i\,\rangle$. If, for each state $|\,j\,\rangle$ the transition rate from $|\,i\,\rangle$ to $|\,j\,\rangle$ is equal to the transition rate from $|\,j\,\rangle$ to $|\,i\,\rangle$, we say that the rates satisfy the condition of *detailed balance*. In other words,

$$W_{ij}\, P_j^{\rm eq} = W_{ji}\, P_i^{\rm eq}. \tag{3.8}$$

Assuming $W_{ij} \neq 0$ and $P_j^{\rm eq} \neq 0$, we can divide to obtain

$$\frac{W_{ji}}{W_{ij}} = \frac{P_j^{\rm eq}}{P_i^{\rm eq}} \,. \tag{3.9}$$

Note that detailed balance is a stronger condition than that required for a stationary solution to the master equation.

If $\Gamma = \Gamma^{\rm t}$ is symmetric, then the right eigenvectors and left eigenvectors are transposes of each other, hence $P^{\rm eq} = 1/N$, where $N$ is the dimension of $\Gamma$. The system then satisfies the conditions of detailed balance. See Appendix II (§3.8) for an example of this formalism applied to a model of radioactive decay.

### 3.2.4 Boltzmann's H-theorem

Suppose for the moment that $\Gamma$ is a symmetric matrix, *i.e.* $\Gamma_{ij} = \Gamma_{ji}$. Then construct the function

$$\mathsf{H}(t) = \sum_i P_i(t)\, \ln P_i(t) \,. \tag{3.10}$$

Then

$$\begin{aligned} \frac{d\mathsf{H}}{dt} &= \sum_i \frac{dP_i}{dt}\,\big(1 + \ln P_i\big) = \sum_i \frac{dP_i}{dt}\, \ln P_i \\ &= -\sum_{i,j} \Gamma_{ij}\, P_j \ln P_i \\ &= \sum_{i,j} \Gamma_{ij}\, P_j \big(\ln P_j - \ln P_i\big) \,, \end{aligned} \tag{3.11}$$

where we have used $\sum_i \Gamma_{ij} = 0$. Now switch $i \leftrightarrow j$ in the above sum and add the terms to get

$$\frac{d\mathsf{H}}{dt} = \frac{1}{2}\sum_{i,j} \Gamma_{ij}\big(P_i - P_j\big)\,\big(\ln P_i - \ln P_j\big) \,. \tag{3.12}$$

Note that the $i = j$ term does not contribute to the sum. For $i \neq j$ we have $\Gamma_{ij} = -W_{ij} \leq 0$, and using the result

$$(x - y)\,(\ln x - \ln y) \geq 0 \; , \tag{3.13}$$

we conclude

$$\frac{d\mathsf{H}}{dt} \leq 0 \; . \tag{3.14}$$

In equilibrium, $P_i^{\text{eq}}$ is a constant, independent of $i$. We write

$$P_i^{\text{eq}} = \frac{1}{\Omega} \quad , \quad \Omega = \sum_i 1 \quad \Longrightarrow \quad \mathsf{H} = -\ln \Omega \; . \tag{3.15}$$

If $\Gamma_{ij} \neq \Gamma_{ji}$, we can still prove a version of the H-theorem. Define a new symmetric matrix

$$\overline{W}_{ij} \equiv W_{ij}\, P_j^{\text{eq}} = W_{ji}\, P_i^{\text{eq}} = \overline{W}_{ji} \; , \tag{3.16}$$

and the generalized H-function,

$$\mathsf{H}(t) \equiv \sum_i P_i(t)\, \ln\!\left(\frac{P_i(t)}{P_i^{\text{eq}}}\right) . \tag{3.17}$$

Then

$$\frac{d\mathsf{H}}{dt} = -\frac{1}{2} \sum_{i,j} \overline{W}_{ij} \left(\frac{P_i}{P_i^{\text{eq}}} - \frac{P_j}{P_j^{\text{eq}}}\right) \left[\ln\!\left(\frac{P_i}{P_i^{\text{eq}}}\right) - \ln\!\left(\frac{P_j}{P_j^{\text{eq}}}\right)\right] \leq 0 \; . \tag{3.18}$$

## 3.3 Phase Flows in Classical Mechanics

### 3.3.1 Hamiltonian evolution

The master equation provides us with a semi-phenomenological description of a dynamical system's relaxation to equilibrium. It explicitly breaks time reversal symmetry. Yet the microscopic laws of Nature are (approximately) time-reversal symmetric. How can a system which obeys Hamilton's equations of motion come to equilibrium?

Let's start our investigation by reviewing the basics of Hamiltonian dynamics. Recall the Lagrangian $L = L(q, \dot{q}, t) = T - V$. The Euler-Lagrange equations of motion for the action $S\big[q(t)\big] = \int\! dt\, L$ are

$$\dot{p}_\sigma = \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_\sigma}\right) = \frac{\partial L}{\partial q_\sigma} \; , \tag{3.19}$$

where $p_\sigma$ is the canonical momentum conjugate to the generalized coordinate $q_\sigma$:

$$p_\sigma = \frac{\partial L}{\partial \dot{q}_\sigma} \; . \tag{3.20}$$

The Hamiltonian, $H(q, p)$ is obtained by a Legendre transformation,

$$H(q, p) = \sum_{\sigma=1}^{r} p_\sigma\, \dot{q}_\sigma - L \; . \tag{3.21}$$

Note that

$$\begin{aligned} dH &= \sum_{\sigma=1}^{r} \left( p_\sigma \, d\dot{q}_\sigma + \dot{q}_\sigma \, dp_\sigma - \frac{\partial L}{\partial q_\sigma} \, dq_\sigma - \frac{\partial L}{\partial \dot{q}_\sigma} \, d\dot{q}_\sigma \right) - \frac{\partial L}{\partial t} \, dt \\ &= \sum_{\sigma=1}^{r} \left( \dot{q}_\sigma \, dp_\sigma - \frac{\partial L}{\partial q_\sigma} \, dq_\sigma \right) - \frac{\partial L}{\partial t} \, dt \ . \end{aligned} \tag{3.22}$$

Thus, we obtain Hamilton's equations of motion,

$$\frac{\partial H}{\partial p_\sigma} = \dot{q}_\sigma \quad , \quad \frac{\partial H}{\partial q_\sigma} = -\frac{\partial L}{\partial q_\sigma} = -\dot{p}_\sigma \tag{3.23}$$

and

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t} \ . \tag{3.24}$$

Define the rank $2r$ vector $\boldsymbol{\varphi}$ by its components,

$$\varphi_i = \begin{cases} q_i & \text{if } 1 \le i \le r \\ & \\ p_{i-r} & \text{if } r \le i \le 2r \ . \end{cases} \tag{3.25}$$

Then we may write Hamilton's equations compactly as

$$\dot{\varphi}_i = J_{ij} \, \frac{\partial H}{\partial \varphi_j} \ , \tag{3.26}$$

where

$$J = \begin{pmatrix} 0_{r\times r} & 1_{r\times r} \\ -1_{r\times r} & 0_{r\times r} \end{pmatrix} \tag{3.27}$$

is a rank $2r$ matrix. Note that $J^{\mathrm{t}} = -J$, *i.e.* $J$ is antisymmetric, and that $J^2 = -1_{2r\times 2r}$.

### 3.3.2 Dynamical systems and the evolution of phase space volumes

Consider a general dynamical system,

$$\frac{d\boldsymbol{\varphi}}{dt} = \boldsymbol{V}(\boldsymbol{\varphi}) \ , \tag{3.28}$$

where $\boldsymbol{\varphi}(t)$ is a point in an $n$-dimensional phase space. Consider now a compact[2] region $\mathcal{R}_0$ in phase space, and consider its evolution under the dynamics. That is, $\mathcal{R}_0$ consists of a set of points $\big\{\boldsymbol{\varphi} \,|\, \boldsymbol{\varphi} \in \mathcal{R}_0\big\}$, and if we regard each $\boldsymbol{\varphi} \in \mathcal{R}_0$ as an initial condition, we can define the time-dependent set $\mathcal{R}(t)$ as the set of points $\boldsymbol{\varphi}(t)$ that *were* in $\mathcal{R}_0$ at time $t = 0$:

$$\mathcal{R}(t) = \big\{\boldsymbol{\varphi}(t) \,\big|\, \boldsymbol{\varphi}(0) \in \mathcal{R}_0\big\} \ . \tag{3.29}$$

Now consider the volume $\Omega(t)$ of the set $\mathcal{R}(t)$. We have

$$\Omega(t) = \int\limits_{\mathcal{R}(t)} d\mu \tag{3.30}$$

---

[2] 'Compact' in the parlance of mathematical analysis means 'closed and bounded'.

where

$$d\mu = d\varphi_1\, d\varphi_2 \,\cdots\, d\varphi_n \ , \tag{3.31}$$

for an $n$-dimensional phase space. We then have

$$\Omega(t+dt) = \int\limits_{\mathcal{R}(t+dt)} \!\! d\mu' = \int\limits_{\mathcal{R}(t)} \! d\mu \left| \frac{\partial\varphi_i(t+dt)}{\partial\varphi_j(t)} \right| \ , \tag{3.32}$$

where

$$\left| \frac{\partial\varphi_i(t+dt)}{\partial\varphi_j(t)} \right| \equiv \frac{\partial(\varphi'_1,\ldots,\varphi'_n)}{\partial(\varphi_1,\ldots,\varphi_n)} \tag{3.33}$$

is a determinant, which is the Jacobean of the transformation from the set of coordinates $\big\{\varphi_i = \varphi_i(t)\big\}$ to the coordinates $\big\{\varphi'_i = \varphi_i(t+dt)\big\}$. But according to the dynamics, we have

$$\varphi_i(t+dt) = \varphi_i(t) + V_i\big(\boldsymbol{\varphi}(t)\big)\, dt + \mathcal{O}(dt^2) \tag{3.34}$$

and therefore

$$\frac{\partial\varphi_i(t+dt)}{\partial\varphi_j(t)} = \delta_{ij} + \frac{\partial V_i}{\partial\varphi_j}\, dt + \mathcal{O}(dt^2) \ . \tag{3.35}$$

We now make use of the equality

$$\ln\det M = \mathsf{Tr}\,\ln M \ , \tag{3.36}$$

for any matrix $M$, which gives us[3], for small $\varepsilon$,

$$\det\big(1+\varepsilon A\big) = \exp \mathsf{Tr}\,\ln\big(1+\varepsilon A\big) = 1 + \varepsilon\ \mathsf{Tr}\,A + \tfrac{1}{2}\,\varepsilon^2\Big(\big(\mathsf{Tr}\,A\big)^2 - \mathsf{Tr}\,(A^2)\Big) + \ldots \tag{3.37}$$

Thus,

$$\Omega(t+dt) = \Omega(t) + \int\limits_{\mathcal{R}(t)} \! d\mu\ \boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\ dt + \mathcal{O}(dt^2) \ , \tag{3.38}$$

which says

$$\frac{d\Omega}{dt} = \int\limits_{\mathcal{R}(t)} \! d\mu\ \boldsymbol{\nabla}\!\cdot\!\boldsymbol{V} = \int\limits_{\partial\mathcal{R}(t)} \! dS\ \hat{\boldsymbol{n}}\cdot\boldsymbol{V} \tag{3.39}$$

Here, the divergence is the *phase space divergence*,

$$\boldsymbol{\nabla}\!\cdot\!\boldsymbol{V} = \sum_{i=1}^{n} \frac{\partial V_i}{\partial\varphi_i} \ , \tag{3.40}$$

and we have used the divergence theorem to convert the volume integral of the divergence to a surface integral of $\hat{\boldsymbol{n}}\cdot\boldsymbol{V}$, where $\hat{\boldsymbol{n}}$ is the surface normal and $dS$ is the differential element of surface area, and $\partial\mathcal{R}$ denotes the boundary of the region $\mathcal{R}$. We see that if $\boldsymbol{\nabla}\!\cdot\!\boldsymbol{V} = 0$ everywhere in phase space, then $\Omega(t)$ is a constant, and phase space volumes are *preserved* by the evolution of the system.

For an alternative derivation, consider a function $\varrho(\boldsymbol{\varphi},t)$ which is defined to be the *density* of some collection of points in phase space at phase space position $\boldsymbol{\varphi}$ and time $t$. This must satisfy the continuity equation,

$$\frac{\partial\varrho}{\partial t} + \boldsymbol{\nabla}\!\cdot\!(\varrho\boldsymbol{V}) = 0 \ . \tag{3.41}$$

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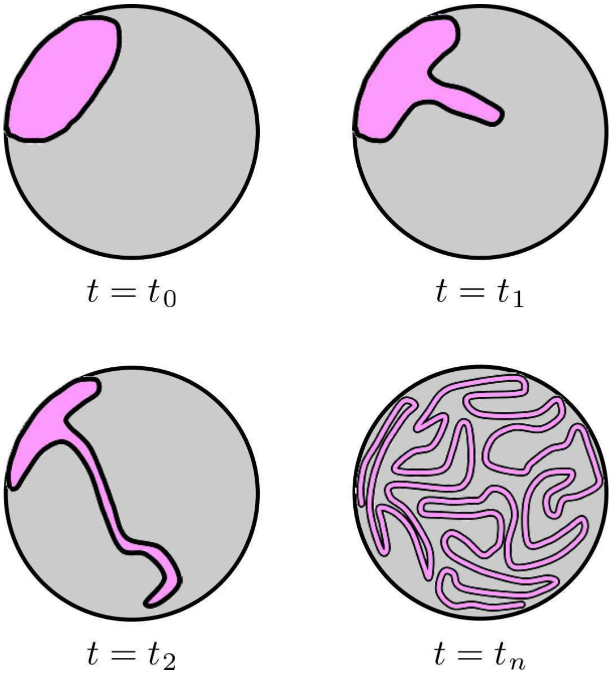
[3] The equality $\ln\det M = \mathsf{Tr}\,\ln M$ is most easily proven by bringing the matrix to diagonal form via a similarity transformation, and proving the equality for diagonal matrices.



$t = t_0$ $t = t_1$

$t = t_2$ $t = t_n$

Figure 3.1: Time evolution of two immiscible fluids. The local density remains constant.

This is called the *continuity equation*. It says that 'nobody gets lost'. If we integrate it over a region of phase space $\mathcal{R}$, we have

$$\frac{d}{dt}\int\limits_{\mathcal{R}} d\mu\,\varrho = -\int\limits_{\mathcal{R}} d\mu\,\boldsymbol{\nabla}\cdot(\varrho\boldsymbol{V}) = -\int\limits_{\partial\mathcal{R}} dS\,\hat{\boldsymbol{n}}\cdot(\varrho\boldsymbol{V})\ . \tag{3.42}$$

It is perhaps helpful to think of $\varrho$ as a charge density, in which case $\boldsymbol{J} = \varrho\boldsymbol{V}$ is the current density. The above equation then says

$$\frac{dQ_{\mathcal{R}}}{dt} = -\int\limits_{\partial\mathcal{R}} dS\,\hat{\boldsymbol{n}}\cdot\boldsymbol{J}\ , \tag{3.43}$$

where $Q_{\mathcal{R}}$ is the total charge contained inside the region $\mathcal{R}$. In other words, the rate of increase or decrease of the charge within the region $\mathcal{R}$ is equal to the total integrated current flowing in or out of $\mathcal{R}$ at its boundary.

The Leibniz rule lets us write the continuity equation as

$$\frac{\partial\varrho}{\partial t} + \boldsymbol{V}\cdot\boldsymbol{\nabla}\varrho + \varrho\,\boldsymbol{\nabla}\cdot\boldsymbol{V} = 0\ . \tag{3.44}$$

But now suppose that the phase flow is divergenceless, *i.e.* $\boldsymbol{\nabla}\cdot\boldsymbol{V} = 0$. Then we have

$$\frac{D\varrho}{Dt} \equiv \bigg(\frac{\partial}{\partial t} + \boldsymbol{V}\cdot\boldsymbol{\nabla}\bigg)\varrho = 0\ . \tag{3.45}$$

The combination inside the brackets above is known as the *convective derivative*. It tells us the total rate of change of $\varrho$ for an observer *moving with the phase flow*. That is

$$\begin{aligned}\frac{d}{dt}\,\varrho\big(\boldsymbol{\varphi}(t),t\big) &= \frac{\partial\varrho}{\partial\varphi_i}\,\frac{d\varphi_i}{dt} + \frac{\partial\varrho}{\partial t} \\ &= \sum_{i=1}^{n} V_i\,\frac{\partial\rho}{\partial\varphi_i} + \frac{\partial\varrho}{\partial t} = \frac{D\varrho}{Dt}\ .\end{aligned} \tag{3.46}$$

If $D\varrho/Dt = 0$, the local density remains the same during the evolution of the system. If we consider the 'characteristic function'

$$\varrho(\boldsymbol{\varphi}, t=0) = \begin{cases} 1 & \text{if } \boldsymbol{\varphi} \in \mathcal{R}_0 \\ 0 & \text{otherwise} \end{cases} \tag{3.47}$$

then the vanishing of the convective derivative means that the image of the set $\mathcal{R}_0$ under time evolution will always have the same volume.

Hamiltonian evolution in classical mechanics is volume preserving. The equations of motion are

$$\dot{q}_i = +\frac{\partial H}{\partial p_i} \qquad , \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \tag{3.48}$$

A point in phase space is specified by $r$ positions $q_i$ and $r$ momenta $p_i$, hence the dimension of phase space is $n = 2r$:

$$\boldsymbol{\varphi} = \begin{pmatrix} \boldsymbol{q} \\ \boldsymbol{p} \end{pmatrix} \qquad , \qquad \boldsymbol{V} = \begin{pmatrix} \dot{\boldsymbol{q}} \\ \dot{\boldsymbol{p}} \end{pmatrix} = \begin{pmatrix} \partial H/\partial \boldsymbol{p} \\ -\partial H/\partial \boldsymbol{q} \end{pmatrix} . \tag{3.49}$$

Hamilton's equations of motion guarantee that the phase space flow is divergenceless:

$$\begin{aligned} \nabla\!\cdot\!\boldsymbol{V} &= \sum_{i=1}^{r} \left\{ \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right\} \\ &= \sum_{i=1}^{r} \left\{ \frac{\partial}{\partial q_i}\left(\frac{\partial H}{\partial p_i}\right) + \frac{\partial}{\partial p_i}\left(-\frac{\partial H}{\partial q_i}\right) \right\} = 0 \, . \end{aligned} \tag{3.50}$$

Thus, we have that the convective derivative vanishes, *viz.*

$$\frac{D\varrho}{Dt} \equiv \frac{\partial \varrho}{\partial t} + \boldsymbol{V}\!\cdot\!\nabla\varrho = 0 \, , \tag{3.51}$$

for any distribution $\varrho(\boldsymbol{\varphi}, t)$ on phase space. Thus, the value of the density $\varrho(\boldsymbol{\varphi}(t), t)$ is constant, which tells us that the phase flow is *incompressible*. In particular, phase space volumes are preserved.

### 3.3.3 Liouville's equation and the microcanonical distribution

Let $\varrho(\boldsymbol{\varphi}) = \varrho(\boldsymbol{q}, \boldsymbol{p})$ be a distribution on phase space. Assuming the evolution is Hamiltonian, we can write

$$\frac{\partial \varrho}{\partial t} = -\dot{\boldsymbol{\varphi}} \cdot \boldsymbol{\nabla}\varrho = -\sum_{k=1}^{r} \left( \dot{q}_k \frac{\partial}{\partial q_k} + \dot{p}_k \frac{\partial}{\partial p_k} \right) \varrho = -i\hat{L}\varrho \, , \tag{3.52}$$

where $\hat{L}$ is a differential operator known as the *Liouvillian*:

$$\hat{L} = -i \sum_{k=1}^{r} \left\{ \frac{\partial H}{\partial p_k} \frac{\partial}{\partial q_k} - \frac{\partial H}{\partial q_k} \frac{\partial}{\partial p_k} \right\} . \tag{3.53}$$

Eqn. 3.52, known as *Liouville's equation*, bears an obvious resemblance to the Schrödinger equation from quantum mechanics.

Suppose that $\Lambda_a(\varphi)$ is conserved by the dynamics of the system. Typical conserved quantities include the components of the total linear momentum (if there is translational invariance), the components of the total angular momentum (if there is rotational invariance), and the Hamiltonian itself (if the Lagrangian is not explicitly time-dependent). Now consider a distribution $\varrho(\boldsymbol{\varphi},t) = \varrho(\Lambda_1,\Lambda_2,\ldots,\Lambda_k)$ which is a function only of these various conserved quantities. Then from the chain rule, we have

$$\dot{\boldsymbol{\varphi}} \cdot \boldsymbol{\nabla}\varrho = \sum_a \frac{\partial \varrho}{\partial \Lambda_a}\, \dot{\boldsymbol{\varphi}} \cdot \boldsymbol{\nabla}\Lambda_a = 0 \ , \tag{3.54}$$

since for each $a$ we have

$$\frac{d\Lambda_a}{dt} = \sum_{\sigma=1}^{r} \left( \frac{\partial \Lambda_a}{\partial q_\sigma}\, \dot{q}_\sigma + \frac{\partial \Lambda_a}{\partial p_\sigma}\, \dot{p}_\sigma \right) = \dot{\boldsymbol{\varphi}} \cdot \boldsymbol{\nabla}\Lambda_a = 0 \ . \tag{3.55}$$

We conclude that any distribution $\varrho(\boldsymbol{\varphi},t) = \varrho(\Lambda_1,\Lambda_2,\ldots,\Lambda_k)$ which is a function solely of conserved dynamical quantities is a stationary solution to Liouville's equation.

Clearly the microcanonical distribution,

$$\varrho_E(\boldsymbol{\varphi}) = \frac{\delta\big(E - H(\boldsymbol{\varphi})\big)}{D(E)} = \frac{\delta\big(E - H(\boldsymbol{\varphi})\big)}{\int\! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big)} \ , \tag{3.56}$$

is a fixed point solution of Liouville's equation.

## 3.4 Irreversibility and Poincaré Recurrence

The dynamics of the master equation describe an approach to equilibrium. These dynamics are irreversible: $d\mathsf{H}/dt \leq 0$, where $\mathsf{H}$ is Boltzmann's H-function. However, the microscopic laws of physics are (almost) time-reversal invariant[4], so how can we understand the emergence of irreversibility? Furthermore, any dynamics which are deterministic and volume-preserving in a finite phase space exhibits the phenomenon of *Poincaré recurrence*, which guarantees that phase space trajectories are arbitrarily close to periodic if one waits long enough.

### 3.4.1 Poincaré recurrence theorem

The proof of the recurrence theorem is simple. Let $g_\tau$ be the '$\tau$-advance mapping' which evolves points in phase space according to Hamilton's equations. Assume that $g_\tau$ is invertible and volume-preserving, as is the case for Hamiltonian flow. Further assume that phase space volume is finite. Since energy is preserved in the case of time-independent Hamiltonians, we simply ask that the volume of phase space *at fixed total energy* $E$ be finite, *i.e.*

$$\int\! d\mu\, \delta\big(E - H(\boldsymbol{q},\boldsymbol{p})\big) < \infty \ , \tag{3.57}$$

where $d\mu = d\boldsymbol{q}\, d\boldsymbol{p}$ is the phase space uniform integration measure.

**Theorem:** In any finite neighborhood $\mathcal{R}_0$ of phase space there exists a point $\boldsymbol{\varphi}_0$ which will return to $\mathcal{R}_0$ after $m$ applications of $g_\tau$, where $m$ is finite.

**Proof:** Assume the theorem fails; we will show this assumption results in a contradiction. Consider the set $\Upsilon$ formed from the union of all sets $g_\tau^k\, \mathcal{R}$ for all $m$:

$$\Upsilon = \bigcup_{k=0}^{\infty} g_\tau^k\, \mathcal{R}_0 \tag{3.58}$$

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[4] Actually, the microscopic laws of physics are *not* time-reversal invariant, but rather are invariant under the product $PCT$, where $P$ is parity, $C$ is charge conjugation, and $T$ is time reversal.

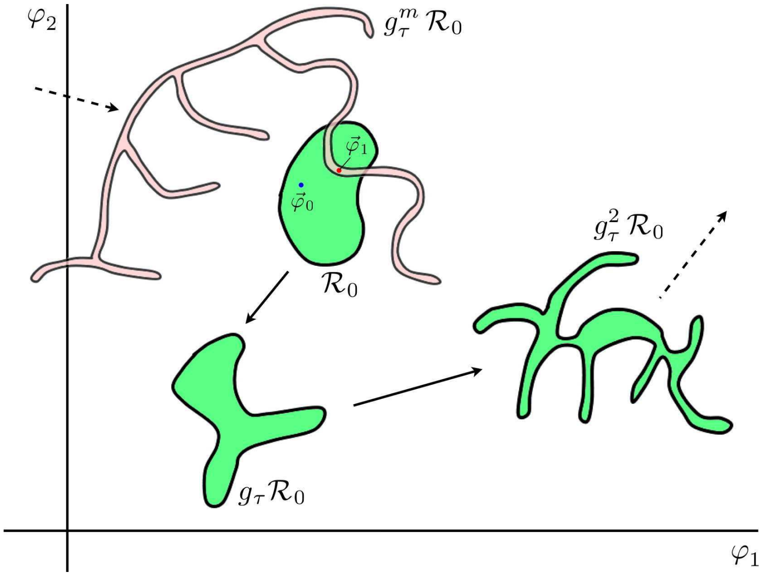

Figure 3.2: Successive images of a set $\mathcal{R}_0$ under the $\tau$-advance mapping $g_\tau$, projected onto a two-dimensional phase plane. The Poincaré recurrence theorem guarantees that if phase space has finite volume, and $g_\tau$ is invertible and volume preserving, then for any set $\mathcal{R}_0$ there exists an integer $m$ such that $\mathcal{R}_0 \cap g_\tau^m\,\mathcal{R}_0 \neq \emptyset$.

We assume that the set $\{g_\tau^k\,\mathcal{R}_0 \,|\, k \in \mathbb{N}\}$ is disjoint[5]. The volume of a union of disjoint sets is the sum of the individual volumes. Thus,

$$\begin{aligned} \mathrm{vol}(\Upsilon) &= \sum_{k=0}^{\infty} \mathrm{vol}\big(g_\tau^k\,\mathcal{R}_0\big) \\ &= \mathrm{vol}(\mathcal{R}_0) \cdot \sum_{k=0}^{\infty} 1 = \infty \ , \end{aligned} \tag{3.59}$$

since $\mathrm{vol}\big(g_\tau^k\,\mathcal{R}_0\big) = \mathrm{vol}\big(\mathcal{R}_0\big)$ from volume preservation. But clearly $\Upsilon$ is a subset of the entire phase space, hence we have a contradiction, because by assumption phase space is of finite volume.

Thus, the assumption that the set $\{g_\tau^k\,\mathcal{R}_0 \,|\, k \in \mathbb{Z}_+\}$ is disjoint fails. This means that there exists some pair of integers $k$ and $l$, with $k \neq l$, such that $g_\tau^k\,\mathcal{R}_0 \cap g_\tau^l\,\mathcal{R}_0 \neq \emptyset$. Without loss of generality we may assume $k < l$. Apply the inverse $g_\tau^{-1}$ to this relation $k$ times to get $g_\tau^{l-k}\,\mathcal{R}_0 \cap \mathcal{R}_0 \neq \emptyset$. Now choose any point $\boldsymbol{\varphi}_1 \in g_\tau^m\,\mathcal{R}_0 \cap \mathcal{R}_0$, where $m = l - k$, and define $\boldsymbol{\varphi}_0 = g_\tau^{-m}\boldsymbol{\varphi}_1$. Then by construction both $\boldsymbol{\varphi}_0$ and $g_\tau^m\,\boldsymbol{\varphi}_0$ lie within $\mathcal{R}_0$ and the theorem is proven.

Poincaré recurrence has remarkable implications. Consider a bottle of perfume which is opened in an otherwise evacuated room, as depicted in fig. 3.3. The perfume molecules evolve according to Hamiltonian evolution. The positions are bounded because physical space is finite. The momenta are bounded because the total energy is conserved, hence no single particle can have a momentum such that $T(\boldsymbol{p}) > E_{\mathrm{TOT}}$, where $T(\boldsymbol{p})$ is the single particle kinetic energy function[6]. Thus, phase space, however large, is still bounded. Hamiltonian evolution, as we have seen, is invertible and volume preserving, therefore the system is recurrent. All the molecules must eventually return to the bottle. What's more, they all must return with momenta arbitrarily close to their initial momenta![7]

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[5] The natural numbers $\mathbb{N}$ is the set of non-negative integers $\{0, 1, 2, \ldots\}$.

[6] In the nonrelativistic limit, $T = p^2/2m$. For relativistic particles, we have $T = (p^2c^2 + m^2c^4)^{1/2} - mc^2$.

[7] Actually, what the recurrence theorem guarantees is that there is a configuration arbitrarily close to the initial one which recurs, to within the same degree of closeness.

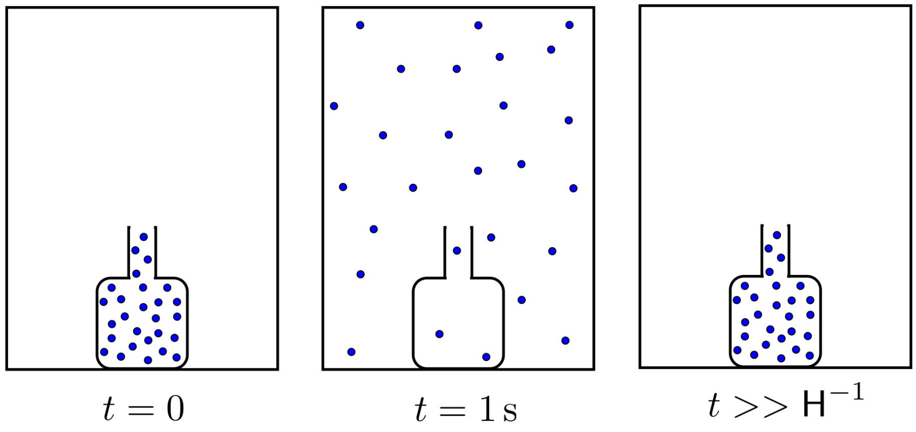

Figure 3.3: Poincaré recurrence guarantees that if we remove the cap from a bottle of perfume in an otherwise evacuated room, all the perfume molecules will eventually return to the bottle! (Here H is the Hubble constant.)

In this case, we could define the region $\mathcal{R}_0$ as

$$\mathcal{R}_0 = \big\{ (q_1, \ldots, q_r, p_1, \ldots, p_r) \,\big|\, |q_i - q_i^0| \le \Delta q \text{ and } |p_j - p_j^0| \le \Delta p \;\forall\, i, j \big\} \ , \tag{3.60}$$

which specifies a hypercube in phase space centered about the point $(\boldsymbol{q}^0, \boldsymbol{p}^0)$.

Each of the three central assumptions – finite phase space, invertibility, and volume preservation – is crucial. If any one of these assumptions does not hold, the proof fails. Obviously if phase space is infinite the flow needn't be recurrent since it can keep moving off in a particular direction. Consider next a volume-preserving map which is not invertible. An example might be a mapping $f : \mathbb{R} \to \mathbb{R}$ which takes any real number to its fractional part. Thus, $f(\pi) = 0.14159265\ldots$. Let us restrict our attention to intervals of width less than unity. Clearly $f$ is then volume preserving. The action of $f$ on the interval $[2, 3)$ is to map it to the interval $[0, 1)$. But $[0, 1)$ remains fixed under the action of $f$, so no point within the interval $[2, 3)$ will ever return under repeated iterations of $f$. Thus, $f$ does not exhibit Poincaré recurrence.

Consider next the case of the damped harmonic oscillator. In this case, phase space volumes contract. For a one-dimensional oscillator obeying $\ddot{x} + 2\beta\dot{x} + \varOmega_0^2\, x = 0$ one has $\nabla\!\cdot\! \boldsymbol{V} = -2\beta < 0$, since $\beta > 0$ for physical damping. Thus the convective derivative is $D_t \varrho = -(\nabla\!\cdot\!\boldsymbol{V})\varrho = 2\beta\varrho$ which says that the density increases exponentially in the comoving frame, as $\varrho(t) = e^{2\beta t}\,\varrho(0)$. Thus, phase space volumes collapse: $\Omega(t) = e^{-2\beta 2}\,\Omega(0)$, and are not preserved by the dynamics. The proof of recurrence therefore fails. In this case, it is possible for the set $\Upsilon$ to be of finite volume, even if it is the union of an infinite number of sets $g_\tau^k\,\mathcal{R}_0$, because the volumes of these component sets themselves decrease exponentially, as $\mathrm{vol}(g_\tau^n\,\mathcal{R}_0) = e^{-2n\beta\tau}\,\mathrm{vol}(\mathcal{R}_0)$. A damped pendulum, released from rest at some small angle $\theta_0$, will not return arbitrarily close to these initial conditions.

### 3.4.2 Kac ring model

The implications of the Poincaré recurrence theorem are surprising – even shocking. If one takes a bottle of perfume in a sealed, evacuated room and opens it, the perfume molecules will diffuse throughout the room. The recurrence theorem guarantees that after some finite time $T$ all the molecules will go back inside the bottle (and arbitrarily close to their initial velocities as well). The hitch is that this could take a very long time, *e.g.* much much longer than the age of the Universe.

On less absurd time scales, we know that most systems come to thermodynamic equilibrium. But how can a system both exhibit equilibration *and* Poincaré recurrence? The two concepts seem utterly incompatible!

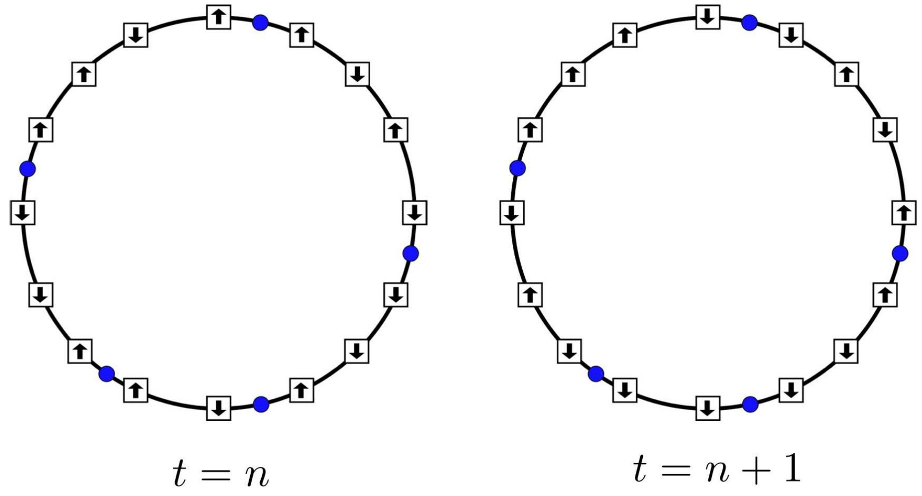

Figure 3.4: Left: A configuration of the Kac ring with $N = 16$ sites and $F = 4$ flippers. The flippers, which live on the links, are represented by blue dots. Right: The ring system after one time step. Evolution proceeds by clockwise rotation. Spins passing through flippers are flipped.

A beautifully simple model due to Kac shows how a recurrent system can exhibit the phenomenon of equilibration. Consider a ring with $N$ sites. On each site, place a 'spin' which can be in one of two states: up or down. Along the $N$ links of the system, $F$ of them contain 'flippers'. The configuration of the flippers is set at the outset and never changes. The dynamics of the system are as follows: during each time step, every spin moves clockwise a distance of one lattice spacing. Spins which pass through flippers reverse their orientation: up becomes down, and down becomes up.

The 'phase space' for this system consists of $2^N$ discrete configurations. Since each configuration maps onto a unique image under the evolution of the system, phase space 'volume' is preserved. The evolution is invertible; the inverse is obtained simply by rotating the spins counterclockwise. Figure 3.4 depicts an example configuration for the system, and its first iteration under the dynamics.

Suppose the flippers were not fixed, but moved about randomly. In this case, we could focus on a single spin and determine its configuration probabilistically. Let $p_n$ be the probability that a given spin is in the up configuration at time $n$. The probability that it is up at time $(n+1)$ is then

$$p_{n+1} = (1-x)\, p_n + x\,(1-p_n)\ , \tag{3.61}$$

where $x = F/N$ is the fraction of flippers in the system. In words: a spin will be up at time $(n+1)$ if it was up at time $n$ and did not pass through a flipper, or if it was down at time $n$ and did pass through a flipper. If the flipper locations are randomized at each time step, then the probability of flipping is simply $x = F/N$. Equation 3.61 can be solved immediately:

$$p_n = \tfrac{1}{2} + (1-2x)^n\,(p_0 - \tfrac{1}{2})\ , \tag{3.62}$$

which decays exponentially to the equilibrium value of $p_{\text{eq}} = \frac{1}{2}$ with time scale

$$\tau(x) = -\frac{1}{\ln|1-2x|}\ . \tag{3.63}$$

We identify $\tau(x)$ as the microscopic relaxation time over which local equilibrium is established. If we define the magnetization $m \equiv (N_\uparrow - N_\downarrow)/N$, then $m = 2p - 1$, so $m_n = (1-2x)^n\, m_0$. The equilibrium magnetization is $m_{\text{eq}} = 0$. Note that for $\frac{1}{2} < x < 1$ that the magnetization reverses sign each time step, as well as decreasing exponentially in magnitude.

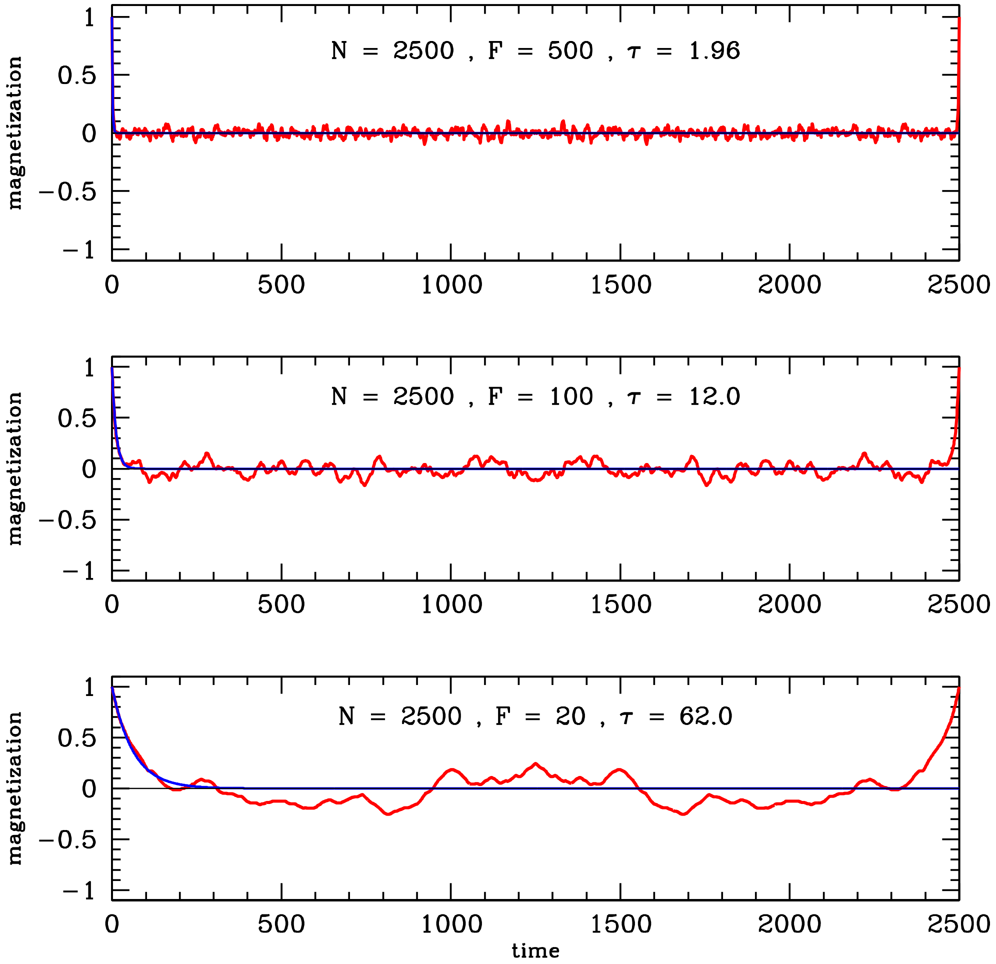

Figure 3.5: Three simulations of the Kac ring model with $N = 2500$ sites and three different concentrations of flippers. The red line shows the magnetization as a function of time, starting from an initial configuration in which 100% of the spins are up. The blue line shows the prediction of the *Stosszahlansatz*, which yields an exponentially decaying magnetization with time constant $\tau$.

The assumption that leads to equation 3.61 is called the *Stosszahlansatz*[8], a long German word meaning, approximately, 'assumption on the counting of hits'. The resulting dynamics are irreversible: the magnetization inexorably decays to zero. However, the Kac ring model is purely deterministic, and the *Stosszahlansatz* can at best be an approximation to the true dynamics. Clearly the *Stosszahlansatz* fails to account for correlations such as the following: if spin $i$ is flipped at time $n$, then spin $i + 1$ will have been flipped at time $n - 1$. Also if spin $i$ is flipped at time $n$, then it also will be flipped at time $n + N$. Indeed, since the dynamics of the Kac ring model are invertible and volume preserving, it must exhibit Poincaré recurrence. We see this most vividly in figs. 3.5 and 3.6.

The model is trivial to simulate. The results of such a simulation are shown in figure 3.5 for a ring of $N = 1000$ sites, with $F = 100$ and $F = 24$ flippers. Note how the magnetization decays and fluctuates about the equilibrium value $m_{\text{eq}} = 0$, but that after $N$ iterations $m$ recovers its initial value: $m_N = m_0$. The recurrence time for this system is simply $N$ if $F$ is even, and $2N$ if $F$ is odd, since every spin will then have flipped an even number of

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[8] Unfortunately, many important physicists were German and we have to put up with a legacy of long German words like *Gedankenexperiment*, *Zitterbewegung*, *Brehmsstrahlung*, *Stosszahlansatz*, *Kartoffelsalat*, *etc.*

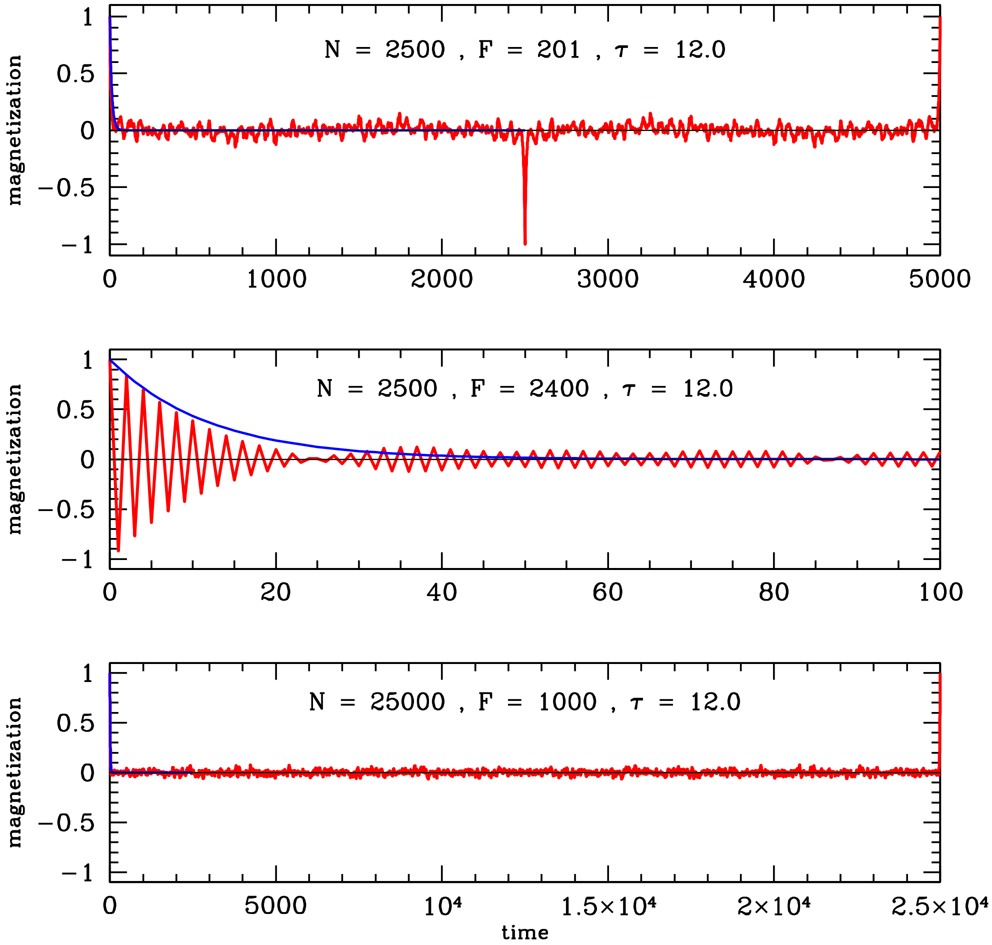

Figure 3.6: Simulations of the Kac ring model. Top: $N = 2500$ sites with $F = 201$ flippers. After $2500$ iterations, each spin has flipped an odd number of times, so the recurrence time is $2N$. Middle: $N = 2500$ with $F = 2400$, resulting in a near-complete reversal of the population with every iteration. Bottom: $N = 25000$ with $N = 1000$, showing long time equilibration and dramatic resurgence of the spin population.

times.

In figure 3.6 we plot two other simulations. The top panel shows what happens when $x > \frac{1}{2}$, so that the magnetization wants to reverse its sign with every iteration. The bottom panel shows a simulation for a larger ring, with $N = 25000$ sites. Note that the fluctuations in $m$ about equilibrium are smaller than in the cases with $N = 1000$ sites. Why?

## 3.5 Remarks on Ergodic Theory

### 3.5.1 Definition of ergodicity

A mechanical system evolves according to Hamilton's equations of motion. We have seen how such a system is *recurrent* in the sense of Poincaré.

There is a level beyond recurrence called *ergodicity*. In an ergodic system, time averages over intervals $[0,T]$ with $T \to \infty$ may be replaced by phase space averages. The time average of a function $f(\boldsymbol{\varphi})$ is defined as

$$\big\langle f(\boldsymbol{\varphi})\big\rangle_T = \lim_{T\to\infty} \frac{1}{T}\int\limits_0^T \! dt\, f\big(\boldsymbol{\varphi}(t)\big) \ . \tag{3.64}$$

For a Hamiltonian system, the *phase space average* of the same function is defined by

$$\big\langle f(\boldsymbol{\varphi})\big\rangle_S = \int\! d\mu\, f(\boldsymbol{\varphi})\, \delta\big(E - H(\boldsymbol{\varphi})\big) \bigg/ \int\! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big) \ , \tag{3.65}$$

where $H(\boldsymbol{\varphi}) = H(\boldsymbol{q},\boldsymbol{p})$ is the Hamiltonian, and where $\delta(x)$ is the Dirac $\delta$-function. Thus,

$$\text{ergodicity} \quad \Longleftrightarrow \quad \big\langle f(\boldsymbol{\varphi})\big\rangle_T = \big\langle f(\boldsymbol{\varphi})\big\rangle_S \ , \tag{3.66}$$

for all smooth functions $f(\boldsymbol{\varphi})$ for which $\big\langle f(\boldsymbol{\varphi})\big\rangle_S$ exists and is finite. Note that we do not average over *all* of phase space. Rather, we average only over a hypersurface along which $H(\boldsymbol{\varphi}) = E$ is fixed, *i.e.* over one of the *level sets* of the Hamiltonian function. This is because the dynamics *preserves the energy*. Ergodicity means that almost all points $\boldsymbol{\varphi}$ will, upon Hamiltonian evolution, move in such a way as to eventually pass through every finite neighborhood on the energy surface, and will spend equal time in equal regions of phase space.

Let $\chi_{\mathcal{R}}(\boldsymbol{\varphi})$ be the characteristic function of a region $\mathcal{R}$:

$$\chi_{\mathcal{R}}(\boldsymbol{\varphi}) = \begin{cases} 1 & \text{if } \boldsymbol{\varphi} \in \mathcal{R} \\ 0 & \text{otherwise,} \end{cases} \tag{3.67}$$

where $H(\boldsymbol{\varphi}) = E$ for all $\boldsymbol{\varphi} \in \mathcal{R}$. Then

$$\big\langle \chi_{\mathcal{R}}(\boldsymbol{\varphi})\big\rangle_T = \lim_{T\to\infty} \left(\frac{\text{time spent in } \mathcal{R}}{T}\right) . \tag{3.68}$$

If the system is ergodic, then

$$\big\langle \chi_{\mathcal{R}}(\boldsymbol{\varphi})\big\rangle_T = P(\mathcal{R}) = \frac{D_{\mathcal{R}}(E)}{D(E)} \ , \tag{3.69}$$

where $P(\mathcal{R})$ is the *a priori* probability to find $\boldsymbol{\varphi} \in \mathcal{R}$, based solely on the relative volumes of $\mathcal{R}$ and of the entire phase space. The latter is given by

$$D(E) = \int\! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big) \ , \tag{3.70}$$

called the *density of states*, is the surface area of phase space at energy $E$, and

$$D_{\mathcal{R}}(E) = \int\limits_{\mathcal{R}}\! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big) \ . \tag{3.71}$$

is the density of states for the phase space subset $\mathcal{R}$. Note that

$$D(E) \equiv \int\! d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big) = \int\limits_{\mathcal{S}_E} \frac{dS}{|\boldsymbol{\nabla} H|} \tag{3.72}$$

$$= \frac{d}{dE}\int\! d\mu\, \Theta\big(E - H(\boldsymbol{\varphi})\big) = \frac{d\Omega(E)}{dE} \ . \tag{3.73}$$

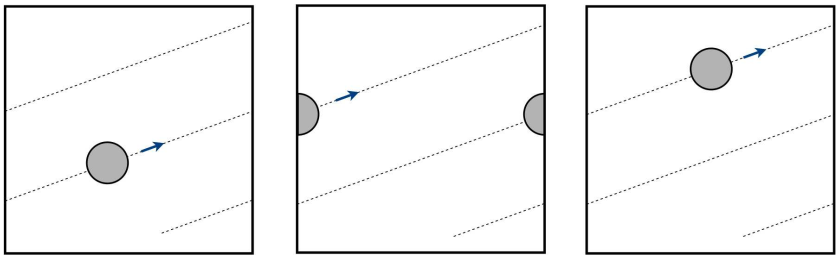

Figure 3.7: Constant phase space velocity at an irrational angle over a toroidal phase space is ergodic, but not mixing. A circle remains a circle, and a blob remains a blob.

Here, $dS$ is the differential surface element, $\mathcal{S}_E$ is the constant $H$ hypersurface $H(\boldsymbol{\varphi}) = E$, and $\Omega(E)$ is the volume of phase space over which $H(\boldsymbol{\varphi}) < E$. Note also that we may write

$$d\mu = dE\, d\Sigma_E \ , \tag{3.74}$$

where

$$d\Sigma_E = \frac{dS}{|\boldsymbol{\nabla} H|}\bigg|_{H(\boldsymbol{\varphi})=E} \tag{3.75}$$

is the the *invariant surface element*.

### 3.5.2 The microcanonical ensemble

The distribution,

$$\varrho_E(\boldsymbol{\varphi}) = \frac{\delta\big(E - H(\boldsymbol{\varphi})\big)}{D(E)} = \frac{\delta\big(E - H(\boldsymbol{\varphi})\big)}{\int d\mu\, \delta\big(E - H(\boldsymbol{\varphi})\big)} \ , \tag{3.76}$$

defines the *microcanonical ensemble* ($\mu$CE) of Gibbs.

We could also write

$$\big\langle f(\boldsymbol{\varphi})\big\rangle_S = \frac{1}{D(E)} \int\limits_{\mathcal{S}_E} d\Sigma_E\, f(\boldsymbol{\varphi}) \ , \tag{3.77}$$

integrating over the hypersurface $\mathcal{S}_E$ rather than the entire phase space.

### 3.5.3 Ergodicity and mixing

Just because a system is ergodic, it doesn't necessarily mean that $\varrho(\varphi, t) \to \varrho^{\mathrm{eq}}(\varphi)$, for consider the following motion on the toroidal space $\big(\boldsymbol{\varphi} = (q, p)\,\big|\, 0 \le q < 1 \ , \ 0 \le p < 1\big\}$, where we identify opposite edges, *i.e.* we impose periodic boundary conditions. We also take $q$ and $p$ to be dimensionless, for simplicity of notation. Let the dynamics be given by

$$\dot{q} = 1 \qquad , \qquad \dot{p} = \alpha \ . \tag{3.78}$$

The solution is

$$q(t) = q_0 + t \qquad , \qquad p(t) = p_0 + \alpha t \ , \tag{3.79}$$

hence the phase curves are given by

$$p = p_0 + \alpha(q - q_0) \ . \tag{3.80}$$

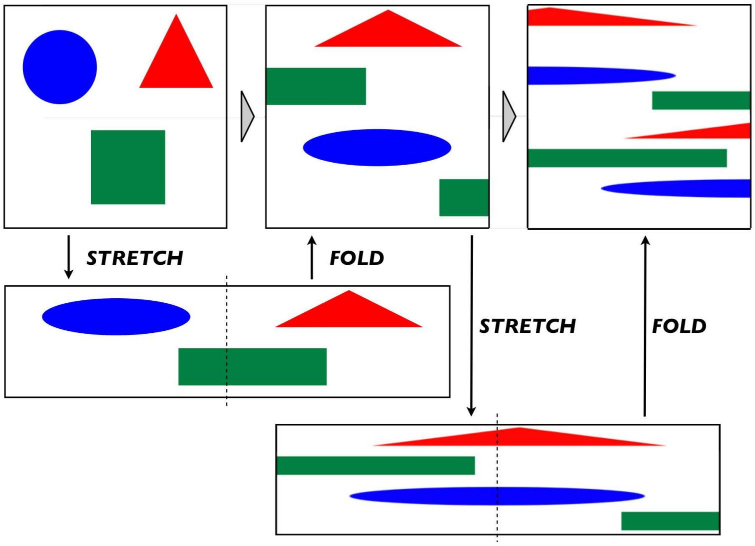

Figure 3.8: The baker's transformation is a successive stretching, cutting, and restacking.

Now consider the average of some function $f(q,p)$. We can write $f(q,p)$ in terms of its Fourier transform,

$$f(q,p) = \sum_{m,n} \hat{f}_{mn}\, e^{2\pi i(mq+np)} \ . \tag{3.81}$$

We have, then,

$$f\big(q(t),p(t)\big) = \sum_{m,n} \hat{f}_{mn}\, e^{2\pi i(mq_0+np_0)}\, e^{2\pi i(m+\alpha n)t} \ . \tag{3.82}$$

We can now perform the time average of $f$:

$$\begin{aligned} \big\langle f(q,p)\big\rangle_T &= \hat{f}_{00} + \lim_{T\to\infty} \frac{1}{T} {\sum_{m,n}}' \hat{f}_{mn}\, e^{2\pi i(mq_0+np_0)}\, \frac{e^{2\pi i(m+\alpha n)T}-1}{2\pi i(m+\alpha n)} \\ &= \hat{f}_{00} \quad \text{if } \alpha \text{ irrational.} \end{aligned} \tag{3.83}$$

Clearly,

$$\big\langle f(q,p)\big\rangle_S = \int\limits_0^1 \!dq \int\limits_0^1 \!dp\, f(q,p) = \hat{f}_{00} = \big\langle f(q,p)\big\rangle_T \ , \tag{3.84}$$

so the system is ergodic.

The situation is depicted in fig. 3.7. If we start with the characteristic function of a disc,

$$\varrho(q,p,t=0) = \Theta\big(a^2 - (q-q_0)^2 - (p-p_0)^2\big) \ , \tag{3.85}$$

then it remains the characteristic function of a disc:

$$\varrho(q,p,t) = \Theta\big(a^2 - (q-q_0-t)^2 - (p-p_0-\alpha t)^2\big) \ , \tag{3.86}$$

A stronger condition one could impose is the following. Let $A$ and $B$ be subsets of $\mathcal{S}_E$. Define the *measure*

$$\nu(A) = \int \! d\Sigma_E\, \chi_A(\varphi) \Big/ \! \int \! d\Sigma_E = \frac{D_A(E)}{D(E)} \ , \tag{3.87}$$

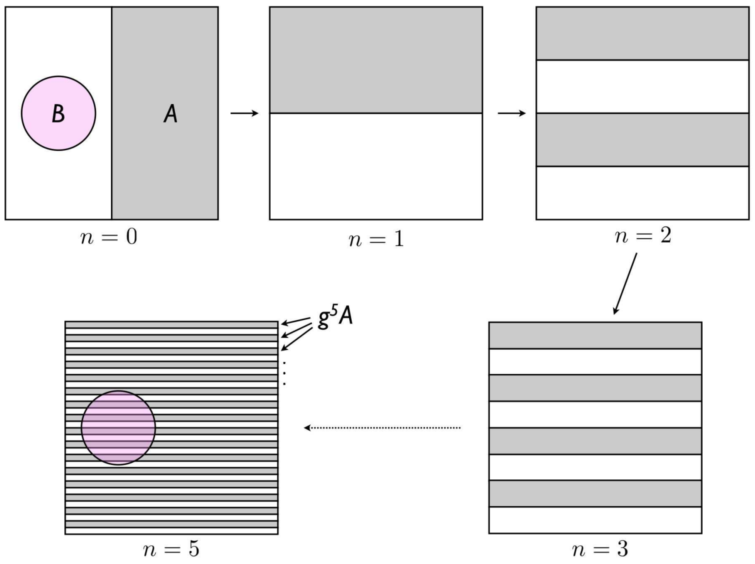

Figure 3.9: The multiply iterated baker's transformation. The set A covers half the phase space and its area is preserved under the map. Initially, the fraction of B covered by A is zero. After many iterations, the fraction of B covered by $g^n$A approaches $\frac{1}{2}$.

where $\chi_A(\boldsymbol{\varphi})$ is the characteristic function of $A$. The measure of a set $A$ is the fraction of the energy surface $\mathcal{S}_E$ covered by $A$. This means $\nu(\mathcal{S}_E)=1$, since $\mathcal{S}_E$ is the entire phase space at energy $E$. Now let $g$ be a volume-preserving map on phase space. Given two measurable sets $A$ and $B$, we say that a system is *mixing* if

$$\text{mixing} \qquad \Longleftrightarrow \qquad \lim_{n\to\infty} \nu\Big(g^n A \cap B\Big) = \nu(A)\,\nu(B)\ . \tag{3.88}$$

In other words, the fraction of $B$ covered by the $n^{\text{th}}$ iterate of $A$, *i.e.* $g^n A$, is, as $n \to \infty$, simply the fraction of $\mathcal{S}_E$ covered by $A$. The iterated map $g^n$ distorts the region $A$ so severely that it eventually spreads out 'evenly' over the entire energy hypersurface. Of course by 'evenly' we mean 'with respect to any finite length scale', because at the very smallest scales, the phase space density is still locally constant as one evolves with the dynamics.

Mixing means that

$$\begin{aligned}\big\langle f(\boldsymbol{\varphi})\big\rangle &= \int\! d\mu\; \varrho(\boldsymbol{\varphi},t)\, f(\boldsymbol{\varphi}) \\ &\xrightarrow[t\to\infty]{} \int\! d\mu\, f(\boldsymbol{\varphi})\,\delta\big(E-H(\boldsymbol{\varphi})\big)\Big/\!\int\! d\mu\,\delta\big(E-H(\boldsymbol{\varphi})\big) \\ &\equiv \mathsf{Tr}\Big[f(\boldsymbol{\varphi})\,\delta\big(E-H(\boldsymbol{\varphi})\big)\Big]\Big/\,\mathsf{Tr}\Big[\delta\big(E-H(\boldsymbol{\varphi})\big)\Big]\ .\end{aligned} \tag{3.89}$$

Physically, we can imagine regions of phase space being successively stretched and folded. During the stretching process, the volume is preserved, so the successive stretch and fold operations map phase space back onto itself.

An example of a mixing system is the *baker's transformation*, depicted in fig. 3.8. The baker map is defined by

$$g(q,p) = \begin{cases} \big(2q\,,\,\frac{1}{2}p\big) & \text{if} \quad 0 \le q < \frac{1}{2} \\ \\ \big(2q-1\,,\,\frac{1}{2}p+\frac{1}{2}\big) & \text{if} \quad \frac{1}{2} \le q < 1\ . \end{cases} \tag{3.90}$$

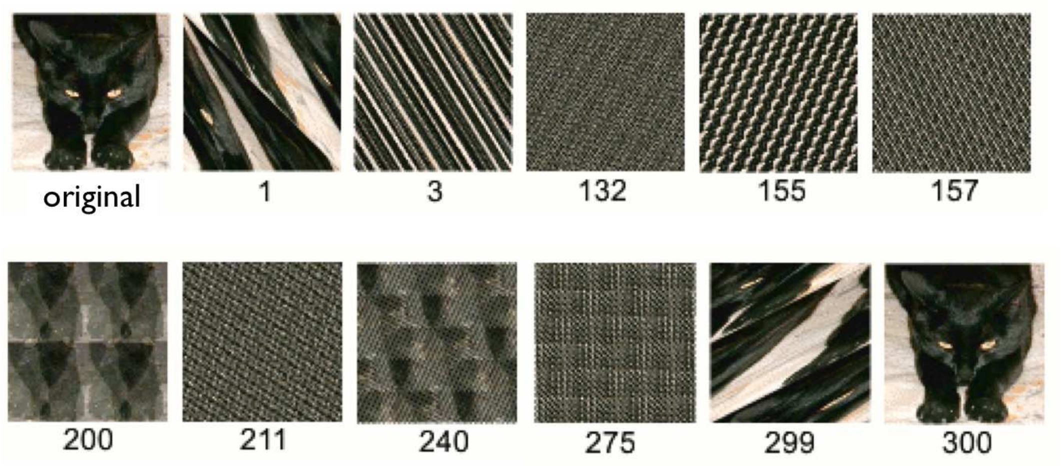

Figure 3.10: The Arnold cat map applied to an image of $150 \times 150$ pixels. After 300 iterations, the image repeats itself. (*Source: Wikipedia*)

Note that $g$ is invertible and volume-preserving. The baker's transformation consists of an initial stretch in which $q$ is expanded by a factor of two and $p$ is contracted by a factor of two, which preserves the total volume. The system is then mapped back onto the original area by cutting and restacking, which we can call a 'fold'. The inverse transformation is accomplished by stretching first in the vertical ($p$) direction and squashing in the horizontal ($q$) direction, followed by a slicing and restacking. Explicitly,

$$g^{-1}(q,p) = \begin{cases} \big(\frac{1}{2}q \,,\, 2p\big) & \text{if} \quad 0 \le p < \frac{1}{2} \\ \\ \big(\frac{1}{2}q + \frac{1}{2} \,,\, 2p - 1\big) & \text{if} \quad \frac{1}{2} \le p < 1 \,. \end{cases} \tag{3.91}$$

Another example of a mixing system is Arnold's 'cat map'[9]

$$g(q,p) = \big(\, [q+p] \,,\, [q+2p] \,\big) \,, \tag{3.92}$$

where $[x]$ denotes the fractional part of $x$. One can write this in matrix form as

$$\begin{pmatrix} q' \\ p' \end{pmatrix} = \overbrace{\begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix}}^{M} \begin{pmatrix} q \\ p \end{pmatrix} \mod \mathbb{Z}^2 \,. \tag{3.93}$$

The matrix $M$ is very special because it has integer entries and its determinant is $\det M = 1$. This means that the inverse also has integer entries. The inverse transformation is then

$$\begin{pmatrix} q \\ p \end{pmatrix} = \overbrace{\begin{pmatrix} 2 & -1 \\ -1 & 1 \end{pmatrix}}^{M^{-1}} \begin{pmatrix} q' \\ p' \end{pmatrix} \mod \mathbb{Z}^2 \,. \tag{3.94}$$

Now for something cool. Suppose that our image consists of a set of discrete points located at $(n_1/k \,,\, n_2/k)$, where the denominator $k \in \mathbb{Z}$ is fixed, and where $n_1$ and $n_2$ range over the set $\{1, \ldots, k\}$. Clearly $g$ and its inverse

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[9] The cat map gets its name from its initial application, by Arnold, to the image of a cat's face.

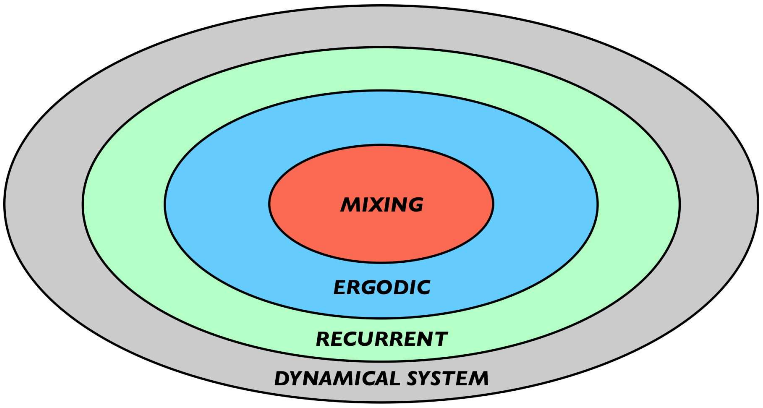

Figure 3.11: The hierarchy of dynamical systems.

preserve this set, since the entries of $M$ and $M^{-1}$ are integers. If there are two possibilities for each pixel (say off and on, or black and white), then there are $2^{(k^2)}$ possible images, and the cat map will map us invertibly from one image to another. Therefore it must exhibit Poincaré recurrence! This phenomenon is demonstrated vividly in fig. 3.10, which shows a $k = 150$ pixel (square) image of a cat subjected to the iterated cat map. The image is stretched and folded with each successive application of the cat map, but after 300 iterations the image is restored! How can this be if the cat map is mixing? The point is that only the discrete set of points $(n_1/k\,,\,n_2/k)$ is periodic. Points with different denominators will exhibit a different periodicity, and points with irrational coordinates will in general never return to their exact initial conditions, although recurrence says they will come arbitrarily close, given enough iterations. The baker's transformation is also different in this respect, since the denominator of the $p$ coordinate is doubled upon each successive iteration.

The student should now contemplate the hierarchy of dynamical systems depicted in fig. 3.11, understanding the characteristic features of each successive refinement[10].

## 3.6 Thermalization of Quantum Systems

### 3.6.1 Quantum dephasing

Thermalization of quantum systems is fundamentally different from that of classical systems. Whereas time evolution in classical mechanics is in general a nonlinear dynamical system, the Schrödinger equation for time evolution in quantum mechanics is linear:

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi\ , \tag{3.95}$$

where $\hat{H}$ is a many-body Hamiltonian. In classical mechanics, the thermal state is constructed by time evolution – this is the content of the ergodic theorem. In quantum mechanics, as we shall see, the thermal distribution must be encoded in the eigenstates themselves.

Let us assume an initial condition at $t = 0$,

$$|\Psi(0)\rangle = \sum_\alpha C_\alpha\,|\Psi_\alpha\rangle\ , \tag{3.96}$$

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[10] There is something beyond mixing, called a $K$-*system*. A $K$-system has positive Kolmogorov-Sinai entropy. For such a system, closed orbits separate exponentially in time, and consequently the Liouvillian $L$ has a Lebesgue spectrum with denumerably infinite multiplicity.

where $\big\{ | \Psi_\alpha \rangle \big\}$ is an orthonormal eigenbasis for $\hat{H}$ satisfying $\hat{H}\,|\Psi_\alpha\rangle = E_\alpha\,|\Psi_\alpha\rangle\dot{}$The expansion coefficients satisfy $C_\alpha = \langle \Psi_\alpha | \Psi(0) \rangle$ and $\sum_\alpha |C_\alpha|^2 = 1$. Normalization requires

$$\langle\, \Psi(0) \,|\, \Psi(0) \,\rangle = \sum_\alpha |C_\alpha|^2 = 1 \ . \tag{3.97}$$

The time evolution of $|\Psi\rangle$ is then given by

$$|\Psi(t)\rangle = \sum_\alpha C_\alpha\, e^{-iE_\alpha t/\hbar}\, |\Psi_\alpha\rangle \ . \tag{3.98}$$

The energy is distributed according to the time-independent function

$$P(E) = \langle\, \Psi(t) \,|\, \delta(E - \hat{H}) \,|\, \Psi(t) \,\rangle = \sum_\alpha |C_\alpha|^2\, \delta(E - E_\alpha) \ . \tag{3.99}$$

Thus, the average energy is time-independent and is given by

$$\langle E \rangle = \langle\, \Psi(t) \,|\, \hat{H} \,|\, \Psi(t) \,\rangle = \int\limits_{-\infty}^{\infty} \! dE\; P(E)\, E = \sum_\alpha |C_\alpha|^2\, E_\alpha \ . \tag{3.100}$$

The root mean square fluctuations of the energy are given by

$$(\Delta E)_{\rm rms} = \Big\langle \big( E - \langle E \rangle \big)^2 \Big\rangle^{1/2} = \sqrt{\sum_\alpha |C_\alpha|^2\, E_\alpha^2 - \Big( \sum_\alpha |C_\alpha|^2\, E_\alpha \Big)^2} \ . \tag{3.101}$$

Typically we assume that the distribution $P(E)$ is narrowly peaked about $\langle E \rangle$, such that $(\Delta E)_{\rm rms} \ll E - E_0$, where $E_0$ is the ground state energy. Note that $P(E) = 0$ for $E < E_0$, *i.e.* the eigenspectrum of $\hat{H}$ is bounded from below.

Now consider a general quantum observable described by an operator $\mathcal{A}$. We have

$$\langle \mathcal{A}(t) \rangle = \langle\, \Psi(t) \,|\, \mathcal{A} \,|\, \Psi(t) \,\rangle = \sum_{\alpha,\beta} C_\alpha^*\, C_\beta\, e^{i(E_\alpha - E_\beta)t/\hbar}\, \mathcal{A}_{\alpha\beta} \ , \tag{3.102}$$

where $\mathcal{A}_{\alpha\beta} = \langle \Psi_\alpha | \mathcal{A} | \Psi_\beta \rangle$. In the limit of large times, we have

$$\langle \mathcal{A} \rangle_T \equiv \lim_{T\to\infty} \frac{1}{T} \int\limits_0^T \! dt\; \langle \mathcal{A}(t) \rangle = \sum_\alpha |C_\alpha|^2\, \mathcal{A}_{\alpha\alpha} \ . \tag{3.103}$$

Note that this implies that all coherence between different eigenstates is lost in the long time limit, due to *dephasing*.

### 3.6.2 Eigenstate thermalization hypothesis

The essential ideas behind the *eigenstate thermalization hypothesis* (ETH) were described independently by J. Deutsch (1991) and by M. Srednicki (1994). The argument goes as follows. If the total energy is the only conserved quantity, and if $\mathcal{A}$ is a local, translationally-invariant, few-body operator, then the time average $\langle \mathcal{A} \rangle$ is given by its microcanonical value,

$$\langle \mathcal{A} \rangle_T = \sum_\alpha |C_\alpha|^2\, \mathcal{A}_{\alpha\alpha} = \frac{\sum_\alpha \mathcal{A}_{\alpha\alpha}\, \Theta(E_\alpha \in I)}{\sum_\alpha \Theta(E_\alpha \in I)} \equiv \langle \mathcal{A} \rangle_E , \tag{3.104}$$

where $I = \big[E, E + \Delta E\big]$ is an energy interval of width $\Delta E$. So once again, time averages are micro canonical averages.

But how is it that this is the case? The hypothesis of Deutsch and of Srednicki is that thermalization in isolated and bounded quantum systems occurs *at the level of individual eigenstates*. That is, for all eigenstates $|\Psi_\alpha\rangle$ with $E_\alpha \in I$, one has

$$\mathcal{A}_{\alpha\alpha} = \langle \mathcal{A} \rangle_{E_\alpha} \ . \tag{3.105}$$

This means that *thermal information is encoded in each eigenstate*. This is called the *eigenstate thermalization hypothesis* (ETH).

An equivalent version of the ETH is the following scenario. Suppose we have an infinite or extremely large quantum system $U$ (the 'universe') fixed in an eigenstate $|\Psi_\alpha\rangle$. Then form the projection operator $P_\alpha = |\Psi_\alpha\rangle\langle\Psi_\alpha|$. Projection operators satisfy $P^2 = P$ and their eigenspectrum consists of one eigenvalue 1 and the rest of the eigenvalues are zero[11]. Now consider a partition of $U = W \cup S$, where $W \gg S$. We imagine $S$ to be the 'system' and $W$ the 'world'. We can always decompose the state $|\Psi_\alpha\rangle$ in a complete product basis for $W$ and $S$, *viz.*

$$|\Psi_\alpha\rangle = \sum_{p=1}^{N_W} \sum_{j=1}^{N_S} \mathcal{Q}^\alpha_{pj} \, |\psi^W_p\rangle \otimes |\psi^S_j\rangle \ . \tag{3.106}$$

Here $N_{W/S}$ is the size of the basis for $W/S$. The *reduced density matrix* for $S$ is defined as

$$\rho_S = \mathop{\mathsf{Tr}}_W P_\alpha = \sum_{j,j'=1}^{N_S} \Bigg( \sum_{p=1}^{N_W} \mathcal{Q}^\alpha_{pj} \, \mathcal{Q}^{\alpha *}_{pj'} \Bigg) \, |\psi^S_j\rangle\langle\psi^S_{j'}| \ . \tag{3.107}$$

The claim is that $\rho_S$ is a *thermal density matrix* on $S$, *i.e.*

$$\rho_S = \frac{1}{Z_S} \, e^{-\beta \hat{H}_S} \ , \tag{3.108}$$

where $\hat{H}_S$ is the Hamiltonian restricted to $S$, and $Z_S = \mathsf{Tr}\, e^{-\beta \hat{H}_S}$, so that $\mathsf{Tr}\, \rho_S = 1$ and $\rho_S$ is properly normalized. Here $\beta = 1/k_{\rm B}T$ with $T$ the temperature. The temperature is fixed by the requirement that $\mathsf{Tr}\,(\rho_S \, \hat{H}_S) = E_\alpha \cdot (V_S/V_U)$, where the last factor is a ratio of volumes.

### 3.6.3 When is the ETH true?

There is no rigorous proof of the ETH. Deutsch showed that the ETH holds for the case of an integrable Hamiltonian weakly perturbed by a single Gaussian random matrix. Horoi *et al.* (1995) showed that nuclear shell model wavefunctions reproduce thermodynamic predictions. Recent numerical work by M. Rigol and collaborators has verified the applicability of the ETH in small interacting boson systems. ETH fails for so-called integrable models, where there are a large number of conserved quantities, which commute with the Hamiltonian. Integrable models are, however, quite special, and as Deutsch showed, integrability is spoiled by weak perturbations, in which case ETH then applies.

Note again that in contrast to the classical case, time evolution of a quantum state does not create the thermal state. Rather, it *reveals* the thermal distribution which is encoded in all eigenstates after sufficient time for dephasing to occur, so that correlations between all the wavefunction expansion coefficients $\{C_\alpha\}$ for $\alpha \neq \alpha'$ are all lost.

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[11] More generally, we could project onto a $K$-dimensional subspace, in which case there would be $K$ eigenvalues of $+1$ and $N - K$ eigenvalues of 0, where $N$ is the dimension of the entire vector space.

## 3.7 Appendix I : Formal Solution of the Master Equation

Recall the master equation $\dot{P}_i = -\Gamma_{ij}\, P_j$. The matrix $\Gamma_{ij}$ is real but not necessarily symmetric. For such a matrix, the left eigenvectors $\phi^\alpha_i$ and the right eigenvectors $\psi^\beta_j$ are not the same: general different:

$$\begin{aligned} \phi^\alpha_i\, \Gamma_{ij} &= \lambda_\alpha\, \phi^\alpha_j \\ \Gamma_{ij}\, \psi^\beta_j &= \lambda_\beta\, \psi^\beta_i \ . \end{aligned} \tag{3.109}$$

Note that the eigenvalue equation for the right eigenvectors is $\Gamma\psi = \lambda\psi$ while that for the left eigenvectors is $\Gamma^{\rm t}\phi = \lambda\phi$. The characteristic polynomial is the same in both cases:

$$F(\lambda) \equiv \det\,(\lambda - \Gamma) = \det\,(\lambda - \Gamma^{\rm t})\ , \tag{3.110}$$

which means that the left and right eigenvalues are the same. Note also that $\big[F(\lambda)\big]^* = F(\lambda^*)$, hence the eigenvalues are either real or appear in complex conjugate pairs. Multiplying the eigenvector equation for $\phi^\alpha$ on the right by $\psi^\beta_j$ and summing over $j$, and multiplying the eigenvector equation for $\psi^\beta$ on the left by $\phi^\alpha_i$ and summing over $i$, and subtracting the two results yields

$$\big(\lambda_\alpha - \lambda_\beta\big)\, \big\langle\, \phi^\alpha \,\big|\, \psi^\beta \,\big\rangle = 0\ , \tag{3.111}$$

where the inner product is

$$\big\langle\, \phi \,\big|\, \psi \,\big\rangle = \sum_i \phi_i\, \psi_i\ . \tag{3.112}$$

We can now demand

$$\big\langle\, \phi^\alpha \,\big|\, \psi^\beta \,\big\rangle = \delta_{\alpha\beta}\ , \tag{3.113}$$

in which case we can write

$$\Gamma = \sum_\alpha \lambda_\alpha\, \big|\, \psi^\alpha \,\big\rangle \big\langle\, \phi^\alpha \,\big| \qquad \Longleftrightarrow \qquad \Gamma_{ij} = \sum_\alpha \lambda_\alpha\, \psi^\alpha_i\, \phi^\alpha_j\ . \tag{3.114}$$

We have seen that $\vec{\phi} = (1, 1, \ldots, 1)$ is a left eigenvector with eigenvalue $\lambda = 0$, since $\sum_i \Gamma_{ij} = 0$. We do not know *a priori* the corresponding right eigenvector, which depends on other details of $\Gamma_{ij}$. Now let's expand $P_i(t)$ in the right eigenvectors of $\Gamma$, writing

$$P_i(t) = \sum_\alpha C_\alpha(t)\, \psi^\alpha_i\ . \tag{3.115}$$

Then

$$\begin{aligned} \frac{dP_i}{dt} &= \sum_\alpha \frac{dC_\alpha}{dt}\, \psi^\alpha_i \\ &= -\Gamma_{ij}\, P_j = -\sum_\alpha C_\alpha\, \Gamma_{ij}\, \psi^\alpha_j \\ &= -\sum_\alpha \lambda_\alpha\, C_\alpha\, \psi^\alpha_i\ . \end{aligned} \tag{3.116}$$

This allows us to write

$$\frac{dC_\alpha}{dt} = -\lambda_\alpha\, C_\alpha \qquad \Longrightarrow \qquad C_\alpha(t) = C_\alpha(0)\, e^{-\lambda_\alpha t}\ . \tag{3.117}$$

Hence, we can write

$$P_i(t) = \sum_\alpha C_\alpha(0)\, e^{-\lambda_\alpha t}\, \psi^\alpha_i\ . \tag{3.118}$$

It is now easy to see that $\mathrm{Re}\,(\lambda_\alpha) \geq 0$ for all $\lambda$, or else the probabilities will become negative. For suppose $\mathrm{Re}\,(\lambda_\alpha) < 0$ for some $\alpha$. Then as $t \to \infty$, the sum in eqn. 3.118 will be dominated by the term for which $\lambda_\alpha$ has the largest negative real part; all other contributions will be subleading. But we must have $\sum_i \psi_i^\alpha = 0$ since $\big|\,\psi^\alpha\,\big\rangle$ must be orthogonal to the left eigenvector $\vec{\phi}^{\alpha=0} = (1, 1, \ldots, 1)$. Therefore, at least one component of $\psi_i^\alpha$ (*i.e.* for some value of $i$) must have a negative real part, which means a negative probability![12] As we have already proven that an initial nonnegative distribution $\{P_i(t=0)\}$ will remain nonnegative under the evolution of the master equation, we conclude that $P_i(t) \to P_i^{\mathrm{eq}}$ as $t \to \infty$, relaxing to the $\lambda = 0$ right eigenvector, with $\mathrm{Re}\,(\lambda_\alpha) \geq 0$ for all $\alpha$.

## 3.8 Appendix II : Radioactive Decay

Consider a group of atoms, some of which are in an excited state which can undergo nuclear decay. Let $P_n(t)$ be the probability that $n$ atoms are excited at some time $t$. We then model the decay dynamics by

$$W_{mn} = \begin{cases} 0 & \text{if } m \geq n \\ n\gamma & \text{if } m = n-1 \\ 0 & \text{if } m < n-1\ . \end{cases} \tag{3.119}$$

Here, $\gamma$ is the decay rate of an individual atom, which can be determined from quantum mechanics. The master equation then tells us

$$\frac{dP_n}{dt} = (n+1)\,\gamma\,P_{n+1} - n\,\gamma\,P_n\ . \tag{3.120}$$

The interpretation here is as follows: let $\big|\,n\,\big\rangle$ denote a state in which $n$ atoms are excited. Then $P_n(t) = \big|\langle\,\psi(t)\,|\,n\,\rangle\big|^2$. Then $P_n(t)$ will increase due to spontaneous transitions from $|\,n{+}1\,\rangle$ to $|\,n\,\rangle$, and will decrease due to spontaneous transitions from $|\,n\,\rangle$ to $|\,n{-}1\,\rangle$.

The average number of particles in the system is

$$N(t) = \sum_{n=0}^\infty n\,P_n(t)\ . \tag{3.121}$$

Note that

$$\begin{aligned} \frac{dN}{dt} &= \sum_{n=0}^\infty n\Big[(n+1)\,\gamma\,P_{n+1} - n\,\gamma\,P_n\Big] \\ &= \gamma \sum_{n=0}^\infty \Big[n(n-1)\,P_n - n^2 P_n\Big] \\ &= -\gamma \sum_{n=0}^\infty n\,P_n = -\gamma\,N\ . \end{aligned} \tag{3.122}$$

Thus,

$$N(t) = N(0)\,e^{-\gamma t}\ . \tag{3.123}$$

The relaxation time is $\tau = \gamma^{-1}$, and the equilibrium distribution is

$$P_n^{\mathrm{eq}} = \delta_{n,0}\ . \tag{3.124}$$

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[12] Since the probability $P_i(t)$ is real, if the eigenvalue with the smallest (*i.e.* largest negative) real part is complex, there will be a corresponding complex conjugate eigenvalue, and summing over all eigenvectors will result in a real value for $P_i(t)$.

Note that this satisfies detailed balance.

We can go a bit farther here. Let us define

$$P(z,t) \equiv \sum_{n=0}^{\infty} z^n \, P_n(t) \ . \tag{3.125}$$

This is sometimes called a *generating function*. Then

$$\begin{aligned} \frac{\partial P}{\partial t} &= \gamma \sum_{n=0}^{\infty} z^n \Big[ (n+1)\, P_{n+1} - n\, P_n \Big] \\ &= \gamma \, \frac{\partial P}{\partial z} - \gamma z \, \frac{\partial P}{\partial z} \ . \end{aligned} \tag{3.126}$$

Thus,

$$\frac{1}{\gamma}\,\frac{\partial P}{\partial t} - (1-z)\,\frac{\partial P}{\partial z} = 0 \ . \tag{3.127}$$

We now see that any function $f(\xi)$ satisfies the above equation, where $\xi = \gamma t - \ln(1-z)$. Thus, we can write

$$P(z,t) = f\big(\gamma t - \ln(1-z)\big) \ . \tag{3.128}$$

Setting $t=0$ we have $P(z,0) = f\big(-\ln(1-z)\big)$, and inverting this result we obtain $f(u) = P(1-e^{-u},0)$, *i.e.*

$$P(z,t) = P\big(1 + (z-1)\, e^{-\gamma t} \, , \, 0\big) \ . \tag{3.129}$$

The total probability is $P(z\!=\!1,t) = \sum_{n=0}^{\infty} P_n$, which clearly is conserved: $P(1,t) = P(1,0)$. The average particle number is

$$N(t) = \sum_{n=0}^{\infty} n\, P_n(t) = \frac{\partial P}{\partial z}\bigg|_{z=1} = \ e^{-\gamma t}\, P(1,0) = N(0)\, e^{-\gamma t} \ . \tag{3.130}$$

## 3.9 Appendix III : Canonical Transformations in Hamiltonian Mechanics

The Euler-Lagrange equations of motion of classical mechanics are invariant under a redefinition of generalized coordinates,

$$Q_\sigma = Q_\sigma(q_1, \ldots, q_r, t) \ , \tag{3.131}$$

called a *point transformation*. That is, if we express the new Lagrangian in terms of the new coordinates and their time derivatives, *viz.*

$$\tilde{L}\big(Q, \dot{Q}, t\big) = L\big(q(Q,t) \, , \, \dot{q}(Q, \dot{Q}, t) \, , \, t\big) \ , \tag{3.132}$$

then the equations of motion remain of the form

$$\frac{\partial \tilde{L}}{\partial Q_\sigma} = \frac{d}{dt}\bigg(\frac{\partial \tilde{L}}{\partial \dot{Q}_\sigma}\bigg) \ . \tag{3.133}$$

Hamilton's equations[13],

$$\dot{q}_\sigma = \frac{\partial H}{\partial p_\sigma} \qquad , \qquad \dot{p}_\sigma = -\frac{\partial H}{\partial q_\sigma} \tag{3.134}$$

---

[13] We revert to using $H$ for the Hamiltonian in this section, rather than $\hat{H}$ as before.

are invariant under a much broader class of transformations which mix all the $q's$ and $p's$, called *canonical transformations*. The general form for a canonical transformation is

$$q_\sigma = q_\sigma\big(Q_1\,,\,\ldots\,,\,Q_r\,,\,P_1\,,\,\ldots\,,\,P_r\,,\,t\big) \tag{3.135}$$

$$p_\sigma = p_\sigma\big(Q_1\,,\,\ldots\,,\,Q_r\,,\,P_1\,,\,\ldots\,,\,P_r\,,\,t\big)\ , \tag{3.136}$$

with $\sigma \in \{1,\ldots,r\}$. We may also write

$$\xi_i = \xi_i\big(\Xi_1\,,\,\ldots\,,\,\Xi_{2r}\,,\,t\big)\ , \tag{3.137}$$

with $i \in \{1,\ldots,2r\}$. Here we have

$$\xi_i = \begin{cases} q_i & \text{if } 1 \le i \le r \\ p_{i-r} & \text{if } n \le i \le 2r \end{cases} \quad , \quad \Xi_i = \begin{cases} Q_i & \text{if } 1 \le i \le r \\ P_{i-r} & \text{if } r \le i \le 2r\ . \end{cases} \tag{3.138}$$

The transformed Hamiltonian is $\tilde{H}(Q,P,t)$.

What sorts of transformations are allowed? Well, if Hamilton's equations are to remain invariant, then

$$\dot{Q}_\sigma = \frac{\partial \tilde{H}}{\partial P_\sigma} \quad , \quad \dot{P}_\sigma = -\frac{\partial \tilde{H}}{\partial Q_\sigma}\ , \tag{3.139}$$

which gives

$$\frac{\partial \dot{Q}_\sigma}{\partial Q_\sigma} + \frac{\partial \dot{P}_\sigma}{\partial P_\sigma} = 0 = \frac{\partial \dot{\Xi}_i}{\partial \Xi_i}\ . \tag{3.140}$$

*I.e.* the flow remains incompressible in the new $(Q,P)$ variables. We will also require that phase space volumes are preserved by the transformation, *i.e.*

$$\det\!\left(\frac{\partial \Xi_i}{\partial \xi_j}\right) = \left|\left|\frac{\partial(Q,P)}{\partial(q,p)}\right|\right| = 1\ . \tag{3.141}$$

This last condition guarantees the invariance of the phase space measure

$$d\mu = h^{-r} \prod_{\sigma=1}^{r} dq_\sigma\, dp_\sigma\ , \tag{3.142}$$

where $h$ in the normalization prefactor is Planck's constant.

# Chapter 4

# Statistical Ensembles

## 4.1 References

- F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1987)
  This has been perhaps the most popular undergraduate text since it first appeared in 1967, and with good reason.
- A. H. Carter, *Classical and Statistical Thermodynamics*
  (Benjamin Cummings, 2000)
  A very relaxed treatment appropriate for undergraduate physics majors.
- D. V. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley, 2000)
  This is the best undergraduate thermodynamics book I've come across, but only 40% of the book treats statistical mechanics.
- C. Kittel, *Elementary Statistical Physics* (Dover, 2004)
  Remarkably crisp, though dated, this text is organized as a series of brief discussions of key concepts and examples. Published by Dover, so you can't beat the price.
- M. Kardar, *Statistical Physics of Particles* (Cambridge, 2007)
  A superb modern text, with many insightful presentations of key concepts.
- M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* (3$^{\text{rd}}$ edition, World Scientific, 2006)
  An excellent graduate level text. Less insightful than Kardar but still a good modern treatment of the subject. Good discussion of mean field theory.
- E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics* (part I, 3$^{\text{rd}}$ edition, Pergamon, 1980)
  This is volume 5 in the famous Landau and Lifshitz *Course of Theoretical Physics*. Though dated, it still contains a wealth of information and physical insight.

## 4.2 Microcanonical Ensemble ($\mu$CE)

### 4.2.1 The microcanonical distribution function

We have seen how in an *ergodic* dynamical system, time averages can be replaced by phase space averages:

$$\text{ergodicity} \quad \Longleftrightarrow \quad \big\langle f(\boldsymbol{\varphi})\big\rangle_T = \big\langle f(\boldsymbol{\varphi})\big\rangle_S \ , \tag{4.1}$$

where

$$\big\langle f(\boldsymbol{\varphi})\big\rangle_T = \lim_{T\to\infty} \frac{1}{T}\int\limits_0^T\! dt\, f\big(\boldsymbol{\varphi}(t)\big) \ . \tag{4.2}$$

and

$$\big\langle f(\boldsymbol{\varphi})\big\rangle_S = \int\! d\mu\, f(\boldsymbol{\varphi})\, \delta\big(E - \hat{H}(\boldsymbol{\varphi})\big) \bigg/ \int\! d\mu\, \delta\big(E - \hat{H}(\boldsymbol{\varphi})\big) \ . \tag{4.3}$$

Here $\hat{H}(\boldsymbol{\varphi}) = \hat{H}(\boldsymbol{q},\boldsymbol{p})$ is the Hamiltonian, and where $\delta(x)$ is the Dirac $\delta$-function[1]. Thus, averages are taken over a constant energy hypersurface which is a subset of the entire phase space.

We've also seen how any phase space distribution $\varrho(\Lambda_1,\ldots,\Lambda_k)$ which is a function of conserved quantitied $\Lambda_a(\boldsymbol{\varphi})$ is automatically a stationary (time-independent) solution to Liouville's equation. Note that the microcanonical distribution,

$$\varrho_E(\boldsymbol{\varphi}) = \delta\big(E - \hat{H}(\boldsymbol{\varphi})\big) \bigg/ \int\! d\mu\, \delta\big(E - \hat{H}(\boldsymbol{\varphi})\big) \ , \tag{4.4}$$

is of this form, since $\hat{H}(\boldsymbol{\varphi})$ is conserved by the dynamics. Linear and angular momentum conservation generally are broken by elastic scattering off the walls of the sample.

So averages in the microcanonical ensemble are computed by evaluating the ratio

$$\big\langle A \big\rangle = \frac{\mathsf{Tr}\ A\,\delta(E-\hat{H})}{\mathsf{Tr}\ \delta(E-\hat{H})} \ , \tag{4.5}$$

where $\mathsf{Tr}$ means 'trace', which entails an integration over all phase space:

$$\mathsf{Tr}\ A(q,p) \equiv \frac{1}{N!}\prod_{i=1}^N \int \frac{d^dp_i\, d^dq_i}{(2\pi\hbar)^d}\, A(q,p) \ . \tag{4.6}$$

Here $N$ is the total number of particles and $d$ is the dimension of physical space in which each particle moves. The factor of $1/N!$, which cancels in the ratio between numerator and denominator, is present for *indistinguishable particles*. The normalization factor $(2\pi\hbar)^{-Nd}$ renders the trace dimensionless. Again, this cancels between numerator and denominator. These factors may then seem arbitrary in the definition of the trace, but we'll see how they in fact are required from quantum mechanical considerations. So we now adopt the following metric for classical phase space integration:

$$d\mu = \frac{1}{N!}\prod_{i=1}^N \frac{d^dp_i\, d^dq_i}{(2\pi\hbar)^d} \ . \tag{4.7}$$

---

[1] We write the Hamiltonian as $\hat{H}$ (classical or quantum) in order to distinguish it from magnetic field ($H$) or enthalpy ($\mathsf{H}$).

### 4.2.2 Density of states

The denominator,

$$D(E) = \mathsf{Tr}\ \delta(E - \hat{H})\ , \tag{4.8}$$

is called the *density of states*. It has dimensions of inverse energy, such that

$$\begin{aligned} D(E)\,\Delta E &= \int\limits_E^{E+\Delta E}\!\! dE' \int\! d\mu\ \delta(E' - \hat{H}) = \int\limits_{E<\hat{H}<E+\Delta E}\!\!\! d\mu \\ &= \text{\# of states with energies between } E \text{ and } E + \Delta E\ . \end{aligned} \tag{4.9}$$

Let us now compute $D(E)$ for the nonrelativistic ideal gas. The Hamiltonian is

$$\hat{H}(q,p) = \sum_{i=1}^N \frac{\boldsymbol{p}_i^2}{2m}\ . \tag{4.10}$$

We assume that the gas is enclosed in a region of volume $V$, and we'll do a purely classical calculation, neglecting discreteness of its quantum spectrum. We must compute

$$D(E) = \frac{1}{N!} \int \prod_{i=1}^N \frac{d^d\!p_i\, d^d\!q_i}{(2\pi\hbar)^d}\ \delta\bigg(E - \sum_{i=1}^N \frac{\boldsymbol{p}_i^2}{2m}\bigg)\ . \tag{4.11}$$

We'll do this calculation in two ways. First, let's rescale $p_i^\alpha \equiv \sqrt{2mE}\ u_i^\alpha$. We then have

$$D(E) = \frac{V^N}{N!} \left(\frac{\sqrt{2mE}}{h}\right)^{\!Nd} \frac{1}{E} \int\! d^M\!u\ \delta\big(u_1^2 + u_2^2 + \ldots + u_M^2 - 1\big)\ . \tag{4.12}$$

Here we have written $\boldsymbol{u} = (u_1, u_2, \ldots, u_M)$ with $M = Nd$ as a $M$-dimensional vector. We've also used the rule $\delta(Ex) = E^{-1}\delta(x)$ for $\delta$-functions. We can now write

$$d^M\!u = u^{M-1}\, du\, d\Omega_M\ , \tag{4.13}$$

where $d\Omega_M$ is the $M$-dimensional differential solid angle. We now have our answer:[2]

$$D(E) = \frac{V^N}{N!} \left(\frac{\sqrt{2m}}{h}\right)^{\!Nd} E^{\frac{1}{2}Nd - 1} \cdot \tfrac{1}{2}\, \Omega_{Nd}\ . \tag{4.14}$$

What remains is for us to compute $\Omega_M$, the total solid angle in $M$ dimensions. We do this by a nifty mathematical trick. Consider the integral

$$\begin{aligned} \mathcal{I}_M &= \int\! d^M\!u\ e^{-u^2} = \Omega_M \int\limits_0^\infty\! du\ u^{M-1}\, e^{-\boldsymbol{u}^2} \\ &= \tfrac{1}{2}\Omega_M \int\limits_0^\infty\! ds\ s^{\frac{1}{2}M-1}\, e^{-s} = \tfrac{1}{2}\Omega_M\, \Gamma\big(\tfrac{1}{2}M\big)\ , \end{aligned} \tag{4.15}$$

---

[2] The factor of $\frac{1}{2}$ preceding $\Omega_M$ in eqn. 4.14 appears because $\delta(u^2 - 1) = \frac{1}{2}\,\delta(u-1) + \frac{1}{2}\,\delta(u+1)$. Since $u = |\boldsymbol{u}| \geq 0$, the second term can be dropped.

where $s = u^2$, and where

$$\Gamma(z) = \int\limits_0^\infty \! dt \, t^{z-1} \, e^{-t} \tag{4.16}$$

is the Gamma function, which satisfies $z\,\Gamma(z) = \Gamma(z+1)$.[3] On the other hand, we can compute $\mathcal{I}_M$ in Cartesian coordinates, writing

$$\mathcal{I}_M = \left( \int\limits_{-\infty}^{\infty} \! du_1 \, e^{-u_1^2} \right)^{\!M} = \big(\sqrt{\pi}\big)^M \ . \tag{4.17}$$

Therefore

$$\Omega_M = \frac{2\pi^{M/2}}{\Gamma(M/2)} \ . \tag{4.18}$$

We thereby obtain $\Omega_2 = 2\pi$, $\Omega_3 = 4\pi$, $\Omega_4 = 2\pi^2$, *etc.*, the first two of which are familiar.

Our final result, then, is

$$D(E,V,N) = \frac{V^N}{N!} \left( \frac{m}{2\pi\hbar^2} \right)^{\!Nd/2} \frac{E^{\frac{1}{2}Nd-1}}{\Gamma(Nd/2)} \ . \tag{4.19}$$

Here we have emphasized that the density of states is a function of $E$, $V$, and $N$. Using Stirling's approximation,

$$\ln N! = N\ln N - N + \tfrac{1}{2}\ln N + \tfrac{1}{2}\ln(2\pi) + \mathcal{O}\big(N^{-1}\big) \ , \tag{4.20}$$

we may define the *statistical entropy*,

$$S(E,V,N) \equiv k_{\rm B} \ln D(E,V,N) = N k_{\rm B} \, \phi\bigg(\frac{E}{N}\,,\,\frac{V}{N}\bigg) + \mathcal{O}(\ln N) \ , \tag{4.21}$$

where

$$\phi\bigg(\frac{E}{N}\,,\,\frac{V}{N}\bigg) = \frac{d}{2}\,\ln\bigg(\frac{E}{N}\bigg) + \ln\bigg(\frac{V}{N}\bigg) + \frac{d}{2}\,\ln\bigg(\frac{m}{d\pi\hbar^2}\bigg) + \big(1 + \tfrac{1}{2}d\big) \ . \tag{4.22}$$

Recall $k_{\rm B} = 1.3806503 \times 10^{-16}\,{\rm erg/K}$ is Boltzmann's constant.

The second way to calculate $D(E)$ is to first compute its *Laplace transform*, $Z(\beta)$:

$$Z(\beta) = \mathcal{L}\big[D(E)\big] \equiv \int\limits_0^\infty \! dE \, e^{-\beta E} \, D(E) = \mathsf{Tr}\; e^{-\beta \hat{H}} \ . \tag{4.23}$$

The inverse Laplace transform is then

$$D(E) = \mathcal{L}^{-1}\big[Z(\beta)\big] \equiv \int\limits_{c-i\infty}^{c+i\infty} \! \frac{d\beta}{2\pi i} \, e^{\beta E} \, Z(\beta) \ , \tag{4.24}$$

where $c$ is such that the integration contour is to the right of any singularities of $Z(\beta)$ in the complex $\beta$-plane. We

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[3] Note that for integer argument, $\Gamma(k) = (k-1)!$

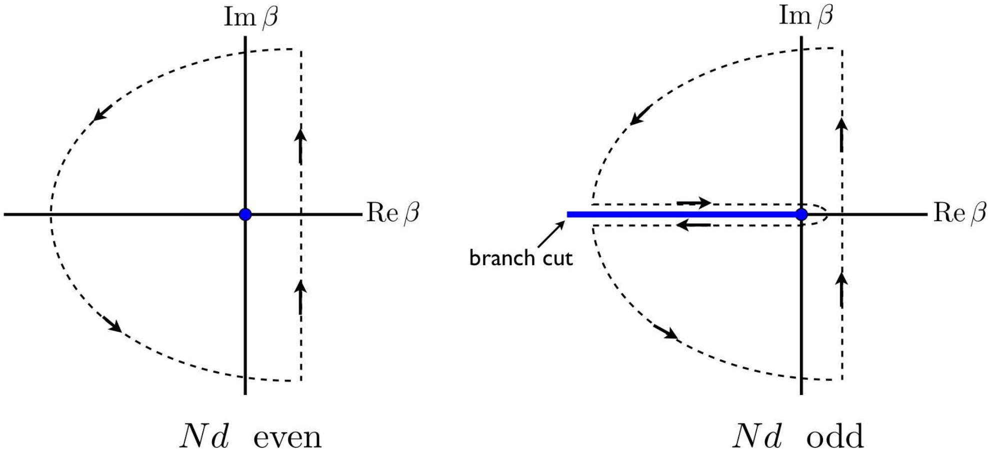

Figure 4.1: Complex integration contours $\mathcal{C}$ for inverse Laplace transform $\mathcal{L}^{-1}\big[Z(\beta)\big] = D(E)$. When the product $dN$ is odd, there is a branch cut along the negative $\mathrm{Re}\,\beta$ axis.

then have

$$\begin{aligned} Z(\beta) &= \frac{1}{N!}\prod_{i=1}^{N}\int\frac{d^dx_i\,d^dp_i}{(2\pi\hbar)^d}\,e^{-\beta\boldsymbol{p}_i^2/2m} \\ &= \frac{V^N}{N!}\left(\int\limits_{-\infty}^{\infty}\frac{dp}{2\pi\hbar}\,e^{-\beta p^2/2m}\right)^{Nd} \\ &= \frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^2}\right)^{Nd/2}\beta^{-Nd/2}\ . \end{aligned} \tag{4.25}$$

The inverse Laplace transform is then

$$\begin{aligned} D(E) &= \frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^2}\right)^{Nd/2}\oint\limits_{\mathcal{C}}\frac{d\beta}{2\pi i}\,e^{\beta E}\,\beta^{-Nd/2} \\ &= \frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^2}\right)^{Nd/2}\frac{E^{\frac{1}{2}Nd-1}}{\Gamma(Nd/2)}\ , \end{aligned} \tag{4.26}$$

exactly as before. The integration contour for the inverse Laplace transform is extended in an infinite semicircle in the left half $\beta$-plane. When $Nd$ is even, the function $\beta^{-Nd/2}$ has a simple pole of order $Nd/2$ at the origin. When $Nd$ is odd, there is a branch cut extending along the negative $\mathrm{Re}\,\beta$ axis, and the integration contour must avoid the cut, as shown in fig. 4.1.

For a general system, the Laplace transform, $Z(\beta) = \mathcal{L}\big[D(E)\big]$ also is called the *partition function*. We shall again meet up with $Z(\beta)$ when we discuss the ordinary canonical ensemble.

### 4.2.3 Arbitrariness in the definition of $S(E)$

Note that $D(E)$ has dimensions of inverse energy, so one might ask how we are to take the logarithm of a dimensionful quantity in eqn. 4.21. We must introduce an energy scale, such as $\Delta E$ in eqn. 4.9, and define

$\tilde{D}(E;\Delta E) = D(E)\,\Delta E$ and $S(E;\Delta E) \equiv k_{\rm B} \ln \tilde{D}(E;\Delta E)$. The definition of statistical entropy then involves the arbitrary parameter $\Delta E$, however this only affects $S(E)$ in an additive way. That is,

$$S(E,V,N;\Delta E_1) = S(E,V,N;\Delta E_2) + k_{\rm B} \ln\!\bigg(\frac{\Delta E_1}{\Delta E_2}\bigg) \ . \tag{4.27}$$

Note that the difference between the two definitions of $S$ depends only on the ratio $\Delta E_1/\Delta E_2$, and is independent of $E$, $V$, and $N$.

### 4.2.4 Ultra-relativistic ideal gas

Consider an ultrarelativistic ideal gas, with single particle dispersion $\varepsilon(p) = cp$. We then have

$$\begin{aligned} Z(\beta) &= \frac{V^N}{N!}\,\frac{\Omega_d^N}{h^N d}\left(\int\limits_0^\infty \!dp\, p^{d-1}\, e^{-\beta c p}\right)^{\!N} \\ &= \frac{V^N}{N!}\left(\frac{\Gamma(d)\,\Omega_d}{c^d\, h^d\, \beta^d}\right)^{\!N} \ . \end{aligned} \tag{4.28}$$

The statistical entropy is $S(E,V,N) = k_{\rm B} \ln D(E,V,N) = N k_{\rm B}\, \phi\big(\frac{E}{N},\frac{V}{N}\big)$, with

$$\phi\bigg(\frac{E}{N}\,,\,\frac{V}{N}\bigg) = d\,\ln\!\bigg(\frac{E}{N}\bigg) + \ln\!\bigg(\frac{V}{N}\bigg) + \ln\!\bigg(\frac{\Omega_d\,\Gamma(d)}{(dhc)^d}\bigg) + (d+1) \tag{4.29}$$

### 4.2.5 Discrete systems

For classical systems where the energy levels are discrete, the states of the system $|\,\boldsymbol{\sigma}\,\rangle$ are labeled by a set of discrete quantities $\{\sigma_1,\sigma_2,\ldots\}$, where each variable $\sigma_i$ takes discrete values. The number of ways of configuring the system at fixed energy $E$ is then

$$\Omega(E,N) = \sum_{\boldsymbol{\sigma}} \delta_{\hat{H}(\boldsymbol{\sigma}),E} \ , \tag{4.30}$$

where the sum is over all possible configurations. Here $N$ labels the total number of particles. For example, if we have $N$ spin-$\frac{1}{2}$ particles on a lattice which are placed in a magnetic field $H$, so the individual particle energy is $\varepsilon_i = -\mu_0 H \sigma$, where $\sigma = \pm 1$, then in a configuration in which $N_\uparrow$ particles have $\sigma_i = +1$ and $N_\downarrow = N - N_\uparrow$ particles have $\sigma_i = -1$, the energy is $E = (N_\downarrow - N_\uparrow)\mu_0 H$. The number of configurations at fixed energy $E$ is

$$\Omega(E,N) = \binom{N}{N_\uparrow} = \frac{N!}{\big(\frac{N}{2} - \frac{E}{2\mu_0 H}\big)!\,\big(\frac{N}{2} + \frac{E}{2\mu_0 H}\big)!} \ , \tag{4.31}$$

since $N_{\uparrow/\downarrow} = \frac{N}{2} \mp \frac{E}{2\mu_0 H}$. The statistical entropy is $S(E,N) = k_{\rm B} \ln \Omega(E,N)$.

## 4.3 The Quantum Mechanical Trace

Thus far our understanding of ergodicity is rooted in the dynamics of classical mechanics. A Hamiltonian flow which is ergodic is one in which time averages can be replaced by phase space averages using the microcanonical ensemble. What happens, though, if our system is quantum mechanical, as all systems ultimately are?

### 4.3.1 The density matrix

First, let us consider that our system $S$ will in general be in contact with a world $W$. We call the union of $S$ and $W$ the universe, $U = W \cup S$. Let $\big| N \big\rangle$ denote a quantum mechanical state of $W$, and let $\big| n \big\rangle$ denote a quantum mechanical state of $S$. Then the most general wavefunction we can write is of the form

$$\big| \Psi \big\rangle = \sum_{N,n} \Psi_{N,n} \, \big| N \big\rangle \otimes \big| n \big\rangle \, . \tag{4.32}$$

Now let us compute the expectation value of some operator $\hat{\mathcal{A}}$ which acts as the identity within $W$, meaning $\big\langle N \big| \hat{\mathcal{A}} \big| N' \big\rangle = \hat{A} \, \delta_{NN'}$, where $\hat{A}$ is the 'reduced' operator which acts within $S$ alone. We then have

$$\begin{aligned} \big\langle \Psi \big| \hat{\mathcal{A}} \big| \Psi \big\rangle &= \sum_{N,N'} \sum_{n,n'} \Psi^*_{N,n} \, \Psi_{N',n'} \, \delta_{NN'} \, \big\langle n \big| \hat{A} \big| n' \big\rangle \\ &= \mathsf{Tr} \, \big( \hat{\varrho} \, \hat{A} \big) \, , \end{aligned} \tag{4.33}$$

where

$$\hat{\varrho} = \sum_{N} \sum_{n,n'} \Psi^*_{N,n} \, \Psi_{N,n'} \, \big| n' \big\rangle \big\langle n \big| \tag{4.34}$$

is the *density matrix*. The time-dependence of $\hat{\varrho}$ is easily found:

$$\begin{aligned} \hat{\varrho}(t) &= \sum_{N} \sum_{n,n'} \Psi^*_{N,n} \, \Psi_{N,n'} \, \big| n'(t) \big\rangle \big\langle n(t) \big| \\ &= e^{-i\hat{H}t/\hbar} \, \hat{\varrho} \, e^{+i\hat{H}t/\hbar} \, , \end{aligned} \tag{4.35}$$

where $\hat{H}$ is the Hamiltonian for the system $S$. Thus, we find

$$i\hbar \, \frac{\partial \hat{\varrho}}{\partial t} = \big[ \hat{H}, \hat{\varrho} \big] \, . \tag{4.36}$$

Note that the density matrix evolves according to a slightly different equation than an operator in the Heisenberg picture, for which

$$\hat{A}(t) = e^{+iHt/\hbar} \, A \, e^{-i\hat{H}t/\hbar} \qquad \Longrightarrow \qquad i\hbar \, \frac{\partial \hat{A}}{\partial t} = \big[ \hat{A}, \hat{H} \big] = -\big[ \hat{H}, \hat{A} \big] \, . \tag{4.37}$$

For Hamiltonian systems, we found that the phase space distribution $\varrho(q,p,t)$ evolved according to the Liouville equation,

$$i \, \frac{\partial \varrho}{\partial t} = L \, \varrho \, , \tag{4.38}$$

where the Liouvillian $L$ is the differential operator

$$L = -i \sum_{j=1}^{Nd} \left\{ \frac{\partial \hat{H}}{\partial p_j} \, \frac{\partial}{\partial q_j} - \frac{\partial \hat{H}}{\partial q_j} \, \frac{\partial}{\partial p_j} \right\} . \tag{4.39}$$

Accordingly, any distribution $\varrho(\Lambda_1, \ldots, \Lambda_k)$ which is a function of constants of the motion $\Lambda_a(q,p)$ is a stationary solution to the Liouville equation: $\partial_t \, \varrho(\Lambda_1, \ldots, \Lambda_k) = 0$. Similarly, any quantum mechanical density matrix which commutes with the Hamiltonian is a stationary solution to eqn. 4.36. The corresponding microcanonical distribution is

$$\hat{\varrho}_E = \delta\big( E - \hat{H} \big) \, . \tag{4.40}$$

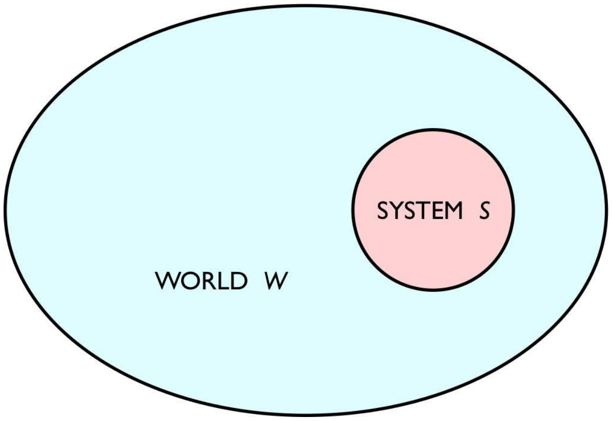

Figure 4.2: A system $S$ in contact with a 'world' $W$. The union of the two, universe $U = W \cup S$, is said to be the 'universe'.

### 4.3.2 Averaging the DOS

If our quantum mechanical system is placed in a finite volume, the energy levels will be discrete, rather than continuous, and the density of states (DOS) will be of the form

$$D(E) = \mathsf{Tr}\;\delta\big(E - \hat{H}\big) = \sum_l \delta(E - E_l)\ , \tag{4.41}$$

where $\{E_l\}$ are the eigenvalues of the Hamiltonian $\hat{H}$. In the thermodynamic limit, $V \to \infty$, and the discrete spectrum of kinetic energies remains discrete for all finite $V$ but must approach the continuum result. To recover the continuum result, we average the DOS over a window of width $\Delta E$:

$$\overline{D(E)} = \frac{1}{\Delta E} \int\limits_E^{E+\Delta E} \! dE'\, D(E')\ . \tag{4.42}$$

If we take the limit $\Delta E \to 0$ but with $\Delta E \gg \delta E$, where $\delta E$ is the spacing between successive quantized levels, we recover a smooth function, as shown in fig. 4.3. We will in general drop the bar and refer to this function as $D(E)$. Note that $\delta E \sim 1/D(E) = e^{-N\phi(\varepsilon,v)}$ is (typically) *exponentially* small in the size of the system, hence if we took $\Delta E \propto V^{-1}$ which vanishes in the thermodynamic limit, there are still exponentially many energy levels within an interval of width $\Delta E$.

### 4.3.3 Coherent states

The quantum-classical correspondence is elucidated with the use of *coherent states*. Recall that the one-dimensional harmonic oscillator Hamiltonian may be written

$$\begin{aligned} \hat{H}_0 &= \frac{p^2}{2m} + \tfrac{1}{2} m\, \omega_0^2\, q^2 \\ &= \hbar\omega_0\, \big(a^\dagger a + \tfrac{1}{2}\big)\ , \end{aligned} \tag{4.43}$$

where $a$ and $a^\dagger$ are *ladder operators* satisfying $\big[a, a^\dagger\big] = 1$, which can be taken to be

$$a = \ell\, \frac{\partial}{\partial q} + \frac{q}{2\ell} \qquad , \qquad a^\dagger = -\ell\, \frac{\partial}{\partial q} + \frac{q}{2\ell}\ , \tag{4.44}$$

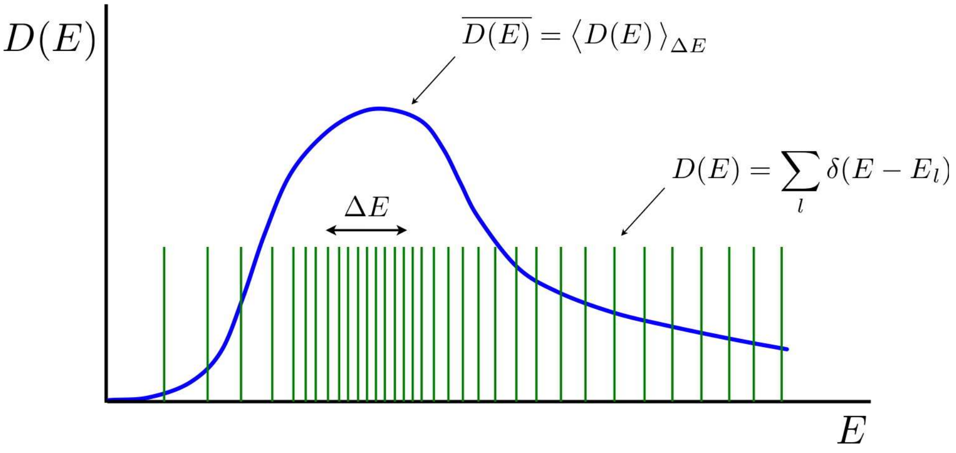

Figure 4.3: Averaging the quantum mechanical discrete density of states yields a continuous curve.

with $\ell = \sqrt{\hbar/2m\omega_0}$ . Note that

$$q = \ell\left(a + a^\dagger\right) \qquad , \qquad p = \frac{\hbar}{2i\ell}\left(a - a^\dagger\right) . \tag{4.45}$$

The ground state satisfies $a\,\psi_0(q) = 0$, which yields

$$\psi_0(q) = (2\pi\ell^2)^{-1/4}\, e^{-q^2/4\ell^2} . \tag{4.46}$$

The normalized *coherent state* $|\,z\,\rangle$ is defined as

$$|\,z\,\rangle = e^{-\frac{1}{2}|z|^2}\, e^{za^\dagger}\,|\,0\,\rangle = e^{-\frac{1}{2}|z|^2} \sum_{n=0}^\infty \frac{z^n}{\sqrt{n!}}\,|\,n\,\rangle . \tag{4.47}$$

The overlap of coherent states is given by

$$\langle\, z_1 \,|\, z_2 \,\rangle = e^{-\frac{1}{2}|z_1|^2}\, e^{-\frac{1}{2}|z_2|^2}\, e^{\bar{z}_1 z_2} , \tag{4.48}$$

hence different coherent states are not orthogonal. Despite this nonorthogonality, the coherent states allow a simple resolution of the identity,

$$1 = \int\!\frac{d^2\!z}{2\pi i}\,|\,z\,\rangle\langle\,z\,| \quad ; \quad \frac{d^2\!z}{2\pi i} \equiv \frac{d\,\mathrm{Re}z\;d\,\mathrm{Im}z}{\pi} \tag{4.49}$$

which is straightforward to establish.

To gain some physical intuition about the coherent states, define

$$z \equiv \frac{Q}{2\ell} + \frac{i\ell P}{\hbar} \tag{4.50}$$

and write $|\,z\,\rangle \equiv |\,Q,P\,\rangle$. One finds (*exercise!*)

$$\psi_{Q,P}(q) = \langle\, q \,|\, z \,\rangle = (2\pi\ell^2)^{-1/4}\, e^{-iPQ/2\hbar}\, e^{iPq/\hbar}\, e^{-(q-Q)^2/4\ell^2} , \tag{4.51}$$

hence the coherent state $\psi_{Q,P}(q)$ is a wavepacket Gaussianly localized about $q = Q$, but oscillating with average momentum $P$.

For example, we can compute

$$\big\langle\, Q,P\,\big|\, q\,\big|\, Q,P\,\big\rangle = \big\langle\, z\,\big|\,\ell\,(a+a^\dagger)\,\big|\, z\,\big\rangle = 2\ell\,\mathrm{Re}\,z = Q \tag{4.52}$$

$$\big\langle\, Q,P\,\big|\, p\,\big|\, Q,P\,\big\rangle = \big\langle\, z\,\big|\,\frac{\hbar}{2i\ell}\,(a-a^\dagger)\,\big|\, z\,\big\rangle = \frac{\hbar}{\ell}\,\mathrm{Im}\,z = P \tag{4.53}$$

as well as

$$\big\langle\, Q,P\,\big|\, q^2\,\big|\, Q,P\,\big\rangle = \big\langle\, z\,\big|\,\ell^2\,(a+a^\dagger)^2\,\big|\, z\,\big\rangle = Q^2+\ell^2 \tag{4.54}$$

$$\big\langle\, Q,P\,\big|\, p^2\,\big|\, Q,P\,\big\rangle = -\big\langle\, z\,\big|\,\frac{\hbar^2}{4\ell^2}(a-a^\dagger)^2\,\big|\, z\,\big\rangle = P^2+\frac{\hbar^2}{4\ell^2}\ . \tag{4.55}$$

Thus, the root mean square fluctuations in the coherent state $|\, Q,P\,\rangle$ are

$$\Delta q = \ell = \sqrt{\frac{\hbar}{2m\omega_0}} \qquad , \qquad \Delta p = \frac{\hbar}{2\ell} = \sqrt{\frac{m\hbar\omega_0}{2}}\ , \tag{4.56}$$

and $\Delta q\cdot\Delta p = \frac{1}{2}\,\hbar$. Thus we learn that the coherent state $\psi_{Q,P}(q)$ is localized in phase space, *i.e.* in both position and momentum. If we have a general operator $\hat{A}(q,p)$, we can then write

$$\big\langle\, Q,P\,\big|\, \hat{A}(q,p)\,\big|\, Q,P\,\big\rangle = A(Q,P) + \mathcal{O}(\hbar)\ , \tag{4.57}$$

where $A(Q,P)$ is formed from $\hat{A}(q,p)$ by replacing $q\to Q$ and $p\to P$.

Since

$$\frac{d^2\!z}{2\pi i} \equiv \frac{d\,\mathrm{Re}z\;d\,\mathrm{Im}z}{\pi} = \frac{dQ\,dP}{2\pi\hbar}\ , \tag{4.58}$$

we can write the trace using coherent states as

$$\mathsf{Tr}\,\hat{A} = \frac{1}{2\pi\hbar}\int\limits_{-\infty}^{\infty}\!dQ\int\limits_{-\infty}^{\infty}\!dP\,\big\langle\, Q,P\,\big|\,\hat{A}\,\big|\, Q,P\,\big\rangle\ . \tag{4.59}$$

We now can understand the origin of the factor $2\pi\hbar$ in the denominator of each $(q_i,p_i)$ integral over classical phase space in eqn. 4.6.

Note that $\omega_0$ is arbitrary in our discussion. By increasing $\omega_0$, the states become more localized in $q$ and more plane wave like in $p$. However, so long as $\omega_0$ is finite, the width of the coherent state in each direction is proportional to $\hbar^{1/2}$, and thus vanishes in the classical limit.

## 4.4 Thermal Equilibrium

Consider two systems in thermal contact, as depicted in fig. 4.4. The two subsystems #1 and #2 are free to exchange energy, but their respective volumes and particle numbers remain fixed. We assume the contact is made over a surface, and that the energy associated with that surface is negligible when compared with the bulk energies $E_1$ and $E_2$. Let the total energy be $E = E_1 + E_2$. Then the density of states $D(E)$ for the combined system is

$$D(E) = \int\! dE_1\, D_1(E_1)\, D_2(E-E_1)\ . \tag{4.60}$$

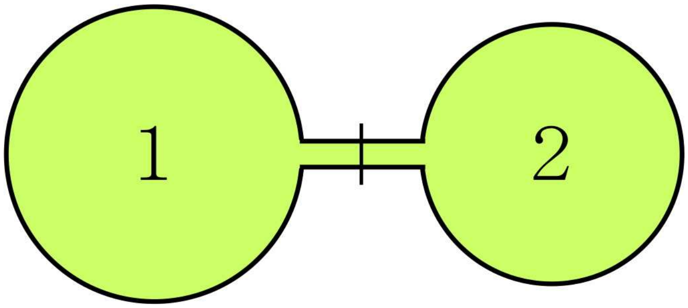

Figure 4.4: Two systems in thermal contact.

The probability density for system #1 to have energy $E_1$ is then

$$P_1(E_1) = \frac{D_1(E_1)\, D_2(E-E_1)}{D(E)} \ . \tag{4.61}$$

Note that $P_1(E_1)$ is normalized: $\int dE_1\, P_1(E_1) = 1$. We now ask: what is the most probable value of $E_1$? We find out by differentiating $P_1(E_1)$ with respect to $E_1$ and setting the result to zero. This requires

$$\begin{aligned} 0 &= \frac{1}{P_1(E_1)}\,\frac{dP_1(E_1)}{dE_1} = \frac{\partial}{\partial E_1}\ln P_1(E_1) \\ &= \frac{\partial}{\partial E_1}\ln D_1(E_1) + \frac{\partial}{\partial E_1}\ln D_2(E-E_1) \ . \end{aligned} \tag{4.62}$$

Thus, we conclude that the maximally likely partition of energy between systems #1 and #2 is realized when

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \ . \tag{4.63}$$

This guarantees that

$$S(E,E_1) = S_1(E_1) + S_2(E-E_1) \tag{4.64}$$

is a maximum with respect to the energy $E_1$, at fixed total energy $E$.

The *temperature* $T$ is defined as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \ , \tag{4.65}$$

a result familiar from thermodynamics. The difference is now we have a more rigorous definition of the entropy. When the total entropy $S$ is maximized, we have that $T_1 = T_2$. Once again, two systems in thermal contact and can exchange energy will in equilibrium have equal temperatures.

According to eqns. 4.22 and 4.29, the entropies of nonrelativistic and ultrarelativistic ideal gases in $d$ space dimensions are given by

$$S_{\rm NR} = \tfrac{1}{2} N d\, k_{\rm B} \ln\left(\frac{E}{N}\right) + N k_{\rm B} \ln\left(\frac{V}{N}\right) + \text{const.} \tag{4.66}$$

$$S_{\rm UR} = N d\, k_{\rm B} \ln\left(\frac{E}{N}\right) + N k_{\rm B} \ln\left(\frac{V}{N}\right) + \text{const.} \ . \tag{4.67}$$

Invoking eqn. 4.65, we then have

$$E_{\rm NR} = \tfrac{1}{2} N d\, k_{\rm B} T \qquad , \qquad E_{\rm UR} = N d\, k_{\rm B} T \ . \tag{4.68}$$

We saw that the probability distribution $P_1(E_1)$ is maximized when $T_1 = T_2$, but how sharp is the peak in the distribution? Let us write $E_1 = E_1^* + \Delta E_1$, where $E_1^*$ is the solution to eqn. 4.62. We then have

$$\ln P_1(E_1^* + \Delta E_1) = \ln P_1(E_1^*) + \frac{1}{2k_{\rm B}} \frac{\partial^2 S_1}{\partial E_1^2}\bigg|_{E_1^*} (\Delta E_1)^2 + \frac{1}{2k_{\rm B}} \frac{\partial^2 S_2}{\partial E_2^2}\bigg|_{E_2^*} (\Delta E_1)^2 + \ldots \ , \tag{4.69}$$

where $E_2^* = E - E_1^*$. We must now evaluate

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\bigg(\frac{1}{T}\bigg) = -\frac{1}{T^2}\bigg(\frac{\partial T}{\partial E}\bigg)_{V,N} = -\frac{1}{T^2\,C_V} \ , \tag{4.70}$$

where $C_V = \big(\partial E/\partial T\big)_{V,N}$ is the heat capacity. Thus,

$$P_1 = P_1^*\, e^{-(\Delta E_1)^2/2k_{\rm B}T^2 \bar{C}_V} \ , \tag{4.71}$$

where

$$\bar{C}_V = \frac{C_{V,1}\, C_{V,2}}{C_{V,1} + C_{V,2}} \ . \tag{4.72}$$

The distribution is therefore a Gaussian, and the fluctuations in $\Delta E_1$ can now be computed:

$$\big\langle (\Delta E_1)^2 \big\rangle = k_{\rm B} T^2\, \bar{C}_V \qquad \Longrightarrow \qquad (\Delta E_1)_{\rm RMS} = k_{\rm B} T \sqrt{\bar{C}_V / k_{\rm B}} \ . \tag{4.73}$$

The individual heat capacities $C_{V,1}$ and $C_{V,2}$ scale with the volumes $V_1$ and $V_2$, respectively. If $V_2 \gg V_1$, then $C_{V,2} \gg C_{V,1}$, in which case $\bar{C}_V \approx C_{V,1}$. Therefore the RMS fluctuations in $\Delta E_1$ are proportional to the *square root* of the system size, whereas $E_1$ itself is extensive. Thus, the ratio $(\Delta E_1)_{\rm RMS}/E_1 \propto V^{-1/2}$ scales as the inverse square root of the volume. The distribution $P_1(E_1)$ is thus *extremely sharp*.

## 4.5 Ordinary Canonical Ensemble (OCE)

### 4.5.1 Canonical distribution and partition function

Consider a system $S$ in contact with a world $W$, and let their union $U = W \cup S$ be called the 'universe'. The situation is depicted in fig. 4.2. The volume $V_{\rm S}$ and particle number $N_{\rm S}$ of the system are held fixed, but the energy is allowed to fluctuate by exchange with the world $W$. We are interested in the limit $N_{\rm S} \to \infty$, $N_{\rm W} \to \infty$, with $N_{\rm S} \ll N_{\rm W}$, with similar relations holding for the respective volumes and energies. We now ask what is the probability that $S$ is in a state $|\, n\,\rangle$ with energy $E_n$. This is given by the ratio

$$\begin{aligned} P_n &= \lim_{\Delta E \to 0} \frac{D_{\rm W}(E_{\rm U} - E_n)\,\Delta E}{D_{\rm U}(E_{\rm U})\,\Delta E} \\ &= \frac{\#\text{ of states accessible to } W \text{ given that } E_{\rm S} = E_n}{\text{total \# of states in } U} \ . \end{aligned} \tag{4.74}$$

Then

$$\begin{aligned} \ln P_n &= \ln D_{\rm W}(E_{\rm U} - E_n) - \ln D_{\rm U}(E_{\rm U}) \\ &= \ln D_{\rm W}(E_{\rm U}) - \ln D_{\rm U}(E_{\rm U}) - E_n\, \frac{\partial \ln D_{\rm W}(E)}{\partial E}\bigg|_{E=E_{\rm U}} + \ldots \\ &\equiv -\alpha - \beta E_n \ . \end{aligned} \tag{4.75}$$

The constant $\beta$ is given by

$$\beta = \frac{\partial \ln D_{\text{W}}(E)}{\partial E}\bigg|_{E=E_{\text{U}}} = \frac{1}{k_{\text{B}} T} \ . \tag{4.76}$$

Thus, we find $P_n = e^{-\alpha}\, e^{-\beta E_n}$. The constant $\alpha$ is fixed by the requirement that $\sum_n P_n = 1$:

$$P_n = \frac{1}{Z}\, e^{-\beta E_n} \qquad , \qquad Z(T,V,N) = \sum_n e^{-\beta E_n} = \textsf{Tr}\; e^{-\beta \hat{H}} \ . \tag{4.77}$$

We've already met $Z(\beta)$ in eqn. 4.23 – it is the Laplace transform of the density of states. It is also called the *partition function* of the system $S$. Quantum mechanically, we can write the ordinary canonical density matrix as

$$\hat{\varrho} = \frac{e^{-\beta \hat{H}}}{\textsf{Tr}\; e^{-\beta \hat{H}}} \ . \tag{4.78}$$

Note that $\big[\hat{\varrho}, \hat{H}\big] = 0$, hence the ordinary canonical distribution is a stationary solution to the evolution equation for the density matrix. Note that the OCE is specified by three parameters: $T$, $V$, and $N$.

### 4.5.2 The difference between $P(E_n)$ and $P_n$

Let the total energy of the Universe be fixed at $E_{\text{U}}$. The joint probability density $P(E_{\text{S}}, E_{\text{W}})$ for the system to have energy $E_{\text{S}}$ and the world to have energy $E_{\text{W}}$ is

$$P(E_{\text{S}}, E_{\text{W}}) = D_{\text{S}}(E_{\text{S}})\, D_{\text{W}}(E_{\text{W}})\, \delta(E_{\text{U}} - E_{\text{S}} - E_{\text{W}}) \big/ D_{\text{U}}(E_{\text{U}}) \ , \tag{4.79}$$

where

$$D_{\text{U}}(E_{\text{U}}) = \int\limits_{-\infty}^{\infty} \! dE_{\text{S}}\; D_{\text{S}}(E_{\text{S}})\, D_{\text{W}}(E_{\text{U}} - E_{\text{S}}) \ , \tag{4.80}$$

which ensures that $\int \! dE_{\text{S}} \int \! dE_{\text{W}}\; P(E_{\text{S}}, E_{\text{W}}) = 1$. The *probability density* $P(E_{\text{S}})$ is defined such that $P(E_{\text{S}})\, dE_{\text{S}}$ is the (differential) probability for the system to have an energy in the range $[E_{\text{S}}, E_{\text{S}} + dE_{\text{S}}]$. The units of $P(E_{\text{S}})$ are $E^{-1}$. To obtain $P(E_{\text{S}})$, we simply integrate the joint probability density $P(E_{\text{S}}, E_{\text{W}})$ over all possible values of $E_{\text{W}}$, obtaining

$$P(E_{\text{S}}) = \frac{D_{\text{S}}(E_{\text{S}})\, D_{\text{W}}(E_{\text{U}} - E_{\text{S}})}{D_{\text{U}}(E_{\text{U}})} \ , \tag{4.81}$$

as we have in eqn. 4.74.

Now suppose we wish to know the probability $P_n$ that the system is in a *particular* state $|\, n\, \rangle$ with energy $E_n$. Clearly

$$P_n = \lim_{\Delta E \to 0} \frac{\text{probability that } E_{\text{S}} \in [E_n, E_n + \Delta E]}{\text{\# of S states with } E_{\text{S}} \in [E_n, E_n + \Delta E]} = \frac{P(E_n)\, \Delta E}{D_{\text{S}}(E_n)\, \Delta E} = \frac{D_{\text{W}}(E_{\text{U}} - E_n)}{D_{\text{U}}(E_{\text{U}})} \ . \tag{4.82}$$

### 4.5.3 Averages within the OCE

To compute averages within the OCE,

$$\big\langle \hat{A} \big\rangle = \textsf{Tr}\,\big(\hat{\varrho}\, \hat{A}\big) = \frac{\sum_n \langle n | \hat{A} | n \rangle\, e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} \ , \tag{4.83}$$

where we have conveniently taken the trace in a basis of energy eigenstates. In the classical limit, we have

$$\varrho(\boldsymbol{\varphi}) = \frac{1}{Z}\, e^{-\beta \hat{H}(\boldsymbol{\varphi})} \quad , \quad Z = \mathsf{Tr}\; e^{-\beta\hat{H}} = \int\! d\mu\, e^{-\beta\hat{H}(\boldsymbol{\varphi})} \ , \tag{4.84}$$

with $d\mu = \frac{1}{N!}\prod_{j=1}^N (d^dq_j\, d^dp_j/h^d)$ for identical particles ('Maxwell-Boltzmann statistics'). Thus,

$$\langle A \rangle = \mathsf{Tr}\,(\varrho A) = \frac{\int\! d\mu\, A(\boldsymbol{\varphi})\, e^{-\beta\hat{H}(\boldsymbol{\varphi})}}{\int\! d\mu\, e^{-\beta\hat{H}(\boldsymbol{\varphi})}} \ . \tag{4.85}$$

### 4.5.4 Entropy and free energy

The *Boltzmann entropy* is defined by

$$S = -k_{\rm B}\, \mathsf{Tr}\,\big(\hat{\varrho}\ln\hat{\varrho}\big) = -k_{\rm B}\sum_n P_n\, \ln P_n \ . \tag{4.86}$$

The Boltzmann entropy and the statistical entropy $S = k_{\rm B}\ln D(E)$ are identical in the thermodynamic limit.

We define the Helmholtz free energy $F(T,V,N)$ as

$$F(T,V,N) = -k_{\rm B}T\ln Z(T,V,N) \ , \tag{4.87}$$

hence

$$P_n = e^{\beta F}\, e^{-\beta E_n} \qquad , \qquad \ln P_n = \beta F - \beta E_n \ . \tag{4.88}$$

Therefore the entropy is

$$\begin{aligned} S &= -k_{\rm B}\sum_n P_n\,\big(\beta F - \beta E_n\big) \\ &= -\frac{F}{T} + \frac{\langle\, \hat{H}\,\rangle}{T} \ , \end{aligned} \tag{4.89}$$

which is to say

$$F = E - TS \ , \tag{4.90}$$

where

$$E = \sum_n P_n\, E_n = \frac{\mathsf{Tr}\; \hat{H}\, e^{-\beta\hat{H}}}{\mathsf{Tr}\; e^{-\beta\hat{H}}} \tag{4.91}$$

is the average energy. We also see that

$$Z = \mathsf{Tr}\; e^{-\beta\hat{H}} = \sum_n e^{-\beta E_n} \quad \Longrightarrow \quad E = \frac{\sum_n E_n\, e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} = -\frac{\partial}{\partial\beta}\,\ln Z = \frac{\partial}{\partial\beta}\big(\beta F\big) \ . \tag{4.92}$$

Thus, $F(T,V,N)$ is a Legendre transform of $E(S,V,N)$, with

$$dF = -S\, dT - p\, dV + \mu\, dN \ , \tag{4.93}$$

which means

$$S = -\bigg(\frac{\partial F}{\partial T}\bigg)_{V,N} \qquad , \qquad p = -\bigg(\frac{\partial F}{\partial V}\bigg)_{T,N} \qquad , \qquad \mu = +\bigg(\frac{\partial F}{\partial N}\bigg)_{T,V} \ . \tag{4.94}$$

### 4.5.5 Fluctuations in the OCE

In the OCE, the energy is not fixed. It therefore fluctuates about its average value $E = \langle \hat{H} \rangle$. Note that

$$\begin{aligned} -\frac{\partial E}{\partial \beta} = k_{\rm B} T^2 \, \frac{\partial E}{\partial T} &= \frac{\partial^2 \ln Z}{\partial \beta^2} \\ &= \frac{\textsf{Tr}\ \hat{H}^2 \, e^{-\beta \hat{H}}}{\textsf{Tr}\ e^{-\beta \hat{H}}} - \left( \frac{\textsf{Tr}\ \hat{H} \, e^{-\beta \hat{H}}}{\textsf{Tr}\ e^{-\beta \hat{H}}} \right)^2 \\ &= \big\langle \hat{H}^2 \big\rangle - \big\langle \hat{H} \big\rangle^2 \ . \end{aligned} \tag{4.95}$$

Thus, the heat capacity is related to the fluctuations in the energy, just as we saw at the end of §4.4:

$$C_V = \left( \frac{\partial E}{\partial T} \right)_{V,N} = \frac{1}{k_{\rm B} T^2} \left( \big\langle \hat{H}^2 \big\rangle - \big\langle \hat{H} \big\rangle^2 \right) \tag{4.96}$$

For the nonrelativistic ideal gas, we found $C_V = \frac{d}{2} N k_{\rm B}$, hence the ratio of RMS fluctuations in the energy to the energy itself is

$$\frac{\sqrt{\big\langle \, (\Delta \hat{H})^2 \, \big\rangle}}{\langle \hat{H} \rangle} = \frac{\sqrt{k_{\rm B} T^2 \, C_V}}{\frac{d}{2} N k_{\rm B} T} = \sqrt{\frac{2}{Nd}} \ , \tag{4.97}$$

and the ratio of the RMS fluctuations to the mean value vanishes in the thermodynamic limit.

The full distribution function for the energy is

$$P(\mathcal{E}) = \big\langle \delta(\mathcal{E} - \hat{H}) \big\rangle = \frac{\textsf{Tr}\ \delta(\mathcal{E} - \hat{H}) \, e^{-\beta \hat{H}}}{\textsf{Tr}\ e^{-\beta \hat{H}}} = \frac{1}{Z} \, D(\mathcal{E}) \, e^{-\beta \mathcal{E}} \ . \tag{4.98}$$

Thus,

$$P(\mathcal{E}) = \frac{e^{-\beta [\mathcal{E} - T S(\mathcal{E})]}}{\int \! d\tilde{\mathcal{E}} \; e^{-\beta [\tilde{\mathcal{E}} - T S(\tilde{\mathcal{E}})]}} \ , \tag{4.99}$$

where $S(\mathcal{E}) = k_{\rm B} \ln D(\mathcal{E})$ is the statistical entropy. Let's write $\mathcal{E} = E + \delta\mathcal{E}$, where $E$ extremizes the combination $\mathcal{E} - T \, S(\mathcal{E})$, *i.e.* the solution to $T \, S'(E) = 1$, where the energy derivative of $S$ is performed at fixed volume $V$ and particle number $N$. We now expand $S(E + \delta\mathcal{E})$ to second order in $\delta\mathcal{E}$, obtaining

$$S(E + \delta\mathcal{E}) = S(E) + \frac{\delta\mathcal{E}}{T} - \frac{\big(\delta\mathcal{E}\big)^2}{2T^2 \, C_V} + \ldots \tag{4.100}$$

Recall that $S''(E) = \frac{\partial}{\partial E} \left( \frac{1}{T} \right) = -\frac{1}{T^2 C_V}$. Thus,

$$\mathcal{E} - T \, S(\mathcal{E}) = E - T \, S(E) + \frac{(\delta\mathcal{E})^2}{2T \, C_V} + \mathcal{O}\big((\delta\mathcal{E})^2\big) \ . \tag{4.101}$$

Applying this to both numerator and denominator of eqn. 4.99, we obtain[4]

$$P(\mathcal{E}) = \mathcal{N} \, \exp \left[ - \frac{(\delta\mathcal{E})^2}{2 k_{\rm B} T^2 \, C_V} \right] \ , \tag{4.102}$$

where $\mathcal{N} = (2\pi k_{\rm B} T^2 C_V)^{-1/2}$ is a normalization constant which guarantees $\int \! d\mathcal{E} \, P(\mathcal{E}) = 1$. Once again, we see that the distribution is a Gaussian centered at $\langle \mathcal{E} \rangle = E$, and of width $(\Delta\mathcal{E})_{\rm RMS} = \sqrt{k_{\rm B} T^2 \, C_V}$. This is a consequence of the Central Limit Theorem.

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[4] In applying eqn. 4.101 to the denominator of eqn. 4.99, we shift $\tilde{\mathcal{E}}$ by $E$ and integrate over the difference $\delta\tilde{\mathcal{E}} \equiv \tilde{\mathcal{E}} - E$, retaining terms up to quadratic order in $\delta\tilde{\mathcal{E}}$ in the argument of the exponent.

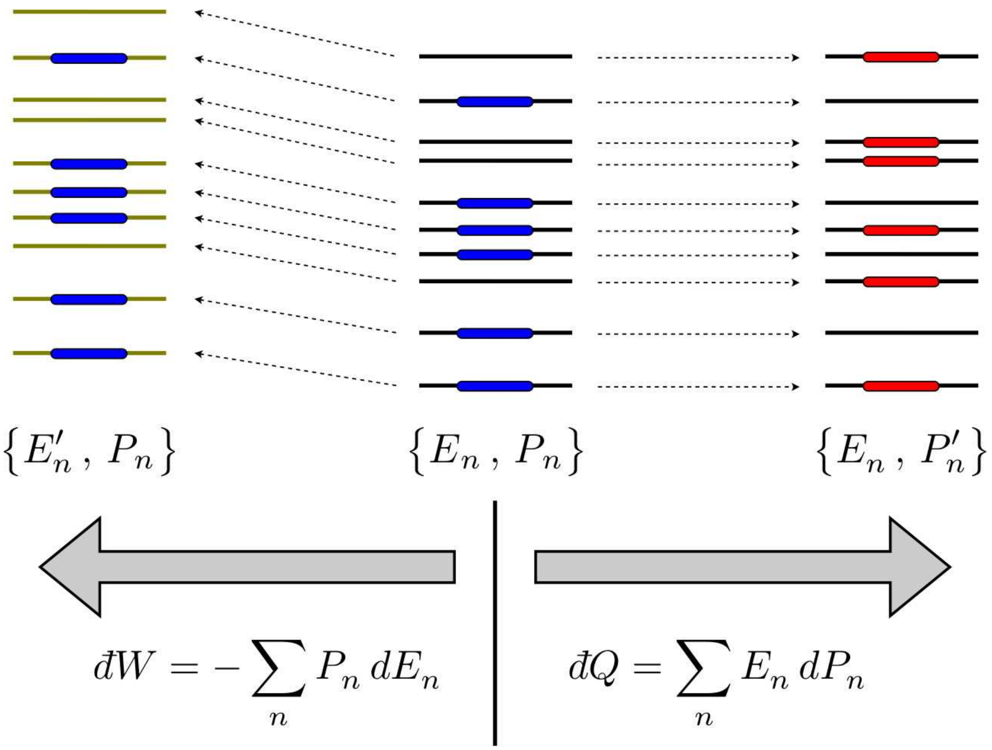

Figure 4.5: Microscopic, statistical interpretation of the First Law of Thermodynamics.

### 4.5.6 Thermodynamics revisited

The average energy within the OCE is

$$E=\sum_n E_n P_n\ , \tag{4.103}$$

and therefore

$$\begin{aligned} dE&=\sum_n E_n\,dP_n+\sum_n P_n\,dE_n \\ &=đQ-đW\ , \end{aligned} \tag{4.104}$$

where

$$đW=-\sum_n P_n\,dE_n \tag{4.105}$$

$$đQ=\sum_n E_n\,dP_n\ . \tag{4.106}$$

Finally, from $P_n=Z^{-1}\,e^{-E_n/k_\mathrm{B}T}$, we can write

$$E_n=-k_\mathrm{B}T\ln Z-k_\mathrm{B}T\ln P_n\ , \tag{4.107}$$

with which we obtain

$$\begin{aligned} đQ &= \sum_n E_n \, dP_n \\ &= -k_{\rm B} T \ln Z \sum_n dP_n - k_{\rm B} T \sum_n \ln P_n \, dP_n \\ &= T \, d\Big( - k_{\rm B} \sum_n P_n \ln P_n \Big) = T \, dS \ . \end{aligned} \tag{4.108}$$

Note also that

$$\begin{aligned} đW &= -\sum_n P_n \, dE_n \\ &= -\sum_n P_n \bigg( \sum_i \frac{\partial E_n}{\partial X_i} \, dX_i \bigg) \\ &= -\sum_{n,i} P_n \, \langle \, n \, | \, \frac{\partial \hat{H}}{\partial X_i} \, | \, n \, \rangle \, dX_i \equiv \sum_i F_i \, dX_i \ , \end{aligned} \tag{4.109}$$

so the generalized force $F_i$ conjugate to the generalized displacement $dX_i$ is

$$F_i = -\sum_n P_n \, \frac{\partial E_n}{\partial X_i} = -\bigg\langle \frac{\partial \hat{H}}{\partial X_i} \bigg\rangle \ . \tag{4.110}$$

This is the force acting *on* the system[5]. In the chapter on thermodynamics, we defined the generalized force conjugate to $X_i$ as $y_i \equiv -F_i$.

Thus we see from eqn. 4.104 that there are two ways that the average energy can change; these are depicted in the sketch of fig. 4.5. Starting from a set of energy levels $\{E_n\}$ and probabilities $\{P_n\}$, we can shift the energies to $\{E'_n\}$. The resulting change in energy $(\Delta E)_{\rm I} = -W$ is identified with the work done *on* the system. We could also modify the probabilities to $\{P'_n\}$ without changing the energies. The energy change in this case is the heat absorbed *by* the system: $(\Delta E)_{\rm II} = Q$. This provides us with a statistical and microscopic interpretation of the First Law of Thermodynamics.

### 4.5.7 Generalized susceptibilities

Suppose our Hamiltonian is of the form

$$\hat{H} = \hat{H}(\lambda) = \hat{H}_0 - \lambda \, \hat{Q} \ , \tag{4.111}$$

where $\lambda$ is an intensive parameter, such as magnetic field. Then

$$Z(\lambda) = \mathsf{Tr} \, e^{-\beta(\hat{H}_0 - \lambda \hat{Q})} \tag{4.112}$$

and

$$\frac{1}{Z} \frac{\partial Z}{\partial \lambda} = \beta \cdot \frac{1}{Z} \, \mathsf{Tr} \, \Big( \hat{Q} \, e^{-\beta \hat{H}(\lambda)} \Big) = \beta \, \langle \hat{Q} \rangle \ . \tag{4.113}$$

But then from $Z = e^{-\beta F}$ we have

$$Q(\lambda, T) = \langle \, \hat{Q} \, \rangle = -\bigg( \frac{\partial F}{\partial \lambda} \bigg)_T \ . \tag{4.114}$$

---

[5] In deriving eqn. 4.110, we have used the so-called Feynman-Hellman theorem of quantum mechanics: $d\langle n|\hat{H}|n\rangle = \langle n| \, d\hat{H} \, |n\rangle$, if $|n\rangle$ is an energy eigenstate.

Typically we will take $Q$ to be an extensive quantity. We can now define the *susceptibility* $\chi$ as

$$\chi = \frac{1}{V}\frac{\partial Q}{\partial \lambda} = -\frac{1}{V}\frac{\partial^2 F}{\partial \lambda^2} \, . \tag{4.115}$$

The volume factor in the denominator ensures that $\chi$ is intensive.

It is important to realize that we have assumed here that $\big[\hat{H}_0 \, , \, \hat{Q}\big] = 0$, *i.e.* the 'bare' Hamiltonian $\hat{H}_0$ and the operator $\hat{Q}$ commute. If they do not commute, then the response functions must be computed within a proper quantum mechanical formalism, which we shall not discuss here.

Note also that we can imagine an entire family of observables $\big\{\hat{Q}_k\big\}$ satisfying $\big[\hat{Q}_k \, , \, \hat{Q}_{k'}\big] = 0$ and $\big[\hat{H}_0 \, , \, \hat{Q}_k\big] = 0$, for all $k$ and $k'$. Then for the Hamiltonian

$$\hat{H}\,(\vec{\lambda}) = \hat{H}_0 - \sum_k \lambda_k \, \hat{Q}_k \, , \tag{4.116}$$

we have that

$$Q_k(\vec{\lambda},T) = \langle\, \hat{Q}_k \,\rangle = -\bigg(\frac{\partial F}{\partial \lambda_k}\bigg)_{T,\,N_a,\,\lambda_{k'\neq k}} \tag{4.117}$$

and we may define an entire matrix of susceptibilities,

$$\chi_{kl} = \frac{1}{V}\frac{\partial Q_k}{\partial \lambda_l} = -\frac{1}{V}\frac{\partial^2 F}{\partial \lambda_k \, \partial \lambda_l} \, . \tag{4.118}$$

## 4.6 Grand Canonical Ensemble (GCE)

### 4.6.1 Grand canonical distribution and partition function

Consider once again the situation depicted in fig. 4.2, where a system $S$ is in contact with a world $W$, their union $U = W \cup S$ being called the 'universe'. We assume that the system's volume $V_{\rm S}$ is fixed, but otherwise it is allowed to exchange energy and particle number with $W$. Hence, the system's energy $E_{\rm S}$ and particle number $N_{\rm S}$ will fluctuate. We ask what is the probability that $S$ is in a state $|\, n\,\rangle$ with energy $E_n$ and particle number $N_n$. This is given by the ratio

$$\begin{aligned} P_n &= \lim_{\Delta E \to 0} \frac{D_{\rm W}(E_{\rm U} - E_n \, , \, N_{\rm U} - N_n)\, \Delta E}{D_{\rm U}(E_{\rm U}, N_{\rm U})\, \Delta E} \\ &= \frac{\text{\# of states accessible to } W \text{ given that } E_{\rm S} = E_n \text{ and } N_{\rm S} = N_n}{\text{total \# of states in } U} \, . \end{aligned} \tag{4.119}$$

Then

$$\begin{aligned} \ln P_n &= \ln D_{\rm W}(E_{\rm U} - E_n \, , \, N_{\rm U} - N_n) - \ln D_{\rm U}(E_{\rm U}, N_{\rm U}) \\ &= \ln D_{\rm W}(E_{\rm U}, N_{\rm U}) - \ln D_{\rm U}(E_{\rm U}, N_{\rm U}) \\ &\qquad - E_n \, \frac{\partial \ln D_{\rm W}(E,N)}{\partial E}\bigg|_{\substack{E=E_{\rm U}\\ N=N_{\rm U}}} - N_n \, \frac{\partial \ln D_{\rm W}(E,N)}{\partial N}\bigg|_{\substack{E=E_{\rm U}\\ N=N_{\rm U}}} + \ldots \\ &\equiv -\alpha - \beta E_n + \beta\mu N_n \, . \end{aligned} \tag{4.120}$$

The constants $\beta$ and $\mu$ are given by

$$\beta = \frac{\partial \ln D_{\rm W}(E,N)}{\partial E}\bigg|_{\substack{E=E_{\rm U}\\ N=N_{\rm U}}} = \frac{1}{k_{\rm B}T} \tag{4.121}$$

$$\mu = -k_{\rm B}T\,\frac{\partial \ln D_{\rm W}(E,N)}{\partial N}\bigg|_{\substack{E=E_{\rm U}\\ N=N_{\rm U}}} \ . \tag{4.122}$$

The quantity $\mu$ has dimensions of energy and is called the *chemical potential*. Nota bene: Some texts define the 'grand canonical Hamiltonian' $\hat{K}$ as

$$\hat{K} \equiv \hat{H} - \mu\hat{N} \ . \tag{4.123}$$

Thus, $P_n = e^{-\alpha}\,e^{-\beta(E_n - \mu N_n)}$. Once again, the constant $\alpha$ is fixed by the requirement that $\sum_n P_n = 1$:

$$P_n = \frac{1}{\Xi}\,e^{-\beta(E_n-\mu N_n)} \quad , \quad \Xi(\beta,V,\mu) = \sum_n e^{-\beta(E_n-\mu N_n)} = \mathsf{Tr}\; e^{-\beta(\hat{H}-\mu\hat{N})} = \mathsf{Tr}\; e^{-\beta\hat{K}} \ . \tag{4.124}$$

Thus, the quantum mechanical *grand canonical density matrix* is given by

$$\hat{\varrho} = \frac{e^{-\beta\hat{K}}}{\mathsf{Tr}\; e^{-\beta\hat{K}}} \ . \tag{4.125}$$

Note that $\big[\hat{\varrho},\hat{K}\big] = 0$.

The quantity $\Xi(T,V,\mu)$ is called the *grand partition function*. It stands in relation to a corresponding free energy in the usual way:

$$\Xi(T,V,\mu) \equiv e^{-\beta\Omega(T,V,\mu)} \qquad \Longleftrightarrow \qquad \Omega = -k_{\rm B}T\,\ln\Xi \ , \tag{4.126}$$

where $\Omega(T,V,\mu)$ is the *grand potential*, also known as the *Landau free energy*. The dimensionless quantity $z \equiv e^{\beta\mu}$ is called the *fugacity*.

If $\big[\hat{H},\hat{N}\big] = 0$, the grand potential may be expressed as a sum over contributions from each $N$ sector, *viz.*

$$\Xi(T,V,\mu) = \sum_N e^{\beta\mu N}\,Z(T,V,N) \ . \tag{4.127}$$

When there is more than one species, we have several chemical potentials $\{\mu_a\}$, and accordingly we define

$$\hat{K} = \hat{H} - \sum_a \mu_a\,\hat{N}_a \ , \tag{4.128}$$

with $\Xi = \mathsf{Tr}\; e^{-\beta\hat{K}}$ as before.

### 4.6.2 Entropy and Gibbs-Duhem relation

In the GCE, the Boltzmann entropy is

$$\begin{aligned} S &= -k_{\rm B}\sum_n P_n \ln P_n \\ &= -k_{\rm B}\sum_n P_n\Big(\beta\Omega - \beta E_n + \beta\mu N_n\Big) \\ &= -\frac{\Omega}{T} + \frac{\langle\hat{H}\rangle}{T} - \frac{\mu\,\langle\hat{N}\rangle}{T} \ , \end{aligned} \tag{4.129}$$

which says

$$\Omega = E - TS - \mu N \ , \tag{4.130}$$

where

$$E = \sum_n E_n \, P_n = \mathsf{Tr}\,\big(\hat{\varrho}\,\hat{H}\big) \tag{4.131}$$

$$N = \sum_n N_n \, P_n = \mathsf{Tr}\,\big(\hat{\varrho}\,\hat{N}\big) \ . \tag{4.132}$$

Therefore, $\Omega(T, V, \mu)$ is a double Legendre transform of $E(S, V, N)$, with

$$d\Omega = -S\,dT - p\,dV - N\,d\mu \ , \tag{4.133}$$

which entails

$$S = -\bigg(\frac{\partial \Omega}{\partial T}\bigg)_{V,\mu} \quad , \quad p = -\bigg(\frac{\partial \Omega}{\partial V}\bigg)_{T,\mu} \quad , \quad N = -\bigg(\frac{\partial \Omega}{\partial \mu}\bigg)_{T,V} \ . \tag{4.134}$$

Since $\Omega(T, V, \mu)$ is an extensive quantity, we must be able to write $\Omega = V\omega(T, \mu)$. We identify the function $\omega(T, \mu)$ as the negative of the pressure:

$$\begin{aligned} \frac{\partial \Omega}{\partial V} &= -\frac{k_\mathrm{B} T}{\Xi}\bigg(\frac{\partial \Xi}{\partial V}\bigg)_{T,\mu} = \frac{1}{\Xi}\sum_n \frac{\partial E_n}{\partial V}\, e^{-\beta(E_n - \mu N_n)} \\ &= \bigg(\frac{\partial E}{\partial V}\bigg)_{T,\mu} = -p(T, \mu) \ . \end{aligned} \tag{4.135}$$

Therefore,

$$\Omega = -pV \quad , \quad p = p(T, \mu) \quad \text{(equation of state)} \ . \tag{4.136}$$

This is consistent with the result from thermodynamics that $G = E - TS + pV = \mu N$. Taking the differential, we obtain the Gibbs-Duhem relation,

$$d\Omega = -S\,dT - p\,dV - N\,d\mu = -p\,dV - V\,dp \quad \Rightarrow \quad S\,dT - V\,dp + N\,d\mu = 0 \ . \tag{4.137}$$

### 4.6.3 Generalized susceptibilities in the GCE

We can appropriate the results from §4.5.7 and apply them, *mutatis mutandis*, to the GCE. Suppose we have a family of observables $\{\hat{Q}_k\}$ satisfying $\big[\hat{Q}_k \, , \, \hat{Q}_{k'}\big] = 0$ and $\big[\hat{H}_0 \, , \, \hat{Q}_k\big] = 0$ and $\big[\hat{N}_a \, , \, \hat{Q}_k\big] = 0$ for all $k$, $k'$, and $a$. Then for the grand canonical Hamiltonian

$$\hat{K}(\vec{\lambda}) = \hat{H}_0 - \sum_a \mu_a \, \hat{N}_a - \sum_k \lambda_k \, \hat{Q}_k \ , \tag{4.138}$$

we have that

$$Q_k(\vec{\lambda}, T) = \langle\, \hat{Q}_k \,\rangle = -\bigg(\frac{\partial \Omega}{\partial \lambda_k}\bigg)_{T, \mu_a, \, \lambda_{k' \neq k}} \tag{4.139}$$

and we may define the matrix of generalized susceptibilities,

$$\chi_{kl} = \frac{1}{V}\,\frac{\partial Q_k}{\partial \lambda_l} = -\frac{1}{V}\,\frac{\partial^2 \Omega}{\partial \lambda_k \, \partial \lambda_l} \ . \tag{4.140}$$

### 4.6.4 Fluctuations in the GCE

Both energy and particle number fluctuate in the GCE. Let us compute the fluctuations in particle number. We have

$$N = \langle\, \hat{N} \,\rangle = \frac{\mathsf{Tr}\ \hat{N}\, e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathsf{Tr}\ e^{-\beta(\hat{H}-\mu\hat{N})}} = \frac{1}{\beta}\,\frac{\partial}{\partial\mu}\,\ln\Xi\,. \tag{4.141}$$

Therefore,

$$\begin{aligned}\frac{1}{\beta}\,\frac{\partial N}{\partial\mu} &= \frac{\mathsf{Tr}\ \hat{N}^2\, e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathsf{Tr}\ e^{-\beta(\hat{H}-\mu\hat{N})}} - \left(\frac{\mathsf{Tr}\ \hat{N}\, e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathsf{Tr}\ e^{-\beta(\hat{H}-\mu\hat{N})}}\right)^{\!2} \\ &= \big\langle \hat{N}^2 \big\rangle - \big\langle \hat{N} \big\rangle^2\,.\end{aligned} \tag{4.142}$$

Note now that

$$\frac{\big\langle \hat{N}^2 \big\rangle - \big\langle \hat{N} \big\rangle^2}{\big\langle \hat{N} \big\rangle^2} = \frac{k_{\rm B}T}{N^2}\left(\frac{\partial N}{\partial\mu}\right)_{\!T,V} = \frac{k_{\rm B}T}{V}\,\kappa_T\,, \tag{4.143}$$

where $\kappa_T$ is the isothermal compressibility. Note:

$$\begin{aligned}\left(\frac{\partial N}{\partial\mu}\right)_{\!T,V} &= \frac{\partial(N,T,V)}{\partial(\mu,T,V)} \\ &= \frac{\partial(N,T,V)}{\partial(N,T,p)}\cdot\frac{\partial(N,T,p)}{\partial(V,T,p)}\cdot\overbrace{\frac{\partial(V,T,p)}{\partial(N,T,\mu)}}^{1}\cdot\frac{\partial(N,T,\mu)}{\partial(V,T,\mu)} \\ &= -\frac{N^2}{V^2}\left(\frac{\partial V}{\partial p}\right)_{\!T,N} = \frac{N^2}{V}\,\kappa_T\,.\end{aligned} \tag{4.144}$$

Thus,

$$\frac{(\Delta N)_{\rm RMS}}{N} = \sqrt{\frac{k_{\rm B}T\,\kappa_T}{V}}\,, \tag{4.145}$$

which again scales as $V^{-1/2}$.

### 4.6.5 Gibbs ensemble

Let the system's particle number $N$ be fixed, but let it exchange energy and volume with the world $W$. *Mutatis mutandis*, we have

$$P_n = \lim_{\Delta E\to 0}\ \lim_{\Delta V\to 0}\ \frac{D_{\rm W}(E_{\rm U}-E_n\,,\,V_{\rm U}-V_n)\,\Delta E\,\Delta V}{D_{\rm U}(E_{\rm U},V_{\rm U})\,\Delta E\,\Delta V}\,. \tag{4.146}$$

Then

$$\begin{aligned}\ln P_n &= \ln D_{\rm W}(E_{\rm U}-E_n\,,\,V_{\rm U}-V_n) - \ln D_{\rm U}(E_{\rm U},V_{\rm U}) \\ &= \ln D_{\rm W}(E_{\rm U},V_{\rm U}) - \ln D_{\rm U}(E_{\rm U},V_{\rm U}) \\ &\qquad - E_n\,\frac{\partial\ln D_{\rm W}(E,V)}{\partial E}\bigg|_{\substack{E=E_{\rm U}\\ V=V_{\rm U}}} - V_n\,\frac{\partial\ln D_{\rm W}(E,V)}{\partial V}\bigg|_{\substack{E=E_{\rm U}\\ V=V_{\rm U}}} + \ldots \\ &\equiv -\alpha - \beta E_n - \beta p\,V_n\,.\end{aligned} \tag{4.147}$$

The constants $\beta$ and $p$ are given by

$$\beta = \frac{\partial \ln D_{\rm W}(E,V)}{\partial E}\bigg|_{\substack{E=E_{\rm U}\\ V=V_{\rm U}}} = \frac{1}{k_{\rm B}T} \tag{4.148}$$

$$p = k_{\rm B}T\,\frac{\partial \ln D_{\rm W}(E,V)}{\partial V}\bigg|_{\substack{E=E_{\rm U}\\ V=V_{\rm U}}} \ . \tag{4.149}$$

The corresponding partition function is

$$Y(T,p,N) = \mathsf{Tr}\ e^{-\beta(\hat{H}+pV)} = \frac{1}{V_0}\int\limits_0^\infty \! dV\, e^{-\beta pV}\, Z(T,V,N) \equiv e^{-\beta G(T,p,N)} \ , \tag{4.150}$$

where $V_0$ is a constant which has dimensions of volume. The factor $V_0^{-1}$ in front of the integral renders $Y$ dimensionless. Note that $G(V_0') = G(V_0) + k_{\rm B}T\ln(V_0'/V_0)$, so the difference is not extensive and can be neglected in the thermodynamic limit. In other words, it doesn't matter what constant we choose for $V_0$ since it contributes subextensively to $G$. Moreover, in computing averages, the constant $V_0$ divides out in the ratio of numerator and denominator. Like the Helmholtz free energy, the Gibbs free energy $G(T,p,N)$ is also a double Legendre transform of the energy $E(S,V,N)$, *viz.*

$$\begin{aligned} G &= E - TS + pV \\ dG &= -S\,dT + V\,dp + \mu\,dN \ , \end{aligned} \tag{4.151}$$

which entails

$$S = -\bigg(\frac{\partial G}{\partial T}\bigg)_{p,N} \quad , \quad V = +\bigg(\frac{\partial G}{\partial p}\bigg)_{T,N} \quad , \quad \mu = +\bigg(\frac{\partial G}{\partial N}\bigg)_{T,p} \ . \tag{4.152}$$

## 4.7 Statistical Ensembles from Maximum Entropy

The basic principle: maximize the entropy,

$$S = -k_{\rm B}\sum_n P_n \ln P_n \ . \tag{4.153}$$

### 4.7.1 $\mu$CE

We maximize $S$ subject to the single constraint

$$C = \sum_n P_n - 1 = 0 \ . \tag{4.154}$$

We implement the constraint $C=0$ with a Lagrange multiplier, $\bar{\lambda} \equiv k_{\rm B}\,\lambda$, writing

$$S^* = S - k_{\rm B}\,\lambda\, C \ , \tag{4.155}$$

and freely extremizing over the distribution $\{P_n\}$ and the Lagrange multiplier $\lambda$. Thus,

$$\begin{aligned} \delta S^* &= \delta S - k_{\rm B}\lambda\,\delta C - k_{\rm B}\,C\,\delta\lambda \\ &= -k_{\rm B}\sum_n \Big[\ln P_n + 1 + \lambda\Big]\delta P_n - k_{\rm B}\,C\,\delta\lambda \equiv 0 \ . \end{aligned} \tag{4.156}$$

We conclude that $C = 0$ and that

$$\ln P_n = -\big(1+\lambda\big) \ , \tag{4.157}$$

and we fix $\lambda$ by the normalization condition $\sum_n P_n = 1$. This gives

$$P_n = \frac{1}{\Omega} \qquad , \qquad \Omega = \sum_n \Theta(E + \Delta E - E_n)\,\Theta(E_n - E) \ . \tag{4.158}$$

Note that $\Omega$ is the number of states with energies between $E$ and $E + \Delta E$.

### 4.7.2 OCE

We maximize $S$ subject to the two constraints

$$C_1 = \sum_n P_n - 1 = 0 \qquad , \qquad C_2 = \sum_n E_n\,P_n - E = 0 \ . \tag{4.159}$$

We now have two Lagrange multipliers. We write

$$S^* = S - k_{\rm B} \sum_{j=1}^2 \lambda_j\, C_j \ , \tag{4.160}$$

and we freely extremize over $\{P_n\}$ and $\{C_j\}$. We therefore have

$$\begin{aligned} \delta S^* &= \delta S - k_{\rm B} \sum_n \big(\lambda_1 + \lambda_2\, E_n\big)\, \delta P_n - k_{\rm B} \sum_{j=1}^2 C_j\, \delta\lambda_j \\ &= -k_{\rm B} \sum_n \Big[ \ln P_n + 1 + \lambda_1 + \lambda_2\, E_n \Big] \delta P_n - k_{\rm B} \sum_{j=1}^2 C_j\, \delta\lambda_j \equiv 0 \ . \end{aligned} \tag{4.161}$$

Thus, $C_1 = C_2 = 0$ and

$$\ln P_n = -\big(1 + \lambda_1 + \lambda_2\, E_n\big) \ . \tag{4.162}$$

We define $\lambda_2 \equiv \beta$ and we fix $\lambda_1$ by normalization. This yields

$$P_n = \frac{1}{Z}\, e^{-\beta E_n} \qquad , \qquad Z = \sum_n e^{-\beta E_n} \ . \tag{4.163}$$

### 4.7.3 GCE

We maximize $S$ subject to the three constraints

$$C_1 = \sum_n P_n - 1 = 0 \quad , \quad C_2 = \sum_n E_n\, P_n - E = 0 \quad , \quad C_3 = \sum_n N_n\, P_n - N = 0 \ . \tag{4.164}$$

We now have three Lagrange multipliers. We write

$$S^* = S - k_{\rm B} \sum_{j=1}^3 \lambda_j\, C_j \ , \tag{4.165}$$

and hence

$$\begin{aligned}\delta S^* &= \delta S - k_B \sum_n \big(\lambda_1 + \lambda_2\, E_n + \lambda_3\, N_n\big)\, \delta P_n - k_B \sum_{j=1}^{3} C_j\, \delta\lambda_j \\ &= -k_B \sum_n \Big[\ln P_n + 1 + \lambda_1 + \lambda_2\, E_n + \lambda_3\, N_n\Big] \delta P_n - k_B \sum_{j=1}^{3} C_j\, \delta\lambda_j \equiv 0\ .\end{aligned} \tag{4.166}$$

Thus, $C_1 = C_2 = C_3 = 0$ and

$$\ln P_n = -\big(1 + \lambda_1 + \lambda_2\, E_n + \lambda_3\, N_n\big)\ . \tag{4.167}$$

We define $\lambda_2 \equiv \beta$ and $\lambda_3 \equiv -\beta\mu$, and we fix $\lambda_1$ by normalization. This yields

$$P_n = \frac{1}{\Xi}\, e^{-\beta(E_n - \mu N_n)} \qquad , \qquad \Xi = \sum_n e^{-\beta(E_n - \mu N_n)}\ . \tag{4.168}$$

## 4.8 Ideal Gas Statistical Mechanics

The ordinary canonical partition function for the ideal gas was computed in eqn. 4.25. We found

$$\begin{aligned}Z(T,V,N) &= \frac{1}{N!} \prod_{i=1}^{N} \int \frac{d^d\!x_i\, d^d\!p_i}{(2\pi\hbar)^d}\, e^{-\beta \boldsymbol{p}_i^2/2m} \\ &= \frac{V^N}{N!} \left( \int\limits_{-\infty}^{\infty} \frac{dp}{2\pi\hbar}\, e^{-\beta p^2/2m} \right)^{Nd} \\ &= \frac{1}{N!} \left(\frac{V}{\lambda_T^d}\right)^{N} ,\end{aligned} \tag{4.169}$$

where $\lambda_T$ is the *thermal wavelength*:

$$\lambda_T = \sqrt{2\pi\hbar^2/m k_B T}\ . \tag{4.170}$$

The physical interpretation of $\lambda_T$ is that it is the de Broglie wavelength for a particle of mass $m$ which has a kinetic energy of $k_B T$.

In the GCE, we have

$$\begin{aligned}\Xi(T,V,\mu) &= \sum_{N=0}^{\infty} e^{\beta\mu N}\, Z(T,V,N) \\ &= \sum_{N=1}^{\infty} \frac{1}{N!} \left(\frac{V e^{\mu/k_B T}}{\lambda_T^d}\right)^{N} = \exp\left(\frac{V e^{\mu/k_B T}}{\lambda_T^d}\right) .\end{aligned} \tag{4.171}$$

From $\Xi = e^{-\Omega/k_B T}$, we have the grand potential is

$$\Omega(T,V,\mu) = -V k_B T\, e^{\mu/k_B T} \big/ \lambda_T^d\ . \tag{4.172}$$

Since $\Omega = -pV$ (see §4.6.2), we have

$$p(T,\mu) = k_B T\, \lambda_T^{-d}\, e^{\mu/k_B T}\ . \tag{4.173}$$

The number density can also be calculated:

$$n = \frac{N}{V} = -\frac{1}{V} \left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = \lambda_T^{-d}\, e^{\mu/k_B T}\ . \tag{4.174}$$

Combined, the last two equations recapitulate the ideal gas law, $pV = N k_B T$.

### 4.8.1 Maxwell velocity distribution

The distribution function for momenta is given by

$$g(\boldsymbol{p}) = \Big\langle \frac{1}{N} \sum_{i=1}^{N} \delta(\boldsymbol{p}_i - \boldsymbol{p}) \Big\rangle \ . \tag{4.175}$$

Note that $g(\boldsymbol{p}) = \big\langle \delta(\boldsymbol{p}_i - \boldsymbol{p}) \big\rangle$ is the same for every particle, independent of its label $i$. We compute the average $\langle A \rangle = \mathsf{Tr}\,\big(A e^{-\beta \hat{H}}\big) / \,\mathsf{Tr}\, e^{-\beta \hat{H}}$. Setting $i=1$, all the integrals other than that over $\boldsymbol{p}_1$ divide out between numerator and denominator. We then have

$$\begin{aligned} g(\boldsymbol{p}) &= \frac{\int\! d^3\!p_1 \; \delta(\boldsymbol{p}_1 - \boldsymbol{p}) \, e^{-\beta \boldsymbol{p}_1^2/2m}}{\int\! d^3\!p_1 \; e^{-\beta \boldsymbol{p}_1^2/2m}} \\ &= (2\pi m k_{\rm B} T)^{-3/2} \, e^{-\beta \boldsymbol{p}^2/2m} \ . \end{aligned} \tag{4.176}$$

Textbooks commonly refer to the *velocity distribution* $f(\boldsymbol{v})$, which is related to $g(\boldsymbol{p})$ by

$$f(\boldsymbol{v}) \, d^3\!v = g(\boldsymbol{p}) \, d^3\!p \ . \tag{4.177}$$

Hence,

$$f(\boldsymbol{v}) = \left( \frac{m}{2\pi k_{\rm B} T} \right)^{3/2} e^{-m\boldsymbol{v}^2/2k_{\rm B}T} \ . \tag{4.178}$$

This is known as the *Maxwell velocity distribution*. Note that the distributions are normalized, *viz.*

$$\int\! d^3\!p \; g(\boldsymbol{p}) = \int\! d^3\!v \; f(\boldsymbol{v}) = 1 \ . \tag{4.179}$$

If we are only interested in averaging functions of $v = |\boldsymbol{v}|$ which are isotropic, then we can define the *Maxwell speed distribution*, $\tilde{f}(v)$, as

$$\tilde{f}(v) = 4\pi \, v^2 f(\boldsymbol{v}) = 4\pi \left( \frac{m}{2\pi k_{\rm B} T} \right)^{3/2} v^2 \, e^{-mv^2/2k_{\rm B}T} \ . \tag{4.180}$$

Note that $\tilde{f}(v)$ is normalized according to

$$\int\limits_0^\infty \! dv \; \tilde{f}(v) = 1 \ . \tag{4.181}$$

It is convenient to represent $v$ in units of $v_0 = \sqrt{k_{\rm B}T/m}$, in which case

$$\tilde{f}(v) = \frac{1}{v_0} \, \varphi(v/v_0) \qquad , \qquad \varphi(s) = \sqrt{\tfrac{2}{\pi}} \, s^2 \, e^{-s^2/2} \ . \tag{4.182}$$

The distribution $\varphi(s)$ is shown in fig. 4.6. Computing averages, we have

$$C_k \equiv \langle s^k \rangle = \int\limits_0^\infty \! ds \; s^k \, \varphi(s) = 2^{k/2} \cdot \frac{2}{\sqrt{\pi}} \, \Gamma\big(\tfrac{3}{2} + \tfrac{k}{2}\big) \ . \tag{4.183}$$

Thus, $C_0 = 1$, $C_1 = \sqrt{\frac{8}{\pi}}$, $C_2 = 3$, *etc.* The speed averages are

$$\big\langle v^k \big\rangle = C_k \left( \frac{k_{\rm B}T}{m} \right)^{k/2} \ . \tag{4.184}$$

Note that the average *velocity* is $\langle \boldsymbol{v} \rangle = 0$, but the average *speed* is $\langle v \rangle = \sqrt{8 k_{\rm B} T/\pi m}$. The speed distribution is plotted in fig. 4.6.

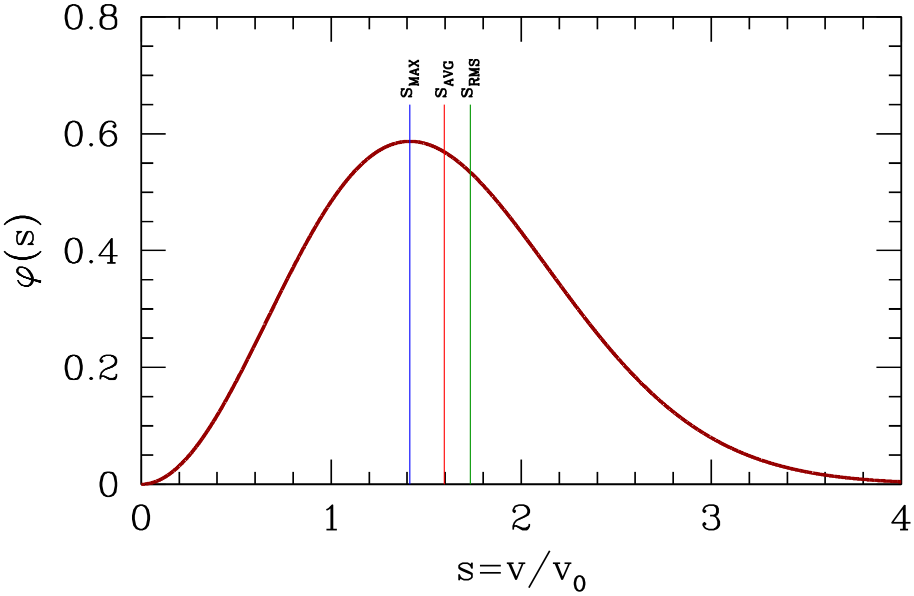

Figure 4.6: Maxwell distribution of speeds $\varphi(v/v_0)$. The most probable speed is $v_{\rm MAX} = \sqrt{2}\, v_0$. The average speed is $v_{\rm AVG} = \sqrt{\frac{8}{\pi}}\, v_0$. The RMS speed is $v_{\rm RMS} = \sqrt{3}\, v_0$.

### 4.8.2 Equipartition

The Hamiltonian for ballistic (*i.e.* massive nonrelativistic) particles is quadratic in the individual components of each momentum $\boldsymbol{p}_i$. There are other cases in which a classical degree of freedom appears quadratically in $\hat{H}$ as well. For example, an individual normal mode $\xi$ of a system of coupled oscillators has the Lagrangian

$$L = \tfrac{1}{2}\dot{\xi}^2 - \tfrac{1}{2}\,\omega_0^2\,\xi^2 \ , \tag{4.185}$$

where the dimensions of $\xi$ are $[\xi] = M^{1/2}L$ by convention. The Hamiltonian for this normal mode is then

$$\hat{H} = \frac{p^2}{2} + \tfrac{1}{2}\,\omega_0^2\,\xi^2 \ , \tag{4.186}$$

from which we see that both the kinetic as well as potential energy terms enter quadratically into the Hamiltonian. The classical rotational kinetic energy is also quadratic in the angular momentum components.

Let us compute the contribution of a single quadratic degree of freedom in $\hat{H}$ to the partition function. We'll call this degree of freedom $\zeta$ – it may be a position or momentum or angular momentum – and we'll write its contribution to $\hat{H}$ as

$$\hat{H}_\zeta = \tfrac{1}{2}K\zeta^2 \ , \tag{4.187}$$

where $K$ is some constant. Integrating over $\zeta$ yields the following factor in the partition function:

$$\int\limits_{-\infty}^{\infty}\! d\zeta\; e^{-\beta K\zeta^2/2} = \bigg(\frac{2\pi}{K\beta}\bigg)^{1/2} \ . \tag{4.188}$$

The contribution to the Helmholtz free energy is then

$$\Delta F_\zeta = \tfrac{1}{2}k_{\rm B}T\ln\bigg(\frac{K}{2\pi k_{\rm B}T}\bigg) \ , \tag{4.189}$$

and therefore the contribution to the internal energy $E$ is

$$\Delta E_\zeta = \frac{\partial}{\partial\beta}\big(\beta\,\Delta F_\zeta\big) = \frac{1}{2\beta} = \tfrac{1}{2}k_{\rm B}T\ . \tag{4.190}$$

We have thus derived what is commonly called the *equipartition theorem* of classical statistical mechanics:

> *To each degree of freedom which enters the Hamiltonian quadratically is associated a contribution $\frac{1}{2}k_{\rm B}T$ to the internal energy of the system. This results in a concomitant contribution of $\frac{1}{2}k_{\rm B}$ to the heat capacity.*

We now see why the internal energy of a classical ideal gas with $f$ degrees of freedom per molecule is $E = \frac{1}{2}fNk_{\rm B}T$, and $C_V = \frac{1}{2}Nk_{\rm B}$. This result also has applications in the theory of solids. The atoms in a solid possess kinetic energy due to their motion, and potential energy due to the spring-like interatomic potentials which tend to keep the atoms in their preferred crystalline positions. Thus, for a three-dimensional crystal, there are *six* quadratic degrees of freedom (three positions and three momenta) per atom, and the classical energy should be $E = 3Nk_{\rm B}T$, and the heat capacity $C_V = 3Nk_{\rm B}$. As we shall see, quantum mechanics modifies this result considerably at temperatures below the highest normal mode (*i.e.* phonon) frequency, but the high temperature limit is given by the classical value $C_V = 3\nu R$ (where $\nu = N/N_{\rm A}$ is the number of moles) derived here, known as the *Dulong-Petit limit*.

### 4.8.3 Quantum statistics and the Maxwell-Boltzmann limit

Consider a system composed of $N$ noninteracting particles. The Hamiltonian is

$$\hat{H} = \sum_{j=1}^N \hat{h}_j\ . \tag{4.191}$$

The single particle Hamiltonian $\hat{h}$ has eigenstates $|\,\alpha\,\rangle$ with corresponding energy eigenvalues $\varepsilon_\alpha$. What is the partition function? Is it

$$H \overset{?}{=} \sum_{\alpha_1} \cdots \sum_{\alpha_N} e^{-\beta\left(\varepsilon_{\alpha_1} + \,\varepsilon_{\alpha_2} + \,\ldots\, + \,\varepsilon_{\alpha_N}\right)} = \zeta^N\ , \tag{4.192}$$

where $\zeta$ is the single particle partition function,

$$\zeta = \sum_\alpha e^{-\beta\varepsilon_\alpha}\ . \tag{4.193}$$

For systems where the individual particles are *distinguishable*, such as spins on a lattice which have fixed positions, this is indeed correct. But for particles free to move in a gas, this equation is *wrong*. The reason is that for *indistinguishable particles* the many particle quantum mechanical states are specified by a collection of *occupation numbers* $n_\alpha$, which tell us how many particles are in the single-particle state $|\,\alpha\,\rangle$. The energy is

$$E = \sum_\alpha n_\alpha\,\varepsilon_\alpha \tag{4.194}$$

and the total number of particles is

$$N = \sum_\alpha n_\alpha\ . \tag{4.195}$$

That is, each collection of occupation numbers $\{n_\alpha\}$ labels a unique many particle state $\big|\,\{n_\alpha\}\,\big\rangle$. In the product $\zeta^N$, the collection $\{n_\alpha\}$ occurs many times. We have therefore *overcounted* the contribution to $Z_N$ due to this state. By what factor have we overcounted? It is easy to see that the overcounting factor is

$$\text{degree of overcounting} \quad = \quad \frac{N!}{\prod_\alpha n_\alpha!} \qquad ,$$

which is the number of ways we can rearrange the labels $\alpha_j$ to arrive at the same collection $\{n_\alpha\}$. This follows from the multinomial theorem,

$$\bigg(\sum_{\alpha=1}^K x_\alpha\bigg)^{\!N} = \sum_{n_1}\sum_{n_2}\cdots\sum_{n_K} \frac{N!}{n_1!\,n_2!\cdots n_K!}\, x_1^{n_1}\, x_2^{n_2}\cdots x_K^{n_K}\;\delta_{N,n_1+\ldots+n_K}\ . \tag{4.196}$$

Thus, the correct expression for $Z_N$ is

$$\begin{aligned} Z_N &= \sum_{\{n_\alpha\}} e^{-\beta\sum_\alpha n_\alpha\varepsilon_\alpha}\,\delta_{N,\sum_\alpha n_\alpha} \\ &= \sum_{\alpha_1}\sum_{\alpha_2}\cdots\sum_{\alpha_N}\bigg(\frac{\prod_\alpha n_\alpha!}{N!}\bigg)\, e^{-\beta(\varepsilon_{\alpha_1}+\,\varepsilon_{\alpha_2}+\,\ldots\,+\,\varepsilon_{\alpha_N})}\ . \end{aligned} \tag{4.197}$$

When we study quantum statistics, we shall learn how to handle these constrained sums. For now it suffices to note that in the high temperature limit, almost all the $n_\alpha$ are either $0$ or $1$, hence

$$Z_N \approx \frac{\zeta^N}{N!}\ . \tag{4.198}$$

This is the classical *Maxwell-Boltzmann limit* of quantum statistical mechanics. We now see the origin of the $1/N!$ term which is so important in the thermodynamics of entropy of mixing.

## 4.9 Selected Examples

### 4.9.1 Spins in an external magnetic field

Consider a system of $N_\mathrm{s}$ spins , each of which can be either up ($\sigma=+1$) or down ($\sigma=-1$). The Hamiltonian for this system is

$$\hat{H} = -\mu_0 H\sum_{j=1}^{N_\mathrm{s}}\sigma_j\ , \tag{4.199}$$

where now we write $\hat{H}$ for the Hamiltonian, to distinguish it from the external magnetic field $H$, and $\mu_0$ is the magnetic moment per particle. We treat this system within the ordinary canonical ensemble. The partition function is

$$Z = \sum_{\sigma_1}\cdots\sum_{\sigma_{N_\mathrm{s}}} e^{-\beta\hat{H}} = \zeta^{N_\mathrm{s}}\ , \tag{4.200}$$

where $\zeta$ is the single particle partition function:

$$\zeta = \sum_{\sigma=\pm1} e^{\mu_0 H\sigma/k_\mathrm{B}T} = 2\cosh\bigg(\frac{\mu_0 H}{k_\mathrm{B}T}\bigg)\ . \tag{4.201}$$

The Helmholtz free energy is then

$$F(T,H,N_{\mathsf{s}}) = -k_{\mathrm{B}}T\ln Z = -N_{\mathsf{s}}\,k_{\mathrm{B}}T\ln\left[2\cosh\!\left(\frac{\mu_0 H}{k_{\mathrm{B}}T}\right)\right] . \tag{4.202}$$

The magnetization is

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,\,N_{\mathsf{s}}} = N_{\mathsf{s}}\,\mu_0\tanh\!\left(\frac{\mu_0 H}{k_{\mathrm{B}}T}\right) . \tag{4.203}$$

The energy is

$$E = \frac{\partial}{\partial\beta}\,(\beta F) = -N_{\mathsf{s}}\,\mu_0 H\tanh\!\left(\frac{\mu_0 H}{k_{\mathrm{B}}T}\right) . \tag{4.204}$$

Hence, $E = -HM$, which we already knew, from the form of $\hat{H}$ itself.

Each spin here is independent. The probability that a given spin has polarization $\sigma$ is

$$P_\sigma = \frac{e^{\beta\mu_0 H\sigma}}{e^{\beta\mu_0 H} + e^{-\beta\mu_0 H}} . \tag{4.205}$$

The total probability is unity, and the average polarization is a weighted average of $\sigma = +1$ and $\sigma = -1$ contributions:

$$P_\uparrow + P_\downarrow = 1 \qquad , \qquad \langle\sigma\rangle = P_\uparrow - P_\downarrow = \tanh\!\left(\frac{\mu_0 H}{k_{\mathrm{B}}T}\right) . \tag{4.206}$$

At low temperatures $T \ll \mu_0 H/k_{\mathrm{B}}$, we have $P_\uparrow \approx 1 - e^{-2\mu_0 H/k_{\mathrm{B}}T}$. At high temperatures $T > \mu_0 H/k_{\mathrm{B}}$, the two polarizations are equally likely, and $P_\sigma \approx \frac{1}{2}\left(1 + \frac{\sigma\mu_0 H}{k_{\mathrm{B}}T}\right)$.

The *isothermal magnetic susceptibility* is defined as

$$\chi_T = \frac{1}{N_{\mathsf{s}}}\left(\frac{\partial M}{\partial H}\right)_T = \frac{\mu_0^2}{k_{\mathrm{B}}T}\,\mathrm{sech}^2\!\left(\frac{\mu_0 H}{k_{\mathrm{B}}T}\right) . \tag{4.207}$$

(Typically this is computed per unit volume rather than per particle.) At $H = 0$, we have $\chi_T = \mu_0^2/k_{\mathrm{B}}T$, which is known as the *Curie law*.

**Aside**

The energy $E = -HM$ here is not the same quantity we discussed in our study of thermodynamics. In fact, the thermodynamic energy for this problem vanishes! Here is why. To avoid confusion, we'll need to invoke a new symbol for the thermodynamic energy, $\mathcal{E}$. Recall that the thermodynamic energy $\mathcal{E}$ is a function of extensive quantities, meaning $\mathcal{E} = \mathcal{E}(S, M, N_{\mathsf{s}})$. It is obtained from the free energy $F(T, H, N_{\mathsf{s}})$ by a double Legendre transform:

$$\mathcal{E}(S,M,N_{\mathsf{s}}) = F(T,H,N_{\mathsf{s}}) + TS + HM . \tag{4.208}$$

Now from eqn. 4.202 we derive the entropy

$$S = -\frac{\partial F}{\partial T} = N_{\mathsf{s}}\,k_{\mathrm{B}}\ln\left[2\cosh\!\left(\frac{\mu_0 H}{k_{\mathrm{B}}T}\right)\right] - N_{\mathsf{s}}\,\frac{\mu_0 H}{T}\,\tanh\!\left(\frac{\mu_0 H}{k_{\mathrm{B}}T}\right) . \tag{4.209}$$

Thus, using eqns. 4.202 and 4.203, we obtain $\mathcal{E}(S, M, N_{\mathsf{s}}) = 0$.

The potential confusion here arises from our use of the expression $F(T, H, N_{\mathsf{s}})$. In thermodynamics, it is the Gibbs free energy $G(T, p, N)$ which is a double Legendre transform of the energy: $G = \mathcal{E} - TS + pV$. By analogy, with magnetic systems we should perhaps write $G = \mathcal{E} - TS - HM$, but in keeping with many textbooks we shall use the symbol $F$ and refer to it as the Helmholtz free energy. The quantity we've called $E$ in eqn. 4.204 is in fact $E = \mathcal{E} - HM$, which means $\mathcal{E} = 0$. The energy $\mathcal{E}(S, M, N_{\mathsf{s}})$ vanishes here because the spins are noninteracting.

### 4.9.2 Negative temperature (!)

Consider again a system of $N_{\mathsf{s}}$ spins, each of which can be either up $(+)$ or down $(-)$. Let $N_\sigma$ be the number of sites with spin $\sigma$, where $\sigma = \pm 1$. Clearly $N_+ + N_- = N_{\mathsf{s}}$. We now treat this system within the microcanonical ensemble.

The energy of the system is

$$E = -HM \ , \tag{4.210}$$

where $H$ is an external magnetic field, and $M = (N_+ - N_-)\mu_0$ is the total magnetization. We now compute $S(E)$ using the ordinary canonical ensemble. The number of ways of arranging the system with $N_+$ up spins is

$$\Omega = \binom{N_{\mathsf{s}}}{N_+} \ , \tag{4.211}$$

hence the entropy is

$$S = k_{\mathrm{B}} \ln \Omega = -N_{\mathsf{s}}\, k_{\mathrm{B}} \Big\{ x \ln x + (1-x) \ln(1-x) \Big\} \tag{4.212}$$

in the thermodynamic limit: $N_{\mathsf{s}} \to \infty$, $N_+ \to \infty$, $x = N_+/N_{\mathsf{s}}$ constant. Now the magnetization is $M = (N_+ - N_-)\mu_0 = (2N_+ - N_{\mathsf{s}})\mu_0$, hence if we define the maximum energy $E_0 \equiv N_{\mathsf{s}}\, \mu_0 H$, then

$$\frac{E}{E_0} = -\frac{M}{N_{\mathsf{s}}\, \mu_0} = 1 - 2x \qquad \Longrightarrow \qquad x = \frac{E_0 - E}{2E_0} \ . \tag{4.213}$$

We therefore have

$$S(E, N_{\mathsf{s}}) = -N_{\mathsf{s}}\, k_{\mathrm{B}} \Bigg[ \bigg(\frac{E_0 - E}{2E_0}\bigg) \ln\bigg(\frac{E_0 - E}{2E_0}\bigg) + \bigg(\frac{E_0 + E}{2E_0}\bigg) \ln\bigg(\frac{E_0 + E}{2E_0}\bigg) \Bigg] \ . \tag{4.214}$$

We now have

$$\frac{1}{T} = \bigg(\frac{\partial S}{\partial E}\bigg)_{N_{\mathsf{s}}} = \frac{\partial S}{\partial x}\, \frac{\partial x}{\partial E} = \frac{N_{\mathsf{s}}\, k_{\mathrm{B}}}{2E_0}\, \ln\bigg(\frac{E_0 - E}{E_0 + E}\bigg) \ . \tag{4.215}$$

We see that the temperature is positive for $-E_0 \le E < 0$ and is *negative* for $0 < E \le E_0$.

What has gone wrong? The answer is that *nothing* has gone wrong – all our calculations are perfectly correct. This system *does* exhibit the possibility of negative temperature. It is, however, unphysical in that we have neglected kinetic degrees of freedom, which result in an entropy function $S(E, N_{\mathsf{s}})$ which is an increasing function of energy. In this system, $S(E, N_{\mathsf{s}})$ achieves a maximum of $S_{\mathrm{max}} = N_{\mathsf{s}}\, k_{\mathrm{B}} \ln 2$ at $E = 0$ (*i.e.* $x = \frac{1}{2}$), and then turns over and starts decreasing. In fact, our results are completely consistent with eqn. 4.204 : the energy $E$ is an odd function of temperature. Positive energy requires negative temperature! Another example of this peculiarity is provided in the appendix in §4.11.2.

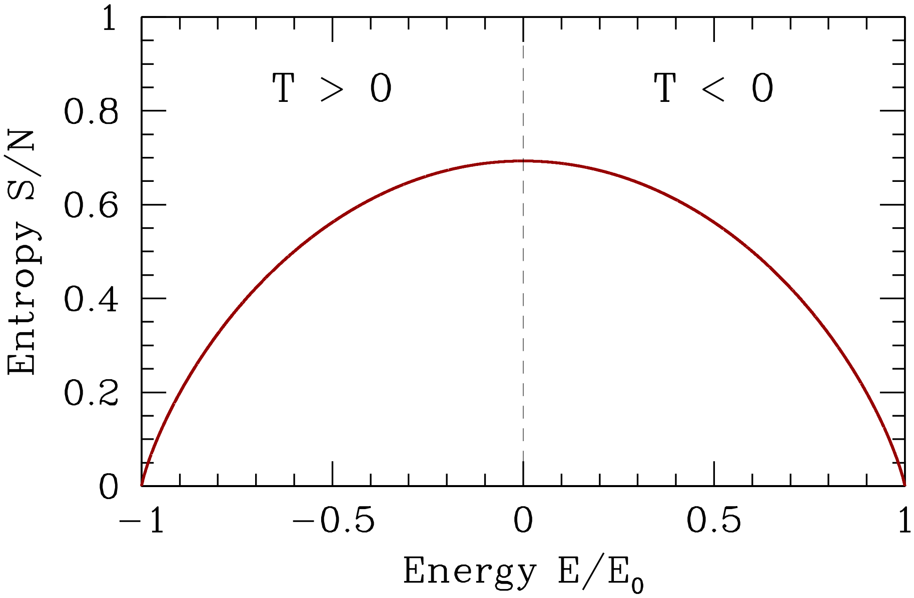

Figure 4.7: When entropy decreases with increasing energy, the temperature is negative. Typically, kinetic degrees of freedom prevent this peculiarity from manifesting in physical systems.

### 4.9.3 Adsorption

`PROBLEM:` A surface containing $N_s$ adsorption sites is in equilibrium with a monatomic ideal gas. Atoms adsorbed on the surface have an energy $-\Delta$ and no kinetic energy. Each adsorption site can accommodate at most one atom. Calculate the fraction $f$ of occupied adsorption sites as a function of the gas density $n$, the temperature $T$, the binding energy $\Delta$, and physical constants.

The grand partition function for the surface is

$$\Xi_{\text{surf}} = e^{-\Omega_{\text{surf}}/k_B T} = \big(1 + e^{\Delta/k_B T}\, e^{\mu/k_B T}\big)^{N_s} \ . \tag{4.216}$$

The fraction of occupied sites is

$$f = \frac{\langle \hat{N}_{\text{surf}} \rangle}{N_s} = -\frac{1}{N_s}\,\frac{\partial \Omega_{\text{surf}}}{\partial \mu} = \frac{e^{\mu/k_B T}}{e^{\mu/k_B T} + e^{-\Delta/k_B T}} \ . \tag{4.217}$$

Since the surface is in equilibrium with the gas, its fugacity $z = \exp(\mu/k_B T)$ and temperature $T$ are the same as in the gas.

`SOLUTION:` For a monatomic ideal gas, the single particle partition function is $\zeta = V\lambda_T^{-3}$, where $\lambda_T = \sqrt{2\pi\hbar^2/mk_B T}$ is the thermal wavelength. Thus, the grand partition function, for indistinguishable particles, is

$$\Xi_{\text{gas}} = \exp\Big(V\lambda_T^{-3}\, e^{\mu/k_B T}\Big) \ . \tag{4.218}$$

The gas density is

$$n = \frac{\langle \hat{N}_{\text{gas}} \rangle}{V} = -\frac{1}{V}\,\frac{\partial \Omega_{\text{gas}}}{\partial \mu} = \lambda_T^{-3}\, e^{\mu/k_B T} \ . \tag{4.219}$$

We can now solve for the fugacity: $z = e^{\mu/k_{\rm B}T} = n\lambda_T^3$. Thus, the fraction of occupied adsorption sites is

$$f = \frac{n\lambda_T^3}{n\lambda_T^3 + e^{-\Delta/k_{\rm B}T}} \ . \tag{4.220}$$

Interestingly, the solution for $f$ involves the constant $\hbar$.

It is always advisable to check that the solution makes sense in various limits. First of all, if the gas density tends to zero at fixed $T$ and $\Delta$, we have $f \to 0$. On the other hand, if $n \to \infty$ we have $f \to 1$, which also makes sense. At fixed $n$ and $T$, if the adsorption energy is $(-\Delta) \to -\infty$, then once again $f = 1$ since every adsorption site wants to be occupied. Conversely, taking $(-\Delta) \to +\infty$ results in $n \to 0$, since the energetic cost of adsorption is infinitely high.

### 4.9.4 Elasticity of wool

Wool consists of interlocking protein molecules which can stretch into an elongated configuration, but reversibly so. This feature gives wool its very useful elasticity. Let us model a chain of these proteins by assuming they can exist in one of two states, which we will call A and B, with energies $\varepsilon_{\rm A}$ and $\varepsilon_{\rm B}$ and lengths $\ell_{\rm A}$ and $\ell_{\rm B}$. The situation is depicted in fig. 4.8. We model these conformational degrees of freedom by a spin variable $\sigma = \pm 1$ for each molecule, where $\sigma = +1$ in the A state and $\sigma = -1$ in the B state. Suppose a chain consisting of $N$ monomers is placed under a tension $\tau$. We then have

$$\hat{H} = \sum_{j=1}^N \Big[ \tfrac{1}{2}\big(\varepsilon_{\rm A} + \varepsilon_{\rm B}\big) + \tfrac{1}{2}\big(\varepsilon_{\rm A} - \varepsilon_{\rm B}\big)\,\sigma_j \Big] \ . \tag{4.221}$$

Similarly, the length is

$$\hat{L} = \sum_{j=1}^N \Big[ \tfrac{1}{2}\big(\ell_{\rm A} + \ell_{\rm B}\big) + \tfrac{1}{2}\big(\ell_{\rm A} - \ell_{\rm B}\big)\,\sigma_j \Big] \ . \tag{4.222}$$

The Gibbs partition function is $Y = {\rm Tr}\, e^{-\hat{K}/k_{\rm B}T}$, with $\hat{K} = \hat{H} - \tau\hat{L}$ :

$$\hat{K} = \sum_{j=1}^N \Big[ \tfrac{1}{2}\big(\tilde{\varepsilon}_{\rm A} + \tilde{\varepsilon}_{\rm B}\big) + \tfrac{1}{2}\big(\tilde{\varepsilon}_{\rm A} - \tilde{\varepsilon}_{\rm B}\big)\,\sigma_j \Big] \ , \tag{4.223}$$

where $\tilde{\varepsilon}_{\rm A} \equiv \varepsilon_{\rm A} - \tau\ell_{\rm A}$ and $\tilde{\varepsilon}_{\rm B} \equiv \varepsilon_{\rm B} - \tau\ell_{\rm B}$. At $\tau = 0$ the A state is preferred for each monomer, but when $\tau$ exceeds $\tau^*$, defined by the relation $\tilde{\varepsilon}_{\rm A} = \tilde{\varepsilon}_{\rm B}$, the B state is preferred. One finds

$$\tau^* = \frac{\varepsilon_{\rm B} - \varepsilon_{\rm A}}{\ell_{\rm B} - \ell_{\rm A}} \ . \tag{4.224}$$

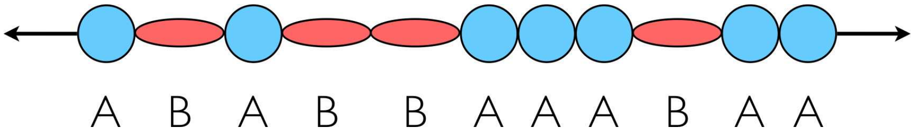

Figure 4.8: The monomers in wool are modeled as existing in one of two states. The low energy undeformed state is A, and the higher energy deformed state is B. Applying tension induces more monomers to enter the B state.

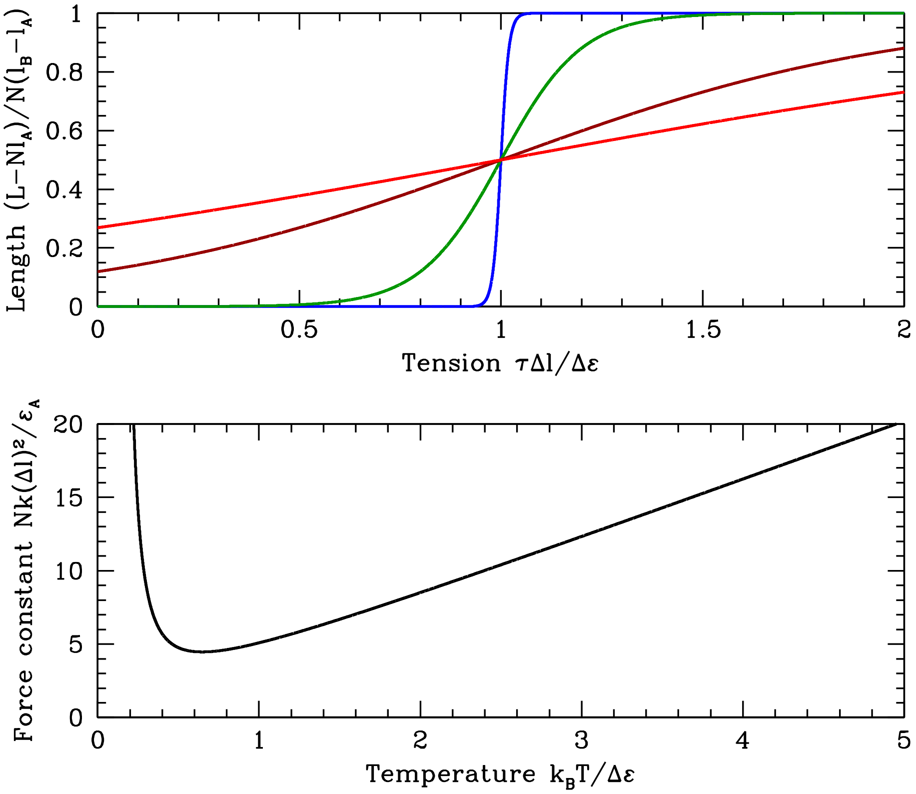

Figure 4.9: Upper panel: length $L(\tau, T)$ for $k_{\mathrm{B}}T/\tilde{\varepsilon} = 0.01$ (blue), $0.1$ (green), $0.5$ (dark red), and $1.0$ (red). Bottom panel: dimensionless force constant $k/N(\Delta\ell)^2$ *versus* temperature.

Once again, we have a set of $N$ noninteracting spins. The partition function is $Y = \zeta^N$, where $\zeta$ is the single monomer partition function,

$$\zeta = \mathrm{Tr}\; e^{-\beta\hat{h}} = e^{-\beta\tilde{\varepsilon}_{\mathrm{A}}} + e^{-\beta\tilde{\varepsilon}_{\mathrm{B}}} \,, \tag{4.225}$$

where

$$\hat{h} = \tfrac{1}{2}\big(\tilde{\varepsilon}_{\mathrm{A}} + \tilde{\varepsilon}_{\mathrm{B}}\big) + \tfrac{1}{2}\big(\tilde{\varepsilon}_{\mathrm{A}} - \tilde{\varepsilon}_{\mathrm{B}}\big)\,\sigma \,, \tag{4.226}$$

is the single spin Hamiltonian. It is convenient to define the differences

$$\Delta\varepsilon = \varepsilon_{\mathrm{B}} - \varepsilon_{\mathrm{A}} \quad , \quad \Delta\ell = \ell_{\mathrm{B}} - \ell_{\mathrm{A}} \quad , \quad \Delta\tilde{\varepsilon} = \tilde{\varepsilon}_{\mathrm{B}} - \tilde{\varepsilon}_{\mathrm{A}} \tag{4.227}$$

in which case the partition function $Y$ is

$$Y(T,\tau,N) = e^{-N\beta\,\tilde{\varepsilon}_{\mathrm{A}}}\Big[1 + e^{-\beta\Delta\tilde{\varepsilon}}\Big]^N \tag{4.228}$$

$$G(T,\tau,N) = N\tilde{\varepsilon}_{\mathrm{A}} - Nk_{\mathrm{B}}T\ln\Big[1 + e^{-\Delta\tilde{\varepsilon}/k_{\mathrm{B}}T}\Big] \tag{4.229}$$

The average length is

$$\begin{aligned} L = \langle\hat{L}\rangle &= -\bigg(\frac{\partial G}{\partial\tau}\bigg)_{T,N} \\ &= N\ell_{\mathrm{A}} + \frac{N\Delta\ell}{e^{(\Delta\varepsilon - \tau\Delta\ell)/k_{\mathrm{B}}T} + 1} \,. \end{aligned} \tag{4.230}$$

The polymer behaves as a spring, and for small $\tau$ the spring constant is

$$k = \frac{\partial\tau}{\partial L}\bigg|_{\tau=0} = \frac{4k_{\rm B}T}{N(\Delta\ell)^2}\,\cosh^2\!\bigg(\frac{\Delta\varepsilon}{2k_{\rm B}T}\bigg)\ . \tag{4.231}$$

The results are shown in fig. 4.9. Note that length increases with temperature for $\tau < \tau^*$ and decreases with temperature for $\tau > \tau^*$. Note also that $k$ diverges at both low and high temperatures. At low $T$, the energy gap $\Delta\varepsilon$ dominates and $L = N\ell_{\rm A}$, while at high temperatures $k_{\rm B}T$ dominates and $L = \frac{1}{2}N(\ell_{\rm A} + \ell_{\rm B})$.

### 4.9.5 Noninteracting spin dimers

Consider a system of noninteracting spin dimers as depicted in fig. 4.10. Each dimer contains two spins, and is described by the Hamiltonian

$$\hat H_{\rm dimer} = -J\,\sigma_1\sigma_2 - \mu_0 H\,(\sigma_1+\sigma_2)\ . \tag{4.232}$$

Here, $J$ is an *interaction energy* between the spins which comprise the dimer. If $J > 0$ the interaction is *ferromagnetic*, which prefers that the spins are aligned. That is, the lowest energy states are $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$. If $J < 0$ the interaction is *antiferromagnetic*, which prefers that spins be anti-aligned: $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$.[6]

Suppose there are $N_{\rm d}$ dimers. Then the OCE partition function is $Z = \zeta^{N_{\rm d}}$, where $\zeta(T,H)$ is the single dimer partition function. To obtain $\zeta(T,H)$, we sum over the four possible states of the two spins, obtaining

$$\begin{aligned}\zeta &= {\rm Tr}\, e^{-\hat H_{\rm dimer}/k_{\rm B}T}\\ &= 2\,e^{-J/k_{\rm B}T} + 2\,e^{J/k_{\rm B}T}\cosh\!\bigg(\frac{2\mu_0 H}{k_{\rm B}T}\bigg)\ .\end{aligned}$$

Thus, the free energy is

$$F(T,H,N_{\rm d}) = -N_{\rm d}\,k_{\rm B}T\ln 2 - N_{\rm d}\,k_{\rm B}T\ln\!\Bigg[e^{-J/k_{\rm B}T} + e^{J/k_{\rm B}T}\cosh\!\bigg(\frac{2\mu_0 H}{k_{\rm B}T}\bigg)\Bigg]\ . \tag{4.233}$$

The magnetization is

$$M = -\bigg(\frac{\partial F}{\partial H}\bigg)_{T,N_{\rm d}} = 2N_{\rm d}\,\mu_0\cdot\frac{e^{J/k_{\rm B}T}\sinh\!\Big(\frac{2\mu_0 H}{k_{\rm B}T}\Big)}{e^{-J/k_{\rm B}T} + e^{J/k_{\rm B}T}\cosh\!\Big(\frac{2\mu_0 H}{k_{\rm B}T}\Big)} \tag{4.234}$$

It is instructive to consider the zero field isothermal susceptibility per spin,

$$\chi_T = \frac{1}{2N_{\rm d}}\,\frac{\partial M}{\partial H}\bigg|_{H=0} = \frac{\mu_0^2}{k_{\rm B}T}\cdot\frac{2\,e^{J/k_{\rm B}T}}{e^{J/k_{\rm B}T} + e^{-J/k_{\rm B}T}}\ . \tag{4.235}$$

The quantity $\mu_0^2/k_{\rm B}T$ is simply the Curie susceptibility for noninteracting classical spins. Note that we correctly recover the Curie result when $J = 0$, since then the individual spins comprising each dimer are in fact noninteracting. For the ferromagnetic case, if $J \gg k_{\rm B}T$, then we obtain

$$\chi_T(J \gg k_{\rm B}T) \approx \frac{2\mu_0^2}{k_{\rm B}T}\ . \tag{4.236}$$

This has the following simple interpretation. When $J \gg k_{\rm B}T$, the spins of each dimer are effectively locked in parallel. Thus, each dimer has an effective magnetic moment $\mu_{\rm eff} = 2\mu_0$. On the other hand, there are only half as many dimers as there are spins, so the resulting Curie susceptibility per spin is $\frac{1}{2}\times(2\mu_0)^2/k_{\rm B}T$.

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[6] *Nota bene* we are concerned with classical spin configurations only – there is no superposition of states allowed in this model!

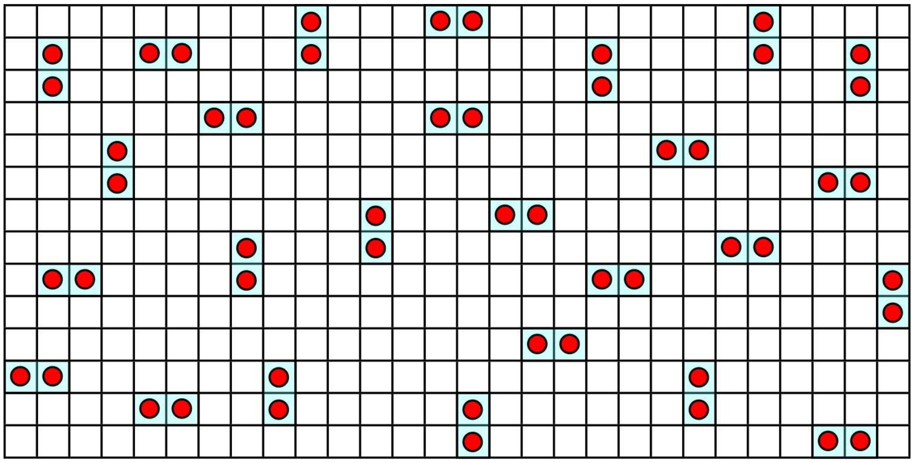

Figure 4.10: A model of noninteracting spin dimers on a lattice. Each red dot represents a classical spin for which $\sigma_j = \pm 1$.

When $-J \gg k_{\rm B}T$, the spins of each dimer are effectively locked in one of the two antiparallel configurations. We then have

$$\chi_T(-J \gg k_{\rm B}T) \approx \frac{2\mu_0^2}{k_{\rm B}T}\, e^{-2|J|/k_{\rm B}T} \ . \tag{4.237}$$

In this case, the individual dimers have essentially zero magnetic moment.

## 4.10 Statistical Mechanics of Molecular Gases

### 4.10.1 Separation of translational and internal degrees of freedom

The states of a noninteracting atom or molecule are labeled by its total momentum $\boldsymbol{p}$ and its internal quantum numbers, which we will simply write with a collective index $\alpha$, specifying rotational, vibrational, and electronic degrees of freedom. The single particle Hamiltonian is then

$$\hat{h} = \frac{\boldsymbol{p}^2}{2m} + \hat{h}_{\rm int} \ , \tag{4.238}$$

with

$$\hat{h}\,|\,\boldsymbol{k}\,,\,\alpha\,\rangle = \left(\frac{\hbar^2\boldsymbol{k}^2}{2m} + \varepsilon_\alpha\right)|\,\boldsymbol{k}\,,\,\alpha\,\rangle \ . \tag{4.239}$$

The partition function is

$$\zeta = \textsf{Tr}\; e^{-\beta\hat{h}} = \sum_{\boldsymbol{p}} e^{-\beta\boldsymbol{p}^2/2m} \sum_j g_j\, e^{-\beta\varepsilon_j} \ . \tag{4.240}$$

Here we have replaced the internal label $\alpha$ with a label $j$ of energy eigenvalues, with $g_j$ being the degeneracy of the internal state with energy $\varepsilon_j$. To do the $\boldsymbol{p}$ sum, we quantize in a box of dimensions $L_1 \times L_2 \times \cdots \times L_d$, using periodic boundary conditions. Then

$$\boldsymbol{p} = \left(\frac{2\pi\hbar n_1}{L_1}\,,\,\frac{2\pi\hbar n_2}{L_2}\,,\,\ldots\,,\,\frac{2\pi\hbar n_d}{L_d}\right) \ , \tag{4.241}$$

where each $n_i$ is an integer. Since the differences between neighboring quantized $\boldsymbol{p}$ vectors are very tiny, we can replace the sum over $\boldsymbol{p}$ by an integral:

$$\sum_{\boldsymbol{p}} \longrightarrow \int \frac{d^d\!p}{\Delta p_1 \cdots \Delta p_d} \tag{4.242}$$

where the volume in momentum space of an elementary rectangle is

$$\Delta p_1 \cdots \Delta p_d = \frac{(2\pi\hbar)^d}{L_1 \cdots L_d} = \frac{(2\pi\hbar)^d}{V} \ . \tag{4.243}$$

Thus,

$$\zeta = V\!\int\!\frac{d^d\!p}{(2\pi\hbar)^d}\, e^{-\boldsymbol{p}^2/2mk_{\rm B}T} \sum_j g_j\, e^{-\varepsilon_j/k_{\rm B}T} = V\lambda_T^{-d}\,\xi \tag{4.244}$$

$$\xi(T) = \sum_j g_j\, e^{-\varepsilon_j/k_{\rm B}T} \ . \tag{4.245}$$

Here, $\xi(T)$ is the *internal coordinate partition function*. The full $N$-particle ordinary canonical partition function is then

$$Z_N = \frac{1}{N!}\bigg(\frac{V}{\lambda_T^d}\bigg)^{\!N} \xi^N(T) \ . \tag{4.246}$$

Using Stirling's approximation, we find the Helmholtz free energy $F = -k_{\rm B}T \ln Z$ is

$$\begin{aligned} F(T,V,N) &= -Nk_{\rm B}T\bigg[\ln\!\bigg(\frac{V}{N\lambda_T^d}\bigg) + 1 + \ln\xi(T)\bigg] \\ &= -Nk_{\rm B}T\bigg[\ln\!\bigg(\frac{V}{N\lambda_T^d}\bigg) + 1\bigg] + N\varphi(T)\ , \end{aligned} \tag{4.247}$$

where

$$\varphi(T) = -k_{\rm B}T\ln\xi(T) \tag{4.248}$$

is the internal coordinate contribution to the single particle free energy. We could also compute the partition function in the Gibbs $(T,p,N)$ ensemble:

$$\begin{aligned} Y(T,p,N) = e^{-\beta G(T,p,N)} &= \frac{1}{V_0}\int\limits_0^\infty\! dV\ e^{-\beta pV}\, Z(T,V,N) \\ &= \bigg(\frac{k_{\rm B}T}{pV_0}\bigg)\bigg(\frac{k_{\rm B}T}{p\,\lambda_T^d}\bigg)^{\!N} \xi^N(T)\ . \end{aligned} \tag{4.249}$$

Thus, in the thermodynamic limit,

$$\begin{aligned} \mu(T,p) = \frac{G(T,p,N)}{N} &= k_{\rm B}T\ln\bigg(\frac{p\,\lambda_T^d}{k_{\rm B}T}\bigg) - k_{\rm B}T\ln\xi(T) \\ &= k_{\rm B}T\ln\bigg(\frac{p\,\lambda_T^d}{k_{\rm B}T}\bigg) + \varphi(T)\ . \end{aligned} \tag{4.250}$$

### 4.10.2 Ideal gas law

Since the internal coordinate contribution to the free energy is volume-independent, we have

$$V = \left(\frac{\partial G}{\partial p}\right)_{T,N} = \frac{N k_{\rm B} T}{p} \ , \tag{4.251}$$

and the ideal gas law applies. The entropy is

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,N} = N k_{\rm B}\left[\ln\left(\frac{k_{\rm B}T}{p\lambda_T^d}\right) + 1 + \tfrac{1}{2}d\right] - N\varphi'(T) \ , \tag{4.252}$$

and therefore the heat capacity is

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = \left(\tfrac{1}{2}d+1\right) N k_{\rm B} - NT\,\varphi''(T) \tag{4.253}$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \tfrac{1}{2}d N k_{\rm B} - NT\,\varphi''(T) \ . \tag{4.254}$$

Thus, any temperature variation in $C_p$ must be due to the internal degrees of freedom.

### 4.10.3 The internal coordinate partition function

At energy scales of interest we can separate the internal degrees of freedom into distinct classes, writing

$$\hat{h}_{\rm int} = \hat{h}_{\rm rot} + \hat{h}_{\rm vib} + \hat{h}_{\rm elec} \tag{4.255}$$

as a sum over internal Hamiltonians governing rotational, vibrational, and electronic degrees of freedom. Then

$$\xi_{\rm int} = \xi_{\rm rot} \cdot \xi_{\rm vib} \cdot \xi_{\rm elec} \ . \tag{4.256}$$

Associated with each class of excitation is a characteristic temperature $\Theta$. Rotational and vibrational temperatures of a few common molecules are listed in table tab. 4.1.

### 4.10.4 Rotations

Consider a class of molecules which can be approximated as an axisymmetric top. The rotational Hamiltonian is then

$$\begin{aligned} \hat{h}_{\rm rot} &= \frac{\mathsf{L}_{\rm a}^2 + \mathsf{L}_{\rm b}^2}{2I_1} + \frac{\mathsf{L}_{\rm c}^2}{2I_3} \\ &= \frac{\hbar^2 L(L+1)}{2I_1} + \left(\frac{1}{2I_3} - \frac{1}{2I_1}\right)\mathsf{L}_c^2 \ , \end{aligned} \tag{4.257}$$

where $\hat{\boldsymbol{n}}_{\rm a.b,c}(t)$ are the principal axes, with $\hat{\boldsymbol{n}}_{\rm c}$ the symmetry axis, and $\mathsf{L}_{\rm a,b,c}$ are the components of the angular momentum vector $\boldsymbol{L}$ about these instantaneous body-fixed principal axes. The components of $\boldsymbol{L}$ along *space-fixed* axes $\{x, y, z\}$ are written as $L^{x,y,z}$. Note that

$$\left[L^\mu \, , \, \mathsf{L}_c\right] = n_{\rm c}^\nu \left[L^\mu \, , \, L^\nu\right] + \left[L^\mu \, , \, n_{\rm c}^\nu\right] L^\nu = i\epsilon_{\mu\nu\lambda}\, n_{\rm c}^\nu \, L^\lambda + i\epsilon_{\mu\nu\lambda}\, n_{\rm c}^\lambda \, L^\nu = 0 \ , \tag{4.258}$$

| molecule | $\Theta_{\text{rot}}(\text{K})$ | $\Theta_{\text{vib}}(\text{K})$ |
|---|---|---|
| $H_2$ | 85.4 | 6100 |
| $N_2$ | 2.86 | 3340 |
| $H_2O$ | 13.7 , 21.0 , 39.4 | 2290 , 5180 , 5400 |

Table 4.1: Some rotational and vibrational temperatures of common molecules.

which is equivalent to the statement that $\mathsf{L}_{\text{c}} = \hat{\boldsymbol{n}}_{\text{c}} \cdot \boldsymbol{L}$ is a rotational scalar. We can therefore simultaneously specify the eigenvalues of $\{\boldsymbol{L}^2, L^z, \mathsf{L}_{\text{c}}\}$, which form a complete set of commuting observables (CSCO)[7]. The eigenvalues of $L^z$ are $m\hbar$ with $m \in \{-L, \ldots, L\}$, while those of $\mathsf{L}_{\text{c}}$ are $k\hbar$ with $k \in \{-L, \ldots, L\}$. There is a $(2L+1)$-fold degeneracy associated with the $L^z$ quantum number.

We assume the molecule is prolate, so that $I_3 < I_1$. We can the define two temperature scales,

$$\Theta = \frac{\hbar^2}{2 I_1 k_{\text{B}}} \qquad , \qquad \widetilde{\Theta} = \frac{\hbar^2}{2 I_3 k_{\text{B}}} \ . \tag{4.259}$$

Prolateness then means $\widetilde{\Theta} > \Theta$. We conclude that the rotational partition function for an axisymmetric molecule is given by

$$\xi_{\text{rot}}(T) = \sum_{L=0}^{\infty} (2L+1)\, e^{-L(L+1)\,\Theta/T} \sum_{k=-L}^{L} e^{-k^2\,(\widetilde{\Theta}-\Theta)/T} \tag{4.260}$$

In diatomic molecules, $I_3$ is extremely small, and $\widetilde{\Theta} \gg k_{\text{B}} T$ at all relevant temperatures. Only the $k=0$ term contributes to the partition sum, and we have

$$\xi_{\text{rot}}(T) = \sum_{L=0}^{\infty} (2L+1)\, e^{-L(L+1)\,\Theta/T} \ . \tag{4.261}$$

When $T \ll \Theta$, only the first few terms contribute, and

$$\xi_{\text{rot}}(T) = 1 + 3\, e^{-2\Theta/T} + 5\, e^{-6\Theta/T} + \ldots \tag{4.262}$$

In the high temperature limit, we have a slowly varying summand. The *Euler-MacLaurin summation formula* may be used to evaluate such a series:

$$\sum_{k=0}^{n} F_k = \int\limits_0^n dk\, F(k) + \tfrac{1}{2}\big[F(0) + F(n)\big] + \sum_{j=1}^{\infty} \frac{B_{2j}}{(2j)!} \Big[F^{(2j-1)}(n) - F^{(2j-1)}(0)\Big] \tag{4.263}$$

where $B_j$ is the $j^{\text{th}}$ *Bernoulli number* where

$$B_0 = 1 \quad , \quad B_1 = -\tfrac{1}{2} \quad , \quad B_2 = \tfrac{1}{6} \quad , \quad B_4 = -\tfrac{1}{30} \quad , \quad B_6 = \tfrac{1}{42} \ . \tag{4.264}$$

Thus,

$$\sum_{k=0}^{\infty} F_k = \int\limits_0^\infty dx\, F(x) + \tfrac{1}{2} F(0) - \tfrac{1}{12} F'(0) - \frac{1}{720} F'''(0) + \ldots \ . \tag{4.265}$$

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[7] Note that while we cannot simultaneously specify the eigenvalues of two components of $\boldsymbol{L}$ along axes fixed in space, we can simultaneously specify the components of $\boldsymbol{L}$ along one axis fixed in space and one axis rotating with a body. See Landau and Lifshitz, *Quantum Mechanics*, §103.

We have $F(x) = (2x+1)\,e^{-x(x+1)\Theta/T}$, for which $\int\limits_0^\infty\!dx\,F(x) = \frac{T}{\Theta}$ , hence

$$\xi_{\rm rot} = \frac{T}{\Theta} + \frac{1}{3} + \frac{1}{15}\,\frac{\Theta}{T} + \frac{4}{315}\bigg(\frac{\Theta}{T}\bigg)^2 + \ldots\ . \tag{4.266}$$

Recall that $\varphi(T) = -k_{\rm B}T\ln\xi(T)$. We conclude that $\varphi_{\rm rot}(T) \approx -3k_{\rm B}T\,e^{-2\Theta/T}$ for $T \ll \Theta$ and $\varphi_{\rm rot}(T) \approx -k_{\rm B}T\ln(T/\Theta)$ for $T \gg \Theta$. We have seen that the internal coordinate contribution to the heat capacity is $\Delta C_V = -NT\varphi''(T)$. For diatomic molecules, then, this contribution is exponentially suppressed for $T \ll \Theta$, while for high temperatures we have $\Delta C_V = Nk_{\rm B}$. One says that the rotational excitations are 'frozen out' at temperatures much below $\Theta$. Including the first few terms, we have

$$\Delta C_V(T \ll \Theta) = 12\,Nk_{\rm B}\bigg(\frac{\Theta}{T}\bigg)^2 e^{-2\Theta/T} + \ldots \tag{4.267}$$

$$\Delta C_V(T \gg \Theta) = Nk_{\rm B}\Bigg\{1 + \frac{1}{45}\bigg(\frac{\Theta}{T}\bigg)^2 + \frac{16}{945}\bigg(\frac{\Theta}{T}\bigg)^3 + \ldots\Bigg\}\ . \tag{4.268}$$

Note that $C_V$ overshoots its limiting value of $Nk_{\rm B}$ and asymptotically approaches it from above.

Special care must be taken in the case of homonuclear diatomic molecules, for then only even or odd $L$ states are allowed, depending on the total nuclear spin. This is discussed below in §4.10.7.

For polyatomic molecules, the moments of inertia generally are large enough that the molecule's rotations can be considered classically. We then have

$$\varepsilon(\mathsf{L}_{\rm a},\mathsf{L}_{\rm b},\mathsf{L}_{\rm c}) = \frac{\mathsf{L}_{\rm a}^2}{2I_1} + \frac{\mathsf{L}_{\rm b}^2}{2I_2} + \frac{\mathsf{L}_{\rm c}^2}{2I_3}\ . \tag{4.269}$$

We then have

$$\xi_{\rm rot}(T) = \frac{1}{g_{\rm rot}}\int\!\frac{d\mathsf{L}_{\rm a}\,d\mathsf{L}_{\rm b}\,d\mathsf{L}_{\rm c}\,d\phi\,d\theta\,d\psi}{(2\pi\hbar)^3}\;e^{-\varepsilon(\mathsf{L}_{\rm a}\,\mathsf{L}_{\rm b}\,\mathsf{L}_{\rm c})/k_{\rm B}T}\ , \tag{4.270}$$

where $(\phi,\theta\,\psi)$ are the Euler angles. Recall $\phi \in [0,2\pi]$, $\theta \in [0,\pi]$, and $\psi \in [0,2\pi]$. The factor $g_{\rm rot}$ accounts for physically indistinguishable orientations of the molecule brought about by rotations, which can happen when more than one of the nuclei is the same. We then have

$$\xi_{\rm rot}(T) = \bigg(\frac{2k_{\rm B}T}{\hbar^2}\bigg)^{3/2}\sqrt{\pi I_1 I_2 I_3}\ . \tag{4.271}$$

This leads to $\Delta C_V = \frac{3}{2}Nk_{\rm B}$.

### 4.10.5 Vibrations

Vibrational frequencies are often given in units of inverse wavelength, such as ${\rm cm}^{-1}$, called a *wavenumber*. To convert to a temperature scale $T^*$, we write $k_{\rm B}T^* = h\nu = hc/\lambda$, hence $T^* = (hc/k_{\rm B})\,\lambda^{-1}$, and we multiply by

$$\frac{hc}{k_{\rm B}} = 1.436\,{\rm K}\cdot{\rm cm}\ . \tag{4.272}$$

For example, infrared absorption ($\sim 50$ ${\rm cm}^{-1}$ to $10^4$ ${\rm cm}^{-1}$) reveals that the 'asymmetric stretch' mode of the $H_2O$ molecule has a vibrational frequency of $\nu = 3756\,{\rm cm}^{-1}$. The corresponding temperature scale is $T^* = 5394\,{\rm K}$.

Vibrations are normal modes of oscillations. A single normal mode Hamiltonian is of the form

$$\hat{h} = \frac{p^2}{2m} + \tfrac{1}{2} m\omega^2 q^2 = \hbar\omega\big(a^\dagger a + \tfrac{1}{2}\big) \ . \tag{4.273}$$

In general there are many vibrational modes, hence many normal mode frequencies $\omega_\alpha$. We then must sum over all of them, resulting in

$$\xi_{\rm vib} = \prod_\alpha \xi^{(\alpha)}_{\rm vib} \ . \tag{4.274}$$

For each such normal mode, the contribution is

$$\begin{aligned}\xi &= \sum_{n=0}^\infty e^{-(n+\frac{1}{2})\hbar\omega/k_{\rm B}T} = e^{-\hbar\omega/2k_{\rm B}T} \sum_{n=0}^\infty \Big(e^{-\hbar\omega/k_{\rm B}T}\Big)^n \\ &= \frac{e^{-\hbar\omega/2k_{\rm B}T}}{1-e^{-\hbar\omega/k_{\rm B}T}} = \frac{1}{2\sinh(\Theta/2T)} \ ,\end{aligned} \tag{4.275}$$

where $\Theta = \hbar\omega/k_{\rm B}$. Then

$$\begin{aligned}\varphi &= k_{\rm B}T \ln\Big(2\sinh(\Theta/2T)\Big) \\ &= \tfrac{1}{2}k_{\rm B}\Theta + k_{\rm B}T\ln\big(1-e^{-\Theta/T}\big) \ .\end{aligned} \tag{4.276}$$

The contribution to the heat capacity is

$$\begin{aligned}\Delta C_V &= N k_{\rm B} \bigg(\frac{\Theta}{T}\bigg)^2 \frac{e^{\Theta/T}}{(e^{\Theta/T}-1)^2} \\ &= \begin{cases} N k_{\rm B}\,(\Theta/T)^2 \,\exp(-\Theta/T) & (T\to 0) \\ N k_{\rm B} & (T\to\infty)\end{cases}\end{aligned} \tag{4.277}$$

### 4.10.6 Two-level systems : Schottky anomaly

Consider now a two-level system, with energies $\varepsilon_0$ and $\varepsilon_1$. We define $\Delta \equiv \varepsilon_1 - \varepsilon_0$ and assume without loss of generality that $\Delta > 0$. The partition function is

$$\zeta = e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1} = e^{-\beta\varepsilon_0}\big(1+e^{-\beta\Delta}\big) \ . \tag{4.278}$$

The free energy is

$$f = -k_{\rm B}T\ln\zeta = \varepsilon_0 - k_{\rm B}T \ln\big(1+e^{-\Delta/k_{\rm B}T}\big) \ . \tag{4.279}$$

The entropy for a given two level system is then

$$s = -\frac{\partial f}{\partial T} = k_{\rm B}\ln\big(1+e^{-\Delta/k_{\rm B}T}\big) + \frac{\Delta}{T}\cdot\frac{1}{e^{\Delta/k_{\rm B}T}+1} \tag{4.280}$$

and the heat capacity is $= T\,(\partial s/\partial T)$, *i.e.*

$$c(T) = \frac{\Delta^2}{k_{\rm B}T^2}\cdot\frac{e^{\Delta/k_{\rm B}T}}{\big(e^{\Delta/k_{\rm B}T}+1\big)^2} \ . \tag{4.281}$$

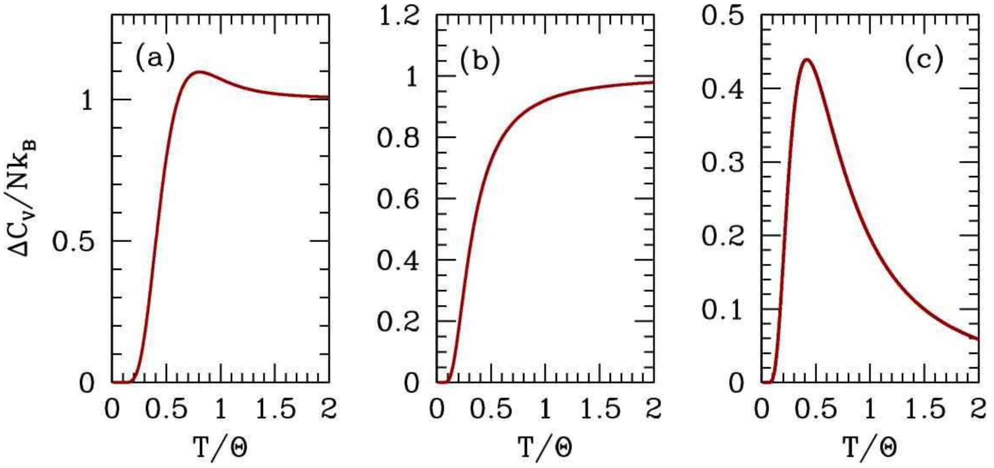

Figure 4.11: Heat capacity per molecule as a function of temperature for (a) heteronuclear diatomic gases, (b) a single vibrational mode, and (c) a single two-level system.

Thus,

$$c\,(T \ll \mathit{\Delta}) = \frac{\Delta^2}{k_{\rm B} T^2}\, e^{-\Delta/k_{\rm B}T} \tag{4.282}$$

$$c\,(T \gg \mathit{\Delta}) = \frac{\Delta^2}{4 k_{\rm B} T^2}\ . \tag{4.283}$$

We find that $c(T)$ has a characteristic peak at $T^* \approx 0.42\,\Delta/k_{\rm B}$. The heat capacity vanishes in both the low temperature and high temperature limits. At low temperatures, the gap to the excited state is much greater than $k_{\rm B}T$, and it is not possible to populate it and store energy. At high temperatures, both ground state and excited state are equally populated, and once again there is no way to store energy.

If we have a distribution of independent two-level systems, the heat capacity of such a system is a sum over the individual Schottky functions:

$$C(T) = \sum_i \widetilde{c}\,(\Delta_i/k_{\rm B}T) = N\int\limits_0^\infty d\Delta\, P(\Delta)\,\widetilde{c}(\Delta/T)\ , \tag{4.284}$$

where $N$ is the number of two level systems, $\widetilde{c}(x) = k_{\rm B}\, x^2\, e^x/(e^x+1)^2$, and where $P(\Delta)$ is the normalized distribution function, which satisfies the normalization condition

$$\int\limits_0^\infty d\Delta\, P(\Delta) = 1\ . \tag{4.285}$$

$N_{\rm s}$ is the total number of two level systems. If $P(\Delta) \propto \Delta^r$ for $\Delta \to 0$, then the low temperature heat capacity behaves as $C(T) \propto T^{1+r}$. Many amorphous or glassy systems contain such a distribution of two level systems, with $r \approx 0$ for glasses, leading to a linear low-temperature heat capacity. The origin of these two-level systems is not always so clear but is generally believed to be associated with local atomic configurations for which there are two low-lying states which are close in energy. The paradigmatic example is the mixed crystalline solid $({\rm KBr})_{1-x}({\rm KCN})_x$ which over the range $0.1 \lesssim x \lesssim 0.6$ forms an 'orientational glass' at low temperatures. The two level systems are associated with different orientation of the cyanide (CN) dipoles.

### 4.10.7 Electronic and nuclear excitations

For a monatomic gas, the internal coordinate partition function arises due to electronic and nuclear degrees of freedom. Let's first consider the electronic degrees of freedom. We assume that $k_{\rm B}T$ is small compared with energy differences between successive electronic shells. The atomic ground state is then computed by filling up the hydrogenic orbitals until all the electrons are used up. If the atomic number is a 'magic number' ($A = 2$ (He), $10$ (Ne), $18$ (Ar), $36$ (Kr), $54$ (Xe), *etc.*) then the atom has all shells filled and $L = 0$ and $S = 0$. Otherwise the last shell is partially filled and one or both of $L$ and $S$ will be nonzero. The atomic ground state configuration ${}^{2J+1}L_S$ is then determined by *Hund's rules*:

1. The $LS$ multiplet with the *largest* $S$ has the lowest energy.
2. If the largest value of $S$ is associated with several multiplets, the multiplet with the *largest* $L$ has the lowest energy.
3. If an incomplete shell is not more than half-filled, then the lowest energy state has $J = |L - S|$. If the shell is more than half-filled, then $J = L + S$.

The last of Hund's rules distinguishes between the $(2S + 1)(2L + 1)$ states which result upon fixing $S$ and $L$ as per rules #1 and #2. It arises due to the atomic spin-orbit coupling, whose effective Hamiltonian may be written $\hat{H} = \varLambda \boldsymbol{L} \cdot \boldsymbol{S}$, where $\varLambda$ is the Russell-Saunders coupling. If the last shell is less than or equal to half-filled, then $\varLambda > 0$ and the ground state has $J = |L - S|$. If the last shell is more than half-filled, the coupling is *inverted*, *i.e.* $\varLambda < 0$, and the ground state has $J = L + S$.[8]

The electronic contribution to $\xi$ is then

$$\xi_{\rm elec} = \sum_{J=|L-S|}^{L+S} (2J+1)\, e^{-\Delta\varepsilon(L,S,J)/k_{\rm B}T} \tag{4.286}$$

where

$$\Delta\varepsilon(L,S,J) = \tfrac{1}{2}\varLambda\Big[J(J+1) - L(L+1) - S(S+1)\Big]\ . \tag{4.287}$$

At high temperatures, $k_{\rm B}T$ is larger than the energy difference between the different $J$ multiplets, and we have $\xi_{\rm elec} \sim (2L + 1)(2S + 1)\, e^{-\beta\varepsilon_0}$, where $\varepsilon_0$ is the ground state energy. At low temperatures, a particular value of $J$ is selected – that determined by Hund's third rule – and we have $\xi_{\rm elec} \sim (2J + 1)\, e^{-\beta\varepsilon_0}$. If, in addition, there is a nonzero nuclear spin $I$, then we also must include a factor $\xi_{\rm nuc} = (2I + 1)$, neglecting the small hyperfine splittings due to the coupling of nuclear and electronic angular momenta.

For *heteronuclear* diatomic molecules, *i.e.* molecules composed from two different atomic nuclei, the internal partition function simply receives a factor of $\xi_{\rm elec} \cdot \xi^{(1)}_{\rm nuc} \cdot \xi^{(2)}_{\rm nuc}$, where the first term is a sum over molecular electronic states, and the second two terms arise from the spin degeneracies of the two nuclei. For *homonuclear* diatomic molecules, the exchange of nuclear centers is a symmetry operation, and does not represent a distinct quantum state. To correctly count the electronic states, we first assume that the total electronic spin is $S = 0$. This is generally a very safe assumption. Exchange symmetry now puts restrictions on the possible values of the molecular angular momentum $L$, depending on the total nuclear angular momentum $I_{\rm tot}$. If $I_{\rm tot}$ is even, then the molecular angular momentum $L$ must also be even. If the total nuclear angular momentum is odd, then $L$ must be odd. This is so because the molecular ground state configuration is ${}^1\varSigma_g^+$.[9]

The total number of nuclear states for the molecule is $(2I + 1)^2$, of which some are even under nuclear exchange, and some are odd. The number of even states, corresponding to even total nuclear angular momentum is written

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[8] See *e.g.* §72 of Landau and Lifshitz, *Quantum Mechanics*, which, in my humble estimation, is the greatest physics book ever written.

[9] See Landau and Lifshitz, *Quantum Mechanics*, §86.

| $2I$ | $g_g$ | $g_u$ |
|---|---|---|
| odd | $I(2I+1)$ | $(I+1)(2I+1)$ |
| even | $(I+1)(2I+1)$ | $I(2I+1)$ |

Table 4.2: Number of even ($g_g$) and odd ($g_u$) total nuclear angular momentum states for a homonuclear diatomic molecule. $I$ is the ground state nuclear spin.

as $g_g$, where the subscript conventionally stands for the (mercifully short) German word *gerade*, meaning 'even'. The number of odd (Ger. *ungerade*) states is written $g_u$. Table 4.2 gives the values of $g_{g,u}$ corresponding to half-odd-integer $I$ and integer $I$.

The final answer for the rotational component of the internal molecular partition function is then

$$\xi_{\rm rot}(T) = g_g\,\zeta_g + g_u\,\zeta_u \ , \tag{4.288}$$

where

$$\begin{aligned}\zeta_g &= \sum_{L \text{ even}} (2L+1)\, e^{-L(L+1)\,\Theta_{\rm rot}/T} \\ \zeta_u &= \sum_{L \text{ odd}} (2L+1)\, e^{-L(L+1)\,\Theta_{\rm rot}/T} \ .\end{aligned} \tag{4.289}$$

For hydrogen, the molecules with the larger nuclear statistical weight are called *orthohydrogen* and those with the smaller statistical weight are called *parahydrogen*. For $H_2$, we have $I = \frac{1}{2}$ hence the ortho state has $g_u = 3$ and the para state has $g_g = 1$. In $D_2$, we have $I = 1$ and the ortho state has $g_g = 6$ while the para state has $g_u = 3$. In equilibrium, the ratio of ortho to para states is then

$$\frac{N^{\rm ortho}_{\rm H_2}}{N^{\rm para}_{\rm H_2}} = \frac{g_u\,\zeta_u}{g_g\,\zeta_g} = \frac{3\,\zeta_u}{\zeta_g} \qquad , \qquad \frac{N^{\rm ortho}_{\rm D_2}}{N^{\rm para}_{\rm D_2}} = \frac{g_g\,\zeta_g}{g_u\,\zeta_u} = \frac{2\,\zeta_g}{\zeta_u} \ . \tag{4.290}$$

Incidentally, how do we derive the results in Tab. 4.10.7 ? The total nuclear angular momentum $I_{\rm tot}$ is the quantum mechanical sum of the two individual nuclear angular momenta, each of which are of magnitude $I$. From elementary addition of angular momenta, we have

$$I \otimes I = 0 \oplus 1 \oplus 2 \oplus \cdots \oplus 2I \ . \tag{4.291}$$

The right hand side of the above equation lists all the possible multiplets. Thus, $I_{\rm tot} \in \{0, 1, \ldots, 2I\}$. Now let us count the total number of states with *even* $I_{\rm tot}$. If $2I$ is even, which is to say if $I$ is an integer, we have

$$g_g^{(2I=\text{even})} = \sum_{n=0}^{I} \Big\{ 2 \cdot (2n) + 1 \Big\} = (I+1)(2I+1) \ , \tag{4.292}$$

because the degeneracy of each multiplet is $2I_{\rm tot} + 1$. It follows that

$$g_u^{(2I=\text{even})} = (2I+1)^2 - g_g = I(2I+1) \ . \tag{4.293}$$

On the other hand, if $2I$ is odd, which is to say $I$ is a half odd integer, then

$$g_g^{(2I=\text{odd})} = \sum_{n=0}^{I-\frac{1}{2}} \Big\{ 2 \cdot (2n) + 1 \Big\} = I(2I+1) \ . \tag{4.294}$$

It follows that

$$g_u^{(2I=\text{odd})} = (2I+1)^2 - g_g = (I+1)(2I+1) \ . \tag{4.295}$$

## 4.11 Appendix I : Additional Examples

### 4.11.1 Three state system

Consider a spin-1 particle where $\sigma = -1, 0, +1$. We model this with the single particle Hamiltonian

$$\hat{h} = -\mu_0 H\,\sigma + \Delta(1-\sigma^2)\ . \tag{4.296}$$

We can also interpret this as describing a spin if $\sigma = \pm 1$ and a vacancy if $\sigma = 0$. The parameter $\Delta$ then represents the vacancy formation energy. The single particle partition function is

$$\zeta = \mathsf{Tr}\ e^{-\beta\hat{h}} = e^{-\beta\Delta} + 2\cosh(\beta\mu_0 H)\ . \tag{4.297}$$

With $N_\mathsf{s}$ distinguishable noninteracting spins (*e.g.* at different sites in a crystalline lattice), we have $Z = \zeta^{N_\mathsf{s}}$ and

$$F \equiv N_\mathsf{s} f = -k_\mathrm{B} T \ln Z = -N_\mathsf{s}\, k_\mathrm{B} T \ln\Big[e^{-\beta\Delta} + 2\cosh(\beta\mu_0 H)\Big]\ , \tag{4.298}$$

where $f = -k_\mathrm{B} T \ln\zeta$ is the free energy of a single particle. Note that

$$\hat{n}_\mathrm{V} = 1 - \sigma^2 = \frac{\partial\hat{h}}{\partial\Delta} \tag{4.299}$$

$$\hat{m} = \mu_0\,\sigma = -\frac{\partial\hat{h}}{\partial H} \tag{4.300}$$

are the vacancy number and magnetization, respectively. Thus,

$$n_\mathrm{V} = \big\langle\, \hat{n}_\mathrm{V} \,\big\rangle = \frac{\partial f}{\partial\Delta} = \frac{e^{-\Delta/k_\mathrm{B}T}}{e^{-\Delta/k_\mathrm{B}T} + 2\cosh(\mu_0 H/k_\mathrm{B}T)} \tag{4.301}$$

and

$$m = \big\langle\, \hat{m} \,\big\rangle = -\frac{\partial f}{\partial H} = \frac{2\mu_0\,\sinh(\mu_0 H/k_\mathrm{B}T)}{e^{-\Delta/k_\mathrm{B}T} + 2\cosh(\mu_0 H/k_\mathrm{B}T)}\ . \tag{4.302}$$

At weak fields we can compute

$$\chi_T = \frac{\partial m}{\partial H}\bigg|_{H=0} = \frac{\mu_0^2}{k_\mathrm{B}T}\cdot\frac{2}{2 + e^{-\Delta/k_\mathrm{B}T}}\ . \tag{4.303}$$

We thus obtain a modified Curie law. At temperatures $T \ll \Delta/k_\mathrm{B}$, the vacancies are frozen out and we recover the usual Curie behavior. At high temperatures, where $T \gg \Delta/k_\mathrm{B}$, the low temperature result is reduced by a factor of $\frac{2}{3}$, which accounts for the fact that one third of the time the particle is in a nonmagnetic state with $\sigma = 0$.

### 4.11.2 Spins and vacancies on a surface

`PROBLEM:` A collection of spin-$\frac{1}{2}$ particles is confined to a surface with $N$ sites. For each site, let $\sigma = 0$ if there is a vacancy, $\sigma = +1$ if there is particle present with spin up, and $\sigma = -1$ if there is a particle present with spin down. The particles are non-interacting, and the energy for each site is given by $\varepsilon = -W\sigma^2$, where $-W < 0$ is the binding energy.

(a) Let $Q = N_\uparrow + N_\downarrow$ be the number of spins, and $N_0$ be the number of vacancies. The surface magnetization is $M = N_\uparrow - N_\downarrow$. Compute, in the microcanonical ensemble, the statistical entropy $S(Q, M)$.

(b) Let $q = Q/N$ and $m = M/N$ be the dimensionless particle density and magnetization density, respectively. Assuming that we are in the thermodynamic limit, where $N$, $Q$, and $M$ all tend to infinity, but with $q$ and $m$ finite, Find the temperature $T(q,m)$. Recall Stirling's formula

$$\ln(N!) = N\ln N - N + \mathcal{O}(\ln N) \ .$$

(c) Show explicitly that $T$ can be negative for this system. What does negative $T$ mean? What physical degrees of freedom have been left out that would avoid this strange property?

`SOLUTION`: There is a constraint on $N_\uparrow$, $N_0$, and $N_\downarrow$:

$$N_\uparrow + N_0 + N_\downarrow = Q + N_0 = N \ . \tag{4.304}$$

The total energy of the system is $E = -WQ$.

(a) The number of states available to the system is

$$\Omega = \frac{N!}{N_\uparrow!\,N_0!\,N_\downarrow!} \ . \tag{4.305}$$

Fixing $Q$ and $M$, along with the above constraint, is enough to completely determine $\{N_\uparrow, N_0, N_\downarrow\}$:

$$N_\uparrow = \tfrac{1}{2}(Q+M) \qquad , \qquad N_0 = N - Q \qquad , \qquad N_\downarrow = \tfrac{1}{2}(Q-M) \ , \tag{4.306}$$

whence

$$\Omega(Q,M) = \frac{N!}{\big[\frac{1}{2}(Q+M)\big]!\,\big[\frac{1}{2}(Q-M)\big]!\,(N-Q)!} \ . \tag{4.307}$$

The statistical entropy is $S = k_{\rm B}\ln\Omega$:

$$S(Q,M) = k_{\rm B}\ln(N!) - k_{\rm B}\ln\big[\tfrac{1}{2}(Q+M)!\big] - k_{\rm B}\ln\big[\tfrac{1}{2}(Q-M)!\big] - k_{\rm B}\ln\big[(N-Q)!\big] \ . \tag{4.308}$$

(b) Now we invoke Stirling's rule,

$$\ln(N!) = N\ln N - N + \mathcal{O}(\ln N) \ , \tag{4.309}$$

to obtain

$$\begin{aligned}\ln\Omega(Q,M) &= N\ln N - N - \tfrac{1}{2}(Q+M)\ln\big[\tfrac{1}{2}(Q+M)\big] + \tfrac{1}{2}(Q+M)\\ &\qquad - \tfrac{1}{2}(Q-M)\ln\big[\tfrac{1}{2}(Q-M)\big] + \tfrac{1}{2}(Q-M)\\ &\qquad - (N-Q)\ln(N-Q) + (N-Q)\\ &= N\ln N - \tfrac{1}{2}Q\ln\Big[\tfrac{1}{4}(Q^2-M^2)\Big] - \tfrac{1}{2}M\ln\left(\frac{Q+M}{Q-M}\right)\end{aligned} \tag{4.310}$$

Combining terms,

$$\ln\Omega(Q,M) = -Nq\ln\Big[\tfrac{1}{2}\sqrt{q^2-m^2}\Big] - \tfrac{1}{2}Nm\ln\left(\frac{q+m}{q-m}\right) - N(1-q)\ln(1-q) \ , \tag{4.311}$$

where $Q = Nq$ and $M = Nm$. Note that the entropy $S = k_{\rm B}\ln\Omega$ is extensive. The statistical entropy per site is thus

$$s(q,m) = -k_{\rm B}\,q\ln\Big[\tfrac{1}{2}\sqrt{q^2-m^2}\Big] - \tfrac{1}{2}k_{\rm B}\,m\ln\left(\frac{q+m}{q-m}\right) - k_{\rm B}\,(1-q)\ln(1-q) \ . \tag{4.312}$$

The temperature is obtained from the relation

$$\begin{aligned}\frac{1}{T} &= \left(\frac{\partial S}{\partial E}\right)_{M} = \frac{1}{W}\left(\frac{\partial s}{\partial q}\right)_{m} \\ &= \frac{1}{W}\,\ln(1-q) - \frac{1}{W}\,\ln\Big[\tfrac{1}{2}\sqrt{q^2-m^2}\,\Big] \ .\end{aligned} \tag{4.313}$$

Thus,

$$T = \frac{W/k_{\rm B}}{\ln\!\big[2(1-q)/\sqrt{q^2-m^2}\,\big]} \ . \tag{4.314}$$

(c) We have $0 \le q \le 1$ and $-q \le m \le q$, so $T$ is real (thank heavens!). But it is easy to choose $\{q, m\}$ such that $T < 0$. For example, when $m = 0$ we have $T = W/k_{\rm B} \ln(2q^{-1} - 2)$ and $T < 0$ for all $q \in \big(\frac{2}{3}, 1\big]$. The reason for this strange state of affairs is that the entropy $S$ is bounded, and is not an monotonically increasing function of the energy $E$ (or the dimensionless quantity $Q$). The entropy is maximized for $N \uparrow = N_0 = N_\downarrow = \frac{1}{3}$, which says $m = 0$ and $q = \frac{2}{3}$. Increasing $q$ beyond this point (with $m = 0$ fixed) starts to reduce the entropy, and hence $(\partial S/\partial E) < 0$ in this range, which immediately gives $T < 0$. What we've left out are kinetic degrees of freedom, such as vibrations and rotations, whose energies are unbounded, and which result in an increasing $S(E)$ function.

### 4.11.3 Fluctuating interface

Consider an interface between two dissimilar fluids. In equilibrium, in a uniform gravitational field, the denser fluid is on the bottom. Let $z = z(x, y)$ be the height the interface between the fluids, relative to equilibrium. The potential energy is a sum of gravitational and surface tension terms, with

$$U_{\rm grav} = \int\! d^2\!x \int_0^z\! dz'\, \Delta\rho\, g\, z' \tag{4.315}$$

$$U_{\rm surf} = \int\! d^2\!x\ \tfrac{1}{2}\sigma\,(\boldsymbol{\nabla} z)^2 \ . \tag{4.316}$$

We won't need the kinetic energy in our calculations, but we can include it just for completeness. It isn't so clear how to model it *a priori* so we will assume a rather general form

$$T = \int\! d^2\!x \int\! d^2\!x'\ \tfrac{1}{2}\mu(\boldsymbol{x}, \boldsymbol{x}')\, \frac{\partial z(\boldsymbol{x}, t)}{\partial t}\, \frac{\partial z(\boldsymbol{x}', t)}{\partial t} \ . \tag{4.317}$$

We assume that the $(x, y)$ plane is a rectangle of dimensions $L_x \times L_y$. We also assume $\mu(\boldsymbol{x}, \boldsymbol{x}') = \mu\big(|\boldsymbol{x} - \boldsymbol{x}'|\big)$. We can then Fourier transform

$$z(\boldsymbol{x}) = \big(L_x\, L_y\big)^{-1/2} \sum_{\boldsymbol{k}} z_{\boldsymbol{k}}\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \ , \tag{4.318}$$

where the wavevectors $\boldsymbol{k}$ are quantized according to

$$\boldsymbol{k} = \frac{2\pi n_x}{L_x}\,\hat{\boldsymbol{x}} + \frac{2\pi n_y}{L_y}\,\hat{\boldsymbol{y}} \ , \tag{4.319}$$

with integer $n_x$ and $n_y$, if we impose periodic boundary conditions (for calculational convenience). The Lagrangian is then

$$L = \frac{1}{2} \sum_{\boldsymbol{k}} \Big[ \mu_{\boldsymbol{k}}\, \big|\dot z_{\boldsymbol{k}}\big|^2 - \big(g\,\Delta\rho + \sigma \boldsymbol{k}^2\big)\, \big|z_{\boldsymbol{k}}\big|^2 \Big] \ , \tag{4.320}$$

where

$$\mu_{\boldsymbol{k}} = \int\! d^2\!x\, \mu\big(|\boldsymbol{x}|\big)\, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}} \ . \tag{4.321}$$

Since $z(\boldsymbol{x},t)$ is real, we have the relation $z_{-\boldsymbol{k}} = z^*_{\boldsymbol{k}}$, therefore the Fourier coefficients at $\boldsymbol{k}$ and $-\boldsymbol{k}$ are not independent. The canonical momenta are given by

$$p_{\boldsymbol{k}} = \frac{\partial L}{\partial \dot z^*_{\boldsymbol{k}}} = \mu_{\boldsymbol{k}}\, \dot z_{\boldsymbol{k}} \qquad , \qquad p^*_{\boldsymbol{k}} = \frac{\partial L}{\partial \dot z_{\boldsymbol{k}}} = \mu_{\boldsymbol{k}}\, \dot z^*_{\boldsymbol{k}} \tag{4.322}$$

The Hamiltonian is then

$$\begin{aligned}\hat H &= \sum_{\boldsymbol{k}}{}' \Big[ p_{\boldsymbol{k}}\, z^*_{\boldsymbol{k}} + p^*_{\boldsymbol{k}}\, z_{\boldsymbol{k}} \Big] - L && (4.323)\\ &= \sum_{\boldsymbol{k}}{}' \left[ \frac{|p_{\boldsymbol{k}}|^2}{\mu_{\boldsymbol{k}}} + \big(g\,\Delta\rho + \sigma\boldsymbol{k}^2\big)\, |z_{\boldsymbol{k}}|^2 \right] \ , && (4.324)\end{aligned}$$

where the prime on the $\boldsymbol{k}$ sum indicates that only one of the pair $\{\boldsymbol{k},-\boldsymbol{k}\}$ is to be included, for each $\boldsymbol{k}$.

We may now compute the ordinary canonical partition function:

$$\begin{aligned} Z &= \prod_{\boldsymbol{k}}{}' \int\! \frac{d^2\!p_{\boldsymbol{k}}\, d^2\!z_{\boldsymbol{k}}}{(2\pi\hbar)^2}\, e^{-|p_{\boldsymbol{k}}|^2/\mu_{\boldsymbol{k}} k_{\rm B}T}\, e^{-(g\,\Delta\rho + \sigma\boldsymbol{k}^2)\,|z_{\boldsymbol{k}}|^2/k_{\rm B}T} \\ &= \prod_{\boldsymbol{k}}{}' \left(\frac{k_{\rm B}T}{2\hbar}\right)^{\!2} \left(\frac{\mu_{\boldsymbol{k}}}{g\,\Delta\rho + \sigma\boldsymbol{k}^2}\right) \ . \end{aligned} \tag{4.325}$$

Thus,

$$F = -k_{\rm B}T \sum_{\boldsymbol{k}} \ln\!\left(\frac{k_{\rm B}T}{2\hbar\varOmega_{\boldsymbol{k}}}\right) \ , \tag{4.326}$$

where[10]

$$\varOmega_{\boldsymbol{k}} = \left(\frac{g\,\Delta\rho + \sigma\boldsymbol{k}^2}{\mu_{\boldsymbol{k}}}\right)^{\!1/2} \ . \tag{4.327}$$

is the normal mode frequency for surface oscillations at wavevector $\boldsymbol{k}$. For deep water waves, it is appropriate to take $\mu_{\boldsymbol{k}} = \Delta\rho\big/|\boldsymbol{k}|$, where $\Delta\rho = \rho_{\rm L} - \rho_{\rm G} \approx \rho_{\rm L}$ is the difference between the densities of water and air.

It is now easy to compute the thermal average

$$\begin{aligned} \big\langle\, |z_{\boldsymbol{k}}|^2 \,\big\rangle &= \int\! d^2\!z_{\boldsymbol{k}}\, |z_{\boldsymbol{k}}|^2\, e^{-(g\,\Delta\rho+\sigma\boldsymbol{k}^2)\,|z_{\boldsymbol{k}}|^2/k_{\rm B}T} \bigg/ \int\! d^2\!z_{\boldsymbol{k}}\, e^{-(g\,\Delta\rho+\sigma\boldsymbol{k}^2)\,|z_{\boldsymbol{k}}|^2/k_{\rm B}T} \\ &= \frac{k_{\rm B}T}{g\,\Delta\rho + \sigma\boldsymbol{k}^2} \ . \end{aligned} \tag{4.328}$$

Note that this result does not depend on $\mu_{\boldsymbol{k}}$, *i.e.* on our choice of kinetic energy. One defines the *correlation function*

$$\begin{aligned} C(\boldsymbol{x}) \equiv \big\langle\, z(\boldsymbol{x})\, z(0) \,\big\rangle &= \frac{1}{L_x L_y} \sum_{\boldsymbol{k}} \big\langle\, |z_{\boldsymbol{k}}|^2 \,\big\rangle\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} = \int\! \frac{d^2\!k}{(2\pi)^2} \left(\frac{k_{\rm B}T}{g\,\Delta\rho + \sigma\boldsymbol{k}^2}\right) e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \\ &= \frac{k_{\rm B}T}{4\pi\sigma} \int\limits_0^\infty\! dq\, \frac{e^{ik|\boldsymbol{x}|}}{\sqrt{q^2+\xi^2}} = \frac{k_{\rm B}T}{4\pi\sigma}\, K_0\big(|\boldsymbol{x}|/\xi\big) \ , \end{aligned} \tag{4.329}$$

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[10] Note that there is no prime on the $\boldsymbol{k}$ sum for $F$, as we have divided the logarithm of $Z$ by two and replaced the half sum by the whole sum.

where $\xi = \sqrt{g\,\Delta\rho/\sigma}$ is the correlation length, and where $K_0(z)$ is the Bessel function of imaginary argument. The asymptotic behavior of $K_0(z)$ for small $z$ is $K_0(z) \sim \ln(2/z)$, whereas for large $z$ one has $K_0(z) \sim (\pi/2z)^{1/2}\, e^{-z}$. We see that on large length scales the correlations decay exponentially, but on small length scales they diverge. This divergence is due to the improper energetics we have assigned to short wavelength fluctuations of the interface. Roughly, it can cured by imposing a cutoff on the integral, or by insisting that the shortest distance scale is a molecular diameter.

### 4.11.4 Dissociation of molecular hydrogen

Consider the reaction

$$\mathrm{H} \rightleftharpoons \mathrm{p}^+ + \mathrm{e}^- \ . \tag{4.330}$$

In equilibrium, we have

$$\mu_\mathrm{H} = \mu_\mathrm{p} + \mu_\mathrm{e} \ . \tag{4.331}$$

What is the relationship between the temperature $T$ and the fraction $x$ of hydrogen which is dissociated?

Let us assume a fraction $x$ of the hydrogen is dissociated. Then the densities of H, p, and e are then

$$n_\mathrm{H} = (1-x)\,n \qquad , \qquad n_\mathrm{p} = xn \qquad , \qquad n_\mathrm{e} = xn \ . \tag{4.332}$$

The single particle partition function for each species is

$$\zeta = \frac{g^N}{N!}\left(\frac{V}{\lambda_T^3}\right)^{\!N} e^{-N\varepsilon_\mathrm{int}/k_\mathrm{B}T} \ , \tag{4.333}$$

where $g$ is the degeneracy and $\varepsilon_\mathrm{int}$ the internal energy for a given species. We have $\varepsilon_\mathrm{int} = 0$ for p and e, and $\varepsilon_\mathrm{int} = -\Delta$ for H, where $\Delta = e^2/2a_\mathrm{B} = 13.6\,\mathrm{eV}$, the binding energy of hydrogen. Neglecting hyperfine splittings[11], we have $g_\mathrm{H} = 4$, while $g_\mathrm{e} = g_\mathrm{p} = 2$ because each has spin $S = \frac{1}{2}$. Thus, the associated grand potentials are

$$\Omega_\mathrm{H} = -g_\mathrm{H}\, V k_\mathrm{B} T\, \lambda_{T,\mathrm{H}}^{-3}\, e^{(\mu_\mathrm{H}+\Delta)/k_\mathrm{B}T} \tag{4.334}$$

$$\Omega_\mathrm{p} = -g_\mathrm{p}\, V k_\mathrm{B} T\, \lambda_{T,\mathrm{p}}^{-3}\, e^{\mu_\mathrm{p}/k_\mathrm{B}T} \tag{4.335}$$

$$\Omega_\mathrm{e} = -g_\mathrm{e}\, V k_\mathrm{B} T\, \lambda_{T,\mathrm{e}}^{-3}\, e^{\mu_\mathrm{e}/k_\mathrm{B}T} \ , \tag{4.336}$$

where

$$\lambda_{T,a} = \sqrt{\frac{2\pi\hbar^2}{m_a k_\mathrm{B} T}} \tag{4.337}$$

for species $a$. The corresponding number densities are

$$n = \frac{1}{V}\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} = g\,\lambda_T^{-3}\, e^{(\mu-\varepsilon_\mathrm{int})/k_\mathrm{B}T} \ , \tag{4.338}$$

and the fugacity $z = e^{\mu/k_\mathrm{B}T}$ of a given species is given by

$$z = g^{-1} n\, \lambda_T^3\, e^{\varepsilon_\mathrm{int}/k_\mathrm{B}T} \ . \tag{4.339}$$

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[11] The hyperfine splitting in hydrogen is on the order of $(m_\mathrm{e}/m_\mathrm{p})\,\alpha^4\, m_\mathrm{e} c^2 \sim 10^{-6}$ eV, which is on the order of 0.01 K. Here $\alpha = e^2/\hbar c$ is the fine structure constant.

We now invoke $\mu_{\rm H} = \mu_{\rm p} + \mu_{\rm e}$, which says $z_{\rm H} = z_{\rm p}\, z_{\rm e}$, or

$$g_{\rm H}^{-1} n_{\rm H}\, \lambda^3_{T,{\rm H}}\, e^{-\Delta/k_{\rm B}T} = \big(g_{\rm p}^{-1} n_{\rm p}\, \lambda^3_{T,{\rm p}}\big)\big(g_{\rm e}^{-1} n_{\rm e}\, \lambda^3_{T,{\rm e}}\big)\ , \tag{4.340}$$

which yields

$$\bigg(\frac{x^2}{1-x}\bigg)\, n\tilde\lambda^3_T = e^{-\Delta/k_{\rm B}T}\ , \tag{4.341}$$

where $\tilde\lambda_T = \sqrt{2\pi\hbar^2/m^* k_{\rm B}T}$, with $m^* = m_{\rm p} m_{\rm e}/m_{\rm H} \approx m_{\rm e}$. Note that

$$\tilde\lambda_T = a_{\rm B}\sqrt{\frac{4\pi m_{\rm H}}{m_{\rm p}}}\,\sqrt{\frac{\Delta}{k_{\rm B}T}}\ , \tag{4.342}$$

where $a_{\rm B} = 0.529\,$Å is the Bohr radius. Thus, we have

$$\bigg(\frac{x^2}{1-x}\bigg)\cdot (4\pi)^{3/2}\,\nu = \bigg(\frac{T}{T_0}\bigg)^{3/2} e^{-T_0/T}\ , \tag{4.343}$$

where $T_0 = \Delta/k_{\rm B} = 1.578\times 10^5\,{\rm K}$ and $\nu = n a_{\rm B}^3$. Consider for example a temperature $T = 3000\,{\rm K}$, for which $T_0/T = 52.6$, and assume that $x = \frac{1}{2}$. We then find $\nu = 1.69\times 10^{-27}$, corresponding to a density of $n = 1.14\times 10^{-2}\,{\rm cm}^{-3}$. At this temperature, the fraction of hydrogen molecules in their first excited (2s) state is $x' \sim e^{-T_0/2T} = 3.8\times 10^{-12}$. This is quite striking: half the hydrogen atoms are completely dissociated, which requires an energy of $\Delta$, yet the number in their first excited state, requiring energy $\frac{1}{2}\Delta$, is twelve orders of magnitude smaller. The student should reflect on why this can be the case.

# Chapter 5

# Noninteracting Quantum Systems

## 5.1 References

- F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1987)
  This has been perhaps the most popular undergraduate text since it first appeared in 1967, and with good reason.

- A. H. Carter, *Classical and Statistical Thermodynamics*
  (Benjamin Cummings, 2000)
  A very relaxed treatment appropriate for undergraduate physics majors.

- D. V. Schroeder, *An Introduction to Thermal Physics* (Addison-Wesley, 2000)
  This is the best undergraduate thermodynamics book I've come across, but only 40% of the book treats statistical mechanics.

- C. Kittel, *Elementary Statistical Physics* (Dover, 2004)
  Remarkably crisp, though dated, this text is organized as a series of brief discussions of key concepts and examples. Published by Dover, so you can't beat the price.

- R. K. Pathria, *Statistical Mechanics* ($2^{\text{nd}}$ edition, Butterworth-Heinemann, 1996)
  This popular graduate level text contains many detailed derivations which are helpful for the student.

- M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* ($3^{\text{rd}}$ edition, World Scientific, 2006)
  An excellent graduate level text. Less insightful than Kardar but still a good modern treatment of the subject. Good discussion of mean field theory.

- E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics* (part I, $3^{\text{rd}}$ edition, Pergamon, 1980)
  This is volume 5 in the famous Landau and Lifshitz *Course of Theoretical Physics*. Though dated, it still contains a wealth of information and physical insight.

## 5.2 Statistical Mechanics of Noninteracting Quantum Systems

### 5.2.1 Bose and Fermi systems in the grand canonical ensemble

A noninteracting many-particle quantum Hamiltonian may be written as

$$\hat{H} = \sum_\alpha \varepsilon_\alpha \, \hat{n}_\alpha \ , \tag{5.1}$$

where $\hat{n}_\alpha$ is the number of particles in the quantum state $\alpha$ with energy $\varepsilon_\alpha$. This form is called the *second quantized representation* of the Hamiltonian. The number eigenbasis is therefore also an energy eigenbasis. Any eigenstate of $\hat{H}$ may be labeled by the integer eigenvalues of the $\hat{n}_\alpha$ number operators, and written as $\big|\, n_1 \,,\, n_2 \,,\, \ldots \,\big\rangle$. We then have

$$\hat{n}_\alpha \,\big|\, \vec{n} \,\big\rangle = n_\alpha \,\big|\, \vec{n} \,\big\rangle \tag{5.2}$$

and

$$\hat{H} \,\big|\, \vec{n} \,\big\rangle = \sum_\alpha n_\alpha \, \varepsilon_\alpha \,\big|\, \vec{n} \,\big\rangle \ . \tag{5.3}$$

The eigenvalues $n_\alpha$ take on different possible values depending on whether the constituent particles are *bosons* or *fermions*, *viz.*

$$\text{bosons} : n_\alpha \in \big\{ 0 \,,\, 1 \,,\, 2 \,,\, 3 \,,\, \ldots \big\} \tag{5.4}$$

$$\text{fermions} : n_\alpha \in \big\{ 0 \,,\, 1 \big\} \ . \tag{5.5}$$

In other words, for bosons, the occupation numbers are nonnegative integers. For fermions, the occupation numbers are either 0 or 1 due to the *Pauli principle*, which says that at most one fermion can occupy any single particle quantum state. There is no Pauli principle for bosons.

The $N$-particle partition function $Z_N$ is then

$$Z_N = \sum_{\{n_\alpha\}} e^{-\beta \sum_\alpha n_\alpha \varepsilon_\alpha} \, \delta_{N, \sum_\alpha n_\alpha} \ , \tag{5.6}$$

where the sum is over all allowed values of the set $\{n_\alpha\}$, which depends on the *statistics* of the particles. Bosons satisfy *Bose-Einstein* (BE) statistics, in which $n_\alpha \in \{0 \,,\, 1 \,,\, 2 \,,\, \ldots\}$. Fermions satisfy *Fermi-Dirac* (FD) statistics, in which $n_\alpha \in \{0 \,,\, 1\}$.

The OCE partition sum is difficult to perform, owing to the constraint $\sum_\alpha n_\alpha = N$ on the total number of particles. This constraint is relaxed in the GCE, where

$$\begin{aligned} \Xi &= \sum_N e^{\beta\mu N} \, Z_N \\ &= \sum_{\{n_\alpha\}} e^{-\beta \sum_\alpha n_\alpha \varepsilon_\alpha} \, e^{\beta\mu \sum_\alpha n_\alpha} \\ &= \prod_\alpha \Bigg( \sum_{n_\alpha} e^{-\beta(\varepsilon_\alpha - \mu)\, n_\alpha} \Bigg) \ . \end{aligned} \tag{5.7}$$

Note that the grand partition function $\Xi$ takes the form of a product over contributions from the individual single particle states.

We now perform the single particle sums:

$$\sum_{n=0}^{\infty} e^{-\beta(\varepsilon-\mu)\,n} = \frac{1}{1-e^{-\beta(\varepsilon-\mu)}} \qquad \text{(bosons)} \tag{5.8}$$

$$\sum_{n=0}^{1} e^{-\beta(\varepsilon-\mu)\,n} = 1+e^{-\beta(\varepsilon-\mu)} \qquad \text{(fermions)}\ . \tag{5.9}$$

Therefore we have

$$\Xi_{\mathrm{BE}} = \prod_\alpha \frac{1}{1-e^{-(\varepsilon_\alpha-\mu)/k_{\mathrm{B}}T}} \tag{5.10}$$

$$\Omega_{\mathrm{BE}} = k_{\mathrm{B}}T\sum_\alpha \ln\Big(1-e^{-(\varepsilon_\alpha-\mu)/k_{\mathrm{B}}T}\Big) \tag{5.11}$$

and

$$\Xi_{\mathrm{FD}} = \prod_\alpha \Big(1+e^{-(\varepsilon_\alpha-\mu)/k_{\mathrm{B}}T}\Big) \tag{5.12}$$

$$\Omega_{\mathrm{FD}} = -k_{\mathrm{B}}T\sum_\alpha \ln\Big(1+e^{-(\varepsilon_\alpha-\mu)/k_{\mathrm{B}}T}\Big)\ . \tag{5.13}$$

We can combine these expressions into one, writing

$$\Omega(T,V,\mu) = \pm k_{\mathrm{B}}T\sum_\alpha \ln\Big(1\mp e^{-(\varepsilon_\alpha-\mu)/k_{\mathrm{B}}T}\Big)\ , \tag{5.14}$$

where we take the upper sign for Bose-Einstein statistics and the lower sign for Fermi-Dirac statistics. Note that the average occupancy of single particle state $\alpha$ is

$$\langle \hat{n}_\alpha\rangle = \frac{\partial\Omega}{\partial\varepsilon_\alpha} = \frac{1}{e^{(\varepsilon_\alpha-\mu)/k_{\mathrm{B}}T}\mp 1}\ , \tag{5.15}$$

and the total particle number is then

$$N(T,V,\mu) = \sum_\alpha \frac{1}{e^{(\varepsilon_\alpha-\mu)/k_{\mathrm{B}}T}\mp 1}\ . \tag{5.16}$$

We will henceforth write $n_\alpha(\mu,T) = \langle \hat{n}_\alpha\rangle$ for the thermodynamic average of this occupancy.

### 5.2.2 Maxwell-Boltzmann limit

Note also that if $n_\alpha(\mu,T) \ll 1$ then $\mu \ll \varepsilon_\alpha - k_{\mathrm{B}}T$, and

$$\Omega \longrightarrow \Omega_{\mathrm{MB}} = -k_{\mathrm{B}}T\sum_\alpha e^{-(\varepsilon_\alpha-\mu)/k_{\mathrm{B}}T}\ . \tag{5.17}$$

This is the Maxwell-Boltzmann limit of quantum statistical mechanics. The occupation number average is then

$$\langle \hat{n}_\alpha\rangle = e^{-(\varepsilon_\alpha-\mu)/k_{\mathrm{B}}T} \tag{5.18}$$

in this limit.

### 5.2.3 Single particle density of states

The single particle density of states per unit volume $g(\varepsilon)$ is defined as

$$g(\varepsilon)=\frac{1}{V}\sum_\alpha \delta(\varepsilon-\varepsilon_\alpha)\ . \tag{5.19}$$

We can then write

$$\Omega(T,V,\mu)=\pm V k_{\rm B}T\int\limits_{-\infty}^{\infty}\!d\varepsilon\; g(\varepsilon)\,\ln\!\Big(1\mp e^{-(\varepsilon-\mu)/k_{\rm B}T}\Big)\ . \tag{5.20}$$

For particles with a dispersion $\varepsilon(\boldsymbol{k})$, with $\boldsymbol{p}=\hbar\boldsymbol{k}$, we have

$$\begin{aligned} g(\varepsilon)&={\sf g}\!\int\!\frac{d^d\!k}{(2\pi)^d}\;\delta\big(\varepsilon-\varepsilon(\boldsymbol{k})\big)\\ &=\frac{{\sf g}\,\Omega_d}{(2\pi)^d}\,\frac{k^{d-1}}{d\varepsilon/dk}\ . \end{aligned} \tag{5.21}$$

where ${\sf g}=2S+1$ is the spin degeneracy. Thus, we have

$$g(\varepsilon)=\frac{{\sf g}\,\Omega_d}{(2\pi)^d}\,\frac{k^{d-1}}{d\varepsilon/dk}=\begin{cases}\frac{\sf g}{\pi}\,\frac{dk}{d\varepsilon} & d=1\\[2ex] \frac{\sf g}{2\pi}\,k\,\frac{dk}{d\varepsilon} & d=2\\[2ex] \frac{\sf g}{2\pi^2}\,k^2\,\frac{dk}{d\varepsilon} & d=3\ .\end{cases} \tag{5.22}$$

In order to obtain $g(\varepsilon)$ as a function of the energy $\varepsilon$ one must invert the dispersion relation $\varepsilon=\varepsilon(k)$ to obtain $k=k(\varepsilon)$.

Note that we can equivalently write

$$g(\varepsilon)\,d\varepsilon={\sf g}\,\frac{d^d\!k}{(2\pi)^d}=\frac{{\sf g}\,\Omega_d}{(2\pi)^d}\,k^{d-1}\,dk \tag{5.23}$$

to derive $g(\varepsilon)$.

For a spin-$S$ particle with ballistic dispersion $\varepsilon(\boldsymbol{k})=\hbar^2\boldsymbol{k}^2/2m$, we have

$$g(\varepsilon)=\frac{2S+1}{\Gamma(d/2)}\bigg(\frac{m}{2\pi\hbar^2}\bigg)^{\!d/2}\varepsilon^{\frac{d}{2}-1}\,\Theta(\varepsilon)\ , \tag{5.24}$$

where $\Theta(\varepsilon)$ is the step function, which takes the value $0$ for $\varepsilon<0$ and $1$ for $\varepsilon\geq 0$. The appearance of $\Theta(\varepsilon)$ simply says that all the single particle energy eigenvalues are nonnegative. Note that we are assuming a box of volume $V$ but we are ignoring the quantization of kinetic energy, and assuming that the difference between successive quantized single particle energy eigenvalues is negligible so that $g(\varepsilon)$ can be replaced by the average in the above expression. Note that

$$n(\varepsilon,T,\mu)=\frac{1}{e^{(\varepsilon-\mu)/k_{\rm B}T}\mp 1}\ . \tag{5.25}$$

This result holds true independent of the form of $g(\varepsilon)$. The average total number of particles is then

$$N(T,V,\mu)=V\!\!\int\limits_{-\infty}^{\infty}\!d\varepsilon\; g(\varepsilon)\,\frac{1}{e^{(\varepsilon-\mu)/k_{\rm B}T}\mp 1}\ , \tag{5.26}$$

which does depend on $g(\varepsilon)$.

## 5.3 Quantum Ideal Gases : Low Density Expansions

### 5.3.1 Expansion in powers of the fugacity

From eqn. 5.26, we have that the number density $n = N/V$ is

$$\begin{aligned} n(T,z) &= \int\limits_{-\infty}^{\infty} d\varepsilon\, \frac{g(\varepsilon)}{z^{-1}\, e^{\varepsilon/k_{\rm B}T} \mp 1} \\ &= \sum_{j=1}^{\infty} (\pm 1)^{j-1}\, C_j(T)\, z^j \ , \end{aligned} \tag{5.27}$$

where $z = \exp(\mu/k_{\rm B}T)$ is the fugacity and

$$C_j(T) = \int\limits_{-\infty}^{\infty} d\varepsilon\; g(\varepsilon)\, e^{-j\varepsilon/k_{\rm B}T} \ . \tag{5.28}$$

From $\Omega = -pV$ and our expression above for $\Omega(T,V,\mu)$, we have

$$\begin{aligned} p(T,z) &= \mp\, k_{\rm B}T \int\limits_{-\infty}^{\infty} d\varepsilon\; g(\varepsilon)\, \ln\Big(1 \mp z\, e^{-\varepsilon/k_{\rm B}T}\Big) \\ &= k_{\rm B}T \sum_{j=1}^{\infty} (\pm 1)^{j-1}\, j^{-1} C_j(T)\, z^j \ . \end{aligned} \tag{5.29}$$

### 5.3.2 Virial expansion of the equation of state

Eqns. 5.27 and 5.29 express $n(T,z)$ and $p(T,z)$ as power series in the fugacity $z$, with $T$-dependent coefficients. In principal, we can eliminate $z$ using eqn. 5.27, writing $z = z(T,n)$ as a power series in the number density $n$, and substitute this into eqn. 5.29 to obtain an equation of state $p = p(T,n)$ of the form

$$p(T,n) = n\, k_{\rm B}T\, \Big(1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots\Big) \ . \tag{5.30}$$

Note that the low density limit $n \to 0$ yields the ideal gas law independent of the density of states $g(\varepsilon)$. This follows from expanding $n(T,z)$ and $p(T,z)$ to lowest order in $z$, yielding $n = C_1\, z + \mathcal{O}(z^2)$ and $p = k_{\rm B}T\, C_1\, z + \mathcal{O}(z^2)$. Dividing the second of these equations by the first yields $p = n\, k_{\rm B}T + \mathcal{O}(n^2)$, which is the ideal gas law. Note that $z = n/C_1 + \mathcal{O}(n^2)$ can formally be written as a power series in $n$.

Unfortunately, there is no general analytic expression for the virial coefficients $B_j(T)$ in terms of the expansion coefficients $n_j(T)$. The only way is to grind things out order by order in our expansions. Let's roll up our sleeves and see how this is done. We start by formally writing $z(T,n)$ as a power series in the density $n$ with $T$-dependent coefficients $A_j(T)$:

$$z = A_1\, n + A_2\, n^2 + A_3\, n^3 + \ldots \ . \tag{5.31}$$

We then insert this into the series for $n(T,z)$:

$$\begin{aligned} n &= C_1\, z \pm C_2\, z^2 + C_3 z^3 + \ldots \\ &= C_1\, \big(A_1\, n + A_2\, n^2 + A_3\, n^3 + \ldots\big) \pm C_2\, \big(A_1\, n + A_2\, n^2 + A_3\, n^3 + \ldots\big)^2 \\ &\qquad + C_3\, \big(A_1\, n + A_2\, n^2 + A_3\, n^3 + \ldots\big)^3 + \ldots \ . \end{aligned} \tag{5.32}$$

Let's expand the RHS to order $n^3$. Collecting terms, we have

$$n = C_1\,A_1\,n + \big(C_1\,A_2 \pm C_2\,A_1^2\big)\,n^2 + \big(C_1\,A_3 \pm 2C_2\,A_1 A_2 + C_3\,A_1^3\big)\,n^3 + \ldots \tag{5.33}$$

In order for this equation to be true we require that the coefficient of $n$ on the RHS be unity, and that the coefficients of $n^j$ for all $j > 1$ must vanish. Thus,

$$\begin{aligned} C_1\,A_1 &= 1 \\ C_1\,A_2 \pm C_2\,A_1^2 &= 0 \\ C_1\,A_3 \pm 2C_2\,A_1 A_2 + C_3\,A_1^3 &= 0\ . \end{aligned} \tag{5.34}$$

The first of these yields $A_1$:

$$A_1 = \frac{1}{C_1}\ . \tag{5.35}$$

We now insert this into the second equation to obtain $A_2$:

$$A_2 = \mp\frac{C_2}{C_1^3}\ . \tag{5.36}$$

Next, insert the expressions for $A_1$ and $A_2$ into the third equation to obtain $A_3$:

$$A_3 = \frac{2C_2^2}{C_1^5} - \frac{C_3}{C_1^4}\ . \tag{5.37}$$

This procedure rapidly gets tedious!

And we're only half way done. We still must express $p$ in terms of $n$:

$$\begin{aligned} \frac{p}{k_\mathrm{B}T} &= C_1\,\big(A_1\,n + A_2\,n^2 + A_3\,n^3 + \ldots\big) \pm \tfrac{1}{2}C_2\,\big(A_1\,n + A_2\,n^2 + A_3\,n^3 + \ldots\big)^2 \\ &\qquad + \tfrac{1}{3}C_3\,\big(A_1\,n + A_2\,n^2 + A_3\,n^3 + \ldots\big)^3 + \ldots \\ &= C_1\,A_1\,n + \big(C_1\,A_2 \pm \tfrac{1}{2}C_2\,A_1^2\big)n^2 + \big(C_1\,A_3 \pm C_2\,A_1\,A_2 + \tfrac{1}{3}\,C_3\,A_1^3\big)\,n^3 + \ldots \\ &= n + B_2\,n^2 + B_3\,n^3 + \ldots \end{aligned} \tag{5.38}$$

We can now write

$$B_2 = C_1\,A_2 \pm \tfrac{1}{2}C_2 A_1^2 = \mp\frac{C_2}{2C_1^2} \tag{5.39}$$

$$B_3 = C_1\,A_3 \pm C_2\,A_1\,A_2 + \tfrac{1}{3}\,C_3\,A_1^3 = \frac{C_2^2}{C_1^4} - \frac{2\,C_3}{3\,C_1^3}\ . \tag{5.40}$$

It is easy to derive the general result that $B_j^\mathrm{F} = (-1)^{j-1} B_j^\mathrm{B}$, where the superscripts denote Fermi (F) or Bose (B) statistics.

We remark that the equation of state for classical (and quantum) *interacting* systems also can be expanded in terms of virial coefficients. Consider, for example, the van der Waals equation of state,

$$\bigg(p + \frac{aN^2}{V^2}\bigg)\big(V - Nb\big) = Nk_\mathrm{B}T\ . \tag{5.41}$$

This may be recast as

$$\begin{aligned} p &= \frac{nk_\mathrm{B}T}{1 - bn} - an^2 \\ &= nk_\mathrm{B}T + \big(b\,k_\mathrm{B}T - a\big)\,n^2 + k_\mathrm{B}T\,b^2 n^3 + k_\mathrm{B}T\,b^3 n^4 + \ldots\ , \end{aligned} \tag{5.42}$$

where $n = N/V$. Thus, for the van der Waals system, we have $B_2 = (b\,k_\mathrm{B}T - a)$ and $B_k = k_\mathrm{B}T\,b^{k-1}$ for all $k \geq 3$.

### 5.3.3 Ballistic dispersion

For the ballistic dispersion $\varepsilon(\boldsymbol{p}) = \boldsymbol{p}^2/2m$ we computed the density of states in eqn. 5.24. One finds

$$C_j(T) = \frac{\mathsf{g}_S\,\lambda_T^{-d}}{\Gamma(d/2)} \int\limits_0^\infty \!dt\, t^{\frac{d}{2}-1}\, e^{-jt} = \mathsf{g}_S\,\lambda_T^{-d}\, j^{-d/2}\ . \tag{5.43}$$

We then have

$$B_2(T) = \mp\, 2^{-\left(\frac{d}{2}+1\right)} \cdot \mathsf{g}_S^{-1}\,\lambda_T^d \tag{5.44}$$

$$B_3(T) = \Big(2^{-(d+1)} - 3^{-\left(\frac{d}{2}+1\right)}\Big) \cdot 2\,\mathsf{g}_S^{-2}\,\lambda_T^{2d}\ . \tag{5.45}$$

Note that $B_2(T)$ is negative for bosons and positive for fermions. This is because bosons have a tendency to bunch and under certain circumstances may exhibit a phenomenon known as *Bose-Einstein condensation* (BEC). Fermions, on the other hand, obey the Pauli principle, which results in an extra positive correction to the pressure in the low density limit.

We may also write

$$n(T,z) = \pm \mathsf{g}_S\,\lambda_T^{-d}\ \mathrm{Li}_{\frac{d}{2}}(\pm z) \tag{5.46}$$

and

$$p(T,z) = \pm \mathsf{g}_S\,k_{\mathrm{B}}T\,\lambda_T^{-d}\ \mathrm{Li}_{\frac{d}{2}+1}(\pm z)\ , \tag{5.47}$$

where

$$\mathrm{Li}_q(z) \equiv \sum_{n=1}^{\infty} \frac{z^n}{n^q} \tag{5.48}$$

is the *polylogarithm function*[1]. Note that $\mathrm{Li}_q(z)$ obeys a recursion relation in its index, *viz.*

$$z\,\frac{\partial}{\partial z}\,\mathrm{Li}_q(z) = \mathrm{Li}_{q-1}(z)\ , \tag{5.49}$$

and that

$$\mathrm{Li}_q(1) = \sum_{n=1}^{\infty} \frac{1}{n^q} = \zeta(q)\ . \tag{5.50}$$

## 5.4 Entropy and Counting States

Suppose we are to partition $N$ particles among $J$ possible distinct single particle states. How many ways $\Omega$ are there of accomplishing this task? The answer depends on the statistics of the particles. If the particles are fermions, the answer is easy: $\Omega_{\mathrm{FD}} = \binom{J}{N}$. For bosons, the number of possible partitions can be evaluated via the following argument. Imagine that we line up all the $N$ particles in a row, and we place $J-1$ barriers among the particles, as shown below in Fig. 5.1. The number of partitions is then the total number of ways of placing the $N$ particles among these $N+J-1$ objects (particles plus barriers), hence we have $\Omega_{\mathrm{BE}} = \binom{N+J-1}{N}$. For Maxwell-Boltzmann statistics, we take $\Omega_{\mathrm{MB}} = J^N/N!$. Note that $\Omega_{\mathrm{MB}}$ is not necessarily an integer, so Maxwell-Boltzmann statistics does not represent any actual state counting. Rather, it manifests itself as a common limit of the Bose and Fermi distributions, as we have seen and shall see again shortly.

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[1] Several texts, such as Pathria and Reichl, write $g_q(z)$ for $\mathrm{Li}_q(z)$. I adopt the latter notation since we are already using the symbol $g$ for the density of states function $g(\varepsilon)$ and for the internal degeneracy $\mathsf{g}$.

Figure 5.1: Partitioning $N$ bosons into $J$ possible states ($N = 14$ and $J = 5$ shown). The $N$ black dots represent bosons, while the $J - 1$ white dots represent markers separating the different single particle populations. Here $n_1 = 3$, $n_2 = 1$, $n_3 = 4$, $n_4 = 2$, and $n_5 = 4$.

The entropy in each case is simply $S = k_B \ln \Omega$. We assume $N \gg 1$ and $J \gg 1$, with $n \equiv N/J$ finite. Then using Stirling's approximation, $\ln(K!) = K \ln K - K + \mathcal{O}(\ln K)$, we have

$$\begin{aligned} S_{MB} &= -Jk_B \, n \ln n \\ S_{BE} &= -Jk_B \big[ n \ln n - (1+n) \ln(1+n) \big] \\ S_{FD} &= -Jk_B \big[ n \ln n + (1-n) \ln(1-n) \big] \ . \end{aligned} \tag{5.51}$$

In the Maxwell-Boltzmann limit, $n \ll 1$, and all three expressions agree. Note that

$$\begin{aligned} \bigg(\frac{\partial S_{MB}}{\partial N}\bigg)_{\!J} &= -k_B \big(1 + \ln n\big) \\ \bigg(\frac{\partial S_{BE}}{\partial N}\bigg)_{\!J} &= k_B \ln\big(n^{-1} + 1\big) \\ \bigg(\frac{\partial S_{FD}}{\partial N}\bigg)_{\!J} &= k_B \ln\big(n^{-1} - 1\big) \ . \end{aligned} \tag{5.52}$$

Now let's imagine grouping the single particle spectrum into intervals of $J$ consecutive energy states. If $J$ is finite and the spectrum is continuous and we are in the thermodynamic limit, then these states will all be degenerate. Therefore, using $\alpha$ as a label for the energies, we have that the grand potential $\Omega = E - TS - \mu N$ is given in each case by

$$\begin{aligned} \Omega_{MB} &= J \sum_\alpha \Big[ (\varepsilon_\alpha - \mu)\, n_\alpha + k_B T \, n_\alpha \ln n_\alpha \Big] \\ \Omega_{BE} &= J \sum_\alpha \Big[ (\varepsilon_\alpha - \mu)\, n_\alpha + k_B T \, n_\alpha \ln n_\alpha - k_B T \, (1 + n_\alpha) \ln(1 + n_\alpha) \Big] \\ \Omega_{FD} &= J \sum_\alpha \Big[ (\varepsilon_\alpha - \mu)\, n_\alpha + k_B T \, n_\alpha \ln n_\alpha + k_B T \, (1 - n_\alpha) \ln(1 - n_\alpha) \Big] \ . \end{aligned} \tag{5.53}$$

Now - *lo and behold!* - treating $\Omega$ as a function of the distribution $\{n_\alpha\}$ and extremizing in each case, subject to the constraint of total particle number $N = J \sum_\alpha n_\alpha$, one obtains the Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac distributions, respectively:

$$\frac{\delta}{\delta n_\alpha} \Big( \Omega - \lambda \, J \sum_{\alpha'} n_{\alpha'} \Big) = 0 \quad \Rightarrow \quad \begin{cases} n^{MB}_\alpha = e^{(\mu - \varepsilon_\alpha)/k_B T} \\ \\ n^{BE}_\alpha = \big[ e^{(\varepsilon_\alpha - \mu)/k_B T} - 1 \big]^{-1} \\ \\ n^{FD}_\alpha = \big[ e^{(\varepsilon_\alpha - \mu)/k_B T} + 1 \big]^{-1} \ . \end{cases} \tag{5.54}$$

As long as $J$ is finite, so the states in each block all remain at the same energy, the results are independent of $J$.

## 5.5 Photon Statistics

### 5.5.1 Thermodynamics of the photon gas

There exists a certain class of particles, including photons and certain elementary excitations in solids such as phonons (*i.e.* lattice vibrations) and magnons (*i.e.* spin waves) which obey bosonic statistics but with zero chemical potential. This is because their overall number is not conserved (under typical conditions) – photons can be emitted and absorbed by the atoms in the wall of a container, phonon and magnon number is also not conserved due to various processes, *etc.* In such cases, the free energy attains its minimum value with respect to particle number when

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T.V} = 0 \, . \tag{5.55}$$

The number distribution, from eqn. 5.15, is then

$$n(\varepsilon) = \frac{1}{e^{\beta\varepsilon} - 1} \, . \tag{5.56}$$

The grand partition function for a system of particles with $\mu = 0$ is

$$\Omega(T,V) = V k_{\rm B} T \int\limits_{-\infty}^{\infty} \! d\varepsilon \, g(\varepsilon) \, \ln\left(1 - e^{-\varepsilon/k_{\rm B}T}\right) \, , \tag{5.57}$$

where $g(\varepsilon)$ is the density of states per unit volume.

Suppose the particle dispersion is $\varepsilon(\boldsymbol{p}) = A|\boldsymbol{p}|^\sigma$. We can compute the density of states $g(\varepsilon)$:

$$\begin{aligned} g(\varepsilon) &= \mathsf{g} \int \! \frac{d^d\!p}{h^d} \, \delta\big(\varepsilon - A|\boldsymbol{p}|^\sigma\big) \\ &= \frac{\mathsf{g}\Omega_d}{h^d} \int\limits_0^\infty \! dp \, p^{d-1} \, \delta(\varepsilon - Ap^\sigma) \\ &= \frac{\mathsf{g}\Omega_d}{\sigma h^d} \, A^{-\frac{d}{\sigma}} \int\limits_0^\infty \! dx \, x^{\frac{d}{\sigma}-1} \, \delta(\varepsilon - x) \\ &= \frac{2\,\mathsf{g}}{\sigma\,\Gamma(d/2)} \left(\frac{\sqrt{\pi}}{hA^{1/\sigma}}\right)^{\! d} \varepsilon^{\frac{d}{\sigma}-1} \, \Theta(\varepsilon) \, , \end{aligned} \tag{5.58}$$

where g is the internal degeneracy, due, for example, to different polarization states of the photon. We have used the result $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ for the solid angle in $d$ dimensions. The step function $\Theta(\varepsilon)$ is perhaps overly formal, but it reminds us that the energy spectrum is bounded from below by $\varepsilon = 0$, *i.e.* there are no negative energy states.

For the photon, we have $\varepsilon(\boldsymbol{p}) = cp$, hence $\sigma = 1$ and

$$g(\varepsilon) = \frac{2\mathsf{g}\,\pi^{d/2}}{\Gamma(d/2)} \, \frac{\varepsilon^{d-1}}{(hc)^d} \, \Theta(\varepsilon) \, . \tag{5.59}$$

In $d = 3$ dimensions the degeneracy is $\mathsf{g} = 2$, the number of independent polarization states. The pressure $p(T)$ is then obtained using $\Omega = -pV$. We have

$$\begin{aligned} p(T) &= -k_{\rm B}T \int\limits_{-\infty}^{\infty} \! d\varepsilon \; g(\varepsilon)\, \ln\!\big(1 - e^{-\varepsilon/k_{\rm B}T}\big) \\ &= -\frac{2\,\mathsf{g}\,\pi^{d/2}}{\Gamma(d/2)}\,(hc)^{-d}\,k_{\rm B}T \int\limits_0^{\infty} \! d\varepsilon\, \varepsilon^{d-1}\, \ln\!\big(1 - e^{-\varepsilon/k_{\rm B}T}\big) \\ &= -\frac{2\,\mathsf{g}\,\pi^{d/2}}{\Gamma(d/2)}\,\frac{(k_{\rm B}T)^{d+1}}{(hc)^d} \int\limits_0^{\infty} \! dt\, t^{d-1} \ln\!\big(1 - e^{-t}\big) \ . \end{aligned} \tag{5.60}$$

We can make some progress with the dimensionless integral:

$$\begin{aligned} \mathcal{I}_d &\equiv -\int\limits_0^{\infty} \! dt\, t^{d-1} \ln\!\big(1 - e^{-t}\big) \\ &= \sum_{n=1}^{\infty} \frac{1}{n} \int\limits_0^{\infty} \! dt\, t^{d-1}\, e^{-nt} \\ &= \Gamma(d) \sum_{n=1}^{\infty} \frac{1}{n^{d+1}} = \Gamma(d)\,\zeta(d+1) \ . \end{aligned} \tag{5.61}$$

Finally, we invoke a result from the mathematics of the gamma function known as the *doubling formula*,

$$\Gamma(z) = \frac{2^{z-1}}{\sqrt{\pi}}\,\Gamma\big(\tfrac{z}{2}\big)\,\Gamma\big(\tfrac{z+1}{2}\big) \ . \tag{5.62}$$

Putting it all together, we find

$$p(T) = \mathsf{g}\,\pi^{-\frac{1}{2}(d+1)}\,\Gamma\big(\tfrac{d+1}{2}\big)\,\zeta(d+1)\,\frac{(k_{\rm B}T)^{d+1}}{(\hbar c)^d} \ . \tag{5.63}$$

The number density is found to be

$$\begin{aligned} n(T) &= \int\limits_{-\infty}^{\infty} \! d\varepsilon \; \frac{g(\varepsilon)}{e^{\varepsilon/k_{\rm B}T} - 1} \\ &= \mathsf{g}\,\pi^{-\frac{1}{2}(d+1)}\,\Gamma\big(\tfrac{d+1}{2}\big)\,\zeta(d) \left(\frac{k_{\rm B}T}{\hbar c}\right)^{\!d} . \end{aligned} \tag{5.64}$$

For photons in $d = 3$ dimensions, we have $\mathsf{g} = 2$ and thus

$$n(T) = \frac{2\,\zeta(3)}{\pi^2}\left(\frac{k_{\rm B}T}{\hbar c}\right)^{\!3} \quad , \quad p(T) = \frac{2\,\zeta(4)}{\pi^2}\,\frac{(k_{\rm B}T)^4}{(\hbar c)^3} \ . \tag{5.65}$$

It turns out that $\zeta(4) = \frac{\pi^4}{90}$.

Note that $\hbar c/k_{\rm B} = 0.22855\,{\rm cm}\cdot{\rm K}$, so

$$\frac{k_{\rm B}T}{\hbar c} = 4.3755\,T[{\rm K}]\,{\rm cm}^{-1} \quad \Longrightarrow \quad n(T) = 20.405 \times T^3[{\rm K}^3]\,{\rm cm}^{-3} \ . \tag{5.66}$$

To find the entropy, we use Gibbs-Duhem:

$$d\mu = 0 = -s\,dT + v\,dp \quad \Longrightarrow \quad s = v\,\frac{dp}{dT}\ , \tag{5.67}$$

where $s$ is the entropy per particle and $v = n^{-1}$ is the volume per particle. We then find

$$s(T) = (d{+}1)\,\frac{\zeta(d{+}1)}{\zeta(d)}\,k_{\mathrm{B}}\ . \tag{5.68}$$

The entropy per particle is constant. The internal energy is

$$E = -\frac{\partial \ln \Xi}{\partial \beta} = -\frac{\partial}{\partial \beta}(\beta p V) = d \cdot p\,V\ , \tag{5.69}$$

and hence the energy per particle is

$$\varepsilon = \frac{E}{N} = d \cdot pv = \frac{d \cdot \zeta(d{+}1)}{\zeta(d)}\,k_{\mathrm{B}}T\ . \tag{5.70}$$

### 5.5.2 Classical arguments for the photon gas

A number of thermodynamic properties of the photon gas can be determined from purely classical arguments. Here we recapitulate a few important ones.

1. Suppose our photon gas is confined to a rectangular box of dimensions $L_x \times L_y \times L_z$. Suppose further that the dimensions are all expanded by a factor $\lambda^{1/3}$, *i.e.* the volume is isotropically expanded by a factor of $\lambda$. The cavity modes of the electromagnetic radiation have quantized wavevectors, even within classical electromagnetic theory, given by

$$\boldsymbol{k} = \left(\frac{2\pi n_x}{L_x}\,,\,\frac{2\pi n_y}{L_y}\,,\,\frac{2\pi n_z}{L_z}\right). \tag{5.71}$$

   Since the energy for a given mode is $\varepsilon(\boldsymbol{k}) = \hbar c|\boldsymbol{k}|$, we see that the energy changes by a factor $\lambda^{-1/3}$ under an adiabatic volume expansion $V \to \lambda V$, where the distribution of different electromagnetic mode occupancies remains fixed. Thus,

$$V\left(\frac{\partial E}{\partial V}\right)_{\!S} = \lambda\left(\frac{\partial E}{\partial \lambda}\right)_{\!S} = -\tfrac{1}{3}E\ . \tag{5.72}$$

   Thus,

$$p = -\left(\frac{\partial E}{\partial V}\right)_{\!S} = \frac{E}{3V}\ , \tag{5.73}$$

   as we found in eqn. 5.69. Since $E = E(T,V)$ is extensive, we must have $p = p(T)$ alone.

2. Since $p = p(T)$ alone, we have

$$\begin{aligned}\left(\frac{\partial E}{\partial V}\right)_{\!T} &= \left(\frac{\partial E}{\partial V}\right)_{\!p} = 3p\\ &= T\left(\frac{\partial p}{\partial T}\right)_{\!V} - p\ ,\end{aligned} \tag{5.74}$$

   where the second line follows the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_p = \left(\frac{\partial p}{\partial T}\right)_V$, after invoking the First Law $dE = TdS - p\,dV$. Thus,

$$T\,\frac{dp}{dT} = 4p \quad \Longrightarrow \quad p(T) = A\,T^4\ , \tag{5.75}$$

   where $A$ is a constant. Thus, we recover the temperature dependence found microscopically in eqn. 5.63.

3. Given an energy density $E/V$, the differential energy flux emitted in a direction $\theta$ relative to a surface normal is
$$dj_\varepsilon = c \cdot \frac{E}{V} \cdot \cos\theta \cdot \frac{d\Omega}{4\pi} \ , \tag{5.76}$$
where $d\Omega$ is the differential solid angle. Thus, the power emitted per unit area is
$$\frac{dP}{dA} = \frac{cE}{4\pi V} \int\limits_0^{\pi/2} \!d\theta \int\limits_0^{2\pi} \!d\phi \ \sin\theta \cdot \cos\theta = \frac{cE}{4V} = \tfrac{3}{4}\, c\, p(T) \equiv \sigma\, T^4 \ , \tag{5.77}$$
where $\sigma = \frac{3}{4} cA$, with $p(T) = A\, T^4$ as we found above. From quantum statistical mechanical considerations, we have
$$\sigma = \frac{\pi^2 k_{\rm B}^4}{60\, c^2\, \hbar^3} = 5.67 \times 10^{-8}\, \frac{\rm W}{\rm m^2\, K^4} \tag{5.78}$$
is *Stefan's constant*.

### 5.5.3 Surface temperature of the earth

We derived the result $P = \sigma T^4 \cdot A$ where $\sigma = 5.67 \times 10^{-8}\,{\rm W/m^2\,K^4}$ for the power emitted by an electromagnetic 'black body'. Let's apply this result to the earth-sun system. We'll need three lengths: the radius of the sun $R_\odot = 6.96 \times 10^8\,{\rm m}$, the radius of the earth $R_{\rm e} = 6.38 \times 10^6\,{\rm m}$, and the radius of the earth's orbit $a_{\rm e} = 1.50 \times 10^{11}\,{\rm m}$. Let's assume that the earth has achieved a steady state temperature of $T_{\rm e}$. We balance the total power incident upon the earth with the power radiated by the earth. The power incident upon the earth is
$$P_{\rm incident} = \frac{\pi R_{\rm e}^2}{4\pi a_{\rm e}^2} \cdot \sigma T_\odot^4 \cdot 4\pi R_\odot^2 = \frac{R_{\rm e}^2\, R_\odot^2}{a_{\rm e}^2} \cdot \pi\sigma T_\odot^4 \ . \tag{5.79}$$
The power radiated by the earth is
$$P_{\rm radiated} = \sigma T_{\rm e}^4 \cdot 4\pi R_{\rm e}^2 \ . \tag{5.80}$$
Setting $P_{\rm incident} = P_{\rm radiated}$, we obtain
$$T_{\rm e} = \left(\frac{R_\odot}{2\, a_{\rm e}}\right)^{1/2} T_\odot \ . \tag{5.81}$$
Thus, we find $T_{\rm e} = 0.04817\, T_\odot$, and with $T_\odot = 5780\,{\rm K}$, we obtain $T_{\rm e} = 278.4\,{\rm K}$. The mean surface temperature of the earth is $\bar{T}_{\rm e} = 287\,{\rm K}$, which is only about $10\,{\rm K}$ higher. The difference is due to the fact that the earth is not a perfect blackbody, *i.e.* an object which absorbs all incident radiation upon it and emits radiation according to Stefan's law. As you know, the earth's atmosphere retraps a fraction of the emitted radiation – a phenomenon known as the *greenhouse effect*.

### 5.5.4 Distribution of blackbody radiation

Recall that the frequency of an electromagnetic wave of wavevector $\boldsymbol{k}$ is $\nu = c/\lambda = ck/2\pi$. Therefore the number of photons $\mathcal{N}_T(\nu, T)$ per unit frequency in thermodynamic equilibrium is (recall there are two polarization states)
$$\mathcal{N}(\nu, T)\, d\nu = \frac{2\, V}{8\pi^3} \cdot \frac{d^3\!k}{e^{\hbar ck/k_{\rm B}T} - 1} = \frac{V}{\pi^2} \cdot \frac{k^2\, dk}{e^{\hbar ck/k_{\rm B}T} - 1} \ . \tag{5.82}$$
We therefore have
$$\mathcal{N}(\nu, T) = \frac{8\pi V}{c^3} \cdot \frac{\nu^2}{e^{h\nu/k_{\rm B}T} - 1} \ . \tag{5.83}$$

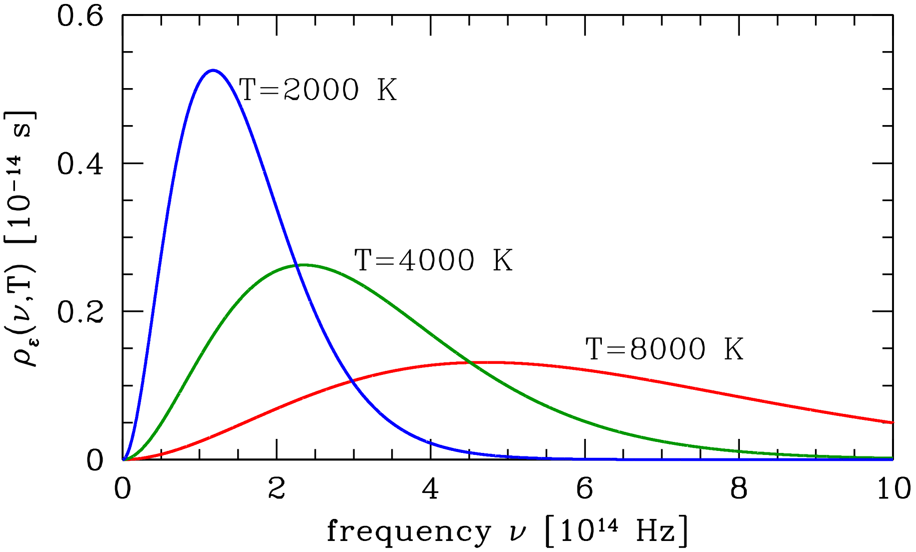

Figure 5.2: Spectral density $\rho_\varepsilon(\nu,T)$ for blackbody radiation at three temperatures.

Since a photon of frequency $\nu$ carries energy $h\nu$, the energy per unit frequency $\mathcal{E}(\nu)$ is

$$\mathcal{E}(\nu,T) = \frac{8\pi hV}{c^3} \cdot \frac{\nu^3}{e^{h\nu/k_B T} - 1} \, . \tag{5.84}$$

Note what happens if Planck's constant $h$ vanishes, as it does in the classical limit. The denominator can then be written

$$e^{h\nu/k_B T} - 1 = \frac{h\nu}{k_B T} + \mathcal{O}(h^2) \tag{5.85}$$

and

$$\mathcal{E}_{CL}(\nu,T) = \lim_{h\to 0} \mathcal{E}(\nu) = V \cdot \frac{8\pi k_B T}{c^3}\, \nu^2 \, . \tag{5.86}$$

In classical electromagnetic theory, then, the total energy integrated over all frequencies *diverges*. This is known as the *ultraviolet catastrophe*, since the divergence comes from the large $\nu$ part of the integral, which in the optical spectrum is the ultraviolet portion. With quantization, the Bose-Einstein factor imposes an effective ultraviolet cutoff $k_B T/h$ on the frequency integral, and the total energy, as we found above, is finite:

$$E(T) = \int\limits_0^\infty d\nu\, \mathcal{E}(\nu) = 3pV = V \cdot \frac{\pi^2}{15}\, \frac{(k_B T)^4}{(\hbar c)^3} \, . \tag{5.87}$$

We can define the spectral density $\rho_\varepsilon(\nu)$ of the radiation as

$$\rho_\varepsilon(\nu,T) \equiv \frac{\mathcal{E}(\nu,T)}{E(T)} = \frac{15}{\pi^4}\, \frac{h}{k_B T}\, \frac{(h\nu/k_B T)^3}{e^{h\nu/k_B T} - 1} \tag{5.88}$$

so that $\rho_\varepsilon(\nu,T)\, d\nu$ is the fraction of the electromagnetic energy, under equilibrium conditions, between frequencies $\nu$ and $\nu + d\nu$, *i.e.* $\int\limits_0^\infty d\nu\, \rho_\varepsilon(\nu,T) = 1$. In fig. 5.2 we plot this in fig. 5.2 for three different temperatures. The maximum occurs when $s \equiv h\nu/k_B T$ satisfies

$$\frac{d}{ds}\left(\frac{s^3}{e^s - 1}\right) = 0 \qquad \Longrightarrow \qquad \frac{s}{1 - e^{-s}} = 3 \qquad \Longrightarrow \qquad s = 2.82144 \, . \tag{5.89}$$

### 5.5.5 What if the sun emitted ferromagnetic spin waves?

We saw in eqn. 5.76 that the power emitted per unit surface area by a blackbody is $\sigma T^4$. The power law here follows from the ultrarelativistic dispersion $\varepsilon = \hbar c k$ of the photons. Suppose that we replace this dispersion with the general form $\varepsilon = \varepsilon(\boldsymbol{k})$. Now consider a large box in equilibrium at temperature $T$. The *energy current* incident on a differential area $dA$ of surface normal to $\hat{\boldsymbol{z}}$ is

$$dP = dA \cdot \int \frac{d^3k}{(2\pi)^3}\, \Theta(\cos\theta) \cdot \varepsilon(\boldsymbol{k}) \cdot \frac{1}{\hbar}\frac{\partial\varepsilon(\boldsymbol{k})}{\partial k_z} \cdot \frac{1}{e^{\varepsilon(\boldsymbol{k})/k_{\rm B}T} - 1} \ . \tag{5.90}$$

Let us assume an isotropic power law dispersion of the form $\varepsilon(\boldsymbol{k}) = Ck^\alpha$. Then after a straightforward calculation we obtain

$$\frac{dP}{dA} = \sigma\, T^{2+\frac{2}{\alpha}} \ , \tag{5.91}$$

where

$$\sigma = \zeta\big(2+\tfrac{2}{\alpha}\big)\, \Gamma\big(2+\tfrac{2}{\alpha}\big) \cdot \frac{\mathsf{g}\, k_{\rm B}^{2+\frac{2}{\alpha}}\, C^{-\frac{2}{\alpha}}}{8\pi^2\hbar} \ . \tag{5.92}$$

One can check that for $\mathsf{g} = 2$, $C = \hbar c$, and $\alpha = 1$ that this result reduces to that of eqn. 5.78.

## 5.6 Lattice Vibrations : Einstein and Debye Models

Crystalline solids support propagating waves called *phonons*, which are quantized vibrations of the lattice. Recall that the quantum mechanical Hamiltonian for a single harmonic oscillator, $\hat{H} = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2$, may be written as $\hat{H} = \hbar\omega_0(a^\dagger a + \frac{1}{2})$, where $a$ and $a^\dagger$ are 'ladder operators' satisfying commutation relations $\big[a\,,a^\dagger\big] = 1$.

### 5.6.1 One-dimensional chain

Consider the linear chain of masses and springs depicted in fig. 5.3. We assume that our system consists of $N$ mass points on a large ring of circumference $L$. In equilibrium, the masses are spaced evenly by a distance $b = L/N$. That is, $x_n^0 = nb$ is the equilibrium position of particle $n$. We define $u_n = x_n - x_n^0$ to be the difference between the position of mass $n$ and The Hamiltonian is then

$$\begin{aligned}\hat{H} &= \sum_n \bigg[\frac{p_n^2}{2m} + \tfrac{1}{2}\kappa\,(x_{n+1} - x_n - a)^2\bigg] \\ &= \sum_n \bigg[\frac{p_n^2}{2m} + \tfrac{1}{2}\kappa\,(u_{n+1} - u_n)^2\bigg] + \tfrac{1}{2}N\kappa(b-a)^2 \ ,\end{aligned} \tag{5.93}$$

where $a$ is the unstretched length of each spring, $m$ is the mass of each mass point, $\kappa$ is the force constant of each spring, and $N$ is the total number of mass points. If $b \neq a$ the springs are under tension in equilibrium, but as we see this only leads to an additive constant in the Hamiltonian, and hence does not enter the equations of motion.

The classical equations of motion are

$$\dot{u}_n = \frac{\partial\hat{H}}{\partial p_n} = \frac{p_n}{m} \tag{5.94}$$

$$\dot{p}_n = -\frac{\partial\hat{H}}{\partial u_n} = \kappa\,\big(u_{n+1} + u_{n-1} - 2u_n\big) \ . \tag{5.95}$$

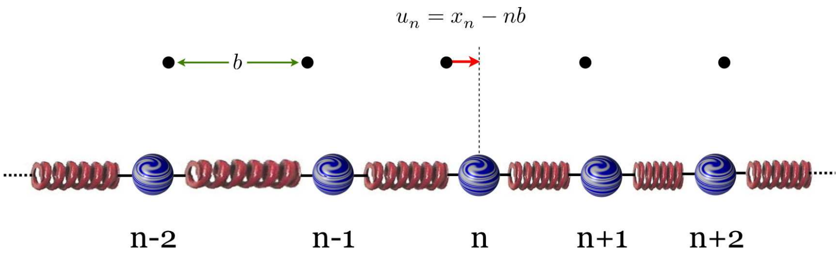

Figure 5.3: A linear chain of masses and springs. The black circles represent the equilibrium positions of the masses. The displacement of mass $n$ relative to its equilibrium value is $u_n$.

Taking the time derivative of the first equation and substituting into the second yields

$$\ddot{u}_n = \frac{\kappa}{m}\big(u_{n+1} + u_{n-1} - 2u_n\big) \, . \tag{5.96}$$

We now write

$$u_n = \frac{1}{\sqrt{N}} \sum_k \tilde{u}_k \, e^{ikna} \, , \tag{5.97}$$

where periodicity $u_{N+n} = u_n$ requires that the $k$ values are quantized so that $e^{ikNa} = 1$, *i.e.* $k = 2\pi j/Na$ where $j \in \{0, 1, \ldots, N-1\}$. The inverse of this discrete Fourier transform is

$$\tilde{u}_k = \frac{1}{\sqrt{N}} \sum_n u_n \, e^{-ikna} \, . \tag{5.98}$$

Note that $\tilde{u}_k$ is in general complex, but that $\tilde{u}^*_k = \tilde{u}_{-k}$. In terms of the $\tilde{u}_k$, the equations of motion take the form

$$\ddot{\tilde{u}}_k = -\frac{2\kappa}{m}\big(1 - \cos(ka)\big)\, \tilde{u}_k \equiv -\omega^2_k \, \tilde{u}_k \, . \tag{5.99}$$

Thus, each $\tilde{u}_k$ is a normal mode, and the normal mode frequencies are

$$\omega_k = 2\sqrt{\frac{\kappa}{m}}\, \big|\sin\big(\tfrac{1}{2}ka\big)\big| \, . \tag{5.100}$$

The density of states for this band of phonon excitations is

$$\begin{aligned} g(\varepsilon) &= \int\limits_{-\pi/a}^{\pi/a} \frac{dk}{2\pi}\, \delta(\varepsilon - \hbar\omega_k) \\ &= \frac{2}{\pi a}\big(J^2 - \varepsilon^2\big)^{-1/2}\, \Theta(\varepsilon)\, \Theta(J - \varepsilon) \, , \end{aligned} \tag{5.101}$$

where $J = 2\hbar\sqrt{\kappa/m}$ is the phonon bandwidth. The step functions require $0 \le \varepsilon \le J$; outside this range there are no phonon energy levels and the density of states accordingly vanishes.

The entire theory can be quantized, taking $\big[p_n \, , u_{n'}\big] = -i\hbar\delta_{nn'}$. We then define

$$p_n = \frac{1}{\sqrt{N}} \sum_k \tilde{p}_k \, e^{ikna} \qquad , \qquad \tilde{p}_k = \frac{1}{\sqrt{N}} \sum_n p_n \, e^{-ikna} \, , \tag{5.102}$$

in which case $\big[\tilde{p}_k \, , \tilde{u}_{k'}\big] = -i\hbar\delta_{kk'}$. Note that $\tilde{u}^\dagger_k = \tilde{u}_{-k}$ and $\tilde{p}^\dagger_k = \tilde{p}_{-k}$. We then define the ladder operator

$$a_k = \bigg(\frac{1}{2m\hbar\omega_k}\bigg)^{1/2} \tilde{p}_k - i\bigg(\frac{m\omega_k}{2\hbar}\bigg)^{1/2} \tilde{u}_k \tag{5.103}$$

and its Hermitean conjugate $a^\dagger_k$, in terms of which the Hamiltonian is

$$\hat{H} = \sum_k \hbar\omega_k \left( a^\dagger_k a_k + \tfrac{1}{2} \right) , \tag{5.104}$$

which is a sum over independent harmonic oscillator modes. Note that the sum over $k$ is restricted to an interval of width $2\pi$, *e.g.* $k \in \big[-\frac{\pi}{a}, \frac{\pi}{a}\big]$, which is the *first Brillouin zone* for the one-dimensional chain structure. The state at wavevector $k + \frac{2\pi}{a}$ is identical to that at $k$, as we see from eqn. 5.98.

### 5.6.2 General theory of lattice vibrations

The most general model of a harmonic solid is described by a Hamiltonian of the form

$$\hat{H} = \sum_{\boldsymbol{R},i} \frac{\boldsymbol{p}_i^2(\boldsymbol{R})}{2M_i} + \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} \sum_{\boldsymbol{R},\boldsymbol{R}'} u_i^\alpha(\boldsymbol{R})\, \Phi_{ij}^{\alpha\beta}(\boldsymbol{R}-\boldsymbol{R}')\, u_j^\beta(\boldsymbol{R}') , \tag{5.105}$$

where the *dynamical matrix* is

$$\Phi_{ij}^{\alpha\beta}(\boldsymbol{R}-\boldsymbol{R}') = \frac{\partial^2 U}{\partial u_i^\alpha(\boldsymbol{R})\, \partial u_j^\beta(\boldsymbol{R}')} , \tag{5.106}$$

where $U$ is the potential energy of interaction among all the atoms. Here we have simply expanded the potential to second order in the local displacements $u_i^\alpha(\boldsymbol{R})$. The lattice sites $\boldsymbol{R}$ are elements of a *Bravais lattice*. The indices $i$ and $j$ specify *basis elements* with respect to this lattice, and the indices $\alpha$ and $\beta$ range over $\{1, \ldots, d\}$, the number of possible directions in space. The subject of crystallography is beyond the scope of these notes, but, very briefly, a Bravais lattice in $d$ dimensions is specified by a set of $d$ linearly independent *primitive direct lattice vectors* $\boldsymbol{a}_l$, such that any point in the Bravais lattice may be written as a sum over the primitive vectors with integer coefficients: $\boldsymbol{R} = \sum_{l=1}^d n_l\, \boldsymbol{a}_l$. The set of all such vectors $\{\boldsymbol{R}\}$ is called the *direct lattice*. The direct lattice is closed under the operation of vector addition: if $\boldsymbol{R}$ and $\boldsymbol{R}'$ are points in a Bravais lattice, then so is $\boldsymbol{R}+\boldsymbol{R}'$.

A crystal is a periodic arrangement of lattice sites. The fundamental repeating unit is called the *unit cell*. Not every crystal is a Bravais lattice, however. Indeed, Bravais lattices are special crystals in which there is only one atom per unit cell. Consider, for example, the structure in fig. 5.4. The blue dots form a square Bravais lattice with primitive direct lattice vectors $\boldsymbol{a}_1 = a\,\hat{\boldsymbol{x}}$ and $\boldsymbol{a}_2 = a\,\hat{\boldsymbol{y}}$, where $a$ is the *lattice constant*, which is the distance between any neighboring pair of blue dots. The red squares and green triangles, along with the blue dots, form a *basis* for the crystal structure which label each *sublattice*. Our crystal in fig. 5.4 is formally classified as a *square Bravais lattice with a three element basis*. To specify an arbitrary site in the crystal, we must specify both a direct lattice vector $\boldsymbol{R}$ as well as a basis index $j \in \{1, \ldots, r\}$, so that the location is $\boldsymbol{R} + \boldsymbol{\eta}_j$. The vectors $\{\boldsymbol{\eta}_j\}$ are the *basis vectors* for our crystal structure. We see that a general crystal structure consists of a repeating unit, known as a *unit cell*. The centers (or corners, if one prefers) of the unit cells form a Bravais lattice. Within a given unit cell, the individual sublattice sites are located at positions $\boldsymbol{\eta}_j$ with respect to the unit cell position $\boldsymbol{R}$.

Upon diagonalization, the Hamiltonian of eqn. 5.105 takes the form

$$\hat{H} = \sum_{\boldsymbol{k},a} \hbar\omega_a(\boldsymbol{k}) \Big( A^\dagger_a(\boldsymbol{k})\, A_a(\boldsymbol{k}) + \tfrac{1}{2} \Big) , \tag{5.107}$$

where

$$\big[A_a(\boldsymbol{k}) \, , \, A^\dagger_b(\boldsymbol{k}')\big] = \delta_{ab}\, \delta_{\boldsymbol{k}\boldsymbol{k}'} \ . \tag{5.108}$$

The eigenfrequencies are solutions to the eigenvalue equation

$$\sum_{j,\beta} \tilde{\Phi}_{ij}^{\alpha\beta}(\boldsymbol{k})\, \mathsf{e}_{j\beta}^{(a)}(\boldsymbol{k}) = M_i\, \omega_a^2(\boldsymbol{k})\, \mathsf{e}_{i\alpha}^{(a)}(\boldsymbol{k}) , \tag{5.109}$$

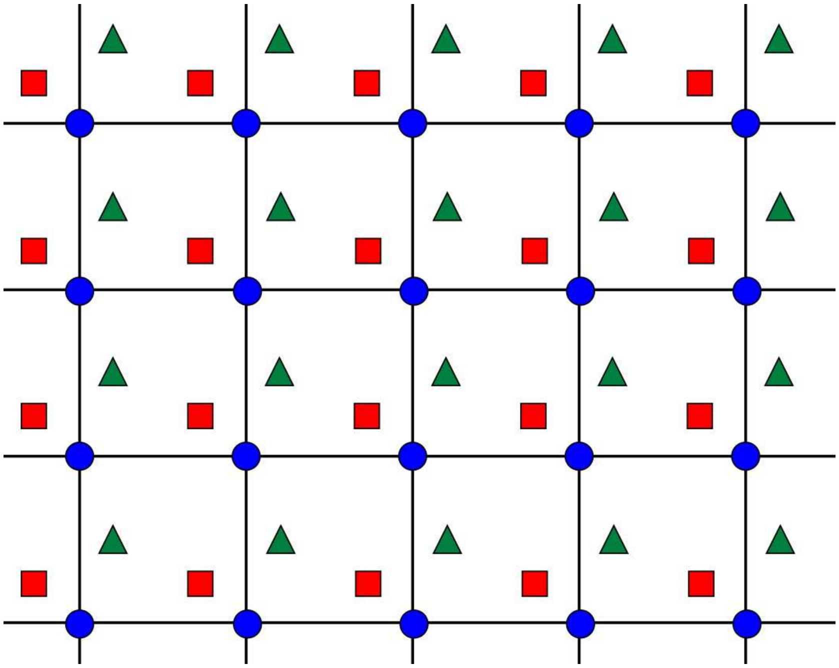

Figure 5.4: A crystal structure with an underlying square Bravais lattice and a three element basis.

where

$$\tilde{\Phi}^{\alpha\beta}_{ij}(\boldsymbol{k}) = \sum_{\boldsymbol{R}} \Phi^{\alpha\beta}_{ij}(\boldsymbol{R})\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \ . \tag{5.110}$$

Here, $\boldsymbol{k}$ lies within the first *Brillouin zone*, which is the unit cell of the *reciprocal lattice* of points $\boldsymbol{G}$ satisfying $e^{i\boldsymbol{G}\cdot\boldsymbol{R}} = 1$ for all $\boldsymbol{G}$ and $\boldsymbol{R}$. The reciprocal lattice is also a Bravais lattice, with primitive reciprocal lattice vectors $\boldsymbol{b}_l$, such that any point on the reciprocal lattice may be written $\boldsymbol{G} = \sum_{l=1}^{d} m_l\, \boldsymbol{b}_l$. One also has that $\boldsymbol{a}_l \cdot \boldsymbol{b}_{l'} = 2\pi\delta_{ll'}$. The index $a$ ranges from $1$ to $d \cdot r$ and labels the *mode* of oscillation at wavevector $\boldsymbol{k}$. The vector $\mathrm{e}^{(a)}_{i\alpha}(\boldsymbol{k})$ is the *polarization vector* for the $a^{\text{th}}$ phonon branch. In solids of high symmetry, phonon modes can be classified as longitudinal or transverse excitations.

For a crystalline lattice with an $r$-element basis, there are then $d \cdot r$ phonon modes for each wavevector $\boldsymbol{k}$ lying in the first Brillouin zone. If we impose periodic boundary conditions, then the $\boldsymbol{k}$ points within the first Brillouin zone are themselves quantized, as in the $d = 1$ case where we found $k = 2\pi n/N$. There are $N$ distinct $\boldsymbol{k}$ points in the first Brillouin zone – one for every direct lattice site. The total number of modes is than $d \cdot r \cdot N$, which is the total number of translational degrees of freedom in our system: $rN$ total atoms ($N$ unit cells each with an $r$ atom basis) each free to vibrate in $d$ dimensions. Of the $d \cdot r$ branches of phonon excitations, $d$ of them will be *acoustic modes* whose frequency vanishes as $\boldsymbol{k} \to 0$. The remaining $d(r-1)$ branches are *optical modes* and oscillate at finite frequencies. Basically, in an acoustic mode, for $\boldsymbol{k}$ close to the (Brillouin) zone center $\boldsymbol{k} = 0$, all the atoms in each unit cell move together in the same direction at any moment of time. In an optical mode, the different basis atoms move in different directions.

There is no number conservation law for phonons – they may be freely created or destroyed in anharmonic processes, where two photons with wavevectors $\boldsymbol{k}$ and $\boldsymbol{q}$ can combine into a single phonon with wavevector $\boldsymbol{k}+\boldsymbol{q}$, and *vice versa*. Therefore the chemical potential for phonons is $\mu = 0$. We define the density of states $g_a(\omega)$ for the

$a^{\rm th}$ phonon mode as

$$g_a(\omega) = \frac{1}{N}\sum_{\boldsymbol{k}} \delta\big(\omega - \omega_a(\boldsymbol{k})\big) = \mathcal{V}_0 \int\limits_{\rm BZ} \frac{d^d\!k}{(2\pi)^d}\, \delta\big(\omega - \omega_a(\boldsymbol{k})\big) \ , \tag{5.111}$$

where $N$ is the number of unit cells, $\mathcal{V}_0$ is the unit cell volume of the direct lattice, and the $\boldsymbol{k}$ sum and integral are over the first Brillouin zone only. Note that $\omega$ here has dimensions of frequency. The functions $g_a(\omega)$ is normalized to unity:

$$\int\limits_0^\infty \! d\omega\, g_a(\omega) = 1\ . \tag{5.112}$$

The total phonon density of states per unit cell is given by[2]

$$g(\omega) = \sum_{a=1}^{dr} g_a(\omega)\ . \tag{5.113}$$

The grand potential for the phonon gas is

$$\begin{aligned} \Omega(T,V) &= -k_{\rm B}T \ln \prod_{\boldsymbol{k},a} \sum_{n_a(\boldsymbol{k})=0}^\infty e^{-\beta\hbar\omega_a(\boldsymbol{k})\big(n_a(\boldsymbol{k}) + \frac{1}{2}\big)} \\ &= k_{\rm B}T \sum_{\boldsymbol{k},a} \ln\left[2\sinh\left(\frac{\hbar\omega_a(\boldsymbol{k})}{2k_{\rm B}T}\right)\right] \\ &= Nk_{\rm B}T \int\limits_0^\infty \! d\omega\, g(\omega)\, \ln\left[2\sinh\left(\frac{\hbar\omega}{2k_{\rm B}T}\right)\right] . \end{aligned} \tag{5.114}$$

Note that $V = N\mathcal{V}_0$ since there are $N$ unit cells, each of volume $\mathcal{V}_0$. The entropy is given by $S = -\big(\frac{\partial\Omega}{\partial T}\big)_V$ and thus the heat capacity is

$$C_V = -T\,\frac{\partial^2\Omega}{\partial T^2} = Nk_{\rm B} \int\limits_0^\infty \! d\omega\, g(\omega) \left(\frac{\hbar\omega}{2k_{\rm B}T}\right)^{\!2} {\rm csch}^2\!\left(\frac{\hbar\omega}{2k_{\rm B}T}\right) \tag{5.115}$$

Note that as $T\to\infty$ we have ${\rm csch}\big(\frac{\hbar\omega}{2k_{\rm B}T}\big) \to \frac{2k_{\rm B}T}{\hbar\omega}$, and therefore

$$\lim_{T\to\infty} C_V(T) = Nk_{\rm B} \int\limits_0^\infty \! d\omega\, g(\omega) = rdNk_{\rm B}\ . \tag{5.116}$$

This is the classical Dulong-Petit limit of $\frac{1}{2}k_{\rm B}$ per quadratic degree of freedom; there are $rN$ atoms moving in $d$ dimensions, hence $d\cdot rN$ positions and an equal number of momenta, resulting in a high temperature limit of $C_V = rdNk_{\rm B}$.

### 5.6.3 Einstein and Debye models

HIstorically, two models of lattice vibrations have received wide attention. First is the so-called *Einstein model*, in which there is no dispersion to the individual phonon modes. We approximate $g_a(\omega) \approx \delta(\omega - \omega_a)$, in which case

$$C_V(T) = Nk_{\rm B} \sum_a \left(\frac{\hbar\omega_a}{2k_{\rm B}T}\right)^{\!2} {\rm csch}^2\!\left(\frac{\hbar\omega_a}{2k_{\rm B}T}\right) . \tag{5.117}$$

---

[2] Note the dimensions of $g(\omega)$ are $({\rm frequency})^{-1}$. By contrast, the dimensions of $g(\varepsilon)$ in eqn. 5.24 are $({\rm energy})^{-1}\cdot({\rm volume})^{-1}$. The difference lies in the a factor of $\mathcal{V}_0\cdot\hbar$, where $\mathcal{V}_0$ is the unit cell volume.

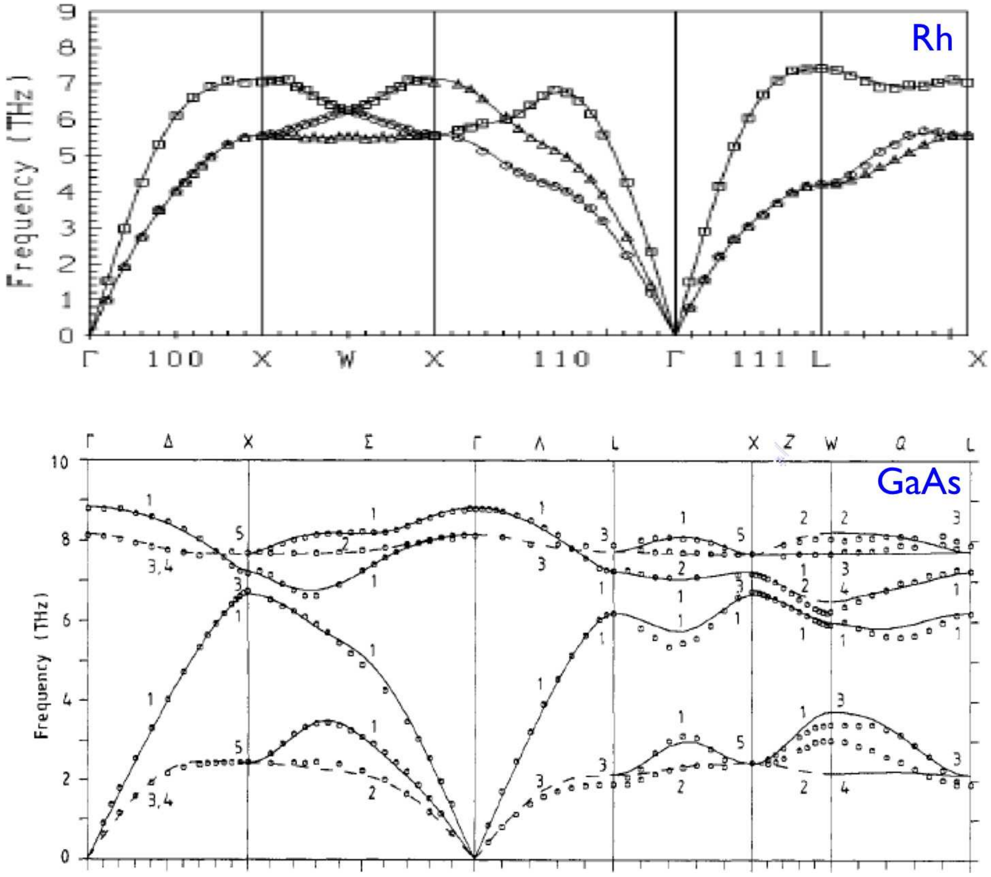

Figure 5.5: Upper panel: phonon spectrum in elemental rhodium (Rh) at $T = 297\,\mathrm{K}$ measured by high precision inelastic neutron scattering (INS) by A. Eichler *et al.*, *Phys. Rev. B* **57**, 324 (1998). Note the three acoustic branches and no optical branches, corresponding to $d = 3$ and $r = 1$. Lower panel: phonon spectrum in gallium arsenide (GaAs) at $T = 12\,\mathrm{K}$, comparing theoretical lattice-dynamical calculations with INS results of D. Strauch and B. Dorner, *J. Phys.: Condens. Matter* **2**, 1457 (1990). Note the three acoustic branches and three optical branches, corresponding to $d = 3$ and $r = 2$. The Greek letters along the $x$-axis indicate points of high symmetry in the Brillouin zone.

At low temperatures, the contribution from each branch vanishes exponentially, since $\mathrm{csch}^2\big(\frac{\hbar\omega_a}{2k_\mathrm{B}T}\big) \simeq 4\,e^{-\hbar\omega_a/k_\mathrm{B}T} \to 0$. Real solids don't behave this way.

A more realistic model. due to Debye, accounts for the low-lying acoustic phonon branches. Since the acoustic phonon dispersion vanishes linearly with $|\boldsymbol{k}|$ as $\boldsymbol{k} \to 0$, there is no temperature at which the acoustic phonons 'freeze out' exponentially, as in the case of Einstein phonons. Indeed, the Einstein model is appropriate in describing the $d\,(r-1)$ optical phonon branches, though it fails miserably for the acoustic branches.

In the vicinity of the zone center $\boldsymbol{k} = 0$ (also called $\Gamma$ in crystallographic notation) the $d$ acoustic modes obey a linear dispersion, with $\omega_a(\boldsymbol{k}) = c_a(\hat{\boldsymbol{k}})\,k$. This results in an acoustic phonon density of states in $d = 3$ dimensions of

$$\begin{aligned}\tilde{g}(\omega) &= \frac{\mathcal{V}_0\,\omega^2}{2\pi^2}\sum_a\int\!\frac{d\hat{\boldsymbol{k}}}{4\pi}\,\frac{1}{c_a^3(\boldsymbol{k})}\;\Theta(\omega_{\rm D}-\omega)\\ &= \frac{3\mathcal{V}_0}{2\pi^2\bar{c}^3}\,\omega^2\,\Theta(\omega_{\rm D}-\omega)\ ,\end{aligned} \tag{5.118}$$

where $\bar{c}$ is an average acoustic phonon velocity (*i.e.* speed of sound) defined by

$$\frac{3}{\bar{c}^3}=\sum_a\int\!\frac{d\hat{\boldsymbol{k}}}{4\pi}\,\frac{1}{c_a^3(\boldsymbol{k})} \tag{5.119}$$

and $\omega_{\rm D}$ is a cutoff known as the *Debye frequency*. The cutoff is necessary because the phonon branch does not extend forever, but only to the boundaries of the Brillouin zone. Thus, $\omega_{\rm D}$ should roughly be equal to the energy of a zone boundary phonon. Alternatively, we can define $\omega_{\rm D}$ by the normalization condition

$$\int\limits_0^\infty\!d\omega\;\tilde{g}(\omega)=3\qquad\Longrightarrow\qquad\omega_{\rm D}=(6\pi^2/\mathcal{V}_0)^{1/3}\,\bar{c}\,. \tag{5.120}$$

This allows us to write $\tilde{g}(\omega)=\big(9\omega^2/\omega_{\rm D}^3\big)\,\Theta(\omega_{\rm D}-\omega)$.

The specific heat due to the acoustic phonons is then

$$\begin{aligned}C_V(T) &= \frac{9Nk_{\rm B}}{\omega_{\rm D}^3}\int\limits_0^{\omega_{\rm D}}\!d\omega\;\omega^2\bigg(\frac{\hbar\omega}{2k_{\rm B}T}\bigg)^2\,{\rm csch}^2\bigg(\frac{\hbar\omega}{2k_{\rm B}T}\bigg)\\ &= 9Nk_{\rm B}\bigg(\frac{2T}{\Theta_{\rm D}}\bigg)^3\,\phi\big(\Theta_{\rm D}/2T\big)\ ,\end{aligned} \tag{5.121}$$

where $\Theta_{\rm D}=\hbar\omega_{\rm D}/k_{\rm B}$ is the *Debye temperature* and

$$\phi(x)=\int\limits_0^x\!dt\;t^4\;{\rm csch}^2 t=\begin{cases}\frac{1}{3}x^3 & x\to 0\\[2ex] \frac{\pi^4}{30} & x\to\infty\ .\end{cases} \tag{5.122}$$

Therefore,

$$C_V(T)=\begin{cases}\frac{12\pi^4}{5}\,Nk_{\rm B}\Big(\frac{T}{\Theta_{\rm D}}\Big)^3 & T\ll\Theta_{\rm D}\\[2ex] 3Nk_{\rm B} & T\gg\Theta_{\rm D}\ .\end{cases} \tag{5.123}$$

Thus, the heat capacity due to acoustic phonons obeys the Dulong-Petit rule in that $C_V(T\to\infty)=3Nk_{\rm B}$, corresponding to the three acoustic degrees of freedom per unit cell. The remaining contribution of $3(r-1)Nk_{\rm B}$ to the high temperature heat capacity comes from the optical modes not considered in the Debye model. The low temperature $T^3$ behavior of the heat capacity of crystalline solids is a generic feature, and its detailed description is a triumph of the Debye model.

| Element | Ag | Al | Au | C | Cd | Cr | Cu | Fe | Mn |
|---|---|---|---|---|---|---|---|---|---|
| $\Theta_{\mathrm{D}}$ (K) | 227 | 433 | 162 | 2250 | 210 | 606 | 347 | 477 | 409 |
| $T_{\mathrm{melt}}$ (K) | 962 | 660 | 1064 | 3500 | 321 | 1857 | 1083 | 1535 | 1245 |
| Element | Ni | Pb | Pt | Si | Sn | Ta | Ti | W | Zn |
| $\Theta_{\mathrm{D}}$ (K) | 477 | 105 | 237 | 645 | 199 | 246 | 420 | 383 | 329 |
| $T_{\mathrm{melt}}$ (K) | 1453 | 327 | 1772 | 1410 | 232 | 2996 | 1660 | 3410 | 420 |

Table 5.1: Debye temperatures (at $T = 0$) and melting points for some common elements (carbon is assumed to be diamond and not graphite). (*Source: the internet!*)

### 5.6.4 Melting and the Lindemann criterion

**Atomic fluctuations in a crystal**

For the one-dimensional chain, eqn. 5.103 gives

$$\tilde{u}_k = i\left(\frac{\hbar}{2m\omega_k}\right)^{1/2} \big(a_k - a^\dagger_{-k}\big)\ . \tag{5.124}$$

Therefore the RMS fluctuations at each site are given by

$$\begin{aligned} \langle u_n^2\rangle &= \frac{1}{N}\sum_k \langle \tilde{u}_k\, \tilde{u}_{-k}\rangle \\ &= \frac{1}{N}\sum_k \frac{\hbar}{m\omega_k}\,\big(n(k) + \tfrac{1}{2}\big)\ , \end{aligned} \tag{5.125}$$

where $n(k,T) = \big[\exp(\hbar\omega_k/k_{\mathrm{B}}T) - 1\big]^{-1}$ is the Bose occupancy function.

Let us now generalize this expression to the case of a $d$-dimensional solid. The appropriate expression for the RMS position fluctuations of the $i^{\mathrm{th}}$ basis atom in each unit cell is

$$\langle \boldsymbol{u}_i^2(\boldsymbol{R})\rangle = \frac{1}{N}\sum_{\boldsymbol{k}}\sum_{a=1}^{dr} \frac{\hbar}{M_{ia}(\boldsymbol{k})\,\omega_a(\boldsymbol{k})}\,\big(n_a(\boldsymbol{k}) + \tfrac{1}{2}\big)\ . \tag{5.126}$$

Here we sum over all wavevectors $\boldsymbol{k}$ in the first Brillioiun zone, and over all normal modes $a$. There are $dr$ normal modes per unit cell *i.e.* $d$ branches of the phonon dispersion $\omega_a(\boldsymbol{k})$. (For the one-dimensional chain with $d = 1$ and $r = 1$ there was only one such branch to consider). Note also the quantity $M_{ia}(\boldsymbol{k})$, which has units of mass and is defined in terms of the polarization vectors $\mathsf{e}^{(a)}_{i\alpha}(\boldsymbol{k})$ as

$$\frac{1}{M_{ia}(\boldsymbol{k})} = \sum_{\mu=1}^{d} \big|\mathsf{e}^{(a)}_{i\mu}(\boldsymbol{k})\big|^2\ . \tag{5.127}$$

The dimensions of the polarization vector are $[\mathrm{mass}]^{-1/2}$, since the generalized orthonormality condition on the normal modes is

$$\sum_{i,\mu} M_i\, \mathsf{e}^{(a)^*}_{i\mu}(\boldsymbol{k})\, \mathsf{e}^{(b)}_{i\mu}(\boldsymbol{k}) = \delta^{ab}\ , \tag{5.128}$$

where $M_i$ is the mass of the atom of species $i$ within the unit cell ($i \in \{1, \ldots, r\}$). For our purposes we can replace $M_{ia}(\boldsymbol{k})$ by an appropriately averaged quantity which we call $\mathsf{M}_i$ ; this 'effective mass' is then independent of the mode index $a$ as well as the wavevector $\boldsymbol{k}$. We may then write

$$\langle\, \boldsymbol{u}_i^2 \,\rangle \approx \int\limits_0^\infty \! d\omega\, g(\omega)\, \frac{\hbar}{\mathsf{M}_i\, \omega} \cdot \left\{ \frac{1}{e^{\hbar\omega/k_\mathrm{B}T} - 1} + \frac{1}{2} \right\} , \tag{5.129}$$

where we have dropped the site label $\boldsymbol{R}$ since translational invariance guarantees that the fluctuations are the same from one unit cell to the next. Note that the fluctuations $\langle\, \boldsymbol{u}_i^2 \,\rangle$ can be divided into a temperature-dependent part $\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{th}$ and a temperature-independent quantum contribution $\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{qu}$ , where

$$\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{th} = \frac{\hbar}{\mathsf{M}_i} \int\limits_0^\infty \! d\omega\, \frac{g(\omega)}{\omega} \cdot \frac{1}{e^{\hbar\omega/k_\mathrm{B}T} - 1} \tag{5.130}$$

$$\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{qu} = \frac{\hbar}{2\mathsf{M}_i} \int\limits_0^\infty \! d\omega\, \frac{g(\omega)}{\omega} \ . \tag{5.131}$$

Let's evaluate these contributions within the Debye model, where we replace $g(\omega)$ by

$$\bar{g}(\omega) = \frac{d^2\, \omega^{d-1}}{\omega_\mathrm{D}^d}\, \Theta(\omega_\mathrm{D} - \omega) \ . \tag{5.132}$$

We then find

$$\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{th} = \frac{d^2 \hbar}{\mathsf{M}_i\, \omega_\mathrm{D}} \left( \frac{k_\mathrm{B}T}{\hbar\omega_\mathrm{D}} \right)^{d-1} F_d(\hbar\omega_\mathrm{D}/k_\mathrm{B}T) \tag{5.133}$$

$$\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{qu} = \frac{d^2}{d-1} \cdot \frac{\hbar}{2\mathsf{M}_i\, \omega_\mathrm{D}} \ , \tag{5.134}$$

where

$$F_d(x) = \int\limits_0^x \! ds\, \frac{s^{d-2}}{e^s - 1} = \begin{cases} \frac{x^{d-2}}{d-2} & x \to 0 \\[2ex] \zeta(d-1) & x \to \infty \end{cases} \ . \tag{5.135}$$

We can now extract from these expressions several important conclusions:

1) The $T = 0$ contribution to the the fluctuations, $\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{qu}$, diverges in $d = 1$ dimensions. *Therefore there are no one-dimensional quantum solids.*

2) The thermal contribution to the fluctuations, $\langle\, \boldsymbol{u}_i^2 \,\rangle_\mathrm{th}$, diverges for any $T > 0$ whenever $d \le 2$. This is because the integrand of $F_d(x)$ goes as $s^{d-3}$ as $s \to 0$. *Therefore, there are no two-dimensional classical solids.*

3) Both the above conclusions are valid in the thermodynamic limit. Finite size imposes a cutoff on the frequency integrals, because there is a smallest wavevector $k_\mathrm{min} \sim 2\pi/L$, where $L$ is the (finite) linear dimension of the system. This leads to a low frequency cutoff $\omega_\mathrm{min} = 2\pi\bar{c}/L$, where $\bar{c}$ is the appropriately averaged acoustic phonon velocity from eqn. 5.119, which mitigates any divergences.

### Lindemann melting criterion

An old phenomenological theory of melting due to Lindemann says that a crystalline solid melts when the RMS fluctuations in the atomic positions exceeds a certain fraction $\eta$ of the lattice constant $a$. We therefore define the ratios

$$x_{i,\mathrm{th}}^2 \equiv \frac{\langle\, \boldsymbol{u}_i^2 \,\rangle_{\mathrm{th}}}{a^2} = d^2 \cdot \left(\frac{\hbar^2}{\mathsf{M}_i\, a^2\, k_{\mathrm{B}}}\right) \cdot \frac{T^{d-1}}{\Theta_{\mathrm{D}}^d} \cdot F(\Theta_{\mathrm{D}}/T) \tag{5.136}$$

$$x_{i,\mathrm{qu}}^2 \equiv \frac{\langle\, \boldsymbol{u}_i^2 \,\rangle_{\mathrm{qu}}}{a^2} = \frac{d^2}{2(d-1)} \cdot \left(\frac{\hbar^2}{\mathsf{M}_i\, a^2\, k_{\mathrm{B}}}\right) \cdot \frac{1}{\Theta_{\mathrm{D}}} \ , \tag{5.137}$$

with $x_i = \sqrt{x_{i,\mathrm{th}}^2 + x_{i,\mathrm{qu}}^2} = \sqrt{\langle\, \boldsymbol{u}_i^2 \,\rangle}\Big/a$.

Let's now work through an example of a three-dimensional solid. We'll assume a single element basis ($r = 1$). We have that

$$\frac{9\hbar^2/4k_{\mathrm{B}}}{1\,\mathtt{amu}\,\text{Å}^2} = 109\,\mathrm{K}\,. \tag{5.138}$$

According to table 5.1, the melting temperature always exceeds the Debye temperature, and often by a great amount. We therefore assume $T \gg \Theta_{\mathrm{D}}$, which puts us in the small $x$ limit of $F_d(x)$. We then find

$$x_{\mathrm{qu}}^2 = \frac{\Theta^\star}{\Theta_{\mathrm{D}}} \qquad , \qquad x_{\mathrm{th}}^2 = \frac{\Theta^\star}{\Theta_{\mathrm{D}}} \cdot \frac{4T}{\Theta_{\mathrm{D}}} \qquad , \qquad x = \sqrt{\left(1 + \frac{4T}{\Theta_{\mathrm{D}}}\right)\frac{\Theta^\star}{\Theta_{\mathrm{D}}}}\,. \tag{5.139}$$

where

$$\Theta^* = \frac{109\,\mathrm{K}}{M[\mathtt{amu}] \cdot \big(a[\text{Å}]\big)^2}\,. \tag{5.140}$$

The total position fluctuation is of course the sum $x^2 = x_{i,\mathrm{th}}^2 + x_{i,\mathrm{qu}}^2$. Consider for example the case of copper, with $M = 56\,\mathtt{amu}$ and $a = 2.87\,$Å. The Debye temperature is $\Theta_{\mathrm{D}} = 347\,\mathrm{K}$. From this we find $x_{\mathrm{qu}} = 0.026$, which says that at $T = 0$ the RMS fluctuations of the atomic positions are not quite three percent of the lattice spacing (*i.e.* the distance between neighboring copper atoms). At room temperature, $T = 293\,\mathrm{K}$, one finds $x_{\mathrm{th}} = 0.048$, which is about twice as large as the quantum contribution. How big are the atomic position fluctuations at the melting point? According to our table, $T_{\mathrm{melt}} = 1083\,\mathrm{K}$ for copper, and from our formulae we obtain $x_{\mathrm{melt}} = 0.096$. The *Lindemann criterion* says that solids melt when $x(T) \approx 0.1$.

We were very lucky to hit the magic number $x_{\mathrm{melt}} = 0.1$ with copper. Let's try another example. Lead has $M = 208\,\mathtt{amu}$ and $a = 4.95\,$Å. The Debye temperature is $\Theta_{\mathrm{D}} = 105\,\mathrm{K}$ ('soft phonons'), and the melting point is $T_{\mathrm{melt}} = 327\,\mathrm{K}$. From these data we obtain $x(T = 0) = 0.014$, $x(293\,\mathrm{K}) = 0.050$ and $x(T = 327\,\mathrm{K}) = 0.053$. Same ballpark.

We can turn the analysis around and predict a melting temperature based on the Lindemann criterion $x(T_{\mathrm{melt}}) = \eta$, where $\eta \approx 0.1$. We obtain

$$T_{\mathrm{L}} = \left(\frac{\eta^2\,\Theta_{\mathrm{D}}}{\Theta^\star} - 1\right) \cdot \frac{\Theta_{\mathrm{D}}}{4}\,. \tag{5.141}$$

We call $T_{\mathrm{L}}$ the *Lindemann temperature*. Most treatments of the Lindemann criterion ignore the quantum correction, which gives the $-1$ contribution inside the above parentheses. But if we are more careful and include it, we see that it may be possible to have $T_{\mathrm{L}} < 0$. This occurs for any crystal where $\Theta_{\mathrm{D}} < \Theta^\star/\eta^2$.

Consider for example the case of $^4$He, which at atmospheric pressure condenses into a liquid at $T_{\mathrm{c}} = 4.2\,\mathrm{K}$ and remains in the liquid state down to absolute zero. At $p = 1\,\mathrm{atm}$, it never solidifies! Why? The number density of liquid $^4$He at $p = 1\,\mathrm{atm}$ and $T = 0\,\mathrm{K}$ is $2.2 \times 10^{22}\,\mathrm{cm}^{-3}$. Let's say the Helium atoms want to form a crystalline lattice. We don't know *a priori* what the lattice structure will be, so let's for the sake of simplicity assume a simple cubic lattice. From the number density we obtain a lattice spacing of $a = 3.57\,$Å. OK now what do we take for the Debye temperature? Theoretically this should depend on the microscopic force constants which enter the small oscillations problem (*i.e.* the spring constants between pairs of helium atoms in equilibrium). We'll use the expression we derived for the Debye frequency, $\omega_{\mathrm{D}} = (6\pi^2/\mathcal{V}_0)^{1/3}\bar{c}$, where $\mathcal{V}_0$ is the unit cell volume. We'll take $\bar{c} = 238\,\mathrm{m/s}$, which is the speed of sound in liquid helium at $T = 0$. This gives $\Theta_{\mathrm{D}} = 19.8\,\mathrm{K}$. We find $\Theta^\star = 2.13\,\mathrm{K}$, and if we take $\eta = 0.1$ this gives $\Theta^\star/\eta^2 = 213\,\mathrm{K}$, which significantly exceeds $\Theta_{\mathrm{D}}$. Thus, the solid should melt because the RMS fluctuations in the atomic positions at absolute zero are huge: $x_{\mathrm{qu}} = (\Theta^\star/\Theta_{\mathrm{D}})^{1/2} = 0.33$. By applying pressure, one can get $^4$He to crystallize above $p_{\mathrm{c}} = 25\,\mathrm{atm}$ (at absolute zero). Under pressure, the unit cell volume $\mathcal{V}_0$ decreases and the phonon velocity $\bar{c}$ increases, so the Debye temperature itself increases.

It is important to recognize that the Lindemann criterion does not provide us with a theory of melting *per se*. Rather it provides us with a heuristic which allows us to predict roughly when a solid should melt.

### 5.6.5 Goldstone bosons

The vanishing of the acoustic phonon dispersion at $\boldsymbol{k} = 0$ is a consequence of *Goldstone's theorem* which says that associated with every *broken generator* of a *continuous symmetry* there is an associated bosonic gapless excitation (*i.e.* one whose frequency $\omega$ vanishes in the long wavelength limit). In the case of phonons, the 'broken generators' are the symmetries under spatial translation in the $x$, $y$, and $z$ directions. The crystal selects a particular location for its center-of-mass, which breaks this symmetry. There are, accordingly, three gapless acoustic phonons.

Magnetic materials support another branch of elementary excitations known as spin waves, or *magnons*. In *isotropic* magnets, there is a global symmetry associated with rotations in internal spin space, described by the group $\mathrm{SU}(2)$. If the system spontaneously magnetizes, meaning there is long-ranged ferromagnetic order ($\uparrow\uparrow\uparrow\cdots$), or long-ranged antiferromagnetic order ($\uparrow\downarrow\uparrow\downarrow\cdots$), then global spin rotation symmetry is broken. Typically a particular direction is chosen for the magnetic moment (or staggered moment, in the case of an antiferromagnet). Symmetry under rotations about this axis is then preserved, but rotations which do not preserve the selected axis are 'broken'. In the most straightforward case, that of the antiferromagnet, there are two such rotations for $\mathrm{SU}(2)$, and concomitantly two gapless magnon branches, with linearly vanishing dispersions $\omega_a(\boldsymbol{k})$. The situation is more subtle in the case of ferromagnets, because the total magnetization is conserved by the dynamics (unlike the total staggered magnetization in the case of antiferromagnets). Another wrinkle arises if there are long-ranged interactions present.

For our purposes, we can safely ignore the deep physical reasons underlying the gaplessness of Goldstone bosons and simply posit a gapless dispersion relation of the form $\omega(\boldsymbol{k}) = A\,|\boldsymbol{k}|^\sigma$. The density of states for this excitation branch is then

$$g(\omega) = \mathcal{C}\,\omega^{\frac{d}{\sigma}-1}\,\Theta(\omega_{\mathrm{c}} - \omega)\ , \tag{5.142}$$

where $\mathcal{C}$ is a constant and $\omega_{\mathrm{c}}$ is the cutoff, which is the bandwidth for this excitation branch.[3] Normalizing the density of states for this branch results in the identification $\omega_{\mathrm{c}} = (d/\sigma\mathcal{C})^{\sigma/d}$.

The heat capacity is then found to be

$$\begin{aligned} C_V &= N k_{\mathrm{B}}\,\mathcal{C}\int\limits_0^{\omega_{\mathrm{c}}}\! d\omega\,\omega^{\frac{d}{\sigma}-1}\left(\frac{\hbar\omega}{k_{\mathrm{B}}T}\right)^{\!2}\mathrm{csch}^2\!\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right) \\ &= \frac{d}{\sigma}\,N k_{\mathrm{B}}\left(\frac{2T}{\Theta}\right)^{\!d/\sigma}\phi(\Theta/2T)\ , \end{aligned} \tag{5.143}$$

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[3] If $\omega(\boldsymbol{k}) = Ak^\sigma$, then $\mathcal{C} = 2^{1-d}\,\pi^{-\frac{d}{2}}\,\sigma^{-1}\,A^{-\frac{d}{\sigma}}\,\mathsf{g}\,/\,\Gamma(d/2)$.

where $\Theta = \hbar\omega_c/k_B$ and

$$\phi(x) = \int_0^x \! dt \, t^{\frac{d}{\sigma}+1} \, \mathrm{csch}^2 t = \begin{cases} \frac{\sigma}{d} \, x^{d/\sigma} & x \to 0 \\ 2^{-d/\sigma} \, \Gamma\big(2+\frac{d}{\sigma}\big) \, \zeta\big(2+\frac{d}{\sigma}\big) & x \to \infty \, , \end{cases} \tag{5.144}$$

which is a generalization of our earlier results. Once again, we recover Dulong-Petit for $k_B T \gg \hbar\omega_c$, with $C_V(T \gg \hbar\omega_c/k_B) = Nk_B$.

In an isotropic ferromagnet, *i.e.*a ferromagnetic material where there is full SU(2) symmetry in internal 'spin' space, the magnons have a $k^2$ dispersion. Thus, a bulk three-dimensional isotropic ferromagnet will exhibit a heat capacity due to spin waves which behaves as $T^{3/2}$ at low temperatures. For sufficiently low temperatures this will overwhelm the phonon contribution, which behaves as $T^3$.

## 5.7 The Ideal Bose Gas

### 5.7.1 General formulation for noninteracting systems

Recall that the grand partition function for noninteracting bosons is given by

$$\Xi = \prod_\alpha \bigg( \sum_{n_\alpha=0}^\infty e^{\beta(\mu-\varepsilon_\alpha)n_\alpha} \bigg) = \prod_\alpha \Big( 1 - e^{\beta(\mu-\varepsilon_\alpha)} \Big)^{-1} \, , \tag{5.145}$$

In order for the sum to converge to the RHS above, we must have $\mu < \varepsilon_\alpha$ for all single-particle states $|\alpha\rangle$. The density of particles is then

$$n(T,\mu) = -\frac{1}{V} \bigg( \frac{\partial\Omega}{\partial\mu} \bigg)_{T,V} = \frac{1}{V} \sum_\alpha \frac{1}{e^{\beta(\varepsilon_\alpha-\mu)} - 1} = \int_{\varepsilon_0}^\infty \! d\varepsilon \, \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)} - 1} \, , \tag{5.146}$$

where $g(\varepsilon) = \frac{1}{V} \sum_\alpha \delta(\varepsilon - \varepsilon_\alpha)$ is the density of single particle states per unit volume. We assume that $g(\varepsilon) = 0$ for $\varepsilon < \varepsilon_0$ ; typically $\varepsilon_0 = 0$, as is the case for any dispersion of the form $\varepsilon(\boldsymbol{k}) = A|\boldsymbol{k}|^r$, for example. However, in the presence of a magnetic field, we could have $\varepsilon(\boldsymbol{k},\sigma) = A|\boldsymbol{k}|^r - g\mu_0 H\sigma$, in which case $\varepsilon_0 = -g\mu_0|H|$.

Clearly $n(T,\mu)$ is an increasing function of both $T$ and $\mu$. At fixed $T$, the maximum possible value for $n(T,\mu)$, called the *critical density* $n_c(T)$, is achieved for $\mu = \varepsilon_0$ , *i.e.*

$$n_c(T) = \int_{\varepsilon_0}^\infty \! d\varepsilon \, \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\varepsilon_0)} - 1} \, .$$

The above integral converges provided $g(\varepsilon_0) = 0$, assuming $g(\varepsilon)$ is continuous. If $g(\varepsilon_0) \neq 0$, the integral diverges, and $n_c(T) = \infty$. In this latter case, one can always invert the equation for $n(T,\mu)$ to obtain the chemical potential $\mu(T,n)$. In the former case, where the $n_c(T)$ is finite, we have a problem – what happens if $n > n_c(T)$ ?

In the former case, where $n_c(T)$ is finite, we can equivalently restate the problem in terms of a *critical temperature* $T_c(n)$, defined by the equation $n_c(T_c) = n$. For $T < T_c$ , we apparently can no longer invert to obtain $\mu(T,n)$, so clearly something has gone wrong. The remedy is to recognize that the single particle energy levels are discrete, and separate out the contribution from the lowest energy state $\varepsilon_0$. *I.e.* we write

$$n(T,\mu) = \overbrace{\frac{1}{V}\,\frac{\mathrm{g}_0}{e^{\beta(\varepsilon_0-\mu)}-1}}^{n_0} + \overbrace{\int\limits_{\varepsilon_0}^{\infty}\!d\varepsilon\;\frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)}-1}}^{n'}\ , \tag{5.147}$$

where $\mathrm{g}_0$ is the degeneracy of the single particle state with energy $\varepsilon_0$. We assume that $n_0$ is finite, which means that $N_0 = V n_0$ is extensive. We say that the particles have *condensed* into the state with energy $\varepsilon_0$. The quantity $n_0$ is the *condensate density*. The remaining particles, with density $n'$, are said to comprise the *overcondensate*. With the total density $n$ fixed, we have $n = n_0 + n'$. Note that $n_0$ finite means that $\mu$ is infinitesimally close to $\varepsilon_0$:

$$\mu = \varepsilon_0 - k_{\rm B}T\ln\!\bigg(1+\frac{\mathrm{g}_0}{Vn_0}\bigg) \approx \varepsilon_0 - \frac{\mathrm{g}_0 k_{\rm B}T}{Vn_0}\ . \tag{5.148}$$

Note also that if $\varepsilon_0-\mu$ is finite, then $n_0 \propto V^{-1}$ is infinitesimal.

Thus, for $T < T_{\rm c}(n)$, we have $\mu = \varepsilon_0$ with $n_0 > 0$, and

$$n(T,n_0) = n_0 + \int\limits_{\varepsilon_0}^{\infty}\!d\varepsilon\;\frac{g(\varepsilon)}{e^{(\varepsilon-\varepsilon_0)/k_{\rm B}T}-1}\ . \tag{5.149}$$

For $T > T_{\rm c}(n)$, we have $n_0 = 0$ and

$$n(T,\mu) = \int\limits_{\varepsilon_0}^{\infty}\!d\varepsilon\;\frac{g(\varepsilon)}{e^{(\varepsilon-\mu)/k_{\rm B}T}-1}\ . \tag{5.150}$$

The equation for $T_{\rm c}(n)$ is

$$n = \int\limits_{\varepsilon_0}^{\infty}\!d\varepsilon\;\frac{g(\varepsilon)}{e^{(\varepsilon-\varepsilon_0)/k_{\rm B}T_{\rm c}}-1}\ .$$

### 5.7.2 Ballistic dispersion

We already derived, in §5.3.3, expressions for $n(T,z)$ and $p(T,z)$ for the ideal Bose gas (IBG) with ballistic dispersion $\varepsilon(\boldsymbol{p}) = \boldsymbol{p}^2/2m$, We found

$$n(T,z) = \mathrm{g}\,\lambda_T^{-d}\ \mathrm{Li}_{\frac{d}{2}}(z) \tag{5.151}$$

$$p(T,z) = \mathrm{g}\,k_{\rm B}T\,\lambda_T^{-d}\ \mathrm{Li}_{\frac{d}{2}+1}(z), \tag{5.152}$$

where g is the internal (*e.g.* spin) degeneracy of each single particle energy level. Here $z = e^{\mu/k_{\rm B}T}$ is the fugacity and

$$\mathrm{Li}_s(z) = \sum_{m=1}^{\infty}\frac{z^m}{m^s} \tag{5.153}$$

is the polylogarithm function. For bosons with a spectrum bounded below by $\varepsilon_0 = 0$, the fugacity takes values on the interval $z \in [0,1]$[4].

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[4] It is easy to see that the chemical potential for noninteracting bosons can never exceed the minimum value $\varepsilon_0$ of the single particle dispersion.

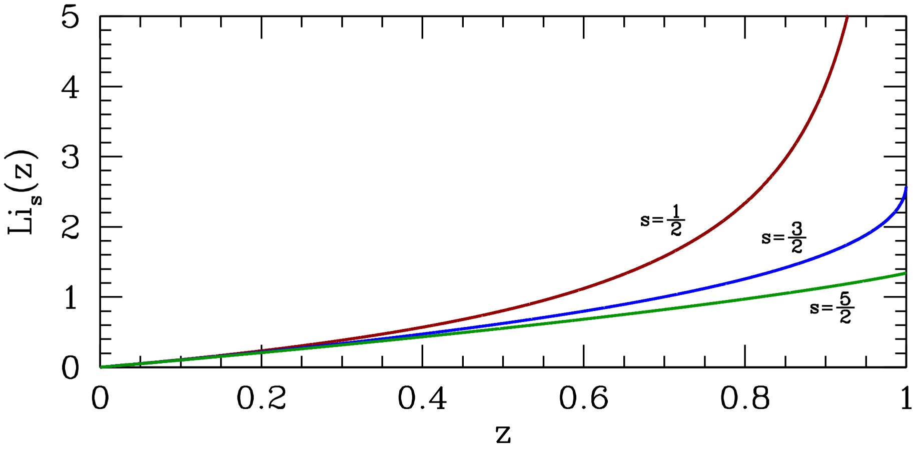

Figure 5.6: The polylogarithm function $\mathrm{Li}_s(z)$ *versus* $z$ for $s=\frac{1}{2}$, $s=\frac{3}{2}$, and $s=\frac{5}{2}$. Note that $\mathrm{Li}_s(1)=\zeta(s)$ diverges for $s\le 1$.

Clearly $n(T,z) = \mathsf{g}\,\lambda_T^{-d}\,\mathrm{Li}_{\frac{d}{2}}(z)$ is an increasing function of $z$ for fixed $T$. In fig. 5.6 we plot the function $\mathrm{Li}_s(z)$ *versus* $z$ for three different values of $s$. We note that the maximum value $\mathrm{Li}_s(z=1)$ is *finite* if $s>1$. Thus, for $d>2$, there is a *maximum density* $n_{\mathrm{max}}(T) = \mathsf{g}\,\mathrm{Li}_{\frac{d}{2}}(z)\,\lambda_T^{-d}$ which is an increasing function of temperature $T$. Put another way, if we fix the density $n$, then there is a *critical temperature* $T_{\mathrm{c}}$ below which there is no solution to the equation $n=n(T,z)$. The critical temperature $T_{\mathrm{c}}(n)$ is then determined by the relation

$$n = \mathsf{g}\,\zeta\big(\tfrac{d}{2}\big)\left(\frac{mk_{\mathrm{B}}T_{\mathrm{c}}}{2\pi\hbar^2}\right)^{d/2} \qquad \Longrightarrow \qquad k_{\mathrm{B}}T_{\mathrm{c}} = \frac{2\pi\hbar^2}{m}\left(\frac{n}{\mathsf{g}\,\zeta\big(\frac{d}{2}\big)}\right)^{2/d} . \tag{5.154}$$

What happens for $T<T_{\mathrm{c}}$?

As shown above in §5.7, we must separate out the contribution from the lowest energy single particle mode, which for ballistic dispersion lies at $\varepsilon_0=0$. Thus writing

$$n = \frac{1}{V}\,\frac{1}{z^{-1}-1} + \frac{1}{V}\sum_{\substack{\alpha\\(\varepsilon_\alpha>0)}} \frac{1}{z^{-1}\,e^{\varepsilon_\alpha/k_{\mathrm{B}}T}-1} , \tag{5.155}$$

where we have taken $\mathsf{g}=1$. Now $V^{-1}$ is of course very small, since $V$ is thermodynamically large, but if $\mu\to 0$ then $z^{-1}-1$ is also very small and their ratio can be finite, as we have seen. Indeed, if the density of $\boldsymbol{k}=0$ bosons $n_0$ is *finite*, then their total number $N_0$ satisfies

$$N_0 = Vn_0 = \frac{1}{z^{-1}-1} \qquad \Longrightarrow \qquad z = \frac{1}{1+N_0^{-1}} . \tag{5.156}$$

The chemical potential is then

$$\mu = k_{\mathrm{B}}T\ln z = -k_{\mathrm{B}}T\ln\big(1+N_0^{-1}\big) \approx -\frac{k_{\mathrm{B}}T}{N_0} \to 0^- . \tag{5.157}$$

In other words, the chemical potential is infinitesimally negative, because $N_0$ is assumed to be thermodynamically large.

According to eqn. 5.14, the contribution to the pressure from the $\boldsymbol{k}=0$ states is

$$p_0 = -\frac{k_{\mathrm{B}}T}{V}\,\ln(1-z) = \frac{k_{\mathrm{B}}T}{V}\ln(1+N_0) \to 0^+ . \tag{5.158}$$

So the $\boldsymbol{k} = 0$ bosons, which we identify as the *condensate*, contribute nothing to the pressure.

Having separated out the $\boldsymbol{k} = 0$ mode, we can now replace the remaining sum over $\alpha$ by the usual integral over $\boldsymbol{k}$. We then have

$$T < T_{\rm c} \ : \qquad n = n_0 + {\sf g}\,\zeta\big(\tfrac{d}{2}\big)\,\lambda_T^{-d} \tag{5.159}$$

$$p = {\sf g}\,\zeta\big(\tfrac{d}{2}{+}1\big)\,k_{\rm B}T\,\lambda_T^{-d} \tag{5.160}$$

and

$$T > T_{\rm c} \ : \qquad n = {\sf g}\,{\rm Li}_{\frac{d}{2}}(z)\,\lambda_T^{-d} \tag{5.161}$$

$$p = {\sf g}\,{\rm Li}_{\frac{d}{2}+1}(z)\,k_{\rm B}T\,\lambda_T^{-d} \ . \tag{5.162}$$

The *condensate fraction* $n_0/n$ is unity at $T = 0$, when all particles are in the condensate with $\boldsymbol{k} = 0$, and decreases with increasing $T$ until $T = T_{\rm c}$, at which point it vanishes identically. Explicitly, we have

$$\frac{n_0(T)}{n} = 1 - \frac{{\sf g}\,\zeta\big(\frac{d}{2}\big)}{n\,\lambda_T^d} = 1 - \bigg(\frac{T}{T_{\rm c}(n)}\bigg)^{d/2} \ . \tag{5.163}$$

Let us compute the internal energy $E$ for the ideal Bose gas. We have

$$\frac{\partial}{\partial\beta}\,(\beta\Omega) = \Omega + \beta\,\frac{\partial\Omega}{\partial\beta} = \Omega - T\,\frac{\partial\Omega}{\partial T} = \Omega + TS \tag{5.164}$$

and therefore

$$\begin{aligned} E = \Omega + TS + \mu N &= \mu N + \frac{\partial}{\partial\beta}\,(\beta\Omega) \\ &= V\bigg(\mu\,n + \frac{\partial}{\partial\beta}\,(\beta p)\bigg) \\ &= \frac{d}{2}\,{\sf g}\,V k_{\rm B}T\,\lambda_T^{-d}\,{\rm Li}_{\frac{d}{2}+1}(z) \ . \end{aligned} \tag{5.165}$$

This expression is valid at all temperatures, both above and below $T_{\rm c}$. Note that the condensate particles do not contribute to $E$, because the $\boldsymbol{k} = 0$ condensate particles carry no energy.

We now investigate the heat capacity $C_{V,N} = \big(\frac{\partial E}{\partial T}\big)_{V,N}$. Since we have been working in the GCE, it is very important to note that $N$ is held constant when computing $C_{V,N}$. We'll also restrict our attention to the case $d = 3$ since the ideal Bose gas does not condense at finite $T$ for $d \le 2$ and $d > 3$ is unphysical. While we're at it, we'll also set ${\sf g} = 1$.

The number of particles is

$$N = \begin{cases} N_0 + \zeta\big(\frac{3}{2}\big)\,V\,\lambda_T^{-3} & (T < T_{\rm c}) \\ \\ V\,\lambda_T^{-3}\,{\rm Li}_{3/2}(z) & (T > T_{\rm c}) \quad , \end{cases} \tag{5.166}$$

and the energy is

$$E = \tfrac{3}{2}\,k_{\rm B}T\,\frac{V}{\lambda_T^3}\,{\rm Li}_{5/2}(z) \ . \tag{5.167}$$

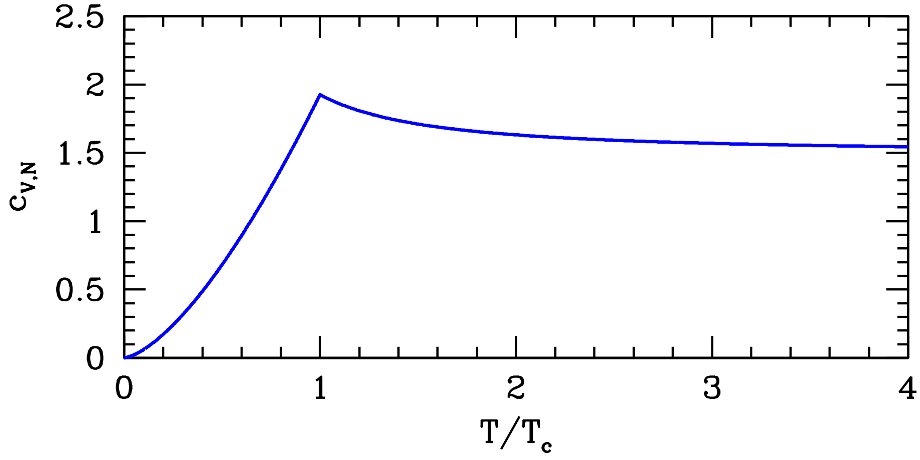

Figure 5.7: Molar heat capacity of the ideal Bose gas. Note the cusp at $T = T_c$.

For $T < T_c$, we have $z = 1$ and

$$C_{V,N} = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \tfrac{15}{4}\,\zeta\big(\tfrac{5}{2}\big)\,k_B\,\frac{V}{\lambda_T^3}\ . \tag{5.168}$$

The molar heat capacity is therefore

$$c_{V,N}(T,n) = N_A \cdot \frac{C_{V,N}}{N} = \tfrac{15}{4}\,\zeta\big(\tfrac{5}{2}\big)\,R\cdot\big(n\,\lambda_T^3\big)^{-1}\ . \tag{5.169}$$

For $T > T_c$, we have

$$dE\big|_V = \tfrac{15}{4}\,k_B T\,\mathrm{Li}_{5/2}(z)\,\frac{V}{\lambda_T^3}\cdot\frac{dT}{T} + \tfrac{3}{2}\,k_B T\,\mathrm{Li}_{3/2}(z)\,\frac{V}{\lambda_T^3}\cdot\frac{dz}{z}\ , \tag{5.170}$$

where we have invoked eqn. 5.49. Taking the differential of $N$, we have

$$dN\big|_V = \tfrac{3}{2}\,\mathrm{Li}_{3/2}(z)\,\frac{V}{\lambda_T^3}\cdot\frac{dT}{T} + \mathrm{Li}_{1/2}(z)\,\frac{V}{\lambda_T^3}\cdot\frac{dz}{z}\ . \tag{5.171}$$

We set $dN = 0$, which fixes $dz$ in terms of $dT$, resulting in

$$c_{V,N}(T,z) = \tfrac{3}{2}\,R\left[\frac{\tfrac{5}{2}\,\mathrm{Li}_{5/2}(z)}{\mathrm{Li}_{3/2}(z)} - \frac{\tfrac{3}{2}\,\mathrm{Li}_{3/2}(z)}{\mathrm{Li}_{1/2}(z)}\right]. \tag{5.172}$$

To obtain $c_{V,N}(T,n)$, we must invert the relation

$$n(T,z) = \lambda_T^{-3}\,\mathrm{Li}_{3/2}(z) \tag{5.173}$$

in order to obtain $z(T,n)$, and then insert this into eqn. 5.172. The results are shown in fig. 5.7. There are several noteworthy features of this plot. First of all, by dimensional analysis the function $c_{V,N}(T,n)$ is $R$ times a function of the dimensionless ratio $T/T_c(n) \propto T\,n^{-2/3}$. Second, the high temperature limit is $\frac{3}{2}R$, which is the classical value. Finally, there is a *cusp* at $T = T_c(n)$.

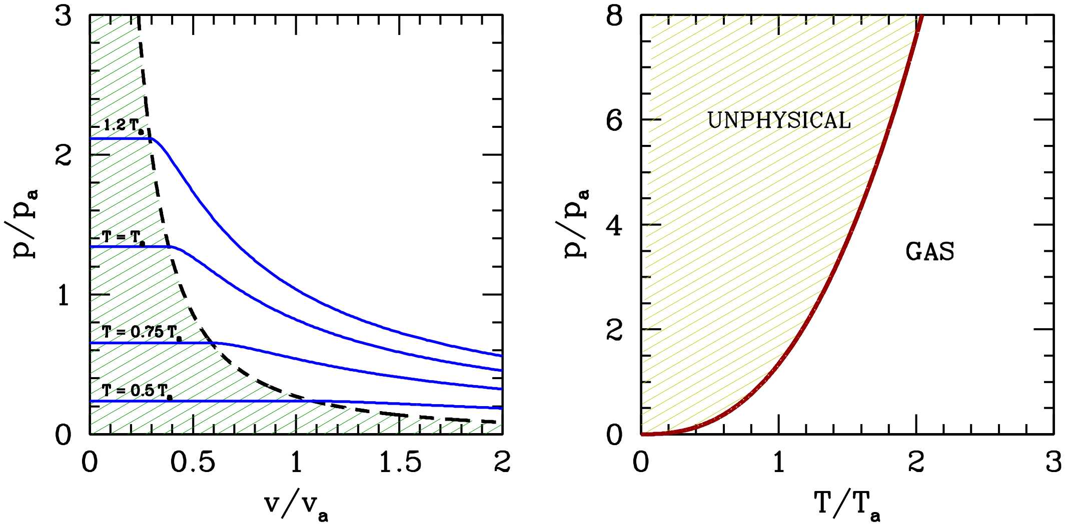

Figure 5.8: Phase diagrams for the ideal Bose gas. Left panel: $(p, v)$ plane. The solid blue curves are isotherms, and the green hatched region denotes $v < v_{\mathrm{c}}(T)$, where the system is partially condensed. Right panel: $(p, T)$ plane. The solid red curve is the coexistence curve $p_{\mathrm{c}}(T)$, along which Bose condensation occurs. No distinct thermodynamic phase exists in the yellow hatched region above $p = p_{\mathrm{c}}(T)$.

### 5.7.3 Isotherms for the ideal Bose gas

Let $a$ be some length scale and define

$$v_a = a^3 \qquad , \qquad p_a = \frac{2\pi\hbar^2}{ma^5} \qquad , \qquad T_a = \frac{2\pi\hbar^2}{ma^2 k_{\mathrm{B}}} \tag{5.174}$$

Then we have

$$\frac{v_a}{v} = \left(\frac{T}{T_a}\right)^{3/2} \mathrm{Li}_{3/2}(z) + v_a\, n_0 \tag{5.175}$$

$$\frac{p}{p_a} = \left(\frac{T}{T_a}\right)^{5/2} \mathrm{Li}_{5/2}(z) \, , \tag{5.176}$$

where $v = V/N$ is the volume per particle[5] and $n_0$ is the condensate number density; $v_0$ vanishes for $T \geq T_{\mathrm{c}}$, when $z = 1$. Note that the pressure is independent of volume for $T < T_{\mathrm{c}}$. The isotherms in the $(p, v)$ plane are then flat for $v < v_{\mathrm{c}}$. This resembles the coexistence region familiar from our study of the thermodynamics of the liquid-gas transition.

Recall the Gibbs-Duhem equation,

$$d\mu = -s\, dT + v\, dp \, . \tag{5.177}$$

Along a coexistence curve, we have the Clausius-Clapeyron relation,

$$\left(\frac{dp}{dT}\right)_{\mathrm{coex}} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T\,\Delta v} \, , \tag{5.178}$$

where $\ell = T\,(s_2 - s_1)$ is the latent heat per mole, and $\Delta v = v_2 - v_1$. For ideal gas Bose condensation, the coexistence curve resembles the red curve in the right hand panel of fig. 5.8. There is no meaning to the shaded

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[5] Note that in the thermodynamics chapter we used $v$ to denote the molar volume, $N_{\mathrm{A}}\, V/N$.

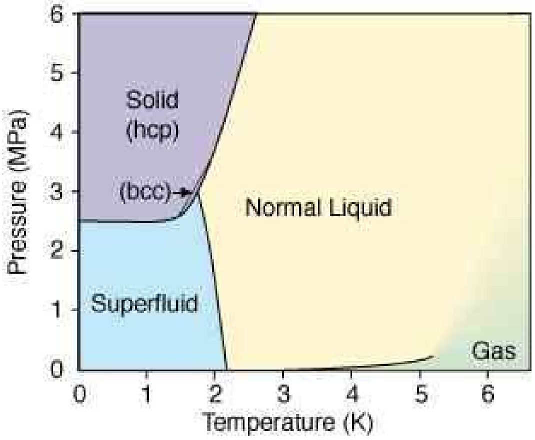

Figure 5.9: Phase diagram of $^4$He. All phase boundaries are first order transition lines, with the exception of the normal liquid-superfluid transition, which is second order. (*Source: University of Helsinki*)

region where $p > p_c(T)$. Nevertheless, it is tempting to associate the curve $p = p_c(T)$ with the coexistence of the $\boldsymbol{k} = 0$ condensate and the remaining uncondensed ($\boldsymbol{k} \neq 0$) bosons[6].

The entropy in the coexistence region is given by

$$s = -\frac{1}{N}\left(\frac{\partial\Omega}{\partial T}\right)_{\!V} = \tfrac{5}{2}\,\zeta\big(\tfrac{5}{2}\big)\,k_B\,v\,\lambda_T^{-3} = \frac{\frac{5}{2}\,\zeta\big(\frac{5}{2}\big)}{\zeta\big(\frac{3}{2}\big)}\,k_B\left(1 - \frac{n_0}{n}\right) . \tag{5.179}$$

All the entropy is thus carried by the uncondensed bosons, and the condensate carries zero entropy. The Clausius-Clapeyron relation can then be interpreted as describing a phase equilibrium between the condensate, for which $s_0 = v_0 = 0$, and the uncondensed bosons, for which $s' = s(T)$ and $v' = v_c(T)$. So this identification forces us to conclude that the specific volume of the condensate is zero. This is certainly false in an interacting Bose gas!

While one can identify, by analogy, a 'latent heat' $\ell = T\,\Delta s = Ts$ in the Clapeyron equation, it is important to understand that there is no distinct thermodynamic phase associated with the region $p > p_c(T)$. Ideal Bose gas condensation is a second order transition, and not a first order transition.

### 5.7.4 The $\lambda$-transition in Liquid $^4$He

Helium has two stable isotopes. $^4$He is a boson, consisting of two protons, two neutrons, and two electrons (hence an even number of fermions). $^3$He is a fermion, with one less neutron than $^4$He. Each $^4$He atom can be regarded as a tiny hard sphere of mass $m = 6.65 \times 10^{-24}$ g and diameter $a = 2.65$ Å. A sketch of the phase diagram is shown in fig. 5.9. At atmospheric pressure, Helium liquefies at $T_l = 4.2$ K. The gas-liquid transition is first order, as usual. However, as one continues to cool, a second transition sets in at $T = T_\lambda = 2.17$ K (at $p = 1$ atm). The $\lambda$-transition, so named for the $\lambda$-shaped anomaly in the specific heat in the vicinity of the transition, as shown in fig. 5.10, is continuous (*i.e.* second order).

If we pretend that $^4$He is a noninteracting Bose gas, then from the density of the liquid $n = 2.2 \times 10^{22}\,\text{cm}^{-3}$, we obtain a Bose-Einstein condensation temperature $T_c = \frac{2\pi\hbar^2}{m}\big(n/\zeta(\frac{3}{2})\big)^{2/3} = 3.16$ K, which is in the right ballpark. The specific heat $C_p(T)$ is found to be singular at $T = T_\lambda$, with

$$C_p(T) = A\,\big|T - T_\lambda(p)\big|^{-\alpha} . \tag{5.180}$$

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[6] The $\boldsymbol{k} \neq 0$ particles are sometimes called the *overcondensate*.

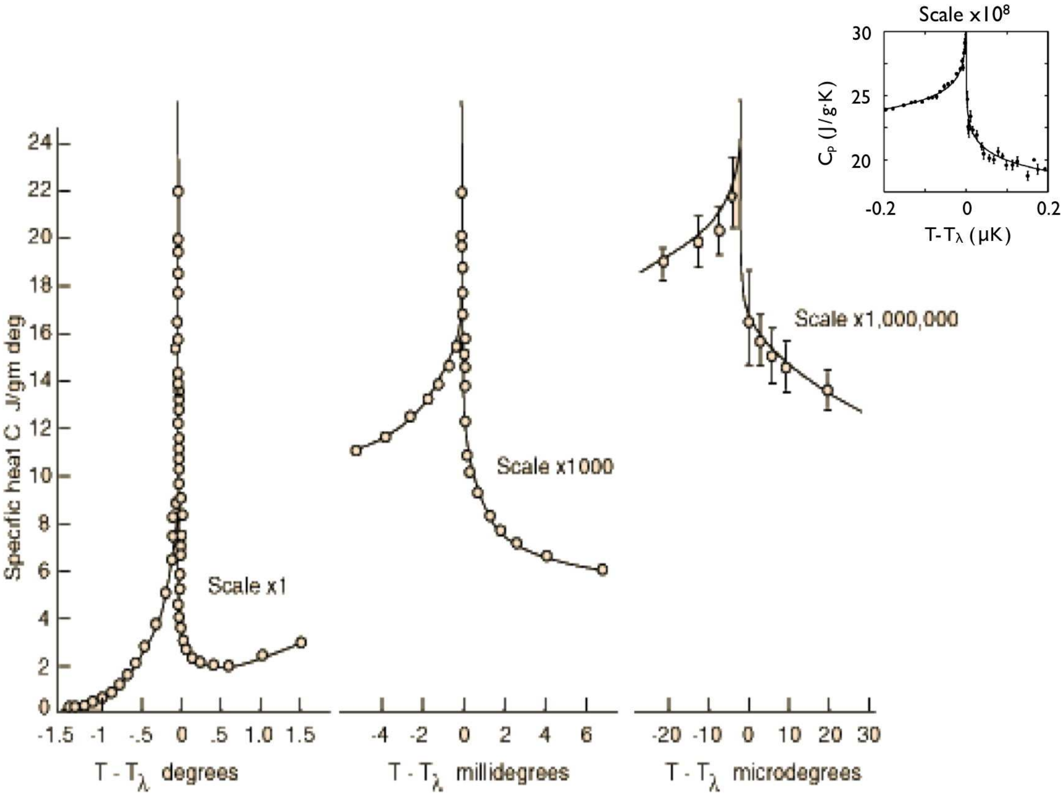

Figure 5.10: Specific heat of liquid $^4$He in the vicinity of the $\lambda$-transition. Data from M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, C. J. Gortner, ed. (North-Holland, 1961). Inset at upper right: more recent data of J. A. Lipa *et al.*, *Phys. Rev. B* **68**, 174518 (2003) performed in zero gravity earth orbit, to within $\Delta T = 2\,\text{nK}$ of the transition.

$\alpha$ is an example of a *critical exponent*. We shall study the physics of critical phenomena later on in this course. For now, note that a cusp singularity of the type found in fig. 5.7 corresponds to $\alpha = -1$. The behavior of $C_p(T)$ in $^4$He is very nearly logarithmic in $|T - T_\lambda|$. In fact, both theory (renormalization group on the O(2) model) and experiment concur that $\alpha$ is almost zero but in fact slightly negative, with $\alpha = -0.0127 \pm 0.0003$ in the best experiments (Lipa *et al.*, 2003). The $\lambda$ transition is most definitely *not* an ideal Bose gas condensation. Theoretically, in the parlance of critical phenomena, IBG condensation and the $\lambda$-transition in $^4$He lie in different *universality classes*[7]. Unlike the IBG, the condensed phase in $^4$He is a distinct thermodynamic phase, known as a *superfluid*.

Note that $C_p(T < T_\text{c})$ for the IBG is not even defined, since for $T < T_\text{c}$ we have $p = p(T)$ and therefore $dp = 0$ requires $dT = 0$.

### 5.7.5 Fountain effect in superfluid $^4$He

At temperatures $T < T_\lambda$, liquid $^4$He has a superfluid component which is a type of Bose condensate. In fact, there is an important difference between condensate fraction $N_{\boldsymbol{k}=0}/N$ and superfluid density, which is denoted by the symbol $\rho_\text{s}$. In $^4$He, for example, at $T = 0$ the condensate fraction is only about 8%, while the superfluid fraction

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[7] IBG condensation is in the universality class of the spherical model. The $\lambda$-transition is in the universality class of the $XY$ model.

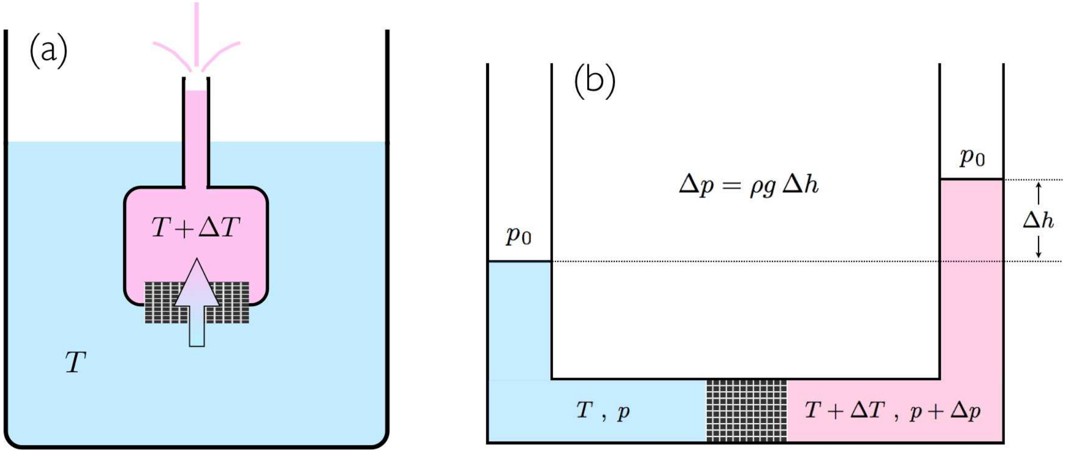

Figure 5.11: The fountain effect. In each case, a temperature gradient is maintained across a porous plug through which only superfluid can flow. This results in a pressure gradient which can result in a fountain or an elevated column in a U-tube.

$\rho_{\rm s}/\rho = 1$. The distinction between $N_0$ and $\rho_s$ is very interesting but lies beyond the scope of this course.

One aspect of the superfluid state is its complete absence of viscosity. For this reason, superfluids can flow through tiny cracks called *microleaks* that will not pass normal fluid. Consider then a porous plug which permits the passage of superfluid but not of normal fluid. The key feature of the superfluid component is that it has zero energy density. Therefore even though there is a transfer of particles across the plug, there is no energy exchange, and therefore a temperature gradient across the plug can be maintained[8].

The elementary excitations in the superfluid state are sound waves called *phonons*. They are compressional waves, just like longitudinal phonons in a solid, but here in a liquid. Their dispersion is acoustic, given by $\omega(k) = ck$ where $c = 238\,{\rm m/s}$.[9] The have no internal degrees of freedom, hence g $= 1$. Like phonons in a solid, the phonons in liquid helium are not conserved. Hence their chemical potential vanishes and these excitations are described by photon statistics. We can now compute the height difference $\Delta h$ in a U-tube experiment.

Clearly $\Delta h = \Delta p/\rho g$. so we must find $p(T)$ for the helium. In the grand canonical ensemble, we have

$$\begin{aligned} p = -\Omega/V &= -k_{\rm B}T \int \frac{d^3\!k}{(2\pi)^3}\,\ln\big(1 - e^{-\hbar ck/k_{\rm B}T}\big) \\ &= -\frac{(k_{\rm B}T)^4}{(\hbar c)^3}\,\frac{4\pi}{8\pi^3}\int\limits_0^\infty \!du\,u^2\,\ln(1-e^{-u}) \\ &= \frac{\pi^2}{90}\,\frac{(k_{\rm B}T)^4}{(\hbar c)^3}\ . \end{aligned} \tag{5.181}$$

---

[8] Recall that two bodies in thermal equilibrium will have identical temperatures *if they are free to exchange energy*.

[9] The phonon velocity $c$ is slightly temperature dependent.

Let's assume $T = 1\,\mathrm{K}$. We'll need the density of liquid helium, $\rho = 148\,\mathrm{kg/m^3}$.

$$\begin{aligned}\frac{dh}{dT} &= \frac{2\pi^2}{45}\left(\frac{k_\mathrm{B}T}{\hbar c}\right)^3 \frac{k_\mathrm{B}}{\rho g} \\ &= \frac{2\pi^2}{45}\left(\frac{(1.38\times10^{-23}\,\mathrm{J/K})(1\,\mathrm{K})}{(1.055\times10^{-34}\,\mathrm{J\cdot s})(238\,\mathrm{m/s})}\right)^3 \times \frac{(1.38\times10^{-23}\,\mathrm{J/K})}{(148\,\mathrm{kg/m^3})(9.8\,\mathrm{m/s^2})} \\ &\simeq 32\,\mathrm{cm/K}\ ,\end{aligned} \tag{5.182}$$

a very noticeable effect!

### 5.7.6 Bose condensation in optical traps

The 2001 Nobel Prize in Physics was awarded to Weiman, Cornell, and Ketterle for the experimental observation of Bose condensation in dilute atomic gases. The experimental techniques required to trap and cool such systems are a true *tour de force*, and we shall not enter into a discussion of the details here[10].

The optical trapping of neutral bosonic atoms, such as $^{87}$Rb, results in a confining potential $V(\boldsymbol{r})$ which is quadratic in the atomic positions. Thus, the single particle Hamiltonian for a given atom is written

$$\hat{H} = -\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}^2 + \tfrac{1}{2}m\big(\omega_1^2\,x^2 + \omega_2^2\,y^2 + \omega_3^2\,z^2\big)\ , \tag{5.183}$$

where $\omega_{1,2,3}$ are the angular frequencies of the trap. This is an anisotropic three-dimensional harmonic oscillator, the solution of which is separable into a product of one-dimensional harmonic oscillator wavefunctions. The eigenspectrum is then given by a sum of one-dimensional spectra, *viz.*

$$E_{n_1,n_2,n_3} = \big(n_1+\tfrac{1}{2}\big)\,\hbar\omega_1 + \big(n_2+\tfrac{1}{2}\big)\,\hbar\omega_2 + \big(n_3+\tfrac{1}{2}\big)\,\hbar\omega_3\ . \tag{5.184}$$

According to eqn. 5.16, the number of particles in the system is

$$\begin{aligned}N &= \sum_{n_1=0}^\infty \sum_{n_2=0}^\infty \sum_{n_3=0}^\infty \Big[y^{-1}\,e^{n_1\hbar\omega_1/k_\mathrm{B}T}\,e^{n_2\hbar\omega_2/k_\mathrm{B}T}\,e^{n_3\hbar\omega_3/k_\mathrm{B}T} - 1\Big]^{-1} \\ &= \sum_{k=1}^\infty y^k \left(\frac{1}{1-e^{-k\hbar\omega_1/k_\mathrm{B}T}}\right)\left(\frac{1}{1-e^{-k\hbar\omega_2/k_\mathrm{B}T}}\right)\left(\frac{1}{1-e^{-k\hbar\omega_3/k_\mathrm{B}T}}\right)\ ,\end{aligned} \tag{5.185}$$

where we've defined

$$y \equiv e^{\mu/k_\mathrm{B}T}\,e^{-\hbar\omega_1/2k_\mathrm{B}T}\,e^{-\hbar\omega_2/2k_\mathrm{B}T}\,e^{-\hbar\omega_3/2k_\mathrm{B}T}\ . \tag{5.186}$$

Note that $y \in [0,1]$.

Let's assume that the trap is approximately anisotropic, which entails that the frequency ratios $\omega_1/\omega_2$ *etc.* are all numbers on the order of one. Let us further assume that $k_\mathrm{B}T \gg \hbar\omega_{1,2,3}$. Then

$$\frac{1}{1-e^{-k\hbar\omega_j/k_\mathrm{B}T}} \approx \begin{cases} \frac{k_\mathrm{B}T}{k\hbar\omega_j} & k \lesssim k^*(T) \\ \\ 1 & k > k^*(T) \end{cases} \tag{5.187}$$

where $k^*(T) = k_\mathrm{B}T/\hbar\bar\omega \gg 1$, with

$$\bar\omega = \big(\omega_1\,\omega_2\,\omega_3\big)^{1/3}\ . \tag{5.188}$$

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[10] Many reliable descriptions may be found on the web. Check Wikipedia, for example.

We then have

$$N(T,y) \approx \frac{y^{k^*+1}}{1-y} + \left(\frac{k_\mathrm{B} T}{\hbar\bar\omega}\right)^3 \sum_{k=1}^{k^*} \frac{y^k}{k^3}\ , \tag{5.189}$$

where the first term on the RHS is due to $k > k^*$ and the second term from $k \le k^*$ in the previous sum. Since $k^* \gg 1$ and since the sum of inverse cubes is convergent, we may safely extend the limit on the above sum to infinity. To help make more sense of the first term, write $N_0 = \big(y^{-1}-1\big)^{-1}$ for the number of particles in the $(n_1,n_2,n_3)=(0,0,0)$ state. Then

$$y = \frac{N_0}{N_0+1}\ . \tag{5.190}$$

This is true always. The issue *vis-a-vis* Bose-Einstein condensation is whether $N_0 \gg 1$. At any rate, we now see that we can write

$$N \approx N_0\,\big(1+N_0^{-1}\big)^{-k^*} + \left(\frac{k_\mathrm{B} T}{\hbar\bar\omega}\right)^3 \mathrm{Li}_3(y)\ . \tag{5.191}$$

As for the first term, we have

$$N_0\,\big(1+N_0^{-1}\big)^{-k^*} = \begin{cases} 0 & N_0 \ll k^* \\ \\ N_0 & N_0 \gg k^* \end{cases} \tag{5.192}$$

Thus, as in the case of IBG condensation of ballistic particles, we identify the critical temperature by the condition $y = N_0/(N_0+1) \approx 1$, and we have

$$T_\mathrm{c} = \frac{\hbar\bar\omega}{k_\mathrm{B}} \left(\frac{N}{\zeta(3)}\right)^{1/3} = 4.5 \left(\frac{\bar\nu}{100\,\mathrm{Hz}}\right) N^{1/3}\ [\,\mathrm{nK}\,]\ , \tag{5.193}$$

where $\bar\nu = \bar\omega/2\pi$. We see that $k_\mathrm{B} T_\mathrm{c} \gg \hbar\bar\omega$ if the number of particles in the trap is large: $N \gg 1$. In this regime, we have

$$T < T_\mathrm{c}\ : \qquad N = N_0 + \zeta(3) \left(\frac{k_\mathrm{B} T}{\hbar\bar\omega}\right)^3 \tag{5.194}$$

$$T > T_\mathrm{c}\ : \qquad N = \left(\frac{k_\mathrm{B} T}{\hbar\bar\omega}\right)^3 \mathrm{Li}_3(y)\ . \tag{5.195}$$

It is interesting to note that BEC can also occur in two-dimensional traps, which is to say traps which are very anisotropic, with oblate equipotential surfaces $V(\boldsymbol{r}) = V_0$. This happens when $\hbar\omega_3 \gg k_\mathrm{B} T \gg \omega_{1,2}$. We then have

$$T_\mathrm{c}^{(d=2)} = \frac{\hbar\bar\omega}{k_\mathrm{B}} \cdot \left(\frac{6N}{\pi^2}\right)^{1/2} \tag{5.196}$$

with $\bar\omega = \big(\omega_1\,\omega_2\big)^{1/2}$. The particle number then obeys a set of equations like those in eqns. 5.194 and 5.195, *mutatis mutandis*[11].

For extremely prolate traps, with $\omega_3 \ll \omega_{1,2}$, the situation is different because $\mathrm{Li}_1(y)$ diverges for $y=1$. We then have

$$N = N_0 + \frac{k_\mathrm{B} T}{\hbar\omega_3}\, \ln\big(1+N_0\big)\ . \tag{5.197}$$

Here we have simply replaced $y$ by the equivalent expression $N_0/(N_0+1)$. If our criterion for condensation is that $N_0 = \alpha N$, where $\alpha$ is some fractional value, then we have

$$T_\mathrm{c}(\alpha) = (1-\alpha)\,\frac{\hbar\omega_3}{k_\mathrm{B}} \cdot \frac{N}{\ln N}\ . \tag{5.198}$$

---

[11] Explicitly, one replaces $\zeta(3)$ with $\zeta(2) = \frac{\pi^2}{6}$, $\mathrm{Li}_3(y)$ with $\mathrm{Li}_2(y)$, and $\big(k_\mathrm{B} T/\hbar\bar\omega\big)^3$ with $\big(k_\mathrm{B} T/\hbar\bar\omega\big)^2$.

### 5.7.7 Example problem from Fall 2004 UCSD graduate written exam

`PROBLEM:` A three-dimensional gas of noninteracting bosonic particles obeys the dispersion relation $\varepsilon(\boldsymbol{k}) = A\,\big|\boldsymbol{k}\big|^{1/2}$.

(a) Obtain an expression for the density $n(T,z)$ where $z = \exp(\mu/k_{\rm B}T)$ is the fugacity. Simplify your expression as best you can, adimensionalizing any integral or infinite sum which may appear. You may find it convenient to define

$$\mathrm{Li}_\nu(z) \equiv \frac{1}{\Gamma(\nu)}\int\limits_0^\infty\!dt\;\frac{t^{\nu-1}}{z^{-1}\,e^t - 1} = \sum_{k=1}^\infty \frac{z^k}{k^\nu}\ . \tag{5.199}$$

Note $\mathrm{Li}_\nu(1) = \zeta(\nu)$, the Riemann zeta function.

(b) Find the critical temperature for Bose condensation, $T_{\rm c}(n)$. Your expression should only include the density $n$, the constant $A$, physical constants, and numerical factors (which may be expressed in terms of integrals or infinite sums).

(c) What is the condensate density $n_0$ when $T = \frac{1}{2}\,T_{\rm c}$?

(d) Do you expect the second virial coefficient to be positive or negative? Explain your reasoning. (You don't have to do any calculation.)

`SOLUTION:` We work in the grand canonical ensemble, using Bose-Einstein statistics.

(a) The density for Bose-Einstein particles are given by

$$\begin{aligned} n(T,z) &= \int\!\frac{d^3\!k}{(2\pi)^3}\,\frac{1}{z^{-1}\,\exp(Ak^{1/2}/k_{\rm B}T) - 1} \\ &= \frac{1}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}\int\limits_0^\infty\!ds\;\frac{s^5}{z^{-1}\,e^s - 1} \\ &= \frac{120}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}\,\mathrm{Li}_6(z)\ , \end{aligned} \tag{5.200}$$

where we have changed integration variables from $k$ to $s = Ak^{1/2}/k_{\rm B}T$, and we have defined the functions $\mathrm{Li}_\nu(z)$ as above, in eqn. 5.199. Note $\mathrm{Li}_\nu(1) = \zeta(\nu)$, the Riemann zeta function.

(b) Bose condensation sets in for $z = 1$, *i.e.* $\mu = 0$. Thus, the critical temperature $T_{\rm c}$ and the density $n$ are related by

$$n = \frac{120\,\zeta(6)}{\pi^2}\bigg(\frac{k_{\rm B}T_{\rm c}}{A}\bigg)^{\!6}, \tag{5.201}$$

or

$$T_{\rm c}(n) = \frac{A}{k_{\rm B}}\bigg(\frac{\pi^2\,n}{120\,\zeta(6)}\bigg)^{\!1/6}\ . \tag{5.202}$$

(c) For $T < T_{\rm c}$, we have

$$\begin{aligned} n &= n_0 + \frac{120\,\zeta(6)}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6} \\ &= n_0 + \bigg(\frac{T}{T_{\rm c}}\bigg)^{\!6}\,n\ , \end{aligned} \tag{5.203}$$

where $n_0$ is the condensate density. Thus, at $T = \frac{1}{2}\,T_{\rm c}$,

$$n_0\big(T=\tfrac{1}{2}T_{\rm c}\big) = \tfrac{63}{64}\,n. \tag{5.204}$$

(d) The virial expansion of the equation of state is

$$p = nk_{\rm B}T\Big(1 + B_2(T)\,n + B_3(T)\,n^2 + \ldots\Big)\ . \tag{5.205}$$

We expect $B_2(T) < 0$ for noninteracting bosons, reflecting the tendency of the bosons to condense. (Correspondingly, for noninteracting fermions we expect $B_2(T) > 0$.)

For the curious, we compute $B_2(T)$ by eliminating the fugacity $z$ from the equations for $n(T,z)$ and $p(T,z)$. First, we find $p(T,z)$:

$$\begin{aligned} p(T,z) &= -k_{\rm B}T\!\int\!\frac{d^3\!k}{(2\pi)^3}\,\ln\Big(1 - z\,\exp(-Ak^{1/2}/k_{\rm B}T)\Big) \\ &= -\frac{k_{\rm B}T}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}\int\limits_0^\infty\!\! ds\, s^5\,\ln\big(1 - z\,e^{-s}\big) \\ &= \frac{120\,k_{\rm B}T}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}{\rm Li}_7(z). \end{aligned} \tag{5.206}$$

Expanding in powers of the fugacity, we have

$$n = \frac{120}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}\bigg\{z + \frac{z^2}{2^6} + \frac{z^3}{3^6} + \ldots\bigg\} \tag{5.207}$$

$$\frac{p}{k_{\rm B}T} = \frac{120}{\pi^2}\bigg(\frac{k_{\rm B}T}{A}\bigg)^{\!6}\bigg\{z + \frac{z^2}{2^7} + \frac{z^3}{3^7} + \ldots\bigg\}\ . \tag{5.208}$$

Solving for $z(n)$ using the first equation, we obtain, to order $n^2$,

$$z = \bigg(\frac{\pi^2A^6\,n}{120\,(k_{\rm B}T)^6}\bigg) - \frac{1}{2^6}\bigg(\frac{\pi^2A^6\,n}{120\,(k_{\rm B}T)^6}\bigg)^{\!2} + \mathcal{O}(n^3)\ . \tag{5.209}$$

Plugging this into the equation for $p(T,z)$, we obtain the first nontrivial term in the virial expansion, with

$$B_2(T) = -\frac{\pi^2}{15360}\bigg(\frac{A}{k_{\rm B}T}\bigg)^{\!6}\ , \tag{5.210}$$

which is negative, as expected. Note also that the ideal gas law is recovered for $T\to\infty$, for fixed $n$.

## 5.8 The Ideal Fermi Gas

### 5.8.1 Grand potential and particle number

The grand potential of the ideal Fermi gas is, per eqn. 5.14,

$$\begin{aligned} \varOmega(T,V,\mu) &= -V k_{\rm B}T\sum_\alpha \ln\Big(1 + e^{\mu/k_{\rm B}T}\,e^{-\varepsilon_\alpha/k_{\rm B}T}\Big) \\ &= -Vk_{\rm B}T\!\int\limits_{-\infty}^{\infty}\!\! d\varepsilon\; g(\varepsilon)\,\ln\Big(1 + e^{(\mu-\varepsilon)/k_{\rm B}T}\Big)\ . \end{aligned} \tag{5.211}$$

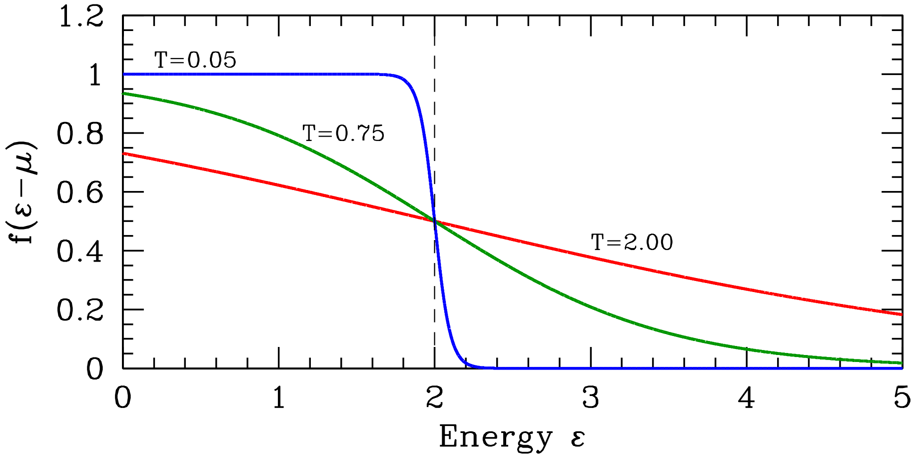

Figure 5.12: The Fermi distribution, $f(\epsilon) = \big[\exp(\epsilon/k_B T) + 1\big]^{-1}$. Here we have set $k_B = 1$ and taken $\mu = 2$, with $T = \frac{1}{20}$ (blue), $T = \frac{3}{4}$ (green), and $T = 2$ (red). In the $T \to 0$ limit, $f(\epsilon)$ approaches a step function $\Theta(-\epsilon)$.

The average number of particles in a state with energy $\varepsilon$ is

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1} \ , \tag{5.212}$$

hence the total number of particles is

$$N = V \int_{-\infty}^{\infty} d\varepsilon \, g(\varepsilon) \, \frac{1}{e^{(\varepsilon-\mu)/k_B T} + 1} \ . \tag{5.213}$$

### 5.8.2 The Fermi distribution

We define the function

$$f(\epsilon) \equiv \frac{1}{e^{\epsilon/k_B T} + 1} \ , \tag{5.214}$$

known as the *Fermi distribution*. In the $T \to \infty$ limit, $f(\epsilon) \to \frac{1}{2}$ for all finite values of $\varepsilon$. As $T \to 0$, $f(\epsilon)$ approaches a step function $\Theta(-\epsilon)$. The average number of particles in a state of energy $\varepsilon$ in a system at temperature $T$ and chemical potential $\mu$ is $n(\varepsilon) = f(\varepsilon - \mu)$. In fig. 5.12 we plot $f(\varepsilon - \mu)$ *versus* $\varepsilon$ for three representative temperatures.

### 5.8.3 $T = 0$ and the Fermi surface

At $T = 0$, we therefore have $n(\varepsilon) = \Theta(\mu - \varepsilon)$, which says that all single particle energy states up to $\varepsilon = \mu$ are filled, and all energy states above $\varepsilon = \mu$ are empty. We call $\mu(T = 0)$ the *Fermi energy*: $\varepsilon_F = \mu(T = 0)$. If the single particle dispersion $\varepsilon(\boldsymbol{k})$ depends only on the wavevector $\boldsymbol{k}$, then the locus of points in $\boldsymbol{k}$-space for which $\varepsilon(\boldsymbol{k}) = \varepsilon_F$ is called the *Fermi surface*. For isotropic systems, $\varepsilon(\boldsymbol{k}) = \varepsilon(k)$ is a function only of the magnitude $k = |\boldsymbol{k}|$, and the Fermi surface is a sphere in $d = 3$ or a circle in $d = 2$. The radius of this circle is the *Fermi wavevector*, $k_F$. When there is internal (*e.g.* spin) degree of freedom, there is a Fermi surface and Fermi wavevector (for isotropic systems) for each polarization state of the internal degree of freedom.

Let's compute the Fermi wavevector $k_{\mathrm{F}}$ and Fermi energy $\varepsilon_{\mathrm{F}}$ for the IFG with a ballistic dispersion $\varepsilon(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$. The number density is

$$n = \mathsf{g}\!\int\! d^d\!k \;\Theta(k_{\mathrm{F}}-k) = \frac{\mathsf{g}\,\Omega_d}{(2\pi)^d}\cdot\frac{k_{\mathrm{F}}^d}{d} = \begin{cases} \mathsf{g}\,k_{\mathrm{F}}/\pi & (d=1) \\[2ex] \mathsf{g}\,k_{\mathrm{F}}^2/4\pi & (d=2) \\[2ex] \mathsf{g}\,k_{\mathrm{F}}^3/6\pi^2 & (d=3)\ . \end{cases} \tag{5.215}$$

Note that the form of $n(k_{\mathrm{F}})$ is independent of the dispersion relation, so long as it remains isotropic. Inverting the above expressions, we obtain $k_{\mathrm{F}}(n)$:

$$k_{\mathrm{F}} = 2\pi\left(\frac{d\,n}{\mathsf{g}\,\Omega_d}\right)^{1/d} = \begin{cases} \pi n/\mathsf{g} & (d=1) \\[2ex] (4\pi n/\mathsf{g})^{1/2} & (d=2) \\[2ex] (6\pi^2 n/\mathsf{g})^{1/3} & (d=3)\ . \end{cases} \tag{5.216}$$

The Fermi energy in each case, for ballistic dispersion, is therefore

$$\varepsilon_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m} = \frac{2\pi^2\hbar^2}{m}\left(\frac{d\,n}{\mathsf{g}\,\Omega_d}\right)^{2/d} = \begin{cases} \frac{\pi^2\hbar^2 n^2}{2\mathsf{g}^2 m} & (d=1) \\[2ex] \frac{2\pi\hbar^2\, n}{\mathsf{g}\, m} & (d=2) \\[2ex] \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{\mathsf{g}}\right)^{2/3} & (d=3)\ . \end{cases} \tag{5.217}$$

Another useful result for the ballistic dispersion, which follows from the above, is that the density of states at the Fermi level is given by

$$g(\varepsilon_{\mathrm{F}}) = \frac{\mathsf{g}\,\Omega_d}{(2\pi)^d}\cdot\frac{m k_{\mathrm{F}}^{d-2}}{\hbar^2} = \frac{d}{2}\cdot\frac{n}{\varepsilon_{\mathrm{F}}}\ . \tag{5.218}$$

For the electron gas, we have $\mathsf{g}=2$. In a metal, one typically has $k_{\mathrm{F}} \sim 0.5\,\text{Å}^{-1}$ to $2\,\text{Å}^{-1}$, and $\varepsilon_{\mathrm{F}} \sim 1\,\mathrm{eV} - 10\,\mathrm{eV}$. Due to the effects of the crystalline lattice, electrons in a solid behave as if they had an *effective mass* $m^*$ which is typically on the order of the electron mass but very often about an order of magnitude smaller, particularly in semiconductors.

Nonisotropic dispersions $\varepsilon(\boldsymbol{k})$ are more interesting in that they give rise to non-spherical Fermi surfaces. The simplest example is that of a two-dimensional 'tight-binding' model of electrons hopping on a square lattice, as may be appropriate in certain layered materials. The dispersion relation is then

$$\varepsilon(k_x,k_y) = -2t\,\cos(k_x a) - 2t\,\cos(k_y a)\ , \tag{5.219}$$

where $k_x$ and $k_y$ are confined to the interval $\big[-\frac{\pi}{a},\frac{\pi}{a}\big]$. The quantity $t$ has dimensions of energy and is known as the *hopping integral*. The Fermi surface is the set of points $(k_x,k_y)$ which satisfies $\varepsilon(k_x,k_y)=\varepsilon_{\mathrm{F}}$. When $\varepsilon_{\mathrm{F}}$ achieves its minimum value of $\varepsilon_{\mathrm{F}}^{\mathrm{min}} = -4t$, the Fermi surface collapses to a point at $(k_x,k_y)=(0,0)$. For energies just above this minimum value, we can expand the dispersion in a power series, writing

$$\varepsilon(k_x,k_y) = -4t + ta^2\left(k_x^2+k_y^2\right) - \tfrac{1}{12}\,ta^4\left(k_x^4+k_y^4\right) + \ldots\ . \tag{5.220}$$

If we only work to quadratic order in $k_x$ and $k_y$, the dispersion is isotropic, and the Fermi surface is a circle, with $k_{\mathrm{F}}^2 = (\varepsilon_{\mathrm{F}}+4t)/ta^2$. As the energy increases further, the continuous $\mathrm{O}(2)$ rotational invariance is broken down to

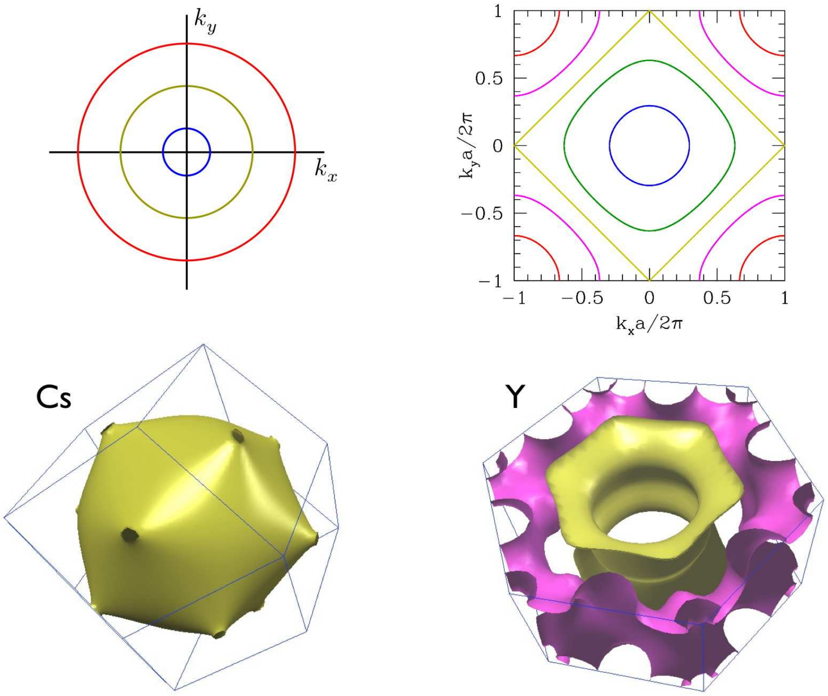

Figure 5.13: Fermi surfaces for two and three-dimensional structures. Upper left: free particles in two dimensions. Upper right: 'tight binding' electrons on a square lattice. Lower left: Fermi surface for cesium, which is predominantly composed of electrons in the $6s$ orbital shell. Lower right: the Fermi surface of yttrium has two parts. One part (yellow) is predominantly due to $5s$ electrons, while the other (pink) is due to $4d$ electrons. (*Source: www.phys.ufl.edu/fermisurface/*)

the discrete group of rotations of the square, $C_{4v}$. The Fermi surfaces distort and eventually, at $\varepsilon_{\mathrm{F}} = 0$, the Fermi surface is itself a square. As $\varepsilon_{\mathrm{F}}$ increases further, the square turns back into a circle, but centered about the point $\left(\frac{\pi}{a}, \frac{\pi}{a}\right)$. Note that everything is periodic in $k_x$ and $k_y$ modulo $\frac{2\pi}{a}$. The Fermi surfaces for this model are depicted in the upper right panel of fig. 5.13.

Fermi surfaces in three dimensions can be very interesting indeed, and of great importance in understanding the electronic properties of solids. Two examples are shown in the bottom panels of fig. 5.13. The electronic configuration of cesium (Cs) is $[\mathrm{Xe}]\,6s^1$. The $6s$ electrons 'hop' from site to site on a body centered cubic (BCC) lattice, a generalization of the simple two-dimensional square lattice hopping model discussed above. The elementary unit cell in $\boldsymbol{k}$ space, known as the *first Brillouin zone*, turns out to be a dodecahedron. In yttrium, the electronic structure is $[\mathrm{Kr}]\,5s^2\,4d^1$, and there are two electronic energy bands at the Fermi level, meaning two Fermi surfaces. Yttrium forms a hexagonal close packed (HCP) crystal structure, and its first Brillouin zone is shaped like a hexagonal pillbox.

### 5.8.4 Spin-split Fermi surfaces

Consider an electron gas in an external magnetic field $H$. The single particle Hamiltonian is then

$$\hat{H} = \frac{\boldsymbol{p}^2}{2m} + \mu_{\mathrm{B}} H\,\sigma\ , \tag{5.221}$$

where $\mu_{\rm B}$ is the *Bohr magneton*,

$$\begin{aligned}\mu_{\rm B} &= \frac{e\hbar}{2mc} = 5.788 \times 10^{-9}\,{\rm eV/G} \\ \mu_{\rm B}/k_{\rm B} &= 6.717 \times 10^{-5}\,{\rm K/G}\ ,\end{aligned} \tag{5.222}$$

where $m$ is the electron mass. What happens at $T = 0$ to a noninteracting electron gas in a magnetic field?

Electrons of each spin polarization form their own Fermi surfaces. That is, there is an up spin Fermi surface, with Fermi wavevector $k_{{\rm F}\uparrow}$, and a down spin Fermi surface, with Fermi wavevector $k_{{\rm F}\downarrow}$. The individual Fermi energies, on the other hand, must be equal, hence

$$\frac{\hbar^2 k^2_{{\rm F}\uparrow}}{2m} + \mu_{\rm B} H = \frac{\hbar^2 k^2_{{\rm F}\downarrow}}{2m} - \mu_{\rm B} H\ , \tag{5.223}$$

which says

$$k^2_{{\rm F}\downarrow} - k^2_{{\rm F}\uparrow} = \frac{2eH}{\hbar c}\ . \tag{5.224}$$

The total density is

$$n = \frac{k^3_{{\rm F}\uparrow}}{6\pi^2} + \frac{k^3_{{\rm F}\downarrow}}{6\pi^2} \qquad \Longrightarrow \qquad k^3_{{\rm F}\uparrow} + k^3_{{\rm F}\downarrow} = 6\pi^2 n\ . \tag{5.225}$$

Clearly the down spin Fermi surface grows and the up spin Fermi surface shrinks with increasing $H$. Eventually, the minority spin Fermi surface vanishes altogether. This happens for the up spins when $k_{{\rm F}\uparrow} = 0$. Solving for the critical field, we obtain

$$H_{\rm c} = \frac{\hbar c}{2e} \cdot \big(6\pi^2 n\big)^{1/3}\ . \tag{5.226}$$

In real magnetic solids, like cobalt and nickel, the spin-split Fermi surfaces are not spheres, just like the case of the (spin degenerate) Fermi surfaces for Cs and Y shown in fig. 5.13.

### 5.8.5 The Sommerfeld expansion

In dealing with the ideal Fermi gas, we will repeatedly encounter integrals of the form

$$\mathcal{I}(T,\mu) \equiv \int\limits_{-\infty}^{\infty}\! d\varepsilon\ f(\varepsilon - \mu)\,\phi(\varepsilon)\ . \tag{5.227}$$

The Sommerfeld expansion provides a systematic way of expanding these expressions in powers of $T$ and is an important analytical tool in analyzing the low temperature properties of the ideal Fermi gas (IFG).

We start by defining

$$\varPhi(\varepsilon) \equiv \int\limits_{-\infty}^{\varepsilon}\! d\varepsilon'\ \phi(\varepsilon') \tag{5.228}$$

so that $\phi(\varepsilon) = \varPhi'(\varepsilon)$. We then have

$$\begin{aligned}\mathcal{I} &= \int\limits_{-\infty}^{\infty}\! d\varepsilon\ f(\varepsilon - \mu)\,\frac{d\varPhi}{d\varepsilon} \\ &= -\int\limits_{-\infty}^{\infty}\! d\varepsilon\ f'(\varepsilon)\,\varPhi(\mu + \varepsilon)\ ,\end{aligned} \tag{5.229}$$

where we assume $\varPhi(-\infty)=0$. Next, we invoke Taylor's theorem, to write

$$\begin{aligned}\varPhi(\mu+\varepsilon)&=\sum_{n=0}^{\infty}\frac{\varepsilon^n}{n\,!}\,\frac{d^n\varPhi}{d\mu^n}\\&=\exp\left(\varepsilon\,\frac{d}{d\mu}\right)\varPhi(\mu)\ .\end{aligned}\tag{5.230}$$

This last expression involving the exponential of a differential operator may appear overly formal but it proves extremely useful. Since

$$f'(\varepsilon)=-\frac{1}{k_\mathrm{B}T}\,\frac{e^{\varepsilon/k_\mathrm{B}T}}{\big(e^{\varepsilon/k_\mathrm{B}T}+1\big)^2}\ ,\tag{5.231}$$

we can write

$$\mathcal{I}=\int\limits_{-\infty}^{\infty}\!dv\;\frac{e^{vD}}{(e^v+1)(e^{-v}+1)}\,\varPhi(\mu)\ ,\tag{5.232}$$

with $v=\varepsilon/k_\mathrm{B}T$, where

$$D=k_\mathrm{B}T\,\frac{d}{d\mu}\tag{5.233}$$

is a dimensionless differential operator. The integral can now be done using the methods of complex integration:[12]

$$\begin{aligned}\int\limits_{-\infty}^{\infty}\!dv\;\frac{e^{vD}}{(e^v+1)(e^{-v}+1)}&=2\pi i\sum_{n=1}^{\infty}\mathrm{Res}\left[\frac{e^{vD}}{(e^v+1)(e^{-v}+1)}\right]_{v=(2n+1)i\pi}\\&=-2\pi i\sum_{n=0}^{\infty}D\,e^{(2n+1)i\pi D}\\&=-\frac{2\pi i D\,e^{i\pi D}}{1-e^{2\pi i D}}=\pi D\,\csc\pi D\end{aligned}\tag{5.234}$$

Thus,

$$\mathcal{I}(T,\mu)=\pi D\csc(\pi D)\,\varPhi(\mu)\ ,\tag{5.235}$$

which is to be understood as the differential operator $\pi D(\csc\pi D)=\pi D/\sin(\pi D)$ acting on the function $\varPhi(\mu)$. Appealing once more to Taylor's theorem, we have

$$\pi D\csc(\pi D)=1+\frac{\pi^2}{6}\,(k_\mathrm{B}T)^2\,\frac{d^2}{d\mu^2}+\frac{7\pi^4}{360}\,(k_\mathrm{B}T)^4\,\frac{d^4}{d\mu^4}+\ldots\ .\tag{5.236}$$

Thus,

$$\begin{aligned}\mathcal{I}(T,\mu)&=\int\limits_{-\infty}^{\infty}\!d\varepsilon\,f(\varepsilon-\mu)\,\phi(\varepsilon)\\&=\int\limits_{-\infty}^{\mu}\!d\varepsilon\,\phi(\varepsilon)+\frac{\pi^2}{6}\,(k_\mathrm{B}T)^2\,\phi'(\mu)+\frac{7\pi^4}{360}\,(k_\mathrm{B}T)^4\,\phi'''(\mu)+\ldots\ .\end{aligned}\tag{5.237}$$

If $\phi(\varepsilon)$ is a polynomial function of its argument, then each derivative effectively reduces the order of the polynomial by one degree, and the dimensionless parameter of the expansion is $(T/\mu)^2$. This procedure is known as the *Sommerfeld expansion*.

---

[12] Note that writing $v=(2n+1)\,i\pi+\epsilon$ we have $e^{\pm v}=-1\mp\epsilon-\frac{1}{2}\epsilon^2+\ldots$, so $(e^v+1)(e^{-v}+1)=-\epsilon^2+\ldots$ We then expand $e^{vD}=e^{(2n+1)i\pi D}\big(1+\epsilon D+\ldots\big)$ to find the residue: $\mathrm{Res}=-D\,e^{(2n+1)i\pi D}$.

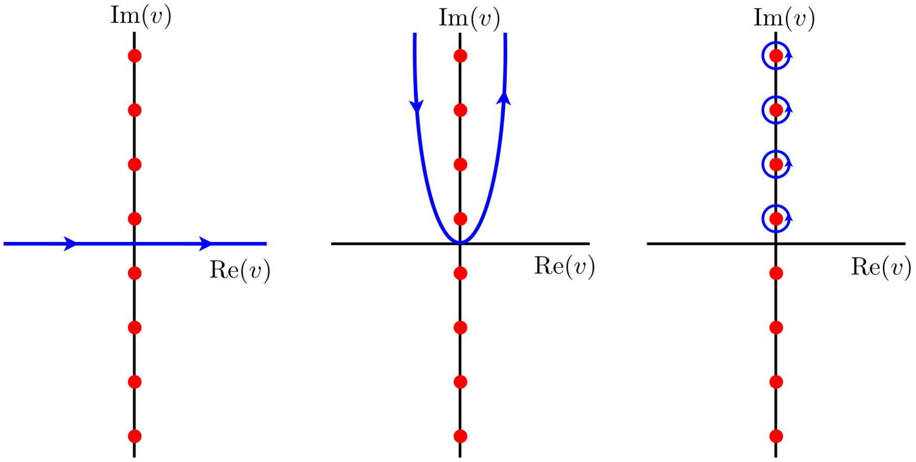

Figure 5.14: Deformation of the complex integration contour in eqn. 5.234.

### 5.8.6 Chemical potential shift

As our first application of the Sommerfeld expansion formalism, let us compute $\mu(n,T)$ for the ideal Fermi gas. The number density $n(T,\mu)$ is

$$\begin{aligned} n &= \int\limits_{-\infty}^{\infty} d\varepsilon\, g(\varepsilon)\, f(\varepsilon-\mu) \\ &= \int\limits_{-\infty}^{\mu} d\varepsilon\, g(\varepsilon) + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g'(\mu) + \ldots\ . \end{aligned} \tag{5.238}$$

Let us write $\mu = \varepsilon_{\rm F} + \delta\mu$, where $\varepsilon_{\rm F} = \mu(T=0,n)$ is the Fermi energy, which is the chemical potential at $T=0$. We then have

$$\begin{aligned} n &= \int\limits_{-\infty}^{\varepsilon_{\rm F}+\delta\mu} d\varepsilon\, g(\varepsilon) + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g'(\varepsilon_{\rm F}+\delta\mu) + \ldots \\ &= \int\limits_{-\infty}^{\varepsilon_{\rm F}} d\varepsilon\, g(\varepsilon) + g(\varepsilon_{\rm F})\,\delta\mu + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g'(\varepsilon_{\rm F}) + \ldots\ , \end{aligned} \tag{5.239}$$

from which we derive

$$\delta\mu = -\frac{\pi^2}{6}\,(k_{\rm B}T)^2\,\frac{g'(\varepsilon_{\rm F})}{g(\varepsilon_{\rm F})} + \mathcal{O}(T^4)\ . \tag{5.240}$$

Note that $g'/g = (\ln g)'$. For a ballistic dispersion, assuming g $= 2$,

$$g(\varepsilon) = 2\int\!\frac{d^3\!k}{(2\pi)^3}\,\delta\bigg(\varepsilon - \frac{\hbar^2 k^2}{2m}\bigg) = \frac{m\,k(\varepsilon)}{\pi^2\hbar^2}\bigg|_{k(\varepsilon)=\frac{1}{\hbar}\sqrt{2m\varepsilon}} \tag{5.241}$$

Thus, $g(\varepsilon) \propto \varepsilon^{1/2}$ and $(\ln g)' = \frac{1}{2}\,\varepsilon^{-1}$, so

$$\mu(n,T) = \varepsilon_{\rm F} - \frac{\pi^2}{12}\,\frac{(k_{\rm B}T)^2}{\varepsilon_{\rm F}} + \ldots\ , \tag{5.242}$$

where $\varepsilon_{\rm F}(n) = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$.

### 5.8.7 Specific heat

The energy of the electron gas is

$$\begin{aligned}\frac{E}{V} &= \int\limits_{-\infty}^{\infty} d\varepsilon\; g(\varepsilon)\,\varepsilon\, f(\varepsilon-\mu)\\ &= \int\limits_{-\infty}^{\mu} d\varepsilon\; g(\varepsilon)\,\varepsilon + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\,\frac{d}{d\mu}\Big(\mu\, g(\mu)\Big) + \ldots\\ &= \int\limits_{-\infty}^{\varepsilon_{\rm F}} d\varepsilon\; g(\varepsilon)\,\varepsilon + g(\varepsilon_{\rm F})\,\varepsilon_{\rm F}\,\delta\mu + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\,\varepsilon_{\rm F}\, g'(\varepsilon_{\rm F}) + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g(\varepsilon_{\rm F}) + \ldots\\ &= \varepsilon_0 + \frac{\pi^2}{6}\,(k_{\rm B}T)^2\, g(\varepsilon_{\rm F}) + \ldots\ ,\end{aligned} \tag{5.243}$$

where

$$\varepsilon_0 = \int\limits_{-\infty}^{\varepsilon_{\rm F}} d\varepsilon\; g(\varepsilon)\,\varepsilon \tag{5.244}$$

is the ground state energy density (*i.e.* ground state energy per unit volume). Thus,

$$C_{V,N} = \bigg(\frac{\partial E}{\partial T}\bigg)_{V,N} = \frac{\pi^2}{3}\,V k_{\rm B}^2\, T\, g(\varepsilon_{\rm F}) \equiv V\gamma\, T\ , \tag{5.245}$$

where

$$\gamma = \frac{\pi^2}{3}\,k_{\rm B}^2\, g(\varepsilon_{\rm F})\ . \tag{5.246}$$

Note that the molar heat capacity is

$$c_V = \frac{N_{\rm A}}{N}\cdot C_V = \frac{\pi^2}{3} R\cdot \frac{k_{\rm B}T\, g(\varepsilon_{\rm F})}{n} = \frac{\pi^2}{2}\bigg(\frac{k_{\rm B}T}{\varepsilon_{\rm F}}\bigg) R\ , \tag{5.247}$$

where in the last expression on the RHS we have assumed a ballistic dispersion, for which

$$\frac{g(\varepsilon_{\rm F})}{n} = \frac{{\sf g}\, m k_{\rm F}}{2\pi^2\hbar^2}\cdot\frac{6\pi^2}{{\sf g}\, k_{\rm F}^3} = \frac{3}{2\,\varepsilon_{\rm F}}\ . \tag{5.248}$$

The molar heat capacity in eqn. 5.247 is to be compared with the classical ideal gas value of $\frac{3}{2}R$. Relative to the classical ideal gas, the IFG value is reduced by a fraction of $(\pi^2/3)\times(k_{\rm B}T/\varepsilon_{\rm F})$, which in most metals is very small and even at room temperature is only on the order of $10^{-2}$. Most of the heat capacity of metals at room temperature is due to the energy stored in lattice vibrations.

### 5.8.8 Magnetic susceptibility and Pauli paramagnetism

Magnetism has two origins: (i) orbital currents of charged particles, and (ii) intrinsic magnetic moment. The intrinsic magnetic moment $\boldsymbol{m}$ of a particle is related to its quantum mechanical *spin* via

$$\boldsymbol{m} = g\mu_0 \boldsymbol{S}/\hbar \qquad , \qquad \mu_0 = \frac{q\hbar}{2mc} = \text{magneton}\ , \tag{5.249}$$

where $g$ is the particle's $g$-factor, $\mu_0$ its magnetic moment, and $\boldsymbol{S}$ is the vector of quantum mechanical spin operators satisfying $\big[S^\alpha\,,\,S^\beta\big]=i\hbar\epsilon_{\alpha\beta\gamma}\,S^\gamma$, *i.e.* SU(2) commutation relations. The Hamiltonian for a single particle is then

$$\begin{aligned}\hat{H}&=\frac{1}{2m^*}\Big(\boldsymbol{p}-\frac{q}{c}\boldsymbol{A}\Big)^2-\boldsymbol{H}\cdot\boldsymbol{m}\\&=\frac{1}{2m^*}\Big(\boldsymbol{p}+\frac{e}{c}\boldsymbol{A}\Big)^2+\frac{g}{2}\,\mu_{\rm B}H\,\sigma\ ,\end{aligned}\tag{5.250}$$

where in the last line we've restricted our attention to the electron, for which $q=-e$. The $g$-factor for an electron is $g=2$ at tree level, and when radiative corrections are accounted for using quantum electrodynamics (QED) one finds $g=2.0023193043617(15)$. For our purposes we can take $g=2$, although we can always absorb the small difference into the definition of $\mu_{\rm B}$, writing $\mu_{\rm B}\to\tilde{\mu}_{\rm B}=ge\hbar/4mc$. We've chosen the $\hat{\boldsymbol{z}}$-axis in spin space to point in the direction of the magnetic field, and we wrote the eigenvalues of $S^z$ as $\frac{1}{2}\hbar\sigma$, where $\sigma=\pm1$. The quantity $m^*$ is the *effective mass* of the electron, which we mentioned earlier. An important distinction is that it is $m^*$ which enters into the kinetic energy term $\boldsymbol{p}^2/2m^*$, but it is the electron mass $m$ itself ($m=511\,$keV) which enters into the definition of the Bohr magneton. We shall discuss the consequences of this further below.

In the absence of orbital magnetic coupling, the single particle dispersion is

$$\varepsilon_\sigma(\boldsymbol{k})=\frac{\hbar^2\boldsymbol{k}^2}{2m^*}+\tilde{\mu}_{\rm B}H\,\sigma\ .\tag{5.251}$$

At $T=0$, we have the results of §5.8.4. At finite $T$, we once again use the Sommerfeld expansion. We then have

$$\begin{aligned}n&=\int\limits_{-\infty}^{\infty}\!d\varepsilon\;g_\uparrow(\varepsilon)\,f(\varepsilon-\mu)\;+\int\limits_{-\infty}^{\infty}\!d\varepsilon\;g_\downarrow(\varepsilon)\,f(\varepsilon-\mu)\\&=\tfrac{1}{2}\int\limits_{-\infty}^{\infty}\!d\varepsilon\;\Big\{g(\varepsilon-\tilde{\mu}_{\rm B}H)+g(\varepsilon+\tilde{\mu}_{\rm B}H)\Big\}\,f(\varepsilon-\mu)\\&=\int\limits_{-\infty}^{\infty}\!d\varepsilon\;\Big\{g(\varepsilon)+(\tilde{\mu}_{\rm B}H)^2\,g''(\varepsilon)+\ldots\Big\}\,f(\varepsilon-\mu)\ .\end{aligned}\tag{5.252}$$

We now invoke the Sommerfeld expension to find the temperature dependence:

$$\begin{aligned}n&=\int\limits_{-\infty}^{\mu}\!d\varepsilon\;g(\varepsilon)+\frac{\pi^2}{6}\,(k_{\rm B}T)^2\,g'(\mu)+(\tilde{\mu}_{\rm B}H)^2\,g'(\mu)+\ldots\\&=\int\limits_{-\infty}^{\varepsilon_{\rm F}}\!d\varepsilon\;g(\varepsilon)+g(\varepsilon_{\rm F})\,\delta\mu+\frac{\pi^2}{6}\,(k_{\rm B}T)^2\,g'(\varepsilon_{\rm F})+(\tilde{\mu}_{\rm B}H)^2\,g'(\varepsilon_{\rm F})+\ldots\ .\end{aligned}\tag{5.253}$$

Note that the density of states for spin species $\sigma$ is

$$g_\sigma(\varepsilon)=\tfrac{1}{2}\,g(\varepsilon-\tilde{\mu}_{\rm B}H\sigma)\ ,\tag{5.254}$$

where $g(\varepsilon)$ is the total density of states per unit volume, for both spin species, in the absence of a magnetic field. We conclude that the chemical potential shift in an external field is

$$\delta\mu(T,n,H)=-\bigg\{\frac{\pi^2}{6}\,(k_{\rm B}T)^2+(\tilde{\mu}_{\rm B}H)^2\bigg\}\,\frac{g'(\varepsilon_{\rm F})}{g(\varepsilon_{\rm F})}+\ldots\ .\tag{5.255}$$

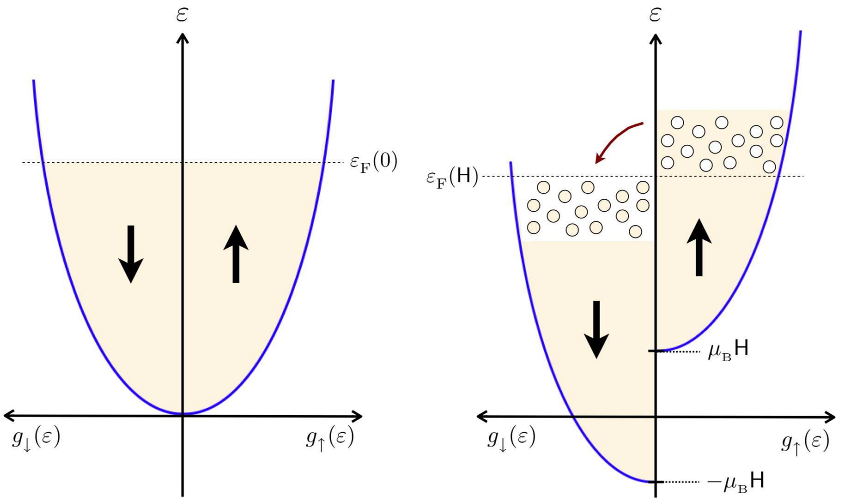

Figure 5.15: Fermi distributions in the presence of an external Zeeman-coupled magnetic field.

We next compute the difference $n_\uparrow - n_\downarrow$ in the densities of up and down spin electrons:

$$\begin{aligned} n_\uparrow - n_\downarrow &= \int\limits_{-\infty}^{\infty} \! d\varepsilon \, \Big\{ g_\uparrow(\varepsilon) - g_\downarrow(\varepsilon) \Big\} \, f(\varepsilon-\mu) \\ &= \tfrac{1}{2} \int\limits_{-\infty}^{\infty} \! d\varepsilon \, \Big\{ g(\varepsilon - \tilde\mu_{\rm B} H) - g(\varepsilon + \tilde\mu_{\rm B} H) \Big\} \, f(\varepsilon-\mu) \\ &= -\tilde\mu_{\rm B} H \cdot \pi D \csc(\pi D) \, g(\mu) + \mathcal{O}(H^3) \ . \end{aligned} \tag{5.256}$$

We needn't go beyond the trivial lowest order term in the Sommerfeld expansion, because $H$ is already assumed to be small. Thus, the magnetization density is

$$M = -\tilde\mu_{\rm B}(n_\uparrow - n_\downarrow) = \tilde\mu^2_{\rm B} \, g(\varepsilon_{\rm F}) \, H \ . \tag{5.257}$$

in which the magnetic susceptibility is

$$\chi = \bigg(\frac{\partial M}{\partial H}\bigg)_{T,N} = \tilde\mu^2_{\rm B} \, g(\varepsilon_{\rm F}) \ . \tag{5.258}$$

This is called the *Pauli paramagnetic susceptibility*.

### 5.8.9 Landau diamagnetism

When orbital effects are included, the single particle energy levels are given by

$$\varepsilon(n,k_z,\sigma) = (n+\tfrac{1}{2})\hbar\omega_{\rm c} + \frac{\hbar^2 k_z^2}{2m^*} + \tilde\mu_{\rm B} H \, \sigma \ . \tag{5.259}$$

Here $n$ is a Landau level index, and $\omega_{\rm c} = eH/m^* c$ is the *cyclotron frequency*. Note that

$$\frac{\tilde\mu_{\rm B} H}{\hbar\omega_{\rm c}} = \frac{ge\hbar H}{4mc} \cdot \frac{m^* c}{\hbar e H} = \frac{g}{4} \cdot \frac{m^*}{m} \ . \tag{5.260}$$

Accordingly, we define the ratio $r \equiv (g/2) \times (m^*/m)$. We can then write

$$\varepsilon(n,k_z,\sigma) = \big(n + \tfrac{1}{2} + \tfrac{1}{2} r\sigma\big)\hbar\omega_{\rm c} + \frac{\hbar^2 k_z^2}{2m^*} \ . \tag{5.261}$$

The grand potential is then given by

$$\Omega = -\frac{HA}{\phi_0} \cdot L_z \cdot k_{\rm B}T \int\limits_{-\infty}^{\infty} \frac{dk_z}{2\pi} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} \ln\Big[1 + e^{\mu/k_{\rm B}T}\, e^{-(n+\frac{1}{2}+\frac{1}{2}r\sigma)\hbar\omega_{\rm c}/k_{\rm B}T}\, e^{-\hbar^2 k_z^2/2mk_{\rm B}T}\Big] \ . \tag{5.262}$$

A few words are in order here regarding the prefactor. In the presence of a uniform magnetic field, the energy levels of a two-dimensional ballistic charged particle collapse into Landau levels. The number of states per Landau level scales with the area of the system, and is equal to the number of flux quanta through the system: $N_\phi = HA/\phi_0$, where $\phi_0 = hc/e$ is the Dirac flux quantum. Note that

$$\frac{HA}{\phi_0} \cdot L_z \cdot k_{\rm B}T = \hbar\omega_{\rm c} \cdot \frac{V}{\lambda_T^3} \ , \tag{5.263}$$

hence we can write

$$\Omega(T,V,\mu,H) = \hbar\omega_{\rm c} \sum_{n=0}^{\infty} \sum_{\sigma=\pm 1} Q\big((n + \tfrac{1}{2} + \tfrac{1}{2}r\sigma)\hbar\omega_{\rm c} - \mu\big) \ , \tag{5.264}$$

where

$$Q(\varepsilon) = -\frac{V}{\lambda_T^2} \int\limits_{-\infty}^{\infty} \frac{dk_z}{2\pi} \ln\Big[1 + e^{-\varepsilon/k_{\rm B}T} e^{-\hbar^2 k_z^2/2m^* k_{\rm B}T}\Big] \ . \tag{5.265}$$

We now invoke the Euler-MacLaurin formula,

$$\sum_{n=0}^{\infty} F(n) = \int\limits_0^{\infty} dx\, F(x) + \tfrac{1}{2}\, F(0) - \tfrac{1}{12}\, F'(0) + \ldots \ , \tag{5.266}$$

resulting in

$$\begin{aligned}\Omega = \sum_{\sigma=\pm 1} \Bigg\{ & \int\limits_{\frac{1}{2}(1+r\sigma)\hbar\omega_{\rm c}}^{\infty} d\varepsilon\, Q(\varepsilon - \mu) + \tfrac{1}{2}\,\hbar\omega_{\rm c}\, Q\big(\tfrac{1}{2}(1+r\sigma)\hbar\omega_{\rm c} - \mu\big) \\ & - \tfrac{1}{12}\,(\hbar\omega_{\rm c})^2\, Q'\big(\tfrac{1}{2}(1+r\sigma)\hbar\omega_{\rm c} - \mu\big) + \ldots \Bigg\}\end{aligned} \tag{5.267}$$

We next expand in powers of the magnetic field $H$ to obtain

$$\Omega(T,V,\mu,H) = 2\int\limits_0^{\infty} d\varepsilon\, Q(\varepsilon - \mu) + \big(\tfrac{1}{4}r^2 - \tfrac{1}{12}\big)\,(\hbar\omega_{\rm c})^2\, Q'(-\mu) + \ldots \ . \tag{5.268}$$

Thus, the magnetic susceptibility is

$$\begin{aligned}\chi = -\frac{1}{V}\frac{\partial^2\Omega}{\partial H^2} &= \big(r^2 - \tfrac{1}{3}\big) \cdot \tilde\mu_{\rm B}^2 \cdot \big(m/m^*\big)^2 \cdot \Big(-\frac{2}{V}\, Q'(-\mu)\Big) \\ &= \left(\frac{g^2}{4} - \frac{m^2}{3m^{*2}}\right) \cdot \tilde\mu_{\rm B}^2 \cdot n^2 \kappa_T \ ,\end{aligned} \tag{5.269}$$

where $\kappa_T$ is the isothermal compressibility[13]. In most metals we have $m^* \approx m$ and the term in brackets is positive (recall $g \approx 2$). In semiconductors, however, we can have $m^* \ll m$; for example in GaAs we have $m^* = 0.067$. Thus, semiconductors can have a *diamagnetic* response. If we take $g = 2$ and $m^* = m$, we see that the orbital currents give rise to a diamagnetic contribution to the magnetic susceptibility which is exactly $-\frac{1}{3}$ times as large as the contribution arising from Zeeman coupling. The net result is then paramagnetic ($\chi > 0$) and $\frac{2}{3}$ as large as the Pauli susceptibility. The orbital currents can be understood within the context of *Lenz's law*.

*Exercise : Show that* $-\frac{2}{V}\,Q'(-\mu) = n^2\kappa_T$.

### 5.8.10 White dwarf stars

There is a nice discussion of this material in R. K. Pathria, *Statistical Mechanics*. As a model, consider a mass $M \sim 10^{33}\,\text{g}$ of helium at nuclear densities of $\rho \sim 10^7\,\text{g/cm}^3$ and temperature $T \sim 10^7\,\text{K}$. This temperature is much larger than the ionization energy of $^4$He, hence we may safely assume that all helium atoms are ionized. If there are $N$ electrons, then the number of $\alpha$ particles (*i.e.* $^4$He nuclei) must be $\frac{1}{2}N$. The mass of the $\alpha$ particle is $m_\alpha \approx 4m_\text{p}$. The total stellar mass $M$ is almost completely due to $\alpha$ particle cores.

The electron density is then

$$n = \frac{N}{V} = \frac{2\cdot M/4m_\text{p}}{V} = \frac{\rho}{2m_\text{p}} \approx 10^{30}\,\text{cm}^{-3}\ , \tag{5.270}$$

since $M = N\cdot m_\text{e} + \frac{1}{2}N\cdot 4m_\text{p}$. From the number density $n$ we find for the electrons

$$k_\text{F} = (3\pi^2 n)^{1/3} = 2.14\times 10^{10}\,\text{cm}^{-1} \tag{5.271}$$

$$p_\text{F} = \hbar k_\text{F} = 2.26\times 10^{-17}\,\text{g cm/s} \tag{5.272}$$

$$mc = (9.1\times 10^{-28}\,\text{g})(3\times 10^{10}\,\text{m/s}) = 2.7\times 10^{-17}\,\text{g cm/s}\ . \tag{5.273}$$

Since $p_\text{F} \sim mc$, we conclude that the electrons are relativistic. The Fermi temperature will then be $T_\text{F} \sim mc^2 \sim 10^6\,\text{eV} \sim 10^{12}\,\text{K}$. Thus, $T \ll T_\text{f}$ which says that the electron gas is degenerate and may be considered to be at $T \sim 0$. So we need to understand the ground state properties of the relativistic electron gas.

The kinetic energy is given by

$$\varepsilon(\boldsymbol{p}) = \sqrt{\boldsymbol{p}^2c^2 + m^2c^4} - mc^2\ . \tag{5.274}$$

The velocity is

$$\boldsymbol{v} = \frac{\partial\varepsilon}{\partial\boldsymbol{p}} = \frac{\boldsymbol{p}c^2}{\sqrt{p^2c^2+m^2c^4}}\ . \tag{5.275}$$

The pressure in the ground state is

$$\begin{aligned} p_0 &= \tfrac{1}{3}n\langle \boldsymbol{p}\cdot\boldsymbol{v}\rangle \\ &= \frac{1}{3\pi^2\hbar^3}\int\limits_0^{p_\text{F}}\!dp\, p^2\cdot\frac{p^2c^2}{\sqrt{p^2c^2+m^2c^4}} \\ &= \frac{m^4c^5}{3\pi^2\hbar^3}\int\limits_0^{\theta_\text{F}}\!d\theta\ \sinh^4\!\theta \\ &= \frac{m^4c^5}{96\pi^2\hbar^3}\big(\sinh(4\theta_\text{F}) - 8\sinh(2\theta_\text{F}) + 12\,\theta_\text{F}\big)\ , \end{aligned} \tag{5.276}$$

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[13] We've used $-\frac{2}{V}Q'(\mu) = -\frac{1}{V}\frac{\partial^2\Omega}{\partial\mu^2} = n^2\kappa_T$.

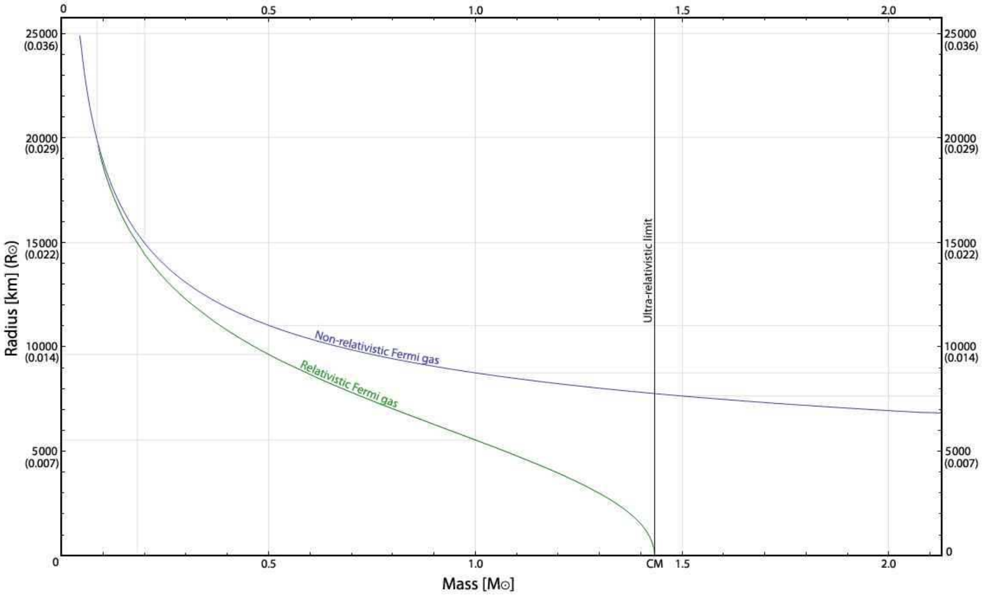

Figure 5.16: Mass-radius relationship for white dwarf stars. (*Source: Wikipedia*).

where we use the substitution

$$p = mc\sinh\theta \quad , \quad v = c\tanh\theta \quad \Longrightarrow \quad \theta = \tfrac{1}{2}\ln\!\left(\frac{c+v}{c-v}\right) . \tag{5.277}$$

Note that $p_{\rm F} = \hbar k_{\rm F} = \hbar(3\pi^2 n)^{1/3}$, and that

$$n = \frac{M}{2m_{\rm p}V} \qquad \Longrightarrow \qquad 3\pi^2 n = \frac{9\pi}{8}\,\frac{M}{R^3\,m_{\rm p}} . \tag{5.278}$$

Now in equilibrium the pressure $p$ is balanced by gravitational pressure. We have

$$dE_0 = -p_0\,dV = -p_0(R)\cdot 4\pi R^2\,dR . \tag{5.279}$$

This must be balanced by gravity:

$$dE_{\rm g} = \gamma\cdot\frac{GM^2}{R^2}\,dR , \tag{5.280}$$

where $\gamma$ depends on the radial mass distribution. Equilibrium then implies

$$p_0(R) = \frac{\gamma}{4\pi}\,\frac{GM^2}{R^4} . \tag{5.281}$$

To find the relation $R = R(M)$, we must solve

$$\frac{\gamma}{4\pi}\,\frac{gM^2}{R^4} = \frac{m^4c^5}{96\pi^2\hbar^3}\,\big(\sinh(4\theta_{\rm F}) - 8\sinh(2\theta_{\rm F}) + 12\,\theta_{\rm F}\big) . \tag{5.282}$$

Note that

$$\sinh(4\theta_{\rm F}) - 8\sinh(2\theta_{\rm F}) + 12\theta_{\rm F} = \begin{cases} \frac{96}{15}\,\theta_{\rm F}^5 & \theta_{\rm F}\to 0 \\[2ex] \frac{1}{2}\,e^{4\theta_{\rm F}} & \theta_{\rm F}\to\infty . \end{cases} \tag{5.283}$$

Thus, we may write

$$p_0(R) = \frac{\gamma}{4\pi}\,\frac{gM^2}{R^4} = \begin{cases} \frac{\hbar^2}{15\pi^2 m}\,\left(\frac{9\pi}{8}\,\frac{M}{R^3\,m_\mathrm{p}}\right)^{5/3} & \theta_\mathrm{F}\to 0 \\ \\ \frac{\hbar c}{12\pi^2}\,\left(\frac{9\pi}{8}\,\frac{M}{R^3\,m_\mathrm{p}}\right)^{4/3} & \theta_\mathrm{F}\to\infty\ . \end{cases} \tag{5.284}$$

In the limit $\theta_\mathrm{F}\to 0$, we solve for $R(M)$ and find

$$R = \tfrac{3}{40\gamma}\,(9\pi)^{2/3}\,\frac{\hbar^2}{G\,m_\mathrm{p}^{5/3}\,m\,M^{1/3}} \propto M^{-1/3}\ . \tag{5.285}$$

In the opposite limit $\theta_\mathrm{F}\to\infty$, the $R$ factors divide out and we obtain

$$M = M_0 = \frac{9}{64}\left(\frac{3\pi}{\gamma^3}\right)^{1/2}\left(\frac{\hbar c}{G}\right)^{3/2}\frac{1}{m_\mathrm{p}^2}\ . \tag{5.286}$$

To find the $R$ dependence, we must go beyond the lowest order expansion of eqn. 5.283, in which case we find

$$R = \left(\frac{9\pi}{8}\right)^{1/3}\left(\frac{\hbar}{mc}\right)\left(\frac{M}{m_\mathrm{p}}\right)^{1/3}\left[1-\left(\frac{M}{M_0}\right)^{2/3}\right]^{1/2}\ . \tag{5.287}$$

The value $M_0$ is the limiting size for a white dwarf. It is called the *Chandrasekhar limit*.

# Chapter 6

# Classical Interacting Systems

## 6.1 References

- M. Kardar, *Statistical Physics of Particles* (Cambridge, 2007)
  A superb modern text, with many insightful presentations of key concepts.
- L. E. Reichl, *A Modern Course in Statistical Physics* (2nd edition, Wiley, 1998)
  A comprehensive graduate level text with an emphasis on nonequilibrium phenomena.
- M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* ($3^{\text{rd}}$ edition, World Scientific, 2006)
  An excellent graduate level text. Less insightful than Kardar but still a good modern treatment of the subject. Good discussion of mean field theory.
- E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics* (part I, $3^{\text{rd}}$ edition, Pergamon, 1980)
  This is volume 5 in the famous Landau and Lifshitz *Course of Theoretical Physics*. Though dated, it still contains a wealth of information and physical insight.
- J.-P Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, 1990)
  An advanced, detailed discussion of liquid state physics.

## 6.2 Ising Model

### 6.2.1 Definition

The simplest model of an interacting system consists of a lattice $\mathcal{L}$ of sites, each of which contains a spin $\sigma_i$ which may be either up ($\sigma_i = +1$) or down ($\sigma_i = -1$). The Hamiltonian is

$$\hat{H} = -J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j - \mu_0 H \sum_i \sigma_i \ . \tag{6.1}$$

When $J > 0$, the preferred (*i.e.* lowest energy) configuration of neighboring spins is that they are aligned, *i.e.* $\sigma_i \, \sigma_j = +1$. The interaction is then called *ferromagnetic*. When $J < 0$ the preference is for anti-alignment, *i.e.* $\sigma_i \, \sigma_j = -1$, which is *antiferromagnetic*.

This model is not exactly solvable in general. In one dimension, the solution is quite straightforward. In two dimensions, Onsager's solution of the model (with $H = 0$) is among the most celebrated results in statistical physics. In higher dimensions the system has been studied by numerical simulations (the Monte Carlo method) and by field theoretic calculations (renormalization group), but no exact solutions exist.

### 6.2.2 Ising model in one dimension

Consider a one-dimensional ring of $N$ sites. The ordinary canonical partition function is then

$$\begin{aligned} Z_{\text{ring}} &= \mathsf{Tr} \; e^{-\beta \hat{H}} \\ &= \sum_{\{\sigma_n\}} \prod_{n=1}^{N} e^{\beta J \sigma_n \sigma_{n+1}} \, e^{\beta \mu_0 H \sigma_n} \\ &= \mathsf{Tr} \left( R^N \right) \ , \end{aligned} \tag{6.2}$$

where $\sigma_{N+1} \equiv \sigma_1$ owing to periodic (ring) boundary conditions, and where $R$ is a $2 \times 2$ *transfer matrix*,

$$\begin{aligned} R_{\sigma\sigma'} &= e^{\beta J \sigma \sigma'} \, e^{\beta \mu_0 H (\sigma + \sigma')/2} \\ &= \begin{pmatrix} e^{\beta J} \, e^{\beta \mu_0 H} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \, e^{-\beta \mu_0 H} \end{pmatrix} \\ &= e^{\beta J} \cosh(\beta \mu_0 H) + e^{\beta J} \sinh(\beta \mu_0 H) \, \tau^z + e^{-\beta J} \, \tau^x \ , \end{aligned} \tag{6.3}$$

where $\tau^\alpha$ are the Pauli matrices. Since the trace of a matrix is invariant under a similarity transformation, we have

$$Z(T, H, N) = \lambda_+^N + \lambda_-^N \ , \tag{6.4}$$

where

$$\lambda_\pm(T, H) = e^{\beta J} \cosh(\beta \mu_0 H) \pm \sqrt{e^{2\beta J} \sinh^2(\beta \mu_0 H) + e^{-2\beta J}} \tag{6.5}$$

are the eigenvalues of $R$. In the thermodynamic limit, $N \to \infty$, and the $\lambda_+^N$ term dominates exponentially. We therefore have

$$F(T, H, N) = -N k_{\mathrm{B}} T \ln \lambda_+(T, H) \ . \tag{6.6}$$

From the free energy, we can compute the magnetization,

$$M = -\left( \frac{\partial F}{\partial H} \right)_{T,N} = \frac{N \mu_0 \, \sinh(\beta \mu_0 H)}{\sqrt{\sinh^2(\beta \mu_0 H) + e^{-4\beta J}}} \tag{6.7}$$

and the zero field isothermal susceptibility,

$$\chi(T) = \frac{1}{N}\,\frac{\partial M}{\partial H}\bigg|_{H=0} = \frac{\mu_0^2}{k_{\rm B}T}\,e^{2J/k_{\rm B}T}\ . \tag{6.8}$$

Note that in the noninteracting limit $J \to 0$ we recover the familiar result for a free spin. The effect of the interactions at low temperature is to vastly increase the susceptibility. Rather than a set of independent single spins, the system effectively behaves as if it were composed of large blocks of spins, where the block size $\xi$ is the *correlation length*, to be derived below.

The physical properties of the system are often elucidated by evaluation of various correlation functions. In this case, we define

$$\begin{aligned} C(n) \equiv \big\langle \sigma_1\,\sigma_{n+1}\big\rangle &= \frac{\mathsf{Tr}\,\big(\sigma_1\,R_{\sigma_1\sigma_2}\cdots R_{\sigma_n\sigma_{n+1}}\,\sigma_{n+1}\,R_{\sigma_{n+1}\sigma_{n+2}}\cdots R_{\sigma_N\sigma_1}\big)}{\mathsf{Tr}\,\big(R^N\big)} \\ &= \frac{\mathsf{Tr}\,\big(\varSigma\,R^n\,\varSigma\,R^{N-n}\big)}{\mathsf{Tr}\,\big(R^N\big)}\ , \end{aligned} \tag{6.9}$$

where $0 < n < N$, and where

$$\varSigma = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\ . \tag{6.10}$$

To compute this ratio, we decompose $R$ in terms of its eigenvectors, writing

$$R = \lambda_+\,|+\rangle\langle+| + \lambda_-\,|-\rangle\langle-|\ . \tag{6.11}$$

Then

$$C(n) = \frac{\lambda_+^N\,\varSigma_{++}^2 + \lambda_-^N\,\varSigma_{--}^2 + \big(\lambda_+^{N-n}\,\lambda_-^n + \lambda_+^n\,\lambda_-^{N-n}\big)\,\varSigma_{+-}\varSigma_{-+}}{\lambda_+^N + \lambda_-^N}\ , \tag{6.12}$$

where

$$\varSigma_{\mu\mu'} = \langle\,\mu\,|\,\varSigma\,|\,\mu'\,\rangle\ . \tag{6.13}$$

### 6.2.3 $H = 0$

Consider the case $H = 0$, where $R = e^{\beta J} + e^{-\beta J}\,\tau^x$, where $\tau^x$ is the Pauli matrix. Then

$$|\pm\,\rangle = \tfrac{1}{\sqrt{2}}\Big(|\!\uparrow\rangle \pm |\!\downarrow\rangle\Big)\ , \tag{6.14}$$

*i.e.* the eigenvectors of $R$ are

$$\psi_\pm = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ \pm 1 \end{pmatrix}\ , \tag{6.15}$$

and $\varSigma_{++} = \varSigma_{--} = 0$, while $\varSigma_{\pm} = \varSigma_{-+} = 1$. The corresponding eigenvalues are

$$\lambda_+ = 2\cosh(\beta J) \qquad , \qquad \lambda_- = 2\sinh(\beta J)\ . \tag{6.16}$$

The correlation function is then found to be

$$\begin{aligned} C(n) \equiv \big\langle \sigma_1\,\sigma_{n+1}\big\rangle &= \frac{\lambda_+^{N-|n|}\,\lambda_-^{|n|} + \lambda_+^{|n|}\,\lambda_-^{N-|n|}}{\lambda_+^N + \lambda_-^N} \\ &= \frac{\tanh^{|n|}(\beta J) + \tanh^{N-|n|}(\beta J)}{1 + \tanh^N(\beta J)} \\ &\approx \tanh^{|n|}(\beta J) \qquad (N \to \infty)\ . \end{aligned} \tag{6.17}$$

This result is also valid for $n < 0$, provided $|n| \le N$. We see that we may write

$$C(n) = e^{-|n|/\xi(T)} \ , \tag{6.18}$$

where the *correlation length* is

$$\xi(T) = \frac{1}{\ln \text{ctnh}(J/k_\text{B}T)} \ . \tag{6.19}$$

Note that $\xi(T)$ grows as $T \to 0$ as $\xi \approx \frac{1}{2}\, e^{2J/k_\text{B}T}$.

### 6.2.4 Chain with free ends

When the chain has free ends, there are $(N-1)$ links, and the partition function is

$$\begin{aligned} Z_\text{chain} &= \sum_{\sigma,\sigma'} \big(R^{N-1}\big)_{\sigma\sigma'} \\ &= \sum_{\sigma,\sigma'} \Big\{ \lambda_+^{N-1}\, \psi_+(\sigma)\, \psi_+(\sigma') + \lambda_-^{N-1}\, \psi_-(\sigma)\, \psi_-(\sigma') \Big\} \ , \end{aligned} \tag{6.20}$$

where $\psi_\pm(\sigma) = \langle\, \sigma \,|\, \pm \,\rangle$. When $H = 0$, we make use of eqn. 6.15 to obtain

$$R^{N-1} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \big(2\cosh\beta J\big)^{N-1} + \frac{1}{2}\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \big(2\sinh\beta J\big)^{N-1} \ , \tag{6.21}$$

and therefore

$$Z_\text{chain} = 2^N \cosh^{N-1}(\beta J) \ . \tag{6.22}$$

There's a nifty trick to obtaining the partition function for the Ising chain which amounts to a change of variables. We define

$$\nu_n \equiv \sigma_n\, \sigma_{n+1} \qquad (n = 1\,,\,\ldots\,,\, N-1) \ . \tag{6.23}$$

Thus, $\nu_1 = \sigma_1\sigma_2$, $\nu_2 = \sigma_2\sigma_3$, *etc.* Note that each $\nu_j$ takes the values $\pm 1$. The Hamiltonian for the chain is

$$H_\text{chain} = -J \sum_{n=1}^{N-1} \sigma_n\, \sigma_{n+1} = -J \sum_{n=1}^{N-1} \nu_n \ . \tag{6.24}$$

The state of the system is defined by the $N$ Ising variables $\{\sigma_1\,,\, \nu_1\,,\, \ldots\,,\, \nu_{N-1}\}$. Note that $\sigma_1$ doesn't appear in the Hamiltonian. Thus, the interacting model is recast as $N-1$ noninteracting Ising spins, and the partition function is

$$\begin{aligned} Z_\text{chain} &= \text{Tr}\, e^{-\beta H_\text{chain}} \\ &= \sum_{\sigma_1} \sum_{\nu_1} \cdots \sum_{\nu_{N-1}} e^{\beta J \nu_1} e^{\beta J \nu_2} \cdots e^{\beta J \nu_{N-1}} \\ &= \sum_{\sigma_1} \bigg( \sum_{\nu} e^{\beta J \nu} \bigg)^{N-1} = 2^N \cosh^{N-1}(\beta J) \ . \end{aligned} \tag{6.25}$$

### 6.2.5 Ising model in two dimensions : Peierls' argument

We have just seen how in one dimension, the Ising model never achieves long-ranged spin order. That is, the spin-spin correlation function decays asymptotically as an exponential function of the distance with a correlation length $\xi(T)$ which is finite for all $> 0$. Only for $T = 0$ does the correlation length diverge. At $T = 0$, there are two ground states, $|\uparrow\uparrow\uparrow\uparrow \cdots \uparrow\rangle$ and $|\downarrow\downarrow\downarrow\downarrow \cdots \downarrow\rangle$. To choose between these ground states, we can specify a boundary condition at the ends of our one-dimensional chain, where we demand that the spins are up. Equivalently, we can apply a magnetic field $H$ of order $1/N$, which vanishes in the thermodynamic limit, but which at zero temperature will select the 'all up' ground state. At finite temperature, there is always a finite probability for any consecutive pair of sites $(n, n+1)$ to be in a high energy state, *i.e.* either $|\uparrow\downarrow\rangle$ or $|\downarrow\uparrow\rangle$. Such a configuration is called a *domain wall*, and in one-dimensional systems domain walls live on individual links. Relative to the configurations $|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$, a domain wall costs energy $2J$. For a system with $M = xN$ domain walls, the free energy is

$$\begin{aligned} F &= 2MJ - k_{\rm B}T \ln \binom{N}{M} \\ &= N \cdot \bigg\{ 2Jx + k_{\rm B}T \Big[ x \ln x + (1-x) \ln(1-x) \Big] \bigg\} , \end{aligned} \tag{6.26}$$

Minimizing the free energy with respect to $x$, one finds $x = 1\big/\big(e^{2J/k_{\rm B}T} + 1\big)$, so the equilibrium concentration of domain walls is finite, meaning there can be no long-ranged spin order. In one dimension, entropy wins and there is always a thermodynamically large number of domain walls in equilibrium. And since the correlation length for $T > 0$ is finite, any boundary conditions imposed at spatial infinity will have no thermodynamic consequences since they will only be 'felt' over a finite range.

As we shall discuss in the following chapter, this consideration is true for any system with sufficiently short-ranged interactions and a discrete global symmetry. Another example is the $q$-state Potts model,

$$H = -J \sum_{\langle ij \rangle} \delta_{\sigma_i, \sigma_j} - h \sum_i \delta_{\sigma_i, 1} \ . \tag{6.27}$$

Here, the spin variables $\sigma_i$ take values in the set $\{1, 2, \ldots, q\}$ on each site. The equivalent of an external magnetic field in the Ising case is a field $h$ which prefers a particular value of $\sigma$ ($\sigma = 1$ in the above Hamiltonian). See the appendix in §6.8 for a transfer matrix solution of the one-dimensional Potts model.

What about higher dimensions? A nifty argument due to R. Peierls shows that there will be a finite temperature phase transition for the Ising model on the square lattice[1]. Consider the Ising model, in zero magnetic field, on a $N_x \times N_y$ square lattice, with $N_{x,y} \to \infty$ in the thermodynamic limit. Along the perimeter of the system we impose the boundary condition $\sigma_i = +1$. Any configuration of the spins may then be represented uniquely in the following manner. Start with a configuration in which all spins are up. Next, draw a set of closed loops on the lattice. By definition, the loops cannot share any links along their boundaries, *i.e.* each link on the lattice is associated with at most one such loop. Now flip all the spins inside each loop from up to down. Identify each such loop configuration with a label $\varGamma$. The partition function is

$$Z = \mathsf{Tr}\, e^{-\beta \hat{H}} = \sum_{\varGamma} e^{-2\beta J L_{\varGamma}} \ , \tag{6.28}$$

where $L_{\varGamma}$ is the total perimeter of the loop configuration $\varGamma$. The domain walls are now loops, rather than individual links, but as in the one-dimensional case, each link of each domain wall contributes an energy $+2J$ relative to the ground state.

Now we wish to compute the average magnetization of the central site (assume $N_{x,y}$ are both odd, so there is a unique central site). This is given by the difference $P_+(0) - P_-(0)$, where $P_\mu(0) = \langle \delta_{\sigma_0\, ,\, \mu} \rangle$ is the probability that

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[1] Here we modify slightly the discussion in chapter 5 of the book by L. Peliti.

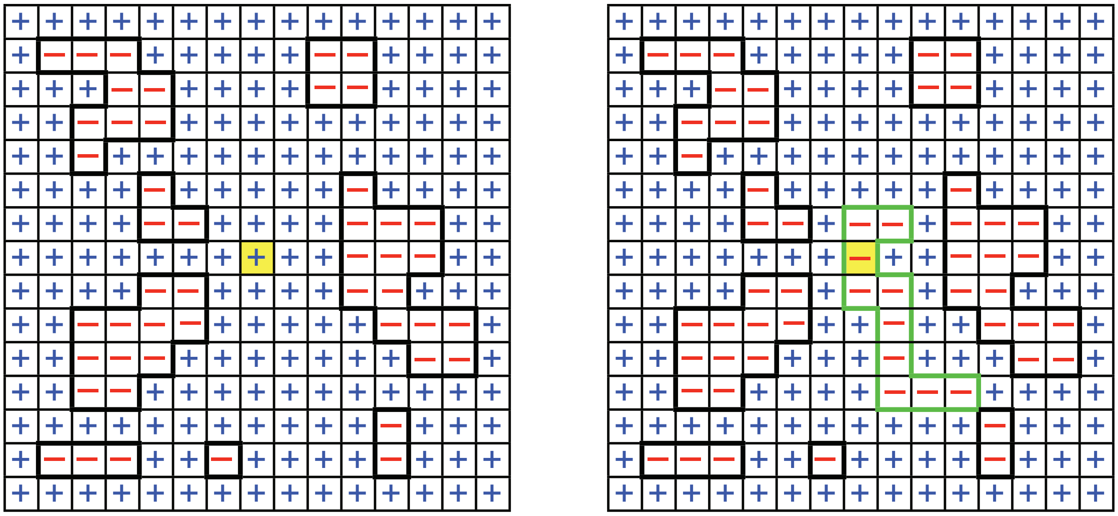

Figure 6.1: Clusters and boundaries for the square lattice Ising model. Left panel: a configuration $\Gamma$ where the central spin is up. Right panel: a configuration $C_\gamma \circ \Gamma$ where the interior spins of a new loop $\gamma$ containing the central spin have been flipped.

the central spin has spin polarization $\mu$. If $P_+(0) > P_-(0)$, then the magnetization per site $m = P_+(0) - P_-(0)$ is finite in the thermodynamic limit, and the system is ordered. Clearly

$$P_+(0) = \frac{1}{Z} \sum_{\Gamma \in \Sigma_+} e^{-2\beta J L_\Gamma} \ , \tag{6.29}$$

where the restriction on the sum indicates that only those configurations where the central spin is up ($\sigma_0 = +1$) are to be included. (see fig. 6.1a). Similarly,

$$P_-(0) = \frac{1}{Z} \sum_{\widetilde{\Gamma} \in \Sigma_-} e^{-2\beta J L_{\widetilde{\Gamma}}} \ , \tag{6.30}$$

where only configurations in which $\sigma_0 = -1$ are included in the sum. Here we have defined

$$\Sigma_\pm = \Big\{ \Gamma \ \big| \ \sigma_0 = \pm \Big\} \ . \tag{6.31}$$

*I.e.* $\Sigma_+ (\Sigma_-)$ is the set of configurations $\Gamma$ in which the central spin is always up (down). Consider now the construction in fig. 6.1b. Any loop configuration $\widetilde{\Gamma} \in \Sigma_-$ may be associated with a unique loop configuration $\Gamma \in \Sigma_+$ by reversing all the spins within the loop of $\widetilde{\Gamma}$ which contains the origin. Note that the map from $\widetilde{\Gamma}$ to $\Gamma$ is many-to-one. That is, we can write $\widetilde{\Gamma} = C_\gamma \circ \Gamma$, where $C_\gamma$ overturns the spins within the loop $\gamma$, with the conditions that (i) $\gamma$ contains the origin, and (ii) none of the links in the perimeter of $\gamma$ coincide with any of the links from the constituent loops of $\Gamma$. Let us denote this set of loops as $\Upsilon_\Gamma$:

$$\Upsilon_\Gamma = \Big\{ \gamma \ : \ 0 \in \text{int}(\gamma) \text{ and } \gamma \cap \Gamma = \emptyset \Big\} \ . \tag{6.32}$$

Then

$$m = P_+(0) - P_-(0) = \frac{1}{Z} \sum_{\Gamma \in \Sigma_+} e^{-2\beta J L_\Gamma} \bigg( 1 - \sum_{\gamma \in \Upsilon_\Gamma} e^{-2\beta J L_\gamma} \bigg) \ . \tag{6.33}$$

If we can prove that $\sum_{\gamma\in\Upsilon_\Gamma} e^{-2\beta J L_\gamma} < 1$, then we will have established that $m > 0$. Let us ask: how many loops $\gamma$ are there in $\Upsilon_\Gamma$ with perimeter $L$? We cannot answer this question exactly, but we can derive a rigorous upper bound for this number, which, following Peliti, we call $g(L)$. We claim that

$$g(L) < \frac{2}{3L} \cdot 3^L \cdot \left(\frac{L}{4}\right)^2 = \frac{L}{24} \cdot 3^L \, . \tag{6.34}$$

To establish this bound, consider any site on such a loop $\gamma$. Initially we have $4$ possible directions to proceed to the next site, but thereafter there are only $3$ possibilities for each subsequent step, since the loop cannot run into itself. This gives $4 \cdot 3^{L-1}$ possibilities. But we are clearly overcounting, since any point on the loop could have been chosen as the initial point, and moreover we could have started by proceeding either clockwise or counterclockwise. So we are justified in dividing this by $2L$. We are still overcounting, because we have not accounted for the constraint that $\gamma$ is a closed loop, nor that $\gamma \cap \Gamma = \emptyset$. We won't bother trying to improve our estimate to account for these constraints. However, we are clearly undercounting due to the fact that a given loop can be translated in space so long as the origin remains within it. To account for this, we multiply by the area of a square of side length $L/4$, which is the maximum area that can be enclosed by a loop of perimeter $L$. We therefore arrive at eqn. 6.34. Finally, we note that the smallest possible value of $L$ is $L = 4$, corresponding to a square enclosing the central site alone. Therefore

$$\sum_{\gamma\in\Upsilon_\Gamma} e^{-2\beta J L_\gamma} < \frac{1}{12} \sum_{k=2}^{\infty} k \cdot \left(3\, e^{-2\beta J}\right)^{2k} = \frac{x^4\,(2 - x^2)}{12\,(1 - x^2)^2} \equiv r \, , \tag{6.35}$$

where $x = 3\, e^{-2\beta J}$. Note that we have accounted for the fact that the perimeter $L$ of each loop $\gamma$ must be an even integer. The sum is smaller than unity provided $x < x_0 = 0.869756\ldots$, hence the system is ordered provided

$$\frac{k_B T}{J} < \frac{2}{\ln(3/x_0)} = 1.61531 \, . \tag{6.36}$$

The exact result is $k_B T_c = 2J/\sinh^{-1}(1) = 2.26918\ldots$ The Peierls argument has been generalized to higher dimensional lattices as well[2].

With a little more work we can derive a bound for the magnetization. We have shown that

$$P_-(0) = \frac{1}{Z} \sum_{\Gamma\in\Sigma_+} e^{-2\beta J L_\Gamma} \sum_{\gamma\in\Upsilon_\Gamma} e^{-2\beta J L_\gamma} < r \cdot \frac{1}{Z} \sum_{\Gamma\in\Sigma_+} e^{-2\beta J L_\Gamma} = r\, P_+(0) \, . \tag{6.37}$$

Thus,

$$1 = P_+(0) + P_-(0) < (1 + r)\, P_+(0) \tag{6.38}$$

and therefore

$$m = P_+(0) - P_-(0) > (1 - r)\, P_+(0) > \frac{1 - r}{1 + r} \, , \tag{6.39}$$

where $r(T)$ is given in eqn. 6.35.

### 6.2.6 Two dimensions or one?

We showed that the one-dimensional Ising model has no finite temperature phase transition, and is disordered at any finite temperature $T$, but in two dimensions on the square lattice there is a finite critical temperature $T_c$ below which there is long-ranged order. Consider now the construction depicted in fig. 6.2, where the sites of

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[2] See. *e.g.* J. L. Lebowitz and A. E. Mazel, *J. Stat. Phys.* **90**, 1051 (1998).

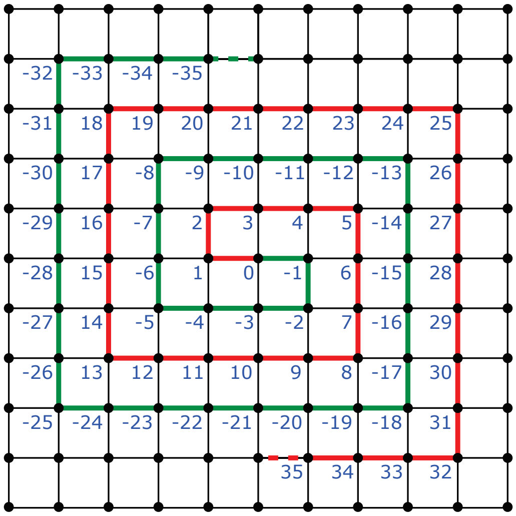


Figure 6.2: A two-dimensional square lattice mapped onto a one-dimensional chain.

a two-dimensional square lattice are mapped onto those of a linear chain[3]. Clearly we can elicit a one-to-one mapping between the sites of a two-dimensional square lattice and those of a one-dimensional chain. That is, the two-dimensional square lattice Ising model may be written as a one-dimensional Ising model, *i.e.*

$$\hat{H} = -J \sum_{\langle ij \rangle}^{\substack{\text{square}\\\text{lattice}}} \sigma_i \, \sigma_j = -\sum_{n,n'}^{\substack{\text{linear}\\\text{chain}}} J_{nn'} \, \sigma_n \, \sigma_{n'} \ . \tag{6.40}$$

How can this be consistent with the results we have just proven?

The fly in the ointment here is that the interaction along the chain $J_{n,n'}$ is long-ranged. This is apparent from inspecting the site labels in fig. 6.2. Note that site $n = 15$ is linked to sites $n' = 14$ and $n' = 16$, but also to sites $n' = -6$ and $n' = -28$. With each turn of the concentric spirals in the figure, the range of the interaction increases. To complicate matters further, the interactions are no longer translationally invariant, *i.e.* $J_{nn'} \neq J(n-n')$. But it is the long-ranged nature of the interactions on our contrived one-dimensional chain which spoils our previous energy-entropy argument, because now the domain walls themselves interact via a long-ranged potential. Consider for example the linear chain with $J_{n,n'} = J \, |n - n'|^{-\alpha}$, where $\alpha > 0$. Let us compute the energy of a domain wall configuration where $\sigma_n = +1$ if $n > 0$ and $\sigma_n = -1$ if $n \leq 0$. The domain wall energy is then

$$\Delta = \sum_{m=0}^{\infty} \sum_{n=1}^{\infty} \frac{2J}{|m+n|^{\alpha}} \ . \tag{6.41}$$

Here we have written one of the sums in terms of $m = -n'$. For asymptotically large $m$ and $n$, we can write $\boldsymbol{R} = (m, n)$ and we obtain an integral over the upper right quadrant of the plane:

$$\int\limits_1^{\infty} \! dR \, R \int\limits_0^{\pi/2} \! d\phi \, \frac{2J}{R^{\alpha} \, (\cos\phi + \sin\phi)^{\alpha}} = 2^{-\alpha/2} \int\limits_{-\pi/4}^{\pi/4} \frac{d\phi}{\cos^{\alpha}\!\phi} \int\limits_1^{\infty} \frac{dR}{R^{\alpha-1}} \ . \tag{6.42}$$

The $\phi$ integral is convergent, but the $R$ integral diverges for $\alpha \leq 2$. For a finite system, the upper bound on the $R$ integral becomes the system size $L$. For $\alpha > 2$ the domain wall energy is finite in the thermodynamic limit

---

[3] A corresponding mapping can be found between a cubic lattice and the linear chain as well.

$L \to \infty$. In this case, entropy again wins. *I.e.* the entropy associated with a single domain wall is $k_{\rm B} \ln L$, and therefore $F = E - k_{\rm B}T$ is always lowered by having a finite density of domain walls. For $\alpha < 2$, the energy of a single domain wall scales as $L^{2-\alpha}$. It was first proven by F. J. Dyson in 1969 that this model has a finite temperature phase transition provided $1 < \alpha < 2$. There is no transition for $\alpha < 1$ or $\alpha > 2$. The case $\alpha = 2$ is special, and is discussed as a special case in the beautiful renormalization group analysis by J. M. Kosterlitz in *Phys. Rev. Lett.* **37**, 1577 (1976).

### 6.2.7 High temperature expansion

Consider once again the ferromagnetic Ising model in zero field ($H = 0$), but on an arbitrary lattice. The partition function is

$$Z = \mathsf{Tr}\, e^{\beta J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j} = \big(\cosh \beta J\big)^{N_{\rm L}} \, \mathsf{Tr} \left\{ \prod_{\langle ij \rangle} \big(1 + x \, \sigma_i \, \sigma_j\big) \right\} , \tag{6.43}$$

where $x = \tanh \beta J$ and $N_{\rm L}$ is the number of links. For regular lattices, $N_{\rm L} = \frac{1}{2} z N$, where $N$ is the number of lattice sites and $z$ is the lattice coordination number, *i.e.* the number of nearest neighbors for each site. We have used

$$e^{\beta J \sigma \sigma'} = \cosh \beta J \cdot \Big\{ 1 + \sigma \sigma' \, \tanh \beta J \Big\} = \begin{cases} e^{+\beta J} & \text{if } \sigma\sigma' = +1 \\ e^{-\beta J} & \text{if } \sigma\sigma' = -1 \, . \end{cases} \tag{6.44}$$

We expand eqn. 6.43 in powers of $x$, resulting in a sum of $2^{N_{\rm L}}$ terms, each of which can be represented graphically in terms of so-called *lattice animals*. A lattice animal is a distinct (including reflections and rotations) arrangement of adjacent plaquettes on a lattice. In order that the trace not vanish, only such configurations and their compositions are permitted. This is because each $\sigma_i$ for every given site $i$ must occur an even number of times in order for a given term in the sum not to vanish. For all such terms, the trace is $2^N$. Let $\varGamma$ represent a collection of lattice animals, and $g_\varGamma$ the multiplicity of $\varGamma$. Then

$$Z = 2^N \big(\cosh \beta J\big)^{N_{\rm L}} \sum_\varGamma g_\varGamma \, \big(\tanh \beta J\big)^{L_\varGamma} \, , \tag{6.45}$$

where $L_\varGamma$ is the total number of sites in the diagram $\varGamma$, and $g_\varGamma$ is the multiplicity of $\varGamma$. Since $x$ vanishes as $T \to \infty$, this procedure is known as the *high temperature expansion* (HTE).

For the square lattice, he enumeration of all lattice animals with up to order eight is given in fig. 6.3. For the diagram represented as a single elementary plaquette, there are $N$ possible locations for the lower left vertex. For the $2 \times 1$ plaquette animal, one has $g = 2N$, because there are two inequivalent orientations as well as $N$ translations. For two disjoint elementary squares, one has $g = \frac{1}{2} N(N-5)$, which arises from subtracting $5N$ 'illegal' configurations involving double lines (remember each link in the partition sum appears only once!), shown in the figure, and finally dividing by two because the individual squares are identical. Note that $N(N-5)$ is always even for any integer value of $N$. Thus, to lowest interesting order on the square lattice,

$$Z = 2^N \big(\cosh \beta J\big)^{2N} \Big\{ 1 + N x^4 + 2 N x^6 + \big(7 - \tfrac{5}{2}\big) N x^8 + \tfrac{1}{2} N^2 x^8 + \mathcal{O}(x^{10}) \Big\} \, . \tag{6.46}$$

The free energy is therefore

$$\begin{aligned} F &= -k_{\rm B}T \ln 2 + N k_{\rm B}T \ln(1 - x^2) - N k_{\rm B}T \Big[ x^4 + 2\, x^6 + \tfrac{9}{2}\, x^8 + \mathcal{O}(x^{10}) \Big] \\ &= N k_{\rm B}T \ln 2 - N k_{\rm B}T \Big\{ x^2 + \tfrac{3}{2}\, x^4 + \tfrac{7}{3}\, x^6 + \tfrac{19}{4}\, x^8 + \mathcal{O}(x^{10}) \Big\}, \end{aligned} \tag{6.47}$$

again with $x = \tanh \beta J$. Note that we've substituted $\cosh^2\!\beta J = 1/(1-x^2)$ to write the final result as a power series in $x$. Notice that the $\mathcal{O}(N^2)$ factor in $Z$ has cancelled upon taking the logarithm, so the free energy is properly extensive.

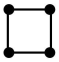
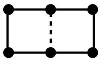
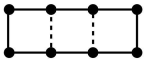
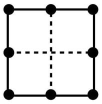
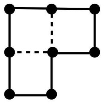
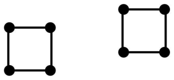
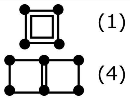
| diagram $\varGamma$ | $L_\varGamma$ | $g_\varGamma$ | remarks |
|---|---|---|---|
|  | $0$ | $1$ | empty lattice |
|  | $4$ | $N$ | *N* translations |
|  | $6$ | $2N$ | 2 rotations, *N* translations |
|  | $8$ | $2N$ | 2 rotations, *N* translations |
|  | $8$ | $N$ | *N* translations |
|  | $8$ | $4N$ | 4 rotations, *N* translations |
|  | $8$ | $\frac{1}{2}(N^2-5N)$ | exclude five invalid diagrams; halve for equivalent squares  |

Figure 6.3: HTE diagrams on the square lattice and their multiplicities.

Note that the high temperature expansion for the one-dimensional Ising chain yields

$$Z_{\rm chain}(T,N) = 2^N \cosh^{N-1}\!\beta J \qquad , \qquad Z_{\rm ring}(T,N) = 2^N \cosh^{N}\!\beta J \ , \tag{6.48}$$

in agreement with the transfer matrix calculations. In higher dimensions, where there is a finite temperature phase transition, one typically computes the specific heat $c(T)$ and tries to extract its singular behavior in the vicinity of $T_{\rm c}$, where $c(T) \sim A\,(T-T_{\rm c})^{-\alpha}$. Since $x(T) = \tanh(J/k_{\rm B}T)$ is analytic in $T$, we have $c(x) \sim A'\,(x-x_{\rm c})^{-\alpha}$, where $x_{\rm c} = x(T_{\rm c})$. One assumes $x_{\rm c}$ is the singularity closest to the origin and corresponds to the radius of convergence of the high temperature expansion. If we write

$$c(x) = \sum_{n=0}^\infty a_n\, x^n \sim A''\bigg(1-\frac{x}{x_{\rm c}}\bigg)^{-\alpha} \ , \tag{6.49}$$

then according to the binomial theorem we should expect

$$\frac{a_n}{a_{n-1}} = \frac{1}{x_{\rm c}}\bigg[1-\frac{1-\alpha}{n}\bigg] \ . \tag{6.50}$$

Thus, by plotting $a_n/a_{n-1}$ *versus* $1/n$, one extracts $1/x_{\rm c}$ as the intercept, and $(\alpha-1)/x_{\rm c}$ as the slope.

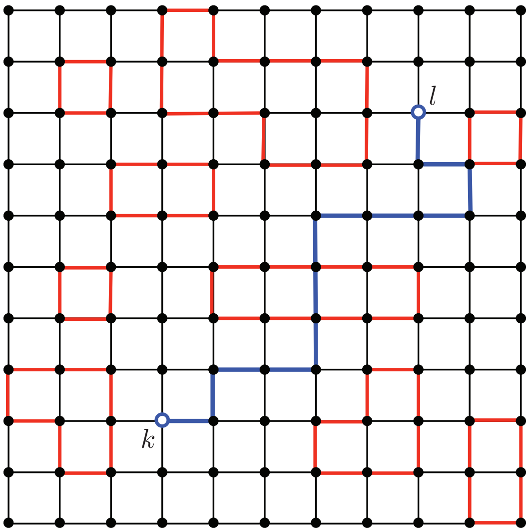


Figure 6.4: HTE diagrams for the numerator $Y_{kl}$ of the correlation function $C_{kl}$. The blue path connecting sites $k$ and $l$ is the string. The remaining red paths are all closed loops.

**High temperature expansion for correlation functions**

Can we also derive a high temperature expansion for the spin-spin correlation function $C_{kl} = \langle \sigma_k \, \sigma_l \rangle$? Yes we can. We have

$$C_{kl} = \frac{\mathsf{Tr}\left[\sigma_k \, \sigma_l \, e^{\beta J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j}\right]}{\mathsf{Tr}\left[e^{\beta J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j}\right]} \equiv \frac{Y_{kl}}{Z} \, . \tag{6.51}$$

Recall our analysis of the partition function $Z$. We concluded that in order for the trace not to vanish, the spin variable $\sigma_i$ on each site $i$ must occur an even number of times in the expansion of the product. Similar considerations hold for $Y_{kl}$, except now due to the presence of $\sigma_k$ and $\sigma_l$, those variables now must occur an *odd* number of times when expanding the product. It is clear that the only nonvanishing diagrams will be those in which there is a finite string connecting sites $k$ and $l$, in addition to the usual closed HTE loops. See fig. 6.4 for an instructive sketch. One then expands both $Y_{kl}$ as well as $Z$ in powers of $x = \tanh \beta J$, taking the ratio to obtain the correlator $C_{kl}$. At high temperatures $(x \to 0)$, both numerator and denominator are dominated by the configurations $\Gamma$ with the shortest possible total perimeter. For $Z$, this means the trivial path $\Gamma = \{\emptyset\}$, while for $Y_{kl}$ this means finding the shortest length path from $k$ to $l$. (If there is no straight line path from $k$ to $l$, there will in general be several such minimizing paths.) Note, however, that the presence of the string between sites $k$ and $l$ complicates the analysis of $g_\Gamma$ for the closed loops, since none of the links of $\Gamma$ can intersect the string. It is worth stressing that this does not mean that the string and the closed loops cannot intersect at isolated *sites*, but only that they share no common *links*; see once again fig. 6.4.

## 6.3 Nonideal Classical Gases

Let's switch gears now and return to the study of continuous classical systems described by a Hamiltonian $\hat{H}\big(\{\boldsymbol{x}_i\}, \{\boldsymbol{p}_i\}\big)$. In the next chapter, we will see how the critical properties of classical fluids can in fact be modeled by an appropriate *lattice gas* Ising model, and we'll derive methods for describing the liquid-gas phase transition in such a model.

### 6.3.1 The configuration integral

Consider the ordinary canonical partition function for a nonideal system of identical point particles interacting via a central two-body potential $u(r)$. We work in the ordinary canonical ensemble. The $N$-particle partition function is

$$\begin{aligned} Z(T,V,N) &= \frac{1}{N!}\int\prod_{i=1}^{N}\frac{d^dp_i\,d^dx_i}{h^d}\,e^{-\hat{H}/k_\mathrm{B}T} \\ &= \frac{\lambda_T^{-Nd}}{N!}\int\prod_{i=1}^{N}d^dx_i\,\exp\bigg(-\frac{1}{k_\mathrm{B}T}\sum_{i<j}u\big(|\boldsymbol{x}_i-\boldsymbol{x}_j|\big)\bigg)\ . \end{aligned} \tag{6.52}$$

Here, we have assumed a many body Hamiltonian of the form

$$\hat{H} = \sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j}u\big(|\boldsymbol{x}_i-\boldsymbol{x}_j|\big)\ , \tag{6.53}$$

in which massive nonrelativistic particles interact via a two-body central potential. As before, $\lambda_T = \sqrt{2\pi\hbar^2/mk_\mathrm{B}T}$ is the thermal wavelength. We can now write

$$Z(T,V,N) = \lambda_T^{-Nd}\,Q_N(T,V)\ , \tag{6.54}$$

where the *configuration integral* $Q_N(T,V)$ is given by

$$Q_N(T,V) = \frac{1}{N!}\int\!d^dx_1\cdots\int\!d^dx_N\,\prod_{i<j}e^{-\beta u(r_{ij})}\ . \tag{6.55}$$

There are no general methods for evaluating the configurational integral exactly.

### 6.3.2 One-dimensional Tonks gas

The Tonks gas is a one-dimensional generalization of the hard sphere gas. Consider a one-dimensional gas of indistinguishable particles of mass $m$ interacting via the potential

$$u(x-x') = \begin{cases} \infty & \text{if } |x-x'| < a \\ 0 & \text{if } |x-x'| \ge a\ . \end{cases} \tag{6.56}$$

Let the gas be placed in a finite volume $L$. The hard sphere nature of the particles means that no particle can get within a distance $\frac{1}{2}a$ of the ends at $x=0$ and $x=L$. That is, there is a one-body potential $v(x)$ acting as well, where

$$v(x) = \begin{cases} \infty & \text{if } x < \frac{1}{2}a \\ 0 & \text{if } \frac{1}{2}a \le x \le L-\frac{1}{2}a \\ \infty & \text{if } x > L-\frac{1}{2}a\ . \end{cases} \tag{6.57}$$

The partition function of the 1D Tonks gas is given by

$$Z(T,L,N) = \frac{\lambda_T^{-N}}{N!}\int\limits_0^L\!dx_1\cdots\int\limits_0^L\!dx_N\,\chi(x_1,\ldots,x_N)\ , \tag{6.58}$$

where $\chi = e^{-U/k_{\mathrm{B}}T}$ is zero if any two 'rods' (of length $a$) overlap, or if any rod overlaps with either boundary at $x = 0$ and $x = L$, and $\chi = 1$ otherwise. Note that $\chi$ does not depend on temperature. Without loss of generality, we can integrate over the subspace where $x_1 < x_2 < \cdots < x_N$ and then multiply the result by $N!$. Clearly $x_j$ must lie to the right of $x_{j-1} + a$ and to the left of $Y_j \equiv L - (N-j)a - \frac{1}{2}a$. Thus,

$$\begin{aligned}
Z(T,L,N) &= \lambda_T^{-N} \int\limits_{a/2}^{Y_1} \! dx_1 \int\limits_{x_1+a}^{Y_2} \! dx_2 \cdots \int\limits_{x_{N-1}+a}^{Y_N} \! dx_N \\
&= \lambda_T^{-N} \int\limits_{a/2}^{Y_1} \! dx_1 \int\limits_{x_1+a}^{Y_2} \! dx_2 \cdots \int\limits_{x_{N-2}+a}^{Y_{N-1}} \! dx_{N-1} \, \big(Y_{N-1} - x_{N-1}\big) \\
&= \lambda_T^{-N} \int\limits_{a/2}^{Y_1} \! dx_1 \int\limits_{x_1+a}^{Y_2} \! dx_2 \cdots \int\limits_{x_{N-3}+a}^{Y_{N-2}} \! dx_{N-2} \, \tfrac{1}{2}\big(Y_{N-2} - x_{N-2}\big)^2 = \cdots \\
&= \frac{\lambda_T^{-N}}{N!} \big(X_1 - \tfrac{1}{2}a\big)^N = \frac{\lambda_T^{-N}}{N!} \, (L - Na)^N \ . \qquad (6.59)
\end{aligned}$$

The $\lambda_T^N$ factor comes from integrating over the momenta; recall $\lambda_T = \sqrt{2\pi\hbar^2/mk_{\mathrm{B}}T}$ .

The free energy is

$$F = -k_{\mathrm{B}}T \ln Z = -Nk_{\mathrm{B}}T \bigg\{ -\ln \lambda_T + 1 + \ln\bigg(\frac{L}{N} - a\bigg)\bigg\} \ , \qquad (6.60)$$

where we have used Stirling's rule to write $\ln N! \approx N \ln N - N$. The pressure is

$$p = -\frac{\partial F}{\partial L} = \frac{k_{\mathrm{B}}T}{\frac{L}{N} - a} = \frac{nk_{\mathrm{B}}T}{1 - na} \ , \qquad (6.61)$$

where $n = N/L$ is the one-dimensional density. Note that the pressure diverges as $n$ approaches $1/a$. The usual one-dimensional ideal gas law, $pL = Nk_{\mathrm{B}}T$, is replaced by $pL_{\text{eff}} = Nk_{\mathrm{B}}T$, where $L_{\text{eff}} = L - Na$ is the 'free' volume obtained by subtracting the total 'excluded volume' $Na$ from the original volume $L$.

### 6.3.3 Mayer cluster expansion

Let us return to the general problem of computing the configuration integral. Consider the function $e^{-\beta u_{ij}}$, where $u_{ij} \equiv u(|\boldsymbol{x}_i - \boldsymbol{x}_j|)$. We assume that at very short distances there is a strong repulsion between particles, *i.e.* $u_{ij} \to \infty$ as $r_{ij} = |\boldsymbol{x}_i - \boldsymbol{x}_j| \to 0$, and that $u_{ij} \to 0$ as $r_{ij} \to \infty$. Thus, $e^{-\beta u_{ij}}$ vanishes as $r_{ij} \to 0$ and approaches unity as $r_{ij} \to \infty$. For our purposes, it will prove useful to define the function

$$f(r) = e^{-\beta u(r)} - 1 \ , \qquad (6.62)$$

called the *Mayer function* after Josef Mayer. We may now write

$$Q_N(T,V) = \frac{1}{N!} \int \! d^d\!x_1 \cdots \int \! d^d\!x_N \, \prod_{i<j} \big(1 + f_{ij}\big) \ . \qquad (6.63)$$

A typical potential we might consider is the semi-phenomenological Lennard-Jones potential,

$$u(r) = 4\,\epsilon \left\{ \Big(\frac{\sigma}{r}\Big)^{12} - \Big(\frac{\sigma}{r}\Big)^{6} \right\} \ . \qquad (6.64)$$

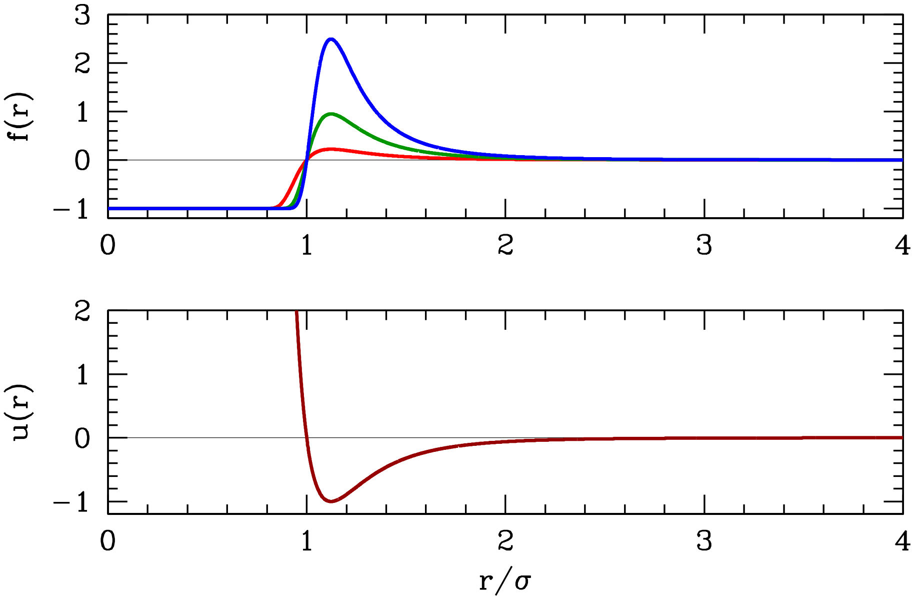


Figure 6.5: Bottom panel: Lennard-Jones potential $u(r)=4\epsilon\left(x^{-12}-x^{-6}\right)$, with $x=r/\sigma$ and $\epsilon=1$. Note the weak attractive tail and the strong repulsive core. Top panel: Mayer function $f(r,T)=e^{-u(r)/k_\text{B}T}-1$ for $k_\text{B}T=0.8\,\epsilon$ (blue), $k_\text{B}T=1.5\,\epsilon$ (green), and $k_\text{B}T=5\,\epsilon$ (red).

This accounts for a long-distance attraction due to mutually induced electric dipole fluctuations, and a strong short-ranged repulsion, phenomenologically modelled with a $r^{-12}$ potential, which mimics a hard core due to overlap of the atomic electron distributions. Setting $u'(r)=0$ we obtain $r^*=2^{1/6}\,\sigma\approx 1.12246\,\sigma$ at the minimum, where $u(r^*)=-\epsilon$. In contrast to the Boltzmann weight $e^{-\beta u(r)}$, the Mayer function $f(r)$ vanishes as $r\to\infty$, behaving as $f(r)\sim -\beta u(r)$. The Mayer function also depends on temperature. Sketches of $u(r)$ and $f(r)$ for the Lennard-Jones model are shown in fig. 6.5.

The Lennard-Jones potential[4] is realistic for certain simple fluids, but it leads to a configuration integral which is in general impossible to evaluate. Indeed, even a potential as simple as that of the hard sphere gas is intractable in more than one space dimension. We can however make progress by deriving a series expansion for the equation of state in powers of the particle density. This is known as the *virial expansion*. As was the case when we investigated noninteracting quantum statistics, it is convenient to work in the grand canonical ensemble and to derive series expansions for the density $n(T,z)$ and the pressure $p(T,z)$ in terms of the fugacity $z$, then solve for $z(T,n)$ to obtain $p(T,n)$. These expansions in terms of fugacity have a nifty diagrammatic interpretation, due to Mayer.

We begin by expanding the product in eqn. 6.63 as

$$\prod_{i<j}\big(1+f_{ij}\big)=1+\sum_{i<j}f_{ij}+\sum_{\substack{i<j\;,\;k<l\\(ij)\neq(kl)}}f_{ij}\,f_{kl}+\ldots\;. \tag{6.65}$$

As there are $\frac{1}{2}N(N-1)$ possible pairings, there are $2^{N(N-1)/2}$ terms in the expansion of the above product. Each such term may be represented by a graph, as shown in fig. 6.7. For each such term, we draw a connection between dots representing different particles $i$ and $j$ if the factor $f_{ij}$ appears in the term under consideration. The contribution for any given graph may be written as a product over contributions from each of its disconnected

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[4] Disambiguation footnote: Take care not to confuse Philipp Lenard (Hungarian-German, cathode ray tubes, Nazi), Alfred-Marie Liénard (French, Liénard-Wiechert potentials, not a Nazi), John Lennard-Jones (British, molecular structure, *definitely* not a Nazi), and Lynyrd Skynyrd (American, "Free Bird", possibly killed by Nazis in 1977 plane crash). I thank my colleague Oleg Shpyrko for setting me straight on this.

Figure 6.6: Left: John Lennard-Jones. Center: Catherine Zeta-Jones. Right: James Earl Jones.

$$\big(f_{1,4}\, f_{4,7}\, f_{4,9}\, f_{7,9}\big)\, \big(f_{2,5}\, f_{2,6}\big)\, \big(f_{3,10}\big)\, \big(f_{8,11}\big)$$

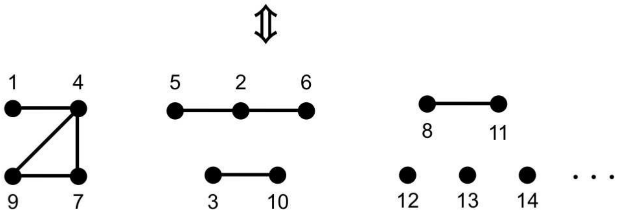

Figure 6.7: Diagrammatic interpretation of a term involving a product of eight Mayer functions.

component clusters. For example, in the case of the term in fig. 6.7, the contribution to the configurational integral would be

$$\begin{aligned} \Delta Q = \frac{1}{N!} & \int \! d^d\!x_1\, d^d\!x_4\, d^d\!x_7\, d^d\!x_9\; f_{1,4}\, f_{4,7}\, f_{4,9}\, f_{7,9} \\ & \times \int \! d^d\!x_2\, d^d\!x_5\, d^d\!x_6\; f_{2,5}\, f_{2,6} \times \int \! d^d\!x_3\, d^d\!x_{10}\; f_{3,10} \times \int \! d^d\!x_8\, d^d\!x_{11}\; f_{8,11}\ . \end{aligned} \tag{6.66}$$

We will refer to a given product of Mayer functions which arises from this expansion as a *term*.

The particular labels we assign to each vertex of a given graph don't affect the overall value of the graph. Now a given unlabeled graph consists of a certain number of connected subgraphs. For a system with $N$ particles, we may then write

$$N = \sum_\gamma m_\gamma\, n_\gamma\ , \tag{6.67}$$

where $\gamma$ ranges over all possible connected subgraphs, and

$$\begin{aligned} m_\gamma &= \text{number of connected subgraphs of type } \gamma \text{ in the unlabeled graph} \\ n_\gamma &= \text{number of vertices in the connected subgraph } \gamma\ . \end{aligned}$$

Note that the single vertex • counts as a connected subgraph, with $n_\bullet = 1$. We now ask: how many ways are there of assigning the $N$ labels to the $N$ vertices of a given unlabeled graph? One might first thing the answer is simply $N!$, however this is too big, because different assignments of the labels to the vertices may not result in a distinct graph. To see this, consider the examples in fig. 6.8. In the first example, an unlabeled graph with four vertices consists of two identical connected subgraphs. Given any assignment of labels to the vertices, then, we can simply exchange the two subgraphs and get the same term. So we should divide $N!$ by the product $\prod_\gamma m_\gamma!$. But even this is not enough, because within each connected subgraph $\gamma$ there may be permutations which leave the integrand unchanged, as shown in the second and third examples in fig. 6.8. We define the *symmetry factor* $s_\gamma$ as the number of permutations of the labels which leaves a given connected subgraphs $\gamma$ invariant. Examples of symmetry factors are shown in fig. 6.9. Consider, for example, the third subgraph in the top row. Clearly one can rotate the figure about its horizontal symmetry axis to obtain a new labeling which represents the same term. This twofold axis is the only symmetry the diagram possesses, hence $s_\gamma = 2$. For the first diagram in the second row, one can rotate *either* of the triangles about the horizontal symmetry axis. One can also rotate the figure in the plane by $180°$ so as to exchange the two triangles. Thus, there are $2 \times 2 \times 2 = 8$ symmetry operations which result in the same term, and $s_\gamma = 8$. Finally, the last subgraph in the second row consists of five vertices each of which is connected to the other four. Therefore any permutation of the labels results in the same term, and $s_\gamma = 5! = 120$. In addition to dividing by the product $\prod_\gamma m_\gamma!$, we must then also divide by $\prod_\gamma s_\gamma^{m_\gamma}$.

We can now write the partition function as

$$Z = \frac{\lambda_T^{-Nd}}{N!} \sum_{\{m_\gamma\}} \frac{N!}{\prod m_\gamma!\, s_\gamma^{m_\gamma}} \cdot \prod_\gamma \bigg( \int \! d^dx_1 \cdots d^dx_{n_\gamma} \prod_{i<j}^{\gamma} f_{ij} \bigg)^{m_\gamma} \cdot \delta_{N\,,\,\sum m_\gamma n_\gamma} \ , \tag{6.68}$$

where the last product is over all links in the subgraph $\gamma$. The final Kronecker delta enforces the constraint $N = \sum_\gamma m_\gamma \, n_\gamma$. We next define the *cluster integral* $b_\gamma$ as

$$b_\gamma(T) \equiv \frac{1}{s_\gamma} \cdot \frac{1}{V} \int \! d^dx_1 \cdots d^dx_{n_\gamma} \prod_{i<j}^{\gamma} f_{ij} \ . \tag{6.69}$$

Since $f_{ij} = f\big(|\boldsymbol{x}_i - \boldsymbol{x}_j|\big)$, the product $\prod_{i<j}^\gamma f_{ij}$ is invariant under simultaneous translation of all the coordinate vectors by any constant vector, and hence the integral over the $n_\gamma$ position variables contains exactly one factor of the volume, which cancels with the prefactor in the above definition of $b_\gamma$. Thus, each cluster integral is *intensive*, scaling as $V^0$.[5]

If we compute the grand partition function, then the fixed $N$ constraint is relaxed, and we can do the sums:

$$\begin{aligned}
\varXi = e^{-\beta\varOmega} &= \sum_{\{m_\gamma\}} \Big( e^{\beta\mu}\, \lambda_T^{-d} \Big)^{\sum m_\gamma n_\gamma} \prod_\gamma \frac{1}{m_\gamma!} \, \big(V\, b_\gamma\big)^{m_\gamma} \\
&= \prod_\gamma \sum_{m_\gamma=0}^{\infty} \frac{1}{m_\gamma!} \, \Big( e^{\beta\mu}\, \lambda_T^{-d} \Big)^{m_\gamma\, n_\gamma} \big(V\, b_\gamma\big)^{m_\gamma} \\
&= \exp\bigg( V \sum_\gamma \big( e^{\beta\mu}\, \lambda_T^{-d} \big)^{n_\gamma} \, b_\gamma \bigg) \ .
\end{aligned} \tag{6.70}$$

Thus,

$$\varOmega(T,V,\mu) = -V k_\mathrm{B} T \sum_\gamma \big( e^{\beta\mu}\, \lambda_T^{-d} \big)^{n_\gamma} \, b_\gamma(T) \ , \tag{6.71}$$

and we can write

$$p = k_\mathrm{B} T \sum_\gamma \big( z \lambda_T^{-d} \big)^{n_\gamma} \, b_\gamma(T) \tag{6.72}$$

$$n = \sum_\gamma n_\gamma \, \big( z \lambda_T^{-d} \big)^{n_\gamma} \, b_\gamma(T) \ , \tag{6.73}$$

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[5] We assume that the long-ranged behavior of $f(r) \approx -\beta u(r)$ is integrable.

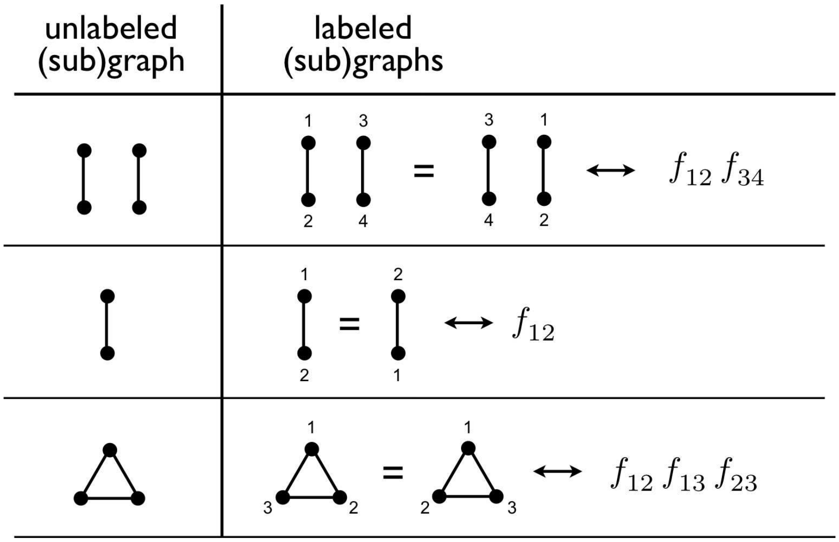

Figure 6.8: Different assignations of labels to vertices may not result in a distinct term in the expansion of the configuration integral.

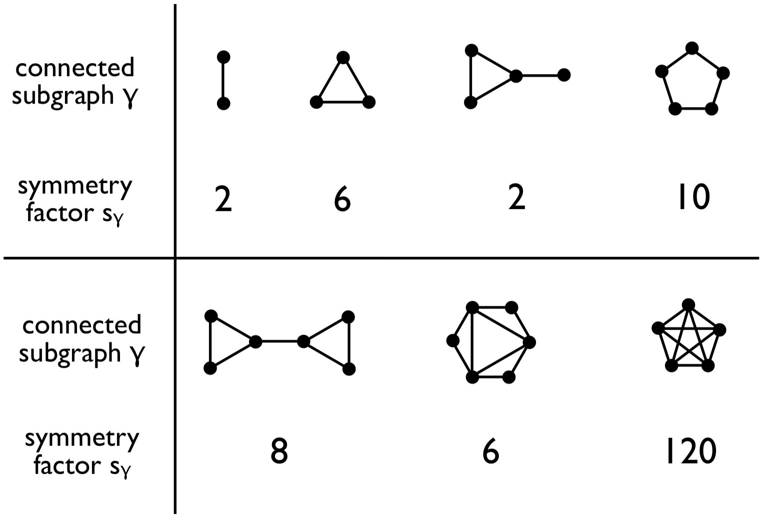

Figure 6.9: The symmetry factor $s_\gamma$ for a connected subgraph $\gamma$ is the number of permutations of its indices which leaves the term $\prod_{(ij)\in\gamma} f_{ij}$ invariant.

where $z = \exp(\beta\mu)$ is the fugacity, and where $b_\bullet \equiv 1$. As we did in the case of ideal quantum gas statistical mechanics, we can systematically invert the relation $n = n(z,T)$ to obtain $z = z(n,T)$, and then insert this into the equation for $p(z,T)$ to obtain the equation of state $p = p(n,T)$. This yields the *virial expansion* of the equation of state,

$$p = nk_{\rm B}T\Big\{1 + B_2(T)\, n + B_3(T)\, n^2 + \ldots\Big\} \,. \tag{6.74}$$

### 6.3.4 Cookbook recipe

Just follow these simple steps!

- The pressure and number density are written as an expansion over unlabeled connected clusters $\gamma$, *viz.*

$$\beta p = \sum_\gamma \big(z\lambda_T^{-d}\big)^{n_\gamma}\, b_\gamma$$
$$n = \sum_\gamma n_\gamma \big(z\lambda_T^{-d}\big)^{n_\gamma}\, b_\gamma\ .$$

- For each term in each of these sums, draw the unlabeled connected cluster $\gamma$.
- Assign labels $1\,,\,2\,,\,\ldots\,,\,n_\gamma$ to the vertices, where $n_\gamma$ is the total number of vertices in the cluster $\gamma$. It doesn't matter how you assign the labels.
- Write down the product $\prod_{i<j}^\gamma f_{ij}$. The factor $f_{ij}$ appears in the product if there is a link in your (now labeled) cluster between sites $i$ and $j$.
- The symmetry factor $s_\gamma$ is the number of elements of the symmetric group $S_{n_\gamma}$ which leave the product $\prod_{i<j}^\gamma f_{ij}$ invariant. The identity permutation always leaves the product invariant, so $s_\gamma \geq 1$.
- The cluster integral is

$$b_\gamma(T) \equiv \frac{1}{s_\gamma}\cdot\frac{1}{V}\int\! d^d\!x_1 \cdots d^d\!x_{n_\gamma} \prod_{i<j}^{\gamma} f_{ij}\ .$$

  Due to translation invariance, $b_\gamma(T) \propto V^0$. One can therefore set $\boldsymbol{x}_{n_\gamma} \equiv 0$, eliminate the volume factor from the denominator, and perform the integral over the remaining $n_\gamma - 1$ coordinates.

- This procedure generates expansions for $p(T,z)$ and $n(T,z)$ in powers of the fugacity $z = e^{\beta\mu}$. To obtain something useful like $p(T,n)$, we invert the equation $n = n(T,z)$ to find $z = z(T,n)$, and then substitute into the equation $p = p(T,z)$ to obtain $p = p\big(T, z(T,n)\big) = p(T,n)$. The result is the virial expansion,

$$p = nk_{\rm B}T\Big\{1 + B_2(T)\,n + B_3(T)\,n^2 + \ldots\Big\}\ .$$

### 6.3.5 Lowest order expansion

We have

$$\begin{aligned} b_{-}(T) &= \frac{1}{2V}\int\! d^d\!x_1\!\int\! d^d\!x_2\; f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_2|\big) \\ &= \tfrac{1}{2}\int\! d^d\!r\; f(r) \end{aligned} \tag{6.75}$$

and

$$\begin{aligned} b_{\wedge}(T) &= \frac{1}{2V}\int\! d^d\!x_1\!\int\! d^d\!x_2\int\! d^d\!x_3\; f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_2|\big)\, f\big(|\boldsymbol{x}_1 - \boldsymbol{x}_3|\big) \\ &= \tfrac{1}{2}\int\! d^d\!r\!\int\! d^d\!r'\; f(r)\, f(r') = 2\big(b_{-}\big)^2 \end{aligned} \tag{6.76}$$

and

$$\begin{aligned} b_{\triangle}(T) &= \frac{1}{6V}\int\! d^d\!x_1 \!\int\! d^d\!x_2 \!\int\! d^d\!x_3 \; f\big(|\boldsymbol{x}_1-\boldsymbol{x}_2|\big)\, f\big(|\boldsymbol{x}_1-\boldsymbol{x}_3|\big)\, f\big(|\boldsymbol{x}_2-\boldsymbol{x}_3|\big) \\ &= \tfrac{1}{6}\int\! d^d\!r \!\int\! d^d\!r' \; f(r)\, f(r')\, f\big(|\boldsymbol{r}-\boldsymbol{r}'|\big) \ . \end{aligned} \tag{6.77}$$

We may now write

$$p = k_{\rm B}T\Big\{ z\lambda_T^{-d} + \big(z\lambda_T^{-d}\big)^2\, b_{-}(T) + \big(z\lambda_T^{-d}\big)^3 \cdot \big(b_{\wedge} + b_{\triangle}\big) + \mathcal{O}(z^4)\Big\} \tag{6.78}$$

$$n = z\lambda_T^{-d} + 2\big(z\lambda_T^{-d}\big)^2\, b_{-}(T) + 3\big(z\lambda_T^{-d}\big)^3 \cdot \big(b_{\wedge} + b_{\triangle}\big) + \mathcal{O}(z^4) \tag{6.79}$$

We invert by writing

$$z\lambda_T^{-d} = n + \alpha_2\, n^2 + \alpha_3\, n^3 + \ldots \tag{6.80}$$

and substituting into the equation for $n(z,T)$, yielding

$$n = (n + \alpha_2\, n^2 + \alpha_3\, n^3) + 2(n + \alpha_2\, n^2)^2\, b_{-} + 3n^3\,\big(b_{\wedge} + b_{\triangle}\big) + \mathcal{O}(n^4) \ . \tag{6.81}$$

Thus,

$$0 = (\alpha_2 + 2b_{-})\, n^2 + (\alpha_3 + 4\alpha_2\, b_{-} + 3b_{\wedge} + 3b_{\triangle})\, n^3 + \ldots \ . \tag{6.82}$$

We therefore conclude

$$\alpha_2 = -2b_{-} \tag{6.83}$$

$$\begin{aligned} \alpha_3 &= -4\alpha_2\, b_{-} - 3b_{\wedge} - 3b_{\triangle} \\ &= 8b_{-}^2 - 6b_{-}^2 - 3b_{\triangle} \\ &= 2b_{-}^2 - 3b_{\triangle} \ . \end{aligned} \tag{6.84}$$

We now insert eqn. 6.80 with the determined values of $\alpha_{2,3}$ into the equation for $p(z,T)$, obtaining

$$\begin{aligned} \frac{p}{k_{\rm B}T} &= n - 2b_{-}n^2 + (2b_{-}^2 - 3b_{\triangle})\, n^3 + (n - 2b_{-}n^2)^2\, b_{-} + n^3\,(2b_{-}^2 + b_{\triangle}) + \mathcal{O}(n^4) \\ &= n - b_{-}\, n^2 - 2b_{\triangle}\, n^3 + \mathcal{O}(n^4) \ . \end{aligned} \tag{6.85}$$

Thus,

$$B_2(T) = -b_{-}(T) \qquad , \qquad B_3(T) = -2b_{\triangle}(T) \ . \tag{6.86}$$

### 6.3.6 Hard sphere gas in three dimensions

The hard sphere potential is given by

$$u(r) = \begin{cases} \infty & \text{if } r \le a \\ 0 & \text{if } r > a \ . \end{cases} \tag{6.87}$$

Here $a$ is the *diameter* of the spheres. The corresponding Mayer function is then temperature independent, and given by

$$f(r) = \begin{cases} -1 & \text{if } r \le a \\ 0 & \text{if } r > a \ . \end{cases} \tag{6.88}$$

We can change variables

$$b_{-}(T) = \tfrac{1}{2}\!\int\! d^3\!r\; f(r) = -\tfrac{2}{3}\pi a^3 \ . \tag{6.89}$$

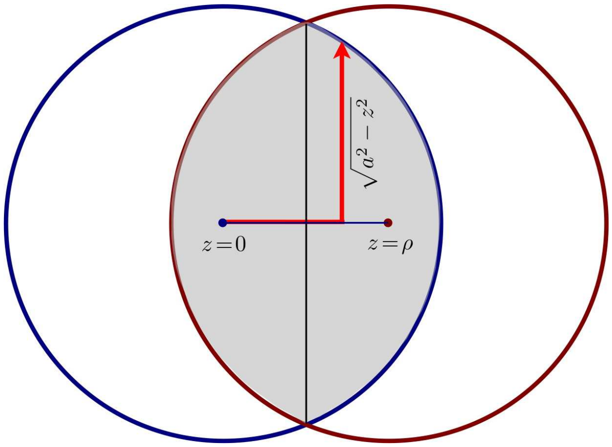

Figure 6.10: The overlap of hard sphere Mayer functions. The shaded volume is $\mathcal{V}$.

The calculation of $b_\triangle$ is more challenging. We have

$$b_\triangle = \tfrac{1}{6}\!\int\! d^3\!\rho\!\int\! d^3\!r\; f(\rho)\,f(r)\,f\big(|\boldsymbol{r}-\boldsymbol{\rho}|\big)\ . \tag{6.90}$$

We must first compute the volume of overlap for spheres of *radius* $a$ (recall $a$ is the *diameter* of the constituent hard sphere particles) centered at $0$ and at $\boldsymbol{\rho}$:

$$\begin{aligned}\mathcal{V} &= \int\! d^3\!r\; f(r)\,f\big(|\boldsymbol{r}-\boldsymbol{\rho}|\big) \\ &= 2\int\limits_{\rho/2}^{a}\! dz\;\pi(a^2-z^2) = \tfrac{4\pi}{3}a^3 - \pi a^2\rho + \tfrac{\pi}{12}\,\rho^3\ .\end{aligned} \tag{6.91}$$

We then integrate over region $|\boldsymbol{\rho}|<a$, to obtain

$$\begin{aligned}b_\triangle &= -\tfrac{1}{6}\cdot 4\pi\!\int\limits_0^a\! d\rho\;\rho^2\cdot\Big\{\tfrac{4\pi}{3}a^3 - \pi a^2\rho + \tfrac{\pi}{12}\,\rho^3\Big\} \\ &= -\tfrac{5\pi^2}{36}\,a^6\ .\end{aligned} \tag{6.92}$$

Thus,

$$p = nk_{\rm B}T\,\Big\{1+\tfrac{2\pi}{3}a^3n + \tfrac{5\pi^2}{18}a^6n^2 + \mathcal{O}(n^3)\Big\}\ . \tag{6.93}$$

### 6.3.7 Weakly attractive tail

Suppose

$$u(r) = \begin{cases} \infty & \text{if } r\le a \\ -u_0(r) & \text{if } r>a\ . \end{cases} \tag{6.94}$$

Then the corresponding Mayer function is

$$f(r) = \begin{cases} -1 & \text{if } r\le a \\ e^{\beta u_0(r)}-1 & \text{if } r>a\ . \end{cases} \tag{6.95}$$

Thus,

$$b_{-}(T)=\tfrac{1}{2}\int\!d^3\!r\,f(r)=-\tfrac{2\pi}{3}a^3+2\pi\int\limits_a^\infty\!dr\,r^2\left[e^{\beta u_0(r)}-1\right]\,. \tag{6.96}$$

Thus, the second virial coefficient is

$$B_2(T)=-b_{-}(T)\approx\tfrac{2\pi}{3}a^3-\frac{2\pi}{k_\mathrm{B}T}\int\limits_a^\infty\!dr\,r^2\,u_0(r)\,, \tag{6.97}$$

where we have assumed $k_\mathrm{B}T \ll u_0(r)$. We see that the second virial coefficient *changes sign* at some temperature $T_0$, from a negative low temperature value to a positive high temperature value.

### 6.3.8 Spherical potential well

Consider an attractive spherical well potential with an infinitely repulsive core,

$$u(r)=\begin{cases}\infty & \text{if } r\le a\\ -\epsilon & \text{if } a<r<R\\ 0 & \text{if } r>R\,.\end{cases} \tag{6.98}$$

Then the corresponding Mayer function is

$$f(r)=\begin{cases}-1 & \text{if } r\le a\\ e^{\beta\epsilon}-1 & \text{if } a<r<R\\ 0 & \text{if } r>R\,.\end{cases} \tag{6.99}$$

Writing $s\equiv R/a$, we have

$$\begin{aligned}B_2(T)=-b_{-}(T)&=-\tfrac{1}{2}\int\!d^3\!r\,f(r)\\ &=-\frac{1}{2}\left\{(-1)\cdot\tfrac{4\pi}{3}a^3+\big(e^{\beta\epsilon}-1\big)\cdot\tfrac{4\pi}{3}a^3(s^3-1)\right\}\\ &=\tfrac{2\pi}{3}a^3\left\{1-(s^3-1)\big(e^{\beta\epsilon}-1\big)\right\}\,.\end{aligned} \tag{6.100}$$

To find the temperature $T_0$ where $B_2(T)$ changes sign, we set $B_2(T_0)=0$ and obtain

$$k_\mathrm{B}T_0=\epsilon\Big/\ln\!\left(\frac{s^3}{s^3-1}\right)\,. \tag{6.101}$$

Recall in our study of the thermodynamics of the Joule-Thompson effect in §1.10.6 that the throttling process is *isenthalpic*. The temperature change, when a gas is pushed (or escapes) through a porous plug from a high pressure region to a low pressure one is

$$\Delta T=\int\limits_{p_1}^{p_2}\!dp\,\left(\frac{\partial T}{\partial p}\right)_{\!H}\,, \tag{6.102}$$

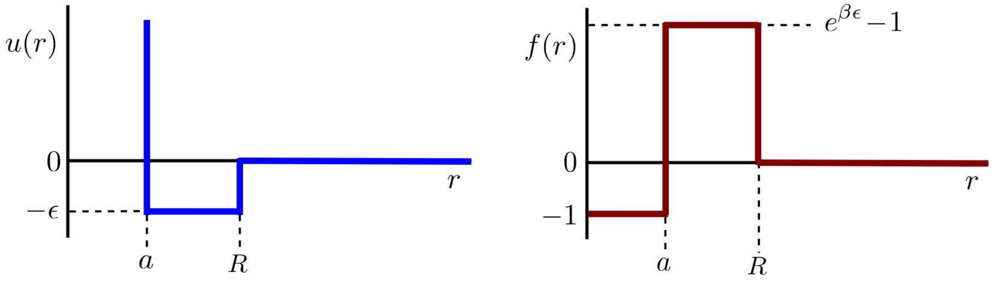

Figure 6.11: An attractive spherical well with a repulsive core $u(r)$ and its associated Mayer function $f(r)$.

where

$$\left(\frac{\partial T}{\partial p}\right)_{H} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_{p} - V\right] . \tag{6.103}$$

Appealing to the virial expansion, and working to lowest order in corrections to the ideal gas law, we have

$$p = \frac{N}{V}\,k_{\rm B}T + \frac{N^2}{V^2}\,k_{\rm B}T\,B_2(T) + \ldots \tag{6.104}$$

and we compute $\left(\frac{\partial V}{\partial T}\right)_p$ by seting

$$0 = dp = -\frac{Nk_{\rm B}T}{V^2}\,dV + \frac{Nk_{\rm B}}{V}\,dT - \frac{2N^2}{V^3}\,k_{\rm B}T\,B_2(T)\,dV + \frac{N^2}{V^2}\,d\big(k_{\rm B}T\,B_2(T)\big) + \ldots\ . \tag{6.105}$$

Dividing by $dT$, we find

$$T\left(\frac{\partial V}{\partial T}\right)_{p} - V = N\left[T\,\frac{\partial B_2}{\partial T} - B_2\right] . \tag{6.106}$$

The temperature where $\left(\frac{\partial T}{\partial p}\right)_H$ changes sign is called the *inversion temperature* $T^*$. To find the inversion point, we set $T^*\,B_2'(T^*) = B_2(T^*)$, *i.e.*

$$\frac{d\ln B_2}{d\ln T}\bigg|_{T^*} = 1 . \tag{6.107}$$

If we approximate $B_2(T) \approx A - \frac{B}{T}$, then the inversion temperature follows simply:

$$\frac{B}{T^*} = A - \frac{B}{T^*} \qquad \Longrightarrow \qquad T^* = \frac{2B}{A} . \tag{6.108}$$

### 6.3.9 Hard spheres with a hard wall

Consider a hard sphere gas in three dimensions in the presence of a hard wall at $z = 0$. The gas is confined to the region $z > 0$. The total potential energy is now

$$W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N) = \sum_i v(\boldsymbol{x}_i) + \sum_{i<j} u(\boldsymbol{x}_i - \boldsymbol{x}_j)\ , \tag{6.109}$$

where

$$v(\boldsymbol{r}) = v(z) = \begin{cases} \infty & \text{if} \quad z \le \frac{1}{2}a \\ 0 & \text{if} \quad z > \frac{1}{2}a\ , \end{cases} \tag{6.110}$$

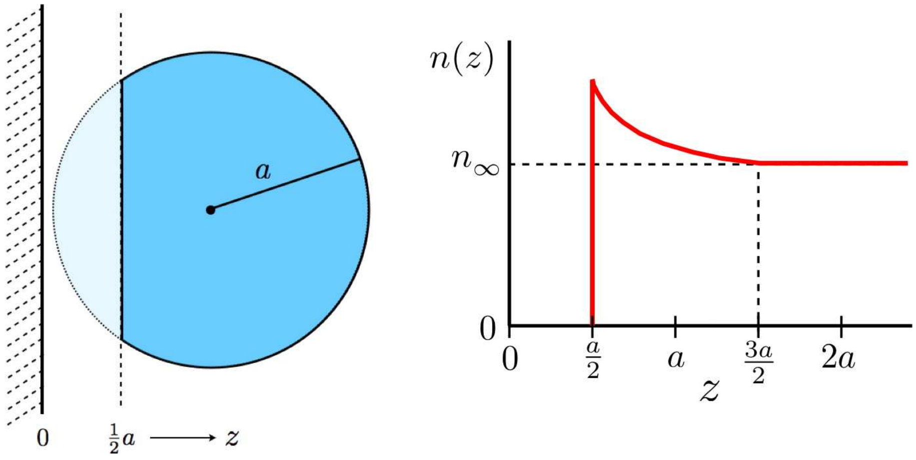

Figure 6.12: In the presence of a hard wall, the Mayer sphere is cut off on the side closest to the wall. The resulting density $n(z)$ vanishes for $z < \frac{1}{2}a$ since the center of each sphere must be at least one radius ($\frac{1}{2}a$) away from the wall. Between $z = \frac{1}{2}a$ and $z = \frac{3}{2}a$ there is a density *enhancement*. If the calculation were carried out to higher order, $n(z)$ would exhibit damped spatial oscillations with wavelength $\lambda \sim a$.

and $u(\boldsymbol{r})$ is given in eqn. 6.87. The grand potential is written as a series in the total particle number $N$, and is given by

$$\varXi = e^{-\beta\varOmega} = 1 + \xi \int\! d^3\!r\, e^{-\beta v(z)} + \tfrac{1}{2}\xi^2 \int\! d^3\!r \int\! d^3\!r'\, e^{-\beta v(z)}\, e^{-\beta v(z')}\, e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} + \ldots\ , \tag{6.111}$$

where $\xi = z\,\lambda_T^{-3}$, with $z = e^{\mu/k_\mathrm{B}T}$ the fugacity. Taking the logarithm, and invoking the Taylor series $\ln(1+\delta) = \delta - \frac{1}{2}\delta^2 + \frac{1}{3}\delta^3 - \ldots$, we obtain

$$-\beta\varOmega = \xi \int\limits_{z>\frac{a}{2}}\! d^3\!r + \tfrac{1}{2}\xi^2 \int\limits_{z>\frac{a}{2}}\! d^3\!r \int\limits_{z'>\frac{a}{2}}\! d^3\!r' \left[e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} - 1\right] + \ldots \tag{6.112}$$

The volume is $V = \int\limits_{z>0} d^3\!r$. Dividing by $V$, we have, in the thermodynamic limit,

$$\begin{aligned} -\frac{\beta\varOmega}{V} = \beta p &= \xi + \tfrac{1}{2}\xi^2 \frac{1}{V} \int\limits_{z>\frac{a}{2}}\! d^3\!r \int\limits_{z'>\frac{a}{2}}\! d^3\!r' \left[e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} - 1\right] + \ldots \\ &= \xi - \tfrac{2}{3}\pi a^3\, \xi^2 + \mathcal{O}(\xi^3)\ . \end{aligned} \tag{6.113}$$

The number density is

$$n = \xi\, \frac{\partial}{\partial\xi}\,(\beta p) = \xi - \tfrac{4}{3}\pi a^3\, \xi^2 + \mathcal{O}(\xi^3)\ , \tag{6.114}$$

and inverting to obtain $\xi(n)$ and then substituting into the pressure equation, we obtain the lowest order virial expansion for the equation of state,

$$p = k_\mathrm{B}T \left\{ n + \tfrac{2}{3}\pi a^3\, n^2 + \ldots \right\} . \tag{6.115}$$

As expected, the presence of the wall does not affect a bulk property such as the equation of state.

Next, let us compute the number density $n(z)$, given by

$$n(z) = \Big\langle \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \Big\rangle\ . \tag{6.116}$$

Due to translational invariance in the $(x, y)$ plane, we know that the density must be a function of $z$ alone. The presence of the wall at $z = 0$ breaks translational symmetry in the $z$ direction. The number density is

$$\begin{aligned} n(z) &= \mathrm{Tr}\Bigg[e^{\beta(\mu\hat{N}-\hat{H})}\sum_{i=1}^{N}\delta(\boldsymbol{r}-\boldsymbol{r}_i)\Bigg]\Bigg/\mathrm{Tr}\,e^{\beta(\mu\hat{N}-\hat{H})} \\ &= \varXi^{-1}\left\{\xi\,e^{-\beta v(z)} + \xi^2\,e^{-\beta v(z)}\!\int\! d^3\!r'\,e^{-\beta v(z')}\,e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} + \ldots\right\} \\ &= \xi\,e^{-\beta v(z)} + \xi^2\,e^{-\beta v(z)}\!\int\! d^3\!r'\,e^{-\beta v(z')}\Big[e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} - 1\Big] + \ldots\ . \end{aligned} \tag{6.117}$$

Note that the term in square brackets in the last line is the Mayer function $f(\boldsymbol{r}-\boldsymbol{r}') = e^{-\beta u(\boldsymbol{r}-\boldsymbol{r}')} - 1$. Consider the function

$$e^{-\beta v(z)}\,e^{-\beta v(z')}\,f(\boldsymbol{r}-\boldsymbol{r}') = \begin{cases} 0 & \text{if } z < \frac{1}{2}a \text{ or } z' < \frac{1}{2}a \\ 0 & \text{if } |\boldsymbol{r}-\boldsymbol{r}'| > a \\ -1 & \text{if } z > \frac{1}{2}a \text{ and } z' > \frac{1}{2}a \text{ and } |\boldsymbol{r}-\boldsymbol{r}'| < a\ . \end{cases} \tag{6.118}$$

Now consider the integral of the above function with respect to $\boldsymbol{r}'$. Clearly the result depends on the value of $z$. If $z > \frac{3}{2}a$, then there is no excluded region in $\boldsymbol{r}'$ and the integral is $(-1)$ times the full Mayer sphere volume, *i.e.* $-\frac{4}{3}\pi a^3$. If $z < \frac{1}{2}a$ the integral vanishes due to the $e^{-\beta v(z)}$ factor. For $z$ infinitesimally larger than $\frac{1}{2}a$, the integral is $(-1)$ times half the Mayer sphere volume, *i.e.* $-\frac{2}{3}\pi a^3$. For $z \in \left[\frac{a}{2}\,,\,\frac{3a}{2}\right]$ the integral interpolates between $-\frac{2}{3}\pi a^3$ and $-\frac{4}{3}\pi a^3$. Explicitly, one finds by elementary integration,

$$\int\! d^3\!r'\,e^{-\beta v(z)}\,e^{-\beta v(z')}\,f(\boldsymbol{r}-\boldsymbol{r}') = \begin{cases} 0 & \text{if } z < \frac{1}{2}a \\ \Big[-1 - \frac{3}{2}\big(\frac{z}{a}-\frac{1}{2}\big) + \frac{1}{2}\big(\frac{z}{a}-\frac{1}{2}\big)^3\Big]\cdot\frac{2}{3}\pi a^3 & \text{if } \frac{1}{2}a < z < \frac{3}{2}a \\ -\frac{4}{3}\pi a^3 & \text{if } z > \frac{3}{2}a\ . \end{cases} \tag{6.119}$$

After substituting $\xi = n + \frac{4}{3}\pi a^3 n^2 + \mathcal{O}(n^3)$ to relate $\xi$ to the bulk density $n = n_\infty$, we obtain the desired result:

$$n(z) = \begin{cases} 0 & \text{if } z < \frac{1}{2}a \\ n + \Big[1 - \frac{3}{2}\big(\frac{z}{a}-\frac{1}{2}\big) + \frac{1}{2}\big(\frac{z}{a}-\frac{1}{2}\big)^3\Big]\cdot\frac{2}{3}\pi a^3\,n^2 & \text{if } \frac{1}{2}a < z < \frac{3}{2}a \\ n & \text{if } z > \frac{3}{2}a\ . \end{cases} \tag{6.120}$$

A sketch is provided in the right hand panel of fig. 6.12. Note that the density $n(z)$ vanishes identically for $z < \frac{1}{2}$ due to the exclusion of the hard spheres by the wall. For $z$ between $\frac{1}{2}a$ and $\frac{3}{2}a$, there is a density *enhancement*, the origin of which has a simple physical interpretation. Since the wall excludes particles from the region $z < \frac{1}{2}$, there is an empty slab of thickness $\frac{1}{2}z$ coating the interior of the wall. There are then no particles in this region to exclude neighbors to their right, hence the density builds up just on the other side of this slab. The effect vanishes to the order of the calculation past $z = \frac{3}{2}a$, where $n(z) = n$ returns to its bulk value. Had we calculated to higher order, we'd have found damped oscillations with spatial period $\lambda \sim a$.

## 6.4 Lee-Yang Theory

### 6.4.1 Analytic properties of the partition function

How can statistical mechanics describe phase transitions? This question was addressed in some beautiful mathematical analysis by Lee and Yang[6]. Consider the grand partition function $\Xi$,

$$\Xi(T,V,z) = \sum_{N=0}^{\infty} z^N \, Q_N(T,V)\, \lambda_T^{-dN} \ , \tag{6.121}$$

where

$$Q_N(T,V) = \frac{1}{N!}\int\! d^d x_1 \cdots \int\! d^d x_N \; e^{-U(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)/k_\text{B}T} \tag{6.122}$$

is the contribution to the $N$-particle partition function from the potential energy $U$ (assuming no momentum-dependent potentials). For two-body central potentials, we have

$$U(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) = \sum_{i<j} v\big(|\boldsymbol{x}_i - \boldsymbol{x}_j|\big) \ . \tag{6.123}$$

Suppose further that these classical particles have hard cores. Then for any *finite* volume, there must be some maximum number $N_V$ such that $Q_N(T,V)$ vanishes for $N > N_V$. This is because if $N > N_V$ at least two spheres must overlap, in which case the potential energy is infinite. The theoretical maximum packing density for hard spheres is achieved for a hexagonal close packed (HCP) lattice[7], for which $f_\text{HCP} = \frac{\pi}{3\sqrt{2}} = 0.74048$. If the spheres have radius $r_0$, then $N_V = V/4\sqrt{2}r_0^3$ is the maximum particle number.

Thus, if $V$ itself is finite, then $\Xi(T,V,z)$ is a *finite* degree polynomial in $z$, and may be factorized as

$$\Xi(T,V,z) = \sum_{N=0}^{N_V} z^N \, Q_N(T,V)\, \lambda_T^{-dN} = \prod_{k=1}^{N_V}\left(1 - \frac{z}{z_k}\right) , \tag{6.124}$$

where $z_k(T,V)$ is one of the $N_V$ zeros of the grand partition function. Note that the $\mathcal{O}(z^0)$ term is fixed to be unity. Note also that since the configuration integrals $Q_N(T,V)$ are all positive, $\Xi(z)$ is an increasing function along the positive real $z$ axis. In addition, since the coefficients of $z^N$ in the polynomial $\Xi(z)$ are all real, then $\Xi(z) = 0$ implies $\overline{\Xi(z)} = \Xi(\bar{z}) = 0$, so the zeros of $\Xi(z)$ are either real and negative or else come in complex conjugate pairs.

For finite $N_V$, the situation is roughly as depicted in the left panel of fig. 6.13, with a set of $N_V$ zeros arranged in complex conjugate pairs (or negative real values). The zeros aren't necessarily distributed along a circle as shown in the figure, though. They could be anywhere, so long as they are symmetrically distributed about the $\text{Re}(z)$ axis, and no zeros occur for $z$ real and nonnegative.

Lee and Yang proved the existence of the limits

$$\frac{p}{k_\text{B}T} = \lim_{V\to\infty} \frac{1}{V}\, \ln \Xi(T,V,z) \tag{6.125}$$

$$n = \lim_{V\to\infty} z\,\frac{\partial}{\partial z}\left[\frac{1}{V}\,\ln\Xi(T,V,z)\right] , \tag{6.126}$$

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[6] See C. N. Yang and R. D. Lee, *Phys. Rev.* **87**, 404 (1952) and *ibid*, p. 410

[7] See *e.g.* http://en.wikipedia.org/wiki/Close-packing . For *randomly* close-packed hard spheres, one finds, from numerical simulations, $f_\text{RCP} = 0.644$.

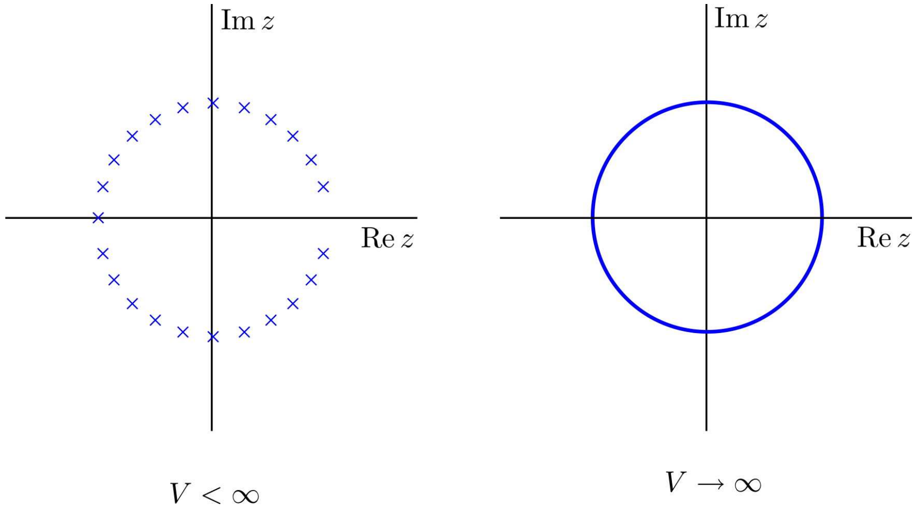


Figure 6.13: In the thermodynamic limit, the grand partition function can develop a singularity at positive real fugacity $z$. The set of discrete zeros fuses into a branch cut.

and notably the result

$$n = z\,\frac{\partial}{\partial z}\bigg(\frac{p}{k_{\rm B}T}\bigg)\ , \tag{6.127}$$

which amounts to the commutativity of the thermodynamic limit $V \to \infty$ with the differential operator $z\,\frac{\partial}{\partial z}$. In particular, $p(T,z)$ is a smooth function of $z$ in regions free of roots. If the roots do coalesce and pinch the positive real axis, then then density $n$ can be discontinuous, as in a first order phase transition, or a higher derivative $\partial^j p/\partial n^j$ can be discontinuous or divergent, as in a second order phase transition.

### 6.4.2 Electrostatic analogy

There is a beautiful analogy to the theory of two-dimensional electrostatics. We write

$$\begin{aligned}\frac{p}{k_{\rm B}T} &= \frac{1}{V}\sum_{k=1}^{N_V} \ln\bigg(1-\frac{z}{z_k}\bigg)\\ &= -\sum_{k=1}^{N_V}\Big[\phi(z-z_k)-\phi(0-z_k)\Big]\ ,\end{aligned} \tag{6.128}$$

where

$$\phi(z) = -\frac{1}{V}\,\ln(z) \tag{6.129}$$

is the complex potential due to a line charge of linear density $\lambda = V^{-1}$ located at origin. The number density is then

$$n = z\,\frac{\partial}{\partial z}\bigg(\frac{p}{k_{\rm B}T}\bigg) = -z\,\frac{\partial}{\partial z}\sum_{k=1}^{N_V}\phi(z-z_k)\ , \tag{6.130}$$

to be evaluated for physical values of $z$, *i.e.* $z \in \mathbb{R}^+$. Since $\phi(z)$ is analytic,

$$\frac{\partial\phi}{\partial\bar z} = \frac{1}{2}\,\frac{\partial\phi}{\partial x} + \frac{i}{2}\,\frac{\partial\phi}{\partial y} = 0\ . \tag{6.131}$$

If we decompose the complex potential $\phi = \phi_1 + i\phi_2$ into real and imaginary parts, the condition of analyticity is recast as the Cauchy-Riemann equations,

$$\frac{\partial \phi_1}{\partial x} = \frac{\partial \phi_2}{\partial y} \qquad , \qquad \frac{\partial \phi_1}{\partial y} = -\frac{\partial \phi_2}{\partial x} \ . \tag{6.132}$$

Thus,

$$\begin{aligned} -\frac{\partial \phi}{\partial z} &= -\frac{1}{2}\,\frac{\partial \phi}{\partial x} + \frac{i}{2}\,\frac{\partial \phi}{\partial y} \\ &= -\frac{1}{2}\bigg(\frac{\partial \phi_1}{\partial x} + \frac{\partial \phi_2}{\partial y}\bigg) + \frac{i}{2}\bigg(\frac{\partial \phi_1}{\partial y} - \frac{\partial \phi_2}{\partial x}\bigg) \\ &= -\frac{\partial \phi_1}{\partial x} + i\,\frac{\partial \phi_1}{\partial y} \\ &= E_x - iE_y \ , \end{aligned} \tag{6.133}$$

where $\boldsymbol{E} = -\boldsymbol{\nabla}\phi_1$ is the electric field. Suppose, then, that as $V \to \infty$ a continuous charge distribution develops, which crosses the positive real $z$ axis at a point $x \in \mathbb{R}^+$. Then

$$\frac{n_+ - n_-}{x} = E_x(x^+) - E_x(x^-) = 4\pi\sigma(x) \ , \tag{6.134}$$

where $\sigma$ is the linear charge density (assuming logarithmic two-dimensional potentials), or the two-dimensional charge density (if we extend the distribution along a third axis).

### 6.4.3 Example

As an example, consider the function

$$\begin{aligned} \Xi(z) &= \frac{(1+z)^M\,(1-z^M)}{1-z} \\ &= (1+z)^M\,\big(1 + z + z^2 + \ldots + z^{M-1}\big) \ . \end{aligned} \tag{6.135}$$

The $(2M-1)$ degree polynomial has an $M^{\rm th}$ order zero at $z=-1$ and $(M-1)$ simple zeros at $z = e^{2\pi i k/M}$, where $k \in \{1, \ldots, M-1\}$. Since $M$ serves as the maximum particle number $N_V$, we may assume that $V = Mv_0$, and the $V \to \infty$ limit may be taken as $M \to \infty$. We then have

$$\begin{aligned} \frac{p}{k_{\rm B}T} &= \lim_{V\to\infty} \frac{1}{V}\,\ln\Xi(z) \\ &= \frac{1}{v_0}\,\lim_{M\to\infty}\frac{1}{M}\ln\Xi(z) \\ &= \frac{1}{v_0}\,\lim_{M\to\infty}\frac{1}{M}\Big[M\ln(1+z) + \ln\big(1-z^M\big) - \ln(1-z)\Big] \ . \end{aligned} \tag{6.136}$$

The limit depends on whether $|z|>1$ or $|z|<1$, and we obtain

$$\frac{p\,v_0}{k_{\rm B}T} = \begin{cases} \ln(1+z) & \text{if} \quad |z|<1 \\[2ex] \Big[\ln(1+z) + \ln z\Big] & \text{if} \quad |z|>1 \ . \end{cases} \tag{6.137}$$

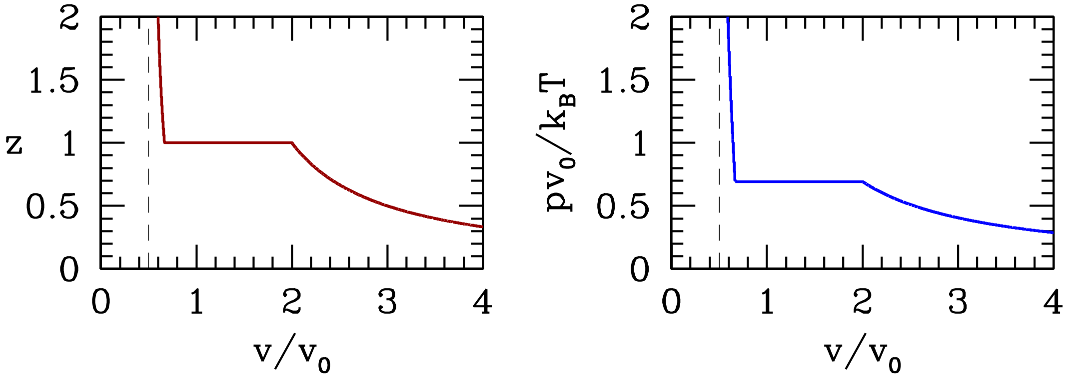


Figure 6.14: Fugacity $z$ and $p\,v_0/k_BT$ *versus* dimensionless specific volume $v/v_0$ for the example problem discussed in the text.

Thus,

$$n = z\,\frac{\partial}{\partial z}\bigg(\frac{p}{k_BT}\bigg) = \begin{cases} \frac{1}{v_0}\cdot\frac{z}{1+z} & \text{if} \quad |z|<1 \\ \\ \frac{1}{v_0}\cdot\Big[\frac{z}{1+z}+1\Big] & \text{if} \quad |z|>1\ . \end{cases} \tag{6.138}$$

If we solve for $z(v)$, where $v = n^{-1}$, we find

$$z = \begin{cases} \frac{v_0}{v-v_0} & \text{if} \quad v > 2v_0 \\ \\ \frac{v_0-v}{2v-v_0} & \text{if} \quad \frac{1}{2}v_0 < v < \frac{2}{3}v_0\ . \end{cases} \tag{6.139}$$

We then obtain the equation of state,

$$\frac{p\,v_0}{k_BT} = \begin{cases} \ln\Big(\frac{v}{v-v_0}\Big) & \text{if} \quad v > 2v_0 \\ \\ \ln 2 & \text{if} \quad \frac{2}{3}v_0 < v < 2v_0 \\ \\ \ln\Big(\frac{v(v_0-v)}{(2v-v_0)^2}\Big) & \text{if} \quad \frac{1}{2}v_0 < v < \frac{2}{3}v_0\ . \end{cases} \tag{6.140}$$

## 6.5 Liquid State Physics

### 6.5.1 The many-particle distribution function

The virial expansion is typically applied to low-density systems. When the density is high, *i.e.* when $na^3 \sim 1$, where $a$ is a typical molecular or atomic length scale, the virial expansion is impractical. There are to many terms to compute, and to make progress one must use sophisticated resummation techniques to investigate the high density regime.

To elucidate the physics of liquids, it is useful to consider the properties of various *correlation functions*. These objects are derived from the general $N$-body Boltzmann distribution,

$$f(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N;\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N)=\begin{cases} Z_N^{-1}\cdot\frac{1}{N!}\,e^{-\beta\hat{H}_N(\boldsymbol{p},\boldsymbol{x})} & \text{OCE}\\ \\ \Xi^{-1}\cdot\frac{1}{N!}\,e^{\beta\mu N}\,e^{-\beta\hat{H}_N(\boldsymbol{p},\boldsymbol{x})} & \text{GCE}\,. \end{cases} \tag{6.141}$$

We assume a Hamiltonian of the form

$$\hat{H}_N=\sum_{i=1}^N\frac{\boldsymbol{p}_i^2}{2m}+W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N). \tag{6.142}$$

The quantity

$$f(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N;\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N)\,\frac{d^dx_1\,d^dp_1}{h^d}\cdots\frac{d^dx_N\,d^dp_N}{h^d} \tag{6.143}$$

is the propability of finding $N$ particles in the system, with particle #1 lying within $d^3x_1$ of $\boldsymbol{x}_1$ and having momentum within $d^dp_1$ of $\boldsymbol{p}_1$, *etc.* If we compute averages of quantities which only depend on the positions $\{\boldsymbol{x}_j\}$ and not on the momenta $\{\boldsymbol{p}_j\}$, then we may integrate out the momenta to obtain, in the OCE,

$$P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)=Q_N^{-1}\cdot\frac{1}{N!}\,e^{-\beta W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)}\,, \tag{6.144}$$

where $W$ is the total potential energy,

$$W(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)=\sum_i v(\boldsymbol{x}_i)+\sum_{i<j}u(\boldsymbol{x}_i-\boldsymbol{x}_j)+\sum_{i<j<k}w(\boldsymbol{x}_i-\boldsymbol{x}_j\,,\,\boldsymbol{x}_j-\boldsymbol{x}_k)+\ldots\,, \tag{6.145}$$

and $Q_N$ is the configuration integral,

$$Q_N(T,V)=\frac{1}{N!}\int\! d^dx_1\cdots\int\! d^dx_N\,e^{-\beta W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)}\,. \tag{6.146}$$

We will, for the most part, consider only two-body central potentials as contributing to $W$, which is to say we will only retain the middle term on the RHS. Note that $P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)$ is invariant under any permutation of the particle labels.

### 6.5.2 Averages over the distribution

To compute an average, one integrates over the distribution:

$$\big\langle F(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)\big\rangle=\int\! d^dx_1\cdots\int\! d^dx_N\,P(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)\,F(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)\,. \tag{6.147}$$

The overall $N$-particle probability density is normalized according to

$$\int\! d^dx_N\,P(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)=1\,. \tag{6.148}$$

The average local density is

$$\begin{aligned} n_1(\boldsymbol{r})&=\big\langle\sum_i\delta(\boldsymbol{r}-\boldsymbol{x}_i)\big\rangle\\ &=N\int\! d^dx_2\cdots\int\! d^dx_N\,P(\boldsymbol{r},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)\,. \end{aligned} \tag{6.149}$$

Note that the local density obeys the sum rule

$$\int\!d^d\!r\; n_1(\boldsymbol{r}) = N \;. \tag{6.150}$$

In a translationally invariant system, $n_1 = n = \frac{N}{V}$ is a constant independent of position. The boundaries of a system will in general break translational invariance, so in order to maintain the notion of a translationally invariant system of finite total volume, one must impose periodic boundary conditions.

The two-particle density matrix $n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is defined by

$$\begin{aligned} n_2(\boldsymbol{r}_1,\boldsymbol{r}_2) &= \Big\langle \sum_{i\neq j} \delta(\boldsymbol{r}_1-\boldsymbol{x}_i)\,\delta(\boldsymbol{r}_2-\boldsymbol{x}_j)\Big\rangle \\ &= N(N-1)\!\int\!d^d\!x_3\cdots\!\int\!d^d\!x_N\; P(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{x}_3,\ldots,\boldsymbol{x}_N)\;. \end{aligned} \tag{6.151}$$

As in the case of the one-particle density matrix, *i.e.* the local density $n_1(\boldsymbol{r})$, the two-particle density matrix satisfies a sum rule:

$$\int\!d^d\!r_1\!\int\!d^d\!r_2\; n_2(\boldsymbol{r}_1,\boldsymbol{r}_2) = N(N-1)\;. \tag{6.152}$$

Generalizing further, one defines the *k-particle density matrix* as

$$\begin{aligned} n_k(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k) &= \Big\langle {\sum_{i_1\cdots i_k}}' \delta(\boldsymbol{r}_1-\boldsymbol{x}_{i_1})\cdots\delta(\boldsymbol{r}_k-\boldsymbol{x}_{i_k})\;\Big\rangle \\ &= \frac{N!}{(N-k)!}\!\int\!d^d\!x_{k+1}\cdots\!\int\!d^d\!x_N\; P(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k,\boldsymbol{x}_{k+1},\ldots,\boldsymbol{x}_N)\;, \end{aligned} \tag{6.153}$$

where the prime on the sum indicates that all the indices $i_1,\ldots,i_k$ are distinct. The corresponding sum rule is then

$$\int\!d^d\!r_1\cdots\!\int\!d^d\!r_k\; n_k(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k) = \frac{N!}{(N-k)!}\;. \tag{6.154}$$

The average potential energy can be expressed in terms of the distribution functions. Assuming only two-body interactions, we have

$$\begin{aligned} \langle W\rangle &= \Big\langle \sum_{i<j} u(\boldsymbol{x}_i-\boldsymbol{x}_j)\Big\rangle \\ &= \tfrac{1}{2}\!\int\!d^d\!r_1\!\int\!d^d\!r_2\; u(\boldsymbol{r}_1-\boldsymbol{r}_2)\,\Big\langle \sum_{i\neq j}\delta(\boldsymbol{r}_1-\boldsymbol{x}_i)\,\delta(\boldsymbol{r}_2-\boldsymbol{x}_j)\Big\rangle \\ &= \tfrac{1}{2}\!\int\!d^d\!r_1\!\int\!d^d\!r_2\; u(\boldsymbol{r}_1-\boldsymbol{r}_2)\, n_2(\boldsymbol{r}_1,\boldsymbol{r}_2)\;. \end{aligned} \tag{6.155}$$

As the separations $r_{ij} = |\boldsymbol{r}_i-\boldsymbol{r}_j|$ get large, we expect the correlations to vanish, in which case

$$\begin{aligned} n_k(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k) &= \Big\langle {\sum_{i_1\cdots i_k}}' \delta(\boldsymbol{r}_1-\boldsymbol{x}_{i_1})\cdots\delta(\boldsymbol{r}_k-\boldsymbol{x}_{i_k})\Big\rangle \\ &\xrightarrow[r_{ij}\to\infty]{} {\sum_{i_1\cdots i_k}}' \big\langle\delta(\boldsymbol{r}_1-\boldsymbol{x}_{i_1})\big\rangle\cdots\big\langle\delta(\boldsymbol{r}_k-\boldsymbol{x}_{i_k})\big\rangle \\ &= \frac{N!}{(N-k)!}\cdot\frac{1}{N^k}\; n_1(\boldsymbol{r}_1)\cdots n_1(\boldsymbol{r}_k) \\ &= \bigg(1-\frac{1}{N}\bigg)\bigg(1-\frac{2}{N}\bigg)\cdots\bigg(1-\frac{k-1}{N}\bigg)\, n_1(\boldsymbol{r}_1)\cdots n_1(\boldsymbol{r}_k)\;. \end{aligned} \tag{6.156}$$

The *k-particle distribution function* is defined as the ratio

$$g_k(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k) \equiv \frac{n_k(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k)}{n_1(\boldsymbol{r}_1)\cdots n_1(\boldsymbol{r}_k)} \ . \tag{6.157}$$

For large separations, then,

$$g_k(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_k) \xrightarrow[r_{ij}\to\infty]{} \prod_{j=1}^{k-1}\left(1-\frac{j}{N}\right) . \tag{6.158}$$

For isotropic systems, the two-particle distribution function $g_2(\boldsymbol{r}_1,\boldsymbol{r}_2)$ depends only on the magnitude $|\boldsymbol{r}_1-\boldsymbol{r}_2|$. As a function of this scalar separation, the function is known as the *radial distribution function*:

$$\begin{aligned} g(r) \equiv g_2(\boldsymbol{r}) &= \frac{1}{n^2}\,\Big\langle \sum_{i\neq j}\delta(\boldsymbol{r}-\boldsymbol{x}_i)\,\delta(\boldsymbol{x}_j)\Big\rangle \\ &= \frac{1}{Vn^2}\,\Big\langle \sum_{i\neq j}\delta(\boldsymbol{r}-\boldsymbol{x}_i+\boldsymbol{x}_j)\Big\rangle \ . \end{aligned} \tag{6.159}$$

The radial distribution function is of great importance in the physics of liquids because

- thermodynamic properties of the system can be related to $g(r)$
- $g(r)$ is directly measurable by scattering experiments

For example, in an isotropic system the average potential energy is given by

$$\begin{aligned} \langle W\rangle &= \tfrac{1}{2}\!\int\! d^d\!r_1\!\int\! d^d\!r_2\; u(\boldsymbol{r}_1-\boldsymbol{r}_2)\,n_2(\boldsymbol{r}_1,\boldsymbol{r}_2) \\ &= \tfrac{1}{2}n^2\!\int\! d^d\!r_1\!\int\! d^d\!r_2\; u(\boldsymbol{r}_1-\boldsymbol{r}_2)\,g\big(|\boldsymbol{r}_1-\boldsymbol{r}_2|\big) \\ &= \frac{N^2}{2V}\int\! d^d\!r\; u(r)\,g(r) \ . \end{aligned} \tag{6.160}$$

For a three-dimensional system, the average internal (*i.e.* potential) energy per particle is

$$\frac{\langle W\rangle}{N} = 2\pi n\int\limits_0^\infty\! dr\; r^2\, g(r)\,u(r) \ . \tag{6.161}$$

Intuitively, $f(r)\,dr \equiv 4\pi r^2\, n\, g(r)\,dr$ is the average number of particles lying at a radial distance between $r$ and $r+dr$ from a given reference particle. The total potential energy of interaction with the reference particle is then $f(r)\,u(r)\,dr$. Now integrate over all $r$ and divide by two to avoid double-counting. This recovers eqn. 6.161.

In the OCE, $g(r)$ obeys the sum rule

$$\int\! d^d\!r\; g(r) = \frac{V}{N^2}\cdot N(N-1) = V - \frac{V}{N} \ , \tag{6.162}$$

hence

$$n\!\int\! d^d\!r\,\big[g(r)-1\big] = -1 \qquad \text{(OCE)} \ . \tag{6.163}$$

The function $h(r)\equiv g(r)-1$ is called the *pair correlation function*.

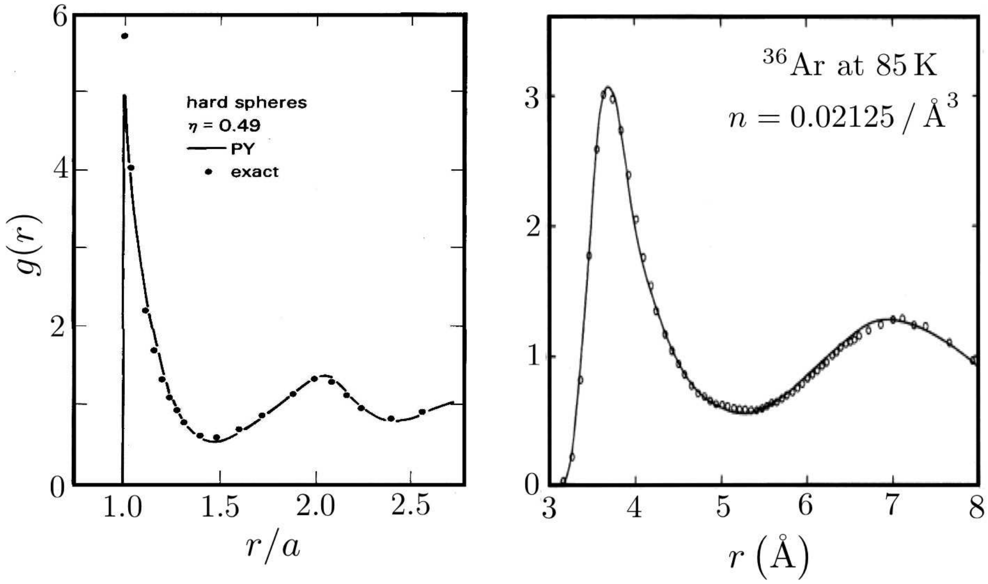


Figure 6.15: Pair distribution functions for hard spheres of diameter $a$ at filling fraction $\eta = \frac{\pi}{6}a^3 n = 0.49$ (left) and for liquid Argon at $T = 85\,\mathrm{K}$ (right). Molecular dynamics data for hard spheres (points) is compared with the result of the Percus-Yevick approximation (see below in §6.5.8). Reproduced (without permission) from J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, fig 5.5. Experimental data on liquid argon are from the neutron scattering work of J. L. Yarnell *et al.*, *Phys. Rev. A* **7**, 2130 (1973). The data (points) are compared with molecular dynamics calculations by Verlet (1967) for a Lennard-Jones fluid.

In the grand canonical formulation, we have

$$\begin{aligned} n\!\int\! d^3\!r\, h(r) &= \frac{\langle N\rangle}{V}\cdot\left[\frac{\langle N(N-1)\rangle}{\langle N\rangle^2}\,V - V\right] \\ &= \frac{\langle N^2\rangle - \langle N\rangle^2}{\langle N\rangle} - 1 \\ &= nk_{\mathrm{B}}T\kappa_T - 1 \qquad \text{(GCE)}\ , \end{aligned} \tag{6.164}$$

where $\kappa_T$ is the isothermal compressibility. Note that in an ideal gas we have $h(r) = 0$ and $\kappa_T = \kappa_T^0 \equiv 1/nk_{\mathrm{B}}T$. Self-condensed systems, such as liquids and solids far from criticality, are nearly incompressible, hence $0 < nk_{\mathrm{B}}T\,\kappa_T \ll 1$, and therefore $n\!\int\! d^3\!r\, h(r) \approx -1$. For incompressible systems, where $\kappa_T = 0$, this becomes an equality.

As we shall see below in §6.5.4, the function $h(r)$, or rather its Fourier transform $\hat{h}(\boldsymbol{k})$, is directly measured in a scattering experiment. The question then arises as to which result applies: the OCE result from eqn. 6.163 or the GCE result from eqn. 6.164. The answer is that under almost all experimental conditions it is the GCE result which applies. The reason for this is that the scattering experiment typically illuminates only a subset of the entire system. This subsystem is in particle equilibrium with the remainder of the system, hence it is appropriate to use the grand canonical ensemble. The OCE results would only apply if the scattering experiment were to measure the entire system.

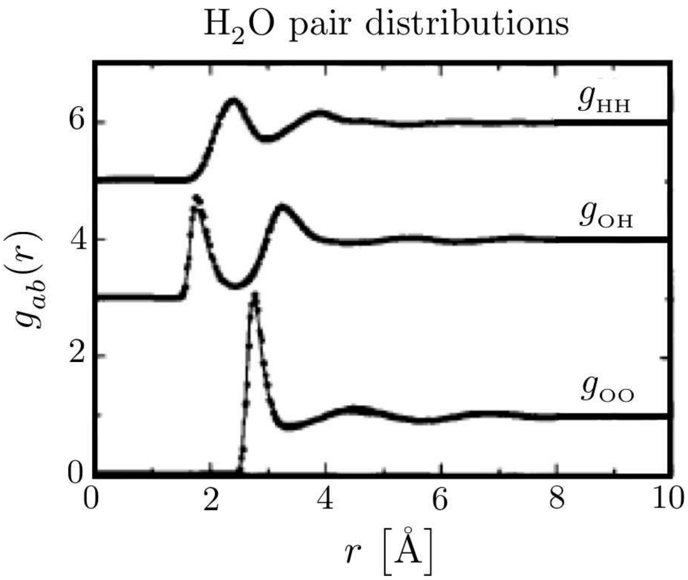


Figure 6.16: Monte Carlo pair distribution functions for liquid water. From A. K. Soper, *Chem Phys.* **202**, 295 (1996).

### 6.5.3 Virial equation of state

The *virial* of a mechanical system is defined to be

$$G = \sum_i \boldsymbol{x}_i \cdot \boldsymbol{F}_i \ , \tag{6.165}$$

where $\boldsymbol{F}_i$ is the total force acting on particle $i$. If we average $G$ over time, we obtain

$$\begin{aligned} \langle G \rangle &= \lim_{T\to\infty} \frac{1}{T} \int\limits_0^T \!dt \, \sum_i \boldsymbol{x}_i \cdot \boldsymbol{F}_i \\ &= -\lim_{T\to\infty} \frac{1}{T} \int\limits_0^T \!dt \, \sum_i m\, \dot{\boldsymbol{x}}_i^2 \\ &= -3Nk_{\rm B}T \ . \end{aligned} \tag{6.166}$$

Here, we have made use of

$$\boldsymbol{x}_i \cdot \boldsymbol{F}_i = m\,\boldsymbol{x}_i \cdot \ddot{\boldsymbol{x}}_i = -\,m\,\dot{\boldsymbol{x}}_i^2 + \frac{d}{dt}\Big(m\,\boldsymbol{x}_i \cdot \dot{\boldsymbol{x}}_i\Big) \ , \tag{6.167}$$

as well as ergodicity and equipartition of kinetic energy. We have also assumed three space dimensions. In a bounded system, there are two contributions to the force $\boldsymbol{F}_i$. One contribution is from the surfaces which enclose the system. This is given by[8]

$$\langle G \rangle_{\rm surfaces} = \Big\langle \sum_i \boldsymbol{x}_i \cdot \boldsymbol{F}_i^{(\rm surf)} \Big\rangle = -3pV \ . \tag{6.168}$$

---

[8] To derive this expression, note that $\boldsymbol{F}^{(\rm surf)}$ is directed inward and vanishes away from the surface. Each Cartesian direction $\alpha = (x, y, z)$ then contributes $-F_\alpha^{(\rm surf)} L_\alpha$, where $L_\alpha$ is the corresponding linear dimension. But $F_\alpha^{(\rm surf)} = pA_\alpha$, where $A_\alpha$ is the area of the corresponding face and $p$. is the pressure. Summing over the three possibilities for $\alpha$, one obtains eqn. 6.168.

The remaining contribution is due to the interparticle forces. Thus,

$$\frac{p}{k_{\mathrm{B}}T} = \frac{N}{V} - \frac{1}{3Vk_{\mathrm{B}}T}\,\Big\langle \sum_i \boldsymbol{x}_i \cdot \boldsymbol{\nabla}_{\!i} W \Big\rangle \ . \tag{6.169}$$

Invoking the definition of $g(r)$, we have

$$p = nk_{\mathrm{B}}T\left\{1 - \frac{2\pi n}{3k_{\mathrm{B}}T}\int\limits_0^\infty\! dr\; r^3\, g(r)\, u'(r)\right\} \ . \tag{6.170}$$

As an alternate derivation, consider the First Law of Thermodynamics,

$$d\Omega = -S\,dT - p\,dV - N\,d\mu \ , \tag{6.171}$$

from which we derive

$$p = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu} = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \ . \tag{6.172}$$

Now let $V \to \ell^3 V$, where $\ell$ is a scale parameter. Then

$$p = -\frac{\partial\Omega}{\partial V} = -\frac{1}{3V}\,\frac{\partial}{\partial\ell}\bigg|_{\ell=1} \Omega(T,\ell^3 V,\mu) \ . \tag{6.173}$$

Now

$$\begin{aligned} \Xi(T,\ell^3 V,\mu) &= \sum_{N=0}^\infty \frac{1}{N!}\, e^{\beta\mu N}\, \lambda_T^{-3N} \int\limits_{\ell^3 V}\! d^3\!x_1 \cdots \int\limits_{\ell^3 V}\! d^3\!x_N \; e^{-\beta W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)} \\ &= \sum_{N=0}^\infty \frac{1}{N!}\left(e^{\beta\mu}\,\lambda_T^{-3}\right)^N \ell^{3N} \int\limits_V\! d^3\!x_1 \cdots \int\limits_V\! d^3\!x_N \; e^{-\beta W(\ell\boldsymbol{x}_1\,,\,\ldots\,,\,\ell\boldsymbol{x}_N)} \end{aligned} \tag{6.174}$$

Thus,

$$\begin{aligned} p &= -\frac{1}{3V}\,\frac{\partial\Omega(\ell^3 V)}{\partial\ell}\bigg|_{\ell=1} = \frac{k_{\mathrm{B}}T}{3V}\,\frac{1}{\Xi}\,\frac{\partial\Xi(\ell^3 V)}{\partial\ell} \\ &= \frac{k_{\mathrm{B}}T}{3V}\,\frac{1}{\Xi}\sum_{N=0}^\infty \frac{1}{N!}\big(z\lambda_T^{-3}\big)^N \left\{ \int\limits_V\! d^3\!x_1 \cdots \int\limits_V\! d^3\!x_N \; e^{-\beta W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)} \left[3N - \beta\sum_i \boldsymbol{x}_i \cdot \frac{\partial W}{\partial\boldsymbol{x}_i}\right]\right\} \\ &= nk_{\mathrm{B}}T - \frac{1}{3V}\,\Big\langle\frac{\partial W}{\partial\ell}\Big\rangle_{\ell=1} \ . \end{aligned} \tag{6.175}$$

Finally, from $W = \sum_{i<j} u(\ell\boldsymbol{x}_{ij})$ we have

$$\begin{aligned} \Big\langle\frac{\partial W}{\partial\ell}\Big\rangle_{\ell=1} &= \sum_{i<j} \boldsymbol{x}_{ij}\cdot\boldsymbol{\nabla} u(\boldsymbol{x}_{ij}) \\ &= \frac{2\pi N^2}{V}\int\limits_0^\infty\! dr\; r^3 g(r)\, u'(r) \ , \end{aligned} \tag{6.176}$$

and hence

$$p = nk_{\mathrm{B}}T - \tfrac{2}{3}\pi n^2 \int\limits_0^\infty\! dr\; r^3\, g(r)\, u'(r) \ . \tag{6.177}$$

Note that the density $n$ enters the equation of state explicitly on the RHS of the above equation, but also implicitly through the pair distribution function $g(r)$, which has implicit dependence on both $n$ and $T$.

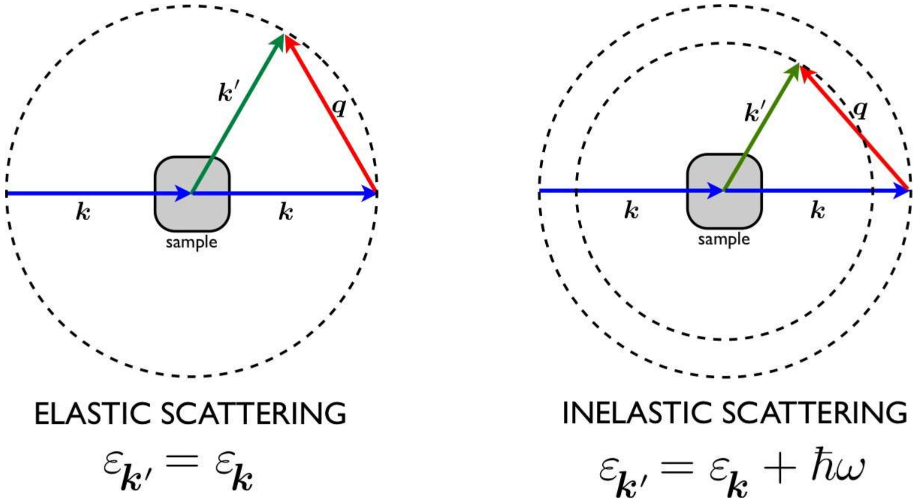


Figure 6.17: In a scattering experiment, a beam of particles interacts with a sample and the beam particles scatter off the sample particles. A momentum $\hbar\boldsymbol{q}$ and energy $\hbar\omega$ are transferred to the beam particle during such a collision. If $\omega = 0$, the scattering is said to be *elastic*. For $\omega \neq 0$, the scattering is *inelastic*.

### 6.5.4 Correlations and scattering

Consider the scattering of a light or particle beam (*i.e.* photons or neutrons) from a liquid. We label the states of the beam particles by their wavevector $\boldsymbol{k}$ and we assume a general dispersion $\varepsilon_{\boldsymbol{k}}$. For photons, $\varepsilon_{\boldsymbol{k}} = \hbar c|\boldsymbol{k}|$, while for neutrons $\varepsilon_{\boldsymbol{k}} = \frac{\hbar^2\boldsymbol{k}^2}{2m_{\rm n}}$. We assume a single scattering process with the liquid, during which the total momentum and energy of the liquid plus beam are conserved. We write

$$\boldsymbol{k}' = \boldsymbol{k} + \boldsymbol{q} \tag{6.178}$$

$$\varepsilon_{\boldsymbol{k}'} = \varepsilon_{\boldsymbol{k}} + \hbar\omega \ , \tag{6.179}$$

where $\boldsymbol{k}'$ is the final state of the scattered beam particle. Thus, the fluid transfers momentum $\Delta\boldsymbol{p} = \hbar\boldsymbol{q}$ and energy $\hbar\omega$ to the beam.

Now consider the scattering process between an initial state $|\, i, \boldsymbol{k}\,\rangle$ and a final state $|\, j, \boldsymbol{k}'\,\rangle$, where these states describe both the beam and the liquid. According to Fermi's Golden Rule, the scattering rate is

$$\varGamma_{i\boldsymbol{k}\to j\boldsymbol{k}'} = \frac{2\pi}{\hbar} \big|\langle\, j, \boldsymbol{k}' \,|\, \mathcal{V} \,|\, i, \boldsymbol{k}\,\rangle\big|^2 \, \delta(E_j - E_i + \hbar\omega) \ , \tag{6.180}$$

where $\mathcal{V}$ is the scattering potential and $E_i$ is the initial internal energy of the liquid. If $\boldsymbol{r}$ is the position of the beam particle and $\{\boldsymbol{x}_l\}$ are the positions of the liquid particles, then

$$\mathcal{V}(\boldsymbol{r}) = \sum_{l=1}^{N} v(\boldsymbol{r} - \boldsymbol{x}_l) \ . \tag{6.181}$$

The differential scattering cross section (per unit frequency per unit solid angle) is

$$\frac{\partial^2\sigma}{\partial\Omega\,\partial\omega} = \frac{\hbar}{4\pi}\,\frac{g(\varepsilon_{\boldsymbol{k}'})}{|\boldsymbol{v}_{\boldsymbol{k}}|} \sum_{i,j} P_i \, \varGamma_{i\boldsymbol{k}\to j\boldsymbol{k}'} \ , \tag{6.182}$$

where

$$g(\varepsilon) = \int\!\frac{d^dk}{(2\pi)^d}\,\delta(\varepsilon - \varepsilon_{\boldsymbol{k}}) \tag{6.183}$$

is the density of states for the beam particle and

$$P_i = \frac{1}{Z}\, e^{-\beta E_i} \ . \tag{6.184}$$

Consider now the matrix element

$$\begin{aligned} \big\langle\, j, \boldsymbol{k}' \,\big|\, \mathcal{V} \,\big|\, i, \boldsymbol{k} \,\big\rangle &= \big\langle\, j \,\big|\, \frac{1}{V} \sum_{l=1}^{N} \int\!\! d^d\!r\, e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{r}}\, v(\boldsymbol{r}-\boldsymbol{x}_l) \,\big|\, i \,\big\rangle \\ &= \frac{1}{V}\, \hat{v}(\boldsymbol{q})\, \big\langle\, j \,\big|\, \sum_{l=1}^{N} e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_l} \,\big|\, i \,\big\rangle \ , \end{aligned} \tag{6.185}$$

where we have assumed that the incident and scattered beams are plane waves. We then have

$$\begin{aligned} \frac{\partial^2\sigma}{\partial\Omega\,\partial\omega} &= \frac{\hbar}{2}\, \frac{g(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{|\boldsymbol{\nabla}_{\!\boldsymbol{k}}\varepsilon_{\boldsymbol{k}}|}\, \frac{|\hat{v}(\boldsymbol{q})|^2}{V^2} \sum_i P_i \sum_j \Big|\big\langle\, j \,\big|\, \sum_{l=1}^{N} e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_l} \,\big|\, i \,\big\rangle\Big|^2\, \delta(E_j - E_i + \hbar\omega) \\ &= \frac{g(\varepsilon_{\boldsymbol{k}+\boldsymbol{q}})}{4\pi\, |\boldsymbol{\nabla}_{\!\boldsymbol{k}}\varepsilon_{\boldsymbol{k}}|}\, \frac{N}{V^2}\, |\hat{v}(\boldsymbol{q})|^2\, S(\boldsymbol{q},\omega) \ , \end{aligned} \tag{6.186}$$

where $S(\boldsymbol{q},\omega)$ is the *dynamic structure factor*,

$$S(\boldsymbol{q},\omega) = \frac{2\pi\hbar}{N} \sum_i P_i \sum_j \Big|\big\langle\, j \,\big|\, \sum_{l=1}^{N} e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_l} \,\big|\, i \,\big\rangle\Big|^2\, \delta(E_j - E_i + \hbar\omega) \tag{6.187}$$

Note that for an arbitrary operator $A$,

$$\begin{aligned} \sum_j \Big|\big\langle\, j \,\big|\, A \,\big|\, i \,\big\rangle\Big|^2\, \delta(E_j - E_i + \hbar\omega) &= \frac{1}{2\pi\hbar} \sum_j \int\limits_{-\infty}^{\infty}\!\! dt\; e^{i(E_j - E_i + \hbar\omega)\,t/\hbar}\, \big\langle\, i \,\big|\, A^\dagger \,\big|\, j \,\big\rangle \big\langle\, j \,\big|\, A \,\big|\, i \,\big\rangle \\ &= \frac{1}{2\pi\hbar} \sum_j \int\limits_{-\infty}^{\infty}\!\! dt\; e^{i\omega t}\, \big\langle\, i \,\big|\, A^\dagger \,\big|\, j \,\big\rangle \big\langle\, j \,\big|\, e^{i\hat{H}t/\hbar}\, A\, e^{-i\hat{H}t/\hbar} \,\big|\, i \,\big\rangle \\ &= \frac{1}{2\pi\hbar} \int\limits_{-\infty}^{\infty}\!\! dt\; e^{i\omega t}\, \big\langle\, i \,\big|\, A^\dagger(0)\, A(t) \,\big|\, i \,\big\rangle \ . \end{aligned} \tag{6.188}$$

Thus,

$$\begin{aligned} S(\boldsymbol{q},\omega) &= \frac{1}{N} \int\limits_{-\infty}^{\infty}\!\! dt\; e^{i\omega t} \sum_i P_i \, \big\langle\, i \,\big|\, \sum_{l,l'} e^{i\boldsymbol{q}\cdot\boldsymbol{x}_l(0)}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_{l'}(t)} \,\big|\, i \,\big\rangle \\ &= \frac{1}{N} \int\limits_{-\infty}^{\infty}\!\! dt\; e^{i\omega t}\, \Big\langle \sum_{l,l'} e^{i\boldsymbol{q}\cdot\boldsymbol{x}_l(0)}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{x}_{l'}(t)} \Big\rangle \ , \end{aligned} \tag{6.189}$$

where the angular brackets in the last line denote a thermal expectation value of a quantum mechanical operator. If we integrate over all frequencies, we obtain the equal time correlator,

$$\begin{aligned} S(\boldsymbol{q}) &= \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, S(\boldsymbol{q},\omega) = \frac{1}{N} \sum_{l,l'} \big\langle e^{i\boldsymbol{q}\cdot(\boldsymbol{x}_l - \boldsymbol{x}_{l'})} \big\rangle \\ &= N\, \delta_{\boldsymbol{q},0} + 1 + n \!\int\!\! d^d\!r\; e^{-i\boldsymbol{q}\cdot\boldsymbol{r}}\, \big[ g(r) - 1 \big] \ . \end{aligned} \tag{6.190}$$

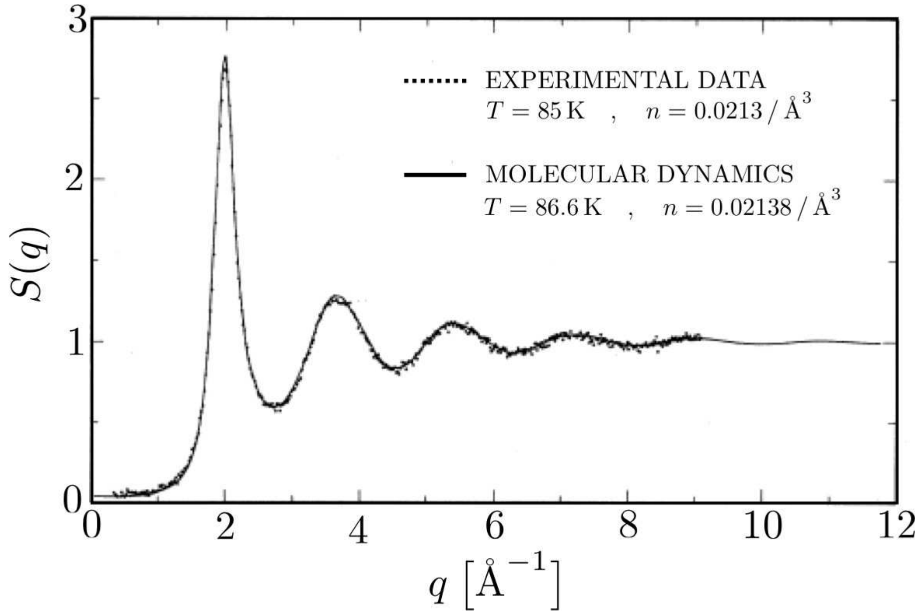


Figure 6.18: Comparison of the static structure factor as determined by neutron scattering work of J. L. Yarnell *et al., Phys. Rev. A* **7**, 2130 (1973) with molecular dynamics calculations by Verlet (1967) for a Lennard-Jones fluid.

known as the *static structure factor*[9]. Note that $S(\boldsymbol{q} = 0) = N$, since all the phases $e^{i\boldsymbol{q}\cdot(\boldsymbol{x}_i - \boldsymbol{x}_j)}$ are then unity. As $q \to \infty$, the phases oscillate rapidly with changes in the distances $|\boldsymbol{x}_i - \boldsymbol{x}_j|$, and average out to zero. However, the 'diagonal' terms in the sum, *i.e.* those with $i = j$, always contribute a total of 1 to $S(\boldsymbol{q})$. Therefore in the $q \to \infty$ limit we have $S(q \to \infty) = 1$.

In general, the detectors used in a scattering experiment are sensitive to the energy of the scattered beam particles, although there is always a finite experimental resolution, both in $\boldsymbol{q}$ and $\omega$. This means that what is measured is actually something like

$$S_{\text{meas}}(\boldsymbol{q}, \omega) = \int\! d^d\!q' \int\! d\omega'\, F(\boldsymbol{q} - \boldsymbol{q}')\, G(\omega - \omega')\, S(\boldsymbol{q}', \omega')\ , \tag{6.191}$$

where $F$ and $G$ are essentially Gaussian functions of their argument, with width given by the experimental resolution. If one integrates over all frequencies $\omega$, *i.e.* if one simply counts scattered particles as a function of $\boldsymbol{q}$ but without any discrimination of their energies, then one measures the static structure factor $S(\boldsymbol{q})$. Elastic scattering is determined by $S(\boldsymbol{q}, \omega = 0$, *i.e.* no energy transfer.

### 6.5.5 Correlation and response

Suppose an external potential $v(\boldsymbol{x})$ is also present. Then

$$P(\boldsymbol{x}_1\,, \ldots\,, \boldsymbol{x}_N) = \frac{1}{Q_N[v]} \cdot \frac{1}{N!}\, e^{-\beta W(\boldsymbol{x}_1\,, \ldots\,, \boldsymbol{x}_N)}\, e^{-\beta \sum_i v(\boldsymbol{x}_i)}\ , \tag{6.192}$$

where

$$Q_N[v] = \frac{1}{N!}\!\int\! d^d\!x_1 \cdots\!\int\! d^d\!x_N\, e^{-\beta W(\boldsymbol{x}_1\,, \ldots\,, \boldsymbol{x}_N)}\, e^{-\beta \sum_i v(\boldsymbol{x}_i)}\ . \tag{6.193}$$

---

[9] We may write $\delta_{\boldsymbol{q},0} = \frac{1}{V}\,(2\pi)^d\,\delta(\boldsymbol{q})$.

The Helmholtz free energy is then

$$F = -\frac{1}{\beta}\,\ln\Big(\lambda_T^{-dN}\,Q_N[v]\Big)\ . \tag{6.194}$$

Now consider the functional derivative

$$\frac{\delta F}{\delta v(\boldsymbol{r})} = -\frac{1}{\beta}\cdot\frac{1}{Q_N}\cdot\frac{\delta Q_N}{\delta v(\boldsymbol{r})}\ . \tag{6.195}$$

Using

$$\sum_i v(\boldsymbol{x}_i) = \int\! d^d\!r\; v(\boldsymbol{r})\,\sum_i \delta(\boldsymbol{r}-\boldsymbol{x}_i)\ , \tag{6.196}$$

hence

$$\begin{aligned}\frac{\delta F}{\delta v(\boldsymbol{r})} &= \int\! d^d\!x_1\cdots\!\int\! d^d\!x_N\; P(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)\,\sum_i \delta(\boldsymbol{r}-\boldsymbol{x}_i)\\ &= n_1(\boldsymbol{r})\ ,\end{aligned} \tag{6.197}$$

which is the local density at $\boldsymbol{r}$.

Next, consider the *response function*,

$$\begin{aligned}\chi(\boldsymbol{r},\boldsymbol{r}') \equiv \frac{\delta n_1(\boldsymbol{r})}{\delta v(\boldsymbol{r}')} &= \frac{\delta^2 F[v]}{\delta v(\boldsymbol{r})\,\delta v(\boldsymbol{r}')}\\ &= \frac{1}{\beta}\cdot\frac{1}{Q_N^2}\,\frac{\delta Q_N}{\delta v(\boldsymbol{r})}\,\frac{\delta Q_N}{\delta v(\boldsymbol{r}')} - \frac{1}{\beta}\cdot\frac{1}{Q_N}\,\frac{\delta^2 Q_N}{\delta v(\boldsymbol{r})\,\delta v(\boldsymbol{r}')}\\ &= \beta\,n_1(\boldsymbol{r})\,n_1(\boldsymbol{r}') - \beta\,n_1(\boldsymbol{r})\,\delta(\boldsymbol{r}-\boldsymbol{r}') - \beta\,n_2(\boldsymbol{r},\boldsymbol{r}')\ .\end{aligned} \tag{6.198}$$

In an isotropic system, $\chi(\boldsymbol{r},\boldsymbol{r}') = \chi(\boldsymbol{r}-\boldsymbol{r}')$ is a function of the coordinate separation, and

$$\begin{aligned}-k_{\rm B}T\,\chi(\boldsymbol{r}-\boldsymbol{r}') &= -n^2 + n\,\delta(\boldsymbol{r}-\boldsymbol{r}') + n^2 g\big(|\boldsymbol{r}-\boldsymbol{r}'|\big)\\ &= n^2\,h\big(|\boldsymbol{r}-\boldsymbol{r}'|\big) + n\,\delta(\boldsymbol{r}-\boldsymbol{r}')\ .\end{aligned} \tag{6.199}$$

Taking the Fourier transform,

$$\begin{aligned}-k_{\rm B}T\,\hat\chi(\boldsymbol{q}) &= n + n^2\,\hat h(\boldsymbol{q})\\ &= n\,S(\boldsymbol{q})\ .\end{aligned} \tag{6.200}$$

We may also write

$$\frac{\kappa_T}{\kappa_T^0} = 1 + n\,\hat h(0) = -nk_{\rm B}T\,\hat\chi(0)\ , \tag{6.201}$$

*i.e.* $\kappa_T = -\hat\chi(0)$.

What does this all mean? Suppose we have an isotropic system which is subjected to a weak, spatially inhomogeneous potential $v(\boldsymbol{r})$. We expect that the density $n(\boldsymbol{r})$ in the presence of the inhomogeneous potential to itself be inhomogeneous. The first corrections to the $v = 0$ value $n = n_0$ are linear in $v$, and given by

$$\begin{aligned}\delta n(\boldsymbol{r}) &= \int\! d^d\!r'\;\chi(\boldsymbol{r},\boldsymbol{r}')\,v(\boldsymbol{r}')\\ &= -\beta n_0\,v(\boldsymbol{r}) - \beta n_0^2\!\int\! d^d\!r'\;h(\boldsymbol{r}-\boldsymbol{r})\,v(\boldsymbol{r}')\ .\end{aligned} \tag{6.202}$$

Note that if $v(\boldsymbol{r}) > 0$ it becomes energetically more costly for a particle to be at $\boldsymbol{r}$. Accordingly, the density response is negative, and proportional to the ratio $v(\boldsymbol{r})/k_{\mathrm{B}}T$ – this is the first term in the above equation. If there were no correlations between the particles, then $h = 0$ and this would be the entire story. However, the particles in general *are* correlated. Consider, for example, the case of hard spheres of diameter $a$, and let there be a repulsive potential at $\boldsymbol{r} = 0$. This means that it is less likely for a particle to be centered anywhere within a distance $a$ of the origin. But then it will be *more* likely to find a particle in the next 'shell' of radial thickness $a$.

### 6.5.6 BBGKY hierarchy

The distribution functions satisfy a hierarchy of integro-differential equations known as the *BBGKY hierarchy*[10]. In homogeneous systems, we have

$$g_k(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k) = \frac{N!}{(N-k)!}\,\frac{1}{n^k}\int\! d^dx_{k+1}\cdots\!\int\! d^dx_N\,P(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k\,,\,\boldsymbol{x}_{k+1}\,,\,\ldots\,,\,\boldsymbol{x}_N)\ , \tag{6.203}$$

where

$$P(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N) = \frac{1}{Q_N}\cdot\frac{1}{N!}\,e^{-\beta W(\boldsymbol{x}_1\,,\,\ldots\,,\,\boldsymbol{x}_N)}\ . \tag{6.204}$$

Taking the gradient with respect to $\boldsymbol{r}_1$, we have

$$\begin{aligned}\frac{\partial}{\partial\boldsymbol{r}_1}g_k(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k) = \frac{1}{Q_N}\cdot\frac{n^{-k}}{(N-k)!}&\int\! d^dx_{k+1}\cdots\!\int\! d^dx_N\,e^{-\beta\sum_{k<i<j}u(\boldsymbol{x}_{ij})}\\ &\times\frac{\partial}{\partial\boldsymbol{r}_1}\Big[e^{-\beta\sum_{i<j\le k}u(\boldsymbol{r}_{ij})}\cdot e^{-\beta\sum_{i\le k<j}u(\boldsymbol{r}_i-\boldsymbol{x}_j)}\Big]\ ,\end{aligned} \tag{6.205}$$

where $\sum_{k<i<j}$ means to sum on indices $i$ and $j$ such that $i < j$ and $k < i$, *i.e.*

$$\begin{aligned}\sum_{k<i<j}u(\boldsymbol{x}_{ij}) &\equiv \sum_{i=k+1}^{N-1}\sum_{j=i+1}^{N}u\big(\boldsymbol{x}_i-\boldsymbol{x}_j\big)\\ \sum_{i<j\le k}u(\boldsymbol{r}_{ij}) &\equiv \sum_{i=1}^{k-1}\sum_{j=i+1}^{k}u\big(\boldsymbol{r}_i-\boldsymbol{r}_j\big)\\ \sum_{i\le k<j}u(\boldsymbol{r}_i-\boldsymbol{x}_j) &= \sum_{i=1}^{k}\sum_{j=k+1}^{N}u(\boldsymbol{r}_i-\boldsymbol{x}_j)\ .\end{aligned}$$

Now

$$\begin{aligned}&\frac{\partial}{\partial\boldsymbol{r}_1}\Big[e^{-\beta\sum_{i<j\le k}u(r_{ij})}\cdot e^{-\beta\sum_{i\le k<j}u(\boldsymbol{r}_i-\boldsymbol{x}_j)}\Big] =\\ &\qquad\beta\left\{\sum_{1<j\le k}\frac{\partial u(\boldsymbol{r}_1-\boldsymbol{r}_j)}{\partial\boldsymbol{r}_1}+\sum_{k<j}\frac{\partial u(\boldsymbol{r}_1-\boldsymbol{r}_j)}{\partial\boldsymbol{r}_1}\right\}\cdot\Big[e^{-\beta\sum_{i<j\le k}u(r_{ij})}\cdot e^{-\beta\sum_{i\le k<j}u(\boldsymbol{r}_i-\boldsymbol{x}_j)}\Big]\ ,\end{aligned} \tag{6.206}$$

---

[10] So named after Bogoliubov, Born, Green, Kirkwood, and Yvon.

hence

$$\begin{aligned}\frac{\partial}{\partial \boldsymbol{r}_1} g_k(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k) = -\beta \sum_{j=2}^{k} \frac{\partial u(\boldsymbol{r}_1 - \boldsymbol{r}_j)}{\partial \boldsymbol{r}_1}\, g_k(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k) & \qquad (6.207)\\ - \beta(N-k)\!\int\! d^d x_{k+1}\, \frac{\partial u(\boldsymbol{r}_1 - \boldsymbol{x}_{k+1})}{\partial \boldsymbol{r}_1}\, P(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k\,,\,\boldsymbol{x}_{k+1}\,,\,\ldots\,,\,\boldsymbol{x}_N) &\\ = -\beta \sum_{j=2}^{k} \frac{\partial u(\boldsymbol{r}_1 - \boldsymbol{r}_j)}{\partial \boldsymbol{r}_1}\, g_k(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k) & \qquad (6.208)\\ + n\!\int\! d^d x_{k+1}\, \frac{\partial u(\boldsymbol{r}_1 - \boldsymbol{x}_{k+1})}{\partial \boldsymbol{r}_1}\, g_{k+1}(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k\,,\,x_{k+1}) &\end{aligned}$$

Thus, we obtain the BBGKY hierarchy:

$$\begin{aligned}-k_{\rm B}T\, \frac{\partial}{\partial \boldsymbol{r}_1} g_k(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k) = \sum_{j=2}^{k} \frac{\partial u(\boldsymbol{r}_1 - \boldsymbol{r}_j)}{\partial \boldsymbol{r}_1}\, g_k(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k) & \qquad (6.209)\\ + n\!\int\! d^d r'\, \frac{\partial u(\boldsymbol{r}_1 - \boldsymbol{r}')}{\partial \boldsymbol{r}_1}\, g_{k+1}(\boldsymbol{r}_1\,,\,\ldots\,,\,\boldsymbol{r}_k\,,\,\boldsymbol{r}')\ . &\end{aligned}$$

The BBGKY hierarchy is an infinite tower of coupled integro-differential equations, relating $g_k$ to $g_{k+1}$ for all $k$. If we approximate $g_k$ at some level $k$ in terms of equal or lower order distributions, then we obtain a closed set of equations which in principle can be solved, at least numerically. For example, the *Kirkwood approximation* closes the hierarchy at order $k = 2$ by imposing the condition

$$g_3(\boldsymbol{r}_1\,,\,\boldsymbol{r}_2\,,\,\boldsymbol{r}_3) \equiv g(\boldsymbol{r}_1 - \boldsymbol{r}_2)\, g(\boldsymbol{r}_1 - \boldsymbol{r}_3)\, g(\boldsymbol{r}_2 - \boldsymbol{r}_2)\ . \qquad (6.210)$$

This results in the single integro-differential equation

$$-k_{\rm B}T\, \boldsymbol{\nabla} g(\boldsymbol{r}) = g(\boldsymbol{r})\, \boldsymbol{\nabla} u + n\!\int\! d^d r'\, g(\boldsymbol{r})\, g(\boldsymbol{r}')\, g(\boldsymbol{r} - \boldsymbol{r}')\, \boldsymbol{\nabla} u(\boldsymbol{r} - \boldsymbol{r}')\ . \qquad (6.211)$$

This is known as the Born-Green-Yvon (BGY) equation. In practice, the BGY equation, which is solved numerically, gives adequate results only at low densities.

### 6.5.7 Ornstein-Zernike theory

The *direct correlation function* $c(\boldsymbol{r})$ is defined by the equation

$$h(\boldsymbol{r}) = c(\boldsymbol{r}) + n\!\int\! d^3 r'\, h(\boldsymbol{r} - \boldsymbol{r}')\, c(\boldsymbol{r}')\ , \qquad (6.212)$$

where $h(r) = g(r) - 1$ and we assume an isotropic system. This is called the *Ornstein-Zernike equation*. The first term, $c(\boldsymbol{r})$, accounts for local correlations, which are then propagated in the second term to account for long-ranged correlations.

The OZ equation is an integral equation, but it becomes a simple algebraic one upon Fourier transforming:

$$\hat{h}(\boldsymbol{q}) = \hat{c}(\boldsymbol{q}) + n\, \hat{h}(\boldsymbol{q})\, \hat{c}(\boldsymbol{q})\ , \qquad (6.213)$$

the solution of which is

$$\hat{h}(\boldsymbol{q}) = \frac{\hat{c}(\boldsymbol{q})}{1 - n\, \hat{c}(\boldsymbol{q})}\ . \qquad (6.214)$$

The static structure factor is then

$$S(\boldsymbol{q}) = 1 + n\,\hat{h}(\boldsymbol{q}) = \frac{1}{1 - n\,\hat{c}(\boldsymbol{q})} \ . \tag{6.215}$$

In the grand canonical ensemble, we can write

$$\kappa_T = \frac{1 + n\,\hat{h}(0)}{nk_{\rm B}T} = \frac{1}{nk_{\rm B}T} \cdot \frac{1}{1 - n\,\hat{c}(0)} \qquad \Longrightarrow \qquad n\,\hat{c}(0) = 1 - \frac{\kappa_T^0}{\kappa_T} \ , \tag{6.216}$$

where $\kappa_T^0 = 1/nk_{\rm B}T$ is the ideal gas isothermal compressibility.

At this point, we have merely substituted one unknown function, $h(\boldsymbol{r})$, for another, namely $c(\boldsymbol{r})$. To close the system, we need to relate $c(\boldsymbol{r})$ to $h(\boldsymbol{r})$ again in some way. There are various approximation schemes which do just this.

### 6.5.8 Percus-Yevick equation

In the Percus-Yevick approximation, we take

$$c(\boldsymbol{r}) = \big[1 - e^{\beta u(\boldsymbol{r})}\big] \cdot g(\boldsymbol{r}) \ . \tag{6.217}$$

Note that $c(\boldsymbol{r})$ vanishes whenever the potential $u(\boldsymbol{r})$ itself vanishes. This results in the following integro-differential equation for the pair distribution function $g(\boldsymbol{r})$:

$$g(\boldsymbol{r}) = e^{-\beta u(\boldsymbol{r})} + n\,e^{-\beta u(\boldsymbol{r})} \!\int\! d^3\!r'\,\big[g(\boldsymbol{r}-\boldsymbol{r}') - 1\big] \cdot \big[1 - e^{\beta u(\boldsymbol{r}')}\big]\,g(\boldsymbol{r}') \ . \tag{6.218}$$

This is the *Percus-Yevick equation*. Remarkably, the Percus-Yevick (PY) equation can be solved analytically for the case of hard spheres, where $u(r) = \infty$ for $r \le a$ and $u(r) = 0$ for $r > a$, where $a$ is the hard sphere diameter. Define the function $y(\boldsymbol{r}) = e^{\beta u(\boldsymbol{r})} g(\boldsymbol{r})$, in which case

$$c(\boldsymbol{r}) = y(\boldsymbol{r})\,f(\boldsymbol{r}) = \begin{cases} -y(\boldsymbol{r}) & ,\ r \le a \\ 0 & ,\ r > a \ . \end{cases} \tag{6.219}$$

Here, $f(\boldsymbol{r}) = e^{-\beta u(\boldsymbol{r})} - 1$ is the Mayer function. We remark that the definition of $y(\boldsymbol{r})$ may cause some concern for the hard sphere system, because of the $e^{\beta u(\boldsymbol{r})}$ term, which diverges severely for $r \le a$. However, $g(r)$ vanishes in this limit, and their product $y(\boldsymbol{r})$ is in fact finite! The PY equation may then be written for the function $y(\boldsymbol{r})$ as

$$y(\boldsymbol{r}) = 1 + n \!\!\int\limits_{r'<a}\!\! d^3\!r'\,y(\boldsymbol{r}') - n \!\!\!\!\int\limits_{\substack{r'<a \\ |\boldsymbol{r}-\boldsymbol{r}'|>a}}\!\!\!\! d^3\!r'\,y(\boldsymbol{r}')\,y(\boldsymbol{r}-\boldsymbol{r}') \ . \tag{6.220}$$

This has been solved using Laplace transform methods by M. S. Wertheim, *J. Math. Phys.* **5**, 643 (1964). The final result for $c(\boldsymbol{r})$ is

$$c(\boldsymbol{r}) = -\left\{\lambda_1 + 6\eta\,\lambda_2\left(\frac{r}{a}\right) + \tfrac{1}{2}\eta\,\lambda_1\left(\frac{r}{a}\right)^3\right\} \cdot \Theta(a - r) \ , \tag{6.221}$$

where $\eta = \frac{1}{6}\pi a^3 n$ is the packing fraction and

$$\lambda_1 = \frac{(1+2\eta)^2}{(1-\eta)^4} \qquad , \qquad \lambda_2 = -\frac{(1+\frac{1}{2}\eta)^2}{(1-\eta)^4} \ . \tag{6.222}$$

This leads to the equation of state

$$p = nk_{\rm B}T \cdot \frac{1 + \eta + \eta^2}{(1-\eta)^3} \ . \tag{6.223}$$

| quantity | exact | PY | HNC |
|---|---|---|---|
| $B_4/B_2^3$ | 0.28695 | 0.2969 | 0.2092 |
| $B_5/B_2^4$ | 0.1103 | 0.1211 | 0.0493 |
| $B_6/B_2^5$ | 0.0386 | 0.0281 | 0.0449 |
| $B_7/B_2^6$ | 0.0138 | 0.0156 | – |

Table 6.1: Comparison of exact (Monte Carlo) results to those of the Percus-Yevick (PY) and hypernetted chains approximation (HCA) for hard spheres in three dimensions. *Sources*: Hansen and McDonald (1990) and Reichl (1998)

This gets $B_2$ and $B_3$ exactly right. The accuracy of the PY approximation for higher order virial coefficients is shown in table 6.1.

To obtain the equation of state from eqn. 6.221, we invoke the compressibility equation,

$$n k_{\mathrm{B}} T \, \kappa_T = \bigg(\frac{\partial n}{\partial p}\bigg)_T = \frac{1}{1 - n\,\hat{c}(0)} \ . \tag{6.224}$$

We therefore need

$$\begin{aligned} \hat{c}(0) &= \int\! d^3\!r \; c(\boldsymbol{r}) \\ &= -4\pi a^3 \int\limits_0^1\! dx\, x^2 \, \big[\lambda_1 + 6\,\eta\,\lambda_2\,x + \tfrac{1}{2}\,\eta\,\lambda_1\,x^3\big] \\ &= -4\pi a^3 \big[\tfrac{1}{3}\,\lambda_1 + \tfrac{3}{2}\,\eta\,\lambda_2 + \tfrac{1}{12}\,\eta\,\lambda_1\big] \ . \end{aligned} \tag{6.225}$$

With $\eta = \frac{1}{6}\pi a^3 n$ and using the definitions of $\lambda_{1,2}$ in eqn. 6.222, one finds

$$1 - n\,\hat{c}(0) = \frac{1 + 4\eta + 4\eta^2}{(1-\eta)^4} \ . \tag{6.226}$$

We then have, from the compressibility equation,

$$\frac{6 k_{\mathrm{B}} T}{\pi a^3} \, \frac{\partial p}{\partial \eta} = \frac{1 + 4\eta + 4\eta^2}{(1-\eta)^4} \ . \tag{6.227}$$

Integrating, we obtain $p(\eta)$ up to a constant. The constant is set so that $p = 0$ when $n = 0$. The result is eqn. 6.223.

Another commonly used scheme is the *hypernetted chains* (HNC) approximation, for which

$$c(\boldsymbol{r}) = -\beta u(\boldsymbol{r}) + h(\boldsymbol{r}) - \ln\Big(1 + h(\boldsymbol{r})\Big) \ . \tag{6.228}$$

The rationale behind the HNC and other such approximation schemes is rooted in diagrammatic approaches, which are extensions of the Mayer cluster expansion to the computation of correlation functions. For details and references to their application in the literature, see Hansen and McDonald (1990) and Reichl (1998).

### 6.5.9 Ornstein-Zernike approximation at long wavelengths

Let's expand the direct correlation function $\hat{c}(\boldsymbol{q})$ in powers of the wavevector $\boldsymbol{q}$, *viz.*

$$\hat{c}(\boldsymbol{q}) = \hat{c}(0) + c_2\, q^2 + c_4\, q^4 + \ldots \ . \tag{6.229}$$

Here we have assumed spatial isotropy. Then

$$\begin{aligned} 1 - n\,\hat{c}(\boldsymbol{q}) = \frac{1}{S(\boldsymbol{q})} &= 1 - n\,\hat{c}(0) - n\,c_2\,q^2 + \ldots \\ &\equiv \xi^{-2}R^2 + q^2R^2 + \mathcal{O}(q^4)\ , \end{aligned} \tag{6.230}$$

where

$$R^2 = -n\,c_2 = 2\pi n \int\limits_0^\infty \! dr\, r^4\, c(r) \tag{6.231}$$

and

$$\xi^{-2} = \frac{1 - n\,\hat{c}(0)}{R^2} = \frac{1 - 4\pi n \int_0^\infty \! dr\, r^2\, c(r)}{2\pi n \int_0^\infty \! dr\, r^4\, c(r)}\ . \tag{6.232}$$

The quantity $R(T)$ tells us something about the effective range of the interactions, while $\xi(T)$ is the *correlation length*. As we approach a critical point, the correlation length diverges as a power law:

$$\xi(T) \sim A|T - T_{\rm c}|^{-\nu}\ . \tag{6.233}$$

The susceptibility is given by

$$\hat{\chi}(\boldsymbol{q}) = -n\beta\, S(\boldsymbol{q}) = -\frac{n\beta R^{-2}}{\xi^{-2} + q^2 + \mathcal{O}(q^4)} \tag{6.234}$$

In the *Ornstein-Zernike approximation*, one drops the $\mathcal{O}(q^4)$ terms in the denominator and retains only the long wavelength behavior. in the direct correlation function. Thus,

$$\hat{\chi}^{\rm OZ}(\boldsymbol{q}) = -\frac{n\beta R^{-2}}{\xi^{-2} + q^2}\ . \tag{6.235}$$

We now apply the inverse Fourier transform back to real space to obtain $\chi^{\rm OZ}(\boldsymbol{r})$. In $d = 1$ dimension the result can be obtained exactly:

$$\begin{aligned} \chi^{\rm OZ}_{d=1}(x) &= -\frac{n}{k_{\rm B}TR^2} \int\limits_{-\infty}^{\infty} \! \frac{dq}{2\pi}\, \frac{e^{iqx}}{\xi^{-2} + q^2} \\ &= -\frac{n\xi}{2k_{\rm B}TR^2}\, e^{-|x|/\xi}\ . \end{aligned} \tag{6.236}$$

In higher dimensions $d > 1$ we can obtain the result asymptotically in two limits:

- Take $r \to \infty$ with $\xi$ fixed. Then

  $$\chi^{\rm OZ}_d(\boldsymbol{r}) \simeq -C_d\, n \cdot \frac{\xi^{(3-d)/2}}{k_{\rm B}T\,R^2} \cdot \frac{e^{-r/\xi}}{r^{(d-1)/2}} \cdot \left\{1 + \mathcal{O}\bigg(\frac{d-3}{r/\xi}\bigg)\right\}\ , \tag{6.237}$$

  where the $C_d$ are dimensionless constants.
- Take $\xi \to \infty$ with $r$ fixed; this is the limit $T \to T_{\rm c}$ at fixed $r$. In dimensions $d > 2$ we obtain

  $$\chi^{\rm OZ}_d(\boldsymbol{r}) \simeq -\frac{C'_d\, n}{k_{\rm B}TR^2} \cdot \frac{e^{-r/\xi}}{r^{d-2}} \cdot \left\{1 + \mathcal{O}\bigg(\frac{d-3}{r/\xi}\bigg)\right\}\ . \tag{6.238}$$

  In $d = 2$ dimensions we obtain

  $$\chi^{\rm OZ}_{d=2}(\boldsymbol{r}) \simeq -\frac{C'_2\, n}{k_{\rm B}TR^2} \cdot \ln\!\bigg(\frac{r}{\xi}\bigg)\, e^{-r/\xi} \cdot \left\{1 + \mathcal{O}\bigg(\frac{1}{\ln(r/\xi)}\bigg)\right\}\ , \tag{6.239}$$

  where the $C'_d$ are dimensionless constants.

At criticality, $\xi \to \infty$, and clearly our results in $d = 1$ and $d = 2$ dimensions are nonsensical, as they are divergent. To correct this behavior, M. E. Fisher in 1963 suggested that the OZ correlation functions in the $r \ll \xi$ limit be replaced by

$$\chi(\boldsymbol{r}) \simeq -C''_d \, n \cdot \frac{\xi^\eta}{k_\text{B} T R^2} \cdot \frac{e^{-r/\xi}}{r^{d-2+\eta}} \ , \tag{6.240}$$

a result known as *anomalous scaling*. Here, $\eta$ is the *anomalous scaling exponent*.

Recall that the isothermal compressibility is given by $\kappa_T = -\hat\chi(0)$. Near criticality, the integral in $\hat\chi(0)$ is dominated by the $r \ll \xi$ part, since $\xi \to \infty$. Thus, using Fisher's anomalous scaling,

$$\begin{aligned}\kappa_T = -\hat\chi(0) &= -\int\! d^d\!r \, \chi(\boldsymbol{r}) \\ &\sim A \int\! d^d\!r \, \frac{e^{-r/\xi}}{r^{d-2+\eta}} \sim B\, \xi^{2-\eta} \sim C \, \big|T - T_\text{c}\big|^{-(2-\eta)\nu} \ ,\end{aligned} \tag{6.241}$$

where $A$, $B$, and $C$ are temperature-dependent constants which are nonsingular at $T = T_\text{c}$. Thus, since $\kappa_T \propto |T - T_\text{c}|^{-\gamma}$, we conclude

$$\gamma = (2 - \eta)\, \nu \ , \tag{6.242}$$

a result known as *hyperscaling*.

## 6.6 Coulomb Systems : Plasmas and the Electron Gas

### 6.6.1 Electrostatic potential

Coulomb systems are particularly interesting in statistical mechanics because of their long-ranged forces, which result in the phenomenon of *screening*. Long-ranged forces wreak havoc with the Mayer cluster expansion, since the Mayer function is no longer integrable. Thus, the virial expansion fails, and new techniques need to be applied to reveal the physics of plasmas.

The potential energy of a Coulomb system is

$$U = \tfrac{1}{2} \int\! d^d\!r \int\! d^d\!r' \, \rho(\boldsymbol{r}) \, u(\boldsymbol{r} - \boldsymbol{r}') \, \rho(\boldsymbol{r}') \ , \tag{6.243}$$

where $\rho(\boldsymbol{r})$ is the charge density and $u(\boldsymbol{r})$, which has the dimensions of (energy)/(charge)$^2$, satisfies

$$\nabla^2 u(\boldsymbol{r} - \boldsymbol{r}') = -4\pi \, \delta(\boldsymbol{r} - \boldsymbol{r}') \ . \tag{6.244}$$

Thus,

$$u(\boldsymbol{r}) = \begin{cases} -2\pi \, |x - x'| & , \ d = 1 \\ \\ -2 \, \ln |\boldsymbol{r} - \boldsymbol{r}'| & , \ d = 2 \\ \\ |\boldsymbol{r} - \boldsymbol{r}'|^{-1} & , \ d = 3 \ . \end{cases} \tag{6.245}$$

For discete particles, the charge density $\rho(\boldsymbol{r})$ is given by

$$\rho(\boldsymbol{r}) = \sum_i q_i \, \delta(\boldsymbol{r} - \boldsymbol{x}_i) \ , \tag{6.246}$$

where $q_i$ is the charge of the $i^{\rm th}$ particle. We will assume two types of charges: $q = \pm e$, with $e > 0$. The electric potential is

$$\begin{aligned}\phi(\boldsymbol{r}) &= \int\! d^d\!r'\, u(\boldsymbol{r}-\boldsymbol{r}')\,\rho(\boldsymbol{r}') \\ &= \sum_i q_i\, u(\boldsymbol{r}-\boldsymbol{x}_i)\ .\end{aligned} \tag{6.247}$$

This satisfies the Poisson equation,

$$\nabla^2\phi(\boldsymbol{r}) = -4\pi\rho(\boldsymbol{r})\ . \tag{6.248}$$

The total potential energy can be written as

$$U = \tfrac{1}{2}\!\int\! d^d\!r\, \phi(\boldsymbol{r})\,\rho(\boldsymbol{r}) \tag{6.249}$$

$$= \tfrac{1}{2}\sum_i q_i\,\phi(\boldsymbol{x}_i)\ , \tag{6.250}$$

## 6.6.2 Debye-Hückel theory

We now write the grand partition function:

$$\begin{aligned}\varXi(T,V,\mu_+,\mu_-) = \sum_{N_+=0}^{\infty}\sum_{N_-=0}^{\infty} &\frac{1}{N_+!}\,e^{\beta\mu_+N_+}\,\lambda_+^{-N_+d}\cdot\frac{1}{N_-!}\,e^{\beta\mu_-N_-}\,\lambda_-^{-N_-d} \\ &\cdot\int\! d^d\!r_1\cdots\!\int\! d^d\!r_{N_++N_-}\;e^{-\beta U(\boldsymbol{r}_1,\,\ldots\,,\,\boldsymbol{r}_{N_++N_-})}\ .\end{aligned} \tag{6.251}$$

We now adopt a *mean field* approach, known as *Debye-Hückel theory*, writing

$$\rho(\boldsymbol{r}) = \rho^{\rm av}(\boldsymbol{r}) + \delta\rho(\boldsymbol{r}) \tag{6.252}$$

$$\phi(\boldsymbol{r}) = \phi^{\rm av}(\boldsymbol{r}) + \delta\phi(\boldsymbol{r})\ . \tag{6.253}$$

We then have

$$\begin{aligned}U &= \tfrac{1}{2}\!\int\! d^d\!r\,\big[\rho^{\rm av}(\boldsymbol{r})+\delta\rho(\boldsymbol{r})\big]\cdot\big[\phi^{\rm av}(\boldsymbol{r})+\delta\phi(\boldsymbol{r})\big] \\ &= \overbrace{-\tfrac{1}{2}\!\int\! d^d\!r\,\rho^{\rm av}(\boldsymbol{r})\,\phi^{\rm av}(\boldsymbol{r})}^{\equiv\,U_0} + \int\! d^d\!r\,\phi^{\rm av}(\boldsymbol{r})\,\rho(\boldsymbol{r}) + \overbrace{\tfrac{1}{2}\!\int\! d^d\!r\,\delta\rho(\boldsymbol{r})\,\delta\phi(\boldsymbol{r})}^{\text{ignore fluctuation term}}\ .\end{aligned} \tag{6.254}$$

We apply the mean field approximation in each region of space, which leads to

$$\begin{aligned}\varOmega(T,V,\mu_+,\mu_-) = -k_{\rm B}T\lambda_+^{-d}\,z_+\!\int\! d^d\!r\,\exp\!\bigg(-\frac{e\,\phi^{\rm av}(\boldsymbol{r})}{k_{\rm B}T}\bigg) \\ - k_{\rm B}T\lambda_-^{-d}\,z_-\!\int\! d^d\!r\,\exp\!\bigg(+\frac{e\,\phi^{\rm av}(\boldsymbol{r})}{k_{\rm B}T}\bigg)\ ,\end{aligned} \tag{6.255}$$

where

$$\lambda_\pm = \bigg(\frac{2\pi\hbar^2}{m_\pm k_{\rm B}T}\bigg) \qquad , \qquad z_\pm = \exp\!\bigg(\frac{\mu_\pm}{k_{\rm B}T}\bigg)\ . \tag{6.256}$$

The charge density is therefore

$$\rho(\boldsymbol{r}) = \frac{\delta\Omega}{\delta\phi^{\text{av}}(\boldsymbol{r})} = e\,\lambda_+^{-d}\,z_+\,\exp\!\bigg(-\frac{e\,\phi(\boldsymbol{r})}{k_{\text{B}}T}\bigg) - e\,\lambda_-^{-d}\,z_-\,\exp\!\bigg(+\frac{e\,\phi(\boldsymbol{r})}{k_{\text{B}}T}\bigg)\ , \tag{6.257}$$

where we have now dropped the superscript on $\phi^{\text{av}}(\boldsymbol{r})$ for convenience. At $r\to\infty$, we assume charge neutrality and $\phi(\infty)=0$. Thus

$$\lambda_+^{-d}\,z_+ = n_+(\infty) = \lambda_-^{-d}\,z_- = n_-(\infty) \equiv n_\infty\ , \tag{6.258}$$

where $n_\infty$ is the ionic density of either species at infinity. Therefore,

$$\rho(\boldsymbol{r}) = -2e\,n_\infty \sinh\!\bigg(\frac{e\,\phi(\boldsymbol{r})}{k_{\text{B}}T}\bigg)\ . \tag{6.259}$$

We now invoke Poisson's equation,

$$\nabla^2\phi = 8\pi e n_\infty \sinh(\beta e\phi) - 4\pi\rho_{\text{ext}}\ , \tag{6.260}$$

where $\rho_{\text{ext}}$ is an externally imposed charge density.

If $e\phi \ll k_{\text{B}}T$, we can expand the sinh function and obtain

$$\nabla^2\phi = \kappa_{\text{D}}^2\,\phi - 4\pi\rho_{\text{ext}}\ , \tag{6.261}$$

where

$$\kappa_{\text{D}} = \bigg(\frac{8\pi n_\infty e^2}{k_{\text{B}}T}\bigg)^{1/2} \qquad , \qquad \lambda_{\text{D}} = \bigg(\frac{k_{\text{B}}T}{8\pi n_\infty e^2}\bigg)^{1/2}\ . \tag{6.262}$$

The quantity $\lambda_{\text{D}}$ is known as the *Debye screening length*. Consider, for example, a point charge $Q$ located at the origin. We then solve Poisson's equation in the weak field limit,

$$\nabla^2\phi = \kappa_{\text{D}}^2\,\phi - 4\pi Q\,\delta(\boldsymbol{r})\ . \tag{6.263}$$

Fourier transforming, we obtain

$$-\boldsymbol{q}^2\,\hat\phi(\boldsymbol{q}) = \kappa_{\text{D}}^2\,\hat\phi(\boldsymbol{q}) - 4\pi Q \qquad\Longrightarrow\qquad \hat\phi(\boldsymbol{q}) = \frac{4\pi Q}{\boldsymbol{q}^2+\kappa_{\text{D}}^2}\ . \tag{6.264}$$

Transforming back to real space, we obtain, in three dimensions, the Yukawa potential,

$$\phi(\boldsymbol{r}) = \int\!\frac{d^3q}{(2\pi)^3}\,\frac{4\pi Q\,e^{i\boldsymbol{q}\cdot\boldsymbol{r}}}{\boldsymbol{q}^2+\kappa_{\text{D}}^2} = \frac{Q}{r}\cdot e^{-\kappa_{\text{D}}r}\ . \tag{6.265}$$

This solution must break down sufficiently close to $r=0$, since the assumption $e\phi(r)\ll k_{\text{B}}T$ is no longer valid there. However, for larger $r$, the Yukawa form is increasingly accurate.

For another example, consider an electrolyte held between two conducting plates, one at potential $\phi(x=0)=0$ and the other at potential $\phi(x=L)=V$, where $\hat{\boldsymbol{x}}$ is normal to the plane of the plates. Again assuming a weak field $e\phi\ll k_{\text{B}}T$, we solve $\nabla^2\phi=\kappa_{\text{D}}^2\,\phi$ and obtain

$$\phi(x) = A\,e^{\kappa_{\text{D}}x} + B\,e^{-\kappa_{\text{D}}\,x}\ . \tag{6.266}$$

We fix the constants $A$ and $B$ by invoking the boundary conditions, which results in

$$\phi(x) = V\cdot\frac{\sinh(\kappa_{\text{D}}x)}{\sinh(\kappa_{\text{D}}L)}\ . \tag{6.267}$$

Debye-Hückel theory is valid provided $n_\infty\,\lambda_{\text{D}}^3 \gg 1$, so that the statistical assumption of many charges in a screening volume is justified.

### 6.6.3 The electron gas : Thomas-Fermi screening

Assuming $k_{\rm B}T \ll \varepsilon_{\rm F}$, thermal fluctuations are unimportant and we may assume $T = 0$. In the same spirit as the Debye-Hückel approach, we assume a slowly varying mean electrostatic potential $\phi(\boldsymbol{r})$. Locally, we can write

$$\varepsilon_{\rm F} = \frac{\hbar^2 k_{\rm F}^2}{2m} - e\phi(\boldsymbol{r}) \ . \tag{6.268}$$

Thus, the Fermi wavevector $k_{\rm F}$ is spatially varying, according to the relation

$$k_{\rm F}(\boldsymbol{r}) = \left[\frac{2m}{\hbar^2}\Big(\varepsilon_{\rm F} + e\phi(\boldsymbol{r})\Big)\right]^{1/2} . \tag{6.269}$$

The local electron number density is

$$n(\boldsymbol{r}) = \frac{k_{\rm F}^3(\boldsymbol{r})}{3\pi^2} = n_\infty \left(1 + \frac{e\phi(\boldsymbol{r})}{\varepsilon_{\rm F}}\right)^{3/2} . \tag{6.270}$$

In the presence of a uniform compensating positive background charge $\rho_+ = en_\infty$, Poisson's equation takes the form

$$\nabla^2\phi = 4\pi e\, n_\infty \cdot \left[\left(1 + \frac{e\phi(\boldsymbol{r})}{\varepsilon_{\rm F}}\right)^{3/2} - 1\right] - 4\pi\rho_{\rm ext}(\boldsymbol{r}) \ . \tag{6.271}$$

If $e\phi \ll \varepsilon_{\rm F}$, we may expand in powers of the ratio, obtaining

$$\nabla^2\phi = \frac{6\pi n_\infty e^2}{\varepsilon_{\rm F}}\,\phi \equiv \kappa_{\rm TF}^2\,\phi - 4\pi\rho_{\rm ext}(\boldsymbol{r}) \ . \tag{6.272}$$

Here, $\kappa_{\rm TF}$ is the *Thomas-Fermi wavevector*,

$$\kappa_{\rm TF} = \left(\frac{6\pi n_\infty e^2}{\varepsilon_{\rm F}}\right)^{1/2} . \tag{6.273}$$

Thomas-Fermi theory is valid provided $n_\infty\, \lambda_{\rm TF}^3 \gg 1$, where $\lambda_{\rm TF} = \kappa_{\rm TF}^{-1}$, so that the statistical assumption of many electrons in a screening volume is justified.

One important application of Thomas-Fermi screening is to the theory of metals. In a metal, the outer, valence electrons of each atom are stripped away from the positively charged ionic core and enter into itinerant, plane-wave-like states. These states disperse with some $\varepsilon(\boldsymbol{k})$ function (that is periodic in the Brillouin zone, *i.e.* under $\boldsymbol{k} \to \boldsymbol{k} + \boldsymbol{G}$, where $\boldsymbol{G}$ is a reciprocal lattice vector), and at $T = 0$ this *energy band* is filled up to the Fermi level $\varepsilon_{\rm F}$, as Fermi statistics dictates. (In some cases, there may be several bands at the Fermi level, as we saw in the case of yttrium.) The set of ionic cores then acts as a neutralizing positive background. In a perfect crystal, the ionic cores are distributed periodically, and the positive background is approximately uniform. A charged impurity in a metal, such as a zinc atom in a copper matrix, has a different nuclear charge and a different valency than the host. The charge of the ionic core, when valence electrons are stripped away, differs from that of the host ions, and therefore the impurity acts as a *local charge impurity*. For example, copper has an electronic configuration of $[\mathrm{Ar}]\,3d^{10}\,4s^1$. The 4s electron forms an energy band which contains the Fermi surface. Zinc has a configuration of $[\mathrm{Ar}]\,3d^{10}\,4s^2$, and in a Cu matrix the Zn gives up its two $4s$ electrons into the $4s$ conduction band, leaving behind a charge +2 ionic core. The Cu cores have charge +1 since each copper atom contributed only one $4s$ electron to the conduction band. The conduction band electrons neutralize the uniform positive background of the Cu ion cores. What is left is an extra $Q = +e$ nuclear charge at the Zn site, and one extra $4s$ conduction band electron. The $Q = +e$ impurity is, however, *screened* by the electrons, and at distances greater than an atomic radius the potential that a given electron sees due to the Zn core is of the Yukawa form,

$$\phi(\boldsymbol{r}) = \frac{Q}{r} \cdot e^{-\kappa_{\rm TF} r} \ . \tag{6.274}$$

We should take care, however, that the dispersion $\varepsilon(\boldsymbol{k})$ for the conduction band in a metal is not necessarily of the free electron form $\varepsilon(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$. To linear order in the potential, however, the change in the local electronic density is

$$\delta n(\boldsymbol{r}) = e\phi(\boldsymbol{r})\, g(\varepsilon_{\rm F}) \ , \tag{6.275}$$

where $g(\varepsilon_{\rm F})$ is the density of states at the Fermi energy. Thus, in a metal, we should write

$$\begin{aligned} \nabla^2\phi &= (-4\pi)(-e\,\delta n) \\ &= 4\pi e^2 g(\varepsilon_{\rm F})\,\phi = \kappa^2_{\rm TF}\,\phi \ , \end{aligned} \tag{6.276}$$

where

$$\kappa_{\rm TF} = \sqrt{4\pi e^2\, g(\varepsilon_{\rm F})} \ . \tag{6.277}$$

The value of $g(\varepsilon_{\rm F})$ will depend on the form of the dispersion. For ballistic bands with an effective mass $m^*$, the formula in eqn. 6.272 still applies.

### The Thomas-Fermi atom

Consider an ion formed of a nucleus of charge $+Ze$ and an electron cloud of charge $-Ne$. The net ionic charge is then $(Z - N)e$. Since we will be interested in atomic scales, we can no longer assume a weak field limit and we must retain the full nonlinear screening theory, for which

$$\nabla^2\phi(\boldsymbol{r}) = 4\pi e \cdot \frac{(2m)^{3/2}}{3\pi^2\hbar^3}\Big(\varepsilon_{\rm F} + e\phi(\boldsymbol{r})\Big)^{3/2} - 4\pi Ze\,\delta(\boldsymbol{r}) \ . \tag{6.278}$$

We assume an isotropic solution. It is then convenient to define

$$\varepsilon_{\rm F} + e\phi(\boldsymbol{r}) = \frac{Ze^2}{r}\cdot\chi(r/r_0) \ , \tag{6.279}$$

where $r_0$ is yet to be determined. As $r \to 0$ we expect $\chi \to 1$ since the nuclear charge is then unscreened. We then have

$$\nabla^2\left\{\frac{Ze^2}{r}\cdot\chi(r/r_0)\right\} = \frac{1}{r_0^2}\,\frac{Ze^2}{r}\,\chi''(r/r_0) \ , \tag{6.280}$$

thus we arrive at the *Thomas-Fermi equation*,

$$\chi''(t) = \frac{1}{\sqrt{t}}\,\chi^{3/2}(t) \ , \tag{6.281}$$

with $r = t\,r_0$, provided we take

$$r_0 = \frac{\hbar^2}{2me^2}\left(\frac{3\pi}{4\sqrt{Z}}\right)^{2/3} = 0.885\,Z^{-1/3}\,a_{\rm B} \ , \tag{6.282}$$

where $a_{\rm B} = \frac{\hbar^2}{me^2} = 0.529$ Å is the Bohr radius. The TF equation is subject to the following boundary conditions:

- At short distances, the nucleus is unscreened, *i.e.*

$$\chi(0) = 1 \ . \tag{6.283}$$

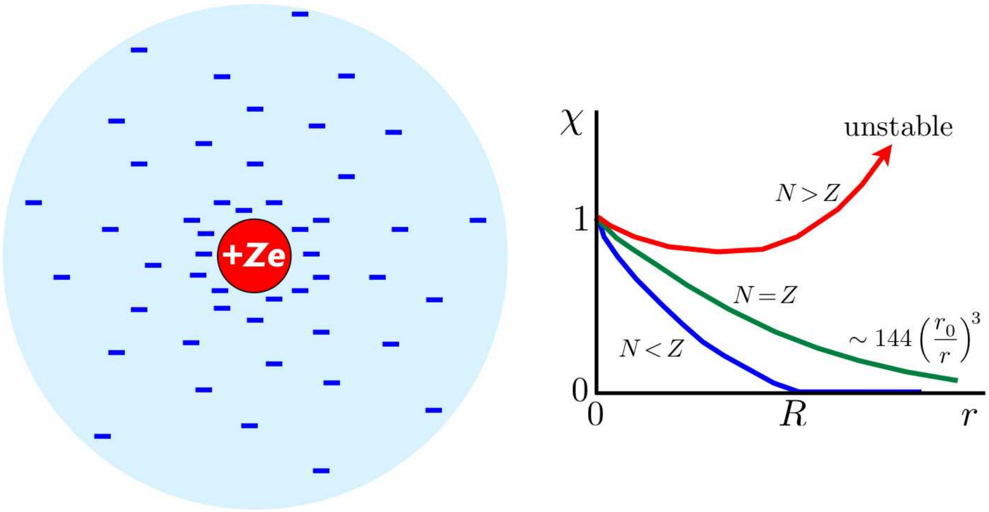


Figure 6.19: The Thomas-Fermi atom consists of a nuclear charge $+Ze$ surrounded by $N$ electrons distributed in a cloud. The electric potential $\phi(\boldsymbol{r})$ felt by any electron at position $\boldsymbol{r}$ is screened by the electrons within this radius, resulting in a self-consistent potential $\phi(\boldsymbol{r}) = \phi_0 + (Ze^2/r)\,\chi(r/r_0)$.

- For positive ions, with $N < Z$, there is perfect screening at the ionic boundary $R = t^*\, r_0$, where $\chi(t^*) = 0$. This requires

  $$\boldsymbol{E} = -\boldsymbol{\nabla}\phi = \left[-\frac{Ze^2}{R^2}\,\chi(R/r_0) + \frac{Ze^2}{R\,r_0}\,\chi'(R/r_0)\right]\hat{\boldsymbol{r}} = \frac{(Z-N)\,e}{R^2}\,\hat{\boldsymbol{r}}\,. \tag{6.284}$$

  This requires

  $$-t^*\,\chi'(t^*) = 1 - \frac{N}{Z}\,. \tag{6.285}$$

For an atom, with $N = Z$, the asymptotic solution to the TF equation is a power law, and by inspection is found to be $\chi(t) \sim C\,t^{-3}$, where $C$ is a constant. The constant follows from the TF equation, which yields $12\,C = C^{3/2}$, hence $C = 144$. Thus, a neutral TF atom has a density with a power law tail, with $\rho \sim r^{-9/2}$. TF ions with $N > Z$ are unstable.

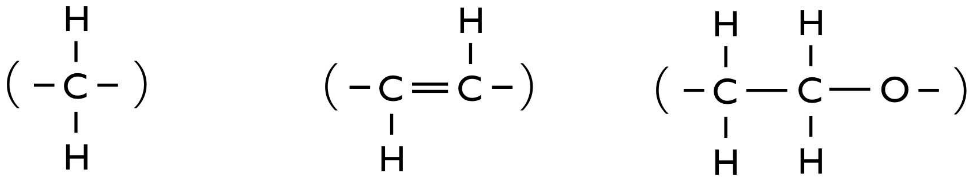
## 6.7 Polymers

### 6.7.1 Basic concepts

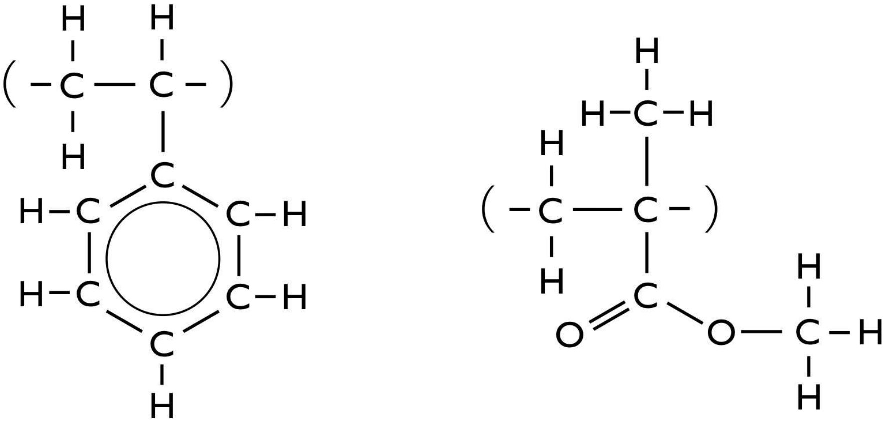
Linear chain polymers are repeating structures with the chemical formula $(A)_x$, where $A$ is the *formula unit* and $x$ is the *degree of polymerization*. In many cases (*e.g.* polystyrene), $x \gtrsim 10^5$ is not uncommon. For a very readable introduction to the subject, see P. G. de Gennes, *Scaling Concepts in Polymer Physics*.

Quite often a given polymer solution will contain a distribution of $x$ values; this is known as *polydispersity*. Various preparation techniques, such as chromatography, can mitigate the degree of polydispersity. Another morphological feature of polymers is *branching* (see fig. 6.21), in which the polymers do not form linear chains.

Polymers exhibit a *static flexibility* which can be understood as follows. Consider a long chain hydrocarbon with a $-\mathrm{C}-\mathrm{C}-\mathrm{C}-$ backbone. The angle between successive $\mathrm{C}-\mathrm{C}$ bonds is fixed at $\theta \approx 68°$, but the azimuthal angle



polyethylene $(\mathrm{CH}_2)_x$ polyacetylene $(\mathrm{CH})_x$ polyoxyethylene $(\mathrm{C}_2\mathrm{H}_4\mathrm{O})_x$



polystyrene $(\mathrm{C}_8\mathrm{H}_8)_x$ poly(methyl methacrylate) $(\mathrm{C}_5\mathrm{H}_8\mathrm{O}_2)_x$

Figure 6.20: Some examples of linear chain polymers.

$\varphi$ can take one of three possible low-energy values, as shown in the right panel of fig. 6.22. Thus, the relative probabilities of *gauche* and *trans* orientations are

$$\frac{\mathrm{Prob}\,(\mathrm{gauche})}{\mathrm{Prob}\,(\mathrm{trans})} = 2\,e^{-\Delta\varepsilon/k_{\mathrm{B}}T} \ , \tag{6.286}$$

where $\Delta\varepsilon$ is the energy difference between *trans* and *gauche* configurations. This means that the polymer chain is in fact a *random coil* with a *persistence length*

$$\ell_{\mathrm{p}} = \ell_0\, e^{\Delta\varepsilon/k_{\mathrm{B}}T} \ , \tag{6.287}$$

where $\ell_0$ is a microscopic length scale, roughly given by the length of a formula unit, which is approximately a few Ångstroms (see fig. 6.23). Let $L$ be the total length of the polymer when it is stretched into a straight line. If $\ell_{\mathrm{p}} > L$, the polymer is *rigid*. If $\ell_{\mathrm{p}} \ll L$, the polymer is rigid on the length scale $\ell_{\mathrm{p}}$ but flexible on longer scales. We have

$$\frac{\ell_{\mathrm{p}}}{L} = \frac{1}{N}\, e^{\Delta\varepsilon/k_{\mathrm{B}}T} \ , \tag{6.288}$$

where we now use $N$ (rather than $x$) for the degree of polymerization.

In the time domain, the polymer exhibits a *dynamical flexibility* on scales longer than a *persistence time*. The persistence time $\tau_{\mathrm{p}}$ is the time required for a *trans-gauche* transition. The rate for such transitions is set by the energy barrier $B$ separating *trans* from *gauche* configurations:

$$\tau_{\mathrm{p}} = \tau_0\, e^{B/k_{\mathrm{B}}T} \ , \tag{6.289}$$

where $\tau_0 \sim 10^{-11}\,\mathrm{s}$. On frequency scales $\omega \ll \tau_{\mathrm{p}}^{-1}$ the polymer is dynamically flexible. If $\Delta\varepsilon \sim k_{\mathrm{B}}T \ll B$ the polymer is flexible from a static point of view, but dynamically rigid. That is, there are many *gauche* orientations of successive carbon bonds which reflect a quenched disorder. The polymer then forms a frozen random coil, like a twisted coat hanger.

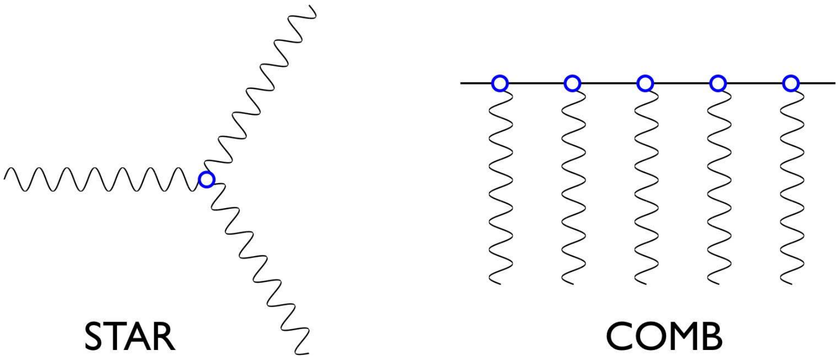


Figure 6.21: Branched polymers.

### 6.7.2 Polymers as random walks

A polymer can be modeled by a *self-avoiding random walk* (SAW). That is, on scales longer than $\ell_{\rm p}$, it twists about randomly in space subject to the constraint that it doesn't overlap itself. Before we consider the mathematics of SAWs, let's first recall some aspects of ordinary random walks which are not self-avoiding.

We'll simplify matters further by considering random walks on a hypercubic lattice of dimension $d$. Such a lattice has coordination number $2d$, *i.e.* there are $2d$ nearest neighbor separations,

$$\boldsymbol{\delta} = \pm a\,\hat{\boldsymbol{e}}_1\,,\,\pm a\,\hat{\boldsymbol{e}}_2\,,\,\ldots\,,\,\pm a\,\hat{\boldsymbol{e}}_d\ , \tag{6.290}$$

where $a$ is the lattice spacing. Consider now a random walk of $N$ steps starting at the origin. After $N$ steps the position is

$$\boldsymbol{R}_N = \sum_{j=1}^N \boldsymbol{\delta}_j\ , \tag{6.291}$$

where $\boldsymbol{\delta}_j$ takes on one of $2d$ possible values. Now $N$ is no longer the degree of polymerization, but more like $L/\ell_{\rm p}$, which is the number of persistence lengths in the chain. We assume each step is independent, hence $\langle \boldsymbol{\delta}_j \cdot \boldsymbol{\delta}_{j'} \rangle = a^2\,\delta_{jj'}$ and $\langle \boldsymbol{R}_N^2 \rangle = Na^2$. The full distribution $P_N(\boldsymbol{R})$ is given by

$$\begin{aligned}
P_N(\boldsymbol{R}) &= (2d)^{-N} \sum_{\boldsymbol{\delta}_1} \cdots \sum_{\boldsymbol{\delta}_N} \delta_{\boldsymbol{R},\sum_j \boldsymbol{\delta}_j} \\
&= a^d \int\limits_{-\pi/a}^{\pi/a} \frac{dk_1}{2\pi} \cdots \int\limits_{-\pi/a}^{\pi/a} \frac{dk_d}{2\pi}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \left[ \frac{1}{d} \sum_{\mu=1}^d \cos(k_\mu a) \right]^N \\
&= a^d \int\limits_{\hat\Omega} \frac{d^d\!k}{(2\pi)^d}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \exp\left[ N \ln\!\left( 1 - \frac{1}{2d}\,\boldsymbol{k}^2 a^2 + \ldots \right) \right] \\
&\approx \left( \frac{a}{2d} \right)^d \int\! d^d\!k\, e^{-N\boldsymbol{k}^2 a^2/2d}\, e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} = \left( \frac{d}{2\pi N} \right)^{d/2} e^{-d\boldsymbol{R}^2/2Na^2}\ .
\end{aligned} \tag{6.292}$$

This is a simple Gaussian, with width $\langle \boldsymbol{R}^2 \rangle = d \cdot (Na^2/d) = Na^2$, as we have already computed. We define $R_0 = \sqrt{N}\,a$ as the *radius of gyration*.

The total number of random walk configurations with end-to-end vector $\boldsymbol{R}$ is then $(2d)^N P_N(\boldsymbol{R})$, so the entropy of

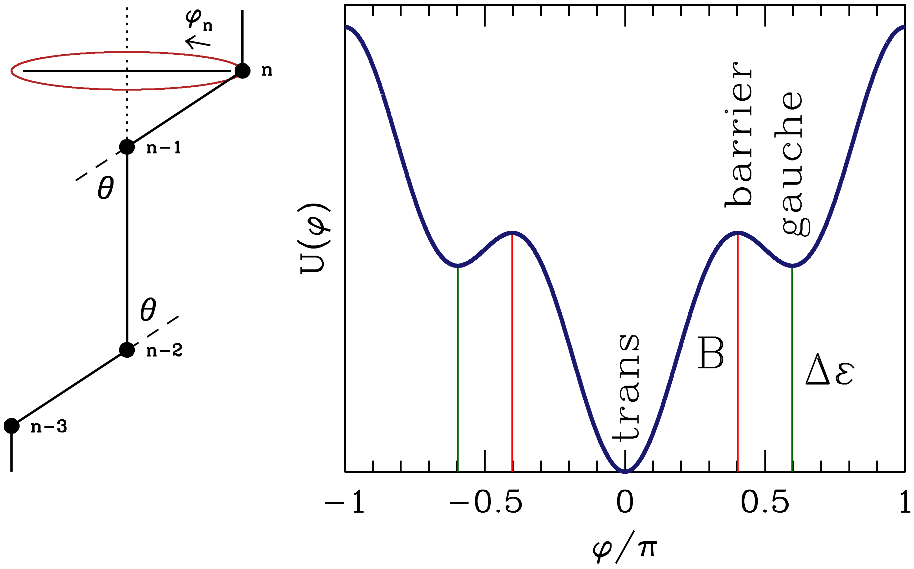


Figure 6.22: Left" *trans* and *gauche* orientations in carbon chains. Right: energy as a function of azimuthal angle $\varphi$. There are three low energy states: *trans* ($\varphi = 0$) and *gauche* ($\varphi = \pm\varphi_0$).

a chain at fixed elongation is

$$S(\boldsymbol{R},N) = k_{\rm B} \ln\Big[(2d)^N P_N(\boldsymbol{R})\Big] = S(0,N) - \frac{dk_{\rm B}\boldsymbol{R}^2}{2Na^2} \ . \tag{6.293}$$

If we assume that the energy of the chain is conformation independent, then $E = E_0(N)$ and

$$F(\boldsymbol{R},N) = F(0,N) + \frac{dk_{\rm B}T\boldsymbol{R}^2}{2Na^2} \ . \tag{6.294}$$

In the presence of an external force $F_{\rm ext}$, the Gibbs free energy is the Legendre transform

$$G(\boldsymbol{F}_{\rm ext},N) = F(\boldsymbol{R},N) - \boldsymbol{F}_{\rm ext}\cdot\boldsymbol{R} \ , \tag{6.295}$$

and $\partial G/\partial\boldsymbol{R} = 0$ then gives the relation

$$\big\langle \boldsymbol{R}(\boldsymbol{F}_{\rm ext},N)\big\rangle = \frac{Na^2}{dk_{\rm B}T}\,\boldsymbol{F}_{\rm ext} \ . \tag{6.296}$$

This may be considered an equation of state for the polymer.

Following de Gennes, consider a chain with charges $\pm e$ at each end, placed in an external electric field of magnitude $E = 30,000\,{\rm V/cm}$. Let $N = 10^4$, $a = 2\,$Å, and $d = 3$. What is the elongation? From the above formula, we have

$$\frac{R}{R_0} = \frac{eER_0}{3k_{\rm B}T} = 0.8 \ . \tag{6.297}$$

### Structure factor

We can also compute the structure factor (see eqn. 6.190),

$$S(\boldsymbol{q}) = \frac{1}{N}\Big\langle \sum_{m=1}^N\sum_{n=1}^N e^{i\boldsymbol{q}\cdot(\boldsymbol{R}_m-\boldsymbol{R}_n)}\Big\rangle \ . \tag{6.298}$$

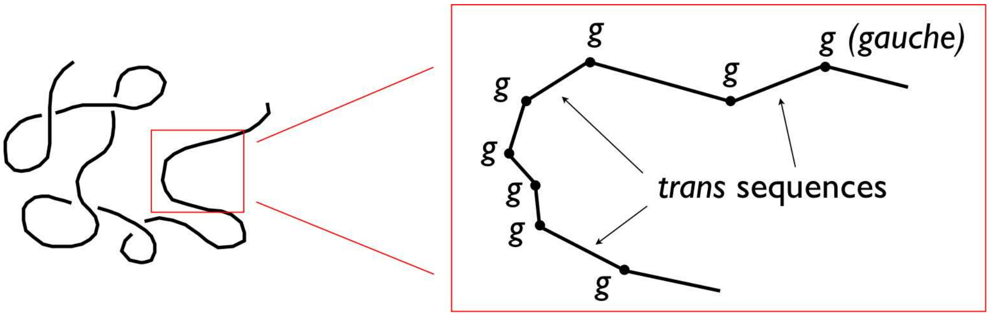


Figure 6.23: The polymer chain as a random coil.

For averages with respect to a Gaussian distribution,

$$\left\langle e^{i\boldsymbol{q}\cdot(\boldsymbol{R}_m-\boldsymbol{R}_n)}\right\rangle = \exp\Big[-\tfrac{1}{2}\big\langle\big(\boldsymbol{q}\cdot(\boldsymbol{R}_m-\boldsymbol{R}_n)\big)^2\big\rangle\Big] \ . \tag{6.299}$$

We then have

$$S(\boldsymbol{q}) = \frac{1}{N}\sum_{m,n=1}^{N} e^{-|m-n|\boldsymbol{q}^2a^2/2} = N f\big(N\boldsymbol{q}^2a^2/2\big) \ , \tag{6.300}$$

where

$$f(x) = \frac{2}{x^2}\left(e^{-x}-1+x\right) = 1 - \frac{x}{3} + \frac{x^2}{12} + \ldots \ . \tag{6.301}$$

**Self-avoiding walks**

On a lattice of coordination number $z$, the number of $N$-step random walks starting from the origin is $\Omega_N = z^N$. If we constrain our random walks to be self-avoiding, the number is reduced to

$$\Omega_N^{\text{SAW}} = \mathcal{C}\, N^{\gamma-1}\, y^N \ , \tag{6.302}$$

where $\mathcal{C}$ and $\gamma$ are dimension-dependent constants, and we expect $y \lesssim z-1$, since at the very least a SAW cannot immediately double back on itself. In fact, on the cubic lattice one has $z=6$ but $y=4.68$, slightly less than $z-1$. One finds $\gamma_{d=2} \simeq \frac{4}{3}$ and $\gamma_{d=3} \simeq \frac{7}{6}$. The RMS end-to-end distance of the SAW is

$$R_{\text{F}} = a\, N^{\nu} \ , \tag{6.303}$$

where $a$ and $\nu$ are $d$-dependent constants,with $\nu_{d=1}=1$, $\nu_{d=2} \simeq \frac{3}{4}$, and $\nu_{d=3} \simeq \frac{3}{5}$. The distribution $P_N(\boldsymbol{R})$ has a scaling form,

$$P_N(R) = \frac{1}{R_{\text{F}}^d}\, f\!\left(\frac{R}{R_{\text{F}}}\right) \qquad (a \ll R \ll Na) \ . \tag{6.304}$$

One finds

$$f(x) \sim \begin{cases} x^g & x \ll 1 \\ \exp(-x^{\delta}) & x \gg 1 \ , \end{cases} \tag{6.305}$$

with $g = (\gamma-1)/\nu$ and $\delta = 1/(1-\nu)$.

### 6.7.3 Flory theory

What is missing from the random walk free energy is the effect of *steric interactions*. Suppose we have a chain of radius $R$. Then the average monomer density within the chain is $c = N/R^d$. Assuming short-ranged interactions, we should then add a term to the free energy which effectively counts the number of near self-intersections of the chain. This number should be roughly $Nc$. Thus, we write

$$F(\boldsymbol{R}, N) = F_0 + u(T)\, \frac{N^2}{R^d} + \tfrac{1}{2} d k_{\rm B} T\, \frac{R^2}{Na^2} \ . \tag{6.306}$$

The effective interaction $u(T)$ is positive in the case of a so-called 'good solvent'.

The free energy is minimized when

$$0 = \frac{\partial F}{\partial R} = -\frac{dvN^2}{R^{d+1}} + d k_{\rm B} T\, \frac{R}{Na^2} \ , \tag{6.307}$$

which yields the result

$$R_{\rm F}(N) = \bigg(\frac{ua^2}{k_{\rm B}T}\bigg)^{\frac{1}{d+2}} N^{\frac{3}{d+2}} \ . \tag{6.308}$$

Thus, we obtain $\nu = 3/(d+2)$, and $\nu_{d=3} = \frac{3}{5}$, which is extremely close to the correct value $\nu = 0.5880$ obtained from numerical work and renormalization group calculations.

For a SAW under an external force, we compute the Gibbs partition function,

$$Y(\boldsymbol{F}_{\rm ext}, N) = \int\! d^d\!R\; P_N(\boldsymbol{R})\, e^{\boldsymbol{F}_{\rm ext}\cdot \boldsymbol{R}/k_{\rm B}T} = \int\! d^d\!x\; f(x)\, e^{s\hat{\boldsymbol{n}}\cdot\boldsymbol{x}} \ , \tag{6.309}$$

where $x = R/R_{\rm F}$ and $s = k_{\rm B}T/R_{\rm F}F_{\rm ext}$ and $\hat{\boldsymbol{n}} = \hat{\boldsymbol{F}}_{\rm ext}$. One than has $R(F_{\rm ext}) = R_{\rm F}\, \varPhi(R_{\rm F}/\xi)$, where $\xi = k_{\rm B}T/F_{\rm ext}$ and $R(F_{\rm ext}) = F_{\rm ext} R_{\rm F}^2/k_{\rm B}T$. For small values of its argument one has $\varPhi(u) \propto u$. For large $u$ it can be shown that $R(F_{\rm ext}) \propto (F_{\rm ext}R_{\rm F}/k_{\rm B}T)^{2/3}$.

### 6.7.4 Polymers and solvents

Consider a solution of monodisperse polymers of length $N$ in a solvent. Let $\phi$ be the dimensionless monomer concentration, so $\phi/N$ is the dimensionless polymer concentration and $\phi_{\rm s} = 1 - \phi$ is the dimensionless solvent concentration. (Dimensionless concentrations are obtained by dividing the corresponding dimensionful concentration by the overall density.) The entropy of mixing for such a system is given by eqn. 2.352. We have

$$S_{\rm mix} = -\frac{Vk_{\rm B}}{v_0} \cdot \left\{ \frac{1}{N} \phi \ln\phi + (1-\phi)\ln(1-\phi) \right\} \ , \tag{6.310}$$

where $v_0 \propto a^3$ is the volume per monomer. Accounting for an interaction between the monomer and the solvent, we have that the free energy of mixing is

$$\frac{v_0\, F_{\rm mix}}{Vk_{\rm B}T} = \frac{1}{N}\, \phi \ln\phi + (1-\phi)\ln(1-\phi) + \chi\, \phi(1-\phi) \ . \tag{6.311}$$

where $\chi$ is the dimensionless polymer-solvent interaction, called the *Flory parameter*. This provides a mean field theory of the polymer-solvent system.

The osmotic pressure $\varPi$ is defined by

$$\varPi = -\frac{\partial F_{\rm mix}}{\partial V}\bigg|_{N_{\rm p}} \ , \tag{6.312}$$

which is the variation of the free energy of mixing with respect to volume *holding the number of polymers constant*. The monomer concentration is $\phi = N N_\mathrm{p} v_0 / V$, so

$$\frac{\partial}{\partial V}\bigg|_{N_\mathrm{p}} = -\frac{\phi^2}{N N_\mathrm{p}\, v_0}\,\frac{\partial}{\partial \phi}\bigg|_{N_\mathrm{p}} \ . \tag{6.313}$$

Now we have

$$F_\mathrm{mix} = N N_\mathrm{p}\, k_\mathrm{B} T \left\{ \frac{1}{N}\, \ln\phi + (\phi^{-1} - 1)\ln(1-\phi) + \chi\,(1-\phi) \right\} \ , \tag{6.314}$$

and therefore

$$\mathit{\Pi} = \frac{k_\mathrm{B} T}{v_0}\Big[ (N^{-1} - 1)\,\phi - \ln(1-\phi) - \chi\,\phi^2 \Big] \ . \tag{6.315}$$

In the limit of vanishing monomer concentration $\phi \to 0$, we recover

$$\mathit{\Pi} = \frac{\phi\, k_\mathrm{B} T}{N v_0} \ , \tag{6.316}$$

which is the ideal gas law for polymers.

For $N^{-1} \ll \phi \ll 1$, we expand the logarithm and obtain

$$\begin{aligned} \frac{v_0\, \mathit{\Pi}}{k_\mathrm{B} T} &= \frac{1}{N}\phi + \tfrac{1}{2}(1 - 2\chi)\,\phi^2 + \mathcal{O}(\phi^3) \\ &\approx \tfrac{1}{2}(1-2\chi)\,\phi^2 \ . \end{aligned} \tag{6.317}$$

Note that $\mathit{\Pi} > 0$ only if $\chi < \frac{1}{2}$, which is the condition for a 'good solvent'.

In fact, eqn. 6.317 is only qualitatively correct. In the limit where $\chi \ll \frac{1}{2}$, Flory showed that the individual polymer coils behave much as hard spheres of radius $R_\mathrm{F}$. The osmotic pressure then satisfies something analogous to a virial equation of state:

$$\begin{aligned} \frac{\mathit{\Pi}}{k_\mathrm{B} T} &= \frac{\phi}{N v_0} + A\left(\frac{\phi}{N v_0}\right)^{\!2} R_\mathrm{F}^3 + \ldots \\ &= \frac{\phi}{N v_0}\, h(\phi/\phi^*) \ . \end{aligned} \tag{6.318}$$

This is generalized to a scaling form in the second line, where $h(x)$ is a scaling function, and $\phi^* = N v_0 / R_\mathrm{F}^3 \propto N^{-4/5}$, assuming $d = 3$ and $\nu = \frac{3}{5}$ from Flory theory. As $x = \phi/\phi^* \to 0$, we must recover the ideal gas law, so $h(x) = 1 + \mathcal{O}(x)$ in this limit. For $x \to \infty$, we require that the result be independent of the degree of polymerization $N$. This means $h(x) \propto x^p$ with $\frac{4}{5}p = 1$, *i.e.* $p = \frac{5}{4}$. The result is known as the des Cloiseaux law:

$$\frac{v_0 \mathit{\Pi}}{k_\mathrm{B} T} = C\, \phi^{9/4} \ , \tag{6.319}$$

where $C$ is a constant. This is valid for what is known as semi-dilute solutions, where $\phi^* \ll \phi \ll 1$. In the dense limit $\phi \sim 1$, the results do not exhibit this universality, and we must appeal to the theory of liquids as discussed in §6.5.

## 6.8 Appendix : Potts Model in One Dimension

### 6.8.1 Definition

The Potts model is defined by the Hamiltonian

$$H = -J \sum_{\langle ij \rangle} \delta_{\sigma_i , \sigma_j} - h \sum_i \delta_{\sigma_i , 1} \, . \tag{6.320}$$

Here, the spin variables $\sigma_i$ take values in the set $\{1, 2, \ldots, q\}$ on each site. The equivalent of an external magnetic field in the Ising case is a field $h$ which prefers a particular value of $\sigma$ ($\sigma = 1$ in the above Hamiltonian). Once again, it is not possible to compute the partition function on general lattices, however in one dimension we may once again find $Z$ using the transfer matrix method.

### 6.8.2 Transfer matrix

On a ring of $N$ sites, we have

$$\begin{aligned} Z &= \mathrm{Tr}\, e^{-\beta H} \\ &= \sum_{\{\sigma_n\}} e^{\beta h \delta_{\sigma_1 , 1}} \, e^{\beta J \delta_{\sigma_1 , \sigma_2}} \, \cdots \, e^{\beta h \delta_{\sigma_N , 1}} \, e^{\beta J \delta_{\sigma_N , \sigma_1}} \\ &= \mathrm{Tr}\, \big( R^N \big) \, , \end{aligned} \tag{6.321}$$

where the $q \times q$ transfer matrix $R$ is given by

$$R_{\sigma\sigma'} = e^{\beta J \delta_{\sigma\sigma'}} \, e^{\frac{1}{2}\beta h \delta_{\sigma,1}} \, e^{\frac{1}{2}\beta h \delta_{\sigma',1}} = \begin{cases} e^{\beta (J+h)} & \text{if } \sigma = \sigma' = 1 \\ e^{\beta J} & \text{if } \sigma = \sigma' \neq 1 \\ e^{\beta h/2} & \text{if } \sigma = 1 \text{ and } \sigma' \neq 1 \\ e^{\beta h/2} & \text{if } \sigma \neq 1 \text{ and } \sigma' = 1 \\ 1 & \text{if } \sigma \neq 1 \text{ and } \sigma' \neq 1 \text{ and } \sigma \neq \sigma' \, . \end{cases} \tag{6.322}$$

In matrix form,

$$R = \begin{pmatrix} e^{\beta (J+h)} & e^{\beta h/2} & e^{\beta h/2} & \cdots & & e^{\beta h/2} \\ e^{\beta h/2} & e^{\beta J} & 1 & \cdots & & 1 \\ e^{\beta h/2} & 1 & e^{\beta J} & \cdots & & 1 \\ \vdots & \vdots & \vdots & \ddots & & \vdots \\ e^{\beta h/2} & 1 & 1 & \cdots & e^{\beta J} & 1 \\ e^{\beta h/2} & 1 & 1 & \cdots & 1 & e^{\beta J} \end{pmatrix} \tag{6.323}$$

The matrix $R$ has $q$ eigenvalues $\lambda_j$, with $j = 1, \ldots, q$. The partition function for the Potts chain is then

$$Z = \sum_{j=1}^{q} \lambda_j^N \, . \tag{6.324}$$

We can actually find the eigenvalues of $R$ analytically. To this end, consider the vectors

$$\phi = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \quad , \quad \psi = \big( q - 1 + e^{\beta h} \big)^{-1/2} \begin{pmatrix} e^{\beta h/2} \\ 1 \\ \vdots \\ 1 \end{pmatrix} \, . \tag{6.325}$$

Then $R$ may be written as

$$R = \big(e^{\beta J} - 1\big)\,\mathbb{I} + \big(q - 1 + e^{\beta h}\big)\,|\,\psi\,\rangle\langle\,\psi\,| + \big(e^{\beta J} - 1\big)\big(e^{\beta h} - 1\big)\,|\,\phi\,\rangle\langle\,\phi\,|\ , \tag{6.326}$$

where $\mathbb{I}$ is the $q \times q$ identity matrix. When $h = 0$, we have a simpler form,

$$R = \big(e^{\beta J} - 1\big)\,\mathbb{I} + q\,|\,\psi\,\rangle\langle\,\psi\,|\ . \tag{6.327}$$

From this we can read off the eigenvalues:

$$\lambda_1 = e^{\beta J} + q - 1 \tag{6.328}$$

$$\lambda_j = e^{\beta J} - 1 \quad , \quad j \in \{2, \ldots, q\}\ , \tag{6.329}$$

since $|\,\psi\,\rangle$ is an eigenvector with eigenvalue $\lambda = e^{\beta J} + q - 1$, and any vector orthogonal to $|\,\psi\,\rangle$ has eigenvalue $\lambda = e^{\beta J} - 1$. The partition function is then

$$Z = \big(e^{\beta J} + q - 1\big)^N + (q - 1)\big(e^{\beta J} - 1\big)^N\ . \tag{6.330}$$

In the thermodynamic limit $N \to \infty$, only the $\lambda_1$ eigenvalue contributes, and we have

$$F(T, N, h = 0) = -N k_{\rm B} T \ln\big(e^{J/k_{\rm B}T} + q - 1\big) \qquad \text{for } N \to \infty\ . \tag{6.331}$$

When $h$ is nonzero, the calculation becomes somewhat more tedious, but still relatively easy. The problem is that $|\,\psi\,\rangle$ and $|\,\phi\,\rangle$ are not orthogonal, so we define

$$|\,\chi\,\rangle = \frac{|\,\phi\,\rangle - |\,\psi\,\rangle\langle\,\psi\,|\,\phi\,\rangle}{\sqrt{1 - \langle\,\phi\,|\,\psi\,\rangle^2}}\ , \tag{6.332}$$

where

$$x \equiv \langle\,\phi\,|\,\psi\,\rangle = \left(\frac{e^{\beta h}}{q - 1 + e^{\beta h}}\right)^{1/2}\ . \tag{6.333}$$

Now we have $\langle\,\chi\,|\,\psi\,\rangle = 0$, with $\langle\,\chi\,|\,\chi\,\rangle = 1$ and $\langle\,\psi\,|\,\psi\,\rangle = 1$, with

$$|\,\phi\,\rangle = \sqrt{1 - x^2}\;|\,\chi\,\rangle + x\,|\,\psi\,\rangle\ . \tag{6.334}$$

and the transfer matrix is then

$$\begin{aligned} R &= \big(e^{\beta J} - 1\big)\,\mathbb{I} + \big(q - 1 + e^{\beta h}\big)\,|\,\psi\,\rangle\langle\,\psi\,| \\ &\qquad + \big(e^{\beta J} - 1\big)\big(e^{\beta h} - 1\big)\left[(1 - x^2)\,|\,\chi\,\rangle\langle\,\chi\,| + x^2\,|\,\psi\,\rangle\langle\,\psi\,| + x\sqrt{1 - x^2}\,\Big(|\,\chi\,\rangle\langle\,\psi\,| + |\,\psi\,\rangle\langle\,\chi\,|\Big)\right] \\ &= \big(e^{\beta J} - 1\big)\,\mathbb{I} + \left[\big(q - 1 + e^{\beta h}\big) + \big(e^{\beta J} - 1\big)\big(e^{\beta h} - 1\big)\left(\frac{e^{\beta h}}{q - 1 + e^{\beta h}}\right)\right]|\,\psi\,\rangle\langle\,\psi\,| \\ &\qquad + \big(e^{\beta J} - 1\big)\big(e^{\beta h} - 1\big)\left(\frac{q - 1}{q - 1 + e^{\beta h}}\right)|\,\chi\,\rangle\langle\,\chi\,| \\ &\qquad + \big(e^{\beta J} - 1\big)\big(e^{\beta h} - 1\big)\left(\frac{(q - 1)\,e^{\beta h}}{q - 1 + e^{\beta h}}\right)^{1/2}\Big(|\,\chi\,\rangle\langle\,\psi\,| + |\,\psi\,\rangle\langle\,\chi\,|\Big)\ , \end{aligned} \tag{6.335}$$

which in the two-dimensional subspace spanned by $|\,\chi\,\rangle$ and $|\,\psi\,\rangle$ is of the form

$$R = \begin{pmatrix} a & c \\ c & b \end{pmatrix}\ . \tag{6.336}$$

Recall that for any $2 \times 2$ Hermitian matrix,

$$\begin{aligned} M &= a_0\,\mathbb{I} + \boldsymbol{a} \cdot \boldsymbol{\tau} \\ &= \begin{pmatrix} a_0 + a_3 & a_1 - i a_2 \\ a_1 + i a_2 & a_0 - a_3 \end{pmatrix} \ , \end{aligned} \tag{6.337}$$

the characteristic polynomial is

$$P(\lambda) = \det\big(\lambda\,\mathbb{I} - M\big) = (\lambda - a_0)^2 - a_1^2 - a_2^2 - a_3^2 \ , \tag{6.338}$$

and hence the eigenvalues are

$$\lambda_{\pm} = a_0 \pm \sqrt{a_1^2 + a_2^2 + a_3^2} \ . \tag{6.339}$$

For the transfer matrix of eqn. 6.335, we obtain, after a little work,

$$\begin{aligned} \lambda_{1,2} &= e^{\beta J} - 1 + \tfrac{1}{2}\Big[q - 1 + e^{\beta h} + \big(e^{\beta J} - 1\big)\big(e^{\beta h} - 1\big)\Big] \\ &\quad \pm \tfrac{1}{2}\sqrt{\Big[q - 1 + e^{\beta h} + \big(e^{\beta J} - 1\big)\big(e^{\beta h} - 1\big)\Big]^2 - 4(q-1)\big(e^{\beta J} - 1\big)\big(e^{\beta h} - 1\big)} \ . \end{aligned} \tag{6.340}$$

There are $q - 2$ other eigenvalues, however, associated with the $(q-2)$-dimensional subspace orthogonal to $|\,\chi\,\rangle$ and $|\,\psi\,\rangle$. Clearly all these eigenvalues are given by

$$\lambda_j = e^{\beta J} - 1 \qquad , \quad j \in \{3\,,\,\ldots\,,\,q\} \ . \tag{6.341}$$

The partition function is then

$$Z = \lambda_1^N + \lambda_2^N + (q-2)\,\lambda_3^N \ , \tag{6.342}$$

and in the thermodynamic limit $N \to \infty$ the maximum eigenvalue $\lambda_1$ dominates. Note that we recover the correct limit as $h \to 0$.

# Chapter 7

# Mean Field Theory of Phase Transitions

## 7.1 References

- M. Kardar, *Statistical Physics of Particles* (Cambridge, 2007)
  A superb modern text, with many insightful presentations of key concepts.
- M. Plischke and B. Bergersen, *Equilibrium Statistical Physics* ($3^{\mathrm{rd}}$ edition, World Scientific, 2006)
  An excellent graduate level text. Less insightful than Kardar but still a good modern treatment of the subject. Good discussion of mean field theory.
- G. Parisi, *Statistical Field Theory* (Addison-Wesley, 1988)
  An advanced text focusing on field theoretic approaches, covering mean field and Landau-Ginzburg theories before moving on to renormalization group and beyond.
- J. P. Sethna, *Entropy, Order Parameters, and Complexity* (Oxford, 2006)
  An excellent introductory text with a very modern set of topics and exercises. Available online at http://www.physics.corn

## 7.2 The van der Waals system

### 7.2.1 Equation of state

Recall the van der Waals equation of state,

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT \ , \tag{7.1}$$

where $v = N_{\rm A} V/N$ is the molar volume. Solving for $p(v,T)$, we have

$$p=\frac{RT}{v-b}-\frac{a}{v^2} \ . \tag{7.2}$$

Let us fix the temperature $T$ and examine the function $p(v)$. Clearly $p(v)$ is a decreasing function of volume for $v$ just above the minimum allowed value $v = b$, as well as for $v \to \infty$. But is $p(v)$ a monotonic function for all $v \in [b, \infty]$?

We can answer this by computing the derivative,

$$\left(\frac{\partial p}{\partial v}\right)_T=\frac{2a}{v^3}-\frac{RT}{(v-b)^2} \ . \tag{7.3}$$

Setting this expression to zero for finite $v$, we obtain the equation[1]

$$\frac{2a}{bRT}=\frac{u^3}{(u-1)^2} \ , \tag{7.4}$$

where $u \equiv v/b$ is dimensionless. It is easy to see that the function $f(u) = u^3/(u-1)^2$ has a unique minimum for $u > 1$. Setting $f'(u^*) = 0$ yields $u^* = 3$, and so $f_{\rm min} = f(3) = \frac{27}{4}$. Thus, for $T > T_{\rm c} = 8a/27bR$, the LHS of eqn. 7.4 lies below the minimum value of the RHS, and there is no solution. This means that $p(v, T > T_{\rm c})$ is a monotonically decreasing function of $v$.

At $T = T_{\rm c}$ there is a saddle-node bifurcation. Setting $v_{\rm c} = bu^* = 3b$ and evaluating $p_{\rm c} = p(v_{\rm c}, T_{\rm c})$, we have that the location of the *critical point* for the van der Waals system is

$$p_{\rm c}=\frac{a}{27\,b^2} \qquad , \qquad v_{\rm c}=3b \qquad , \qquad T_{\rm c}=\frac{8a}{27\,bR} \ . \tag{7.5}$$

For $T < T_{\rm c}$, there are two solutions to eqn. 7.4, corresponding to a local minimum and a local maximum of the function $p(v)$. The locus of points in the $(v, p)$ plane for which $(\partial p/\partial v)_T = 0$ is obtained by setting eqn. 7.3 to zero and solving for $T$, then substituting this into eqn. 7.2. The result is

$$p^*(v)=\frac{a}{v^3}-\frac{2ab}{v^2} \ . \tag{7.6}$$

Expressed in terms of dimensionless quantities $\bar{p} = p/p_{\rm c}$ and $\bar{v} = v/v_{\rm c}$, this equation becomes

$$\bar{p}^*(\bar{v})=\frac{3}{\bar{v}^3}-\frac{2}{\bar{v}^2} \ . \tag{7.7}$$

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[1] There is always a solution to $(\partial p/\partial v)_T = 0$ at $v = \infty$.

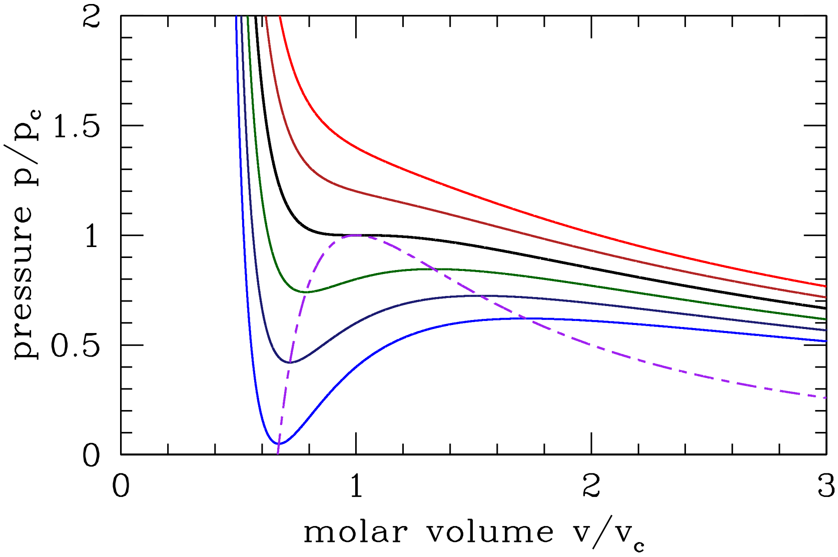

Figure 7.1: Pressure *versus* molar volume for the van der Waals gas at temperatures in equal intervals from $T = 1.10\,T_c$ (red) to $T = 0.85\,T_c$ (blue). The purple curve is $\bar{p}^*(\bar{v})$.

Along the curve $p = p^*(v)$, the isothermal compressibility, $\kappa_T = -\frac{1}{v}\big(\frac{\partial v}{\partial p}\big)_T$ diverges, heralding a *thermodynamic instability*. To understand better, let us compute the free energy of the van der Waals system, $F = E - TS$. Regarding the energy $E$, we showed back in chapter 2 that

$$\left(\frac{\partial \varepsilon}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p = \frac{a}{v^2} \ , \tag{7.8}$$

which entails

$$\varepsilon(T, v) = \tfrac{1}{2} f R T - \frac{a}{v} \ , \tag{7.9}$$

where $\varepsilon = E/\nu$ is the molar internal energy. The first term is the molar energy of an ideal gas, where $f$ is the number of molecular freedoms, which is the appropriate low density limit. The molar specific heat is then $c_V = \big(\frac{\partial \varepsilon}{\partial T}\big)_v = \frac{f}{2} R$, which means that the molar entropy is

$$s(T, v) = \int^T \! dT' \, \frac{c_V}{T'} = \tfrac{f}{2} R \ln(T/T_c) + s_1(v) \ . \tag{7.10}$$

We then write $f = \varepsilon - Ts$, and we fix the function $s_1(v)$ by demanding that $p = -\big(\frac{\partial f}{\partial v}\big)_T$. This yields $s_1(v) = R\ln(v - b) + s_0$, where $s_0$ is a constant. Thus[2],

$$f(T, v) = \tfrac{f}{2} R T \Big(1 - \ln\big(T/T_c\big)\Big) - \frac{a}{v} - RT\ln(v - b) - T s_0 \ . \tag{7.11}$$

We know that under equilibrium conditions, $f$ is driven to a minimum by spontaneous processes. Now suppose that $\frac{\partial^2 f}{\partial v^2}\big|_T < 0$ over some range of $v$ at a given temperature $T$. This would mean that one mole of the system at volume $v$ and temperature $T$ could lower its energy by rearranging into two half-moles, with respective molar volumes $v \pm \delta v$, each at temperature $T$. The total volume and temperature thus remain fixed, but the free energy changes by an amount $\Delta f = \frac{1}{2}\frac{\partial^2 f}{\partial v^2}\big|_T (\delta v)^2 < 0$. This means that the system is unstable – it can lower its energy by

---

[2] Don't confuse the molar free energy ($f$) with the number of molecular degrees of freedom ($f$)!

| gas | $a$ $\left(\frac{\mathrm{L}^2\cdot\mathrm{bar}}{\mathrm{mol}^2}\right)$ | $b$ $\left(\frac{\mathrm{L}}{\mathrm{mol}}\right)$ | $p_\mathrm{c}$ (bar) | $T_\mathrm{c}$ (K) | $v_\mathrm{c}$ (L/mol) |
|---|---|---|---|---|---|
| Acetone | 14.09 | 0.0994 | 52.82 | 505.1 | 0.2982 |
| Argon | 1.363 | 0.03219 | 48.72 | 150.9 | 0.0966 |
| Carbon dioxide | 3.640 | 0.04267 | 7404 | 304.0 | 0.1280 |
| Ethanol | 12.18 | 0.08407 | 63.83 | 516.3 | 0.2522 |
| Freon | 10.78 | 0.0998 | 40.09 | 384.9 | 0.2994 |
| Helium | 0.03457 | 0.0237 | 2.279 | 5.198 | 0.0711 |
| Hydrogen | 0.2476 | 0.02661 | 12.95 | 33.16 | 0.0798 |
| Mercury | 8.200 | 0.01696 | 1055 | 1723 | 0.0509 |
| Methane | 2.283 | 0.04278 | 46.20 | 190.2 | 0.1283 |
| Nitrogen | 1.408 | 0.03913 | 34.06 | 128.2 | 0.1174 |
| Oxygen | 1.378 | 0.03183 | 50.37 | 154.3 | 0.0955 |
| Water | 5.536 | 0.03049 | 220.6 | 647.0 | 0.0915 |

Table 7.1: Van der Waals parameters for some common gases. (Source: *Wikipedia*)

dividing up into two subsystems each with different densities (*i.e.* molar volumes). Note that the onset of stability occurs when

$$\frac{\partial^2 f}{\partial v^2}\bigg|_T = -\frac{\partial p}{\partial v}\bigg|_T = \frac{1}{v\kappa_p} = 0 \ , \tag{7.12}$$

which is to say when $\kappa_p = \infty$. As we saw, this occurs at $p = p^*(v)$, given in eqn. 7.6.

However, this condition, $\frac{\partial^2 f}{\partial v^2}\big|_T < 0$, is in fact too strong. That is, the system can be unstable even at molar volumes where $\frac{\partial^2 f}{\partial v^2}\big|_T > 0$. The reason is shown graphically in fig. 7.2. At the fixed temperature $T$, for any molar volume $v$ between $v_\mathrm{liquid} \equiv v_1$ and $v_\mathrm{gas} \equiv v_2$ , the system can lower its free energy by *phase separating* into regions of different molar volumes. In general we can write

$$v = (1-x)\,v_1 + x\,v_2 \ , \tag{7.13}$$

so $v = v_1$ when $x = 0$ and $v = v_2$ when $x = 1$. The free energy upon phase separation is simply

$$f = (1-x)\,f_1 + x\,f_2 \ , \tag{7.14}$$

where $f_j = f(v_j, T)$. This function is given by the straight black line connecting the points at volumes $v_1$ and $v_2$ in fig. 7.2.

The two equations which give us $v_1$ and $v_2$ are

$$\frac{\partial f}{\partial v}\bigg|_{v_1,T} = \frac{\partial f}{\partial v}\bigg|_{v_2,T} \tag{7.15}$$

and

$$f(T,v_1) - f(T,v_2) = (v_2 - v_1)\,\frac{\partial f}{\partial v}\bigg|_{v_1,T} \ . \tag{7.16}$$

In terms of the pressure, $p = -\frac{\partial f}{\partial v}\big|_T$, these equations are equivalent to

$$p(T,v_1) = p(T,v_2) \tag{7.17}$$

$$\int\limits_{v_1}^{v_2} dv\, p(T,v) = \big(v_2 - v_1\big)\, p(T,v_1) \ . \tag{7.18}$$

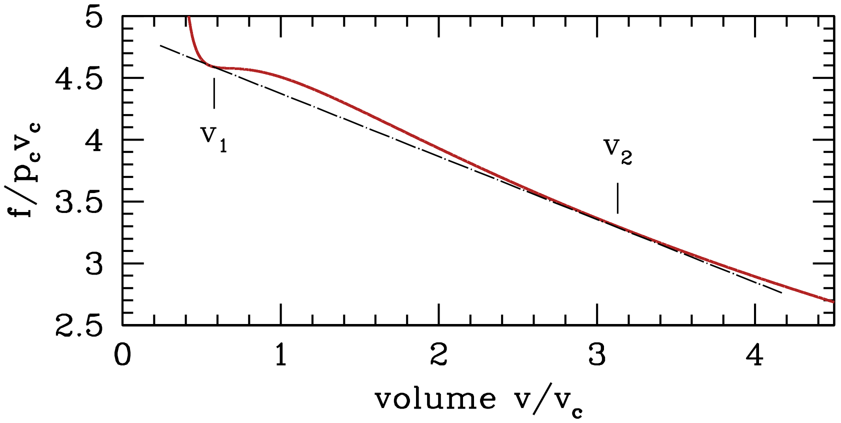

Figure 7.2: Molar free energy $f(T,v)$ of the van der Waals system $T = 0.85\,T_c$, with dot-dashed black line showing Maxwell construction connecting molar volumes $v_{1,2}$ on opposite sides of the coexistence curve.

This procedure is known as the *Maxwell construction*, and is depicted graphically in Fig. 7.3. When the Maxwell construction is enforced, the isotherms resemble the curves in Fig. 7.4. In this figure, all points within the purple shaded region have $\frac{\partial^2 f}{\partial v^2} < 0$, hence this region is unstable to infinitesimal fluctuations. The boundary of this region is called the *spinodal*, and the spontaneous phase separation into two phases is a process known as *spinodal decomposition*. The dot-dashed orange curve, called the *coexistence curve*, marks the instability boundary for *nucleation*. In a nucleation process, an energy barrier must be overcome in order to achieve the lower free energy state. There is no energy barrier for spinodal decomposition – it is a spontaneous process.

### 7.2.2 Analytic form of the coexistence curve near the critical point

We write $v_{\mathsf{L}} = v_{\mathsf{c}} + w_{\mathsf{L}}$ and $v_{\mathsf{G}} = v_{\mathsf{c}} + w_{\mathsf{G}}$. One of our equations is $p(v_{\mathsf{c}} + w_{\mathsf{L}}, T) = p(v_{\mathsf{c}} + w_{\mathsf{G}}, T)$. Taylor expanding in powers of $w_{\mathsf{L}}$ and $w_{\mathsf{G}}$, we have

$$0 = p_v(v_{\mathsf{c}},T)\,(w_{\mathsf{G}} - w_{\mathsf{L}}) + \tfrac{1}{2}\,p_{vv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^2 - w_{\mathsf{L}}^2\big) + \tfrac{1}{6}\,p_{vvv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^3 - w_{\mathsf{L}}^3\big) + \ldots\ , \tag{7.19}$$

where

$$p_v \equiv \frac{\partial p}{\partial v} \quad , \quad p_{vv} \equiv \frac{\partial^2 p}{\partial v^2} \quad , \quad p_{vvv} \equiv \frac{\partial^3 p}{\partial v^3} \quad , \quad p_{vT} \equiv \frac{\partial^2 p}{\partial v\,\partial T} \quad , \quad \text{etc.} \tag{7.20}$$

The second equation we write as

$$\int\limits_{w_{\mathsf{L}}}^{w_{\mathsf{G}}}\!\! dw\; p(v_{\mathsf{c}} + w, T) = \tfrac{1}{2}(w_{\mathsf{G}} - w_{\mathsf{L}})\Big(p(v_{\mathsf{c}} + w_{\mathsf{L}}, T) + p(v_{\mathsf{c}} + w_{\mathsf{G}}, T)\Big)\ . \tag{7.21}$$

Expanding in powers of $w_{\mathsf{L}}$ and $w_{\mathsf{G}}$, this becomes

$$\begin{aligned} p(v_{\mathsf{c}},T)\,(w_{\mathsf{G}} - w_{\mathsf{L}}) &+ \tfrac{1}{2}\,p_v(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^2 - w_{\mathsf{L}}^2\big) + \tfrac{1}{6}\,p_{vv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^3 - w_{\mathsf{L}}^3\big) \\ &+ \tfrac{1}{24}\,p_{vvv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^4 - w_{\mathsf{L}}^4\big) + \tfrac{1}{120}\,p_{vvvv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^5 - w_{\mathsf{L}}^5\big) + \ldots \\ &= \tfrac{1}{2}(w_{\mathsf{G}} - w_{\mathsf{L}})\Big\{2\,p(v_{\mathsf{c}},T) + p_v(v_{\mathsf{c}},T)\,(w_{\mathsf{G}} + w_{\mathsf{L}}) + \tfrac{1}{2}\,p_{vv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^2 + w_{\mathsf{L}}^2\big) \\ &\qquad + \tfrac{1}{6}\,p_{vvv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^3 + w_{\mathsf{L}}^3\big) + \tfrac{1}{24}\,p_{vvvv}(v_{\mathsf{c}},T)\,\big(w_{\mathsf{G}}^4 + w_{\mathsf{L}}^4\big) + \ldots\Big\} \end{aligned} \tag{7.22}$$

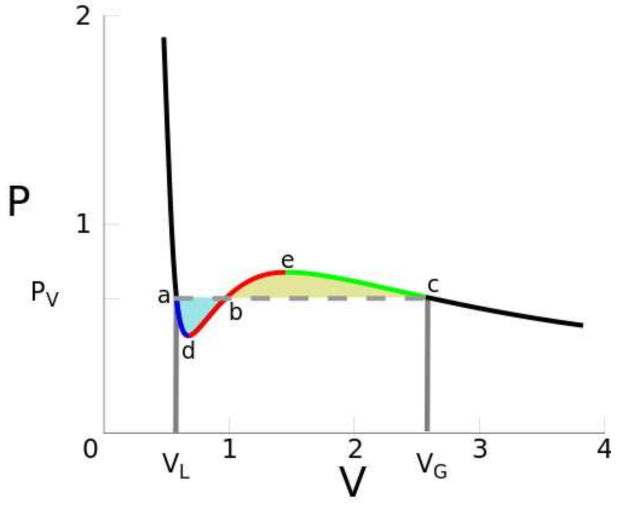

Figure 7.3: Maxwell construction in the $(v,p)$ plane. The system is absolutely unstable between volumes $v_\mathrm{d}$ and $v_\mathrm{e}$. For $v \in [v_\mathrm{a}, v_\mathrm{d}]$ of $v \in [v_\mathrm{e}, v_\mathrm{c}]$, the solution is unstable with respect to phase separation. Source: *Wikipedia*.

Subtracting the LHS from the RHS, we find that we can then divide by $\frac{1}{6}\big(w_\mathsf{G}^2 - w_\mathsf{L}^2\big)$, resulting in

$$0 = p_{vv}(v_\mathsf{c},T) + \tfrac{1}{2}\, p_{vvv}(v_\mathsf{c},T)\,(w_\mathsf{G} + w_\mathsf{L}) + \tfrac{1}{20}\, p_{vvvv}(v_\mathsf{c},T)\,\big(3w_\mathsf{G}^2 + 4w_\mathsf{G}w_\mathsf{L} + 3w_\mathsf{L}^2\big) + \mathcal{O}\big(w_{\mathsf{G},\mathsf{L}}^3\big)\ . \tag{7.23}$$

We now define $w_\pm \equiv w_\mathsf{G} \pm w_\mathsf{L}$. In terms of these variables, eqns. 7.19 and 7.23 become

$$0 = p_v(v_\mathsf{c},T) + \tfrac{1}{2}\, p_{vv}(v_\mathsf{c},T)\, w_+ + \tfrac{1}{8}\, p_{vvv}(v_\mathsf{c},T)\,\big(w_+^2 + \tfrac{1}{3}\, w_-^2\big) + \mathcal{O}\big(w_\pm^3\big) \tag{7.24}$$

$$0 = p_{vv}(v_\mathsf{c},T) + \tfrac{1}{2}\, p_{vvv}(v_\mathsf{c},T)\, w_+ + \tfrac{1}{8}\, p_{vvvv}(v_\mathsf{c},T)\,\big(w_+^2 + \tfrac{1}{5}\, w_-^2\big) + \mathcal{O}\big(w_\pm^3\big)\ . \tag{7.25}$$

We now evaluate $w_\pm$ to order $T$. Note that $p_v(v_\mathsf{c},T_\mathsf{c}) = p_{vv}(v_\mathsf{c},T_\mathsf{c}) = 0$, since the critical point is an inflection point in the $(v,p)$ plane. Thus, we have $p_v(v_\mathsf{c},T) = p_{vT}\,\Theta + \mathcal{O}(\Theta^2)$, where $T = T_\mathsf{c} + \Theta$ and $p_{vT} = p_{vT}(v_\mathsf{c},T_\mathsf{c})$. We can then see that $w_-$ is of leading order $\sqrt{-\Theta}$, while $w_+$ is of leading order $\Theta$. This allows us to write

$$0 = p_{vT}\,\Theta + \tfrac{1}{24}\, p_{vvv}\, w_-^2 + \mathcal{O}(\Theta^2) \tag{7.26}$$

$$0 = p_{vvT}\,\Theta + \tfrac{1}{2}\, p_{vvv}\, w_+ + \tfrac{1}{40}\, p_{vvvv}\, w_-^2 + \mathcal{O}(\Theta^2)\ . \tag{7.27}$$

Thus,

$$w_- = \bigg(\frac{24\,p_{vT}}{p_{vvv}}\bigg)^{1/2} \sqrt{-\Theta} + \ldots \tag{7.28}$$

$$w_+ = \bigg(\frac{6\,p_{vT}\,p_{vvvv} - 10\,p_{vvv}\,p_{vvT}}{5\,p_{vvv}^2}\bigg)\,\Theta + \ldots\ . \tag{7.29}$$

We then have

$$w_\mathsf{L} = -\bigg(\frac{6\,p_{vT}}{p_{vvv}}\bigg)^{1/2} \sqrt{-\Theta} + \bigg(\frac{3\,p_{vT}\,p_{vvvv} - 5\,p_{vvv}\,p_{vvT}}{5\,p_{vvv}^2}\bigg)\Theta + \mathcal{O}\big(\Theta^{3/2}\big) \tag{7.30}$$

$$w_\mathsf{G} = \bigg(\frac{6\,p_{vT}}{p_{vvv}}\bigg)^{1/2} \sqrt{-\Theta} + \bigg(\frac{3\,p_{vT}\,p_{vvvv} - 5\,p_{vvv}\,p_{vvT}}{5\,p_{vvv}^2}\bigg)\Theta + \mathcal{O}\big(\Theta^{3/2}\big)\ . \tag{7.31}$$

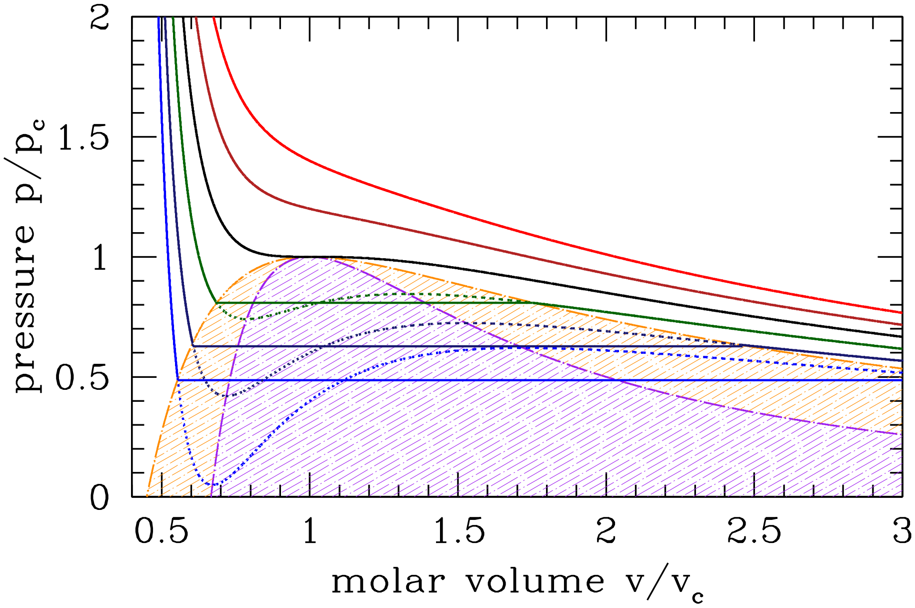

Figure 7.4: Pressure-volume isotherms for the van der Waals system, as in Fig. 7.1, but corrected to account for the Maxwell construction. The boundary of the purple shaded region is the spinodal line $\bar{p}^*(\bar{v})$. The boundary of the orange shaded region is the stability boundary with respect to phase separation.

Suppose we follow along an isotherm starting from the high molar volume (gas) phase. If $T > T_c$, the volume $v$ decreases continuously as the pressure $p$ increases. If $T < T_c$, then at the instant the isotherm first intersects the orange boundary curve in Fig. 7.4, there is a discontinuous change in the molar volume from high (gas) to low (liquid). This discontinuous change is the hallmark of a *first order phase transition*. Note that the volume discontinuity, $\Delta v = w_- \propto (T_c - T)^{1/2}$. This is an example of a *critical behavior* in which the *order parameter* $\phi$, which in this case may be taken to be the difference $\phi = v_G - v_L$, behaves as a power law in $\left|T - T_c\right|$, where $T_c$ is the *critical temperature*. In this case, we have $\phi(T) \propto (T_c - T)_+^\beta$, where $\beta = \frac{1}{2}$ is the exponent, and where $(T_c - T)_+$ is defined to be $T_c - T$ if $T < T_c$ and $0$ otherwise. The isothermal compressibility is $\kappa_T = -v/p_v(v, T)$. This is finite along the coexistence curve – it diverges only along the spinodal. It therefore diverges at the critical point, which lies at the intersection of the spinodal and the coexistence curve.

It is convenient to express the equation of state and the coexistence curve in terms of dimensionless variables. Write

$$\bar{p} = \frac{p}{p_c} \quad , \quad \bar{v} = \frac{v}{v_c} \quad , \quad \bar{T} = \frac{T}{T_c} \; . \tag{7.32}$$

The van der Waals equation of state then becomes

$$\bar{p} = \frac{8\bar{T}}{3\bar{v} - 1} - \frac{3}{\bar{v}^2} \; . \tag{7.33}$$

Further expressing these dimensionless quantities in terms of distance from the critical point, we write

$$\bar{p} = 1 + \pi \quad , \quad \bar{v} = 1 + \epsilon \quad , \quad \bar{T} = 1 + t \; . \tag{7.34}$$

Thus,

$$\pi(\epsilon, t) = \frac{8(1+t)}{2 + 3\epsilon} - \frac{3}{(1+\epsilon)^2} - 1 \; . \tag{7.35}$$

Note that the LHS and the RHS of this equation vanish identically for $(\pi, \epsilon, t) = (0, 0, 0)$. We can then write

$$\epsilon_{\mathsf{L,G}} = \mp\bigg(\frac{6\,\pi_{\epsilon t}}{\pi_{\epsilon\epsilon\epsilon}}\bigg)^{1/2} (-t)^{1/2} + \bigg(\frac{3\,\pi_{\epsilon t}\,\pi_{\epsilon\epsilon\epsilon\epsilon} - 5\,\pi_{\epsilon\epsilon\epsilon}\,\pi_{\epsilon\epsilon t}}{5\,\pi_{\epsilon\epsilon\epsilon}^2}\bigg) t + \mathcal{O}\big((-t)^{3/2}\big)\ . \tag{7.36}$$

### 7.2.3 History of the van der Waals equation

The van der Waals equation of state first appears in van der Waals' 1873 PhD thesis[3], *"Over de Continuïteit van den Gas - en Vloeistoftoestand"* ("On the continuity of the gas and liquid state"). In his Nobel lecture[4], van der Waals writes of how he was inspired by Rudolf Clausius' 1857 treatise on the nature of heat, where it is posited that a gas in fact consists of microscopic particles whizzing around at high velocities. van der Waals reasoned that liquids, which result when gases are compressed, also consist of 'small moving particles': *"Thus I conceived the idea that there is no essential difference between the gaseous and the liquid state of matter…"*

Clausius' treatise showed how his kinetic theory of heat was consistent with Boyle's law for gases ($pV = \text{constant}$ at fixed temperature). van der Waals pondered why this might fail for the non-dilute liquid phase, and he reasoned that there were two principal differences: inter-particle attraction and excluded volume. These considerations prompted him to posit his famous equation,

$$p = \frac{RT}{v-b} - \frac{a}{v^2}\ . \tag{7.37}$$

The first term on the RHS accounts for excluded volume effects, and the second for mutual attractions.

In the limiting case of $p \to \infty$, the molar volume approaches $v = b$. On physical grounds it seems that one should take $b = N_{\text{A}} \cdot 8v_0$, where $v_0$ is the molecular volume. The factor of eight arises from the hard core intermolecular potential effective for separations less than the molecular diameter (*i.e.* twice the molecular radius). Expanding in inverse powers of $v$, though,

$$p = \frac{RT}{v} + \bigg(b - \frac{a}{RT}\bigg) \cdot \frac{RT}{v^2} + \mathcal{O}\big(v^{-3}\big)\ , \tag{7.38}$$

and we read of the second virial coefficient $B_2 = \big(b - \frac{a}{RT}\big)/N_{\text{A}}$. But we have computed from the Mayer expansion that $B_2 = 4v_0$, so the naïve guess for $b$ is twice too large.

Another of van der Waals' great achievements was his articulation of the *law of corresponding states*. Recall that the van der Waals equation of state, when written in terms of dimensionless quantities $\bar{p} = p/p_{\text{c}}$, $\bar{v} = v/v_{\text{c}}$, and $\bar{T} = T/T_{\text{c}}$, takes the form of eqn. 7.33. Thus, while the $a$ and $b$ parameters are specific to each fluid – see Tab. 7.1 – when written in terms of these scaled dimensionless variables, the equation of state and all its consequent properties (*i.e.* the liquid-gas phase transition) are *universal*.

The van der Waals equation is best viewed as semi-phenomenological. Interaction and excluded volume effects surely are present, but the van der Waals equation itself only captures them in a very approximate way. It is applicable to gases, where it successfully predicts features that are not present in ideal systems (*e.g.* throttling). It is of only qualitative and pedagogical use in the study of fluids, the essential physics of which lies in the behavior of quantities like the pair distribution function $g(r)$. As we saw in chapter 6, any adequate first principles derivation of $g(r)$ - a function which can be measured in scattering experiments - involves rather complicated approximation schemes to close the BBGKY hierarchy. Else one must resort to numerical simulations such as the Monte Carlo method. Nevertheless, the lessons learned from the van der Waals system are invaluable and they provide us

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[3] Johannes Diderik van der Waals, the eldest of ten children, was the son of a carpenter. As a child he received only a primary school education. He worked for a living until age 25, and was able to enroll in a three-year industrial evening school for working class youth. Afterward he continued his studies independently, in his spare time, working as a teacher. By the time he obtained his PhD, he was 36 years old. He received the Nobel Prize for Physics in 1910.

[4] See http://www.nobelprize.org/nobel_prizes/physics/laureates/1910/waals-lecture.pdf

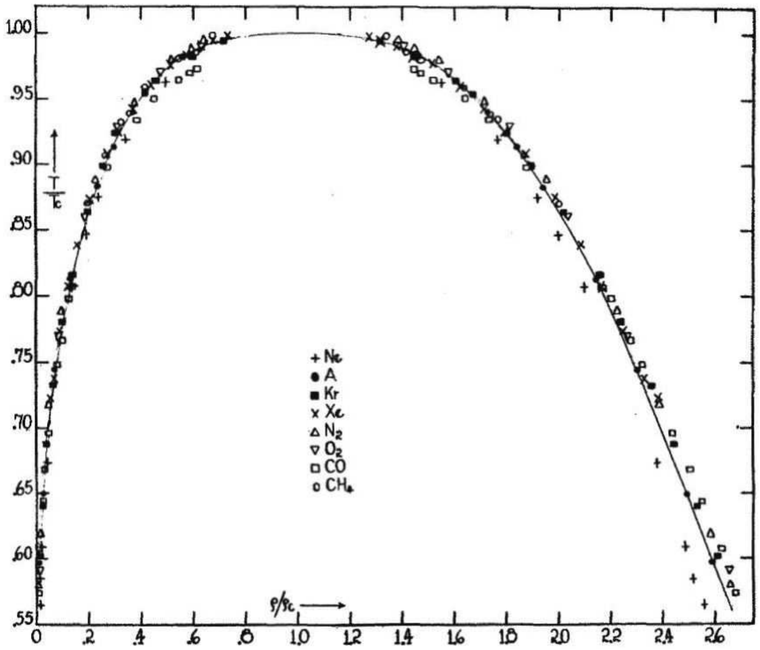

Figure 7.5: ‘Universality’ of the liquid-gas transition for eight different atomic and molecular fluids, from E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945). Dimensionless pressure $p/p_{\mathrm{c}}$ *versus* dimensionless density $\rho/\rho_{\mathrm{c}} = v_{\mathrm{c}}/v$ is shown. The van der Waals / mean field theory gives $\Delta v = v_{\mathrm{gas}} - v_{\mathrm{liquid}} \propto (-t)^{1/2}$, while experiments show a result closer to $\Delta v \propto (-t)^{1/3}$. Here $t \equiv \bar{T} - 1 = (T - T_{\mathrm{c}})/T_{\mathrm{c}}$ is the dimensionless temperature deviation with respect to the critical point.

with a first glimpse of what is going on in the vicinity of a phase transition, and how nonanalytic behavior, such as $v_{\mathsf{G}} - v_{\mathsf{L}} \propto (T_{\mathrm{c}} - T)^{\beta}$ with noninteger exponent $\beta$ may result due to singularities in the free energy at the critical point.

## 7.3 Fluids, Magnets, and the Ising Model

### 7.3.1 Lattice gas description of a fluid

The usual description of a fluid follows from a continuum Hamiltonian of the form

$$\hat{H}(\boldsymbol{p}, \boldsymbol{x}) = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j} u(\boldsymbol{x}_i - \boldsymbol{x}_j) \ . \tag{7.39}$$

The potential $u(\boldsymbol{r})$ is typically central, depending only on the magnitude $|\boldsymbol{r}|$, and short-ranged. Now consider a discretized version of the fluid, in which we divide up space into cells (cubes, say), each of which can accommodate at most one fluid particle (due to excluded volume effects). That is, each cube has a volume on the order of $a^3$, where $a$ is the diameter of the fluid particles. In a given cube $i$ we set the occupancy $n_i = 1$ if a fluid particle is present and $n_i = 0$ if there is no fluid particle present. We then have that the potential energy is

$$U = \sum_{i<j} u(\boldsymbol{x}_i - \boldsymbol{x}_j) = \tfrac{1}{2} \sum_{\boldsymbol{R} \neq \boldsymbol{R}'} V_{\boldsymbol{R}\boldsymbol{R}'} \, n_{\boldsymbol{R}} \, n_{\boldsymbol{R}'} \ , \tag{7.40}$$

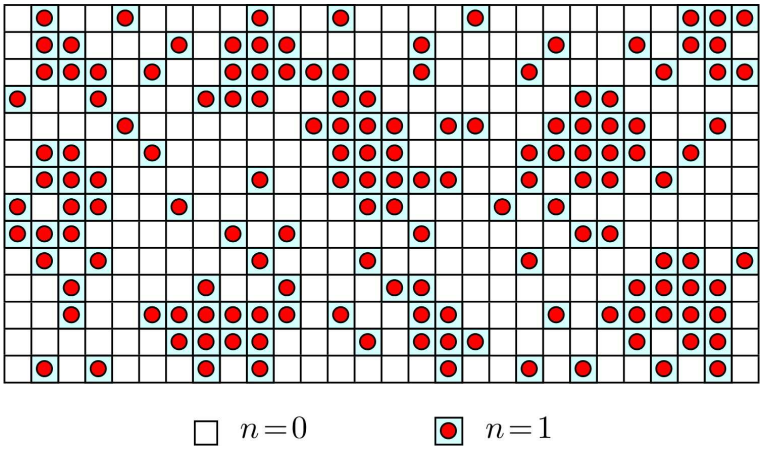

Figure 7.6: The lattice gas model. An occupied cell corresponds to $n = 1$ ($\sigma = +1$), and a vacant cell to $n = 0$ ($\sigma = -1$).

where $V_{\boldsymbol{R}\boldsymbol{R}'} \approx v(\boldsymbol{R} - \boldsymbol{R}')$, where $R_k$ is the position at the center of cube $k$. The grand partition function is then approximated as

$$\Xi(T, V, \mu) \approx \sum_{\{n_{\boldsymbol{R}}\}} \bigg( \prod_{\boldsymbol{R}} \xi^{n_{\boldsymbol{R}}} \bigg) \exp\bigg( -\tfrac{1}{2}\beta \sum_{\boldsymbol{R}\neq\boldsymbol{R}'} V_{\boldsymbol{R}\boldsymbol{R}'}\, n_{\boldsymbol{R}}\, n_{\boldsymbol{R}'} \bigg) , \tag{7.41}$$

where

$$\xi = e^{\beta\mu}\, \lambda_T^{-d}\, a^d , \tag{7.42}$$

where $a$ is the side length of each cube (chosen to be on the order of the hard sphere diameter). The $\lambda_T^{-d}$ factor arises from the integration over the momenta. Note $\sum_{\boldsymbol{R}} n_{\boldsymbol{R}} = N$ is the total number of fluid particles, so

$$\prod_{\boldsymbol{R}} \xi^{\, n_{\boldsymbol{R}}} = \xi^N = e^{\beta\mu N}\, \lambda_T^{-Nd}\, a^{Nd} . \tag{7.43}$$

Thus, we can write a lattice Hamiltonian,

$$\begin{aligned} \hat{H} &= \tfrac{1}{2} \sum_{\boldsymbol{R}\neq\boldsymbol{R}'} V_{\boldsymbol{R}\boldsymbol{R}'}\, n_{\boldsymbol{R}}\, n_{\boldsymbol{R}'} - k_{\mathrm{B}} T \ln \xi \sum_{\boldsymbol{R}} n_{\boldsymbol{R}} \\ &= -\tfrac{1}{2} \sum_{\boldsymbol{R}\neq\boldsymbol{R}'} J_{\boldsymbol{R}\boldsymbol{R}'}\, \sigma_{\boldsymbol{R}}\, \sigma_{\boldsymbol{R}'} - H \sum_{\boldsymbol{R}} \sigma_{\boldsymbol{R}} + E_0 , \end{aligned} \tag{7.44}$$

where $\sigma_{\boldsymbol{R}} \equiv 2n_{\boldsymbol{R}} - 1$ is a spin variable taking the possible values $\{-1, +1\}$, and

$$\begin{aligned} J_{\boldsymbol{R}\boldsymbol{R}'} &= -\tfrac{1}{4} V_{\boldsymbol{R}\boldsymbol{R}'} \\ H &= \tfrac{1}{2} k_{\mathrm{B}} T \ln \xi - \tfrac{1}{4} {\sum_{\boldsymbol{R}'}}' V_{\boldsymbol{R}\boldsymbol{R}'} , \end{aligned} \tag{7.45}$$

where the prime on the sum indicates that $\boldsymbol{R}' = \boldsymbol{R}$ is to be excluded. For the Lennard-Jones system, $V_{\boldsymbol{R}\boldsymbol{R}'} = v(\boldsymbol{R} - \boldsymbol{R}') < 0$ is due to the attractive tail of the potential, hence $J_{\boldsymbol{R}\boldsymbol{R}'}$ is positive, which prefers alignment of the spins $\sigma_{\boldsymbol{R}}$ and $\sigma_{\boldsymbol{R}'}$. This interaction is therefore *ferromagnetic*. The spin Hamiltonian in eqn. 7.44 is known as the Ising model.

### 7.3.2 Phase diagrams and critical exponents

The physics of the liquid-gas transition in fact has a great deal in common with that of the transition between a magnetized and unmagnetized state of a magnetic system. The correspondences are[5]

$$p \longleftrightarrow H \qquad , \qquad v \longleftrightarrow m \ ,$$

where $m$ is the magnetization density, defined here to be the total magnetization $M$ divided by the number of lattice sites $N_{\mathsf{s}}$:[6]

$$m = \frac{M}{N_{\mathsf{s}}} = \frac{1}{N_{\mathsf{s}}} \sum_{\boldsymbol{R}} \langle \sigma_{\boldsymbol{R}} \rangle \ . \tag{7.46}$$

Sketches of the phase diagrams are reproduced in fig. 7.7. Of particular interest is the *critical point*, which occurs at $(T_{\mathrm{c}}, p_{\mathrm{c}})$ in the fluid system and $(T_{\mathrm{c}}, H_{\mathrm{c}})$ in the magnetic system, with $H_{\mathrm{c}} = 0$ by symmetry.

In the fluid, the coexistence curve in the $(p, T)$ plane separates high density (liquid) and low density (vapor) phases. The specific volume $v$ (or the density $n = v^{-1}$) jumps discontinuously across the coexistence curve. In the magnet, the coexistence curve in the $(H, T)$ plane separates positive magnetization and negative magnetization phases. The magnetization density $m$ jumps discontinuously across the coexistence curve. For $T > T_{\mathrm{c}}$, the latter system is a *paramagnet*, in which the magnetization varies smoothly as a function of $H$. This behavior is most apparent in the bottom panel of the figure, where $v(p)$ and $m(H)$ curves are shown.

For $T < T_{\mathrm{c}}$, the fluid exists in a *two phase region*, which is spatially inhomogeneous, supporting local regions of high and low density. There is no stable homogeneous thermodynamic phase for $(T, v)$ within the two phase region shown in the middle left panel. Similarly, for the magnet, there is no stable homogeneous thermodynamic phase at fixed temperature $T$ and magnetization $m$ if $(T, m)$ lies within the coexistence region. Rather, the system consists of blobs where the spin is predominantly up, and blobs where the spin is predominantly down.

Note also the analogy between the isothermal compressibility $\kappa_T$ and the isothermal susceptibility $\chi_T$:

$$\kappa_T = -\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T \quad , \quad \kappa_T(T_{\mathrm{c}}, p_{\mathrm{c}}) = \infty$$

$$\chi_T = \left( \frac{\partial m}{\partial H} \right)_T \quad , \quad \chi_T(T_{\mathrm{c}}, H_{\mathrm{c}}) = \infty$$

The 'order parameter' for a second order phase transition is a quantity which vanishes in the disordered phase and is finite in the ordered phase. For the fluid, the order parameter can be chosen to be $\Psi \propto (v_{\mathrm{vap}} - v_{\mathrm{liq}})$, the difference in the specific volumes of the vapor and liquid phases. In the vicinity of the critical point, the system exhibits power law behavior in many physical quantities, *viz.*

$$\begin{aligned} m(T, H_{\mathrm{c}}) &\sim \big(T_{\mathrm{c}} - T\big)_{+}^{\beta} \\ \chi(T, H_{\mathrm{c}}) &\sim |T - T_{\mathrm{c}}|^{-\gamma} \\ C_M(T, H_{\mathrm{c}}) &\sim |T - T_{\mathrm{c}}|^{-\alpha} \\ m(T_{\mathrm{c}}, H) &\sim \pm |H|^{1/\delta} \ . \end{aligned} \tag{7.47}$$

---

[5] One could equally well identify the second correspondence as $n \longleftrightarrow m$ between density (rather than specific volume) and magnetization. One might object that $H$ is more properly analogous to $\mu$. However, since $\mu = \mu(p, T)$ it can equally be regarded as analogous to $p$. Note also that $\beta p = z \lambda_T^{-d}$ for the ideal gas, in which case $\xi = z(a/\lambda_T)^d$ is proportional to $p$.

[6] Note the distinction between the number of lattice sites $N_{\mathsf{s}}$ and the number of occupied cells $N$. According to our definitions, $N = \frac{1}{2}(M + N_{\mathsf{s}})$.

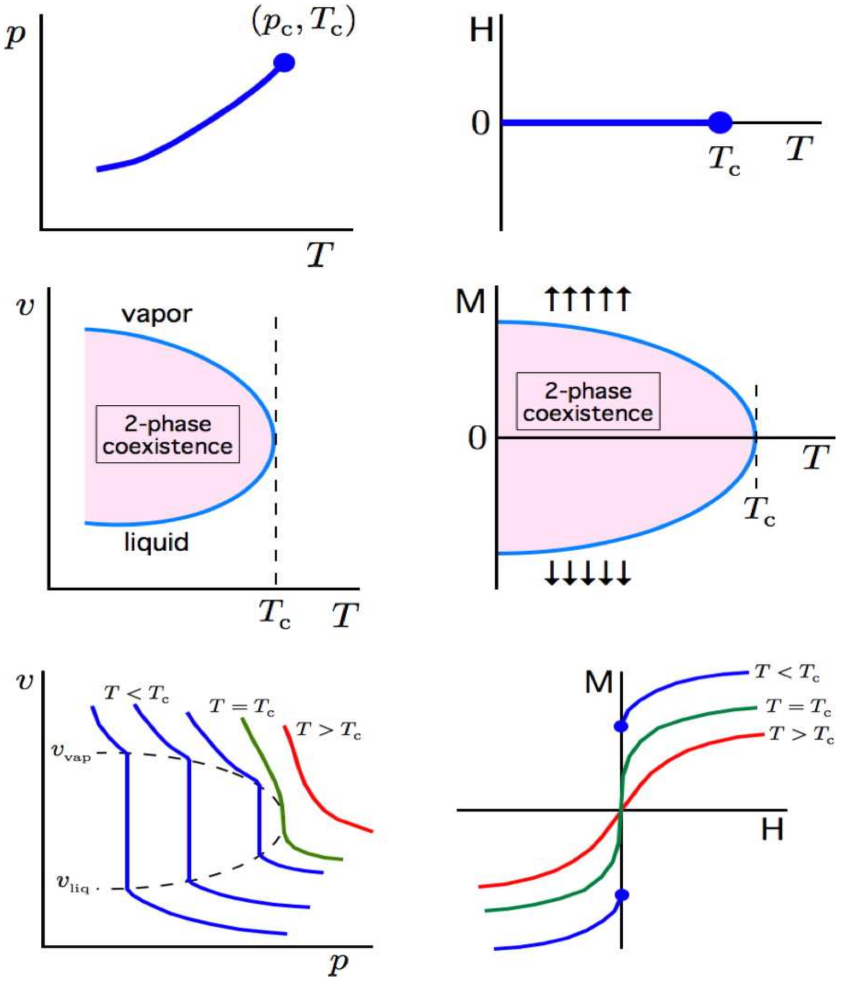

Figure 7.7: Comparison of the liquid-gas phase diagram with that of the Ising ferromagnet.

The quantities $\alpha$, $\beta$, $\gamma$, and $\delta$ are the *critical exponents* associated with the transition. These exponents satisfy certain equalities, such as the Rushbrooke and Griffiths relations and hyperscaling,[7]

$$\begin{aligned} \alpha + 2\beta + \gamma &= 2 \qquad \text{(Rushbrooke)} \\ \beta + \gamma &= \beta\delta \qquad \text{(Griffiths)} \\ 2 - \alpha &= d\,\nu \qquad \text{(hyperscaling)}\ . \end{aligned} \tag{7.48}$$

Originally such relations were derived as inequalities, and only after the advent of scaling and renormalization group theories it was realized that they held as equalities. We shall have much more to say about critical behavior later on, when we discuss scaling and renormalization.

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[7] In the third of the following exponent equalities, $d$ is the dimension of space and $\nu$ is the correlation length exponent.

### 7.3.3 Gibbs-Duhem relation for magnetic systems

Homogeneity of $E(S,M,N_{\mathsf{s}})$ means $E = TS + HM + \mu N_{\mathsf{s}}$, and, after invoking the First Law $dE = T\,dS + H\,dM + \mu\,dN_{\mathsf{s}}$, we have

$$S\,dT + M\,dH + N_{\mathsf{s}} d\mu = 0 \; . \tag{7.49}$$

Now consider two magnetic phases in coexistence. We must have $d\mu_1 = d\mu_2$, hence

$$d\mu_1 = -s_1\,dT - m_1\,dH = -s_2\,dT - m_2\,dH = d\mu_2 \; , \tag{7.50}$$

where $m = M/N_{\mathsf{s}}$ is the magnetization per site and $s = S/N_{\mathsf{s}}$ is the specific entropy. Thus, we obtain the Clapeyron equation for magnetic systems,

$$\bigg(\frac{dH}{dT}\bigg)_{\rm coex} = -\frac{s_1 - s_2}{m_1 - m_2} \; . \tag{7.51}$$

Thus, if $m_1 \neq m_2$ and $\big(\frac{dH}{dT}\big)_{\rm coex} = 0$, then we must have $s_1 = s_2$, which says that there is *no latent heat associated with the transition*. This absence of latent heat is a consequence of the *symmetry* which guarantees that $F(T,H,N_{\mathsf{s}}) = F(T,-H,N_{\mathsf{s}})$.

### 7.3.4 Order-disorder transitions

Another application of the Ising model lies in the theory of order-disorder transitions in alloys. Examples include Cu$_3$Au, CuZn, and other compounds. In CuZn, the Cu and Zn atoms occupy sites of a body centered cubic (BCC) lattice, forming an alloy known as $\beta$-brass. Below $T_{\rm c} \simeq 740\,{\rm K}$, the atoms are ordered, with the Cu preferentially occupying one simple cubic sublattice and the Zn preferentially occupying the other.

The energy is a sum of pairwise interactions, with a given link contributing $\varepsilon_{\rm AA}$, $\varepsilon_{\rm BB}$, or $\varepsilon_{\rm AB}$, depending on whether it is an A-A, B-B, or A-B/B-A link. Here A and B represent Cu and Zn, respectively. Thus, we can write the energy of the link $\langle ij \rangle$ as

$$E_{ij} = \varepsilon_{\rm AA}\, P^{\rm A}_i\, P^{\rm A}_j + \varepsilon_{\rm BB}\, P^{\rm B}_i\, P^{\rm B}_j + \varepsilon_{\rm AB}\left(P^{\rm A}_i\, P^{\rm B}_j + P^{\rm B}_i\, P^{\rm A}_j\right) , \tag{7.52}$$

where

$$P^{\rm A}_i = \tfrac{1}{2}(1+\sigma_i) = \begin{cases} 1 & \text{if site } i \text{ contains Cu} \\ 0 & \text{if site } i \text{ contains Zn} \end{cases}$$

$$P^{\rm B}_i = \tfrac{1}{2}(1-\sigma_i) = \begin{cases} 1 & \text{if site } i \text{ contains Zn} \\ 0 & \text{if site } i \text{ contains Cu} \; . \end{cases}$$

The Hamiltonian is then

$$\begin{aligned} \hat{H} &= \sum_{\langle ij \rangle} E_{ij} \\ &= \sum_{\langle ij \rangle} \Big\{ \tfrac{1}{4}\big(\varepsilon_{\rm AA} + \varepsilon_{\rm BB} - 2\varepsilon_{\rm AB}\big)\,\sigma_i\,\sigma_j + \tfrac{1}{4}\big(\varepsilon_{\rm AA} - \varepsilon_{\rm BB}\big)\,(\sigma_i + \sigma_j) + \tfrac{1}{4}\big(\varepsilon_{\rm AA} + \varepsilon_{\rm BB} + 2\varepsilon_{\rm AB}\big) \Big\} \\ &= -J \sum_{\langle ij \rangle} \sigma_i\,\sigma_j - H \sum_i \sigma_i + E_0 \; , \end{aligned} \tag{7.53}$$

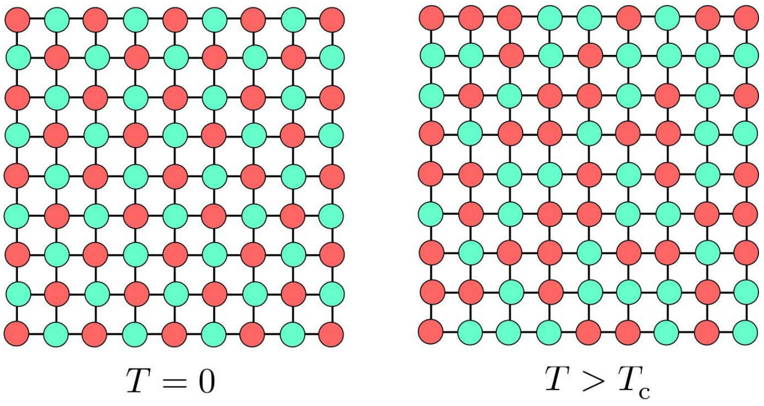

Figure 7.8: Order-disorder transition on the square lattice. Below $T = T_c$, order develops spontaneously on the two $\sqrt{2} \times \sqrt{2}$ sublattices. There is perfect sublattice order at $T = 0$ (left panel).

where the exchange constant $J$ and the magnetic field $H$ are given by

$$\begin{aligned} J &= \tfrac{1}{4}\big(2\varepsilon_{\rm AB} - \varepsilon_{\rm AA} - \varepsilon_{\rm BB}\big) \\ H &= \tfrac{1}{4}\big(\varepsilon_{\rm BB} - \varepsilon_{\rm AA}\big) \ , \end{aligned} \tag{7.54}$$

and $E_0 = \frac{1}{8}Nz\big(\varepsilon_{\rm AA} + \varepsilon_{\rm BB} + 2\varepsilon_{\rm AB}\big)$, where $N$ is the total number of lattice sites and $z = 8$ is the *lattice coordination number*, which is the number of nearest neighbors of any given site.

Note that

$$\begin{aligned} 2\varepsilon_{\rm AB} > \varepsilon_{\rm AA} + \varepsilon_{\rm BB} \quad &\Longrightarrow \quad J > 0 \quad \text{(ferromagnetic)} \\ 2\varepsilon_{\rm AB} < \varepsilon_{\rm AA} + \varepsilon_{\rm BB} \quad &\Longrightarrow \quad J < 0 \quad \text{(antiferromagnetic)} \ . \end{aligned} \tag{7.55}$$

The antiferromagnetic case is depicted in fig. 7.8.

## 7.4 Mean Field Theory

Consider the Ising model Hamiltonian,

$$\hat{H} = -J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j - H \sum_i \sigma_i \ , \tag{7.56}$$

where the first sum on the RHS is over all links of the lattice. Each spin can be either 'up' ($\sigma = +1$) or 'down' ($\sigma = -1$). We further assume that the spins are located on a Bravais lattice[8] and that the coupling $J_{ij} = J\big(|\boldsymbol{R}_i - \boldsymbol{R}_j|\big)$, where $\boldsymbol{R}_i$ is the position of the $i^{\rm th}$ spin.

On each site $i$ we decompose $\sigma_i$ into a contribution from its thermodynamic average and a fluctuation term, *i.e.*

$$\sigma_i = \langle \sigma_i \rangle + \delta\sigma_i \ . \tag{7.57}$$

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[8] A Bravais lattice is one in which any site is equivalent to any other site through an appropriate discrete translation. Examples of Bravais lattices include the linear chain, square, triangular, simple cubic, face-centered cubic, *etc.* lattices. The honeycomb lattice is not a Bravais lattice, because there are two sets of inequivalent sites – those in the center of a Y and those in the center of an upside down Y.

We will write $\langle\sigma_i\rangle \equiv m$, the local magnetization (dimensionless), and assume that $m$ is independent of position $i$. Then

$$\begin{aligned}\sigma_i\,\sigma_j &= (m+\delta\sigma_i)\,(m+\delta\sigma_j)\\ &= m^2 + m\,(\delta\sigma_i+\delta\sigma_j) + \delta\sigma_i\,\delta\sigma_j\\ &= -m^2 + m\,(\sigma_i+\sigma_j) + \delta\sigma_i\,\delta\sigma_j\ .\end{aligned} \tag{7.58}$$

The last term on the RHS of the second equation above is quadratic in the fluctuations, and we assume this to be negligibly small. Thus, we obtain the *mean field Hamiltonian*

$$\hat{H}_{\text{MF}} = \tfrac{1}{2}NzJ\,m^2 - \big(H+zJm\big)\sum_i \sigma_i\ , \tag{7.59}$$

where $N$ is the total number of lattice sites. The first term is a constant, although the value of $m$ is yet to be determined. The Boltzmann weights are then completely determined by the second term, which is just what we would write down for a Hamiltonian of *noninteracting* spins in an effective 'mean field'

$$H_{\text{eff}} = H + zJm\ . \tag{7.60}$$

In other words, $H_{\text{eff}} = H_{\text{ext}} + H_{\text{int}}$, where the external field is applied field $H_{\text{ext}} = H$, and the 'internal field' is $H_{\text{int}} = zJm$. The internal field accounts for the interaction with the *average* values of all other spins coupled to a spin at a given site, hence it is often called the 'mean field'. Since the spins are noninteracting, we have

$$m = \frac{e^{\beta H_{\text{eff}}} - e^{-\beta H_{\text{eff}}}}{e^{\beta H_{\text{eff}}} + e^{-\beta H_{\text{eff}}}} = \tanh\!\bigg(\frac{H+zJm}{k_{\text{B}}T}\bigg)\ . \tag{7.61}$$

It is a simple matter to solve for the free energy, given the noninteracting Hamiltonian $\hat{H}_{\text{MF}}$. The partition function is

$$Z = \mathsf{Tr}\ e^{-\beta\hat{H}_{\text{MF}}} = e^{-\frac{1}{2}\beta NzJ\,m^2}\bigg(\sum_\sigma e^{\beta(H+zJm)\sigma}\bigg)^{N} = e^{-\beta F}\ . \tag{7.62}$$

We now define dimensionless variables:

$$f \equiv \frac{F}{NzJ} \qquad , \qquad \theta \equiv \frac{k_{\text{B}}T}{zJ} \qquad , \qquad h \equiv \frac{H}{zJ}\ , \tag{7.63}$$

and obtain the dimensionless free energy

$$f(m,h,\theta) = \tfrac{1}{2}m^2 - \theta\,\ln\Big(e^{(m+h)/\theta} + e^{-(m+h)/\theta}\Big)\ . \tag{7.64}$$

Differentiating with respect to $m$ gives the mean field equation,

$$m = \tanh\Big(\frac{m+h}{\theta}\Big)\ , \tag{7.65}$$

which is equivalent to the self-consistency requirement, $m = \langle\sigma_i\rangle$.

### 7.4.1 $h = 0$

When $h = 0$ the mean field equation becomes

$$m = \tanh\Big(\frac{m}{\theta}\Big)\ . \tag{7.66}$$

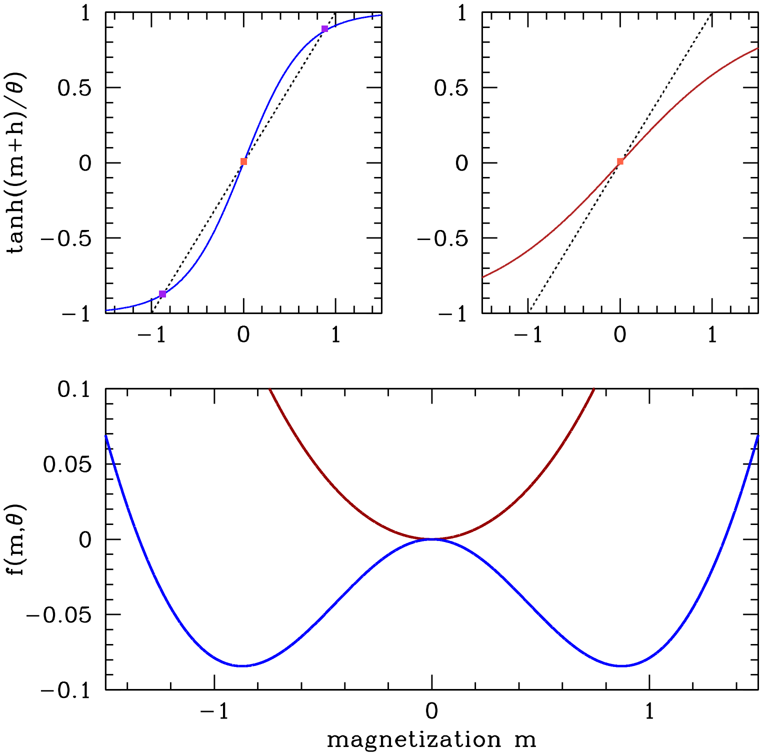

Figure 7.9: Results for $h = 0$. Upper panels: graphical solution to self-consistency equation $m = \tanh(m/\theta)$ at temperatures $\theta = 0.65$ (blue) and $\theta = 1.5$ (dark red). Lower panel: mean field free energy, with energy shifted by $\theta \ln 2$ so that $f(m = 0, \theta) = 0$.

This nonlinear equation can be solved graphically, as in the top panel of fig. 7.9. The RHS in a tanh function which gets steeper with decreasing $t$. If, at $m = 0$, the slope of $\tanh(m/\theta)$ is smaller than unity, then the curve $y = \tanh(m/h)$ will intersect $y = m$ only at $m = 0$. However, if the slope is larger than unity, there will be three such intersections. Since the slope is $1/\theta$, we identify $\theta_c = 1$ as the *mean field transition temperature*.

In the low temperature phase $\theta < 1$, there are three solutions to the mean field equations. One solution is always at $m = 0$. The other two solutions must be related by the $m \leftrightarrow -m$ symmetry of the free energy (when $h = 0$). The exact free energies are plotted in the bottom panel of fig. 7.9, but it is possible to make analytical progress by assuming $m$ is small and Taylor expanding the free energy $f(m, \theta)$ in powers of $m$:

$$\begin{aligned} f(m,\theta) &= \tfrac{1}{2} m^2 - \theta \ln 2 - \theta \, \ln\cosh\left(\frac{m}{\theta}\right) \\ &= -\theta \, \ln 2 + \tfrac{1}{2} \left(1 - \theta^{-1}\right) m^2 + \frac{m^4}{12\,\theta^3} - \frac{m^6}{45\,\theta^5} + \ldots \; . \end{aligned} \tag{7.67}$$

Note that the sign of the quadratic term is positive for $\theta > 1$ and negative for $\theta < 1$. Thus, the shape of the free energy $f(m, \theta)$ as a function of $m$ qualitatively changes at this point, $\theta_c = 1$, the mean field transition temperature, also known as the *critical temperature*.

For $\theta > \theta_c$, the free energy $f(m, \theta)$ has a single minimum at $m = 0$. Below $\theta_c$, the curvature at $m = 0$ reverses, and $m = 0$ becomes a local maximum. There are then two equivalent minima symmetrically displaced on either side of $m = 0$. Differentiating with respect to $m$, we find these local minima. For $\theta < \theta_c$, the local minima are found at

$$m^2 = 3\theta^2(1 - \theta) = 3(1 - \theta) + \mathcal{O}\big((1 - \theta)^2\big) \; . \tag{7.68}$$

Thus, we find for $|\theta - 1| \ll 1$,

$$m(\theta, h=0) = \pm\sqrt{3}\,\big(1-\theta\big)^{1/2}_{+} \ , \tag{7.69}$$

where the $+$ subscript indicates that this solution is only for $1-\theta > 0$. For $\theta > 1$ the only solution is $m = 0$. The exponent with which $m(\theta)$ vanishes as $\theta \to \theta_{\rm c}^{-}$ is denoted $\beta$. *I.e.* $m(\theta, h=0) \propto (\theta_{\rm c} - \theta)^{\beta}_{+}$.

### 7.4.2 Specific heat

We can now expand the free energy $f(\theta, h=0)$. We find

$$f(\theta, h=0) = \begin{cases} -\theta \ln 2 & \text{if } \theta > \theta_{\rm c} \\ -\theta \ln 2 - \frac{3}{4}(1-\theta)^2 + \mathcal{O}\big((1-\theta)^4\big) & \text{if } \theta < \theta_{\rm c} \ . \end{cases} \tag{7.70}$$

Thus, if we compute the heat capacity, we find in the vicinity of $\theta = \theta_{\rm c}$

$$c_V = -\theta\,\frac{\partial^2 f}{\partial \theta^2} = \begin{cases} 0 & \text{if } \theta > \theta_{\rm c} \\ \frac{3}{2} & \text{if } \theta < \theta_{\rm c} \ . \end{cases} \tag{7.71}$$

Thus, the specific heat is *discontinuous* at $\theta = \theta_{\rm c}$. We emphasize that this is only valid near $\theta = \theta_{\rm c} = 1$. The general result valid for all $\theta$ is[9]

$$c_V(\theta) = \frac{1}{\theta} \cdot \frac{m^2(\theta) - m^4(\theta)}{\theta - 1 + m^2(\theta)} \ , \tag{7.72}$$

With this expression one can check both limits $\theta \to 0$ and $\theta \to \theta_{\rm c}$. As $\theta \to 0$ the magnetization saturates and one has $m^2(\theta) \simeq 1 - 4\,e^{-2/\theta}$. The numerator then vanishes as $e^{-2/\theta}$, which overwhelms the denominator that itself vanishes as $\theta^2$. As a result, $c_V(\theta \to 0) = 0$, as expected. As $\theta \to 1$, invoking $m^2 \simeq 3(1-\theta)$ we recover $c_V(\theta_{\rm c}^{-}) = \frac{3}{2}$.

In the theory of critical phenomena, $c_V(\theta) \propto |\theta - \theta_{\rm c}|^{-\alpha}$ as $\theta \to \theta_{\rm c}$. We see that mean field theory yields $\alpha = 0$.

### 7.4.3 $h \neq 0$

Consider without loss of generality the case $h > 0$. The minimum of the free energy $f(m, h, \theta)$ now lies at $m > 0$ for any $\theta$. At low temperatures, the double well structure we found in the $h = 0$ case is tilted so that the right well lies lower in energy than the left well. This is depicted in fig. 7.10. As the temperature is raised, the local minimum at $m < 0$ vanishes, annihilating with the local maximum in a saddle-node bifurcation. To find where this happens, one sets $\frac{\partial f}{\partial m} = 0$ and $\frac{\partial^2 f}{\partial m^2} = 0$ simultaneously, resulting in

$$h^*(\theta) = \sqrt{1-\theta} - \frac{\theta}{2} \ln\!\left(\frac{1+\sqrt{1-\theta}}{1-\sqrt{1-\theta}}\right). \tag{7.73}$$

The solutions lie at $h = \pm h^*(\theta)$. For $\theta < \theta_{\rm c} = 1$ and $h \in \big[-h^*(\theta)\,,\,+h^*(\theta)\big]$, there are three solutions to the mean field equation. Equivalently we could in principle invert the above expression to obtain $\theta^*(h)$. For $\theta > \theta^*(h)$, there is only a single global minimum in the free energy $f(m)$ and there is no local minimum. Note $\theta^*(h=0) = 1$.

Assuming $h \ll |\theta - 1| \ll 1$, the mean field solution for $m(\theta, h)$ will also be small, and we expand the free energy in $m$, and to linear order in $h$:

$$\begin{aligned} f(m, h, \theta) &= -\theta\,\ln 2 + \tfrac{1}{2}(1-\theta^{-1})\,m^2 + \frac{m^4}{12\,\theta^3} - \frac{hm}{\theta} \\ &= f_0 + \tfrac{1}{2}\,(\theta - 1)\,m^2 + \tfrac{1}{12} m^4 - hm + \ldots \ . \end{aligned} \tag{7.74}$$

---

[9] To obtain this result, one writes $f = f\big(\theta, m(\theta)\big)$ and then differentiates twice with respect to $\theta$, using the chain rule. Along the way, any naked (*i.e.* undifferentiated) term proportional to $\frac{\partial f}{\partial m}$ may be dropped, since this vanishes at any $\theta$ by the mean field equation.

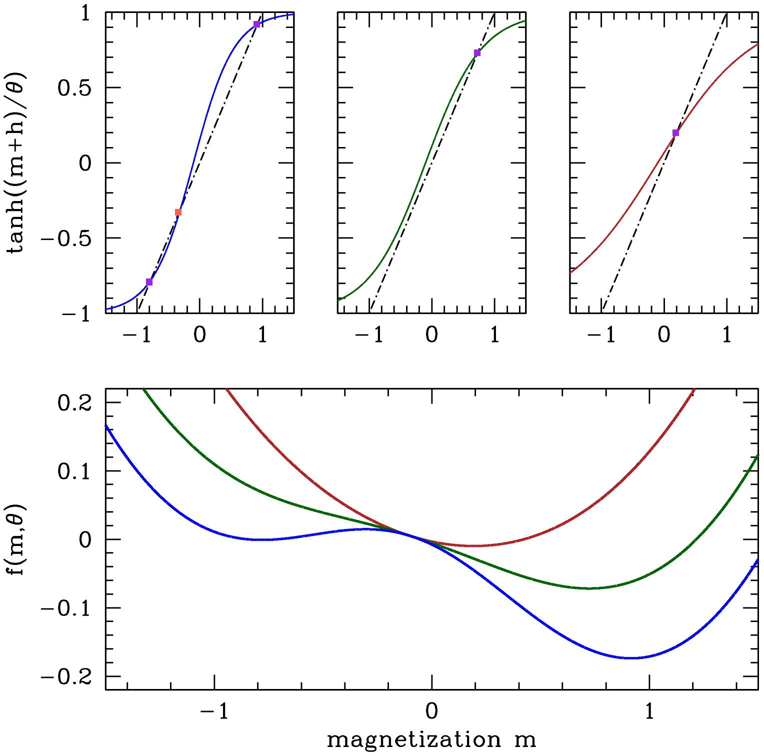

Figure 7.10: Results for $h = 0.1$. Upper panels: graphical solution to self-consistency equation $m = \tanh\big((m+h)/\theta\big)$ at temperatures $\theta = 0.65$ (blue), $\theta = 0.9$ (dark green), and $\theta = 1.5$ (dark red). Lower panel: mean field free energy, with energy shifted by $\theta \ln 2$ so that $f(m = 0, \theta) = 0$.

Setting $\frac{\partial f}{\partial m} = 0$, we obtain

$$\tfrac{1}{3} m^3 + (\theta - 1) \cdot m - h = 0\ . \tag{7.75}$$

If $\theta > 1$ then we have a solution $m = h/(\theta - 1)$. The $m^3$ term can be ignored because it is higher order in $h$, and we have assumed $h \ll |\theta - 1| \ll 1$. This is known as the *Curie-Weiss law*[10]. The magnetic susceptibility behaves as

$$\chi(\theta) = \frac{\partial m}{\partial h} = \frac{1}{\theta - 1} \propto |\theta - 1|^{-\gamma}\ , \tag{7.76}$$

where the magnetization critical exponent $\gamma$ is $\gamma = 1$. If $\theta < 1$ then while there is still a solution at $m = h/(\theta - 1)$, it lies at a local maximum of the free energy, as shown in fig. 7.10. The minimum of the free energy occurs close to the $h = 0$ solution $m = m_0(\theta) \equiv \sqrt{3}\,(1 - \theta)$, and writing $m = m_0 + \delta m$ we find $\delta m$ to linear order in $h$ as $\delta m(\theta, h) = h/2(1 - \theta)$. Thus,

$$m(\theta, h) = \sqrt{3}\,(1 - \theta) + \frac{h}{2(1 - \theta)}\ . \tag{7.77}$$

---

[10] Pierre Curie was a pioneer in the fields of crystallography, magnetism, and radiation physics. In 1880, Pierre and his older brother Jacques discovered piezoelectricity. He was 21 years old at the time. It was in 1895 that Pierre made the first systematic studies of the effects of temperature on magnetic materials, and he formulated what is known as *Curie's Law*, $\chi = C/T$, where $C$ is a constant. Curie married Marie Sklodowska in the same year. Their research turned toward radiation, recently discovered by Becquerel and Röntgen. In 1898, Pierre and Marie Curie discovered radium. They shared the 1903 Nobel Prize in Physics with Becquerel. Marie went on to win the 1911 Nobel Prize in Chemistry and was the first person ever awarded two Nobel Prizes. Their daughter Irène Joliot Curie shared the 1935 Prize in Chemistry (with her husband), also for work on radioactivity. Pierre Curie met an untimely and unfortunate end in the Spring of 1906. Walking across the Place Dauphine, he slipped and fell under a heavy horse-drawn wagon carrying military uniforms. His skull was crushed by one of the wagon wheels, killing him instantly. Later on that year, Pierre-Ernest Weiss proposed a modification of Curie's Law to account for ferromagnetism. This became known as the Curie-Weiss law, $\chi = C/(T - T_c)$.

| Exponent | MFT | 2D Ising (exact) | 3D Ising (numerical) | $CO_2$ (expt.) |
|---|---|---|---|---|
| $\alpha$ | 0 | 0 | 0.125 | $\lesssim 0.1$ |
| $\beta$ | 1/2 | 1/8 | 0.313 | 0.35 |
| $\gamma$ | 1 | 7/4 | 1.25 | 1.26 |
| $\delta$ | 3 | 15 | 5 | 4.2 |

Table 7.2: Critical exponents from mean field theory as compared with exact results for the two-dimensional Ising model, numerical results for the three-dimensional Ising model, and experiments on the liquid-gas transition in $CO_2$. *Source*: H. E. Stanley, *Phase Transitions and Critical Phenomena*.

Once again, we find that $\chi(\theta)$ diverges as $|\theta - 1|^{-\gamma}$ with $\gamma = 1$. The exponent $\gamma$ on either side of the transition is the same.

Finally, we can set $\theta = \theta_c$ and examine $m(h)$. We find, from eqn. 7.76,

$$m(\theta = \theta_c, h) = (3h)^{1/3} \propto h^{1/\delta} , \tag{7.78}$$

where $\delta$ is a new critical exponent. Mean field theory gives $\delta = 3$. Note that at $\theta = \theta_c = 1$ we have $m = \tanh(m+h)$, and inverting we find

$$h(m, \theta = \theta_c) = \tfrac{1}{2} \ln\left(\frac{1+m}{1-m}\right) - m = \frac{m^3}{3} + \frac{m^5}{5} + \ldots , \tag{7.79}$$

which is consistent with what we just found for $m(h, \theta = \theta_c)$.

How well does mean field theory do in describing the phase transition of the Ising model? In table 7.2 we compare our mean field results for the exponents $\alpha$, $\beta$, $\gamma$, and $\delta$ with exact values for the two-dimensional Ising model, numerical work on the three-dimensional Ising model, and experiments on the liquid-gas transition in $CO_2$. The first thing to note is that the exponents are dependent on the dimension of space, and this is something that mean field theory completely misses. In fact, it turns out that the mean field exponents are exact provided $d > d_u$, where $d_u$ is the *upper critical dimension* of the theory. For the Ising model, $d_u = 4$, and above four dimensions (which is of course unphysical) the mean field exponents are in fact exact. We see that all in all the MFT results compare better with the three dimensional exponent values than with the two-dimensional ones – this makes sense since MFT does better in higher dimensions. The reason for this is that higher dimensions means more nearest neighbors, which has the effect of reducing the relative importance of the fluctuations we neglected to include.

### 7.4.4 Magnetization dynamics

Dissipative processes drive physical systems to minimum energy states. We can crudely model the dissipative dynamics of a magnet by writing the phenomenological equation

$$\frac{dm}{ds} = -\frac{\partial f}{\partial m} , \tag{7.80}$$

where $s$ is a dimensionless time variable. Under these dynamics, the free energy is never increasing:

$$\frac{df}{ds} = \frac{\partial f}{\partial m} \frac{\partial m}{\partial s} = -\left(\frac{\partial f}{\partial m}\right)^2 \leq 0 . \tag{7.81}$$

Clearly the *fixed point* of these dynamics, where $\dot{m} = 0$, is a solution to the mean field equation $\frac{\partial f}{\partial m} = 0$.

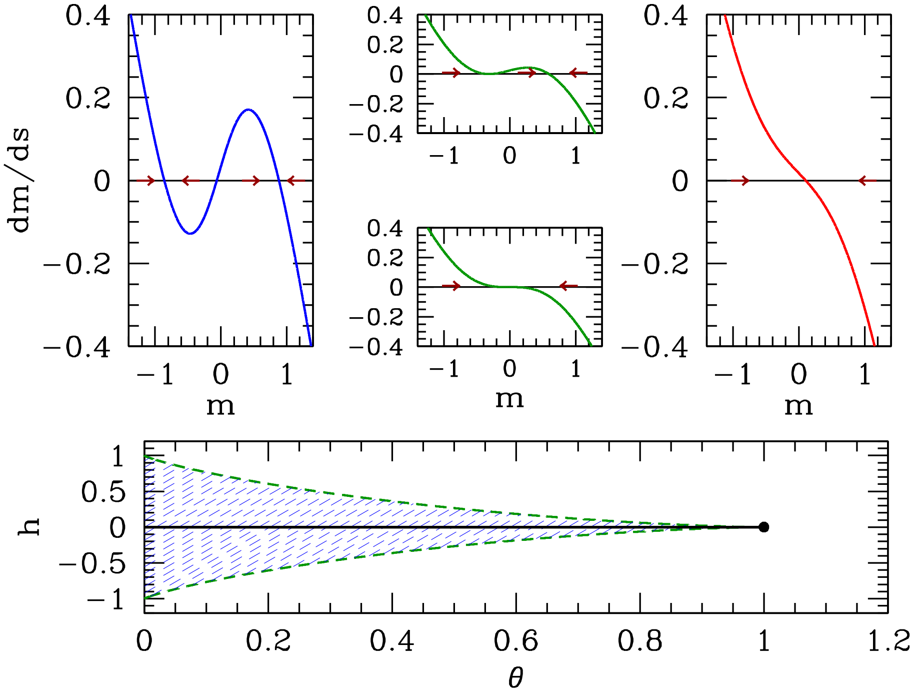

Figure 7.11: Dissipative magnetization dynamics $\dot{m} = -f'(m)$. Bottom panel shows $h^*(\theta)$ from eqn. 7.73. For $(\theta, h)$ within the blue shaded region, the free energy $f(m)$ has a global minimum plus a local minimum and a local maximum. Otherwise $f(m)$ has only a single global minimum. Top panels show an imperfect bifurcation in the magnetization dynamics at $h = 0.0215$ , for which $\theta^* = 0.90$. Temperatures shown: $\theta = 0.65$ (blue), $\theta = \theta^*(h) = 0.90$ (green), and $\theta = 1.2$. The rightmost stable fixed point corresponds to the global minimum of the free energy. The bottom of the middle two upper panels shows $h = 0$, where both of the attractive fixed points and the repulsive fixed point coalesce into a single attractive fixed point (supercritical pitchfork bifurcation).

The phase flow for the equation $\dot{m} = -f'(m)$ is shown in fig. 7.11. As we have seen, for any value of $h$ there is a temperature $\theta^*$ below which the free energy $f(m)$ has two local minima and one local maximum. When $h = 0$ the minima are degenerate, but at finite $h$ one of the minima is a global minimum. Thus, for $\theta < \theta^*(h)$ there are three solutions to the mean field equations. In the language of dynamical systems, under the dynamics of eqn. 7.80, minima of $f(m)$ correspond to attractive fixed points and maxima to repulsive fixed points. If $h > 0$, the rightmost of these fixed points corresponds to the global minimum of the free energy. As $\theta$ is increased, this fixed point evolves smoothly. At $\theta = \theta^*$, the (metastable) local minimum and the local maximum coalesce and annihilate in a saddle-note bifurcation. However at $h = 0$ all three fixed points coalesce at $\theta = \theta_c$ and the bifurcation is a supercritical pitchfork. As a function of $t$ at finite $h$, the dynamics are said to exhibit an *imperfect bifurcation*, which is a deformed supercritical pitchfork.

The solution set for the mean field equation is simply expressed by inverting the tanh function to obtain $h(\theta, m)$. One readily finds

$$h(\theta, m) = \frac{\theta}{2} \ln\!\left(\frac{1+m}{1-m}\right) - m \, . \tag{7.82}$$

As we see in the bottom panel of fig. 7.12, $m(h)$ becomes multivalued for $h \in \big[-h^*(\theta)\,,\,+h^*(\theta)\big]$, where $h^*(\theta)$ is given in eqn. 7.73. Now imagine that $\theta < \theta_c$ and we slowly ramp the field $h$ from a large negative value to a large positive value, and then slowly back down to its original value. On the time scale of the magnetization dynamics, we can regard $h(s)$ as a constant. (Remember the time variable is $s$ here.) Thus, $m(s)$ will flow to the nearest stable fixed point. Initially the system starts with $m = -1$ and $h$ large and negative, and there is only

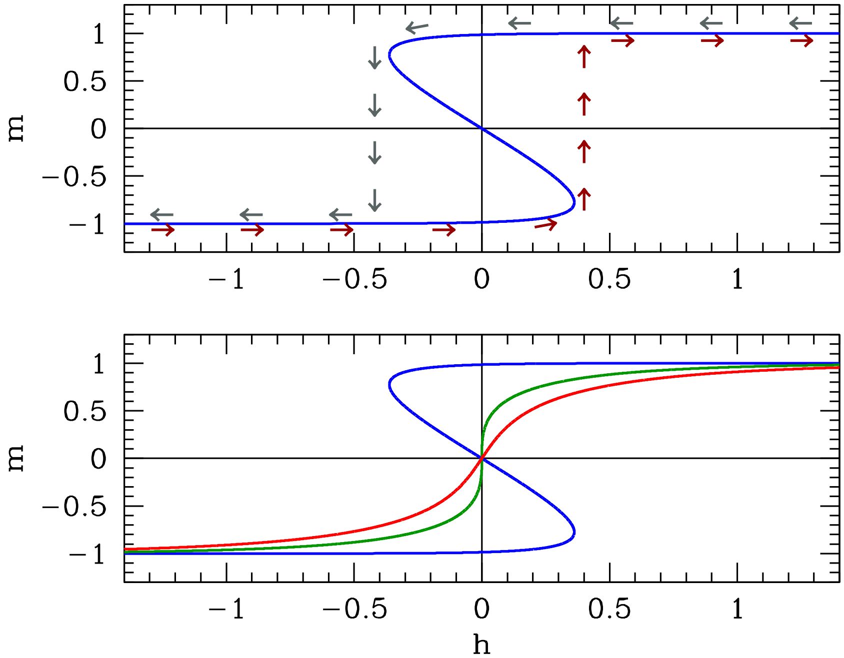

Figure 7.12: Top panel : hysteresis as a function of ramping the dimensionless magnetic field $h$ at $\theta = 0.40$. Dark red arrows below the curve follow evolution of the magnetization on slow increase of $h$. Dark grey arrows above the curve follow evolution of the magnetization on slow decrease of $h$. Bottom panel : solution set for $m(\theta, h)$ as a function of $h$ at temperatures $\theta = 0.40$ (blue), $\theta = \theta_c = 1.0$ (dark green), and $t = 1.25$ (red).

one fixed point, at $m^* \approx -1$. As $h$ slowly increases, the fixed point value $m^*$ also slowly increases. As $h$ exceeds $-h^*(\theta)$, a saddle-node bifurcation occurs, and two new fixed points are created at positive $m$, one stable and one unstable. The global minimum of the free energy still lies at the fixed point with $m^* < 0$. However, when $h$ crosses $h = 0$, the global minimum of the free energy lies at the most positive fixed point $m^*$. The dynamics, however, keep the system stuck in what is a metastable phase. This persists until $h = +h^*(\theta)$, at which point another saddle-note bifurcation occurs, and the attractive fixed point at $m^* < 0$ annihilates with the repulsive fixed point. The dynamics then act quickly to drive $m$ to the only remaining fixed point. This process is depicted in the top panel of fig. 7.12. As one can see from the figure, the the system follows a stable fixed point until the fixed point disappears, even though that fixed point may not always correspond to a global minimum of the free energy. The resulting $m(h)$ curve is then not reversible as a function of time, and it possesses a characteristic shape known as a *hysteresis loop*. Etymologically, the word *hysteresis* derives from the Greek $\upsilon\sigma\tau\varepsilon\rho\eta\sigma\iota\varsigma$, which means 'lagging behind'. Systems which are hysteretic exhibit a *history-dependence* to their status, which is not uniquely determined by external conditions. Hysteresis may be exhibited with respect to changes in applied magnetic field, changes in temperature, or changes in other externally determined parameters.

### 7.4.5 Beyond nearest neighbors

Suppose we had started with the more general model,

$$\begin{aligned}\hat{H} &= -\sum_{i<j} J_{ij}\,\sigma_i\,\sigma_j - H\sum_i \sigma_i \\ &= -\tfrac{1}{2}\sum_{i\neq j} J_{ij}\,\sigma_i\,\sigma_j - H\sum_i \sigma_i\ ,\end{aligned} \tag{7.83}$$

where $J_{ij}$ is the coupling between spins on sites $i$ and $j$. In the top equation above, each pair $(ij)$ is counted once in the interaction term; this may be replaced by a sum over all $i$ and $j$ if we include a factor of $\frac{1}{2}$.[11] The resulting mean field Hamiltonian is then

$$\hat{H}_{\text{MF}} = \tfrac{1}{2}N\hat{J}(0)\,m^2 - \big(H + \hat{J}(0)\,m\big)\sum_i \sigma_i \ . \tag{7.84}$$

Here, $\hat{J}(\boldsymbol{q})$ is the Fourier transform of the interaction matrix $J_{ij}$:[12]

$$\hat{J}(\boldsymbol{q}) = \sum_{\boldsymbol{R}} J(\boldsymbol{R})\, e^{-i\boldsymbol{q}\cdot\boldsymbol{R}} \ . \tag{7.85}$$

For nearest neighbor interactions only, one has $\hat{J}(0) = zJ$, where $z$ is the *lattice coordination number*, *i.e.* the number of nearest neighbors of any given site. The scaled free energy is as in eqn. 7.64, with $f = F/N\hat{J}(0)$, $\theta = k_{\text{B}}T/\hat{J}(0)$, and $h = H/\hat{J}(0)$. The analysis proceeds precisely as before, and we conclude $\theta_{\text{c}} = 1$, *i.e.* $k_{\text{B}}T_{\text{c}}^{\text{MF}} = \hat{J}(0)$.

### 7.4.6 Ising model with long-ranged forces

Consider an Ising model where $J_{ij} = J/N$ for all $i$ and $j$, so that there is a very weak interaction between every pair of spins. The Hamiltonian is then

$$\hat{H} = -\frac{J}{2N}\bigg(\sum_i \sigma_i\bigg)^2 - H\sum_k \sigma_k \ . \tag{7.86}$$

The partition function is

$$Z = \mathsf{Tr}_{\,\{\sigma_i\}} \, \exp\Bigg[\frac{\beta J}{2N}\bigg(\sum_i \sigma_i\bigg)^2 + \beta H \sum_i \sigma_i\Bigg] \ . \tag{7.87}$$

We now invoke the Gaussian integral,

$$\int\limits_{-\infty}^{\infty}\! dx\; e^{-\alpha x^2 - \beta x} = \sqrt{\frac{\pi}{\alpha}}\; e^{\beta^2/4\alpha} \ . \tag{7.88}$$

Thus,

$$\exp\Bigg[\frac{\beta J}{2N}\bigg(\sum_i \sigma_i\bigg)^2\Bigg] = \bigg(\frac{N\beta J}{2\pi}\bigg)^{1/2} \int\limits_{-\infty}^{\infty}\! dm\; e^{-\frac{1}{2}N\beta J m^2 + \beta J m \sum_i \sigma_i} \ , \tag{7.89}$$

and we can write the partition function as

$$\begin{aligned} Z &= \bigg(\frac{N\beta J}{2\pi}\bigg)^{1/2} \int\limits_{-\infty}^{\infty}\! dm\; e^{-\frac{1}{2}N\beta J m^2} \bigg(\sum_\sigma e^{\beta(H + Jm)\sigma}\bigg)^N \\ &= \bigg(\frac{N}{2\pi\theta}\bigg)^{1/2} \int\limits_{-\infty}^{\infty}\! dm\; e^{-NA(m)/\theta} \ , \end{aligned} \tag{7.90}$$

---

[11] The self-interaction terms with $i = j$ contribute a constant to $\hat{H}$ and may be either included or excluded. However, this property only pertains to the $\sigma_i = \pm 1$ model. For higher spin versions of the Ising model, say where $S_i \in \{-1, 0, +1\}$, then $S_i^2$ is not constant and we should explicitly exclude the self-interaction terms.

[12] The sum in the discrete Fourier transform is over all 'direct Bravais lattice vectors' and the wavevector $\boldsymbol{q}$ may be restricted to the 'first Brillouin zone'. These terms are familiar from elementary solid state physics.

where $\theta = k_{\rm B}T/J$, $h = H/J$, and

$$A(m) = \tfrac{1}{2}m^2 - \theta \ln\!\bigg[2\cosh\!\bigg(\frac{h+m}{\theta}\bigg)\bigg] \ . \tag{7.91}$$

Since $N \to \infty$, we can perform the integral using the method of steepest descents. Thus, we must set

$$\frac{dA}{dm}\bigg|_{m^*} = 0 \qquad \Longrightarrow \qquad m^* = \tanh\!\bigg(\frac{m^*+h}{\theta}\bigg) \ . \tag{7.92}$$

Expanding about $m = m^*$, we write

$$A(m) = A(m^*) + \tfrac{1}{2}A''(m^*)\,(m-m^*)^2 + \tfrac{1}{6}\,A'''(m^*)\,(m-m^*)^3 + \ldots \ . \tag{7.93}$$

Performing the integrations, we obtain

$$\begin{aligned} Z &= \bigg(\frac{N}{2\pi\theta}\bigg)^{1/2} e^{-NA(m^*)/\theta} \int\limits_{-\infty}^{\infty}\!d\nu\ \exp\bigg[-\frac{NA''(m^*)}{2\theta}\,m^2 - \frac{NA'''(m^*)}{6\theta}\,m^3 + \ldots\bigg] \\ &= \frac{1}{\sqrt{A''(m^*)}}\,e^{-NA(m^*)/\theta}\cdot\Big\{1+\mathcal{O}(N^{-1})\Big\} \ . \end{aligned} \tag{7.94}$$

The corresponding free energy per site

$$f = \frac{F}{NJ} = A(m^*) + \frac{\theta}{2N}\,\ln A''(m^*) + \mathcal{O}(N^{-2}) \ , \tag{7.95}$$

where $m^*$ is the solution to the mean field equation which minimizes $A(m)$. Mean field theory is *exact* for this model!

## 7.5 Variational Density Matrix Method

### 7.5.1 The variational principle

Suppose we are given a Hamiltonian $\hat{H}$. From this we construct the free energy, $F$:

$$\begin{aligned} F &= E - TS \\ &= {\rm Tr}\,(\varrho\,\hat{H}) + k_{\rm B}T\,{\rm Tr}\,(\varrho\,\ln\varrho) \ . \end{aligned} \tag{7.96}$$

Here, $\varrho$ is the *density matrix*[13]. A physical density matrix must be (i) normalized (*i.e.* ${\rm Tr}\,\varrho = 1$), (ii) Hermitian, and (iii) non-negative definite (*i.e.* all the eigenvalues of $\varrho$ must be non-negative).

Our goal is to extremize the free energy subject to the various constraints on $\varrho$. Let us assume that $\varrho$ is diagonal in the basis of eigenstates of $\hat{H}$, *i.e.*

$$\varrho = \sum_\gamma P_\gamma \,|\,\gamma\,\rangle\langle\,\gamma\,| \ , \tag{7.97}$$

---

[13] How do we take the logarithm of a matrix? The rule is this: $A = \ln B$ if $B = \exp(A)$. The exponential of a matrix may be evaluated via its Taylor expansion.

where $P_\gamma$ is the probability that the system is in state $\big|\,\gamma\,\big\rangle$. Then

$$F = \sum_\gamma E_\gamma \, P_\gamma + k_{\rm B}T \sum_\gamma P_\gamma \ln P_\gamma \ . \tag{7.98}$$

Thus, the free energy is a function of the set $\{P_\gamma\}$. We now extremize $F$ subject to the normalization constraint. This means we form the extended function

$$F^*\big(\{P_\gamma\},\lambda\big) = F\big(\{P_\gamma\}\big) + \lambda\Big(\sum_\gamma P_\gamma - 1\Big) \ , \tag{7.99}$$

and then freely extremize over both the probabilities $\{P_\gamma\}$ as well as the Lagrange multiplier $\lambda$. This yields the Boltzmann distribution,

$$P_\gamma^{\rm eq} = \frac{1}{Z}\,\exp(-E_\gamma/k_{\rm B}T) \ , \tag{7.100}$$

where $Z = \sum_\gamma e^{-E_\gamma/k_{\rm B}T} = {\rm Tr}\, e^{-\hat{H}/k_{\rm B}T}$ is the canonical partition function, which is related to $\lambda$ through

$$\lambda = k_{\rm B}T\,(\ln Z - 1) \ . \tag{7.101}$$

Note that the Boltzmann weights are, appropriately, all positive.

If the spectrum of $\hat{H}$ is bounded from below, our extremum should in fact yield a minimum for the free energy $F$. Furthermore, since we have freely minimized over all the probabilities, subject to the single normalization constraint, *any distribution $\{P_\gamma\}$ other than the equilibrium one must yield a greater value of $F$.*

Alas, the Boltzmann distribution, while exact, is often intractable to evaluate. For one-dimensional systems, there are general methods such as the transfer matrix approach which do permit an exact evaluation of the free energy. However, beyond one dimension the situation is in general hopeless. A family of solvable ("integrable") models exists in two dimensions, but their solutions require specialized techniques and are extremely difficult. The idea behind the variational density matrix approximation is to construct a tractable *trial* density matrix $\varrho$ which depends on a set of variational parameters $\{x_\alpha\}$, and to minimize with respect to this (finite) set.

### 7.5.2 Variational density matrix for the Ising model

Consider once again the Ising model Hamiltonian,

$$\hat{H} = -\sum_{i<j} J_{ij}\,\sigma_i\,\sigma_j - H\sum_i \sigma_i \ . \tag{7.102}$$

The states of the system $\big|\,\gamma\,\big\rangle$ may be labeled by the values of the spin variables: $\big|\,\gamma\,\big\rangle \longleftrightarrow \big|\,\sigma_1,\sigma_2,\ldots\,\big\rangle$. We assume the density matrix is diagonal in this basis, *i.e.*

$$\varrho_N\big(\gamma\big|\gamma'\big) \equiv \varrho(\gamma)\,\delta_{\gamma,\gamma'} \ , \tag{7.103}$$

where

$$\delta_{\gamma,\gamma'} = \prod_i \delta_{\sigma_i,\sigma'_i} \ . \tag{7.104}$$

Indeed, this is the case for the exact density matrix, which is to say the Boltzmann weight,

$$\varrho_N(\sigma_1,\sigma_2,\ldots) = \frac{1}{Z}\,e^{-\beta\hat{H}(\sigma_1,\ldots,\sigma_N)} \ . \tag{7.105}$$

We now write a *trial density matrix* which is a product over contributions from independent single sites:

$$\varrho_N(\sigma_1, \sigma_2, \ldots) = \prod_i \varrho(\sigma_i) \ , \tag{7.106}$$

where

$$\varrho(\sigma) = \Big(\frac{1+m}{2}\Big)\, \delta_{\sigma,1} + \Big(\frac{1-m}{2}\Big)\, \delta_{\sigma,-1} \ . \tag{7.107}$$

Note that we've changed our notation slightly. We are denoting by $\varrho(\sigma)$ the corresponding diagonal element of the matrix

$$\varrho = \begin{pmatrix} \frac{1+m}{2} & 0 \\ 0 & \frac{1-m}{2} \end{pmatrix} \ , \tag{7.108}$$

and the full density matrix is a tensor product over the single site matrices:

$$\varrho_N = \varrho \otimes \varrho \otimes \cdots \otimes \varrho \ . \tag{7.109}$$

Note that $\varrho$ and hence $\varrho_N$ are appropriately normalized. The variational parameter here is $m$, which, if $\rho$ is to be non-negative definite, must satisfy $-1 \leq m \leq 1$. The quantity $m$ has the physical interpretation of the average spin on any given site, since

$$\langle \sigma_i \rangle = \sum_\sigma \varrho(\sigma)\, \sigma = m. \tag{7.110}$$

We may now evaluate the average energy:

$$\begin{aligned} E = \mathsf{Tr}\,(\varrho_N \hat{H}) &= -\sum_{i<j} J_{ij}\, m^2 - H \sum_i m \\ &= -\tfrac{1}{2} N \hat{J}(0)\, m^2 - NH\, m \ , \end{aligned} \tag{7.111}$$

where once again $\hat{J}(0)$ is the discrete Fourier transform of $J(\boldsymbol{R})$ at wavevector $\boldsymbol{q} = 0$. The entropy is given by

$$\begin{aligned} S &= -k_{\rm B}\, \mathsf{Tr}\,(\varrho_N \ln \varrho_N) = -N k_{\rm B}\, \mathsf{Tr}\,(\varrho \ln \varrho) \\ &= -N k_{\rm B} \bigg\{ \Big(\frac{1+m}{2}\Big) \ln \Big(\frac{1+m}{2}\Big) + \Big(\frac{1-m}{2}\Big) \ln \Big(\frac{1-m}{2}\Big) \bigg\} \ . \end{aligned} \tag{7.112}$$

We now define the dimensionless free energy per site: $f \equiv F/N\hat{J}(0)$. We have

$$f(m,h,\theta) = -\tfrac{1}{2}\, m^2 - hm + \theta \,\bigg\{ \Big(\frac{1+m}{2}\Big) \ln \Big(\frac{1+m}{2}\Big) + \Big(\frac{1-m}{2}\Big) \ln \Big(\frac{1-m}{2}\Big) \bigg\} \ , \tag{7.113}$$

where $\theta \equiv k_{\rm B}T/\hat{J}(0)$ is the dimensionless temperature, and $h \equiv H/\hat{J}(0)$ the dimensionless magnetic field, as before. We extremize $f(m)$ by setting

$$\frac{\partial f}{\partial m} = 0 = -m - h + \frac{\theta}{2} \ln \Big(\frac{1+m}{1-m}\Big) \ . \tag{7.114}$$

Solving for $m$, we obtain

$$m = \tanh\left(\frac{m+h}{\theta}\right) \ , \tag{7.115}$$

which is precisely what we found in eqn. 7.65.

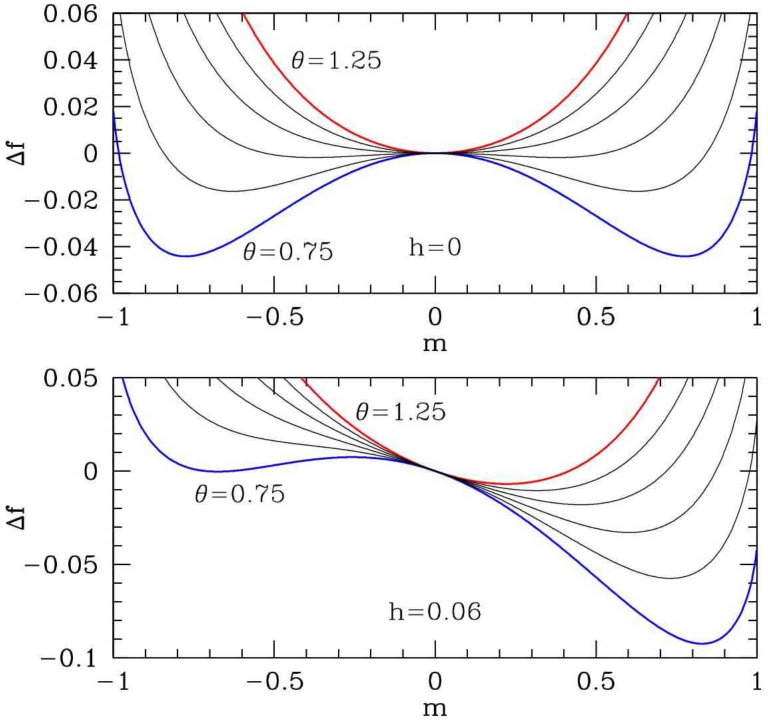

Figure 7.13: Variational field free energy $\Delta f = f(m,h,\theta) + \theta\,\ln 2$ *versus* magnetization $m$ at six equally spaced temperatures interpolating between 'high' ($\theta = 1.25$, red) and 'low' ($\theta = 0.75$, blue) values. Top panel: $h = 0$. Bottom panel: $h = 0.06$.

Note that the optimal value of $m$ indeed satisfies the requirement $|m| \le 1$ of non-negative probability. This nonlinear equation may be solved graphically. For $h = 0$, the unmagnetized solution $m = 0$ always applies. However, for $\theta < 1$ there are two additional solutions at $m = \pm m_{\rm A}(\theta)$, with $m_{\rm A}(\theta) = \sqrt{3(1-\theta)} + \mathcal{O}\big((1-\theta)^{3/2}\big)$ for $t$ close to (but less than) one. These solutions, which are related by the $\mathbb{Z}_2$ symmetry of the $h = 0$ model, are in fact the low energy solutions. This is shown clearly in figure 7.13, where the variational free energy $f(m,t)$ is plotted as a function of $m$ for a range of temperatures interpolating between 'high' and 'low' values. At the *critical temperature* $\theta_{\rm c} = 1$, the lowest energy state changes from being unmagnetized (high temperature) to magnetized (low temperature).

For $h > 0$, there is no longer a $\mathbb{Z}_2$ symmetry (*i.e.* $\sigma_i \to -\sigma_i\ \forall\ i$). The high temperature solution now has $m > 0$ (or $m < 0$ if $h < 0$), and this smoothly varies as $t$ is lowered, approaching the completely polarized limit $m = 1$ as $\theta \to 0$. At very high temperatures, the argument of the $\tanh$ function is small, and we may approximate $\tanh(x) \simeq x$, in which case

$$m(h,\theta) = \frac{h}{\theta - \theta_{\rm c}}\ . \tag{7.116}$$

This is called the *Curie-Weiss law*. One can infer $\theta_{\rm c}$ from the high temperature susceptibility $\chi(\theta) = (\partial m/\partial h)_{h=0}$ by plotting $\chi^{-1}$ *versus* $\theta$ and extrapolating to obtain the $\theta$-intercept. In our case, $\chi(\theta) = (\theta - \theta_{\rm c})^{-1}$. For low $\theta$ and weak $h$, there are two inequivalent minima in the free energy.

When $m$ is small, it is appropriate to expand $f(m,h,\theta)$, obtaining

$$f(m,h,\theta) = -\theta\,\ln 2 - hm + \tfrac{1}{2}\,(\theta - 1)\,m^2 + \tfrac{\theta}{12}\,m^4 + \tfrac{\theta}{30}\,m^6 + \tfrac{\theta}{56}\,m^8 + \ldots\ . \tag{7.117}$$

This is known as the *Landau expansion* of the free energy in terms of the *order parameter* $m$. An order parameter is a thermodynamic variable $\phi$ which distinguishes ordered and disordered phases. Typically $\phi = 0$ in the disordered (high temperature) phase, and $\phi \neq 0$ in the ordered (low temperature) phase. When the order sets in continuously, *i.e.* when $\phi$ is continuous across $\theta_{\rm c}$, the phase transition is said to be *second order.* When $\phi$ changes abruptly, the transition is *first order.* It is also quite commonplace to observe phase transitions between two ordered states. For example, a crystal, which is an ordered state, may change its lattice structure, say from a high temperature tetragonal phase to a low temperature orthorhombic phase. When the high $T$ phase possesses the same symmetries as the low $T$ phase, as in the tetragonal-to-orthorhombic example, the transition may be second order. When the two symmetries are completely unrelated, for example in a hexagonal-to-tetragonal transition, or in a transition between a ferromagnet and an antiferromagnet, the transition is in general first order.

Throughout this discussion, we have assumed that the interactions $J_{ij}$ are predominantly *ferromagnetic*, *i.e.* $J_{ij} > 0$, so that all the spins prefer to align. When $J_{ij} < 0$, the interaction is said to be *antiferromagnetic* and prefers anti-alignment of the spins (*i.e.* $\sigma_i\,\sigma_j = -1$). Clearly not every pair of spins can be anti-aligned – there are two possible spin states and a thermodynamically extensive number of spins. But on the square lattice, for example, if the only interactions $J_{ij}$ are between nearest neighbors and the interactions are antiferromagnetic, then the lowest energy configuration ($T = 0$ ground state) will be one in which spins on opposite sublattices are anti-aligned. The square lattice is *bipartite* – it breaks up into two interpenetrating sublattices A and B (which are themselves square lattices, rotated by 45° with respect to the original, and with a larger lattice constant by a factor of $\sqrt{2}$), such that any site in A has nearest neighbors in B, and *vice versa*. The honeycomb lattice is another example of a bipartite lattice. So is the simple cubic lattice. The triangular lattice, however, is not bipartite (it is *tripartite*). Consequently, with nearest neighbor antiferromagnetic interactions, the triangular lattice Ising model is highly *frustrated*. The moral of the story is this: antiferromagnetic interactions can give rise to complicated magnetic ordering, and, when frustrated by the lattice geometry, may have finite specific entropy even at $T = 0$.

### 7.5.3 Mean Field Theory of the Potts Model

The Hamiltonian for the Potts model is

$$\hat{H} = -\sum_{i<j} J_{ij}\,\delta_{\sigma_i,\sigma_j} - H\sum_i \delta_{\sigma_i,1}\ . \tag{7.118}$$

Here, $\sigma_i \in \{1,\ldots,q\}$, with integer $q$. This is the so-called '$q$-state Potts model'. The quantity $H$ is analogous to an external magnetic field, and preferentially aligns (for $H > 0$) the local spins in the $\sigma = 1$ direction. We will assume $H \geq 0$.

The $q$-component set is conveniently taken to be the integers from $1$ to $q$, but it could be anything, such as

$$\sigma_i \in \{\text{tomato, penny, ostrich, Grateful Dead ticket from 1987},\ \ldots\}\ . \tag{7.119}$$

The interaction energy is $-J_{ij}$ if sites $i$ and $j$ contain the same object ($q$ possibilities), and $0$ if $i$ and $j$ contain different objects ($q^2 - q$ possibilities).

The two-state Potts model is equivalent to the Ising model. Let the allowed values of $\sigma$ be $\pm 1$. Then the quantity

$$\delta_{\sigma,\sigma'} = \tfrac{1}{2} + \tfrac{1}{2}\,\sigma\sigma' \tag{7.120}$$

equals $1$ if $\sigma = \sigma'$, and is zero otherwise. The three-state Potts model cannot be written as a simple three-state Ising model, *i.e.* one with a bilinear interaction $\sigma\,\sigma'$ where $\sigma \in \{-1, 0, +1\}$. However, it is straightforward to verify the identity

$$\delta_{\sigma,\sigma'} = 1 + \tfrac{1}{2}\,\sigma\sigma' + \tfrac{3}{2}\,\sigma^2\sigma'^2 - (\sigma^2 + \sigma'^2)\ . \tag{7.121}$$

Thus, the $q = 3$-state Potts model is equivalent to a $S = 1$ (three-state) Ising model which includes both bilinear ($\sigma\sigma'$) and biquadratic ($\sigma^2\sigma'^2$) interactions, as well as a local field term which couples to the square of the spin,

$\sigma^2$. In general one can find such correspondences for higher $q$ Potts models, but, as should be expected, the interactions become increasingly complex, with bi-cubic, bi-quartic, bi-quintic, *etc.* terms.

Getting back to the mean field theory, we write the single site variational density matrix $\varrho$ as a diagonal matrix with entries

$$\varrho(\sigma) = x\,\delta_{\sigma,1} + \left(\frac{1-x}{q-1}\right)\left(1-\delta_{\sigma,1}\right) , \tag{7.122}$$

with $\varrho_N(\sigma_1,\ldots,\sigma_N) = \varrho(\sigma_1)\cdots\varrho(\sigma_N)$. Note that $\mathsf{Tr}\,(\varrho) = 1$. The variational parameter is $x$. When $x = q^{-1}$, all states are equally probable. But for $x > q^{-1}$, the state $\sigma = 1$ is preferred, and the other $(q-1)$ states have identical but smaller probabilities. It is a simple matter to compute the energy and entropy:

$$\begin{aligned} E &= \mathsf{Tr}\,(\varrho_N \hat{H}) = -\tfrac{1}{2}N\hat{J}(0)\bigg\{x^2 + \frac{(1-x)^2}{q-1}\bigg\} - NHx \\ S &= -k_{\rm B}\,\mathsf{Tr}\,(\varrho_N \ln \varrho_N) = -Nk_{\rm B}\bigg\{x\ln x + (1-x)\ln\left(\frac{1-x}{q-1}\right)\bigg\} . \end{aligned} \tag{7.123}$$

The dimensionless free energy per site is then

$$f(x,\theta,h) = -\tfrac{1}{2}\bigg\{x^2 + \frac{(1-x)^2}{q-1}\bigg\} + \theta\,\bigg\{x\ln x + (1-x)\ln\left(\frac{1-x}{q-1}\right)\bigg\} - hx , \tag{7.124}$$

where $h = H/\hat{J}(0)$. We now extremize with respect to $x$ to obtain the mean field equation,

$$\frac{\partial f}{\partial x} = 0 = -x + \frac{1-x}{q-1} + \theta\,\ln x - \theta\,\ln\left(\frac{1-x}{q-1}\right) - h . \tag{7.125}$$

Note that for $h = 0$, $x = q^{-1}$ is a solution, corresponding to a disordered state in which all states are equally probable. At high temperatures, for small $h$, we expect $x - q^{-1} \propto h$. Indeed, using `Mathematica` one can set

$$x \equiv q^{-1} + s , \tag{7.126}$$

and expand the mean field equation in powers of $s$. One obtains

$$h = \frac{q\,(q\theta-1)}{q-1}\,s + \frac{q^3\,(q-2)\,\theta}{2\,(q-1)^2}\,s^2 + \mathcal{O}(s^3) . \tag{7.127}$$

For weak fields, $|h| \ll 1$, and we have

$$s(\theta) = \frac{(q-1)\,h}{q\,(q\theta-1)} + \mathcal{O}(h^2) , \tag{7.128}$$

which again is of the Curie-Weiss form. The difference $s = x - q^{-1}$ is the order parameter for the transition.

Finally, one can expand the free energy in powers of $s$, obtaining the Landau expansion,

$$\begin{aligned} f(s,\theta,h) = -\frac{2h+1}{2q} - \theta\ln q - hs &+ \frac{q\,(q\theta-1)}{2\,(q-1)}\,s^2 - \frac{(q-2)\,q^3\,\theta}{6\,(q-1)^2}\,s^3 \\ &+ \frac{q^3\theta}{12}\Big[1+(q-1)^{-3}\Big]s^4 - \frac{q^4\theta}{20}\Big[1-(q-1)^{-4}\Big]s^5 \\ &+ \frac{q^5\theta}{30}\Big[1+(q-1)^{-5}\Big]s^6 + \ldots \end{aligned} \tag{7.129}$$

Note that, for $q = 2$, the coefficients of $s^3$, $s^5$, and higher order odd powers of $s$ vanish in the Landau expansion. This is consistent with what we found for the Ising model, and is related to the $\mathbb{Z}_2$ symmetry of that model. For $q > 3$, there is a cubic term in the mean field free energy, and thus we generically expect a first order transition, as we shall see below when we discuss Landau theory.

### 7.5.4 Mean Field Theory of the $XY$ Model

Consider the so-called $XY$ model, in which each site contains a continuous planar spin, represented by an angular variable $\phi_i \in [-\pi, \pi]$:

$$\hat{H} = -\sum_{i<j} J_{ij} \, \cos\big(\phi_i - \phi_j\big) - H \sum_i \cos\phi_i \ . \tag{7.130}$$

We write the (diagonal elements of the) full density matrix once again as a product:

$$\varrho_N(\phi_1, \phi_2, \ldots) = \prod_i \varrho(\phi_i) \ . \tag{7.131}$$

Our goal will be to extremize the free energy with respect to the *function* $\varrho(\phi)$. To this end, we compute

$$E = \mathsf{Tr}\,(\varrho_N \, \hat{H}) = -\tfrac{1}{2} N \hat{J}(0) \, \Big|\mathsf{Tr}\,\big(\varrho \, e^{i\phi}\big)\Big|^2 - N\,H\,\mathsf{Tr}\,\big(\varrho\,\cos\phi\big) \ . \tag{7.132}$$

The entropy is

$$S = -N k_{\rm B} \, \mathsf{Tr}\,(\varrho\,\ln\varrho) \ . \tag{7.133}$$

Note that for any function $A(\phi)$, we have[14]

$$\mathsf{Tr}\,\big(\varrho\,A\big) \equiv \int\limits_{-\pi}^{\pi} \frac{d\phi}{2\pi} \, \varrho(\phi)\,A(\phi) \ . \tag{7.134}$$

We now extremize the *functional* $F\big[\varrho(\phi)\big] = E - TS$ with respect to $\varrho(\phi)$, under the condition that $\mathsf{Tr}\;\varrho = 1$. We therefore use Lagrange's method of undetermined multipliers, writing

$$\tilde{F} = F - N k_{\rm B} T\,\lambda\,\Big(\,\mathsf{Tr}\,\varrho - 1\Big) \ . \tag{7.135}$$

Note that $\tilde{F}$ is a *function* of the Lagrange multiplier $\lambda$ and a *functional* of the density matrix $\varrho(\phi)$. The prefactor $Nk_{\rm B}T$ which multiplies $\lambda$ is of no mathematical consequence – we could always redefine the multiplier to be $\lambda' \equiv Nk_{\rm B}T\lambda$. It is present only to maintain homogeneity and proper dimensionality of $F^*$ with $\lambda$ itself dimensionless and of order $N^0$. We now have

$$\begin{aligned}\frac{\delta\tilde{F}}{\delta\varrho(\phi)} = \frac{\delta}{\delta\varrho(\phi)}\bigg\{ &-\tfrac{1}{2} N\hat{J}(0)\,\Big|\mathsf{Tr}\big(\varrho\,e^{i\phi}\big)\Big|^2 - N\,H\,\mathsf{Tr}\big(\varrho\,\cos\phi\big) \\ &+ Nk_{\rm B}T \;\mathsf{Tr}\,\big(\varrho\,\ln\varrho\big) - Nk_{\rm B}T\,\lambda\,\Big(\,\mathsf{Tr}\,\varrho - 1\Big)\bigg\} \ .\end{aligned}$$

To this end, we note that

$$\frac{\delta}{\delta\varrho(\phi)}\,\mathsf{Tr}\,(\varrho\,A) = \frac{\delta}{\delta\varrho(\phi)} \int\limits_{-\pi}^{\pi} \frac{d\phi}{2\pi}\,\varrho(\phi)\,A(\phi) = \frac{1}{2\pi}\,A(\phi) \ . \tag{7.136}$$

Thus, we have

$$\begin{aligned}\frac{\delta\tilde{F}}{\delta\varrho(\phi)} = -\tfrac{1}{2} N\hat{J}(0) \cdot \frac{1}{2\pi}\bigg[\underset{\phi'}{\mathsf{Tr}}\big(\varrho\,e^{i\phi'}\big)\,e^{-i\phi} + \underset{\phi'}{\mathsf{Tr}}\big(\varrho\,e^{-i\phi'}\big)\,e^{i\phi}\bigg] - NH \cdot \frac{\cos\phi}{2\pi} \\ + Nk_{\rm B}T \cdot \frac{1}{2\pi}\Big[\ln\varrho(\phi) + 1\Big] - Nk_{\rm B}T \cdot \frac{\lambda}{2\pi} \ .\end{aligned} \tag{7.137}$$

---

[14] The denominator of $2\pi$ in the measure is not necessary, and in fact it is even slightly cumbersome. It divides out whenever we take a ratio to compute a thermodynamic average. I introduce this factor to preserve the relation $\mathsf{Tr}\;1 = 1$. I personally find unnormalized traces to be profoundly unsettling on purely aesthetic grounds.

Now let us define

$$\mathop{\mathsf{Tr}}_{\phi}\big(\varrho\, e^{i\phi}\big) = \int\limits_{-\pi}^{\pi}\!\frac{d\phi}{2\pi}\;\varrho(\phi)\, e^{i\phi} \equiv m\, e^{i\phi_0} \ . \tag{7.138}$$

We then have

$$\ln\varrho(\phi) = \frac{\hat{J}(0)}{k_{\rm B}T}\, m\, \cos(\phi-\phi_0) + \frac{H}{k_{\rm B}T}\, \cos\phi + \lambda - 1. \tag{7.139}$$

Clearly the free energy will be reduced if $\phi_0 = 0$ so that the mean field is maximal and aligns with the external field, which prefers $\phi = 0$. Thus, we conclude

$$\varrho(\phi) = \mathcal{C}\, \exp\!\bigg(\frac{H_{\rm eff}}{k_{\rm B}T}\, \cos\phi\bigg) \ , \tag{7.140}$$

where

$$H_{\rm eff} = \hat{J}(0)\, m + H \tag{7.141}$$

and $\mathcal{C} = e^{\lambda-1}$. The value of $\lambda$ is then determined by invoking the constraint,

$$\mathsf{Tr}\,\varrho = 1 = \mathcal{C}\!\int\limits_{-\pi}^{\pi}\!\frac{d\phi}{2\pi}\; \exp\!\bigg(\frac{H_{\rm eff}}{k_{\rm B}T}\, \cos\phi\bigg) = \mathcal{C}\, I_0(H_{\rm eff}/k_{\rm B}T) \ , \tag{7.142}$$

where $I_0(z)$ is the Bessel function. We are free to define

$$\varepsilon \equiv \frac{H_{\rm eff}}{k_{\rm B}T} \ , \tag{7.143}$$

and to treat $\varepsilon$ as our single variational parameter.

We then have the normalized density matrix

$$\varrho(\phi) = \frac{e^{\varepsilon\cos\phi}}{\int\limits_{-\pi}^{\pi}\frac{d\phi'}{2\pi}\; e^{\varepsilon\cos\phi'}} = \frac{e^{\varepsilon\cos\phi}}{I_0(\varepsilon)} \ . \tag{7.144}$$

We next compute the following averages:

$$\big\langle e^{\pm i\phi}\big\rangle = \int\limits_{-\pi}^{\pi}\!\frac{d\phi}{2\pi}\;\varrho(\phi)\, e^{\pm i\phi} = \frac{I_1(\varepsilon)}{I_0(\varepsilon)} \tag{7.145}$$

$$\big\langle\cos(\phi-\phi')\big\rangle = {\rm Re}\,\big\langle e^{i\phi}\, e^{-i\phi'}\big\rangle = \bigg(\frac{I_1(\varepsilon)}{I_0(\varepsilon)}\bigg)^2 \ , \tag{7.146}$$

as well as

$$\mathsf{Tr}\,(\varrho\,\ln\varrho) = \int\limits_{-\pi}^{\pi}\!\frac{d\phi}{2\pi}\;\frac{e^{\varepsilon\cos\phi}}{I_0(\varepsilon)}\,\Big\{\varepsilon\cos\phi - \ln I_0(\varepsilon)\Big\} = \varepsilon\,\frac{I_1(\varepsilon)}{I_0(\varepsilon)} - \ln I_0(\varepsilon) \ . \tag{7.147}$$

The dimensionless free energy per site is therefore

$$f(\varepsilon,h,\theta) = -\tfrac{1}{2}\bigg(\frac{I_1(\varepsilon)}{I_0(\varepsilon)}\bigg)^2 + (\varepsilon\,\theta - h)\,\frac{I_1(\varepsilon)}{I_0(\varepsilon)} - \theta\,\ln I_0(\varepsilon) \ , \tag{7.148}$$

with $\theta = k_{\rm B}T/\hat{J}(0)$ and $h = H/\hat{J}(0)$ and $f = F/N\hat{J}(0)$ as before.

For small $\varepsilon$, we may expand the Bessel functions, using

$$I_\nu(z) = (\tfrac{1}{2}z)^\nu \sum_{k=0}^\infty \frac{(\frac{1}{4}z^2)^k}{k!\,\Gamma(k+\nu+1)} \ , \tag{7.149}$$

to obtain

$$f(\varepsilon,h,\theta) = \tfrac{1}{4}\left(\theta - \tfrac{1}{2}\right)\varepsilon^2 + \tfrac{1}{64}\left(2-3\theta\right)\varepsilon^4 - \tfrac{1}{2}\,h\varepsilon + \tfrac{1}{16}\,h\varepsilon^3 + \ldots \ . \tag{7.150}$$

This predicts a second order phase transition at $\theta_c = \frac{1}{2}$.[15] Note also the Curie-Weiss form of the susceptibility at high $\theta$:

$$\frac{\partial f}{\partial \varepsilon} = 0 \quad \Longrightarrow \quad \varepsilon = \frac{h}{\theta - \theta_c} + \ldots \ . \tag{7.151}$$

## 7.6 Landau Theory of Phase Transitions

Landau's theory of phase transitions is based on an expansion of the free energy of a thermodynamic system in terms of an *order parameter*, which is nonzero in an ordered phase and zero in a disordered phase. For example, the magnetization $M$ of a ferromagnet in zero external field but at finite temperature typically vanishes for temperatures $T > T_c$, where $T_c$ is the *critical temperature*, also called the *Curie temperature* in a ferromagnet. A low order expansion in powers of the order parameter is appropriate sufficiently close to the phase transition, *i.e.* at temperatures such that the order parameter, if nonzero, is still small.

The simplest example is the quartic free energy,

$$f(m,h=0,\theta) = f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 \ , \tag{7.152}$$

where $f_0 = f_0(\theta)$, $a = a(\theta)$, and $b = b(\theta)$. Here, $\theta$ is a dimensionless measure of the temperature. If for example the local exchange energy in the ferromagnet is $J$, then we might define $\theta = k_B T/zJ$, as before. Let us assume $b > 0$, which is necessary if the free energy is to be bounded from below[16]. The equation of state ,

$$\frac{\partial f}{\partial m} = 0 = am + bm^3 \ , \tag{7.153}$$

has three solutions in the complex $m$ plane: (i) $m = 0$, (ii) $m = \sqrt{-a/b}$, and (iii) $m = -\sqrt{-a/b}$. The latter two solutions lie along the (physical) real axis if $a < 0$. We assume that there exists a unique temperature $\theta_c$ where $a(\theta_c) = 0$. Minimizing $f$, we find

$$\begin{aligned} \theta < \theta_c \quad &: \quad f(\theta) = f_0 - \frac{a^2}{4b} \\ \theta > \theta_c \quad &: \quad f(\theta) = f_0 \ . \end{aligned} \tag{7.154}$$

The free energy is continuous at $\theta_c$ since $a(\theta_c) = 0$. The specific heat, however, is discontinuous across the transition, with

$$c(\theta_c^+) - c(\theta_c^-) = -\theta_c \, \frac{\partial^2}{\partial \theta^2}\bigg|_{\theta=\theta_c} \left(\frac{a^2}{4b}\right) = -\frac{\theta_c \left[a'(\theta_c)\right]^2}{2b(\theta_c)} \ . \tag{7.155}$$

---

[15] Note that the coefficient of the quartic term in $\varepsilon$ is negative for $\theta > \frac{2}{3}$. At $\theta = \theta_c = \frac{1}{2}$, the coefficient is positive, but for larger $\theta$ one must include higher order terms in the Landau expansion.

[16] It is always the case that $f$ is bounded from below, on physical grounds. Were $b$ negative, we'd have to consider higher order terms in the Landau expansion.

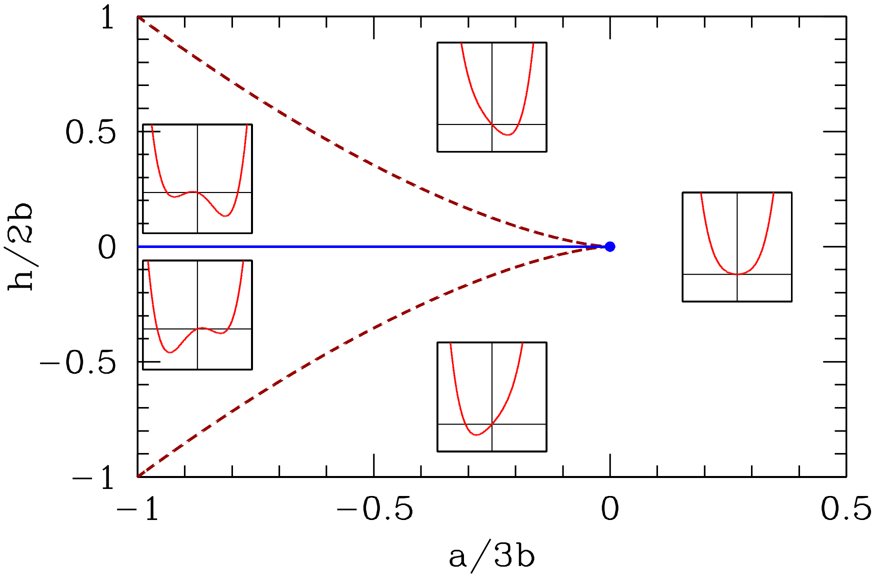

Figure 7.14: Phase diagram for the quartic mean field theory $f = f_0 + \frac{1}{2}am^2 + \frac{1}{4}bm^4 - hm$, with $b > 0$. There is a first order line at $h = 0$ extending from $a = -\infty$ and terminating in a critical point at $a = 0$. For $|h| < h^*(a)$ (dashed red line) there are three solutions to the mean field equation, corresponding to one global minimum, one local minimum, and one local maximum. Insets show behavior of the free energy $f(m)$.

The presence of a magnetic field $h$ breaks the $\mathbb{Z}_2$ symmetry of $m \to -m$. The free energy becomes

$$f(m, h, \theta) = f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 - hm \ , \tag{7.156}$$

and the mean field equation is

$$bm^3 + am - h = 0 \ . \tag{7.157}$$

This is a cubic equation for $m$ with real coefficients, and as such it can either have three real solutions or one real solution and two complex solutions related by complex conjugation. Clearly we must have $a < 0$ in order to have three real roots, since $bm^3 + am$ is monotonically increasing otherwise. The boundary between these two classes of solution sets occurs when two roots coincide, which means $f''(m) = 0$ as well as $f'(m) = 0$. Simultaneously solving these two equations, we find

$$h^*(a) = \pm \frac{2}{3^{3/2}} \, \frac{(-a)^{3/2}}{b^{1/2}} \ , \tag{7.158}$$

or, equivalently,

$$a^*(h) = -\frac{3}{2^{2/3}} \, b^{1/3} \, |h|^{2/3} . \tag{7.159}$$

If, for fixed $h$, we have $a < a^*(h)$, then there will be three real solutions to the mean field equation $f'(m) = 0$, one of which is a global minimum (the one for which $m \cdot h > 0$). For $a > a^*(h)$ there is only a single global minimum, at which $m$ also has the same sign as $h$. If we solve the mean field equation perturbatively in $h/a$, we find

$$\begin{aligned} m(a,h) &= \frac{h}{a} - \frac{b}{a^4} \, h^3 + \mathcal{O}(h^5) && (a > 0) \\ &= \pm \frac{|a|^{1/2}}{b^{1/2}} + \frac{h}{2\,|a|} \pm \frac{3\,b^{1/2}}{8\,|a|^{5/2}} \, h^2 + \mathcal{O}(h^3) && (a < 0) \ . \end{aligned} \tag{7.160}$$

### 7.6.1 Cubic terms in Landau theory : first order transitions

Next, consider a free energy with a cubic term,

$$f = f_0 + \tfrac{1}{2}am^2 - \tfrac{1}{3}ym^3 + \tfrac{1}{4}bm^4 \ , \tag{7.161}$$

with $b > 0$ for stability. Without loss of generality, we may assume $y > 0$ (else send $m \to -m$). Note that we no longer have $m \to -m$ (*i.e.* $\mathbb{Z}_2$) symmetry. The cubic term favors positive $m$. What is the phase diagram in the $(a, y)$ plane?

Extremizing the free energy with respect to $m$, we obtain

$$\frac{\partial f}{\partial m} = 0 = am - ym^2 + bm^3 \ . \tag{7.162}$$

This cubic equation factorizes into a linear and quadratic piece, and hence may be solved simply. The three solutions are $m = 0$ and

$$m = m_\pm \equiv \frac{y}{2b} \pm \sqrt{\left(\frac{y}{2b}\right)^2 - \frac{a}{b}} \ . \tag{7.163}$$

We now see that for $y^2 < 4ab$ there is only one real solution, at $m = 0$, while for $y^2 > 4ab$ there are three real solutions. Which solution has lowest free energy? To find out, we compare the energy $f(0)$ with $f(m_+)$[17]. Thus, we set

$$f(m) = f(0) \quad \Longrightarrow \quad \tfrac{1}{2}am^2 - \tfrac{1}{3}ym^3 + \tfrac{1}{4}bm^4 = 0 \ , \tag{7.164}$$

and we now have two quadratic equations to solve simultaneously:

$$\begin{aligned} 0 &= a - ym + bm^2 \\ 0 &= \tfrac{1}{2}a - \tfrac{1}{3}ym + \tfrac{1}{4}bm^2 = 0 \ . \end{aligned} \tag{7.165}$$

Eliminating the quadratic term gives $m = 3a/y$. Finally, substituting $m = m_+$ gives us a relation between $a$, $b$, and $y$:

$$y^2 = \tfrac{9}{2}\,ab \ . \tag{7.166}$$

Thus, we have the following:

$$\begin{aligned} a > \frac{y^2}{4b} \quad &: \quad \text{1 real root } m = 0 \\ \frac{y^2}{4b} > a > \frac{2y^2}{9b} \quad &: \quad \text{3 real roots; minimum at } m = 0 \\ \frac{2y^2}{9b} > a \quad &: \quad \text{3 real roots; minimum at } m = \frac{y}{2b} + \sqrt{\left(\frac{y}{2b}\right)^2 - \frac{a}{b}} \end{aligned} \tag{7.167}$$

The solution $m = 0$ lies at a local minimum of the free energy for $a > 0$ and at a local maximum for $a < 0$. Over the range $\frac{y^2}{4b} > a > \frac{2y^2}{9b}$, then, there is a global minimum at $m = 0$, a local minimum at $m = m_+$, and a local maximum at $m = m_-$, with $m_+ > m_- > 0$. For $\frac{2y^2}{9b} > a > 0$, there is a local minimum at $a = 0$, a global minimum at $m = m_+$, and a local maximum at $m = m_-$, again with $m_+ > m_- > 0$. For $a < 0$, there is a local maximum at $m = 0$, a local minimum at $m = m_-$, and a global minimum at $m = m_+$, with $m_+ > 0 > m_-$. See fig. 7.15.

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[17] We needn't waste our time considering the $m = m_-$ solution, since the cubic term prefers positive $m$.

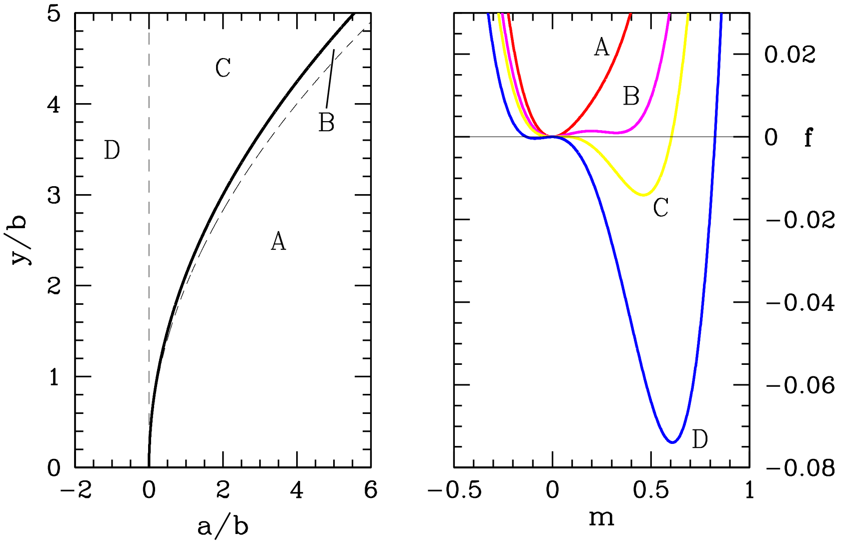

Figure 7.15: Behavior of the quartic free energy $f(m) = \frac{1}{2}am^2 - \frac{1}{3}ym^3 + \frac{1}{4}bm^4$. A: $y^2 < 4ab$ ; B: $4ab < y^2 < \frac{9}{2}ab$ ; C and D: $y^2 > \frac{9}{2}ab$. The thick black line denotes a line of first order transitions, where the order parameter is discontinuous across the transition.

### 7.6.2 Magnetization dynamics

Suppose we now impose some dynamics on the system, of the simple relaxational type

$$\frac{\partial m}{\partial t} = -\Gamma\,\frac{\partial f}{\partial m}\,, \tag{7.168}$$

where $\Gamma$ is a phenomenological kinetic coefficient. Assuming $y > 0$ and $b > 0$, it is convenient to adimensionalize by writing

$$m \equiv \frac{y}{b}\cdot u \qquad , \qquad a \equiv \frac{y^2}{b}\cdot r \qquad , \qquad t \equiv \frac{b}{\Gamma y^2}\cdot s\,. \tag{7.169}$$

Then we obtain

$$\frac{\partial u}{\partial s} = -\frac{\partial \varphi}{\partial u}\,, \tag{7.170}$$

where the dimensionless free energy function is

$$\varphi(u) = \tfrac{1}{2}ru^2 - \tfrac{1}{3}u^3 + \tfrac{1}{4}u^4\,. \tag{7.171}$$

We see that there is a single control parameter, $r$. The fixed points of the dynamics are then the stationary points of $\varphi(u)$, where $\varphi'(u) = 0$, with

$$\varphi'(u) = u\,(r - u + u^2)\,. \tag{7.172}$$

The solutions to $\varphi'(u) = 0$ are then given by

$$u^* = 0 \qquad , \qquad u^* = \tfrac{1}{2} \pm \sqrt{\tfrac{1}{4} - r}\,. \tag{7.173}$$

For $r > \frac{1}{4}$ there is one fixed point at $u = 0$, which is attractive under the dynamics $\dot{u} = -\varphi'(u)$ since $\varphi''(0) = r$. At $r = \frac{1}{4}$ there occurs a saddle-node bifurcation and a pair of fixed points is generated, one stable and one unstable. As we see from fig. 7.14, the interior fixed point is always unstable and the two exterior fixed points are always

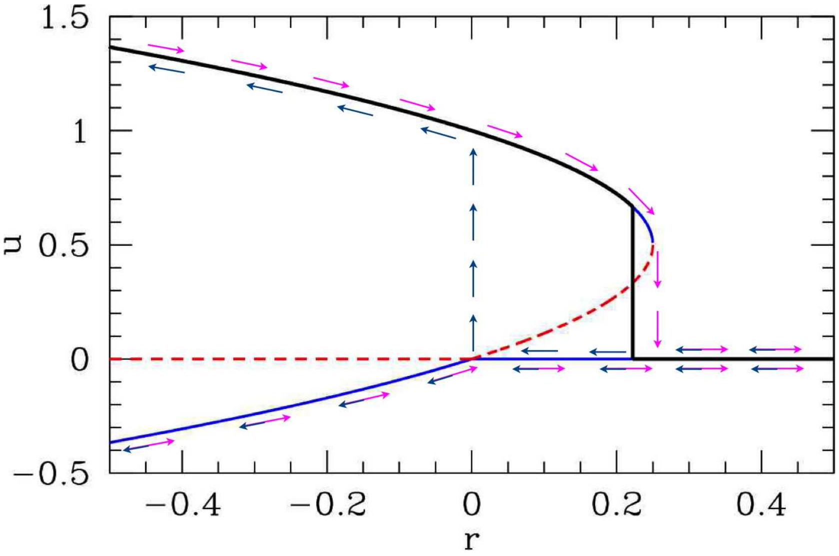

Figure 7.16: Fixed points for $\varphi(u) = \frac{1}{2}ru^2 - \frac{1}{3}u^3 + \frac{1}{4}u^4$ and flow under the dynamics $\dot{u} = -\varphi'(u)$. Solid curves represent stable fixed points and dashed curves unstable fixed points. Magenta arrows show behavior under slowly increasing control parameter $r$ and dark blue arrows show behavior under slowly decreasing $r$. For $u > 0$ there is a hysteresis loop. The thick black curve shows the equilibrium thermodynamic value of $u(r)$, *i.e.* that value which minimizes the free energy $\varphi(u)$. There is a first order phase transition at $r = \frac{2}{9}$, where the thermodynamic value of $u$ jumps from $u = 0$ to $u = \frac{2}{3}$.

stable. At $r = 0$ there is a transcritical bifurcation where two fixed points of opposite stability collide and bounce off one another (metaphorically speaking).

At the saddle-node bifurcation, $r = \frac{1}{4}$ and $u = \frac{1}{2}$, and we find $\varphi(u = \frac{1}{2}; r = \frac{1}{4}) = \frac{1}{192}$, which is positive. Thus, the thermodynamic state of the system remains at $u = 0$ until the value of $\varphi(u_+)$ crosses zero. This occurs when $\varphi(u) = 0$ and $\varphi'(u) = 0$, the simultaneous solution of which yields $r = \frac{2}{9}$ and $u = \frac{2}{3}$.

Suppose we slowly ramp the control parameter $r$ up and down as a function of the dimensionless time $s$. Under the dynamics of eqn. 7.170, $u(s)$ flows to the first stable fixed point encountered – this is always the case for a dynamical system with a one-dimensional phase space. Then as $r$ is further varied, $u$ follows the position of whatever locally stable fixed point it initially encountered. Thus, $u\big(r(s)\big)$ evolves smoothly until a bifurcation is encountered. The situation is depicted by the arrows in fig. 7.16. The equilibrium thermodynamic value for $u(r)$ is discontinuous; there is a first order phase transition at $r = \frac{2}{9}$, as we've already seen. As $r$ is increased, $u(r)$ follows a trajectory indicated by the magenta arrows. For an negative initial value of $u$, the evolution as a function of $r$ will be *reversible*. However, if $u(0)$ is initially positive, then the system exhibits *hysteresis*, as shown. Starting with a large positive value of $r$, $u(s)$ quickly evolves to $u = 0^+$, which means a positive infinitesimal value. Then as $r$ is decreased, the system remains at $u = 0^+$ even through the first order transition, because $u = 0$ is an attractive fixed point. However, once $r$ begins to go negative, the $u = 0$ fixed point becomes repulsive, and $u(s)$ quickly flows to the stable fixed point $u_+ = \frac{1}{2} + \sqrt{\frac{1}{4} - r}$. Further decreasing $r$, the system remains on this branch. If $r$ is later increased, then $u(s)$ remains on the upper branch past $r = 0$, until the $u_+$ fixed point annihilates with the unstable fixed point at $u_- = \frac{1}{2} - \sqrt{\frac{1}{4} - r}$, at which time $u(s)$ quickly flows down to $u = 0^+$ again.

### 7.6.3 Sixth order Landau theory : tricritical point

Finally, consider a model with $\mathbb{Z}_2$ symmetry, with the Landau free energy

$$f = f_0 + \tfrac{1}{2}am^2 + \tfrac{1}{4}bm^4 + \tfrac{1}{6}cm^6 \ , \tag{7.174}$$

with $c > 0$ for stability. We seek the phase diagram in the $(a, b)$ plane. Extremizing $f$ with respect to $m$, we obtain

$$\frac{\partial f}{\partial m} = 0 = m\,(a + bm^2 + cm^4) \ , \tag{7.175}$$

which is a quintic with five solutions over the complex $m$ plane. One solution is obviously $m = 0$. The other four are

$$m = \pm\sqrt{-\frac{b}{2c} \pm \sqrt{\left(\frac{b}{2c}\right)^2 - \frac{a}{c}}} \ . \tag{7.176}$$

For each ± symbol in the above equation, there are two options, hence four roots in all.

If $a > 0$ and $b > 0$, then four of the roots are imaginary and there is a unique minimum at $m = 0$.

For $a < 0$, there are only three solutions to $f'(m) = 0$ for real $m$, since the $-$ choice for the $\pm$ sign under the radical leads to imaginary roots. One of the solutions is $m = 0$. The other two are

$$m = \pm\sqrt{-\frac{b}{2c} + \sqrt{\left(\frac{b}{2c}\right)^2 - \frac{a}{c}}} \ . \tag{7.177}$$

The most interesting situation is $a > 0$ and $b < 0$. If $a > 0$ and $b < -2\sqrt{ac}$, all five roots are real. There must be three minima, separated by two local maxima. Clearly if $m^*$ is a solution, then so is $-m^*$. Thus, the only question is whether the outer minima are of lower energy than the minimum at $m = 0$. We assess this by demanding $f(m^*) = f(0)$, where $m^*$ is the position of the largest root (*i.e.* the rightmost minimum). This gives a second quadratic equation,

$$0 = \tfrac{1}{2}a + \tfrac{1}{4}bm^2 + \tfrac{1}{6}cm^4 \ , \tag{7.178}$$

which together with equation 7.175 gives

$$b = -\tfrac{4}{\sqrt{3}}\,\sqrt{ac} \ . \tag{7.179}$$

Thus, we have the following, for fixed $a > 0$:

$$\begin{aligned} b > -2\sqrt{ac} \quad &: \quad \text{1 real root } m = 0 \\ -2\sqrt{ac} > b > -\tfrac{4}{\sqrt{3}}\,\sqrt{ac} \quad &: \quad \text{5 real roots; minimum at } m = 0 \\ -\tfrac{4}{\sqrt{3}}\,\sqrt{ac} > b \quad &: \quad \text{5 real roots; minima at } m = \pm\sqrt{-\frac{b}{2c} + \sqrt{\left(\frac{b}{2c}\right)^2 - \frac{a}{c}}} \end{aligned} \tag{7.180}$$

The point $(a, b) = (0, 0)$, which lies at the confluence of a first order line and a second order line, is known as a *tricritical point*.

### 7.6.4 Hysteresis for the sextic potential

Once again, we consider the dissipative dynamics $\dot{m} = -\Gamma\, f'(m)$. We adimensionalize by writing

$$m \equiv \sqrt{\frac{|b|}{c}} \cdot u \qquad , \qquad a \equiv \frac{b^2}{c} \cdot r \qquad , \qquad t \equiv \frac{c}{\Gamma\, b^2} \cdot s \ . \tag{7.181}$$

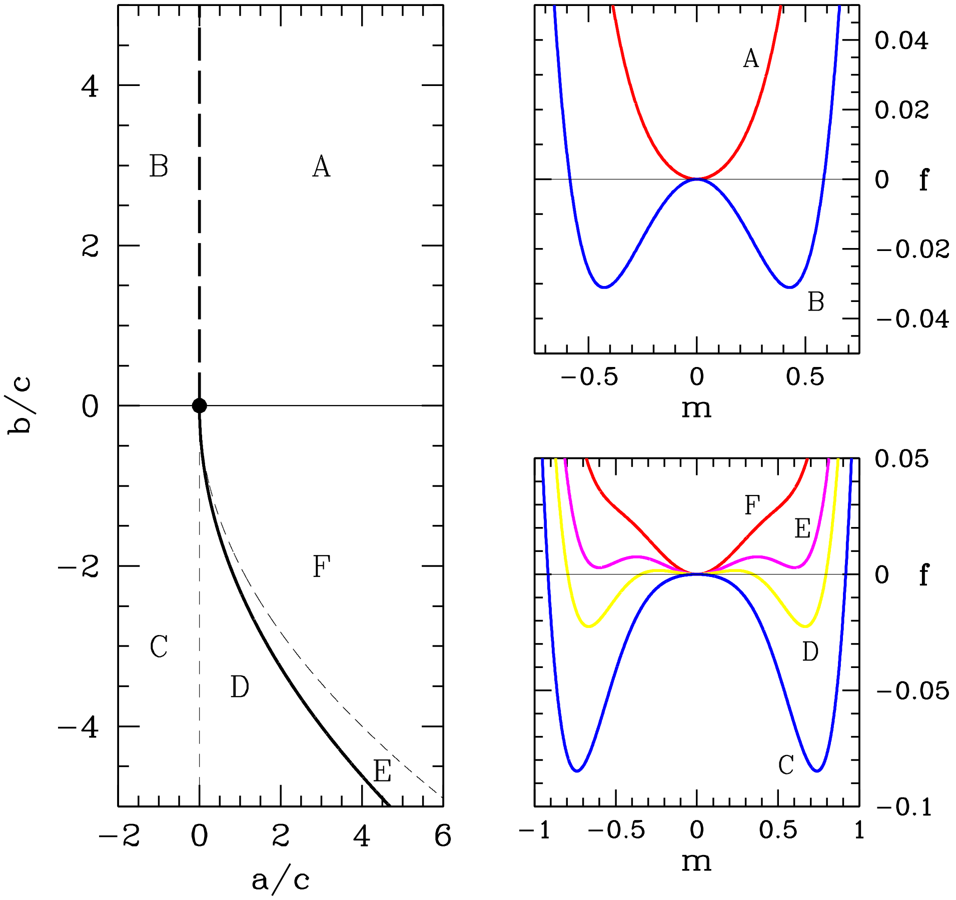

Figure 7.17: Behavior of the sextic free energy $f(m) = \frac{1}{2}am^2 + \frac{1}{4}bm^4 + \frac{1}{6}cm^6$. A: $a > 0$ and $b > 0$ ; B: $a < 0$ and $b > 0$ ; C: $a < 0$ and $b < 0$ ; D: $a > 0$ and $b < -\frac{4}{\sqrt{3}}\sqrt{ac}$ ; E: $a > 0$ and $-\frac{4}{\sqrt{3}}\sqrt{ac} < b < -2\sqrt{ac}$ ; F: $a > 0$ and $-2\sqrt{ac} < b < 0$. The thick dashed line is a line of second order transitions, which meets the thick solid line of first order transitions at the tricritical point, $(a, b) = (0, 0)$.

Then we obtain once again the dimensionless equation

$$\frac{\partial u}{\partial s} = -\frac{\partial \varphi}{\partial u} \,, \tag{7.182}$$

where

$$\varphi(u) = \tfrac{1}{2}ru^2 \pm \tfrac{1}{4}u^4 + \tfrac{1}{6}u^6 \,. \tag{7.183}$$

In the above equation, the coefficient of the quartic term is positive if $b > 0$ and negative if $b < 0$. That is, the coefficient is $\mathrm{sgn}(b)$. When $b > 0$ we can ignore the sextic term for sufficiently small $u$, and we recover the quartic free energy studied earlier. There is then a second order transition at $r = 0$. .

New and interesting behavior occurs for $b > 0$. The fixed points of the dynamics are obtained by setting $\varphi'(u) = 0$. We have

$$\begin{aligned} \varphi(u) &= \tfrac{1}{2}ru^2 - \tfrac{1}{4}u^4 + \tfrac{1}{6}u^6 \\ \varphi'(u) &= u\,(r - u^2 + u^4) \,. \end{aligned} \tag{7.184}$$

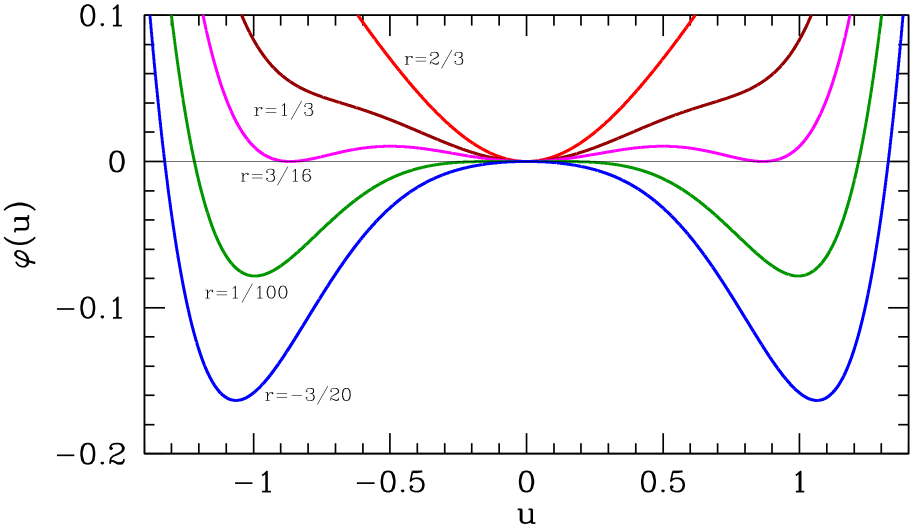

Figure 7.18: Free energy $\varphi(u) = \frac{1}{2}ru^2 - \frac{1}{4}u^4 + \frac{1}{6}u^6$ for several different values of the control parameter $r$.

Thus, the equation $\varphi'(u) = 0$ factorizes into a linear factor $u$ and a quartic factor $u^4 - u^2 + r$ which is quadratic in $u^2$. Thus, we can easily obtain the roots:

$$\begin{aligned} r < 0 \quad &: \quad u^* = 0 \, , \; u^* = \pm\sqrt{\tfrac{1}{2} + \sqrt{\tfrac{1}{4} - r}} \\ 0 < r < \tfrac{1}{4} \quad &: \quad u^* = 0 \, , \; u^* = \pm\sqrt{\tfrac{1}{2} + \sqrt{\tfrac{1}{4} - r}} \; , \; u^* = \pm\sqrt{\tfrac{1}{2} - \sqrt{\tfrac{1}{4} - r}} \\ r > \tfrac{1}{4} \quad &: \quad u^* = 0 \, . \end{aligned} \tag{7.185}$$

In fig. 7.19, we plot the fixed points and the hysteresis loops for this system. At $r = \frac{1}{4}$, there are two symmetrically located saddle-node bifurcations at $u = \pm\frac{1}{\sqrt{2}}$. We find $\varphi(u = \pm\frac{1}{\sqrt{2}}, r = \frac{1}{4}) = \frac{1}{48}$, which is positive, indicating that the stable fixed point $u^* = 0$ remains the thermodynamic minimum for the free energy $\varphi(u)$ as $r$ is decreased through $r = \frac{1}{4}$. Setting $\varphi(u) = 0$ and $\varphi'(u) = 0$ simultaneously, we obtain $r = \frac{3}{16}$ and $u = \pm\frac{\sqrt{3}}{2}$. The thermodynamic value for $u$ therefore jumps discontinuously from $u = 0$ to $u = \pm\frac{\sqrt{3}}{2}$ (either branch) at $r = \frac{3}{16}$; this is a first order transition.

Under the dissipative dynamics considered here, the system exhibits hysteresis, as indicated in the figure, where the arrows show the evolution of $u(s)$ for very slowly varying $r(s)$. When the control parameter $r$ is large and positive, the flow is toward the sole fixed point at $u^* = 0$. At $r = \frac{1}{4}$, two simultaneous saddle-node bifurcations take place at $u^* = \pm\frac{1}{\sqrt{2}}$; the outer branch is stable and the inner branch unstable in both cases. At $r = 0$ there is a subcritical pitchfork bifurcation, and the fixed point at $u^* = 0$ becomes unstable.

Suppose one starts off with $r \gg \frac{1}{4}$ with some value $u > 0$. The flow $\dot{u} = -\varphi'(u)$ then rapidly results in $u \to 0^+$. This is the 'high temperature phase' in which there is no magnetization. Now let $r$ increase slowly, using $s$ as the dimensionless time variable. The scaled magnetization $u(s) = u^*\big(r(s)\big)$ will remain pinned at the fixed point $u^* = 0^+$. As $r$ passes through $r = \frac{1}{4}$, two new stable values of $u^*$ appear, but our system remains at $u = 0^+$, since $u^* = 0$ is a stable fixed point. But after the subcritical pitchfork, $u^* = 0$ becomes unstable. The magnetization $u(s)$ then flows rapidly to the stable fixed point at $u^* = \frac{1}{\sqrt{2}}$, and follows the curve $u^*(r) = \big(\frac{1}{2} + (\frac{1}{4} - r)^{1/2}\big)^{1/2}$ for all $r < 0$.

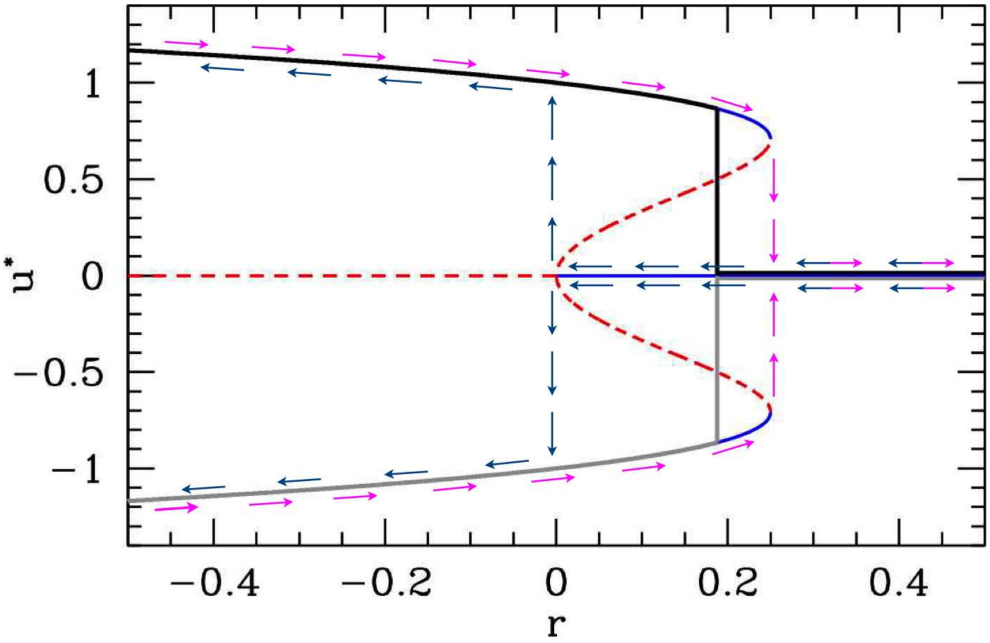

Figure 7.19: Fixed points $\varphi'(u^*) = 0$ for the sextic potential $\varphi(u) = \frac{1}{2}ru^2 - \frac{1}{4}u^4 + \frac{1}{6}u^6$, and corresponding dynamical flow (arrows) under $\dot{u} = -\varphi'(u)$. Solid curves show stable fixed points and dashed curves show unstable fixed points. The thick solid black and solid grey curves indicate the equilibrium thermodynamic values for $u$; note the overall $u \to -u$ symmetry. Within the region $r \in [0, \frac{1}{4}]$ the dynamics are irreversible and the system exhibits the phenomenon of hysteresis. There is a first order phase transition at $r = \frac{3}{16}$.

Now suppose we start increasing $r$ (*i.e.* increasing temperature). The magnetization follows the stable fixed point $u^*(r) = \big(\frac{1}{2} + (\frac{1}{4} - r)^{1/2}\big)^{1/2}$ past $r = 0$, beyond the first order phase transition point at $r = \frac{3}{16}$, and all the way up to $r = \frac{1}{4}$, at which point this fixed point is annihilated at a saddle-node bifurcation. The flow then rapidly takes $u \to u^* = 0^+$, where it remains as $r$ continues to be increased further.

Within the region $r \in \big[0, \frac{1}{4}\big]$ of control parameter space, the dynamics are said to be *irreversible* and the behavior of $u(s)$ is said to be *hysteretic*.

## 7.7 Mean Field Theory of Fluctuations

### 7.7.1 Correlation and response in mean field theory

Consider the Ising model,

$$\hat{H} = -\tfrac{1}{2}\sum_{i,j} J_{ij}\,\sigma_i\,\sigma_j - \sum_k H_k\,\sigma_k \ , \tag{7.186}$$

where the local magnetic field on site $k$ is now $H_k$. We assume without loss of generality that the diagonal terms vanish: $J_{ii} = 0$. Now consider the partition function $Z = \mathsf{Tr}\ e^{-\beta\hat{H}}$ as a function of the temperature $T$ and the local field values $\{H_i\}$. We have

$$\begin{aligned}\frac{\partial Z}{\partial H_i} &= \beta\,\mathsf{Tr}\Big[\sigma_i\, e^{-\beta\hat{H}}\Big] = \beta Z\cdot\langle\sigma_i\rangle \\ \frac{\partial^2 Z}{\partial H_i\,\partial H_j} &= \beta^2\,\mathsf{Tr}\Big[\sigma_i\,\sigma_j\, e^{-\beta\hat{H}}\Big] = \beta^2 Z\cdot\langle\sigma_i\,\sigma_j\rangle\ .\end{aligned} \tag{7.187}$$

Thus,

$$\begin{aligned}m_i &= -\frac{\partial F}{\partial H_i} = \langle\sigma_i\rangle \\ \chi_{ij} &= \frac{\partial m_i}{\partial H_j} = -\frac{\partial^2 F}{\partial H_i \partial H_j} = \frac{1}{k_{\rm B}T}\cdot\Big\{\langle\sigma_i\,\sigma_j\rangle - \langle\sigma_i\rangle\,\langle\sigma_j\rangle\Big\}\ .\end{aligned} \tag{7.188}$$

Expressions such as $\langle\sigma_i\rangle$, $\langle\sigma_i\,\sigma_j\rangle$, *etc.* are in general called *correlation functions*. For example, we define the *spin-spin correlation function* $C_{ij}$ as

$$C_{ij} \equiv \langle\sigma_i\,\sigma_j\rangle - \langle\sigma_i\rangle\,\langle\sigma_j\rangle\ . \tag{7.189}$$

Expressions such as $\frac{\partial F}{\partial H_i}$ and $\frac{\partial^2 F}{\partial H_i\,\partial H_j}$ are called *response functions*. The above relation between correlation functions and response functions, $C_{ij} = k_{\rm B}T\,\chi_{ij}$, is valid *only for the equilibrium distribution*. In particular, this relationship is *invalid* if one uses an approximate distribution, such as the variational density matrix formalism of mean field theory.

The question then arises: within mean field theory, which is more accurate: correlation functions or response functions? A simple argument suggests that the *response functions* are more accurate representations of the real physics. To see this, let's write the variational density matrix $\varrho^{\rm var}$ as the sum of the exact equilibrium (Boltzmann) distribution $\varrho^{\rm eq} = Z^{-1}\exp(-\beta\hat{H})$ plus a deviation $\delta\varrho$:

$$\varrho^{\rm var} = \varrho^{\rm eq} + \delta\varrho\ . \tag{7.190}$$

Then if we calculate a correlator using the variational distribution, we have

$$\begin{aligned}\langle\sigma_i\,\sigma_j\rangle_{\rm var} &= \mathsf{Tr}\Big[\varrho^{\rm var}\,\sigma_i\,\sigma_j\Big] \\ &= \mathsf{Tr}\Big[\varrho^{\rm eq}\,\sigma_i\,\sigma_j\Big] + \mathsf{Tr}\Big[\delta\varrho\,\sigma_i\,\sigma_j\Big]\ .\end{aligned} \tag{7.191}$$

Thus, the variational density matrix gets the correlator right to first order in $\delta\varrho$. On the other hand, the free energy is given by

$$F^{\rm var} = F^{\rm eq} + \sum_{\boldsymbol{\sigma}} \frac{\partial F}{\partial\varrho_{\boldsymbol{\sigma}}}\bigg|_{\varrho^{\rm eq}} \delta\varrho_{\boldsymbol{\sigma}} + \frac{1}{2}\sum_{\boldsymbol{\sigma},\boldsymbol{\sigma}'} \frac{\partial^2 F}{\partial\varrho_{\boldsymbol{\sigma}}\,\partial\varrho_{\boldsymbol{\sigma}'}}\bigg|_{\varrho^{\rm eq}} \delta\varrho_{\boldsymbol{\sigma}}\,\delta\varrho_{\boldsymbol{\sigma}'} + \ldots\ . \tag{7.192}$$

Here $\boldsymbol{\sigma}$ denotes a state of the system, *i.e.* $|\,\boldsymbol{\sigma}\,\rangle = |\,\sigma_1,\ldots,\sigma_N\,\rangle$, where every spin polarization is specified. Since the free energy is an extremum (and in fact an absolute minimum) with respect to the distribution, the second term on the RHS vanishes. This means that the free energy is accurate to second order in the deviation $\delta\varrho$.

### 7.7.2 Calculation of the response functions

Consider the variational density matrix

$$\varrho(\boldsymbol{\sigma}) = \prod_i \varrho_i(\sigma_i)\ , \tag{7.193}$$

where

$$\varrho_i(\sigma_i) = \left(\frac{1+m_i}{2}\right)\delta_{\sigma_i,1} + \left(\frac{1-m_i}{2}\right)\delta_{\sigma_i,-1}\ . \tag{7.194}$$

The variational energy $E = \mathsf{Tr}\,(\varrho\,\hat{H})$ is

$$E = -\tfrac{1}{2}\sum_{ij} J_{i,j}\, m_i\, m_j - \sum_i H_i\, m_i \tag{7.195}$$

and the entropy $S = -k_{\rm B}T\,\mathsf{Tr}\,(\varrho\ln\varrho)$ is

$$S = -k_{\rm B}\sum_i \left\{ \left(\frac{1+m_i}{2}\right)\ln\!\left(\frac{1+m_i}{2}\right) + \left(\frac{1-m_i}{2}\right)\ln\!\left(\frac{1-m_i}{2}\right)\right\}\ . \tag{7.196}$$

Setting the variation $\frac{\partial F}{\partial m_i} = 0$, with $F = E - TS$, we obtain the mean field equations,

$$m_i = \tanh\big(\beta J_{ij}\, m_j + \beta H_i\big)\ , \tag{7.197}$$

where we use the summation convention: $J_{ij}\, m_j \equiv \sum_j J_{ij}\, m_j$. Suppose $T > T_{\rm c}$ and $m_i$ is small. Then we can expand the RHS of the above mean field equations, obtaining

$$\big(\delta_{ij} - \beta J_{ij}\big)\, m_j = \beta H_i\ . \tag{7.198}$$

Thus, the susceptibility tensor $\chi$ is the inverse of the matrix $(k_{\rm B}T\cdot\mathbb{I} - \mathbb{J})$:

$$\chi_{ij} = \frac{\partial m_i}{\partial H_j} = \big(k_{\rm B}T\cdot\mathbb{I} - \mathbb{J}\big)^{-1}_{ij}\ , \tag{7.199}$$

where $\mathbb{I}$ is the identity. Note also that so-called *connected averages* of the kind in eqn. 7.189 vanish identically if we compute them using our variational density matrix, since all the sites are independent, hence

$$\langle \sigma_i\, \sigma_j\rangle = \mathsf{Tr}\,\big(\varrho^{\rm var}\,\sigma_i\,\sigma_j\big) = \mathsf{Tr}\,\big(\varrho_i\,\sigma_i\big)\cdot \mathsf{Tr}\,\big(\varrho_j\,\sigma_j\big) = \langle\sigma_i\rangle\cdot\langle\sigma_j\rangle\ , \tag{7.200}$$

and therefore $\chi_{ij} = 0$ if we compute the correlation functions themselves from the variational density matrix, rather than from the free energy $F$. As we have argued above, the latter approximation is more accurate.

Assuming $J_{ij} = J(\boldsymbol{R}_i - \boldsymbol{R}_j)$, where $\boldsymbol{R}_i$ is a Bravais lattice site, we can Fourier transform the above equation, resulting in

$$\hat{m}(\boldsymbol{q}) = \frac{\hat{H}(\boldsymbol{q})}{k_{\rm B}T - \hat{J}(\boldsymbol{q})} \equiv \hat{\chi}(\boldsymbol{q})\,\hat{H}(\boldsymbol{q})\ . \tag{7.201}$$

Once again, our definition of lattice Fourier transform of a function $\phi(\boldsymbol{R})$ is

$$\begin{aligned} \hat{\phi}(\boldsymbol{q}) &\equiv \sum_{\boldsymbol{R}} \phi(\boldsymbol{R})\, e^{-i\boldsymbol{q}\cdot\boldsymbol{R}} \\ \phi(\boldsymbol{R}) &= \Omega\int\limits_{\hat{\Omega}} \frac{d^dq}{(2\pi)^d}\ \hat{\phi}(\boldsymbol{q})\, e^{i\boldsymbol{q}\cdot\boldsymbol{R}}\ , \end{aligned} \tag{7.202}$$

where $\Omega$ is the unit cell in real space, called the *Wigner-Seitz cell*, and $\hat{\Omega}$ is the first Brillouin zone, which is the unit cell in *reciprocal space*. Similarly, we have

$$\begin{aligned} \hat{J}(\boldsymbol{q}) &= \sum_{\boldsymbol{R}} J(\boldsymbol{R})\Big(1 - i\boldsymbol{q}\cdot\boldsymbol{R} - \tfrac{1}{2}(\boldsymbol{q}\cdot\boldsymbol{R})^2 + \ldots\Big) \\ &= \hat{J}(0)\cdot\Big\{1 - q^2 R_*^2 + \mathcal{O}(q^4)\Big\}\ , \end{aligned} \tag{7.203}$$

where

$$R_*^2 = \frac{\sum_{\boldsymbol{R}} \boldsymbol{R}^2 J(\boldsymbol{R})}{2d \sum_{\boldsymbol{R}} J(\boldsymbol{R})} \ . \tag{7.204}$$

Here we have assumed inversion symmetry for the lattice, in which case

$$\sum_{\boldsymbol{R}} R^\mu R^\nu J(\boldsymbol{R}) = \frac{1}{d} \cdot \delta^{\mu\nu} \sum_{\boldsymbol{R}} \boldsymbol{R}^2 J(\boldsymbol{R}) \ . \tag{7.205}$$

On cubic lattices with nearest neighbor interactions only, one has $R_* = a/\sqrt{2d}$, where $a$ is the lattice constant and $d$ is the dimension of space.

Thus, with the identification $k_{\rm B} T_{\rm c} = \hat{J}(0)$, we have

$$\begin{aligned} \hat{\chi}(\boldsymbol{q}) &= \frac{1}{k_{\rm B}(T - T_{\rm c}) + k_{\rm B} T_{\rm c}\, R_*^2\, \boldsymbol{q}^2 + \mathcal{O}(q^4)} \\ &= \frac{1}{k_{\rm B} T_{\rm c}\, R_*^2} \cdot \frac{1}{\xi^{-2} + q^2 + \mathcal{O}(q^4)} \ , \end{aligned} \tag{7.206}$$

where

$$\xi = R_* \cdot \left( \frac{T - T_{\rm c}}{T_{\rm c}} \right)^{-1/2} \tag{7.207}$$

is the *correlation length*. With the definition

$$\xi(T) \propto |T - T_{\rm c}|^{-\nu} \tag{7.208}$$

as $T \to T_{\rm c}$, we obtain the mean field correlation length exponent $\nu = \frac{1}{2}$. The exact result for the two-dimensional Ising model is $\nu = 1$, whereas $\nu \approx 0.6$ for the $d = 3$ Ising model. Note that $\hat{\chi}(\boldsymbol{q} = 0, T)$ diverges as $(T - T_{\rm c})^{-1}$ for $T > T_{\rm c}$.

In real space, we have

$$m_i = \sum_j \chi_{ij}\, H_j \ , \tag{7.209}$$

where

$$\chi_{ij} = \Omega \!\int\! \frac{d^d q}{(2\pi)^d}\, \hat{\chi}(\boldsymbol{q})\, e^{i\boldsymbol{q}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)} \ . \tag{7.210}$$

Note that $\hat{\chi}(\boldsymbol{q})$ is properly periodic under $\boldsymbol{q} \to \boldsymbol{q} + \boldsymbol{G}$, where $\boldsymbol{G}$ is a reciprocal lattice vector, which satisfies $e^{i\boldsymbol{G}\cdot\boldsymbol{R}} = 1$ for any direct Bravais lattice vector $\boldsymbol{R}$. Indeed, we have

$$\begin{aligned} \hat{\chi}^{-1}(\boldsymbol{q}) &= k_{\rm B} T - \hat{J}(\boldsymbol{q}) \\ &= k_{\rm B} T - J \sum_{\boldsymbol{\delta}} e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}} \ , \end{aligned} \tag{7.211}$$

where $\boldsymbol{\delta}$ is a nearest neighbor separation vector, and where in the second line we have assumed nearest neighbor interactions only. On cubic lattices in $d$ dimensions, there are $2d$ nearest neighbor separation vectors, $\boldsymbol{\delta} = \pm a\, \hat{\boldsymbol{e}}_\mu$, where $\mu \in \{1, \ldots, d\}$. The real space susceptibility is then

$$\chi(\boldsymbol{R}) = \int\limits_{-\pi}^{\pi} \!\frac{d\theta_1}{2\pi} \cdots \int\limits_{-\pi}^{\pi} \!\frac{d\theta_d}{2\pi}\, \frac{e^{i n_1 \theta_1} \ldots e^{i n_d \theta_d}}{k_{\rm B} T - (2J \cos\theta_1 + \ldots + 2J \cos\theta_d)} \ , \tag{7.212}$$

where $\boldsymbol{R} = a \sum_{\mu=1}^d n_\mu\, \hat{\boldsymbol{e}}_\mu$ is a general direct lattice vector for the cubic Bravais lattice in $d$ dimensions, and the $\{n_\mu\}$ are integers.

The long distance behavior was discussed in chapter 6 (see §6.4.9 on Ornstein-Zernike theory[18]). For convenience we reiterate those results:

- In $d = 1$,
$$\chi_{d=1}(x) = \left(\frac{\xi}{2k_{\rm B}T_{\rm c}R_*^2}\right) e^{-|x|/\xi} \ . \tag{7.213}$$
- In $d > 1$, with $r \to \infty$ and $\xi$ fixed,
$$\chi_d^{\rm OZ}(\boldsymbol{r}) \simeq C_d \cdot \frac{\xi^{(3-d)/2}}{k_{\rm B}T\,R_*^2} \cdot \frac{e^{-r/\xi}}{r^{(d-1)/2}} \cdot \left\{1 + \mathcal{O}\left(\frac{d-3}{r/\xi}\right)\right\} \ , \tag{7.214}$$
where the $C_d$ are dimensionless constants.
- In $d > 2$, with $\xi \to \infty$ and $r$ fixed (*i.e.* $T \to T_{\rm c}$ at fixed separation $\boldsymbol{r}$),
$$\chi_d(\boldsymbol{r}) \simeq \frac{C'_d}{k_{\rm B}TR_*^2} \cdot \frac{e^{-r/\xi}}{r^{d-2}} \cdot \left\{1 + \mathcal{O}\left(\frac{d-3}{r/\xi}\right)\right\} \ . \tag{7.215}$$
In $d = 2$ dimensions we obtain
$$\chi_{d=2}(\boldsymbol{r}) \simeq \frac{C'_2}{k_{\rm B}TR_*^2} \cdot \ln\left(\frac{r}{\xi}\right) e^{-r/\xi} \cdot \left\{1 + \mathcal{O}\left(\frac{1}{\ln(r/\xi)}\right)\right\} \ , \tag{7.216}$$
where the $C'_d$ are dimensionless constants.

## 7.8 Global Symmetries

### 7.8.1 Symmetries and symmetry groups

Interacting systems can be broadly classified according to their *global symmetry group*. Consider the following five examples:

$$\begin{aligned}
\hat{H}_{\rm Ising} &= -\sum_{i<j} J_{ij}\,\sigma_i\,\sigma_j & \sigma_i &\in \{-1,+1\} \\
\hat{H}_{p-{\rm clock}} &= -\sum_{i<j} J_{ij}\,\cos\left(\frac{2\pi(n_i-n_j)}{p}\right) & n_i &\in \{1,2,\ldots,p\} \\
\hat{H}_{q-{\rm Potts}} &= -\sum_{i<j} J_{ij}\,\delta_{\sigma_i,\sigma_j} & \sigma_i &\in \{1,2,\ldots,q\} \\
\hat{H}_{XY} &= -\sum_{i<j} J_{ij}\,\cos(\phi_i-\phi_j) & \phi_i &\in \big[0,2\pi\big] \\
\hat{H}_{{\sf O}(n)} &= -\sum_{i<j} J_{ij}\,\hat{\boldsymbol{\Omega}}_i\cdot\hat{\boldsymbol{\Omega}}_j & \hat{\boldsymbol{\Omega}}_i &\in S^{n-1} \ .
\end{aligned} \tag{7.217}$$

The Ising Hamiltonian is left invariant by the global symmetry group $\mathbb{Z}_2$, which has two elements, $\mathbb{I}$ and $\eta$, with
$$\eta\,\sigma_i = -\sigma_i \ . \tag{7.218}$$

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[18] There is a sign difference between the particle susceptibility defined in chapter 6 and the spin susceptibility defined here. The origin of the difference is that the single particle potential $v$ as defined was repulsive for $v > 0$, meaning the local density response $\delta n$ should be negative, while in the current discussion a positive magnetic field $H$ prefers $m > 0$.

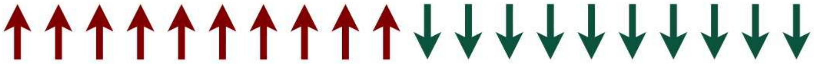

Figure 7.20: A domain wall in a one-dimensional Ising model.

$\mathbb{I}$ is the identity, and $\eta^2 = \mathbb{I}$. By simultaneously reversing *all* the spins $\sigma_i \to -\sigma_i$, the interactions remain invariant.

The degrees of freedom of the *p-state clock model* are integer variables $n_i$ each of which ranges from $1$ to $p$. The Hamiltonian is invariant under the discrete group $\mathbb{Z}_p$, whose $p$ elements are generated by the single operation $\eta$, where

$$\eta\, n_i = \begin{cases} n_i + 1 & \text{if} \quad n_i \in \{1, 2, \ldots, p-1\} \\ 1 & \text{if} \quad n_i = p\,. \end{cases} \tag{7.219}$$

Think of a clock with one hand and $p$ 'hour' markings consecutively spaced by an angle $2\pi/p$. In each site $i$, a hand points to one of the $p$ hour marks; this determines $n_i$. The operation $\eta$ simply advances *all* the hours by one tick, with hour $p$ advancing to hour 1, just as 23:00 military time is followed one hour later by 00:00. The interaction $\cos\big(2\pi(n_i - n_j)/p\big)$ is invariant under such an operation. The $p$ elements of the group $\mathbb{Z}_p$ are then

$$\mathbb{I}\,,\ \eta\,,\ \eta^2\,,\ \ldots\,,\ \eta^{p-1}\,. \tag{7.220}$$

We've already met up with the $q$-state Potts model, where each site supports a 'spin' $\sigma_i$ which can be in any of $q$ possible states, which we may label by integers $\{1\,,\,\ldots\,,\,q\}$. The energy of two interacting sites $i$ and $j$ is $-J_{ij}$ if $\sigma_i = \sigma_j$ and zero otherwise. This energy function is invariant under global operations of the *symmetric group on $q$ characters*, $S_q$, which is the group of permutations of the sequence $\{1\,,\,2\,,\,3\,,\,\ldots\,,\,q\}$. The group $S_q$ has $q!$ elements. Note the difference between a $\mathbb{Z}_q$ symmetry and an $S_q$ symmetry. In the former case, the Hamiltonian is invariant only under the $q$-element cyclic permutations, *e.g.*

$$\eta \equiv \begin{pmatrix} 1 & 2 & \cdots & q\!-\!1 & q \\ 2 & 3 & \cdots & q & 1 \end{pmatrix}$$

and its powers $\eta^l$ with $l = 0, \ldots, q-1$.

All these models – the Ising, $p$-state clock, and $q$-state Potts models – possess a global symmetry group which is *discrete*. That is, each of the symmetry groups $\mathbb{Z}_2$, $\mathbb{Z}_p$, $S_q$ is a discrete group, with a finite number of elements. The $XY$ Hamiltonian $\hat{H}_{XY}$ on the other hand is invariant under a *continuous* group of transformations $\phi_i \to \phi_i + \alpha$, where $\phi_i$ is the angle variable on site $i$. More to the point, we could write the interaction term $\cos(\phi_i - \phi_j)$ as $\frac{1}{2}\big(z_i^* z_j + z_i z_j^*\big)$, where $z_i = e^{i\phi_i}$ is a phase which lives on the unit circle, and $z_i^*$ is the complex conjugate of $z_i$. The model is then invariant under the global transformation $z_i \to e^{i\alpha} z_i$. The phases $e^{i\alpha}$ form a group under multiplication, called $\mathsf{U}(1)$, which is the same as $\mathsf{O}(2)$. Equivalently, we could write the interaction as $\hat{\boldsymbol{\Omega}}_i \cdot \hat{\boldsymbol{\Omega}}_j$, where $\hat{\boldsymbol{\Omega}}_i = (\cos\phi_i\,,\,\sin\phi_i)$, which explains the $\mathsf{O}(2)$, symmetry, since the symmetry operations are global rotations in the plane, which is to say the two-dimensional orthogonal group. This last representation generalizes nicely to unit vectors in $n$ dimensions, where

$$\hat{\boldsymbol{\Omega}} = (\Omega^1\,,\,\Omega^2\,,\,\ldots\,,\,\Omega^n) \tag{7.221}$$

with $\hat{\boldsymbol{\Omega}}^2 = 1$. The dot product $\hat{\boldsymbol{\Omega}}_i \cdot \hat{\boldsymbol{\Omega}}_j$ is then invariant under global rotations in this $n$-dimensional space, which is the group $\mathsf{O}(n)$.

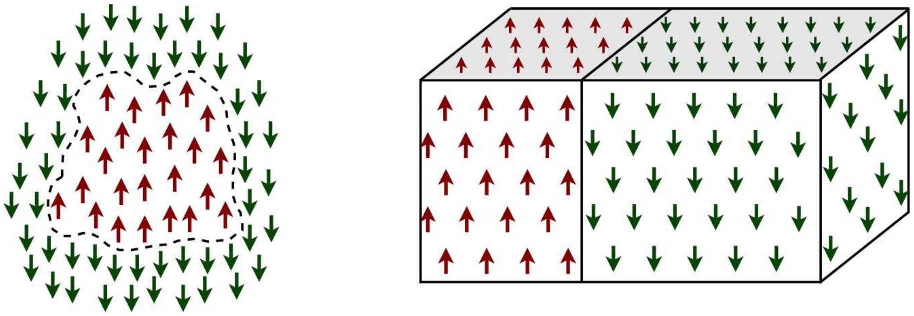

Figure 7.21: Domain walls in the two-dimensional (left) and three-dimensional (right) Ising model.

### 7.8.2 Lower critical dimension

Depending on whether the global symmetry group of a model is discrete or continuous, there exists a *lower critical dimension* $d_\ell$ at or below which no phase transition may take place at finite temperature. That is, for $d \le d_\ell$, the critical temperature is $T_c = 0$. Owing to its neglect of fluctuations, mean field theory generally *overestimates* the value of $T_c$ because it overestimates the stability of the ordered phase. Indeed, there are many examples where mean field theory predicts a finite $T_c$ when the actual critical temperature is $T_c = 0$. This happens whenever $d \le d_\ell$.

Let's test the stability of the ordered (ferromagnetic) state of the one-dimensional Ising model at low temperatures. We consider order-destroying *domain wall* excitations which interpolate between regions of degenerate, symmetry-related ordered phase, *i.e.* ↑↑↑↑↑ and ↓↓↓↓↓. For a system with a discrete symmetry at low temperatures, the domain wall is abrupt, on the scale of a single lattice spacing. If the exchange energy is $J$, then the energy of a single domain wall is $2J$, since a link of energy $-J$ is replaced with one of energy $+J$. However, there are $N$ possible locations for the domain wall, hence its entropy is $k_B \ln N$. For a system with $M$ domain walls, the free energy is

$$\begin{aligned} F &= 2MJ - k_B T \ln \binom{N}{M} \\ &= N \cdot \bigg\{ 2Jx + k_B T \Big[ x \ln x + (1-x)\ln(1-x) \Big] \bigg\} , \end{aligned} \tag{7.222}$$

where $x = M/N$ is the density of domain walls, and where we have used Stirling's approximation for $k!$ when $k$ is large. Extremizing with respect to $x$, we find

$$\frac{x}{1-x} = e^{-2J/k_B T} \qquad \Longrightarrow \qquad x = \frac{1}{e^{2J/k_B T} + 1} . \tag{7.223}$$

The average distance between domain walls is $x^{-1}$, which is finite for finite $T$. Thus, the thermodynamic state of the system is *disordered*, with no net average magnetization.

Consider next an Ising domain wall in $d$ dimensions. Let the linear dimension of the system be $L \cdot a$, where $L$ is a real number and $a$ is the lattice constant. Then the energy of a single domain wall which partitions the entire system is $2J \cdot L^{d-1}$. The domain wall entropy is difficult to compute, because the wall can fluctuate significantly, but for a single domain wall we have $S \gtrsim k_B \ln L$. Thus, the free energy $F = 2JL^{d-1} - k_B T \ln L$ is dominated by the energy term if $d > 1$, suggesting that the system *may* be ordered. We can do a slightly better job in $d = 2$ by writing

$$Z \approx \exp\bigg( L^d \sum_P N_P \, e^{-2PJ/k_B T} \bigg) , \tag{7.224}$$

where the sum is over all closd loops of perimeter $P$, and $N_P$ is the number of such loops. An example of such a loop circumscribing a domain is depicted in the left panel of fig. 7.21. It turns out that

$$N_P \simeq \kappa^P P^{-\theta} \cdot \Big\{1 + \mathcal{O}(P^{-1})\Big\} \ , \tag{7.225}$$

where $\kappa = z - 1$ with $z$ the lattice coordination number, and $\theta$ is some exponent. We can understand the $\kappa^P$ factor in the following way. At each step along the perimeter of the loop, there are $\kappa = z - 1$ possible directions to go (since one doesn't backtrack). The fact that the loop must avoid overlapping itself and must return to its original position to be closed leads to the power law term $P^{-\theta}$, which is subleading since $\kappa^P P^{-\theta} = \exp(P \ln\kappa - \theta \ln P)$ and $P \gg \ln P$ for $P \gg 1$. Thus,

$$F \approx -\frac{1}{\beta}\, L^d \sum_P P^{-\theta}\, e^{(\ln\kappa - 2\beta J)P} \ , \tag{7.226}$$

which diverges if $\ln\kappa > 2\beta J$, *i.e.* if $T > 2J/k_\text{B} \ln(z-1)$. We identify this singularity with the phase transition. The high temperature phase involves a proliferation of such loops. The excluded volume effects between the loops, which we have not taken into account, then enter in an essential way so that the sum converges. Thus, we have the following picture:

$$\begin{aligned} \ln\kappa < 2\beta J &: \text{ large loops suppressed ; ordered phase} \\ \ln\kappa > 2\beta J &: \text{ large loops proliferate ; disordered phase .} \end{aligned}$$

On the square lattice, we obtain

$$\begin{aligned} k_\text{B} T_\text{c}^\text{approx} &= \frac{2J}{\ln 3} = 1.82\, J \\ k_\text{B} T_\text{c}^\text{exact} &= \frac{2J}{\sinh^{-1}(1)} = 2.27\, J \ . \end{aligned}$$

The agreement is better than we should reasonably expect from such a crude argument.

*Nota bene* : Beware of arguments which allegedly prove the existence of an ordered phase. Generally speaking, any approximation will *underestimate* the entropy, and thus will overestimate the stability of the putative ordered phase.

### 7.8.3 Continuous symmetries

When the global symmetry group is continuous, the domain walls interpolate smoothly between ordered phases. The energy generally involves a stiffness term,

$$E = \tfrac{1}{2}\rho_\text{s} \int d^d\!r\, (\boldsymbol{\nabla}\theta)^2 \ , \tag{7.227}$$

where $\theta(\boldsymbol{r})$ is the angle of a local rotation about a single axis and where $\rho_\text{s}$ is the *spin stiffness*. Of course, in $\mathsf{O}(n)$ models, the rotations can be with respect to several different axes simultaneously.

In the ordered phase, we have $\theta(\boldsymbol{r}) = \theta_0$, a constant. Now imagine a domain wall in which $\theta(\boldsymbol{r})$ rotates by $2\pi$ across the width of the sample. We write $\theta(\boldsymbol{r}) = 2\pi n x/L$, where $L$ is the linear size of the sample (here with dimensions of length) and $n$ is an integer telling us how many complete twists the order parameter field makes. The domain wall then resembles that in fig. 7.22. The gradient energy is

$$E = \tfrac{1}{2}\rho_\text{s}\, L^{d-1} \int_0^L dx \left(\frac{2\pi n}{L}\right)^2 = 2\pi^2 n^2 \rho_\text{s}\, L^{d-2} \ . \tag{7.228}$$

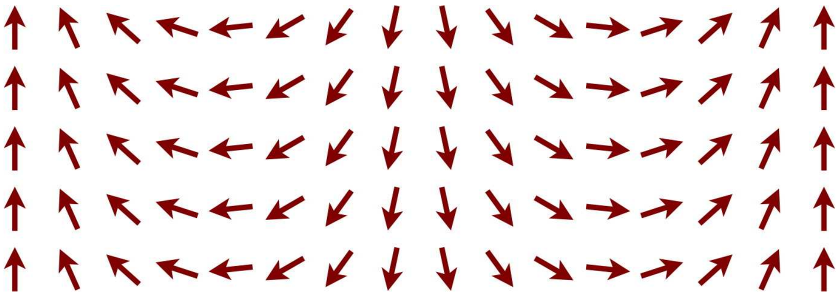

Figure 7.22: A domain wall in an $XY$ ferromagnet.

Recall that in the case of discrete symmetry, the domain wall energy scaled as $E \propto L^{d-1}$. Thus, with $S \gtrsim k_{\rm B} \ln L$ for a single wall, we see that the entropy term dominates if $d \leq 2$, in which case there is no finite temperature phase transition. Thus, the lower critical dimension $d_\ell$ depends on whether the global symmetry is discrete or continuous, with

$$\begin{aligned} \text{discrete global symmetry} \quad &\Longrightarrow \quad d_\ell = 1 \\ \text{continuous global symmetry} \quad &\Longrightarrow \quad d_\ell = 2 \ . \end{aligned}$$

Note that all along we have assumed local, *short-ranged* interactions. Long-ranged interactions can enhance order and thereby suppress $d_\ell$.

Thus, we expect that for models with discrete symmetries, $d_\ell = 1$ and there is no finite temperature phase transition for $d \leq 1$. For models with continuous symmetries, $d_\ell = 2$, and we expect $T_{\rm c} = 0$ for $d \leq 2$. In this context we should emphasize that the two-dimensional $XY$ model *does* exhibit a phase transition at finite temperature, called the *Kosterlitz-Thouless* transition. However, this phase transition is *not* associated with the breaking of the continuous global $\mathsf{O}(2)$ symmetry and rather has to do with the unbinding of vortices and antivortices. So there is still no true long-ranged order below the critical temperature $T_{\rm KT}$, even though there is a phase transition!

### 7.8.4 Random systems : Imry-Ma argument

Oftentimes, particularly in condensed matter systems, intrinsic randomness exists due to quenched impurities, grain boundaries, immobile vacancies, *etc.* How does this quenched randomness affect a system's attempt to order at $T = 0$? This question was taken up in a beautiful and brief paper by J. Imry and S.-K. Ma, *Phys. Rev. Lett.* **35**, 1399 (1975). Imry and Ma considered models in which there are short-ranged interactions and a random local field coupling to the local order parameter:

$$\hat{H}_{\rm RFI} = -J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j - \sum_i H_i \, \sigma_i \tag{7.229}$$

$$\hat{H}_{{\rm RF}\mathsf{O}(n)} = -J \sum_{\langle ij \rangle} \hat{\boldsymbol{\Omega}}_i \cdot \hat{\boldsymbol{\Omega}}_j - \sum_i H_i^\alpha \, \Omega_i^\alpha \ , \tag{7.230}$$

where

$$\langle\!\langle \, H_i^\alpha \, \rangle\!\rangle = 0 \qquad , \qquad \langle\!\langle \, H_i^\alpha \, H_j^\beta \, \rangle\!\rangle = \varGamma \, \delta^{\alpha\beta} \, \delta_{ij} \ , \tag{7.231}$$

where $\langle\!\langle \, \cdot \, \rangle\!\rangle$ denotes a configurational average over the disorder. Imry and Ma reasoned that a system could try to lower its free energy by forming *domains* in which the order parameter takes advantage of local fluctuations in the random field. The size of these domains is assumed to be $L_{\rm d}$, a length scale to be determined. See the sketch in the left panel of fig. 7.23.

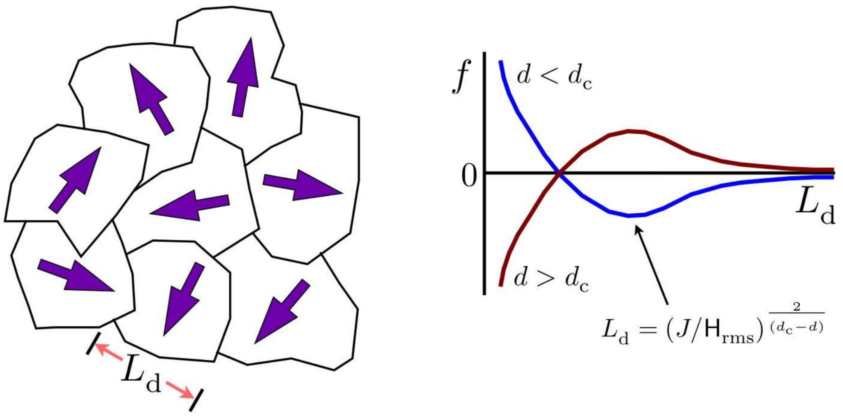

Figure 7.23: Left panel : Imry-Ma domains for an $\mathsf{O}(2)$ model. The arrows point in the direction of the local order parameter field $\langle\hat{\boldsymbol{\Omega}}(\boldsymbol{r})\rangle$. Right panel : free energy density as a function of domain size $L_\mathrm{d}$. Keep in mind that the minimum possible value for $L_\mathrm{d}$ is the lattice spacing $a$.

There are two contributions to the energy of a given domain: bulk and surface terms. The bulk energy is

$$E_\mathrm{bulk} = -H_\mathrm{rms}\,(L_\mathrm{d}/a)^{d/2} \,, \tag{7.232}$$

where $a$ is the lattice spacing. This is because when we add together $(L_\mathrm{d}/a)^d$ random fields, the magnitude of the result is proportional to the square root of the number of terms, *i.e.* to $(L_\mathrm{d}/a)^{d/2}$. The quantity $H_\mathrm{rms} = \sqrt{\Gamma}$ is the root-mean-square fluctuation in the random field at a given site. The surface energy is

$$E_\mathrm{surface} \propto \begin{cases} J\,(L_\mathrm{d}/a)^{d-1} & \text{(discrete symmetry)} \\ J\,(L_\mathrm{d}/a)^{d-2} & \text{(continuous symmetry)} \,. \end{cases} \tag{7.233}$$

We compute the critical dimension $d_\mathrm{c}$ by balancing the bulk and surface energies,

$$\begin{aligned} d - 1 = \tfrac{1}{2}d \qquad &\Longrightarrow \qquad d_\mathrm{c} = 2 \qquad \text{(discrete)} \\ d - 2 = \tfrac{1}{2}d \qquad &\Longrightarrow \qquad d_\mathrm{c} = 4 \qquad \text{(continuous)}\,. \end{aligned}$$

The total free energy is $F = (V/L_\mathrm{d}^d)\cdot\Delta E$, where $\Delta E = E_\mathrm{bulk} + E_\mathrm{surf}$. Thus, the free energy per unit cell is

$$f = \frac{F}{V/a^d} \approx J\left(\frac{a}{L_\mathrm{d}}\right)^{\frac{1}{2}d_\mathrm{c}} - H_\mathrm{rms}\left(\frac{a}{L_\mathrm{d}}\right)^{\frac{1}{2}d} \,. \tag{7.234}$$

If $d < d_\mathrm{c}$, the surface term dominates for small $L_\mathrm{d}$ and the bulk term dominates for large $L_\mathrm{d}$ There is global minimum at

$$\frac{L_\mathrm{d}}{a} = \left(\frac{d_\mathrm{c}}{d}\cdot\frac{J}{H_\mathrm{rms}}\right)^{\frac{2}{d_\mathrm{c}-d}} \,. \tag{7.235}$$

For $d > d_\mathrm{c}$, the relative dominance of the bulk and surface terms is reversed, and there is a global maximum at this value of $L_\mathrm{d}$.

Sketches of the free energy $f(L_\mathrm{d})$ in both cases are provided in the right panel of fig. 7.23. We must keep in mind that the domain size $L_\mathrm{d}$ cannot become smaller than the lattice spacing $a$. Hence we should draw a vertical line on the graph at $L_d = a$ and discard the portion $L_d < a$ as unphysical. For $d < d_\mathrm{c}$, we see that the state with $L_d = \infty$, *i.e.* the ordered state, is never the state of lowest free energy. *In dimensions $d < d_{\mathrm{c}}$, the ordered state is always unstable to domain formation in the presence of a random field.*

For $d > d_{\mathrm{c}}$, there are two possibilities, depending on the relative size of $J$ and $H_{\mathrm{rms}}$. We can see this by evaluating $f(L_d = a) = J - H_{\mathrm{rms}}$ and $f(L_{\mathrm{d}} = \infty) = 0$. Thus, if $J > H_{\mathrm{rms}}$, the minimum energy state occurs for $L_{\mathrm{d}} = \infty$. In this case, the system has an ordered ground state, and we expect a finite temperature transition to a disordered state at some critical temperature $T_{\mathrm{c}} > 0$. If, on the other hand, $J < H_{\mathrm{rms}}$, then the fluctuations in $H$ overwhelm the exchange energy at $T = 0$, and the ground state is disordered down to the very smallest length scale (*i.e.* the lattice spacing $a$).

Please read the essay, "Memories of Shang-Keng Ma," at `http://sip.clarku.edu/skma.html`.

## 7.9 Ginzburg-Landau Theory

### 7.9.1 Ginzburg-Landau free energy

Including gradient terms in the free energy, we write

$$F\big[m(\boldsymbol{x})\,,\,h(\boldsymbol{x})\big] = \int\!\!d^d\!x\,\bigg\{f_0 + \tfrac{1}{2}a\,m^2 + \tfrac{1}{4}b\,m^4 + \tfrac{1}{6}c\,m^6\ - h\,m + \tfrac{1}{2}\kappa\,(\boldsymbol{\nabla} m)^2 + \ldots\bigg\}\ . \tag{7.236}$$

In principle, any term which does not violate the appropriate global symmetry will turn up in such an expansion of the free energy, with some coefficient. Examples include $hm^3$ (both $m$ and $h$ are odd under time reversal), $m^2(\boldsymbol{\nabla} m)^2$, *etc.* We now ask: what function $m(\boldsymbol{x})$ extremizes the free energy functional $F\big[m(\boldsymbol{x})\,,\,h(\boldsymbol{x})\big]$? The answer is that $m(\boldsymbol{x})$ must satisfy the corresponding Euler-Lagrange equation, which for the above functional is

$$a\,m + b\,m^3 + c\,m^5 - h - \kappa\,\nabla^2 m = 0\ . \tag{7.237}$$

If $a > 0$ and $h$ is small (we assume $b > 0$ and $c > 0$), we may neglect the $m^3$ and $m^5$ terms and write

$$\big(a - \kappa\,\nabla^2\big)\,m = h\ , \tag{7.238}$$

whose solution is obtained by Fourier transform as

$$\hat{m}(\boldsymbol{q}) = \frac{\hat{h}(\boldsymbol{q})}{a + \kappa\boldsymbol{q}^2}\ , \tag{7.239}$$

which, with $h(\boldsymbol{x})$ appropriately defined, recapitulates the result in eqn. 7.201. Thus, we conclude that

$$\hat{\chi}(\boldsymbol{q}) = \frac{1}{a + \kappa\boldsymbol{q}^2}\ , \tag{7.240}$$

which should be compared with eqn. 7.206. For continuous functions, we have

$$\hat{m}(\boldsymbol{q}) = \int\!\!d^d\!x\; m(\boldsymbol{x})\,e^{-i\boldsymbol{q}\cdot\boldsymbol{x}} \tag{7.241}$$

$$m(\boldsymbol{x}) = \int\!\!\frac{d^d\!q}{(2\pi)^d}\;\hat{m}(\boldsymbol{q})\,e^{i\boldsymbol{q}\cdot\boldsymbol{x}}\ . \tag{7.242}$$

We can then derive the result

$$m(\boldsymbol{x}) = \int\!\!d^d\!x'\;\chi(\boldsymbol{x} - \boldsymbol{x}')\,h(\boldsymbol{x}')\ , \tag{7.243}$$

where

$$\chi(\boldsymbol{x}-\boldsymbol{x}') = \frac{1}{\kappa}\int\!\frac{d^d q}{(2\pi)^d}\,\frac{e^{i\boldsymbol{q}\cdot(\boldsymbol{x}-\boldsymbol{x}')}}{\boldsymbol{q}^2+\xi^{-2}}\ , \tag{7.244}$$

where the correlation length is $\xi=\sqrt{\kappa/a}\propto(T-T_{\rm c})^{-1/2}$, as before.

If $a<0$ then there is a spontaneous magnetization and we write $m(\boldsymbol{x})=m_0+\delta m(\boldsymbol{x})$. Assuming $h$ is weak, we then have two equations

$$a+b\,m_0^2+c\,m_0^4=0 \tag{7.245}$$

$$(a+3b\,m_0^2+5c\,m_0^4-\kappa\,\nabla^2)\,\delta m=h\ . \tag{7.246}$$

If $-a>0$ is small, we have $m_0^2=-a/3b$ and

$$\delta\hat{m}(\boldsymbol{q})=\frac{\hat{h}(\boldsymbol{q})}{-2a+\kappa\boldsymbol{q}^2}\ , \tag{7.247}$$

### 7.9.2 Domain wall profile

A particularly interesting application of Ginzburg-Landau theory is its application toward modeling the spatial profile of defects such as vortices and domain walls. Consider, for example, the case of Ising ($\mathbb{Z}_2$) symmetry with $h=0$. We expand the free energy density to order $m^4$:

$$F\big[m(\boldsymbol{x})\big]=\int\!d^d\!x\,\Big\{f_0+\tfrac{1}{2}a\,m^2+\tfrac{1}{4}b\,m^4+\tfrac{1}{2}\kappa\,(\boldsymbol{\nabla}m)^2\Big\}\ . \tag{7.248}$$

We assume $a<0$, corresponding to $T<T_{\rm c}$. Consider now a domain wall, where $m(x\to-\infty)=-m_0$ and $m(x\to+\infty)=+m_0$, where $m_0$ is the equilibrium magnetization, which we obtain from the Euler-Lagrange equation,

$$a\,m+b\,m^3-\kappa\,\nabla^2 m=0\ , \tag{7.249}$$

assuming a uniform solution where $\boldsymbol{\nabla}m=0$. This gives $m_0=\sqrt{|a|/b}$. It is useful to scale $m(\boldsymbol{x})$ by $m_0$, writing $m(\boldsymbol{x})=m_0\,\phi(\boldsymbol{x})$. The scaled order parameter function $\phi(\boldsymbol{x})$ interpolates between $\phi(-\infty)=-1$ and $\phi(+\infty)=1$.

It also proves useful to rescale position, writing $\boldsymbol{x}=\big(2\kappa/|a|\big)^{1/2}\boldsymbol{\zeta}$. Then we obtain

$$\tfrac{1}{2}\boldsymbol{\nabla}^2\phi=-\phi+\phi^3\ . \tag{7.250}$$

We assume $\phi(\boldsymbol{\zeta})=\phi(\zeta)$ is only a function of one coordinate, $\zeta\equiv\zeta^1$. Then the Euler-Lagrange equation becomes

$$\frac{d^2\phi}{d\zeta^2}=-2\phi+2\phi^3\equiv-\frac{\partial U}{\partial\phi}\ , \tag{7.251}$$

where

$$U(\phi)=-\tfrac{1}{2}\big(\phi^2-1\big)^2\ . \tag{7.252}$$

The 'potential' $U(\phi)$ is an inverted double well, with maxima at $\phi=\pm1$. The equation $\ddot{\phi}=-U'(\phi)$, where dot denotes differentiation with respect to $\zeta$, is simply Newton's second law with time replaced by space. In order to have a stationary solution at $\zeta\to\pm\infty$ where $\phi=\pm1$, the total energy must be $E=U(\phi=\pm1)=0$, where $E=\frac{1}{2}\dot{\phi}^2+U(\phi)$. This leads to the first order differential equation

$$\frac{d\phi}{d\zeta}=1-\phi^2\ , \tag{7.253}$$

with solution

$$\phi(\zeta) = \tanh(\zeta)\ . \tag{7.254}$$

Restoring the dimensionful constants,

$$m(x) = m_0\, \tanh\!\bigg(\frac{x}{\sqrt{2}\,\xi}\bigg)\ , \tag{7.255}$$

where the coherence length $\xi \equiv \big(\kappa/|a|\big)^{1/2}$ diverges at the Ising transition $a = 0$.

### 7.9.3 Derivation of Ginzburg-Landau free energy

We can make some progress in systematically deriving the Ginzburg-Landau free energy. Consider the Ising model,

$$\frac{\hat{H}}{k_{\rm B}T} = -\tfrac{1}{2}\sum_{i,j} K_{ij}\,\sigma_i\,\sigma_j - \sum_i h_i\,\sigma_i + \tfrac{1}{2}\sum_i K_{ii}\ , \tag{7.256}$$

where now $K_{ij} = J_{ij}/k_{\rm B}T$ and $h_i = H_i/k_{\rm B}T$ are the interaction energies and local magnetic fields in units of $k_{\rm B}T$. The last term on the RHS above cancels out any contribution from diagonal elements of $K_{ij}$. Our derivation makes use of a generalization of the Gaussian integral,

$$\int\limits_{-\infty}^{\infty}\!dx\; e^{-\frac{1}{2}ax^2 - bx} = \bigg(\frac{2\pi}{a}\bigg)^{1/2} e^{b^2/2a}\ . \tag{7.257}$$

The generalization is

$$\int\limits_{-\infty}^{\infty}\!dx_1 \cdots \int\limits_{-\infty}^{\infty}\!dx_N\; e^{-\frac{1}{2}A_{ij}x_i x_j - b_i x_i} = \frac{(2\pi)^{N/2}}{\sqrt{\det A}}\; e^{\frac{1}{2}A^{-1}_{ij}\,b_i b_j}\ , \tag{7.258}$$

where we use the Einstein convention of summing over repeated indices, and where we assume that the matrix $A$ is positive definite (else the integral diverges). This allows us to write

$$\begin{aligned} Z &= e^{-\frac{1}{2}K_{ii}}\ \mathsf{Tr}\,\Big[e^{\frac{1}{2}K_{ij}\sigma_i\,\sigma_j}\ e^{h_i\,\sigma_i}\Big] \\ &= \det{}^{-1/2}(2\pi K)\ e^{-\frac{1}{2}K_{ii}}\int\limits_{-\infty}^{\infty}\!d\phi_1\cdots\int\limits_{-\infty}^{\infty}\!d\phi_N\ e^{-\frac{1}{2}K^{-1}_{ij}\phi_i\phi_j}\ \mathsf{Tr}\ e^{(\phi_i+h_i)\sigma_i} \\ &= \det{}^{-1/2}(2\pi K)\ e^{-\frac{1}{2}K_{ii}}\int\limits_{-\infty}^{\infty}\!d\phi_1\cdots\int\limits_{-\infty}^{\infty}\!d\phi_N\ e^{-\frac{1}{2}K^{-1}_{ij}\phi_i\phi_j}\ e^{\sum_i \ln[2\cosh(\phi_i+h_i)]} \\ &\equiv \int\limits_{-\infty}^{\infty}\!d\phi_1\cdots\int\limits_{-\infty}^{\infty}\!d\phi_N\ e^{-\Phi(\phi_1,\ldots,\phi_N)}\ , \end{aligned} \tag{7.259}$$

where

$$\Phi = \tfrac{1}{2}\sum_{i,j} K^{-1}_{ij}\,\phi_i\,\phi_j - \sum_i \ln\cosh(\phi_i + h_i) + \tfrac{1}{2}\ln\mathsf{det}\,(2\pi K) + \tfrac{1}{2}\,\mathsf{Tr}\ K - N\ln 2\ . \tag{7.260}$$

We assume the model is defined on a Bravais lattice, in which case we can write $\phi_i = \phi_{\boldsymbol{R}_i}$. We can then define the Fourier transforms,

$$\phi_{\boldsymbol{R}} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{q}} \hat{\phi}_{\boldsymbol{q}}\, e^{i\boldsymbol{q}\cdot\boldsymbol{R}} \tag{7.261}$$

$$\hat{\phi}_{\boldsymbol{q}} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}} \phi_{\boldsymbol{R}}\, e^{-i\boldsymbol{q}\cdot\boldsymbol{R}} \tag{7.262}$$

and

$$\hat{K}(\boldsymbol{q}) = \sum_{\boldsymbol{R}} K(\boldsymbol{R})\, e^{-i\boldsymbol{q}\cdot\boldsymbol{R}} \ . \tag{7.263}$$

A few remarks about the lattice structure and periodic boundary conditions are in order. For a Bravais lattice, we can write each direct lattice vector $\boldsymbol{R}$ as a sum over $d$ basis vectors with integer coefficients, *viz.*

$$\boldsymbol{R} = \sum_{\mu=1}^{d} n_\mu\, \boldsymbol{a}_\mu \ , \tag{7.264}$$

where $d$ is the dimension of space. The reciprocal lattice vectors $\boldsymbol{b}_\mu$ satisfy

$$\boldsymbol{a}_\mu \cdot \boldsymbol{b}_\nu = 2\pi\, \delta_{\mu\nu} \ , \tag{7.265}$$

and any wavevector $\boldsymbol{q}$ may be expressed as

$$\boldsymbol{q} = \frac{1}{2\pi} \sum_{\mu=1}^{d} \theta_\mu\, \boldsymbol{b}_\mu \ . \tag{7.266}$$

We can impose periodic boundary conditions on a system of size $M_1 \times M_2 \times \cdots \times M_d$ by requiring

$$\phi_{\boldsymbol{R}+\sum_{\mu=1}^{d} l_\mu M_\mu \boldsymbol{a}_\mu} = \phi_{\boldsymbol{R}} \ . \tag{7.267}$$

This leads to the *quantization* of the wavevectors, which must then satisfy

$$e^{iM_\mu\, \boldsymbol{q}\cdot\boldsymbol{a}_\mu} = e^{iM_\mu \theta_\mu} = 1 \ , \tag{7.268}$$

and therefore $\theta_\mu = 2\pi m_\mu / M_\mu$ , where $m_\mu$ is an integer. There are then $M_1 M_2 \cdots M_d = N$ independent values of $\boldsymbol{q}$, which can be taken to be those corresponding to $m_\mu \in \{1, \ldots, M_\mu\}$.

Let's now expand the function $\Phi(\vec{\phi})$ in powers of the $\phi_i$, and to first order in the external fields $h_i$. We obtain

$$\begin{aligned}\Phi = \tfrac{1}{2} \sum_{\boldsymbol{q}} \Big(\hat{K}^{-1}(\boldsymbol{q}) - 1\Big)\, |\hat{\phi}_{\boldsymbol{q}}|^2 + \tfrac{1}{12} \sum_{\boldsymbol{R}} \phi_{\boldsymbol{R}}^4 - \sum_{\boldsymbol{R}} h_{\boldsymbol{R}}\, \phi_{\boldsymbol{R}} + \mathcal{O}\big(\phi^6, h^2\big) \\ + \tfrac{1}{2}\, \mathsf{Tr}\, K + \tfrac{1}{2}\, \mathsf{Tr}\, \ln(2\pi K) - N \ln 2\end{aligned} \tag{7.269}$$

On a $d$-dimensional lattice, for a model with nearest neighbor interactions $K_1$ only, we have $\hat{K}(\boldsymbol{q}) = K_1 \sum_{\boldsymbol{\delta}} e^{i\boldsymbol{q}\cdot\boldsymbol{\delta}}$, where $\boldsymbol{\delta}$ is a nearest neighbor separation vector. These are the eigenvalues of the matrix $K_{ij}$. We note that $K_{ij}$ is then not positive definite, since there are negative eigenvalues[19]. To fix this, we can add a term $K_0$ everywhere along the diagonal. We then have

$$\hat{K}(\boldsymbol{q}) = K_0 + K_1 \sum_{\boldsymbol{\delta}} \cos(\boldsymbol{q}\cdot\boldsymbol{\delta}) \ . \tag{7.270}$$

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[19] To evoke a negative eigenvalue on a $d$-dimensional cubic lattice, set $q_\mu = \frac{\pi}{a}$ for all $\mu$. The eigenvalue is then $-2dK_1$.

Here we have used the inversion symmetry of the Bravais lattice to eliminate the imaginary term. The eigenvalues are all positive so long as $K_0 > zK_1$, where $z$ is the lattice coordination number. We can therefore write $\hat{K}(\boldsymbol{q}) = \hat{K}(0) - \alpha\,\boldsymbol{q}^2$ for small $\boldsymbol{q}$, with $\alpha > 0$. Thus, we can write

$$\hat{K}^{-1}(\boldsymbol{q}) - 1 = a + \kappa\,\boldsymbol{q}^2 + \ldots\ . \tag{7.271}$$

To lowest order in $\boldsymbol{q}$ the RHS is isotropic if the lattice has cubic symmetry, but anisotropy will enter in higher order terms. We'll assume isotropy at this level. This is not necessary but it makes the discussion somewhat less involved. We can now write down our Ginzburg-Landau free energy density:

$$\mathcal{F} = a\,\phi^2 + \tfrac{1}{2}\kappa\,|\boldsymbol{\nabla}\phi|^2 + \tfrac{1}{12}\,\phi^4 - h\,\phi\ , \tag{7.272}$$

valid to lowest nontrivial order in derivatives, and to sixth order in $\phi$.

One might wonder what we have gained over the inhomogeneous variational density matrix treatment, where we found

$$\begin{aligned} F = -\tfrac{1}{2}\sum_{\boldsymbol{q}} \hat{J}(\boldsymbol{q})\,|\hat{m}(\boldsymbol{q})|^2 - \sum_{\boldsymbol{q}} \hat{H}(-\boldsymbol{q})\,\hat{m}(\boldsymbol{q}) \\ + k_{\rm B}T\sum_i \bigg\{ \bigg(\frac{1+m_i}{2}\bigg)\ln\bigg(\frac{1+m_i}{2}\bigg) + \bigg(\frac{1-m_i}{2}\bigg)\ln\bigg(\frac{1-m_i}{2}\bigg)\bigg\}\ . \end{aligned} \tag{7.273}$$

Surely we could expand $\hat{J}(\boldsymbol{q}) = \hat{J}(0) - \frac{1}{2}a\boldsymbol{q}^2 + \ldots$ and obtain a similar expression for $\mathcal{F}$. However, such a derivation using the variational density matrix is only approximate. The method outlined in this section is exact.

Let's return to our complete expression for $\Phi$:

$$\Phi(\vec{\phi}) = \Phi_0(\vec{\phi}) + \sum_{\boldsymbol{R}} v(\phi_{\boldsymbol{R}})\ , \tag{7.274}$$

where

$$\Phi_0(\vec{\phi}) = \tfrac{1}{2}\sum_{\boldsymbol{q}} G^{-1}(\boldsymbol{q})\,\big|\hat{\phi}(\boldsymbol{q})\big|^2 + \tfrac{1}{2}\,\mathsf{Tr}\left(\frac{1}{1+G^{-1}}\right) + \tfrac{1}{2}\,\mathsf{Tr}\,\ln\left(\frac{2\pi}{1+G^{-1}}\right) - N\ln 2\ . \tag{7.275}$$

Here we have defined

$$\begin{aligned} v(\phi) &= \tfrac{1}{2}\phi^2 - \ln\cosh\phi \\ &= \tfrac{1}{12}\,\phi^4 - \tfrac{1}{45}\,\phi^6 + \tfrac{17}{2520}\,\phi^8 + \ldots \end{aligned} \tag{7.276}$$

and

$$G(\boldsymbol{q}) = \frac{\hat{K}(\boldsymbol{q})}{1-\hat{K}(\boldsymbol{q})}\ . \tag{7.277}$$

We now want to compute

$$Z = \int\! D\vec{\phi}\; e^{-\Phi_0(\vec{\phi})}\; e^{-\sum_{\boldsymbol{R}} v(\phi_{\boldsymbol{R}})} \tag{7.278}$$

where

$$D\vec{\phi} \equiv d\phi_1\, d\phi_2 \cdots d\phi_N\ . \tag{7.279}$$

We expand the second exponential factor in a Taylor series, allowing us to write

$$Z = Z_0\left(1 - \sum_{\boldsymbol{R}} \big\langle v(\phi_{\boldsymbol{R}})\big\rangle + \tfrac{1}{2}\sum_{\boldsymbol{R}}\sum_{\boldsymbol{R}'} \big\langle v(\phi_{\boldsymbol{R}})\,v(\phi_{\boldsymbol{R}'})\big\rangle + \ldots\right)\ , \tag{7.280}$$

where

$$\begin{aligned} Z_0 &= \int\!D\vec{\phi}\; e^{-\Phi_0(\vec{\phi})} \\ \ln Z_0 &= \tfrac{1}{2}\,\mathsf{Tr}\left[\ln(1+G) - \frac{G}{1+G}\right] + N\ln 2 \end{aligned} \tag{7.281}$$

and

$$\big\langle F(\vec{\phi})\big\rangle = \frac{\int\!D\vec{\phi}\; F\, e^{-\Phi_0}}{\int\!D\vec{\phi}\; e^{-\Phi_0}}\ . \tag{7.282}$$

To evaluate the various terms in the expansion of eqn. 7.280, we invoke Wick's theorem, which says

$$\begin{aligned} \big\langle x_{i_1}\, x_{i_2}\cdots x_{i_{2L}}\big\rangle &= \int\limits_{-\infty}^{\infty}\!dx_1\cdots\!\int\limits_{-\infty}^{\infty}\!dx_N\; e^{-\frac{1}{2}\,\mathcal{G}^{-1}_{ij}x_i x_j}\; x_{i_1}\, x_{i_2}\cdots x_{i_{2L}} \bigg/ \int\limits_{-\infty}^{\infty}\!dx_1\cdots\!\int\limits_{-\infty}^{\infty}\!dx_N\; e^{-\frac{1}{2}\,\mathcal{G}^{-1}_{ij}x_i x_j} \\ &= \sum_{\substack{\text{all distinct}\\ \text{pairings}}} \mathcal{G}_{j_1 j_2}\,\mathcal{G}_{j_3 j_4}\cdots\mathcal{G}_{j_{2L-1} j_{2L}}\ , \end{aligned} \tag{7.283}$$

where the sets $\{j_1,\ldots,j_{2L}\}$ are all permutations of the set $\{i_1,\ldots,i_{2L}\}$. In particular, we have

$$\big\langle x_i^4\big\rangle = 3\big(\mathcal{G}_{ii}\big)^2\ . \tag{7.284}$$

In our case, we have

$$\big\langle\phi^4_{\boldsymbol{R}}\big\rangle = 3\left(\frac{1}{N}\sum_{\boldsymbol{q}} G(\boldsymbol{q})\right)^2\ . \tag{7.285}$$

Thus, if we write $v(\phi) \approx \frac{1}{12}\,\phi^4$ and retain only the quartic term in $v(\phi)$, we obtain

$$\begin{aligned} \frac{F}{k_{\rm B}T} = -\ln Z_0 &= \tfrac{1}{2}\,\mathsf{Tr}\left[\frac{G}{1+G} - \ln(1+G)\right] + \frac{1}{4N}\big(\,\mathsf{Tr}\; G\big)^2 - N\ln 2 \\ &= -N\ln 2 + \frac{1}{4N}\big(\,\mathsf{Tr}\; G\big)^2 - \frac{1}{4}\,\mathsf{Tr}\,\big(G^2\big) + \mathcal{O}\big(G^3\big)\ . \end{aligned} \tag{7.286}$$

Note that if we set $K_{ij}$ to be diagonal, then $\hat{K}(\boldsymbol{q})$ and hence $G(\boldsymbol{q})$ are constant functions of $\boldsymbol{q}$. The $\mathcal{O}\big(G^2\big)$ term then vanishes, which is required since the free energy cannot depend on the diagonal elements of $K_{ij}$.

### 7.9.4 Ginzburg criterion

Let us define $A(T,H,V,N)$ to be the usual (*i.e.* thermodynamic) Helmholtz free energy. Then

$$e^{-\beta A} = \int\!Dm\; e^{-\beta F[m(\boldsymbol{x})]}\ , \tag{7.287}$$

where the functional $F[m(\boldsymbol{x})]$ is of the Ginzburg-Landau form, given in eqn. 7.248. The integral above is a *functional integral*. We can give it a more precise meaning by defining its measure in the case of periodic functions $m(\boldsymbol{x})$ confined to a rectangular box. Then we can expand

$$m(\boldsymbol{x}) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{q}} \hat{m}_{\boldsymbol{q}}\, e^{i\boldsymbol{q}\cdot\boldsymbol{x}}\ , \tag{7.288}$$

and we define the measure

$$Dm \equiv dm_0 \prod_{\substack{\boldsymbol{q} \\ q_x > 0}} d\,\mathrm{Re}\,\hat{m}_{\boldsymbol{q}}\, d\,\mathrm{Im}\,\hat{m}_{\boldsymbol{q}} \ . \tag{7.289}$$

Note that the fact that $m(\boldsymbol{x}) \in \mathbb{R}$ means that $\hat{m}_{-\boldsymbol{q}} = \hat{m}^*_{\boldsymbol{q}}$. We'll assume $T > T_\mathrm{c}$ and $H = 0$ and we'll explore limit $T \to T_\mathrm{c}^+$ from above to analyze the properties of the critical region close to $T_\mathrm{c}$. In this limit we can ignore all but the quadratic terms in $m$, and we have

$$\begin{aligned} e^{-\beta A} &= \int\! Dm\, \exp\bigg( -\tfrac{1}{2}\beta \sum_{\boldsymbol{q}} (a + \kappa\, \boldsymbol{q}^2)\, |\hat{m}_{\boldsymbol{q}}|^2 \bigg) \\ &= \prod_{\boldsymbol{q}} \bigg( \frac{\pi k_\mathrm{B} T}{a + \kappa\, \boldsymbol{q}^2} \bigg)^{1/2} \ . \end{aligned} \tag{7.290}$$

Thus,

$$A = \tfrac{1}{2} k_\mathrm{B} T \sum_{\boldsymbol{q}} \ln\bigg( \frac{a + \kappa\, \boldsymbol{q}^2}{\pi k_\mathrm{B} T} \bigg) \ . \tag{7.291}$$

We now assume that $a(T) = \alpha t$, where $t$ is the dimensionless quantity

$$t = \frac{T - T_\mathrm{c}}{T_\mathrm{c}} \ , \tag{7.292}$$

known as the *reduced temperature*.

We now compute the heat capacity $C_V = -T\,\frac{\partial^2 A}{\partial T^2}$. We are really only interested in the singular contributions to $C_V$, which means that we're only interested in differentiating with respect to $T$ as it appears in $a(T)$. We divide by $N_\mathsf{s} k_\mathrm{B}$ where $N_\mathsf{s}$ is the number of unit cells of our system, which we presume is a lattice-based model. Note $N_\mathsf{s} \sim V/\mathsf{a}^d$ where $V$ is the volume and $\mathsf{a}$ the lattice constant. The dimensionless heat capacity per lattice site is then

$$c \equiv \frac{C_V}{N_\mathsf{s}} = \frac{\alpha^2 \mathsf{a}^d}{2\kappa^2} \int^{\Lambda}\! \frac{d^d q}{(2\pi)^d}\, \frac{1}{(\xi^{-2} + \boldsymbol{q}^2)^2} \ , \tag{7.293}$$

where $\xi = (\kappa/\alpha t)^{1/2} \propto |t|^{-1/2}$ is the correlation length, and where $\Lambda \sim \mathsf{a}^{-1}$ is an ultraviolet cutoff. We define $R_* \equiv (\kappa/\alpha)^{1/2}$, in which case

$$c = R_*^{-4}\, \mathsf{a}^d\, \xi^{4-d} \cdot \tfrac{1}{2} \int^{\Lambda\xi}\! \frac{d^d \bar{q}}{(2\pi)^d}\, \frac{1}{(1 + \bar{q}^2)^2} \ , \tag{7.294}$$

where $\bar{\boldsymbol{q}} \equiv \boldsymbol{q}\xi$. Thus,

$$c(t) \sim \begin{cases} \text{const.} & \text{if } d > 4 \\ -\ln t & \text{if } d = 4 \\ t^{\frac{d}{2}-2} & \text{if } d < 4 \ . \end{cases} \tag{7.295}$$

For $d > 4$, mean field theory is qualitatively accurate, with finite corrections. In dimensions $d \le 4$, the mean field result is overwhelmed by fluctuation contributions as $t \to 0^+$ (*i.e.* as $T \to T_\mathrm{c}^+$). We see that MFT is sensible provided the fluctuation contributions are small, *i.e.* provided

$$R_*^{-4}\, \mathsf{a}^d\, \xi^{4-d} \ll 1 \ , \tag{7.296}$$

which entails $t \gg t_\mathrm{G}$, where

$$t_\mathrm{G} = \bigg( \frac{\mathsf{a}}{R_*} \bigg)^{\frac{2d}{4-d}} \tag{7.297}$$

is the *Ginzburg reduced temperature*. The criterion for the sufficiency of mean field theory, namely $t \gg t_{\rm G}$, is known as the *Ginzburg criterion*. The region $|t| < t_{\rm G}$ is known as the *critical region*.

In a lattice ferromagnet, as we have seen, $R_* \sim \mathsf{a}$ is on the scale of the lattice spacing itself, hence $t_{\rm G} \sim 1$ and the critical regime is very large. Mean field theory then fails quickly as $T \to T_{\rm c}$. In a (conventional) three-dimensional superconductor, $R_*$ is on the order of the Cooper pair size, and $R_*/\mathsf{a} \sim 10^2 - 10^3$, hence $t_{\rm G} = (a/R_*)^6 \sim 10^{-18} - 10^{-12}$ is negligibly narrow. The mean field theory of the superconducting transition – BCS theory – is then valid essentially all the way to $T = T_{\rm c}$.

## 7.10 Appendix I : Equivalence of the Mean Field Descriptions

In both the variational density matrix and mean field Hamiltonian methods as applied to the Ising model, we obtained the same result $m = \tanh\big((m+h)/\theta\big)$. What is perhaps not obvious is whether these theories are in fact the same, *i.e.* if their respective free energies agree. Indeed, the two free energy functions,

$$\begin{aligned} f_{\rm A}(m,h,\theta) &= -\tfrac{1}{2}\,m^2 - hm + \theta\left\{\left(\frac{1+m}{2}\right)\ln\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\ln\left(\frac{1-m}{2}\right)\right\} \\ f_{\rm B}(m,h,\theta) &= +\tfrac{1}{2}\,m^2 - \theta\,\ln\left(e^{+(m+h)/\theta} + e^{-(m+h)/\theta}\right)\ , \end{aligned} \tag{7.298}$$

where $f_{\rm A}$ is the variational density matrix result and $f_{\rm B}$ is the mean field Hamiltonian result, clearly are different functions of their arguments. However, it turns out that upon minimizing with respect to $m$ in each cast, the resulting free energies obey $f_{\rm A}(h,\theta) = f_{\rm B}(h,\theta)$. This agreement may seem surprising. The first method utilizes an approximate (variational) density matrix applied to the exact Hamiltonian $\hat{H}$. The second method approximates the Hamiltonian as $\hat{H}_{\rm MF}$, but otherwise treats it exactly. The two Landau expansions seem hopelessly different:

$$f_{\rm A}(m,h,\theta) = -\theta\,\ln 2 - hm + \tfrac{1}{2}\,(\theta-1)\,m^2 + \tfrac{\theta}{12}\,m^4 + \tfrac{\theta}{30}\,m^6 + \ldots \tag{7.299}$$

$$f_{\rm B}(m,h,\theta) = -\theta\,\ln 2 + \tfrac{1}{2}m^2 - \frac{(m+h)^2}{2\,\theta} + \frac{(m+h)^4}{12\,\theta^3} - \frac{(m+h)^6}{45\,\theta^5} + \ldots\ . \tag{7.300}$$

We shall now prove that these two methods, the variational density matrix and the mean field approach, are in fact equivalent, and yield the *same* free energy $f(h,\theta)$.

Let us generalize the Ising model and write

$$\hat{H} = -\sum_{i<j} J_{ij}\,\varepsilon(\sigma_i,\sigma_j) - \sum_i \Phi(\sigma_i)\ . \tag{7.301}$$

Here, each 'spin' $\sigma_i$ may take on any of $K$ possible values, $\{s_1,\ldots,s_K\}$. For the $S=1$ Ising model, we would have $K=3$ possibilities, with $s_1=-1$, $s_2=0$, and $s_3=+1$. But the set $\{s_\alpha\}$, with $\alpha\in\{1,\ldots,K\}$, is completely arbitrary[20]. The 'local field' term $\Phi(\sigma)$ is also a completely arbitrary function. It may be linear, with $\Phi(\sigma)=H\sigma$, for example, but it could also contain terms quadratic in $\sigma$, or whatever one desires.

The symmetric, dimensionless interaction function $\varepsilon(\sigma,\sigma')=\varepsilon(\sigma',\sigma)$ is areal symmetric $K\times K$ matrix. According to the singular value decomposition theorem, any such matrix may be written in the form

$$\varepsilon(\sigma,\sigma') = \sum_{p=1}^{N_{\rm s}} A_p\,\lambda_p(\sigma)\,\lambda_p(\sigma')\ , \tag{7.302}$$

where the $\{A_p\}$ are coefficients (the singular values), and the $\big\{\lambda_p(\sigma)\big\}$ are the singular vectors. The number of terms $N_{\rm s}$ in this decomposition is such that $N_{\rm s}\le K$. This treatment can be generalized to account for continuous $\sigma$.

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[20] It needn't be an equally spaced sequence, for example.

### 7.10.1 Variational Density Matrix

The most general single-site variational density matrix is written

$$\varrho(\sigma) = \sum_{\alpha=1}^{K} x_\alpha \, \delta_{\sigma,s_\alpha} \ . \tag{7.303}$$

Thus, $x_\alpha$ is the probability for a given site to be in state $\alpha$, with $\sigma = s_\alpha$. *The* $\{x_\alpha\}$ *are the* $K$ *variational parameters, subject to the single normalization constraint,* $\sum_\alpha x_\alpha = 1$. We now have

$$\begin{aligned} f &= \frac{1}{N\hat{J}(0)} \Big\{ \mathsf{Tr}\,(\varrho \hat{H}) + k_\text{B} T \ \mathsf{Tr}\,(\varrho \ln \varrho) \Big\} \\ &= -\tfrac{1}{2} \sum_p \sum_{\alpha,\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_\alpha \, x_{\alpha'} - \sum_\alpha \varphi(s_\alpha) \, x_\alpha + \theta \sum_\alpha x_\alpha \ln x_\alpha \ , \end{aligned} \tag{7.304}$$

where $\varphi(\sigma) = \Phi(\sigma)/\hat{J}(0)$. We extremize in the usual way, introducing a Lagrange undetermined multiplier $\zeta$ to enforce the constraint. This means we extend the function $f\big(\{x_\alpha\}\big)$, writing

$$f^*(x_1, \ldots, x_K, \zeta) = f(x_1, \ldots, x_K) + \zeta \left( \sum_{\alpha=1}^{K} x_\alpha - 1 \right) , \tag{7.305}$$

and freely extremizing with respect to the $(K+1)$ parameters $\{x_1, \ldots, x_K, \zeta\}$. This yields $K$ nonlinear equations,

$$0 = \frac{\partial f^*}{\partial x_\alpha} = -\sum_p \sum_{\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_{\alpha'} - \varphi(s_\alpha) + \theta \, \ln x_\alpha + \zeta + \theta \ , \tag{7.306}$$

for each $\alpha$, and one linear equation, which is the normalization condition,

$$0 = \frac{\partial f^*}{\partial \zeta} = \sum_\alpha x_\alpha - 1 \ . \tag{7.307}$$

We cannot solve these nonlinear equations analytically, but they may be recast, by exponentiating them, as

$$x_\alpha = \frac{1}{Z} \, \exp\left\{ \frac{1}{\theta} \left[ \sum_p \sum_{\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_{\alpha'} + \varphi(s_\alpha) \right] \right\} , \tag{7.308}$$

with

$$Z = e^{(\zeta/\theta)+1} = \sum_\alpha \exp\left\{ \frac{1}{\theta} \left[ \sum_p \sum_{\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_{\alpha'} + \varphi(s_\alpha) \right] \right\} . \tag{7.309}$$

From the logarithm of $x_\alpha$, we may compute the entropy, and, finally, the free energy:

$$f(h,\theta) = \tfrac{1}{2} \sum_p \sum_{\alpha,\alpha'} A_p \, \lambda_p(s_\alpha) \, \lambda_p(s_{\alpha'}) \, x_\alpha \, x_{\alpha'} - \theta \ln Z \ , \tag{7.310}$$

which is to be evaluated at the solution of 7.306, $\big\{x^*_\alpha(h,\theta)\big\}$

### 7.10.2 Mean Field Approximation

We now derive a mean field approximation in the spirit of that used in the Ising model above. We write

$$\lambda_p(\sigma) = \big\langle \lambda_p(\sigma) \big\rangle + \delta\lambda_p(\sigma) \ , \tag{7.311}$$

and abbreviate $\bar{\lambda}_p = \big\langle \lambda_p(\sigma) \big\rangle$, the thermodynamic average of $\lambda_p(\sigma)$ on any given site. We then have

$$\begin{aligned} \lambda_p(\sigma)\, \lambda_p(\sigma') &= \bar{\lambda}_p^2 + \bar{\lambda}_p\, \delta\lambda_p(\sigma) + \bar{\lambda}_p\, \delta\lambda_p(\sigma') + \delta\lambda_p(\sigma)\, \delta\lambda_p(\sigma') \\ &= -\bar{\lambda}_p^2 + \bar{\lambda}_p\, \big(\lambda_p(\sigma) + \lambda_p(\sigma')\big) + \delta\lambda_p(\sigma)\, \delta\lambda_p(\sigma') \ . \end{aligned} \tag{7.312}$$

The product $\delta\lambda_p(\sigma)\, \delta\lambda_p(\sigma')$ is of second order in fluctuations, and we neglect it. This leads us to the mean field Hamiltonian,

$$\hat{H}_{\rm MF} = +\tfrac{1}{2} N \hat{J}(0) \sum_p A_p\, \bar{\lambda}_p^2 - \sum_i \Big[ \hat{J}(0) \sum_p A_p\, \bar{\lambda}_p\, \lambda_p(\sigma_i) + \Phi(\sigma_i) \Big] \ . \tag{7.313}$$

The free energy is then

$$f\big(\{\bar{\lambda}_p\}, h, \theta\big) = \tfrac{1}{2} \sum_p A_p\, \bar{\lambda}_p^2 - \theta\, \ln \sum_\alpha \exp\left\{ \frac{1}{\theta} \Big[ \sum_p A_p\, \bar{\lambda}_p\, \lambda_p(s_\alpha) + \varphi(s_\alpha) \Big] \right\} \ . \tag{7.314}$$

*The variational parameters are the mean field values* $\big\{\bar{\lambda}_p\big\}$.

The single site probabilities $\{x_\alpha\}$ are then

$$x_\alpha = \frac{1}{Z} \exp\left\{ \frac{1}{\theta} \Big[ \sum_p A_p\, \bar{\lambda}_p\, \lambda_p(s_\alpha) + \varphi(s_\alpha) \Big] \right\} \ , \tag{7.315}$$

with $Z$ implied by the normalization $\sum_\alpha x_\alpha = 1$. These results reproduce exactly what we found in eqn. 7.306, since the mean field equation here, $\partial f / \partial \bar{\lambda}_p = 0$, yields

$$\bar{\lambda}_p = \sum_{\alpha=1}^{K} \lambda_p(s_\alpha)\, x_\alpha \ . \tag{7.316}$$

The free energy is immediately found to be

$$f(h,\theta) = \tfrac{1}{2} \sum_p A_p\, \bar{\lambda}_p^2 - \theta\, \ln Z \ , \tag{7.317}$$

which again agrees with what we found using the variational density matrix.

Thus, whether one extremizes with respect to the set $\{x_1, \ldots, x_K, \zeta\}$, or with respect to the set $\{\bar{\lambda}_p\}$, the results are the same, in terms of all these parameters, as well as the free energy $f(h,\theta)$. Generically, both approaches may be termed 'mean field theory' since the variational density matrix corresponds to a mean field which acts on each site independently.

## 7.11 Appendix II : Additional Examples

### 7.11.1 Blume-Capel model

The Blume-Capel model provides a simple and convenient way to model systems with vacancies. The simplest version of the model is written

$$\hat{H} = -\tfrac{1}{2} \sum_{i,j} J_{ij}\, S_i\, S_j + \Delta \sum_i S_i^2 \ . \tag{7.318}$$

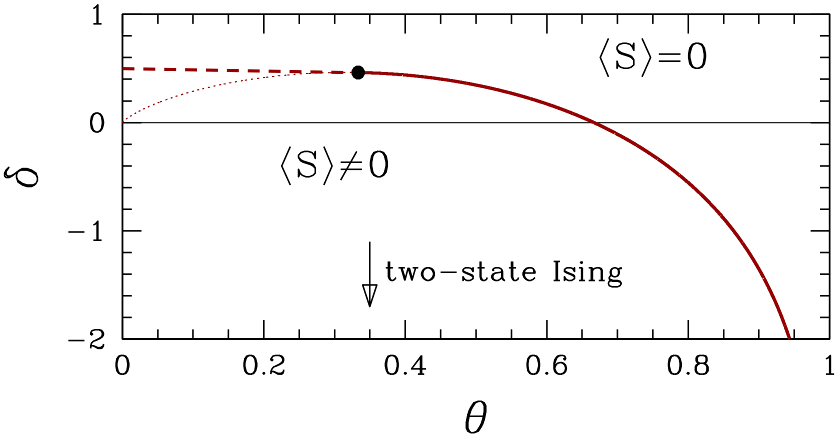

Figure 7.24: Mean field phase diagram for the Blume-Capel model. The black dot signifies a tricritical point, where the coefficients of $m^2$ and $m^4$ in the Landau free energy expansion both vanish. The dashed curve denotes a first order transition, and the solid curve a second order transition. The thin dotted line is the continuation of the $\theta_c(\delta)$ relation to zero temperature.

The spin variables $S_i$ range over the values $\{-1\,,\,0\,,\,+1\}$, so this is an extension of the $S=1$ Ising model. We explicitly separate out the diagonal terms, writing $J_{ii}\equiv 0$, and placing them in the second term on the RHS above. We say that site $i$ is occupied if $S_i=\pm 1$ and vacant if $S_i=0$, and we identify $-\Delta$ as the vacancy creation energy, which may be positive or negative, depending on whether vacancies are disfavored or favored in our system.

We make the mean field *Ansatz*, writing $S_i = m + \delta S_i$. This results in the mean field Hamiltonian,

$$\hat{H}_{\text{MF}} = \tfrac{1}{2} N \hat{J}(0)\, m^2 - \hat{J}(0)\, m \sum_i S_i + \Delta \sum_i S_i^2\ . \tag{7.319}$$

Once again, we adimensionalize, writing $f \equiv F/N\hat{J}(0)$, $\theta = k_{\text{B}}T/\hat{J}(0)$, and $\delta = \Delta/\hat{J}(0)$. We assume $\hat{J}(0)>0$. The free energy per site is then

$$f(\theta,\delta,m) = \tfrac{1}{2}m^2 - \theta \ln\Big(1 + 2e^{-\delta/\theta}\,\cosh(m/\theta)\Big)\ . \tag{7.320}$$

Extremizing with respect to $m$, we obtain the mean field equation,

$$m = \frac{2\sinh(m/\theta)}{\exp(\delta/\theta) + 2\cosh(m/\theta)}\ . \tag{7.321}$$

Note that $m=0$ is always a solution. Finding the slope of the RHS at $m=0$ and setting it to unity gives us the critical temperature:

$$\theta_c = \frac{2}{\exp(\delta/\theta_c) + 2}\ . \tag{7.322}$$

This is an implicit equation for $\theta_c$ in terms of the vacancy energy $\delta$.

Let's now expand the free energy in terms of the magnetization $m$. We find, to fourth order,

$$\begin{aligned} f = -\theta \ln\big(1 + 2e^{-\delta/\theta}\big) &+ \frac{1}{2\theta}\bigg(\theta - \frac{2}{2+\exp(\delta/\theta)}\bigg)m^2 \\ &+ \frac{1}{12\,\big(2+\exp(\delta/\theta)\big)\theta^3}\,\bigg(\frac{6}{2+\exp(\delta/\theta)} - 1\bigg)m^4 + \ldots\ . \end{aligned} \tag{7.323}$$

Note that setting the coefficient of the $m^2$ term to zero yields the equation for $\theta_c$. However, upon further examination, we see that the coefficient of the $m^4$ term can also vanish. As we have seen, when both the coefficients of the $m^2$ and the $m^4$ terms vanish, we have a tricritical point[21]. Setting both coefficients to zero, we obtain

$$\theta_t = \tfrac{1}{3} \quad , \quad \delta_t = \tfrac{2}{3}\ln 2 \; . \tag{7.324}$$

At $\theta = 0$, it is easy to see we have a first order transition, simply by comparing the energies of the paramagnetic ($S_i = 0$) and ferromagnetic ($S_i = +1$ or $S_i = -1$) states. We have

$$\frac{E_{\text{MF}}}{N\hat{J}(0)} = \begin{cases} 0 & \text{if } m = 0 \\ \frac{1}{2} - \Delta & \text{if } m = \pm 1 \; . \end{cases} \tag{7.325}$$

These results are in fact exact, and not only valid for the mean field theory. Mean field theory is approximate because it neglects fluctuations, but at zero temperature, there are no fluctuations to neglect!

The phase diagram is shown in fig. 7.24. Note that for $\delta$ large and negative, vacancies are strongly disfavored, hence the only allowed states on each site have $S_i = \pm 1$, which is our old friend the two-state Ising model. Accordingly, the phase boundary there approaches the vertical line $\theta_c = 1$, which is the mean field transition temperature for the two-state Ising model.

### 7.11.2 Ising antiferromagnet in an external field

Consider the following model:

$$\hat{H} = J \sum_{\langle ij \rangle} \sigma_i \, \sigma_j - H \sum_i \sigma_i \; , \tag{7.326}$$

with $J > 0$ and $\sigma_i = \pm 1$. We've solved for the mean field phase diagram of the Ising ferromagnet; what happens if the interactions are antiferromagnetic?

It turns out that under certain circumstances, the ferromagnet and the antiferromagnet behave exactly the same in terms of their phase diagram, response functions, *etc.* This occurs when $H = 0$, and when the interactions are between nearest neighbors on a *bipartite lattice*. A bipartite lattice is one which can be divided into two sublattices, which we call A and B, such that an A site has only B neighbors, and a B site has only A neighbors. The square, honeycomb, and body centered cubic (BCC) lattices are bipartite. The triangular and face centered cubic lattices are non-bipartite. Now if the lattice is bipartite and the interaction matrix $J_{ij}$ is nonzero only when $i$ and $j$ are from different sublattices (they needn't be nearest neighbors only), then we can simply redefine the spin variables such that

$$\sigma'_j = \begin{cases} +\sigma_j & \text{if } j \in \text{A} \\ -\sigma_j & \text{if } j \in \text{B} \; . \end{cases} \tag{7.327}$$

Then $\sigma'_i \sigma'_j = -\sigma_i \, \sigma_j$, and in terms of the new spin variables the exchange constant has reversed. The thermodynamic properties are invariant under such a redefinition of the spin variables.

We can see why this trick doesn't work in the presence of a magnetic field, because the field $H$ would have to be reversed on the B sublattice. In other words, the thermodynamics of an Ising ferromagnet on a bipartite lattice in a uniform applied field is identical to that of the Ising antiferromagnet, with the same exchange constant (in magnitude), in the presence of a *staggered field* $H_{\text{A}} = +H$ and $H_{\text{B}} = -H$.

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[21] We should really check that the coefficient of the sixth order term is positive, but that is left as an exercise to the eager student.

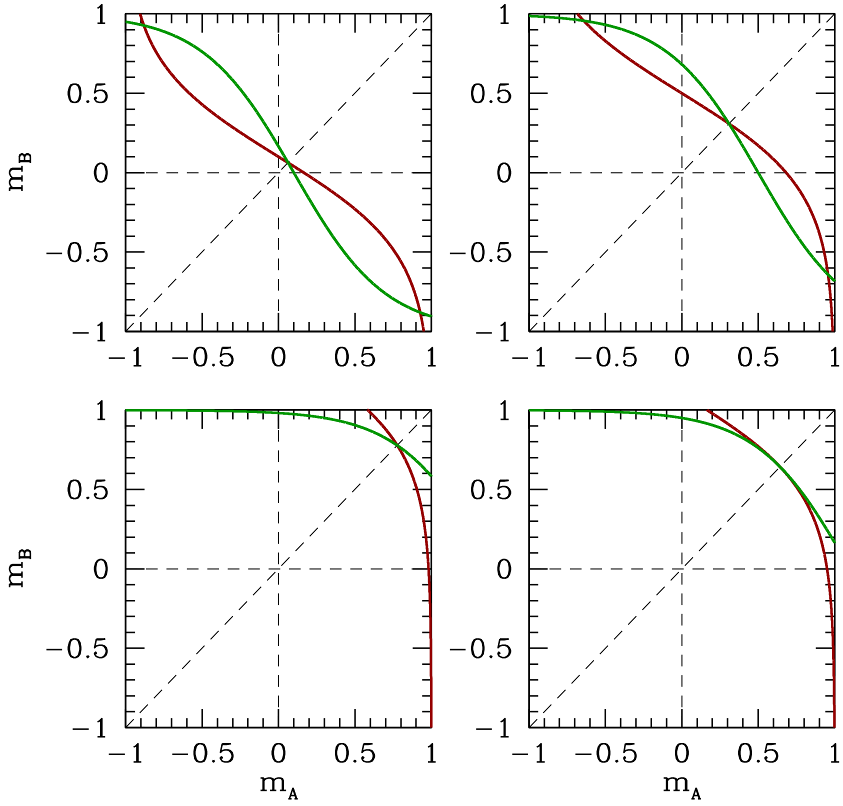

Figure 7.25: Graphical solution to the mean field equations for the Ising antiferromagnet in an external field, here for $\theta = 0.6$. Clockwise from upper left: (a) $h = 0.1$, (b) $h = 0.5$, (c) $h = 1.1$, (d) $h = 1.4$.

We treat this problem using the variational density matrix method, using two independent variational parameters $m_{\rm A}$ and $m_{\rm B}$ for the two sublattices:

$$\begin{aligned} \varrho_{\rm A}(\sigma) &= \frac{1+m_{\rm A}}{2}\,\delta_{\sigma,1} + \frac{1-m_{\rm A}}{2}\,\delta_{\sigma,-1} \\ \varrho_{\rm B}(\sigma) &= \frac{1+m_{\rm B}}{2}\,\delta_{\sigma,1} + \frac{1-m_{\rm B}}{2}\,\delta_{\sigma,-1}\ . \end{aligned} \tag{7.328}$$

With the usual adimensionalization, $f = F/NzJ$, $\theta = k_{\rm B}T/zJ$, and $h = H/zJ$, we have the free energy

$$f(m_{\rm A}, m_{\rm B}) = \tfrac{1}{2} m_{\rm A} m_{\rm B} - \tfrac{1}{2}\,h\,(m_{\rm A} + m_{\rm B}) - \tfrac{1}{2}\,\theta\,s(m_{\rm A}) - \tfrac{1}{2}\,\theta\,s(m_{\rm B})\ , \tag{7.329}$$

where the entropy function is

$$s(m) = -\bigg[\frac{1+m}{2}\,\ln\!\bigg(\frac{1+m}{2}\bigg) + \frac{1-m}{2}\,\ln\!\bigg(\frac{1-m}{2}\bigg)\bigg]\ . \tag{7.330}$$

Note that

$$\frac{ds}{dm} = -\tfrac{1}{2}\,\ln\!\bigg(\frac{1+m}{1-m}\bigg) \qquad , \qquad \frac{d^2 s}{dm^2} = -\frac{1}{1-m^2}\ . \tag{7.331}$$

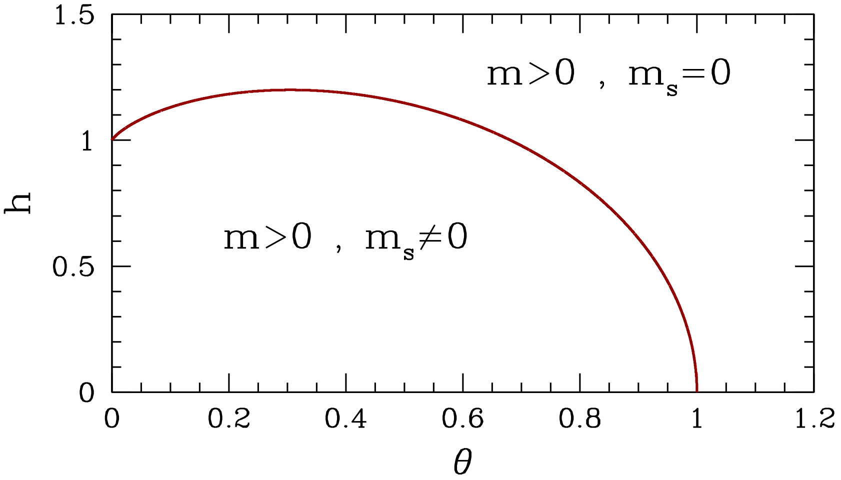

Figure 7.26: Mean field phase diagram for the Ising antiferromagnet in an external field. The phase diagram is symmetric under reflection in the $h = 0$ axis.

Differentiating $f(m_{\rm A}, m_{\rm B})$ with respect to the variational parameters, we obtain two coupled mean field equations:

$$\begin{aligned} \frac{\partial f}{\partial m_{\rm A}} = 0 \quad &\Longrightarrow \quad m_{\rm B} = h - \frac{\theta}{2} \ln\!\left(\frac{1+m_{\rm A}}{1-m_{\rm A}}\right) \\ \frac{\partial f}{\partial m_{\rm B}} = 0 \quad &\Longrightarrow \quad m_{\rm A} = h - \frac{\theta}{2} \ln\!\left(\frac{1+m_{\rm B}}{1-m_{\rm B}}\right) . \end{aligned} \tag{7.332}$$

Recognizing $\tanh^{-1}(x) = \frac{1}{2} \ln\Big[(1+x)/(1-x)\Big]$, we may write these equations in an equivalent but perhaps more suggestive form:

$$m_{\rm A} = \tanh\left(\frac{h - m_{\rm B}}{\theta}\right) \qquad , \qquad m_{\rm B} = \tanh\left(\frac{h - m_{\rm A}}{\theta}\right) . \tag{7.333}$$

In other words, the A sublattice sites see an internal field $H_{\rm A,int} = -zJm_{\rm B}$ from their B neighbors, and the B sublattice sites see an internal field $H_{\rm B,int} = -zJm_{\rm A}$ from their A neighbors.

We can solve these equations graphically, as in fig. 7.25. Note that there is always a paramagnetic solution with $m_{\rm A} = m_{\rm B} = m$, where

$$m = h - \frac{\theta}{2} \ln\left(\frac{1+m}{1-m}\right) \qquad \Longleftrightarrow \qquad m = \tanh\left(\frac{h-m}{\theta}\right) . \tag{7.334}$$

However, we can see from the figure that there will be *three* solutions to the mean field equations provided that $\frac{\partial m_{\rm A}}{\partial m_{\rm B}} < -1$ at the point of the solution where $m_{\rm A} = m_{\rm B} = m$. This gives us two equations with which to eliminate $m_{\rm A}$ and $m_{\rm B}$, resulting in the curve

$$h^*(\theta) = m + \frac{\theta}{2} \ln\left(\frac{1+m}{1-m}\right) \qquad \text{with} \ \ m = \sqrt{1-\theta} \ . \tag{7.335}$$

Thus, for $\theta < 1$ and $|h| < h^*(\theta)$ there are three solutions to the mean field equations. It is *usually* the case, the broken symmetry solutions, which mean those for which $m_{\rm A} \neq m_{\rm B}$ in our case, are of lower energy than the symmetric solution(s). We show the curve $h^*(\theta)$ in fig. 7.26.

We can make additional progress by defining the average and staggered magnetizations $m$ and $m_{\rm s}$,

$$m \equiv \tfrac{1}{2}(m_{\rm A} + m_{\rm B}) \qquad , \qquad m_{\rm s} \equiv \tfrac{1}{2}(m_{\rm A} - m_{\rm B}) \, . \tag{7.336}$$

We expand the free energy in terms of $m_{\rm s}$:

$$\begin{aligned} f(m,m_{\rm s}) &= \tfrac{1}{2}m^2 - \tfrac{1}{2}m_{\rm s}^2 - h\,m - \tfrac{1}{2}\,\theta\,s(m+m_{\rm s}) - \tfrac{1}{2}\,\theta\,s(m-m_{\rm s}) \\ &= \tfrac{1}{2}m^2 - h\,m - \theta\,s(m) - \tfrac{1}{2}\Big(1+\theta\,s''(m)\Big)\,m_{\rm s}^2 - \tfrac{1}{24}\,\theta\,s''''(m)\,m_{\rm s}^4 + \ldots\ . \end{aligned} \tag{7.337}$$

The term quadratic in $m_{\rm s}$ vanishes when $\theta\,s''(m) = -1$, *i.e.* when $m = \sqrt{1-\theta}$. It is easy to obtain

$$\frac{d^3 s}{dm^3} = -\frac{2m}{(1-m^2)^2} \qquad , \qquad \frac{d^4 s}{dm^4} = -\frac{2\,(1+3m^2)}{(1-m^2)^3}\ , \tag{7.338}$$

from which we learn that the coefficient of the quartic term, $-\frac{1}{24}\,\theta\,s''''(m)$, never vanishes. Therefore the transition remains second order down to $\theta = 0$, where it finally becomes first order.

We can confirm the $\theta \to 0$ limit directly. The two competing states are the ferromagnet, with $m_{\rm A} = m_{\rm B} = \pm 1$, and the antiferromagnet, with $m_{\rm A} = -m_{\rm B} = \pm 1$. The free energies of these states are

$$f^{\rm FM} = \tfrac{1}{2} - h \qquad , \qquad f^{\rm AFM} = -\tfrac{1}{2}\ . \tag{7.339}$$

There is a first order transition when $f^{\rm FM} = f^{\rm AFM}$, which yields $h = 1$.

### 7.11.3 Canted quantum antiferromagnet

Consider the following model for *quantum* $S = \frac{1}{2}$ spins:

$$\hat H = \sum_{\langle ij \rangle} \Big[ -J\big(\sigma_i^x \sigma_j^x + \sigma_i^y \sigma_j^y\big) + \Delta\,\sigma_i^z \sigma_j^z \Big] + \tfrac{1}{4}K \sum_{\langle ijkl \rangle} \sigma_i^z \sigma_j^z \sigma_k^z \sigma_l^z\ , \tag{7.340}$$

where $\boldsymbol{\sigma}_i$ is the vector of Pauli matrices on site $i$. The spins live on a square lattice. The second sum is over all square plaquettes. All the constants $J$, $\Delta$, and $K$ are positive.

Let's take a look at the Hamiltonian for a moment. The $J$ term clearly wants the spins to align ferromagnetically in the $(x,y)$ plane (in internal spin space). The $\Delta$ term prefers antiferromagnetic alignment along the $\hat{\boldsymbol{z}}$ axis. The $K$ term discourages any kind of moment along $\hat{\boldsymbol{z}}$ and works against the $\Delta$ term. We'd like our mean field theory to capture the physics behind this competition.

Accordingly, we break up the square lattice into two interpenetrating $\sqrt{2} \times \sqrt{2}$ square sublattices (each rotated by 45° with respect to the original), in order to be able to describe an antiferromagnetic state. In addition, we include a parameter $\alpha$ which describes the *canting angle* that the spins on these sublattices make with respect to the $\hat{\boldsymbol{x}}$-axis. That is, we write

$$\begin{aligned} \varrho_{\rm A} &= \tfrac{1}{2} + \tfrac{1}{2}m\,\big(\sin\alpha\,\sigma^x + \cos\alpha\,\sigma^z\big) \\ \varrho_{\rm B} &= \tfrac{1}{2} + \tfrac{1}{2}m\,\big(\sin\alpha\,\sigma^x - \cos\alpha\,\sigma^z\big)\ . \end{aligned} \tag{7.341}$$

Note that $\mathsf{Tr}\ \varrho_{\rm A} = \mathsf{Tr}\ \varrho_{\rm B} = 1$ so these density matrices are normalized. Note also that the mean direction for a spin on the A and B sublattices is given by

$$\boldsymbol{m}_{\rm A,B} = \mathsf{Tr}\,(\varrho_{\rm A,B}\,\boldsymbol{\sigma}) = \pm\,m\cos\alpha\,\hat{\boldsymbol{z}} + m\sin\alpha\,\hat{\boldsymbol{x}}\ . \tag{7.342}$$

Thus, when $\alpha = 0$, the system is an antiferromagnet with its staggered moment lying along the $\hat{\boldsymbol{z}}$ axis. When $\alpha = \frac{1}{2}\pi$, the system is a ferromagnet with its moment lying along the $\hat{\boldsymbol{x}}$ axis.

Finally, the eigenvalues of $\varrho_{\mathrm{A,B}}$ are still $\lambda_{\pm} = \frac{1}{2}(1 \pm m)$, hence

$$\begin{aligned} s(m) &\equiv -\,\mathsf{Tr}\,(\varrho_{\mathrm{A}} \ln \varrho_{\mathrm{A}}) = -\,\mathsf{Tr}\,(\varrho_{\mathrm{B}} \ln \varrho_{\mathrm{B}}) \\ &= -\left[\frac{1+m}{2}\,\ln\!\left(\frac{1+m}{2}\right) + \frac{1-m}{2}\,\ln\!\left(\frac{1-m}{2}\right)\right] . \end{aligned} \tag{7.343}$$

Note that we have taken $m_{\mathrm{A}} = m_{\mathrm{B}} = m$, unlike the case of the antiferromagnet in a uniform field. The reason is that there remains in our model a symmetry between A and B sublattices.

The free energy is now easily calculated:

$$\begin{aligned} F &= \mathsf{Tr}\,(\varrho \hat{H}) + k_{\mathrm{B}}T\,\mathsf{Tr}\,(\varrho \ln \varrho) \\ &= -2N\Big(J\,\sin^2\!\alpha + \Delta\,\cos^2\!\alpha\Big)\,m^2 + \tfrac{1}{4}NKm^4\cos^4\!\alpha - Nk_{\mathrm{B}}T\,s(m) \end{aligned} \tag{7.344}$$

We can adimensionalize by defining $\delta \equiv \Delta/J$, $\kappa \equiv K/4J$, and $\theta \equiv k_{\mathrm{B}}T/4J$. Then the free energy per site is $f \equiv F/4NJ$ is

$$f(m,\alpha) = -\tfrac{1}{2}m^2 + \tfrac{1}{2}\big(1-\delta\big)\,m^2\cos^2\!\alpha + \tfrac{1}{4}\kappa\,m^4\cos^4\!\alpha - \theta\,s(m)\ . \tag{7.345}$$

There are two variational parameters: $m$ and $\theta$. We thus obtain two coupled mean field equations,

$$\frac{\partial f}{\partial m} = 0 = -m + \big(1-\delta\big)\,m\,\cos^2\!\alpha + \kappa\,m^3\cos^4\!\alpha + \tfrac{1}{2}\theta\,\ln\!\left(\frac{1+m}{1-m}\right) \tag{7.346}$$

$$\frac{\partial f}{\partial \alpha} = 0 = \Big(1-\delta+\kappa\,m^2\cos^2\!\alpha\Big)\,m^2\sin\alpha\,\cos\alpha\ . \tag{7.347}$$

Let's start with the second of the mean field equations. Assuming $m \neq 0$, it is clear from eqn. 7.345 that

$$\cos^2\!\alpha = \begin{cases} 0 & \text{if }\ \delta < 1 \\ (\delta-1)/\kappa m^2 & \text{if }\ 1 \le \delta \le 1+\kappa\,m^2 \\ 1 & \text{if }\ \delta \ge 1+\kappa\,m^2\ . \end{cases} \tag{7.348}$$

Suppose $\delta < 1$. Then we have $\cos\alpha = 0$ and the first mean field equation yields the familiar result

$$m = \tanh\big(m/\theta\big)\ . \tag{7.349}$$

Along the $\theta$ axis, then, we have the usual ferromagnet-paramagnet transition at $\theta_{\mathrm{c}} = 1$.

For $1 < \delta < 1 + \kappa m^2$ we have canting with an angle

$$\alpha = \alpha^*(m) = \cos^{-1}\sqrt{\frac{\delta-1}{\kappa\,m^2}}\ . \tag{7.350}$$

Substituting this into the first mean field equation, we once again obtain the relation $m = \tanh\big(m/\theta\big)$. However, eventually, as $\theta$ is increased, the magnetization will dip below the value $m_0 \equiv \sqrt{(\delta-1)/\kappa}$. This occurs at a dimensionless temperature

$$\theta_0 = \frac{m_0}{\tanh^{-1}(m_0)} < 1 \qquad ; \qquad m_0 = \sqrt{\frac{\delta-1}{\kappa}}\ . \tag{7.351}$$

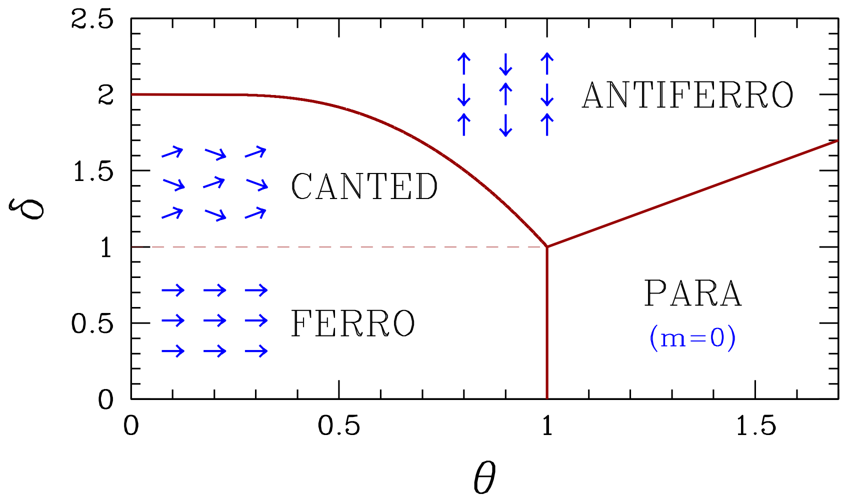

Figure 7.27: Mean field phase diagram for the model of eqn. 7.340 for the case $\kappa = 1$.

For $\theta > \theta_0$, we have $\delta > 1 + \kappa m^2$, and we must take $\cos^2\!\alpha = 1$. The first mean field equation then becomes

$$\delta m - \kappa m^3 = \frac{\theta}{2} \ln\!\left(\frac{1+m}{1-m}\right) , \tag{7.352}$$

or, equivalently, $m = \tanh\big((\delta m - \kappa m^3)/\theta\big)$. A simple graphical analysis shows that a nontrivial solution exists provided $\theta < \delta$. Since $\cos\alpha = \pm 1$, this solution describes an antiferromagnet, with $\boldsymbol{m}_{\rm A} = \pm m\hat{\boldsymbol{z}}$ and $\boldsymbol{m}_{\rm B} = \mp m\hat{\boldsymbol{z}}$. The resulting mean field phase diagram is then as depicted in fig. 7.27.

### 7.11.4 Coupled order parameters

Consider the Landau free energy

$$f(m,\phi) = \tfrac{1}{2}\, a_m\, m^2 + \tfrac{1}{4}\, b_m\, m^4 + \tfrac{1}{2}\, a_\phi\, \phi^2 + \tfrac{1}{4}\, b_\phi\, \phi^4 + \tfrac{1}{2} \Lambda\, m^2\, \phi^2 \, . \tag{7.353}$$

We write

$$a_m \equiv \alpha_m\, \theta_m \qquad , \qquad a_\phi = \alpha_\phi\, \theta_\phi \, , \tag{7.354}$$

where

$$\theta_m = \frac{T - T_{{\rm c},m}}{T_0} \qquad , \qquad \theta_\phi = \frac{T - T_{{\rm c},\phi}}{T_0} \, , \tag{7.355}$$

where $T_0$ is some temperature scale. We assume without loss of generality that $T_{{\rm c},m} > T_{{\rm c},\phi}$. We begin by rescaling:

$$m \equiv \left(\frac{\alpha_m}{b_m}\right)^{\!1/2} \tilde{m} \qquad , \qquad \phi \equiv \left(\frac{\alpha_m}{b_m}\right)^{\!1/2} \tilde{\phi} \, . \tag{7.356}$$

We then have

$$f = \varepsilon_0 \left\{ r \left(\tfrac{1}{2}\theta_m\, \tilde{m}^2 + \tfrac{1}{4}\, \tilde{m}^4\right) + r^{-1} \left(\tfrac{1}{2}\, \theta_\phi\, \tilde{\phi}^2 + \tfrac{1}{4}\, \tilde{\phi}^4\right) + \tfrac{1}{2}\, \lambda\, \tilde{m}^2 \tilde{\phi}^2 \right\} , \tag{7.357}$$

where

$$\varepsilon_0 = \frac{\alpha_m\, \alpha_\phi}{(b_m\, b_\phi)^{1/2}} \qquad , \qquad r = \frac{\alpha_m}{\alpha_\phi} \left(\frac{b_\phi}{b_m}\right)^{\!1/2} \qquad , \qquad \lambda = \frac{\Lambda}{(b_m\, b_\phi)^{1/2}} \, . \tag{7.358}$$

It proves convenient to perform one last rescaling, writing

$$\tilde{m} \equiv r^{-1/4}\,\mathsf{m} \quad , \quad \tilde{\phi} \equiv r^{1/4}\,\varphi\,. \tag{7.359}$$

Then

$$f = \varepsilon_0 \bigg\{ \tfrac{1}{2} q\,\theta_m\,\mathsf{m}^2 + \tfrac{1}{4}\,\mathsf{m}^4 + \tfrac{1}{2} q^{-1}\,\theta_\phi\,\varphi^2 + \tfrac{1}{4}\,\varphi^4 + \tfrac{1}{2}\,\lambda\,\mathsf{m}^2\,\varphi^2 \bigg\}\,, \tag{7.360}$$

where

$$q = \sqrt{r} = \bigg(\frac{\alpha_m}{\alpha_\phi}\bigg)^{1/2} \bigg(\frac{b_\phi}{b_m}\bigg)^{1/4}\,. \tag{7.361}$$

Note that we may write

$$f(\mathsf{m},\varphi) = \frac{\varepsilon_0}{4}\begin{pmatrix}\mathsf{m}^2 & \varphi^2\end{pmatrix}\begin{pmatrix}1 & \lambda \\ \lambda & 1\end{pmatrix}\begin{pmatrix}\mathsf{m}^2 \\ \varphi^2\end{pmatrix} + \frac{\varepsilon_0}{2}\begin{pmatrix}\mathsf{m}^2 & \varphi^2\end{pmatrix}\begin{pmatrix}q\,\theta_m \\ q^{-1}\,\theta_\phi\end{pmatrix}\,. \tag{7.362}$$

The eigenvalues of the above $2 \times 2$ matrix are $1 \pm \lambda$, with corresponding eigenvectors $\binom{1}{\pm 1}$. Since $\varphi^2 > 0$, we are only interested in the first eigenvector $\binom{1}{1}$, corresponding to the eigenvalue $1 + \lambda$. Clearly when $\lambda < 1$ the free energy is unbounded from below, which is unphysical.

We now set

$$\frac{\partial f}{\partial \mathsf{m}} = 0 \quad , \quad \frac{\partial f}{\partial \varphi} = 0\,, \tag{7.363}$$

and identify four possible phases:

- Phase I : $\mathsf{m} = 0$, $\varphi = 0$. The free energy is $f_{\rm I} = 0$.
- Phase II : $\mathsf{m} \neq 0$ with $\varphi = 0$. The free energy is

$$f = \frac{\varepsilon_0}{2}\left(q\,\theta_m\,\mathsf{m}^2 + \tfrac{1}{2}\,\mathsf{m}^4\right)\,, \tag{7.364}$$

  hence we require $\theta_m < 0$ in this phase, in which case

$$\mathsf{m}_{\rm II} = \sqrt{-q\,\theta_m} \quad , \quad f_{\rm II} = -\frac{\varepsilon_0}{4}\,q^2\,\theta_m^2\,. \tag{7.365}$$

- Phase III : $m = 0$ with $\varphi \neq 0$. The free energy is

$$f = \frac{\varepsilon_0}{2}\left(q^{-1}\,\theta_\phi\,\varphi^2 + \tfrac{1}{2}\,\varphi^4\right)\,, \tag{7.366}$$

  hence we require $\theta_\phi < 0$ in this phase, in which case

$$\varphi_{\rm III} = \sqrt{-q^{-1}\,\theta_\phi} \quad , \quad f_{\rm III} = -\frac{\varepsilon_0}{4}\,q^{-2}\,\theta_\phi^2\,. \tag{7.367}$$

- Phase IV : $\mathsf{m} \neq 0$ and $\varphi \neq 0$. Varying $f$ yields

$$\begin{pmatrix}1 & \lambda \\ \lambda & 1\end{pmatrix}\begin{pmatrix}\mathsf{m}^2 \\ \varphi^2\end{pmatrix} = -\begin{pmatrix}q\,\theta_m \\ q^{-1}\,\theta_\phi\end{pmatrix}\,, \tag{7.368}$$

with solution

$$\mathsf{m}^2 = \frac{q\,\theta_m - q^{-1}\,\theta_\phi\,\lambda}{\lambda^2 - 1} \tag{7.369}$$

$$\varphi^2 = \frac{q^{-1}\,\theta_\phi - q\,\theta_m\,\lambda}{\lambda^2 - 1} \ . \tag{7.370}$$

Since $\mathsf{m}^2$ and $\varphi^2$ must each be nonnegative, phase IV exists only over a yet-to-be-determined subset of the entire parameter space. The free energy is

$$f_{\text{IV}} = \frac{q^2\,\theta_m^2 + q^{-2}\,\theta_\phi^2 - 2\lambda\,\theta_m\,\theta_\phi}{4(\lambda^2 - 1)} \ . \tag{7.371}$$

We now define $\theta \equiv \theta_m$ and $\tau \equiv \theta_\phi - \theta_m = (T_{\text{c},m} - T_{\text{c},\phi)}/T_0$. Note that $\tau > 0$. There are three possible temperature ranges to consider.

(1) $\theta_\phi > \theta_m > 0$. The only possible phases are I and IV. For phase IV, we must impose the conditions $m^2 > 0$ and $\phi^2 > 0$. If $\lambda^2 > 1$, then the numerators in eqns. 7.369 and 7.370 must each be positive:

$$\lambda < \frac{q^2\,\theta_m}{\theta_\phi} \quad , \quad \lambda < \frac{\theta_\phi}{q^2\,\theta_m} \quad \Rightarrow \quad \lambda < \min\!\bigg(\frac{q^2\,\theta_m}{\theta_\phi} \, , \, \frac{\theta_\phi}{q^2\theta_m}\bigg) \ . \tag{7.372}$$

But since either $q^2\theta_m/\theta_\phi$ or its inverse must be less than or equal to unity, this requires $\lambda < -1$, which is unphysical.

If on the other hand we assume $\lambda^2 < 1$, the non-negativeness of $\mathsf{m}^2$ and $\varphi^2$ requires

$$\lambda > \frac{q^2\,\theta_m}{\theta_\phi} \quad , \quad \lambda > \frac{\theta_\phi}{q^2\,\theta_m} \quad \Rightarrow \quad \lambda > \max\!\bigg(\frac{q^2\,\theta_m}{\theta_\phi} \, , \, \frac{\theta_\phi}{q^2\theta_m}\bigg) > 1 \ . \tag{7.373}$$

Thus, $\lambda > 1$ and we have a contradiction.

Therefore, the only allowed phase for $\theta > 0$ is phase I.

(2) $\theta_\phi > 0 > \theta_m$. Now the possible phases are I, II, and IV. We can immediately rule out phase I because $f_{\text{II}} < f_{\text{I}}$. To compare phases II and IV, we compute

$$\Delta f = f_{\text{IV}} - f_{\text{II}} = \frac{(q\,\lambda\,\theta_m - q^{-1}\,\theta_\phi)^2}{4(\lambda^2 - 1)} \ . \tag{7.374}$$

Thus, phase II has the lower energy if $\lambda^2 > 1$. For $\lambda^2 < 1$, phase IV has the lower energy, but the conditions $\mathsf{m}^2 > 0$ and $\varphi^2 > 0$ then entail

$$\frac{q^2\theta_m}{\theta_\phi} < \lambda < \frac{\theta_\phi}{q^2\theta_m} \quad \Rightarrow \quad q^2|\theta_m| > \theta_\phi > 0 \ . \tag{7.375}$$

Thus, $\lambda$ is restricted to the range

$$\lambda \in \bigg[ -1 \, , \, -\frac{\theta_\phi}{q^2|\theta_m|} \bigg] \ . \tag{7.376}$$

With $\theta_m \equiv \theta < 0$ and $\theta_\phi \equiv \theta + \tau > 0$, the condition $q^2|\theta_m| > \theta_\phi$ is found to be

$$-\tau < \theta < -\frac{\tau}{q^2 + 1} \ . \tag{7.377}$$

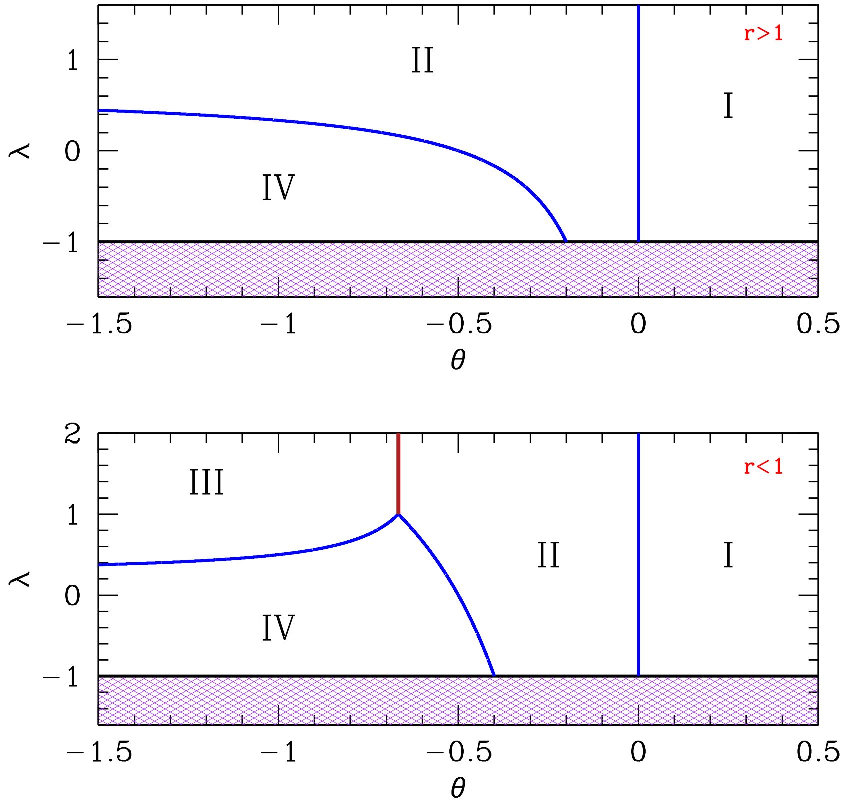

Figure 7.28: Phase diagram for $\tau = 0.5$, $r = 1.5$ (top) and $\tau = 0.5$, $r = 0.25$ (bottom). The hatched purple region is unphysical, with a free energy unbounded from below. The blue lines denote second order transitions. The thick red line separating phases II and III is a first order line.

Thus, phase IV exists and has lower energy when

$$-\tau < \theta < -\frac{\tau}{r+1} \quad \text{and} \quad -1 < \lambda < -\frac{\theta+\tau}{r\theta} \ , \tag{7.378}$$

where $r = q^2$.

(3) $0 > \theta_\phi > \theta_m$. In this regime, any phase is possible, however once again phase I can be ruled out since phases II and III are of lower free energy. The condition that phase II have lower free energy than phase III is

$$f_{\text{II}} - f_{\text{III}} = \frac{\varepsilon_0}{4}\left(q^{-2}\theta_\phi^2 - q^2\theta_m^2\right) < 0 \ , \tag{7.379}$$

*i.e.* $|\theta_\phi| < r|\theta_m|$, which means $r|\theta| > |\theta| - \tau$. If $r > 1$ this is true for all $\theta < 0$, while if $r < 1$ phase II is lower in energy only for $|\theta| < \tau/(1-r)$.

We next need to test whether phase IV has an even lower energy than the lower of phases II and III. We have

$$f_{\text{IV}} - f_{\text{II}} = \frac{(q\,\lambda\,\theta_m - q^{-1}\,\theta_\phi)^2}{4(\lambda^2-1)} \tag{7.380}$$

$$f_{\text{IV}} - f_{\text{III}} = \frac{(q\,\theta_m - q^{-1}\,\lambda\,\theta_\phi)^2}{4(\lambda^2-1)} \ . \tag{7.381}$$

In both cases, phase IV can only be the true thermodynamic phase if $\lambda^2 < 1$. We then require $\mathsf{m}^2 > 0$ and $\varphi^2 > 0$, which fixes

$$\lambda \in \left[ -1 \, , \, \min\!\left( \frac{q^2\,\theta_m}{\theta_\phi} \, , \, \frac{\theta_\phi}{q^2\theta_m} \right) \right] . \tag{7.382}$$

The upper limit will be the first term inside the rounded brackets if $q^2|\theta_m| < \theta_\phi$, *i.e.* if $r|\theta| < |\theta| - \tau$. This is impossible if $r > 1$, hence the upper limit is given by the second term in the rounded brackets:

$$r > 1 \ : \ \lambda \in \left[ -1 \, , \, \frac{\theta + \tau}{r\,\theta} \right] \qquad \text{(condition for phase IV)} \ . \tag{7.383}$$

If $r < 1$, then the upper limit will be $q^2\theta_m/\theta_\phi = r\theta/(\theta+\tau)$ if $|\theta| > \tau/(1-r)$, and will be $\theta_\phi/q^2\theta_m = (\theta+\tau)/r\theta$ if $|\theta| < \tau/(1-r)$.

$$r < 1 \, , \ -\frac{\tau}{1-r} < \theta < -\tau \ : \ \lambda \in \left[ -1 \, , \, \frac{\theta + \tau}{r\theta} \right] \qquad \text{(phase IV)} \tag{7.384}$$

$$r < 1 \, , \ \theta < -\frac{\tau}{1-r} \ : \ \lambda \in \left[ -1 \, , \, \frac{r\theta}{\theta + \tau} \right] \qquad \text{(phase IV)} \ . \tag{7.385}$$

Representative phase diagrams for the cases $r > 1$ and $r < 1$ are shown in fig. 7.28.

# Chapter 8

# Nonequilibrium Phenomena

## 8.1 References

- H. Smith and H. H. Jensen, *Transport Phenomena* (Oxford, 1989)
  An outstanding, thorough, and pellucid presentation of the theory of Boltzmann transport in classical and quantum systems.
- P. L. Krapivsky, S. Redner, and E. Ben-Naim, *A Kinetic View of Statistical Physics* (Cambridge, 2010)
  Superb, modern discussion of a broad variety of issues and models in nonequilibrium statistical physics.
- E. M. Lifshitz and L. P. Pitaevskii, *Physical Kinetics* (Pergamon, 1981)
  Volume 10 in the famous Landau and Lifshitz *Course of Theoretical Physics*. Surprisingly readable, and with many applications (some advanced).
- M. Kardar, *Statistical Physics of Particles* (Cambridge, 2007)
  A superb modern text, with many insightful presentations of key concepts. Includes a very instructive derivation of the Boltzmann equation starting from the BBGKY hierarchy.
- J. A. McLennan, *Introduction to Non-equilibrium Statistical Mechanics* (Prentice-Hall, 1989)
  Though narrow in scope, this book is a good resource on the Boltzmann equation.
- F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, 1987)
  This has been perhaps the most popular undergraduate text since it first appeared in 1967, and with good reason. The later chapters discuss transport phenomena at an undergraduate level.
- N. G. Van Kampen, *Stochastic Processes in Physics and Chemistry* ($3^{\mathrm{rd}}$ edition, North-Holland, 2007)
  This is a very readable and useful text. A relaxed but meaty presentation.

## 8.2 Equilibrium, Nonequilibrium and Local Equilibrium

Classical equilibrium statistical mechanics is described by the full $N$-body distribution,

$$f^0(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N;\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N)=\begin{cases} Z_N^{-1}\cdot\frac{1}{N!}\,e^{-\beta\hat{H}_N(\boldsymbol{p},\boldsymbol{x})} & \text{OCE}\\ \\ \Xi^{-1}\cdot\frac{1}{N!}\,e^{\beta\mu N}e^{-\beta\hat{H}_N(\boldsymbol{p},\boldsymbol{x})} & \text{GCE}\,. \end{cases} \tag{8.1}$$

We assume a Hamiltonian of the form

$$\hat{H}_N=\sum_{i=1}^N\frac{\boldsymbol{p}_i^2}{2m}+\sum_{i=1}^N v(\boldsymbol{x}_i)+\sum_{i<j}^N u(\boldsymbol{x}_i-\boldsymbol{x}_j), \tag{8.2}$$

typically with $v=0$, *i.e.* only two-body interactions. The quantity

$$f^0(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N;\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N)\,\frac{d^dx_1\,d^dp_1}{h^d}\cdots\frac{d^dx_N\,d^dp_N}{h^d} \tag{8.3}$$

is the probability, under equilibrium conditions, of finding $N$ particles in the system, with particle #1 lying within $d^3x_1$ of $\boldsymbol{x}_1$ and having momentum within $d^dp_1$ of $\boldsymbol{p}_1$, *etc.* The temperature $T$ and chemical potential $\mu$ are constants, independent of position. Note that $f(\{\boldsymbol{x}_i\},\{\boldsymbol{p}_i\})$ is dimensionless.

Nonequilibrium statistical mechanics seeks to describe thermodynamic systems which are out of equilibrium, meaning that the distribution function is not given by the Boltzmann distribution above. For a general nonequilibrium setting, it is hopeless to make progress – we'd have to integrate the equations of motion for all the constituent particles. However, typically we are concerned with situations where external forces or constraints are imposed over some macroscopic scale. Examples would include the imposition of a voltage drop across a metal, or a temperature differential across any thermodynamic sample. In such cases, scattering at microscopic length and time scales described by the *mean free path* $\ell$ and the *collision time* $\tau$ work to establish *local equilibrium* throughout the system. A local equilibrium is a state described by a space and time varying temperature $T(\boldsymbol{r},t)$ and chemical potential $\mu(\boldsymbol{r},t)$. As we will see, the Boltzmann distribution with $T=T(\boldsymbol{r},t)$ and $\mu=\mu(\boldsymbol{r},t)$ will not be a solution to the evolution equation governing the distribution function. Rather, the distribution for systems slightly out of equilibrium will be of the form $f=f^0+\delta f$, where $f^0$ describes a state of local equilibrium.

We will mainly be interested in the one-body distribution

$$\begin{aligned} f(\boldsymbol{r},\boldsymbol{p};t)&=\sum_{i=1}^N\big\langle\,\delta\big(\boldsymbol{x}_i(t)-\boldsymbol{r}\big)\,\delta\big(\boldsymbol{p}_i(t)-\boldsymbol{p}\big)\,\big\rangle\\ &=N\!\int\prod_{i=2}^N d^dx_i\,d^dp_i\;f(\boldsymbol{r},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N;\boldsymbol{p},\boldsymbol{p}_2,\ldots,\boldsymbol{p}_N;t)\,. \end{aligned} \tag{8.4}$$

In this chapter, we will drop the $1/\hbar$ normalization for phase space integration. Thus, $f(\boldsymbol{r},\boldsymbol{p},t)$ has dimensions of $h^{-d}$, and $f(\boldsymbol{r},\boldsymbol{p},t)\,d^3r\,d^3p$ is the average number of particles found within $d^3r$ of $\boldsymbol{r}$ and $d^3p$ of $\boldsymbol{p}$ at time $t$.

In the GCE, we sum the RHS above over $N$. Assuming $v=0$ so that there is no one-body potential to break translational symmetry, the equilibrium distribution is time-independent and space-independent:

$$f^0(\boldsymbol{r},\boldsymbol{p})=n\,(2\pi mk_{\rm B}T)^{-3/2}\,e^{-\boldsymbol{p}^2/2mk_{\rm B}T}\,, \tag{8.5}$$

where $n=N/V$ or $n=n(T,\mu)$ is the particle density in the OCE or GCE. From the one-body distribution we can compute things like the particle current, $\boldsymbol{j}$, and the energy current, $\boldsymbol{j}_\varepsilon$:

$$\boldsymbol{j}(\boldsymbol{r},t) = \int\! d^d\!p\; f(\boldsymbol{r},\boldsymbol{p};t)\, \frac{\boldsymbol{p}}{m} \tag{8.6}$$

$$\boldsymbol{j}_\varepsilon(\boldsymbol{r},t) = \int\! d^d\!p\; f(\boldsymbol{r},\boldsymbol{p};t)\; \varepsilon(\boldsymbol{p})\, \frac{\boldsymbol{p}}{m}\ , \tag{8.7}$$

where $\varepsilon(\boldsymbol{p}) = \boldsymbol{p}^2/2m$. Clearly these currents both vanish in equilibrium, when $f = f^0$, since $f^0(\boldsymbol{r},\boldsymbol{p})$ depends only on $\boldsymbol{p}^2$ and not on the direction of $\boldsymbol{p}$. In a *steady state* nonequilibrium situation, the above quantities are time-independent.

Thermodynamics says that

$$dq = T\,ds = d\varepsilon - \mu\,dn\ , \tag{8.8}$$

where $s$, $\varepsilon$, and $n$ are entropy density, energy density, and particle density, respectively, and $dq$ is the differential heat density. This relation may be case as one among the corresponding current densities:

$$\boldsymbol{j}_q = T\boldsymbol{j}_s = \boldsymbol{j}_\varepsilon - \mu\,\boldsymbol{j}\ . \tag{8.9}$$

Thus, in a system with no particle flow, $\boldsymbol{j} = 0$ and the *heat current* $\boldsymbol{j}_q$ is the same as the energy current $\boldsymbol{j}_\varepsilon$.

When the individual particles are not point particles, they possess angular momentum as well as linear momentum. Following Lifshitz and Pitaevskii, we abbreviate $\varGamma = (\boldsymbol{p},\boldsymbol{L})$ for these two variables for the case of diatomic molecules, and $\varGamma = (\boldsymbol{p},\boldsymbol{L},\hat{\boldsymbol{n}}\cdot\boldsymbol{L})$ in the case of spherical top molecules, where $\hat{\boldsymbol{n}}$ is the symmetry axis of the top. We then have, in $d = 3$ dimensions,

$$d\varGamma = \begin{cases} d^3\!p & \text{point particles} \\ d^3\!p\; L\,dL\,d\varOmega_L & \text{diatomic molecules} \\ d^3\!p\; L^2\,dL\,d\varOmega_L\,d\cos\vartheta & \text{symmetric tops ,} \end{cases} \tag{8.10}$$

where $\vartheta = \cos^{-1}(\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{L}})$. We will call the set $\varGamma$ the ‘kinematic variables’. The instantaneous number density at $\boldsymbol{r}$ is then

$$n(\boldsymbol{r},t) = \int\! d\varGamma\; f(\boldsymbol{r},\varGamma;t)\ . \tag{8.11}$$

One might ask why we do not also keep track of the angular orientation of the individual molecules. There are two reasons. First, the rotations of the molecules are generally extremely rapid, so we are justified in averaging over these motions. Second, the orientation of, say, a rotor does not enter into its energy. While the same can be said of the spatial position in the absence of external fields, (i) in the presence of external fields one must keep track of the position coordinate $\boldsymbol{r}$ since there is physical transport of particles from one region of space to another, and (iii) the collision process, which as we shall see enters the dynamics of the distribution function, takes place in real space.

## 8.3 Boltzmann Transport Theory

### 8.3.1 Derivation of the Boltzmann equation

For simplicity of presentation, we assume point particles. Recall that

$$f(\boldsymbol{r},\boldsymbol{p},t)\, d^3\!r\, d^3\!p \equiv \begin{cases} \text{\# of particles with positions within } d^3r \text{ of} \\ \boldsymbol{r} \text{ and momenta within } d^3p \text{ of } \boldsymbol{p} \text{ at time } t. \end{cases} \tag{8.12}$$

We now ask how the distribution functions $f(\boldsymbol{r},\boldsymbol{p},t)$ evolves in time. It is clear that in the absence of collisions, the distribution function must satisfy the continuity equation,

$$\frac{\partial f}{\partial t} + \boldsymbol{\nabla}\cdot(\boldsymbol{u} f) = 0 \; . \tag{8.13}$$

This is just the condition of number conservation for particles. Take care to note that $\boldsymbol{\nabla}$ and $\boldsymbol{u}$ are *six*-dimensional *phase space* vectors:

$$\boldsymbol{u} = (\, \dot{x} \; , \; \dot{y} \; , \; \dot{z} \; , \; \dot{p}_x \; , \; \dot{p}_y \; , \; \dot{p}_z \,) \tag{8.14}$$

$$\boldsymbol{\nabla} = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial}{\partial p_x}, \frac{\partial}{\partial p_y}, \frac{\partial}{\partial p_z} \right) \; . \tag{8.15}$$

The continuity equation describes a distribution in which each constituent particle evolves according to a prescribed dynamics, which for a mechanical system is specified by

$$\frac{d\boldsymbol{r}}{dt} = \frac{\partial H}{\partial \boldsymbol{p}} = \boldsymbol{v}(\boldsymbol{p}) \qquad , \qquad \frac{d\boldsymbol{p}}{dt} = -\frac{\partial H}{\partial \boldsymbol{r}} = \boldsymbol{F}_{\rm ext} \; , \tag{8.16}$$

where $\boldsymbol{F}$ is an external applied force. Here,

$$H(\boldsymbol{p},\boldsymbol{r}) = \varepsilon(\boldsymbol{p}) + U_{\rm ext}(\boldsymbol{r}) \; . \tag{8.17}$$

For example, if the particles are under the influence of gravity, then $U_{\rm ext}(\boldsymbol{r}) = m\boldsymbol{g}\cdot\boldsymbol{r}$ and $\boldsymbol{F} = -\boldsymbol{\nabla} U_{\rm ext} = -m\boldsymbol{g}$.

Note that as a consequence of the dynamics, we have $\boldsymbol{\nabla}\cdot\boldsymbol{u} = 0$, *i.e.* phase space flow is *incompressible*, provided that $\varepsilon(\boldsymbol{p})$ is a function of $\boldsymbol{p}$ alone, and not of $\boldsymbol{r}$. Thus, in the absence of collisions, we have

$$\frac{\partial f}{\partial t} + \boldsymbol{u}\cdot\boldsymbol{\nabla} f = 0 \; . \tag{8.18}$$

The differential operator $D_t \equiv \partial_t + \boldsymbol{u}\cdot\boldsymbol{\nabla}$ is sometimes called the 'convective derivative', because $D_t f$ is the time derivative of $f$ in a comoving frame of reference.

Next we must consider the effect of collisions, which are not accounted for by the semiclassical dynamics. In a collision process, a particle with momentum $\boldsymbol{p}$ and one with momentum $\tilde{\boldsymbol{p}}$ can instantaneously convert into a pair with momenta $\boldsymbol{p}'$ and $\tilde{\boldsymbol{p}}'$, provided total momentum is conserved: $\boldsymbol{p} + \tilde{\boldsymbol{p}} = \boldsymbol{p}' + \tilde{\boldsymbol{p}}'$. This means that $D_t f \neq 0$. Rather, we should write

$$\frac{\partial f}{\partial t} + \dot{\boldsymbol{r}}\cdot\frac{\partial f}{\partial \boldsymbol{r}} + \dot{\boldsymbol{p}}\cdot\frac{\partial f}{\partial \boldsymbol{p}} = \left(\frac{\partial f}{\partial t}\right)_{\rm coll} \tag{8.19}$$

where the right side is known as the *collision integral*. The collision integral is in general a *function* of $\boldsymbol{r}$, $\boldsymbol{p}$, and $t$ and a *functional* of the distribution $f$.

After a trivial rearrangement of terms, we can write the Boltzmann equation as

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_{\rm str} + \left(\frac{\partial f}{\partial t}\right)_{\rm coll} \; , \tag{8.20}$$

where

$$\left(\frac{\partial f}{\partial t}\right)_{\rm str} \equiv -\dot{\boldsymbol{r}}\cdot\frac{\partial f}{\partial \boldsymbol{r}} - \dot{\boldsymbol{p}}\cdot\frac{\partial f}{\partial \boldsymbol{p}} \tag{8.21}$$

is known as the *streaming term*. Thus, there are two contributions to $\partial f/\partial t$: streaming and collisions.

### 8.3.2 Collisionless Boltzmann equation

In the absence of collisions, the Boltzmann equation is given by

$$\frac{\partial f}{\partial t} + \frac{\partial \varepsilon}{\partial \boldsymbol{p}} \cdot \frac{\partial f}{\partial \boldsymbol{r}} - \boldsymbol{\nabla} U_{\rm ext} \cdot \frac{\partial f}{\partial \boldsymbol{p}} = 0 \ . \tag{8.22}$$

In order to gain some intuition about how the streaming term affects the evolution of the distribution $f(\boldsymbol{r},\boldsymbol{p},t)$, consider a case where $\boldsymbol{F}_{\rm ext}=0$. We then have

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \frac{\partial f}{\partial \boldsymbol{r}} = 0 \ . \tag{8.23}$$

Clearly, then, *any* function of the form

$$f(\boldsymbol{r},\boldsymbol{p},t) = \varphi\big(\boldsymbol{r} - \boldsymbol{v}(\boldsymbol{p})\, t \, , \, \boldsymbol{p}\big) \tag{8.24}$$

will be a solution to the collisionless Boltzmann equation, where $\boldsymbol{v}(\boldsymbol{p}) = \frac{\partial \varepsilon}{\partial \boldsymbol{p}}$. One possible solution would be the Boltzmann distribution,

$$f(\boldsymbol{r},\boldsymbol{p},t) = e^{\mu/k_{\rm B}T} e^{-\boldsymbol{p}^2/2mk_{\rm B}T} \ , \tag{8.25}$$

which is time-independent[1]. Here we have assumed a ballistic dispersion, $\varepsilon(\boldsymbol{p}) = \boldsymbol{p}^2/2m$.

For a slightly less trivial example, let the initial distribution be $\varphi(\boldsymbol{r},\boldsymbol{p}) = A\, e^{-\boldsymbol{r}^2/2\sigma^2} e^{-\boldsymbol{p}^2/2\kappa^2}$, so that

$$f(\boldsymbol{r},\boldsymbol{p},t) = A\, e^{-\left(\boldsymbol{r}-\frac{\boldsymbol{p}t}{m}\right)^2/2\sigma^2} \, e^{-\boldsymbol{p}^2/2\kappa^2} \ . \tag{8.26}$$

Consider the one-dimensional version, and rescale position, momentum, and time so that

$$f(x,p,t) = A\, e^{-\frac{1}{2}(\bar{x}-\bar{p}\,\bar{t})^2} \, e^{-\frac{1}{2}\bar{p}^2} \ . \tag{8.27}$$

Consider the level sets of $f$, where $f(x,p,t) = A\, e^{-\frac{1}{2}\alpha^2}$. The equation for these sets is

$$\bar{x} = \bar{p}\,\bar{t} \pm \sqrt{\alpha^2 - \bar{p}^2} \ . \tag{8.28}$$

For fixed $\bar{t}$, these level sets describe the loci in phase space of equal probability densities, with the probability density decreasing exponentially in the parameter $\alpha^2$. For $\bar{t}=0$, the initial distribution describes a Gaussian cloud of particles with a Gaussian momentum distribution. As $\bar{t}$ increases, the distribution widens in $\bar{x}$ but not in $\bar{p}$ – each particle moves with a constant momentum, so the set of momentum values never changes. However, the level sets in the $(\bar{x}\, , \, \bar{p})$ plane become elliptical, with a semimajor axis oriented at an angle $\theta = {\rm ctn}^{-1}(t)$ with respect to the $\bar{x}$ axis. For $\bar{t}>0$, he particles at the outer edges of the cloud are more likely to be moving away from the center. See the sketches in fig. 8.1

Suppose we add in a constant external force $\boldsymbol{F}_{\rm ext}$. Then it is easy to show (and left as an exercise to the reader to prove) that any function of the form

$$f(\boldsymbol{r},\boldsymbol{p},t) = A\,\varphi\bigg(\boldsymbol{r} - \frac{\boldsymbol{p}\,t}{m} + \frac{\boldsymbol{F}_{\rm ext}t^2}{2m} \, , \, \boldsymbol{p} - \frac{\boldsymbol{F}_{\rm ext}t}{m}\bigg) \tag{8.29}$$

satisfies the collisionless Boltzmann equation (ballistic dispersion assumed).

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[1] Indeed, any arbitrary function of $\boldsymbol{p}$ alone would be a solution. Ultimately, we require some energy exchanging processes, such as collisions, in order for any initial nonequilibrium distribution to converge to the Boltzmann distribution.

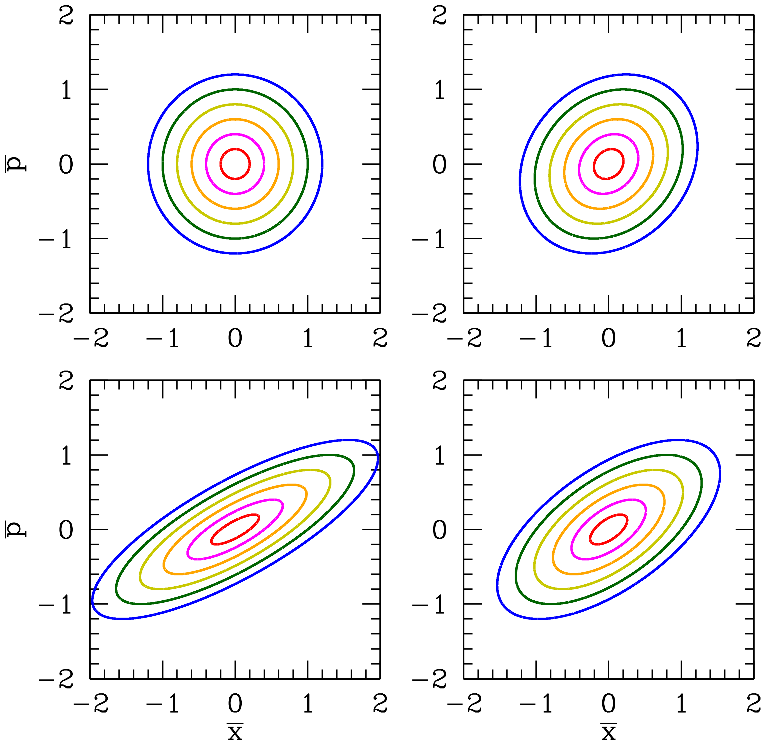

Figure 8.1: Level sets for a sample $f(\bar{x},\bar{p},\bar{t}) = A\,e^{-\frac{1}{2}(\bar{x}-\bar{p}\bar{t})^2}\,e^{-\frac{1}{2}\bar{p}^2}$, for values $f = A\,e^{-\frac{1}{2}\alpha^2}$ with $\alpha$ in equally spaced intervals from $\alpha = 0.2$ (red) to $\alpha = 1.2$ (blue). The time variable $\bar{t}$ is taken to be $\bar{t} = 0.0$ (upper left), $0.2$ (upper right), $0.8$ (lower right), and $1.3$ (lower left).

### 8.3.3 Collisional invariants

Consider a function $A(\boldsymbol{r},\boldsymbol{p})$ of position and momentum. Its average value at time $t$ is

$$A(t) = \int\! d^3\!r\, d^3\!p\; A(\boldsymbol{r},\boldsymbol{p})\, f(\boldsymbol{r},\boldsymbol{p},t)\ . \tag{8.30}$$

Taking the time derivative,

$$\begin{aligned}
\frac{dA}{dt} &= \int\! d^3\!r\, d^3\!p\; A(\boldsymbol{r},\boldsymbol{p})\, \frac{\partial f}{\partial t} \\
&= \int\! d^3\!r\, d^3\!p\; A(\boldsymbol{r},\boldsymbol{p}) \left\{ -\frac{\partial}{\partial \boldsymbol{r}} \cdot (\dot{\boldsymbol{r}} f) - \frac{\partial}{\partial \boldsymbol{p}} \cdot (\dot{\boldsymbol{p}} f) + \left(\frac{\partial f}{\partial t}\right)_{\!\rm coll} \right\} \\
&= \int\! d^3\!r\, d^3\!p\; \left\{ \left( \frac{\partial A}{\partial \boldsymbol{r}} \cdot \frac{d\boldsymbol{r}}{dt} + \frac{\partial A}{\partial \boldsymbol{p}} \cdot \frac{d\boldsymbol{p}}{dt} \right) f + A(\boldsymbol{r},\boldsymbol{p}) \left(\frac{\partial f}{\partial t}\right)_{\!\rm coll} \right\} .
\end{aligned} \tag{8.31}$$

Hence, if $A$ is preserved by the dynamics between collisions, then[2]

$$\frac{dA}{dt} = \frac{\partial A}{\partial \boldsymbol{r}} \cdot \frac{d\boldsymbol{r}}{dt} + \frac{\partial A}{\partial \boldsymbol{p}} \cdot \frac{d\boldsymbol{p}}{dt} = 0\ . \tag{8.32}$$

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[2] Recall from classical mechanics the definition of the *Poisson bracket*, $\{A,B\} = \frac{\partial A}{\partial \boldsymbol{r}} \cdot \frac{\partial B}{\partial \boldsymbol{p}} - \frac{\partial B}{\partial \boldsymbol{r}} \cdot \frac{\partial A}{\partial \boldsymbol{p}}$. Then from Hamilton's equations $\dot{\boldsymbol{r}} = \frac{\partial H}{\partial \boldsymbol{p}}$ and $\dot{\boldsymbol{p}} = -\frac{\partial H}{\partial \boldsymbol{r}}$, where $H(\boldsymbol{p},\boldsymbol{r},t)$ is the Hamiltonian, we have $\frac{dA}{dt} = \{A,H\}$. Invariants have zero Poisson bracket with the Hamiltonian.

We therefore have that the rate of change of $A$ is determined wholly by the collision integral

$$\frac{dA}{dt} = \int\!d^3\!r\, d^3\!p\, A(\boldsymbol{r},\boldsymbol{p}) \left(\frac{\partial f}{\partial t}\right)_{\rm coll} . \tag{8.33}$$

Quantities which are then conserved in the collisions satisfy $\dot{A} = 0$. Such quantities are called *collisional invariants*. Examples of collisional invariants include the particle number ($A = 1$), the components of the total momentum ($A = p_\mu$) (in the absence of broken translational invariance, due *e.g.* to the presence of walls), and the total energy ($A = \varepsilon(\boldsymbol{p})$).

### 8.3.4 Scattering processes

What sort of processes contribute to the collision integral? There are two broad classes to consider. The first involves potential scattering, where a particle in state $|\varGamma\rangle$ scatters, in the presence of an external potential, to a state $|\varGamma'\rangle$. Recall that $\varGamma$ is an abbreviation for the set of kinematic variables, *e.g.* $\varGamma = (\boldsymbol{p},\boldsymbol{L})$ in the case of a diatomic molecule. For point particles, $\varGamma = (p_x, p_y, p_z)$ and $d\varGamma = d^3\!p$.

We now define the function $w\big(\varGamma'|\varGamma\big)$ such that

$$w\big(\varGamma'|\varGamma\big)\, f(\boldsymbol{r},\varGamma;t)\, d\varGamma\, d\varGamma' = \begin{cases} \text{rate at which a particle within } d\varGamma \text{ of } (\boldsymbol{r},\varGamma) \\ \text{scatters to within } d\varGamma' \text{ of } (\boldsymbol{r},\varGamma') \text{ at time } t. \end{cases} \tag{8.34}$$

The units of $w\, d\varGamma$ are therefore $1/T$. The differential scattering cross section for particle scattering is then

$$d\sigma = \frac{w\big(\varGamma'|\varGamma\big)}{n\,|\boldsymbol{v}|}\, d\varGamma' , \tag{8.35}$$

where $\boldsymbol{v} = \boldsymbol{p}/m$ is the particle's velocity and $n$ the density.

The second class is that of two-particle scattering processes, *i.e.* $|\varGamma\varGamma_1\rangle \to |\varGamma'\varGamma_1'\rangle$. We define the scattering function $w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big)$ by

$$w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big)\, f_2(\boldsymbol{r},\varGamma;\boldsymbol{r},\varGamma_1\,;\,t)\, d\varGamma\, d\varGamma_1\, d\varGamma'\, d\varGamma_1' = \begin{cases} \text{rate at which two particles within } d\varGamma \text{ of } (\boldsymbol{r},\varGamma) \\ \text{and within } d\varGamma_1 \text{ of } (\boldsymbol{r},\varGamma_1) \text{ scatter into states within} \\ d\varGamma' \text{ of } (\boldsymbol{r},\varGamma') \text{ and } d\varGamma_1' \text{ of } (\boldsymbol{r},\varGamma_1') \text{ at time } t\,, \end{cases} \tag{8.36}$$

where

$$f_2(\boldsymbol{r},\boldsymbol{p}\,;\,\boldsymbol{r}',\boldsymbol{p}'\,;\,t) = \Big\langle \sum_{i,j} \delta\big(\boldsymbol{x}_i(t)-\boldsymbol{r}\big)\, \delta\big(\boldsymbol{p}_i(t)-\boldsymbol{p}\big)\, \delta\big(\boldsymbol{x}_j(t)-\boldsymbol{r}'\big)\, \delta\big(\boldsymbol{p}_j(t)-\boldsymbol{p}'\big) \Big\rangle \tag{8.37}$$

is the nonequilibrium two-particle distribution for point particles. The differential scattering cross section is

$$d\sigma = \frac{w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big)}{|\boldsymbol{v}-\boldsymbol{v}_1|}\, d\varGamma'\, d\varGamma_1' . \tag{8.38}$$

We assume, in both cases, that any scattering occurs *locally*, *i.e.* the particles attain their asymptotic kinematic states on distance scales small compared to the mean interparticle separation. In this case we can treat each scattering process independently. This assumption is particular to rarefied systems, *i.e.* gases, and is not appropriate for dense liquids. The two types of scattering processes are depicted in fig. 8.2.

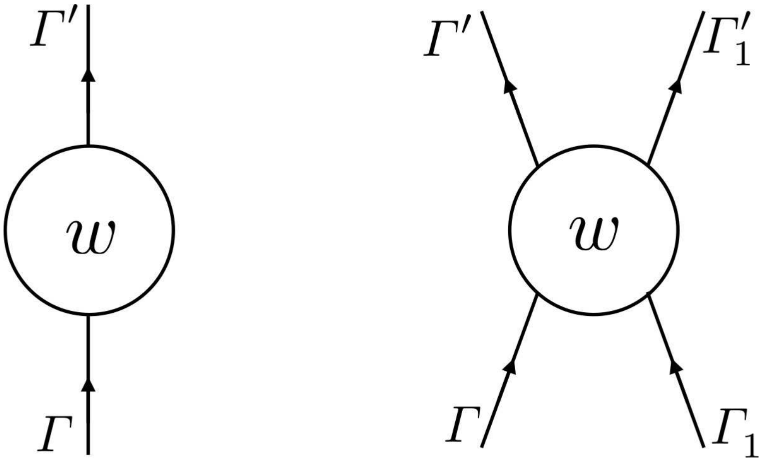

Figure 8.2: Left: single particle scattering process $|\varGamma\rangle \to |\varGamma'\rangle$. Right: two-particle scattering process $|\varGamma\varGamma_1\rangle \to |\varGamma'\varGamma_1'\rangle$.

In computing the collision integral for the state $|\boldsymbol{r},\varGamma\rangle$, we must take care to sum over contributions from transitions *out of* this state, *i.e.* $|\varGamma\rangle \to |\varGamma'\rangle$, which reduce $f(\boldsymbol{r},\varGamma)$, and transitions *into* this state, *i.e.* $|\varGamma'\rangle \to |\varGamma\rangle$, which increase $f(\boldsymbol{r},\varGamma)$. Thus, for one-body scattering, we have

$$\frac{D}{Dt}\,f(\boldsymbol{r},\varGamma;t) = \left(\frac{\partial f}{\partial t}\right)_{\rm coll} = \int\! d\varGamma'\,\Big\{ w(\varGamma\,|\,\varGamma')\,f(\boldsymbol{r},\varGamma';t) - w(\varGamma'\,|\,\varGamma)\,f(\boldsymbol{r},\varGamma;t)\Big\}\ . \tag{8.39}$$

For two-body scattering, we have

$$\begin{aligned}\frac{D}{Dt}\,f(\boldsymbol{r},\varGamma;t) &= \left(\frac{\partial f}{\partial t}\right)_{\rm coll}\\ &= \int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1'\,\Big\{ w\big(\varGamma\varGamma_1\,|\,\varGamma'\varGamma_1'\big)\,f_2(\boldsymbol{r},\varGamma';\boldsymbol{r},\varGamma_1';t)\\ &\qquad\qquad - w\big(\varGamma'\varGamma_1'\,|\,\varGamma\varGamma_1\big)\,f_2(\boldsymbol{r},\varGamma;\boldsymbol{r},\varGamma_1;t)\Big\}\ .\end{aligned} \tag{8.40}$$

Unlike the one-body scattering case, the kinetic equation for two-body scattering does not close, since the LHS involves the one-body distribution $f \equiv f_1$ and the RHS involves the two-body distribution $f_2$. To close the equations, we make the *approximation*

$$f_2(\boldsymbol{r},\varGamma';\tilde{\boldsymbol{r}},\tilde{\varGamma};t) \approx f(\boldsymbol{r},\varGamma;t)\,f(\tilde{\boldsymbol{r}},\tilde{\varGamma};t)\ . \tag{8.41}$$

We then have

$$\begin{aligned}\frac{D}{Dt}\,f(\boldsymbol{r},\varGamma;t) = \int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1'\,\Big\{ & w\big(\varGamma\varGamma_1\,|\,\varGamma'\varGamma_1'\big)\,f(\boldsymbol{r},\varGamma';t)\,f(\boldsymbol{r},\varGamma_1';t)\\ & - w\big(\varGamma'\varGamma_1'\,|\,\varGamma\varGamma_1\big)\,f(\boldsymbol{r},\varGamma;t)\,f(\boldsymbol{r},\varGamma_1;t)\Big\}\ .\end{aligned} \tag{8.42}$$

### 8.3.5 Detailed balance

Classical mechanics places some restrictions on the form of the kernel $w\big(\varGamma\varGamma_1\,|\,\varGamma'\varGamma_1'\big)$. In particular, if $\varGamma^T = (-\boldsymbol{p},-\boldsymbol{L})$ denotes the kinematic variables under time reversal, then

$$w\big(\varGamma'\varGamma_1'\,|\,\varGamma\varGamma_1\big) = w\big(\varGamma^T\varGamma_1^T\,|\,\varGamma'^T\varGamma_1'^T\big)\ . \tag{8.43}$$

This is because the time reverse of the process $|\varGamma\varGamma_1\rangle \to |\varGamma'\varGamma_1'\rangle$ is $|\varGamma'^{\mathrm{T}}\varGamma_1'^{\mathrm{T}}\rangle \to |\varGamma^{\mathrm{T}}\varGamma_1^{\mathrm{T}}\rangle$.

In equilibrium, we must have

$$w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big)\; f^0(\varGamma)\, f^0(\varGamma_1)\, d^4\!\varGamma = w\big(\varGamma^T\varGamma_1^T \,|\, \varGamma'^T\varGamma_1'^T\big)\, f^0(\varGamma'^T)\, f^0(\varGamma_1'^T)\, d^4\!\varGamma^T \tag{8.44}$$

where

$$d^4\!\varGamma \equiv d\varGamma\, d\varGamma_1\, d\varGamma' d\varGamma_1' \qquad , \qquad d^4\!\varGamma^T \equiv d\varGamma^T\, d\varGamma_1^T\, d\varGamma'^T d\varGamma_1'^T \; . \tag{8.45}$$

Since $d\varGamma = d\varGamma^T$ *etc.*, we may cancel the differentials above, and after invoking eqn. 8.43 and suppressing the common $\boldsymbol{r}$ label, we find

$$f^0(\varGamma)\, f^0(\varGamma_1) = f^0(\varGamma'^T)\, f^0(\varGamma_1'^T) \; . \tag{8.46}$$

This is the condition of *detailed balance*. For the Boltzmann distribution, we have

$$f^0(\varGamma) = A\, e^{-\varepsilon/k_{\mathrm{B}}T} \; , \tag{8.47}$$

where $A$ is a constant and where $\varepsilon = \varepsilon(\varGamma)$ is the kinetic energy, *e.g.* $\varepsilon(\varGamma) = \boldsymbol{p}^2/2m$ in the case of point particles. Note that $\varepsilon(\varGamma^T) = \varepsilon(\varGamma)$. Detailed balance is satisfied because the kinematics of the collision requires energy conservation:

$$\varepsilon + \varepsilon_1 = \varepsilon' + \varepsilon_1' \; . \tag{8.48}$$

Since momentum is also kinematically conserved, *i.e.*

$$\boldsymbol{p} + \boldsymbol{p}_1 = \boldsymbol{p}' + \boldsymbol{p}_1' \; , \tag{8.49}$$

any distribution of the form

$$f^0(\varGamma) = A\, e^{-(\varepsilon - \boldsymbol{p}\cdot\boldsymbol{V})/k_{\mathrm{B}}T} \tag{8.50}$$

also satisfies detailed balance, for any velocity parameter $\boldsymbol{V}$. This distribution is appropriate for gases which are flowing with average particle $\boldsymbol{V}$.

In addition to time-reversal, parity is also a symmetry of the microscopic mechanical laws. Under the parity operation $P$, we have $\boldsymbol{r} \to -\boldsymbol{r}$ and $\boldsymbol{p} \to -\boldsymbol{p}$. Note that a pseudovector such as $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ is unchanged under $P$. Thus, $\varGamma^P = (-\boldsymbol{p}, \boldsymbol{L})$. Under the combined operation of $C = PT$, we have $\varGamma^C = (\boldsymbol{p}, -\boldsymbol{L})$. If the microscopic Hamiltonian is invariant under $C$, then we must have

$$w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big) = w\big(\varGamma^C\varGamma_1^C \,|\, \varGamma'^C\varGamma_1'^C\big) \; . \tag{8.51}$$

For point particles, invariance under $T$ and $P$ then means

$$w(\boldsymbol{p}', \boldsymbol{p}_1' \,|\, \boldsymbol{p}, \boldsymbol{p}_1) = w(\boldsymbol{p}, \boldsymbol{p}_1 \,|\, \boldsymbol{p}', \boldsymbol{p}_1') \; , \tag{8.52}$$

and therefore the collision integral takes the simplified form,

$$\begin{aligned} \frac{Df(\boldsymbol{p})}{Dt} &= \bigg(\frac{\partial f}{\partial t}\bigg)_{\!\mathrm{coll}} \\ &= \int\! d^3\!p_1 \!\int\! d^3\!p' \!\int\! d^3\!p_1'\; w(\boldsymbol{p}', \boldsymbol{p}_1' \,|\, \boldsymbol{p}, \boldsymbol{p}_1)\, \Big\{ f(\boldsymbol{p}')\, f(\boldsymbol{p}_1') - f(\boldsymbol{p})\, f(\boldsymbol{p}_1) \Big\} \; , \end{aligned} \tag{8.53}$$

where we have suppressed both $\boldsymbol{r}$ and $t$ variables.

The most general statement of detailed balance is

$$\frac{f^0(\varGamma')\, f^0(\varGamma_1')}{f^0(\varGamma)\, f^0(\varGamma_1)} = \frac{w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big)}{w\big(\varGamma\varGamma_1 \,|\, \varGamma'\varGamma_1'\big)} \; . \tag{8.54}$$

Under this condition, the collision term vanishes for $f = f^0$, which is the equilibrium distribution.

### 8.3.6 Kinematics and cross section

We can rewrite eqn. 8.53 in the form

$$\frac{Df(\boldsymbol{p})}{Dt} = \int\! d^3\!p_1 \!\int\! d\Omega \, |\boldsymbol{v}-\boldsymbol{v}_1| \, \frac{\partial\sigma}{\partial\Omega} \Big\{ f(\boldsymbol{p}')\, f(\boldsymbol{p}_1') - f(\boldsymbol{p})\, f(\boldsymbol{p}_1) \Big\} \ , \tag{8.55}$$

where $\frac{\partial\sigma}{\partial\Omega}$ is the *differential scattering cross section*. If we recast the scattering problem in terms of center-of-mass and relative coordinates, we conclude that the total momentum is conserved by the collision, and furthermore that the energy in the CM frame is conserved, which means that the magnitude of the *relative* momentum is conserved. Thus, we may write $\boldsymbol{p}'-\boldsymbol{p}_1' = |\boldsymbol{p}-\boldsymbol{p}_1|\,\hat{\boldsymbol{\Omega}}$, where $\hat{\boldsymbol{\Omega}}$ is a unit vector. Then $\boldsymbol{p}'$ and $\boldsymbol{p}_1'$ are determined to be

$$\begin{aligned} \boldsymbol{p}' &= \tfrac{1}{2}\big(\boldsymbol{p}+\boldsymbol{p}_1 + |\boldsymbol{p}-\boldsymbol{p}_1|\,\hat{\boldsymbol{\Omega}}\big) \\ \boldsymbol{p}_1' &= \tfrac{1}{2}\big(\boldsymbol{p}+\boldsymbol{p}_1 - |\boldsymbol{p}-\boldsymbol{p}_1|\,\hat{\boldsymbol{\Omega}}\big) \ . \end{aligned} \tag{8.56}$$

### 8.3.7 H-theorem

Let's consider the Boltzmann equation with two particle collisions. We define the local (*i.e.* $\boldsymbol{r}$-dependent) quantity

$$\rho_\varphi(\boldsymbol{r},t) \equiv \int\! d\varGamma \ \varphi(\varGamma,f)\, f(\varGamma,\boldsymbol{r},t) \ . \tag{8.57}$$

At this point, $\varphi(\varGamma,f)$ is arbitrary. Note that the $\varphi(\varGamma,f)$ factor has $\boldsymbol{r}$ and $t$ dependence through its dependence on $f$, which itself is a function of $\boldsymbol{r}$, $\varGamma$, and $t$. We now compute

$$\begin{aligned} \frac{\partial\rho_\varphi}{\partial t} &= \int\! d\varGamma\ \frac{\partial(\varphi f)}{\partial t} = \int\! d\varGamma\ \frac{\partial(\varphi f)}{\partial f}\,\frac{\partial f}{\partial t} \\ &= -\int\! d\varGamma\ \boldsymbol{u}\cdot\boldsymbol{\nabla}(\varphi f) - \int\! d\varGamma\ \frac{\partial(\varphi f)}{\partial f}\left(\frac{\partial f}{\partial t}\right)_{\rm coll} \\ &= -\oint\! d\Sigma\ \hat{\boldsymbol{n}}\cdot(\boldsymbol{u}\,\varphi f) - \int\! d\varGamma\ \frac{\partial(\varphi f)}{\partial f}\left(\frac{\partial f}{\partial t}\right)_{\rm coll} \ . \end{aligned} \tag{8.58}$$

The first term on the last line follows from the divergence theorem, and vanishes if we assume $f=0$ for infinite values of the kinematic variables, which is the only physical possibility. Thus, the rate of change of $\rho_\varphi$ is entirely due to the collision term. Thus,

$$\begin{aligned} \frac{\partial\rho_\varphi}{\partial t} &= \int\! d\varGamma\!\int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1' \Big\{ w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big)\, f f_1\,\chi - w\big(\varGamma\varGamma_1 \,|\, \varGamma'\varGamma_1'\big)\, f' f_1'\,\chi \Big\} \\ &= \int\! d\varGamma\!\int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1'\ w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big)\, f f_1\,(\chi-\chi') \ , \end{aligned} \tag{8.59}$$

where $f\equiv f(\varGamma)$, $f'\equiv f(\varGamma')$, $f_1\equiv f(\varGamma_1)$, $f_1'\equiv f(\varGamma_1')$, $\chi=\chi(\varGamma)$, with

$$\chi = \frac{\partial(\varphi f)}{\partial f} = \varphi + f\,\frac{\partial\varphi}{\partial f} \ . \tag{8.60}$$

We now invoke the symmetry

$$w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big) = w\big(\varGamma_1'\varGamma' \,|\, \varGamma_1\varGamma\big) \ , \tag{8.61}$$

which allows us to write

$$\frac{\partial\rho_\varphi}{\partial t} = \tfrac{1}{2}\!\int\! d\varGamma\!\int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1'\ w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big)\, f f_1\,(\chi+\chi_1-\chi'-\chi_1') \ . \tag{8.62}$$

This shows that $\rho_\varphi$ is preserved by the collision term if $\chi(\varGamma)$ is a collisional invariant.

Now let us consider $\varphi(f) = \ln f$. We define $\mathsf{h} \equiv \rho\big|_{\varphi=\ln f}$. We then have

$$\frac{\partial \mathsf{h}}{\partial t} = -\tfrac{1}{2}\!\int\! d\varGamma\!\int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1'\; w\, f' f_1' \cdot x \ln x \;, \tag{8.63}$$

where $w \equiv w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big)$ and $x \equiv f f_1 / f' f_1'$. We next invoke the result

$$\int\! d\varGamma'\!\int\! d\varGamma_1'\; w\big(\varGamma'\varGamma_1' \,|\, \varGamma\varGamma_1\big) = \int\! d\varGamma'\!\int\! d\varGamma_1'\; w\big(\varGamma\varGamma_1 \,|\, \varGamma'\varGamma_1'\big) \tag{8.64}$$

which is a statement of unitarity of the scattering matrix[3]. Multiplying both sides by $f(\varGamma)\, f(\varGamma_1)$, then integrating over $\varGamma$ and $\varGamma_1$, and finally changing variables $(\varGamma,\varGamma_1) \leftrightarrow (\varGamma',\varGamma_1')$, we find

$$0 = \int\! d\varGamma\!\int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1'\; w\,\big(f f_1 - f' f_1'\big) = \int\! d\varGamma\!\int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1'\; w\, f' f_1'\,(x-1)\;. \tag{8.65}$$

Multiplying this result by $\frac{1}{2}$ and adding it to the previous equation for $\dot{\mathsf{h}}$, we arrive at our final result,

$$\frac{\partial \mathsf{h}}{\partial t} = -\tfrac{1}{2}\!\int\! d\varGamma\!\int\! d\varGamma_1\!\int\! d\varGamma'\!\int\! d\varGamma_1'\; w\, f' f_1'\,(x\ln x - x + 1)\;. \tag{8.66}$$

Note that $w$, $f'$, and $f_1'$ are all nonnegative. It is then easy to prove that the function $g(x) = x\ln x - x + 1$ is nonnegative for all positive $x$ values[4], which therefore entails the important result

$$\frac{\partial \mathsf{h}(\boldsymbol{r},t)}{\partial t} \le 0\;. \tag{8.67}$$

Boltzmann's $\mathsf{H}$ function is the space integral of the $\mathsf{h}$ density: $\mathsf{H} = \int d^3\!r\; \mathsf{h}$.

Thus, everywhere in space, the function $\mathsf{h}(\boldsymbol{r},t)$ is monotonically decreasing or constant, due to collisions. In equilibrium, $\dot{\mathsf{h}} = 0$ everywhere, which requires $x = 1$, *i.e.*

$$f^0(\varGamma)\, f^0(\varGamma_1) = f^0(\varGamma')\, f^0(\varGamma_1')\;, \tag{8.68}$$

or, taking the logarithm,

$$\ln f^0(\varGamma) + \ln f^0(\varGamma_1) = \ln f^0(\varGamma') + \ln f^0(\varGamma_1')\;. \tag{8.69}$$

But this means that $\ln f^0$ is itself a collisional invariant, and if $1$, $\boldsymbol{p}$, and $\varepsilon$ are the only collisional invariants, then $\ln f^0$ must be expressible in terms of them. Thus,

$$\ln f^0 = \frac{\mu}{k_{\rm B}T} + \frac{\boldsymbol{V}\!\cdot\!\boldsymbol{p}}{k_{\rm B}T} - \frac{\varepsilon}{k_{\rm B}T}\;, \tag{8.70}$$

where $\mu$, $\boldsymbol{V}$, and $T$ are constants which parameterize the equilibrium distribution $f^0(\boldsymbol{p})$, corresponding to the chemical potential, flow velocity, and temperature, respectively.

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[3] See Lifshitz and Pitaevskii, *Physical Kinetics*, §2.

[4] The function $g(x) = x\ln x - x + 1$ satisfies $g'(x) = \ln x$, hence $g'(x) < 0$ on the interval $x \in [0,1)$ and $g'(x) > 0$ on $x \in (1,\infty]$. Thus, $g(x)$ monotonically decreases from $g(0) = 1$ to $g(1) = 0$, and then monotonically increases to $g(\infty) = \infty$, never becoming negative.

## 8.4 Weakly Inhomogeneous Gas

Consider a gas which is only weakly out of equilibrium. We follow the treatment in Lifshitz and Pitaevskii, §6. As the gas is only slightly out of equilibrium, we seek a solution to the Boltzmann equation of the form $f = f^0 + \delta f$, where $f^0$ is describes a local equilibrium. Recall that such a distribution function is annihilated by the collision term in the Boltzmann equation but not by the streaming term, hence a correction $\delta f$ must be added in order to obtain a solution.

The most general form of local equilibrium is described by the distribution

$$f^0(\boldsymbol{r},\Gamma) = C\exp\left(\frac{\mu - \varepsilon(\Gamma) + \boldsymbol{V}\cdot\boldsymbol{p}}{k_{\rm B}T}\right) , \tag{8.71}$$

where $\mu = \mu(\boldsymbol{r},t)$, $T = T(\boldsymbol{r},t)$, and $\boldsymbol{V} = \boldsymbol{V}(\boldsymbol{r},t)$ vary in both space and time. Note that

$$\begin{aligned} df^0 &= \left(d\mu + \boldsymbol{p}\cdot d\boldsymbol{V} + (\varepsilon - \mu - \boldsymbol{V}\cdot\boldsymbol{p})\,\frac{dT}{T} - d\varepsilon\right)\left(-\frac{\partial f^0}{\partial\varepsilon}\right) \\ &= \left(\frac{1}{n}\,dp + \boldsymbol{p}\cdot d\boldsymbol{V} + (\varepsilon - h)\,\frac{dT}{T} - d\varepsilon\right)\left(-\frac{\partial f^0}{\partial\varepsilon}\right) \end{aligned} \tag{8.72}$$

where we have assumed $\boldsymbol{V} = 0$ on average, and used

$$\begin{aligned} d\mu &= \left(\frac{\partial\mu}{\partial T}\right)_{\!p} dT + \left(\frac{\partial\mu}{\partial p}\right)_{\!T} dp \\ &= -s\,dT + \frac{1}{n}\,dp\ , \end{aligned} \tag{8.73}$$

where $s$ is the entropy per particle and $n$ is the number density. We have further written $h = \mu + Ts$, which is the enthalpy per particle. Here, $c_p$ is the heat capacity per particle at constant pressure[5]. Finally, note that when $f^0$ is the Maxwell-Boltzmann distribution, we have

$$-\frac{\partial f^0}{\partial\varepsilon} = \frac{f^0}{k_{\rm B}T}\ . \tag{8.74}$$

The Boltzmann equation is written

$$\left(\frac{\partial}{\partial t} + \frac{\boldsymbol{p}}{m}\cdot\frac{\partial}{\partial\boldsymbol{r}} + \boldsymbol{F}\cdot\frac{\partial}{\partial\boldsymbol{p}}\right)\big(f^0 + \delta f\big) = \left(\frac{\partial f}{\partial t}\right)_{\rm coll}\ . \tag{8.75}$$

The RHS of this equation must be of order $\delta f$ because the local equilibrium distribution $f^0$ is annihilated by the collision integral. We therefore wish to evaluate one of the contributions to the LHS of this equation,

$$\begin{aligned} \frac{\partial f^0}{\partial t} + \frac{\boldsymbol{p}}{m}\cdot\frac{\partial f^0}{\partial\boldsymbol{r}} + \boldsymbol{F}\cdot\frac{\partial f^0}{\partial\boldsymbol{p}} = \left(-\frac{\partial f^0}{\partial\varepsilon}\right)&\left\{\frac{1}{n}\,\frac{\partial p}{\partial t} + \frac{\varepsilon - h}{T}\,\frac{\partial T}{\partial t} + m\boldsymbol{v}\cdot\Big[(\boldsymbol{v}\cdot\boldsymbol{\nabla})\,\boldsymbol{V}\Big]\right. \\ &\left. + \boldsymbol{v}\cdot\left(m\,\frac{\partial\boldsymbol{V}}{\partial t} + \frac{1}{n}\,\boldsymbol{\nabla}p\right) + \frac{\varepsilon - h}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla}T - \boldsymbol{F}\cdot\boldsymbol{v}\right\} . \end{aligned} \tag{8.76}$$

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[5] In the chapter on thermodynamics, we adopted a slightly different definition of $c_p$ as the heat capacity per mole. In this chapter $c_p$ is the heat capacity per particle.

To simplify this, first note that Newton's laws applied to an ideal fluid give $\rho\dot{\boldsymbol{V}} = -\boldsymbol{\nabla} p$, where $\rho = mn$ is the mass density. Corrections to this result, *e.g.* viscosity and nonlinearity in $\boldsymbol{V}$, are of higher order.

Next, continuity for particle number means $\dot{n} + \boldsymbol{\nabla}\cdot(n\boldsymbol{V}) = 0$. We assume $\boldsymbol{V}$ is zero on average and that all derivatives are small, hence $\boldsymbol{\nabla}\cdot(n\boldsymbol{V}) = \boldsymbol{V}\cdot\boldsymbol{\nabla} n + n\,\boldsymbol{\nabla}\cdot\boldsymbol{V} \approx n\,\boldsymbol{\nabla}\cdot\boldsymbol{V}$. Thus,

$$\frac{\partial \ln n}{\partial t} = \frac{\partial \ln p}{\partial t} - \frac{\partial \ln T}{\partial t} = -\boldsymbol{\nabla}\cdot\boldsymbol{V}\ , \tag{8.77}$$

where we have invoked the ideal gas law $n = p/k_{\rm B}T$ above.

Next, we invoke conservation of entropy. If $s$ is the entropy per particle, then $ns$ is the entropy per unit volume, in which case we have the continuity equation

$$\frac{\partial(ns)}{\partial t} + \boldsymbol{\nabla}\cdot(ns\boldsymbol{V}) = n\bigg(\frac{\partial s}{\partial t} + \boldsymbol{V}\cdot\boldsymbol{\nabla} s\bigg) + s\bigg(\frac{\partial n}{\partial t} + \boldsymbol{\nabla}\cdot(n\boldsymbol{V})\bigg) = 0\ . \tag{8.78}$$

The second bracketed term on the RHS vanishes because of particle continuity, leaving us with $\dot{s} + \boldsymbol{V}\cdot\boldsymbol{\nabla} s \approx \dot{s} = 0$ (since $\boldsymbol{V} = 0$ on average, and any gradient is first order in smallness). Now thermodynamics says

$$\begin{aligned} ds &= \bigg(\frac{\partial s}{\partial T}\bigg)_{\!p} dT + \bigg(\frac{\partial s}{\partial p}\bigg)_{\!T} dp \\ &= \frac{c_p}{T}\,dT - \frac{k_{\rm B}}{p}\,dp\ , \end{aligned} \tag{8.79}$$

since $T\big(\frac{\partial s}{\partial T}\big)_p = c_p$ and $\big(\frac{\partial s}{\partial p}\big)_T = \big(\frac{\partial v}{\partial T}\big)_p$, where $v = V/N$. Thus,

$$\frac{c_p}{k_{\rm B}}\,\frac{\partial \ln T}{\partial t} - \frac{\partial \ln p}{\partial t} = 0\ . \tag{8.80}$$

We now have in eqns. 8.77 and 8.80 two equations in the two unknowns $\frac{\partial \ln T}{\partial t}$ and $\frac{\partial \ln p}{\partial t}$, yielding

$$\frac{\partial \ln T}{\partial t} = -\frac{k_{\rm B}}{c_V}\,\boldsymbol{\nabla}\cdot\boldsymbol{V} \tag{8.81}$$

$$\frac{\partial \ln p}{\partial t} = -\frac{c_p}{c_V}\,\boldsymbol{\nabla}\cdot\boldsymbol{V}\ . \tag{8.82}$$

Thus eqn. 8.76 becomes

$$\begin{aligned} \frac{\partial f^0}{\partial t} + \frac{\boldsymbol{p}}{m}\cdot\frac{\partial f^0}{\partial \boldsymbol{r}} + \boldsymbol{F}\cdot\frac{\partial f^0}{\partial \boldsymbol{p}} = \bigg(-\frac{\partial f^0}{\partial \varepsilon}\bigg)\bigg\{&\frac{\varepsilon(\varGamma) - h}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla} T + m\,v_\alpha v_\beta\,\mathcal{Q}_{\alpha\beta} \\ &+ \frac{h - Tc_p - \varepsilon(\varGamma)}{c_V/k_{\rm B}}\,\boldsymbol{\nabla}\cdot\boldsymbol{V} - \boldsymbol{F}\cdot\boldsymbol{v}\bigg\}\ , \end{aligned} \tag{8.83}$$

where

$$\mathcal{Q}_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha}\right)\ . \tag{8.84}$$

Therefore, the Boltzmann equation takes the form

$$\left\{\frac{\varepsilon(\varGamma) - h}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla} T + m\,v_\alpha v_\beta\,\mathcal{Q}_{\alpha\beta} - \frac{\varepsilon(\varGamma) - h + Tc_p}{c_V/k_{\rm B}}\,\boldsymbol{\nabla}\cdot\boldsymbol{V} - \boldsymbol{F}\cdot\boldsymbol{v}\right\}\frac{f^0}{k_{\rm B}T} + \frac{\partial\,\delta f}{\partial t} = \bigg(\frac{\partial f}{\partial t}\bigg)_{\rm coll}\ . \tag{8.85}$$

Notice we have dropped the terms $\boldsymbol{v}\cdot\frac{\partial\,\delta f}{\partial\boldsymbol{r}}$ and $\boldsymbol{F}\cdot\frac{\partial\,\delta f}{\partial\boldsymbol{p}}$, since $\delta f$ must already be first order in smallness, and both the $\frac{\partial}{\partial\boldsymbol{r}}$ operator as well as $\boldsymbol{F}$ add a second order of smallness, which is negligible. Typically $\frac{\partial\,\delta f}{\partial t}$ is nonzero if the applied force $\boldsymbol{F}(t)$ is time-dependent. We use the convention of summing over repeated indices. Note that $\delta_{\alpha\beta}\,\mathcal{Q}_{\alpha\beta}=\mathcal{Q}_{\alpha\alpha}=\boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}$. For ideal gases in which only translational and rotational degrees of freedom are excited, $h=c_{\mathrm{p}}T$.

## 8.5 Relaxation Time Approximation

### 8.5.1 Approximation of collision integral

We now consider a very simple model of the collision integral,

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{coll}}=-\,\frac{f-f^0}{\tau}=-\frac{\delta f}{\tau}\ . \tag{8.86}$$

This model is known as the *relaxation time approximation*. Here, $f^0=f^0(\boldsymbol{r},\boldsymbol{p},t)$ is a distribution function which describes a *local equilibrium* at each position $\boldsymbol{r}$ and time $t$. The quantity $\tau$ is the *relaxation time*, which can in principle be momentum-dependent, but which we shall first consider to be constant. In the absence of streaming terms, we have

$$\frac{\partial\,\delta f}{\partial t}=-\frac{\delta f}{\tau}\qquad\Longrightarrow\qquad\delta f(\boldsymbol{r},\boldsymbol{p},t)=\delta f(\boldsymbol{r},\boldsymbol{p},0)\,e^{-t/\tau}\ . \tag{8.87}$$

The distribution $f$ then relaxes to the equilibrium distribution $f^0$ on a time scale $\tau$. We note that this approximation is obviously flawed in that all quantities – even the collisional invariants – relax to their equilibrium values on the scale $\tau$. In the Appendix, we consider a model for the collision integral in which the collisional invariants are all preserved, but everything else relaxes to local equilibrium at a single rate.

### 8.5.2 Computation of the scattering time

Consider two particles with velocities $\boldsymbol{v}$ and $\boldsymbol{v}'$. The average of their relative *speed* is

$$\langle\,|\boldsymbol{v}-\boldsymbol{v}'|\,\rangle=\int\!d^3\!v\!\int\!d^3\!v'\;P(\boldsymbol{v})\,P(\boldsymbol{v}')\,|\boldsymbol{v}-\boldsymbol{v}'|\ , \tag{8.88}$$

where $P(\boldsymbol{v})$ is the Maxwell velocity distribution,

$$P(\boldsymbol{v})=\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2}\exp\left(-\frac{m\boldsymbol{v}^2}{2k_{\mathrm{B}}T}\right)\ , \tag{8.89}$$

which follows from the Boltzmann form of the equilibrium distribution $f^0(\boldsymbol{p})$. It is left as an exercise for the student to verify that

$$\bar{v}_{\mathrm{rel}}\equiv\langle\,|\boldsymbol{v}-\boldsymbol{v}'|\,\rangle=\frac{4}{\sqrt{\pi}}\left(\frac{k_{\mathrm{B}}T}{m}\right)^{1/2}\ . \tag{8.90}$$

Note that $\bar{v}_{\mathrm{rel}}=\sqrt{2}\,\bar{v}$, where $\bar{v}$ is the average particle speed. Let $\sigma$ be the total scattering cross section, which for hard spheres is $\sigma=\pi d^2$, where $d$ is the hard sphere diameter. Then the rate at which particles scatter is

$$\frac{1}{\tau}=n\,\bar{v}_{\mathrm{rel}}\,\sigma\ . \tag{8.91}$$

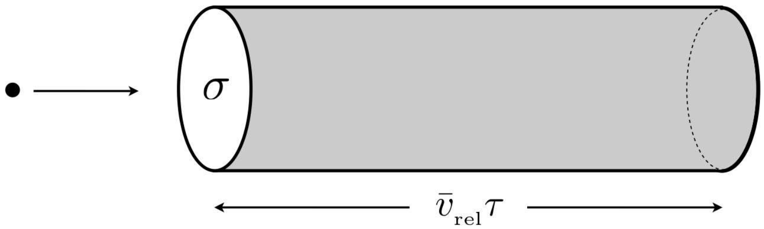

Figure 8.3: Graphic representation of the equation $n\,\sigma\,\bar{v}_{\mathrm{rel}}\,\tau=1$, which yields the scattering time $\tau$ in terms of the number density $n$, average particle pair relative velocity $\bar{v}_{\mathrm{rel}}$, and two-particle total scattering cross section $\sigma$. The equation says that on average there must be one particle within the tube.

The particle *mean free path* is simply

$$\ell=\bar{v}\,\tau=\frac{1}{\sqrt{2}\,n\,\sigma}\ . \tag{8.92}$$

While the scattering length is not temperature-dependent within this formalism, the scattering time *is* $T$-dependent, with

$$\tau(T)=\frac{1}{n\,\bar{v}_{\mathrm{rel}}\,\sigma}=\frac{\sqrt{\pi}}{4n\sigma}\bigg(\frac{m}{k_{\mathrm{B}}T}\bigg)^{1/2}\ . \tag{8.93}$$

As $T\to 0$, the collision time diverges as $\tau\propto T^{-1/2}$, because the particles on average move more slowly at lower temperatures. The mean free path, however, is independent of $T$, and is given by $\ell=1/\sqrt{2}n\sigma$.

### 8.5.3 Thermal conductivity

We consider a system with a temperature gradient $\boldsymbol{\nabla}T$ and seek a steady state (*i.e.* time-independent) solution to the Boltzmann equation. We assume $F_\alpha=\mathcal{Q}_{\alpha\beta}=0$. Appealing to eqn. 8.85, and using the relaxation time approximation for the collision integral, we have

$$\delta f=-\frac{\tau(\varepsilon-c_p\,T)}{k_{\mathrm{B}}T^2}\,(\boldsymbol{v}\cdot\boldsymbol{\nabla}T)\,f^0\ . \tag{8.94}$$

We are now ready to compute the energy and particle currents. In order to compute the *local density* of any quantity $A(\boldsymbol{r},\boldsymbol{p})$, we multiply by the distribution $f(\boldsymbol{r},\boldsymbol{p})$ and integrate over momentum:

$$\rho_{A}(\boldsymbol{r},t)=\int\!d^3\!p\;A(\boldsymbol{r},\boldsymbol{p})\,f(\boldsymbol{r},\boldsymbol{p},t)\ , \tag{8.95}$$

For the energy (thermal) current, we let $A=\varepsilon\,v_\alpha=\varepsilon\,p_\alpha/m$, in which case $\rho_A=j_\alpha$. Note that $\int\!d^3\!p\,\boldsymbol{p}\,f^0=0$ since $f^0$ is isotropic in $\boldsymbol{p}$ even when $\mu$ and $T$ depend on $\boldsymbol{r}$. Thus, only $\delta f$ enters into the calculation of the various currents. Thus, the energy (thermal) current is

$$\begin{aligned}j^\alpha_\varepsilon(\boldsymbol{r})&=\int\!d^3\!p\;\varepsilon\,v^\alpha\,\delta f\\&=-\frac{n\tau}{k_{\mathrm{B}}T^2}\,\big\langle\,v^\alpha v^\beta\,\varepsilon\,(\varepsilon-c_p\,T)\,\big\rangle\,\frac{\partial T}{\partial x^\beta}\ ,\end{aligned} \tag{8.96}$$

where the repeated index $\beta$ is summed over, and where momentum averages are defined relative to the equilibrium distribution, *i.e.*

$$\langle\,\phi(\boldsymbol{p})\,\rangle=\int\!d^3\!p\;\phi(\boldsymbol{p})\,f^0(\boldsymbol{p})\bigg/\!\!\int\!d^3\!p\;f^0(\boldsymbol{p})=\!\int\!d^3\!v\;P(\boldsymbol{v})\,\phi(m\boldsymbol{v})\ . \tag{8.97}$$

In this context, it is useful to point out the identity

$$d^3\!p\, f^0(\boldsymbol{p}) = n\, d^3\!v\, P(\boldsymbol{v}) \ , \tag{8.98}$$

where

$$P(\boldsymbol{v}) = \bigg(\frac{m}{2\pi k_{\rm B}T}\bigg)^{3/2} e^{-m(\boldsymbol{v}-\boldsymbol{V})^2/2k_{\rm B}T} \tag{8.99}$$

is the Maxwell velocity distribution.

Note that if $\phi = \phi(\varepsilon)$ is a function of the energy, and if $\boldsymbol{V} = 0$, then

$$d^3\!p\, f^0(\boldsymbol{p}) = n\, d^3\!v\, P(\boldsymbol{v}) = n\, \widetilde{P}(\varepsilon)\, d\varepsilon \ , \tag{8.100}$$

where

$$\widetilde{P}(\varepsilon) = \tfrac{2}{\sqrt{\pi}}(k_{\rm B}T)^{-3/2}\, \varepsilon^{1/2}\, e^{-\varepsilon/k_{\rm B}T} \ , \tag{8.101}$$

is the Maxwellian distribution of single particle energies. This distribution is normalized with $\int\limits_0^\infty \! d\varepsilon\, \widetilde{P}(\varepsilon) = 1$. Averages with respect to this distribution are given by

$$\langle\, \phi(\varepsilon)\, \rangle = \int\limits_0^\infty \! d\varepsilon\ \phi(\varepsilon)\, \widetilde{P}(\varepsilon) = \tfrac{2}{\sqrt{\pi}}(k_{\rm B}T)^{-3/2} \int\limits_0^\infty \! d\varepsilon\ \varepsilon^{1/2}\, \phi(\varepsilon)\, e^{-\varepsilon/k_{\rm B}T} \ . \tag{8.102}$$

If $\phi(\varepsilon)$ is homogeneous, then for any $\alpha$ we have

$$\langle\, \varepsilon^\alpha\, \rangle = \tfrac{2}{\sqrt{\pi}}\,\Gamma\big(\alpha + \tfrac{3}{2}\big)(k_{\rm B}T)^\alpha \ . \tag{8.103}$$

Due to spatial isotropy, it is clear that we can replace

$$v^\alpha\, v^\beta \to \tfrac{1}{3}\boldsymbol{v}^2\, \delta_{\alpha\beta} = \frac{2\varepsilon}{3m}\, \delta_{\alpha\beta} \tag{8.104}$$

in eqn. 8.96. We then have $\boldsymbol{j}_\varepsilon = -\kappa\, \boldsymbol{\nabla} T$, with

$$\kappa = \frac{2n\tau}{3mk_{\rm B}T^2}\, \langle\, \varepsilon^2\big(\varepsilon - c_p\, T\big)\, \rangle = \frac{5n\tau k_{\rm B}^2 T}{2m} = \tfrac{\pi}{8} n\ell\bar{v}\, c_p \ , \tag{8.105}$$

where we have used $c_p = \frac{5}{2}k_{\rm B}$ and $\bar{v}^2 = \frac{8k_{\rm B}T}{\pi m}$. The quantity $\kappa$ is called the *thermal conductivity*. Note that $\kappa \propto T^{1/2}$.

### 8.5.4 Viscosity

Consider the situation depicted in fig. 8.4. A fluid filling the space between two large flat plates at $z = 0$ and $z = d$ is set in motion by a force $\boldsymbol{F} = F\hat{\boldsymbol{x}}$ applied to the upper plate; the lower plate is fixed. It is assumed that the fluid's velocity locally matches that of the plates. Fluid particles at the top have an average $x$-component of their momentum $\langle p_x \rangle = mV$. As these particles move downward toward lower $z$ values, they bring their $x$-momenta with them. Therefore there is a downward ($-\hat{\boldsymbol{z}}$-directed) flow of $\langle p_x \rangle$. Since $x$-momentum is constantly being drawn away from $z = d$ plane, this means that there is a $-\boldsymbol{x}$-directed *viscous drag* on the upper plate. The viscous drag force per unit area is given by $F_{\rm drag}/A = -\eta V/d$, where $V/d = \partial V_x/\partial z$ is the velocity gradient and $\eta$ is the *shear viscosity*. In steady state, the applied force balances the drag force, *i.e.* $F + F_{\rm drag} = 0$. Clearly in the steady state the net momentum density of the fluid does not change, and is given by $\frac{1}{2}\rho V\hat{\boldsymbol{x}}$, where $\rho$ is the fluid mass density. The momentum per unit time injected into the fluid by the upper plate at $z = d$ is then extracted by the

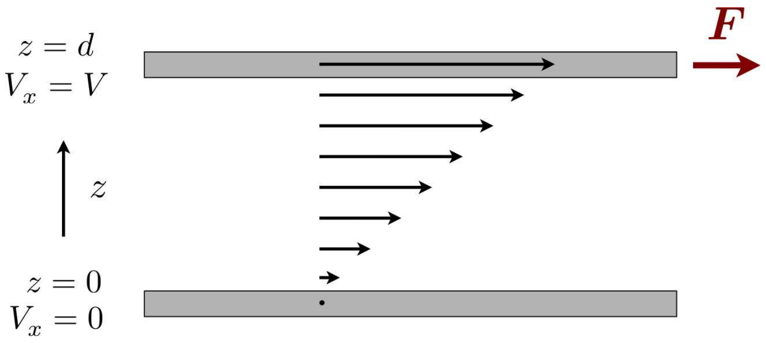

Figure 8.4: *Gedankenexperiment* to measure shear viscosity $\eta$ in a fluid. The lower plate is fixed. The viscous drag force per unit area on the upper plate is $F_{\text{drag}}/A = -\eta V/d$. This must be balanced by an applied force $F$.

lower plate at $z = 0$. The *momentum flux density* $\Pi_{xz} = n\,\langle\, p_x\, v_z\,\rangle$ is the drag force on the upper surface per unit area: $\Pi_{xz} = -\eta\,\frac{\partial V_x}{\partial z}$. The units of viscosity are $[\eta] = M/LT$.

We now provide some formal definitions of viscosity. As we shall see presently, there is in fact a second type of viscosity, called second viscosity or *bulk viscosity*, which is measurable although not by the type of experiment depicted in fig. 8.4.

The momentum flux tensor $\Pi_{\alpha\beta} = n\,\langle\, p_\alpha\, v_\beta\,\rangle$ is defined to be the current of momentum component $p_\alpha$ in the direction of increasing $x_\beta$. For a gas in motion with average velocity $\boldsymbol{V}$, we have

$$\begin{aligned}\Pi_{\alpha\beta} &= nm\,\langle\,(V_\alpha + v'_\alpha)(V_\beta + v'_\beta)\,\rangle \\ &= nm\,V_\alpha V_\beta + nm\,\langle\, v'_\alpha v'_\beta\,\rangle \\ &= nm\,V_\alpha V_\beta + \tfrac{1}{3}nm\,\langle\, \boldsymbol{v}'^2\,\rangle\,\delta_{\alpha\beta} \\ &= \rho\,V_\alpha V_\beta + p\,\delta_{\alpha\beta}\ ,\end{aligned} \tag{8.106}$$

where $\boldsymbol{v}'$ is the particle velocity in a frame moving with velocity $\boldsymbol{V}$, and where we have invoked the ideal gas law $p = nk_{\text{B}}T$. The mass density is $\rho = nm$.

When $\boldsymbol{V}$ is spatially varying,

$$\Pi_{\alpha\beta} = p\,\delta_{\alpha\beta} + \rho\,V_\alpha V_\beta - \tilde{\sigma}_{\alpha\beta}\ , \tag{8.107}$$

where $\tilde{\sigma}_{\alpha\beta}$ is the *viscosity stress tensor*. Any symmetric tensor, such as $\tilde{\sigma}_{\alpha\beta}$, can be decomposed into a sum of (i) a traceless component, and (ii) a component proportional to the identity matrix. Since $\tilde{\sigma}_{\alpha\beta}$ should be, to first order, linear in the spatial derivatives of the components of the velocity field $\boldsymbol{V}$, there is a unique two-parameter decomposition:

$$\begin{aligned}\tilde{\sigma}_{\alpha\beta} &= \eta\left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha} - \tfrac{2}{3}\,\boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\,\delta_{\alpha\beta}\right) + \zeta\,\boldsymbol{\nabla}\!\cdot\!\boldsymbol{V}\,\delta_{\alpha\beta} \\ &= 2\eta\,\Big(\mathcal{Q}_{\alpha\beta} - \tfrac{1}{3}\,\mathsf{Tr}\,(\mathcal{Q})\,\delta_{\alpha\beta}\Big) + \zeta\ \mathsf{Tr}\,(\mathcal{Q})\,\delta_{\alpha\beta}\ .\end{aligned} \tag{8.108}$$

The coefficient of the traceless component is $\eta$, known as the *shear viscosity*. The coefficient of the component proportional to the identity is $\zeta$, known as the *bulk viscosity*. The full stress tensor $\sigma_{\alpha\beta}$ contains a contribution from the pressure:

$$\sigma_{\alpha\beta} = -p\,\delta_{\alpha\beta} + \tilde{\sigma}_{\alpha\beta}\ . \tag{8.109}$$

The differential force $dF_\alpha$ that a fluid exerts on on a surface element $\hat{\boldsymbol{n}}\,dA$ is

$$dF_\alpha = -\sigma_{\alpha\beta}\,n_\beta\,dA\ , \tag{8.110}$$

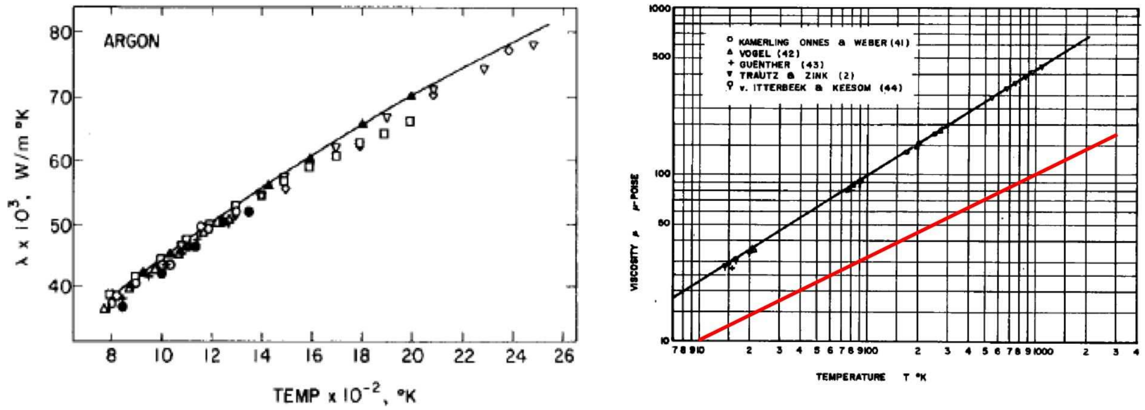

Figure 8.5: Left: thermal conductivity ($\lambda$ in figure) of Ar between $T = 800\,\text{K}$ and $T = 2600\,\text{K}$. The best fit to a single power law $\lambda = aT^b$ results in $b = 0.651$. Source: G. S. Springer and E. W. Wingeier, *J. Chem Phys.* **59**, 1747 (1972). Right: log-log plot of shear viscosity ($\mu$ in figure) of He between $T \approx 15\,\text{K}$ and $T \approx 1000\,\text{K}$. The red line has slope $\frac{1}{2}$. The slope of the data is approximately $0.633$. Source: J. Kestin and W. Leidenfrost, *Physica* **25**, 537 (1959).

where we are using the Einstein summation convention and summing over the repeated index $\beta$. We will now compute the shear viscosity $\eta$ using the Boltzmann equation in the relaxation time approximation.

Appealing again to eqn. 8.85, with $\boldsymbol{F} = 0$ and $h = c_p T$, we find

$$\delta f = -\frac{\tau}{k_\text{B}T}\left\{ m\, v_\alpha v_\beta\, \mathcal{Q}_{\alpha\beta} + \frac{\varepsilon - c_p\, T}{T}\, \boldsymbol{v}\cdot\boldsymbol{\nabla} T - \frac{\varepsilon}{c_V/k_\text{B}}\, \boldsymbol{\nabla}\cdot\boldsymbol{V}\right\} f^0 \ . \tag{8.111}$$

We assume $\boldsymbol{\nabla} T = \boldsymbol{\nabla}\cdot\boldsymbol{V} = 0$, and we compute the momentum flux:

$$\begin{aligned} \Pi_{xz} &= n\!\int\! d^3\!p\; p_x v_z\, \delta f \\ &= -\frac{nm^2\tau}{k_\text{B}T}\, \mathcal{Q}_{\alpha\beta}\, \langle\, v_x\, v_z\, v_\alpha\, v_\beta\,\rangle \\ &= -\frac{n\tau}{k_\text{B}T}\left(\frac{\partial V_x}{\partial z} + \frac{\partial V_z}{\partial x}\right) \langle\, mv_x^2 \cdot mv_z^2\,\rangle \\ &= -n\tau k_\text{B}T\left(\frac{\partial V_z}{\partial x} + \frac{\partial V_x}{\partial z}\right) . \end{aligned} \tag{8.112}$$

Thus, if $V_x = V_x(z)$, we have

$$\Pi_{xz} = -n\tau k_\text{B}T\, \frac{\partial V_x}{\partial z} \tag{8.113}$$

from which we read off the viscosity,

$$\eta = nk_\text{B}T\tau = \tfrac{\pi}{8} nm\ell\bar{v} \ . \tag{8.114}$$

Note that $\eta(T) \propto T^{1/2}$.

How well do these predictions hold up? In fig. 8.5, we plot data for the thermal conductivity of argon and the shear viscosity of helium. Both show a clear sublinear behavior as a function of temperature, but the slope $d\ln\kappa/dT$ is approximately $0.65$ and $d\ln\eta/dT$ is approximately $0.63$. Clearly the simple model is not even getting the functional dependence on $T$ right, let alone its coefficient. Still, our crude theory is at least qualitatively correct.

Why do both $\kappa(T)$ as well as $\eta(T)$ decrease at low temperatures? The reason is that the heat current which flows in response to $\boldsymbol{\nabla} T$ as well as the momentum current which flows in response to $\partial V_x/\partial z$ are due to the presence of collisions, which result in momentum and energy transfer between particles. This is true even when total energy and momentum are conserved, which they are not in the relaxation time approximation. Intuitively, we might think that the viscosity should *increase* as the temperature is lowered, since common experience tells us that fluids 'gum up' as they get colder – think of honey as an extreme example. But of course honey is nothing like an ideal gas, and the physics behind the crystallization or glass transition which occurs in real fluids when they get sufficiently cold is completely absent from our approach. In our calculation, viscosity results from collisions, and with no collisions there is no momentum transfer and hence no viscosity. If, for example, the gas particles were to simply pass through each other, as though they were ghosts, then there would be no opposition to maintaining an arbitrary velocity gradient.

### 8.5.5 Oscillating external force

Suppose a uniform oscillating external force $\boldsymbol{F}_{\rm ext}(t) = \boldsymbol{F}\, e^{-i\omega t}$ is applied. For a system of charged particles, this force would arise from an external electric field $\boldsymbol{F}_{\rm ext} = q\boldsymbol{E}\, e^{-i\omega t}$, where $q$ is the charge of each particle. We'll assume $\boldsymbol{\nabla} T = 0$. The Boltzmann equation is then written

$$\frac{\partial f}{\partial t} + \frac{\boldsymbol{p}}{m} \cdot \frac{\partial f}{\partial \boldsymbol{r}} + \boldsymbol{F} e^{-i\omega t} \cdot \frac{\partial f}{\partial \boldsymbol{p}} = -\frac{f - f^0}{\tau} \ . \tag{8.115}$$

We again write $f = f^0 + \delta f$, and we assume $\delta f$ is spatially constant. Thus,

$$\frac{\partial\, \delta f}{\partial t} + \boldsymbol{F} e^{-i\omega t} \cdot \boldsymbol{v}\, \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f}{\tau} \ . \tag{8.116}$$

If we assume $\delta f(t) = \delta f(\omega)\, e^{-i\omega t}$ then the above differential equation is converted to an algebraic equation, with solution

$$\delta f(t) = -\frac{\tau\, e^{-i\omega t}}{1 - i\omega\tau}\, \frac{\partial f^0}{\partial \varepsilon}\, \boldsymbol{F} \cdot \boldsymbol{v} \ . \tag{8.117}$$

We now compute the particle current:

$$\begin{aligned} j_\alpha(\boldsymbol{r}, t) &= \int\! d^3\!p\; \boldsymbol{v}\; \delta f \\ &= \frac{\tau\, e^{-i\omega t}}{1 - i\omega\tau} \cdot \frac{F_\beta}{k_{\rm B} T} \int\! d^3\!p\; f^0(\boldsymbol{p})\, v_\alpha\, v_\beta \\ &= \frac{\tau\, e^{-i\omega t}}{1 - i\omega\tau} \cdot \frac{n F_\alpha}{3 k_{\rm B} T} \int\! d^3\!v\; P(\boldsymbol{v})\, \boldsymbol{v}^2 \\ &= \frac{n\tau}{m} \cdot \frac{F_\alpha\, e^{-i\omega t}}{1 - i\omega\tau} \ . \end{aligned} \tag{8.118}$$

If the particles are electrons, with charge $q = -e$, then the electrical current is $(-e)$ times the particle current. We then obtain

$$j_\alpha^{\rm (elec)}(t) = \frac{ne^2\tau}{m} \cdot \frac{E_\alpha\, e^{-i\omega t}}{1 - i\omega\tau} \equiv \sigma_{\alpha\beta}(\omega)\, E_\beta\, e^{-i\omega t} \ , \tag{8.119}$$

where

$$\sigma_{\alpha\beta}(\omega) = \frac{ne^2\tau}{m} \cdot \frac{1}{1 - i\omega\tau}\, \delta_{\alpha\beta} \tag{8.120}$$

is the frequency-dependent electrical conductivity tensor. Of course for fermions such as electrons, we should be using the Fermi distribution in place of the Maxwell-Boltzmann distribution for $f^0(\boldsymbol{p})$. This affects the relation between $n$ and $\mu$ only, and the final result for the conductivity tensor $\sigma_{\alpha\beta}(\omega)$ is unchanged.

### 8.5.6 Quick and Dirty Treatment of Transport

Suppose we have some averaged intensive quantity $\phi$ which is spatially dependent through $T(\boldsymbol{r})$ or $\mu(\boldsymbol{r})$ or $\boldsymbol{V}(\boldsymbol{r})$. For simplicity we will write $\phi=\phi(z)$. We wish to compute the current of $\phi$ across some surface whose equation is $dz=0$. If the mean free path is $\ell$, then the value of $\phi$ for particles crossing this surface in the $+\hat{\boldsymbol{z}}$ direction is $\phi(z-\ell\cos\theta)$, where $\theta$ is the angle the particle's velocity makes with respect to $\hat{\boldsymbol{z}}$, *i.e.* $\cos\theta=v_z/v$. We perform the same analysis for particles moving in the $-\hat{\boldsymbol{z}}$ direction, for which $\phi=\phi(z+\ell\cos\theta)$. The current of $\phi$ through this surface is then

$$\begin{aligned}\boldsymbol{j}_\phi&=n\hat{\boldsymbol{z}}\int\limits_{v_z>0}\!d^3v\,P(\boldsymbol{v})\,v_z\,\phi(z-\ell\cos\theta)+n\hat{\boldsymbol{z}}\int\limits_{v_z<0}\!d^3v\,P(\boldsymbol{v})\,v_z\,\phi(z+\ell\cos\theta)\\&=-n\ell\,\frac{\partial\phi}{\partial z}\,\hat{\boldsymbol{z}}\int\!d^3v\,P(\boldsymbol{v})\,\frac{v_z^2}{v}=-\tfrac{1}{3}n\bar{v}\ell\,\frac{\partial\phi}{\partial z}\,\hat{\boldsymbol{z}}\ ,\end{aligned}\tag{8.121}$$

where $\bar{v}=\sqrt{\frac{8k_BT}{\pi m}}$ is the average particle speed. If the $z$-dependence of $\phi$ comes through the dependence of $\phi$ on the local temperature $T$, then we have

$$\boldsymbol{j}_\phi=-\tfrac{1}{3}\,n\ell\bar{v}\,\frac{\partial\phi}{\partial T}\,\boldsymbol{\nabla}T\equiv-K\,\boldsymbol{\nabla}T\ ,\tag{8.122}$$

where

$$K=\tfrac{1}{3}n\ell\bar{v}\,\frac{\partial\phi}{\partial T}\tag{8.123}$$

is the transport coefficient. If $\phi=\langle\varepsilon\rangle$, then $\frac{\partial\phi}{\partial T}=c_p$, where $c_p$ is the heat capacity per particle at constant pressure. We then find $\boldsymbol{j}_\varepsilon=-\kappa\,\boldsymbol{\nabla}T$ with thermal conductivity

$$\kappa=\tfrac{1}{3}n\ell\bar{v}\,c_p\ .\tag{8.124}$$

Our Boltzmann equation calculation yielded the same result, but with a prefactor of $\frac{\pi}{8}$ instead of $\frac{1}{3}$.

We can make a similar argument for the viscosity. In this case $\phi=\langle p_x\rangle$ is spatially varying through its dependence on the flow velocity $\boldsymbol{V}(\boldsymbol{r})$. Clearly $\partial\phi/\partial V_x=m$, hence

$$j^z_{p_x}=\Pi_{xz}=-\tfrac{1}{3}nm\ell\bar{v}\,\frac{\partial V_x}{\partial z}\ ,\tag{8.125}$$

from which we identify the viscosity, $\eta=\frac{1}{3}nm\ell\bar{v}$. Once again, this agrees in its functional dependences with the Boltzmann equation calculation in the relaxation time approximation. Only the coefficients differ. The ratio of the coefficients is $K_{\text{QDC}}/K_{\text{BRT}}=\frac{8}{3\pi}=0.849$ in both cases[6].

### 8.5.7 Thermal diffusivity, kinematic viscosity, and Prandtl number

Suppose, under conditions of constant pressure, we add heat $q$ per unit volume to an ideal gas. We know from thermodynamics that its temperature will then increase by an amount $\Delta T=q/nc_p$. If a heat current $\boldsymbol{j}_q$ flows, then the continuity equation for energy flow requires

$$nc_p\,\frac{\partial T}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{j}_q=0\ .\tag{8.126}$$

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[6] Here we abbreviate QDC for *'quick and dirty calculation'* and BRT for *'Boltzmann equation in the relaxation time approximation'*.

| Gas | $\eta$ ($\mu$Pa · s) | $\kappa$ (mW/m · K) | $c_p/k_{\rm B}$ | Pr |
|---|---|---|---|---|
| He | 19.5 | 149 | 2.50 | 0.682 |
| Ar | 22.3 | 17.4 | 2.50 | 0.666 |
| Xe | 22.7 | 5.46 | 2.50 | 0.659 |
| $H_2$ | 8.67 | 179 | 3.47 | 0.693 |
| $N_2$ | 17.6 | 25.5 | 3.53 | 0.721 |
| $O_2$ | 20.3 | 26.0 | 3.50 | 0.711 |
| $CH_4$ | 11.2 | 33.5 | 4.29 | 0.74 |
| $CO_2$ | 14.8 | 18.1 | 4.47 | 0.71 |
| $NH_3$ | 10.1 | 24.6 | 4.50 | 0.90 |

Table 8.1: Viscosities, thermal conductivities, and Prandtl numbers for some common gases at $T = 293\,$K and $p = 1\,$atm. (Source: Table 1.1 of Smith and Jensen, with data for triatomic gases added.)

In a system where there is no net particle current, the heat current $\boldsymbol{j}_q$ is the same as the energy current $\boldsymbol{j}_\varepsilon$, and since $\boldsymbol{j}_\varepsilon = -\kappa\, \boldsymbol{\nabla} T$, we obtain a diffusion equation for temperature,

$$\frac{\partial T}{\partial t} = \frac{\kappa}{n c_p}\, \nabla^2 T \ . \tag{8.127}$$

The combination

$$a \equiv \frac{\kappa}{n c_p} \tag{8.128}$$

is known as the *thermal diffusivity*. Our Boltzmann equation calculation in the relaxation time approximation yielded the result $\kappa = n k_{\rm B} T \tau c_p / m$. Thus, we find $a = k_{\rm B} T \tau / m$ via this method. Note that the dimensions of $a$ are the same as for any diffusion constant $D$, namely $[a] = L^2/T$.

Another quantity with dimensions of $L^2/T$ is the *kinematic viscosity*, $\nu = \eta/\rho$, where $\rho = nm$ is the mass density. We found $\eta = n k_{\rm B} T \tau$ from the relaxation time approximation calculation, hence $\nu = k_{\rm B} T \tau / m$. The ratio $\nu/a$, called the *Prandtl number*, $\mathrm{Pr} = \eta c_p / m\kappa$, is dimensionless. According to our calculations, $\mathrm{Pr} = 1$. According to table 8.1, most monatomic gases have $\mathrm{Pr} \approx \frac{2}{3}$.

## 8.6 Diffusion and the Lorentz model

### 8.6.1 Failure of the relaxation time approximation

As we remarked above, the relaxation time approximation fails to conserve any of the collisional invariants. It is therefore unsuitable for describing hydrodynamic phenomena such as diffusion. To see this, let $f(\boldsymbol{r}, \boldsymbol{v}, t)$ be the distribution function, here written in terms of position, velocity, and time rather than position, momentum, and time as befor[7]. In the absence of external forces, the Boltzmann equation in the relaxation time approximation is

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} = -\frac{f - f^0}{\tau} \ . \tag{8.129}$$

The density of particles in velocity space is given by

$$\tilde{n}(\boldsymbol{v}, t) = \int\! d^3\!r\ f(\boldsymbol{r}, \boldsymbol{v}, t) \ . \tag{8.130}$$

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[7] The difference is trivial, since $\boldsymbol{p} = m\boldsymbol{v}$.

In equilibrium, this is the Maxwell distribution times the total number of particles: $\tilde{n}_0(\boldsymbol{v}) = N P_{\rm M}(\boldsymbol{v})$. The number of particles as a function of time, $N(t) = \int d^3\!v\, \tilde{n}(\boldsymbol{v},t)$, should be a constant.

Integrating the Boltzmann equation one has

$$\frac{\partial \tilde{n}}{\partial t} = -\frac{\tilde{n} - \tilde{n}_0}{\tau} \ . \tag{8.131}$$

Thus, with $\delta\tilde{n}(\boldsymbol{v},t) = \tilde{n}(\boldsymbol{v},t) - \tilde{n}_0(\boldsymbol{v})$, we have

$$\delta\tilde{n}(\boldsymbol{v},t) = \delta\tilde{n}(\boldsymbol{v},0)\, e^{-t/\tau} \ . \tag{8.132}$$

Thus, $\tilde{n}(\boldsymbol{v},t)$ decays exponentially to zero with time constant $\tau$, from which it follows that the total particle number exponentially relaxes to $N_0$. This is physically incorrect; local density perturbations can't just *vanish*. Rather, they *diffuse*.

### 8.6.2 Modified Boltzmann equation and its solution

To remedy this unphysical aspect, consider the modified Boltzmann equation,

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} = \frac{1}{\tau}\bigg[ - f + \int \frac{d\hat{\boldsymbol{v}}}{4\pi}\, f \bigg] \equiv \frac{1}{\tau}\big(\mathbb{P} - 1\big) f \ , \tag{8.133}$$

where $\mathbb{P}$ is a projector onto a space of isotropic functions of $\boldsymbol{v}$: $\mathbb{P}\, F = \int \frac{d\hat{\boldsymbol{v}}}{4\pi}\, F(\boldsymbol{v})$ for any function $F(\boldsymbol{v})$. Note that $\mathbb{P}\, F$ is a function of the speed $v = |\boldsymbol{v}|$. For this modified equation, known as the *Lorentz model*, one finds $\partial_t \tilde{n} = 0$.

The model in eqn. 8.133 is known as the *Lorentz model*[8]. To solve it, we consider the Laplace transform,

$$\hat{f}(\boldsymbol{k},\boldsymbol{v},s) = \int\limits_0^\infty \! dt\, e^{-st} \!\int\! d^3\!r\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, f(\boldsymbol{r},\boldsymbol{v},t) \ . \tag{8.134}$$

Taking the Laplace transform of eqn. 8.133, we find

$$\big(s + i\boldsymbol{v}\cdot\boldsymbol{k} + \tau^{-1}\big)\, \hat{f}(\boldsymbol{k},\boldsymbol{v},s) = \tau^{-1}\, \mathbb{P}\, \hat{f}(\boldsymbol{k},\boldsymbol{v},s) + f(\boldsymbol{k},\boldsymbol{v},t=0) \ . \tag{8.135}$$

We now solve for $\mathbb{P}\,\hat{f}(\boldsymbol{k},\boldsymbol{v},s)$:

$$\hat{f}(\boldsymbol{k},\boldsymbol{v},s) = \frac{\tau^{-1}}{s + i\boldsymbol{v}\cdot\boldsymbol{k} + \tau^{-1}}\, \mathbb{P}\, \hat{f}(\boldsymbol{k},\boldsymbol{v},s) + \frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s + i\boldsymbol{v}\cdot\boldsymbol{k} + \tau^{-1}} \ , \tag{8.136}$$

which entails

$$\mathbb{P}\,\hat{f}(\boldsymbol{k},\boldsymbol{v},s) = \bigg[\int \!\frac{d\hat{\boldsymbol{v}}}{4\pi}\, \frac{\tau^{-1}}{s + i\boldsymbol{v}\cdot\boldsymbol{k} + \tau^{-1}}\bigg]\, \mathbb{P}\,\hat{f}(\boldsymbol{k},\boldsymbol{v},\boldsymbol{s}) + \int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\, \frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s + i\boldsymbol{v}\cdot\boldsymbol{k} + \tau^{-1}} \ . \tag{8.137}$$

Now we have

$$\begin{aligned} \int \!\frac{d\hat{\boldsymbol{v}}}{4\pi}\, \frac{\tau^{-1}}{s + i\boldsymbol{v}\cdot\boldsymbol{k} + \tau^{-1}} &= \int\limits_{-1}^{1}\! dx\, \frac{\tau^{-1}}{s + ivkx + \tau^{-1}} \\ &= \frac{1}{vk}\, \tan^{-1}\!\bigg(\frac{vk\tau}{1+\tau s}\bigg) \ . \end{aligned} \tag{8.138}$$

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[8] See the excellent discussion in the book by Krapivsky, Redner, and Ben-Naim, cited in §8.1.

Thus,

$$\mathbb{P}\, f(\boldsymbol{k},\boldsymbol{v},s) = \left[1 - \frac{1}{vk\tau}\tan^{-1}\!\left(\frac{vk\tau}{1+\tau s}\right)\right]^{-1} \int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\ . \tag{8.139}$$

We now have the solution to Lorentz's modified Boltzmann equation:

$$\begin{aligned}\hat{f}(\boldsymbol{k},\boldsymbol{v},s) = \frac{\tau^{-1}}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\left[1 - \frac{1}{vk\tau}\tan^{-1}\!\left(\frac{vk\tau}{1+\tau s}\right)\right]^{-1} \int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\\ + \frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\ .\end{aligned} \tag{8.140}$$

Let us assume an initial distribution which is perfectly localized in both $\boldsymbol{r}$ and $\boldsymbol{v}$:

$$f(\boldsymbol{r},\boldsymbol{v},t=0) = \delta(\boldsymbol{v}-\boldsymbol{v}_0)\ . \tag{8.141}$$

For these initial conditions, we find

$$\int\!\frac{d\hat{\boldsymbol{v}}}{4\pi}\,\frac{f(\boldsymbol{k},\boldsymbol{v},t=0)}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}} = \frac{1}{s+i\boldsymbol{v}_0\cdot\boldsymbol{k}+\tau^{-1}}\cdot\frac{\delta(v-v_0)}{4\pi v_0^2}\ . \tag{8.142}$$

We further have that

$$1 - \frac{1}{vk\tau}\tan^{-1}\!\left(\frac{vk\tau}{1+\tau s}\right) = s\tau + \tfrac{1}{3}k^2v^2\tau^2 + \ldots\ , \tag{8.143}$$

and therefore

$$\begin{aligned}\hat{f}(\boldsymbol{k},\boldsymbol{v},s) = \frac{\tau^{-1}}{s+i\boldsymbol{v}\cdot\boldsymbol{k}+\tau^{-1}}\cdot\frac{\tau^{-1}}{s+i\boldsymbol{v}_0\cdot\boldsymbol{k}+\tau^{-1}}\cdot\frac{1}{s+\frac{1}{3}v_0^2\,k^2\,\tau+\ldots}\cdot\frac{\delta(v-v_0)}{4\pi v_0^2}\\ + \frac{\delta(\boldsymbol{v}-\boldsymbol{v}_0)}{s+i\boldsymbol{v}_0\cdot\boldsymbol{k}+\tau^{-1}}\ .\end{aligned} \tag{8.144}$$

We are interested in the long time limit $t \gg \tau$ for $f(\boldsymbol{r},\boldsymbol{v},t)$. This is dominated by $s \sim t^{-1}$, and we assume that $\tau^{-1}$ is dominant over $s$ and $i\boldsymbol{v}\cdot\boldsymbol{k}$. We then have

$$\hat{f}(\boldsymbol{k},\boldsymbol{v},s) \approx \frac{1}{s+\frac{1}{3}v_0^2\,k^2\,\tau}\cdot\frac{\delta(v-v_0)}{4\pi v_0^2}\ . \tag{8.145}$$

Performing the inverse Laplace and Fourier transforms, we obtain

$$f(\boldsymbol{r},\boldsymbol{v},t) = (4\pi Dt)^{-3/2}\,e^{-r^2/4Dt}\cdot\frac{\delta(v-v_0)}{4\pi v_0^2}\ , \tag{8.146}$$

where the *diffusion constant* is

$$D = \tfrac{1}{3}v_0^2\,\tau\ . \tag{8.147}$$

The units are $[D] = L^2/T$. Integrating over velocities, we have the density

$$n(\boldsymbol{r},t) = \int\! d^3\!v\, f(\boldsymbol{r},\boldsymbol{v},t) = (4\pi Dt)^{-3/2}\,e^{-r^2/4Dt}\ . \tag{8.148}$$

Note that

$$\int\! d^3\!r\; n(\boldsymbol{r},t) = 1 \tag{8.149}$$

for all time. Total particle number is conserved!

## 8.7 Linearized Boltzmann Equation

### 8.7.1 Linearizing the collision integral

We now return to the classical Boltzmann equation and consider a more formal treatment of the collision term in the linear approximation. We will assume time-reversal symmetry, in which case

$$\bigg(\frac{\partial f}{\partial t}\bigg)_{\rm coll} = \int\! d^3\!p_1 \!\int\! d^3\!p' \!\int\! d^3\!p_1'\; w(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1)\,\Big\{ f(\boldsymbol{p}')\,f(\boldsymbol{p}_1') - f(\boldsymbol{p})\,f(\boldsymbol{p}_1)\Big\} \ . \tag{8.150}$$

The collision integral is nonlinear in the distribution $f$. We *linearize* by writing

$$f(\boldsymbol{p}) = f^0(\boldsymbol{p}) + f^0(\boldsymbol{p})\,\psi(\boldsymbol{p}) \ , \tag{8.151}$$

where we assume $\psi(\boldsymbol{p})$ is small. We then have, to first order in $\psi$,

$$\bigg(\frac{\partial f}{\partial t}\bigg)_{\rm coll} = f^0(\boldsymbol{p})\,\hat{L}\psi + \mathcal{O}(\psi^2) \ , \tag{8.152}$$

where the action of the *linearized collision operator* is given by

$$\begin{aligned}\hat{L}\psi &= \int\! d^3\!p_1 \!\int\! d^3\!p' \!\int\! d^3\!p_1'\; w(\boldsymbol{p}',\boldsymbol{p}_1'\,|\,\boldsymbol{p},\boldsymbol{p}_1)\,f^0(\boldsymbol{p}_1)\,\Big\{ \psi(\boldsymbol{p}') + \psi(\boldsymbol{p}_1') - \psi(\boldsymbol{p}) - \psi(\boldsymbol{p}_1)\Big\}\\ &= \int\! d^3\!p_1 \!\int\! d\Omega\, |\boldsymbol{v}-\boldsymbol{v}_1|\, \frac{\partial\sigma}{\partial\Omega}\, f^0(\boldsymbol{p}_1)\,\Big\{ \psi(\boldsymbol{p}') + \psi(\boldsymbol{p}_1') - \psi(\boldsymbol{p}) - \psi(\boldsymbol{p}_1)\Big\} \ ,\end{aligned} \tag{8.153}$$

where we have invoked eqn. 8.55 to write the RHS in terms of the differential scattering cross section. In deriving the above result, we have made use of the detailed balance relation,

$$f^0(\boldsymbol{p})\,f^0(\boldsymbol{p}_1) = f^0(\boldsymbol{p}')\,f^0(\boldsymbol{p}_1') \ . \tag{8.154}$$

We have also suppressed the $\boldsymbol{r}$ dependence in writing $f(\boldsymbol{p})$, $f^0(\boldsymbol{p})$, and $\psi(\boldsymbol{p})$.

From eqn. 8.85, we then have the linearized equation

$$\bigg(\hat{L} - \frac{\partial}{\partial t}\bigg)\psi = Y, \tag{8.155}$$

where, for point particles,

$$Y = \frac{1}{k_{\rm B}T}\bigg\{ \frac{\varepsilon(\boldsymbol{p}) - c_pT}{T}\,\boldsymbol{v}\cdot\boldsymbol{\nabla} T + m\,v_\alpha v_\beta\,\mathcal{Q}_{\alpha\beta} - \frac{k_{\rm B}\,\varepsilon(\boldsymbol{p})}{c_V}\,\boldsymbol{\nabla}\cdot\boldsymbol{V} - \boldsymbol{F}\cdot\boldsymbol{v}\bigg\} \ . \tag{8.156}$$

Eqn. 8.155 is an inhomogeneous linear equation, which can be solved by inverting the operator $\hat{L} - \frac{\partial}{\partial t}$.

### 8.7.2 Linear algebraic properties of $\hat{L}$

Although $\hat{L}$ is an integral operator, it shares many properties with other linear operators with which you are familiar, such as matrices and differential operators. We can define an *inner product*[9],

$$\langle\,\psi_1\,|\,\psi_2\,\rangle \equiv \int\! d^3\!p\; f^0(\boldsymbol{p})\,\psi_1(\boldsymbol{p})\,\psi_2(\boldsymbol{p}) \ . \tag{8.157}$$

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[9] The requirements of an inner product $\langle f|g\rangle$ are symmetry, linearity, and non-negative definiteness.

Note that this is not the usual Hilbert space inner product from quantum mechanics, since the factor $f^0(\boldsymbol{p})$ is included in the metric. This is necessary in order that $\hat{L}$ be *self-adjoint*:

$$\langle\, \psi_1 \,|\, \hat{L}\psi_2 \,\rangle = \langle\, \hat{L}\psi_1 \,|\, \psi_2 \,\rangle \ . \tag{8.158}$$

We can now define the spectrum of *normalized eigenfunctions* of $\hat{L}$, which we write as $\phi_n(\boldsymbol{p})$. The eigenfunctions satisfy the eigenvalue equation,

$$\hat{L}\phi_n = -\lambda_n \, \phi_n \ , \tag{8.159}$$

and may be chosen to be orthonormal,

$$\langle\, \phi_m \,|\, \phi_n \,\rangle = \delta_{mn} \ . \tag{8.160}$$

Of course, in order to obtain the eigenfunctions $\phi_n$ we must have detailed knowledge of the function $w(\boldsymbol{p}', \boldsymbol{p}_1' \,|\, \boldsymbol{p}, \boldsymbol{p}_1)$.

Recall that there are five collisional invariants, which are the particle number, the three components of the total particle momentum, and the particle energy. To each collisional invariant, there is an associated eigenfunction $\phi_n$ with eigenvalue $\lambda_n = 0$. One can check that these normalized eigenfunctions are

$$\phi_n(\boldsymbol{p}) = \frac{1}{\sqrt{n}} \tag{8.161}$$

$$\phi_{p_\alpha}(\boldsymbol{p}) = \frac{p_\alpha}{\sqrt{nmk_{\rm B}T}} \tag{8.162}$$

$$\phi_\varepsilon(\boldsymbol{p}) = \sqrt{\frac{2}{3n}}\left(\frac{\varepsilon(\boldsymbol{p})}{k_{\rm B}T} - \frac{3}{2}\right) . \tag{8.163}$$

If there are no temperature, chemical potential, or bulk velocity gradients, and there are no external forces, then $Y = 0$ and the only changes to the distribution are from collisions. The linearized Boltzmann equation becomes

$$\frac{\partial\psi}{\partial t} = \hat{L}\psi \ . \tag{8.164}$$

We can therefore write the most general solution in the form

$$\psi(\boldsymbol{p}, t) = {\sum_n}' C_n \, \phi_n(\boldsymbol{p}) \, e^{-\lambda_n t} \ , \tag{8.165}$$

where the prime on the sum reminds us that collisional invariants are to be excluded. All the eigenvalues $\lambda_n$, aside from the five zero eigenvalues for the collisional invariants, must be positive. Any negative eigenvalue would cause $\psi(\boldsymbol{p}, t)$ to increase without bound, and an initial nonequilibrium distribution would not relax to the equilibrium $f^0(\boldsymbol{p})$, which we regard as unphysical. Henceforth we will drop the prime on the sum but remember that $C_n = 0$ for the five collisional invariants.

Recall also the particle, energy, and thermal (heat) currents,

$$\begin{aligned}
\boldsymbol{j} &= \int\! d^3\!p \; \boldsymbol{v} \, f(\boldsymbol{p}) = \int\! d^3\!p \; f^0(\boldsymbol{p}) \, \boldsymbol{v} \, \psi(\boldsymbol{p}) = \langle\, \boldsymbol{v} \,|\, \psi \,\rangle \\
\boldsymbol{j}_\varepsilon &= \int\! d^3\!p \; \boldsymbol{v} \, \varepsilon \, f(\boldsymbol{p}) = \int\! d^3\!p \; f^0(\boldsymbol{p}) \, \boldsymbol{v} \, \varepsilon \, \psi(\boldsymbol{p}) = \langle\, \boldsymbol{v} \, \varepsilon \,|\, \psi \,\rangle \\
\boldsymbol{j}_q &= \int\! d^3\!p \; \boldsymbol{v} \, (\varepsilon - \mu) \, f(\boldsymbol{p}) = \int\! d^3\!p \; f^0(\boldsymbol{p}) \, \boldsymbol{v} \, (\varepsilon - \mu) \, \psi(\boldsymbol{p}) = \langle\, \boldsymbol{v} \, (\varepsilon - \mu) \,|\, \psi \,\rangle \ .
\end{aligned} \tag{8.166}$$

Note $\boldsymbol{j}_q = \boldsymbol{j}_\varepsilon - \mu \boldsymbol{j}$.

### 8.7.3 Steady state solution to the linearized Boltzmann equation

Under steady state conditions, there is no time dependence, and the linearized Boltzmann equation takes the form

$$\hat{L}\psi = Y \; . \tag{8.167}$$

We may expand $\psi$ in the eigenfunctions $\phi_n$ and write $\psi = \sum_n C_n \, \phi_n$. Applying $\hat{L}$ and taking the inner product with $\phi_j$, we have

$$C_j = -\frac{1}{\lambda_j} \, \langle \, \phi_j \, | \, Y \, \rangle \; . \tag{8.168}$$

Thus, the formal solution to the linearized Boltzmann equation is

$$\psi(\boldsymbol{p}) = -\sum_n \frac{1}{\lambda_n} \, \langle \, \phi_n \, | \, Y \, \rangle \; \phi_n(\boldsymbol{p}) \; . \tag{8.169}$$

This solution is applicable provided $| \, Y \, \rangle$ is orthogonal to the five collisional invariants.

**Thermal conductivity**

For the thermal conductivity, we take $\boldsymbol{\nabla} T = \partial_z T \, \hat{\boldsymbol{x}}$, and

$$Y = \frac{1}{k_{\rm B} T^2} \, \frac{\partial T}{\partial x} \cdot X_\kappa \; , \tag{8.170}$$

where $X_\kappa \equiv (\varepsilon - c_p T) \, v_x$. Under the conditions of no particle flow ($\boldsymbol{j} = 0$), we have $\boldsymbol{j}_q = -\kappa \, \partial_x T \, \hat{\boldsymbol{x}}$. Then we have

$$\langle \, X_\kappa \, | \, \psi \, \rangle = -\kappa \, \frac{\partial T}{\partial x} \; . \tag{8.171}$$

**Viscosity**

For the viscosity, we take

$$Y = \frac{m}{k_{\rm B} T} \, \frac{\partial V_x}{\partial y} \cdot X_\eta \; , \tag{8.172}$$

with $X_\eta = v_x \, v_y$. We then

$$\Pi_{xy} = \langle \, m \, v_x \, v_y \, | \, \psi \, \rangle = -\eta \, \frac{\partial V_x}{\partial y} \; . \tag{8.173}$$

Thus,

$$\langle \, X_\eta \, | \, \psi \, \rangle = -\frac{\eta}{m} \, \frac{\partial V_x}{\partial y} \; . \tag{8.174}$$

### 8.7.4 Variational approach

Following the treatment in chapter 1 of Smith and Jensen, define $\hat{H} \equiv -\hat{L}$. We have that $\hat{H}$ is a positive semidefinite operator, whose only zero eigenvalues correspond to the collisional invariants. We then have the Schwarz inequality,

$$\langle \, \psi \, | \, \hat{H} \, | \, \psi \, \rangle \cdot \langle \, \phi \, | \, \hat{H} \, | \, \phi \, \rangle \geq \langle \, \phi \, | \, \hat{H} \, | \, \psi \, \rangle^2 \; , \tag{8.175}$$

for any two Hilbert space vectors $|\,\psi\,\rangle$ and $|\,\phi\,\rangle$. Consider now the above calculation of the thermal conductivity. We have

$$\hat{H}\psi = -\frac{1}{k_{\rm B}T^2}\,\frac{\partial T}{\partial x}\,X_\kappa \tag{8.176}$$

and therefore

$$\kappa = \frac{k_{\rm B}T^2}{(\partial T/\partial x)^2}\,\langle\,\psi\,|\,\hat{H}\,|\,\psi\,\rangle \geq \frac{1}{k_{\rm B}T^2}\,\frac{\langle\,\phi\,|\,X_\kappa\,\rangle^2}{\langle\,\phi\,|\,\hat{H}\,|\,\phi\,\rangle}\ . \tag{8.177}$$

Similarly, for the viscosity, we have

$$\hat{H}\psi = -\frac{m}{k_{\rm B}T}\,\frac{\partial V_x}{\partial y}\,X_\eta\ , \tag{8.178}$$

from which we derive

$$\eta = \frac{k_{\rm B}T}{(\partial V_x/\partial y)^2}\,\langle\,\psi\,|\,\hat{H}\,|\,\psi\,\rangle \geq \frac{m^2}{k_{\rm B}T}\,\frac{\langle\,\phi\,|\,X_\eta\,\rangle^2}{\langle\,\phi\,|\,\hat{H}\,|\,\phi\,\rangle}\ . \tag{8.179}$$

In order to get a good lower bound, we want $\phi$ in each case to have a good overlap with $X_{\kappa,\eta}$. One approach then is to take $\phi = X_{\kappa,\eta}$, which guarantees that the overlap will be finite (and not zero due to symmetry, for example). We illustrate this method with the viscosity calculation. We have

$$\eta \geq \frac{m^2}{k_{\rm B}T}\,\frac{\langle\,v_x v_y\,|\,v_x v_y\,\rangle^2}{\langle\,v_x v_y\,|\,\hat{H}\,|\,v_x v_y\,\rangle}\ . \tag{8.180}$$

Now the linearized collision operator $\hat{L}$ acts as

$$\langle\,\phi\,|\,\hat{L}\,|\,\psi\,\rangle = \int\! d^3\!p\, g^0(\boldsymbol{p})\,\phi(\boldsymbol{p}) \int\! d^3\!p_1 \int\! d\Omega\,\frac{\partial\sigma}{\partial\Omega}\,|\boldsymbol{v}-\boldsymbol{v}_1|\,f^0(\boldsymbol{p}_1)\Big\{\psi(\boldsymbol{p})+\psi(\boldsymbol{p}_1)-\psi(\boldsymbol{p}')-\psi(\boldsymbol{p}_1')\Big\}\ . \tag{8.181}$$

Here the kinematics of the collision guarantee total energy and momentum conservation, so $\boldsymbol{p}'$ and $\boldsymbol{p}_1'$ are determined as in eqn. 8.56.

Now we have

$$d\Omega = \sin\chi\,d\chi\,d\varphi\ , \tag{8.182}$$

where $\chi$ is the scattering angle depicted in Fig. 8.6 and $\varphi$ is the azimuthal angle of the scattering. The differential scattering cross section is obtained by elementary mechanics and is known to be

$$\frac{\partial\sigma}{\partial\Omega} = \left|\frac{d(b^2/2)}{d\sin\chi}\right|\ , \tag{8.183}$$

where $b$ is the *impact parameter*. The scattering angle is

$$\chi(b,u) = \pi - 2\int\limits_{r_{\rm p}}^{\infty}\! dr\,\frac{b}{\sqrt{r^4 - b^2r^2 - \frac{2U(r)r^4}{\tilde{m}u^2}}}\ , \tag{8.184}$$

where $\tilde{m} = \frac{1}{2}m$ is the reduced mass, and $r_{\rm p}$ is the relative coordinate separation at periapsis, *i.e.* the distance of closest approach, which occurs when $\dot{r} = 0$, *i.e.*

$$\tfrac{1}{2}\tilde{m}u^2 = \frac{\ell^2}{2\tilde{m}r_{\rm p}^2} + U(r_{\rm p})\ , \tag{8.185}$$

where $\ell = \tilde{m}ub$ is the relative coordinate angular momentum.

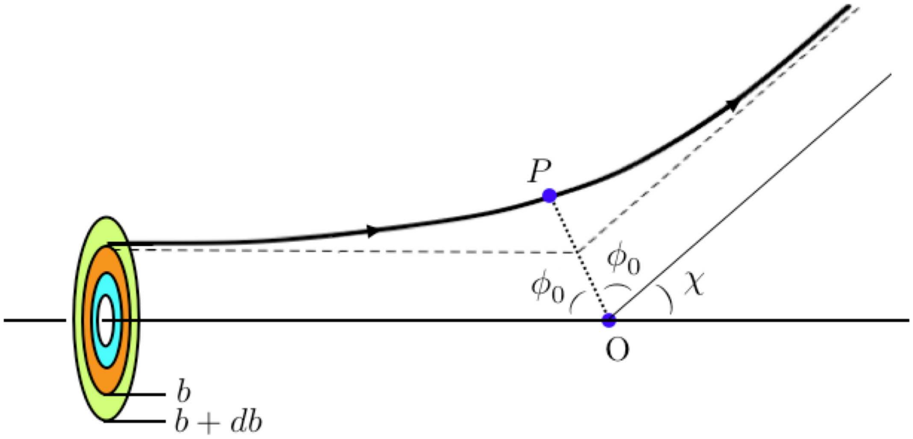

Figure 8.6: Scattering in the CM frame. O is the force center and $P$ is the point of periapsis. The impact parameter is $b$, and $\chi$ is the scattering angle. $\phi_0$ is the angle through which the relative coordinate moves between periapsis and infinity.

We work in center-of-mass coordinates, so the velocities are

$$\boldsymbol{v} = \boldsymbol{V} + \tfrac{1}{2}\boldsymbol{u} \qquad \boldsymbol{v}' = \boldsymbol{V} + \tfrac{1}{2}\boldsymbol{u}' \tag{8.186}$$

$$\boldsymbol{v}_1 = \boldsymbol{V} - \tfrac{1}{2}\boldsymbol{u} \qquad \boldsymbol{v}_1' = \boldsymbol{V} - \tfrac{1}{2}\boldsymbol{u}' \quad , \tag{8.187}$$

with $|\boldsymbol{u}| = |\boldsymbol{u}'|$ and $\hat{\boldsymbol{u}} \cdot \hat{\boldsymbol{u}}' = \cos\chi$. Then if $\psi(\boldsymbol{p}) = v_x v_y$, we have

$$\Delta(\psi) \equiv \psi(\boldsymbol{p}) + \psi(\boldsymbol{p}_1) - \psi(\boldsymbol{p}') - \psi(\boldsymbol{p}_1') = \tfrac{1}{2}\big(u_x u_y - u_x' u_y'\big) \ . \tag{8.188}$$

We may write

$$\boldsymbol{u}' = u\Big(\sin\chi\cos\varphi\,\hat{\boldsymbol{e}}_1 + \sin\chi\sin\varphi\,\hat{\boldsymbol{e}}_2 + \cos\chi\,\hat{\boldsymbol{e}}_3\Big) \ , \tag{8.189}$$

where $\hat{\boldsymbol{e}}_3 = \hat{\boldsymbol{u}}$. With this parameterization, we have

$$\int\limits_0^{2\pi}\! d\varphi\,\tfrac{1}{2}\big(u_\alpha u_\beta - u_\alpha' u_\beta'\big) = -\pi\sin^2\!\chi\,\big(u^2\,\delta_{\alpha\beta} - 3u_\alpha u_\beta\big) \ . \tag{8.190}$$

Note that we have used here the relation

$$e_{1\alpha}\,e_{1\beta} + e_{2\alpha}\,e_{2\beta} + e_{3\alpha}\,e_{3\beta} = \delta_{\alpha\beta} \ , \tag{8.191}$$

which holds since the LHS is a projector $\sum_{i=1}^3 |\hat{\boldsymbol{e}}_i\rangle\langle\hat{\boldsymbol{e}}_i|$.

It is convenient to define the following integral:

$$R(u) \equiv \int\limits_0^\infty\! db\, b\ \sin^2\!\chi(b,u) \ . \tag{8.192}$$

Since the Jacobian

$$\left|\,\mathsf{det}\,\frac{(\partial\boldsymbol{v},\partial\boldsymbol{v}_1)}{(\partial\boldsymbol{V},\partial\boldsymbol{u})}\right| = 1 \ , \tag{8.193}$$

we have

$$\langle\, v_x v_y \,|\, \hat{L} \,|\, v_x v_y \,\rangle = n^2 \bigg(\frac{m}{2\pi k_{\rm B} T}\bigg)^3 \!\int\! d^3\!V \!\int\! d^3\!u \; e^{-m\boldsymbol{V}^2/k_{\rm B}T}\; e^{-m\boldsymbol{u}^2/4k_{\rm B}T} \cdot u \cdot \tfrac{3\pi}{2} u_x u_y \cdot R(u) \cdot v_x v_y \ . \tag{8.194}$$

This yields

$$\langle\, v_x v_y \,|\, \hat{L} \,|\, v_x v_y \,\rangle = \tfrac{\pi}{40}\, n^2\, \big\langle u^5\, R(u) \big\rangle \ , \tag{8.195}$$

where

$$\big\langle F(u) \big\rangle \equiv \int\limits_0^\infty \! du\, u^2\, e^{-mu^2/4k_{\rm B}T}\, F(u) \bigg/ \int\limits_0^\infty \! du\, u^2\, e^{-mu^2/4k_{\rm B}T} \ . \tag{8.196}$$

It is easy to compute the term in the numerator of eqn. 8.180:

$$\langle\, v_x v_y \,|\, v_x v_y \,\rangle = n \left(\frac{m}{2\pi k_{\rm B} T}\right)^{3/2} \int\! d^3\!v \; e^{-m\boldsymbol{v}^2/2k_{\rm B}T}\, v_x^2\, v_y^2 = n\bigg(\frac{k_{\rm B}T}{m}\bigg)^2 \ . \tag{8.197}$$

Putting it all together, we find

$$\eta \ge \frac{40\,(k_{\rm B}T)^3}{\pi\, m^2} \bigg/ \big\langle u^5\, R(u) \big\rangle \ . \tag{8.198}$$

The computation for $\kappa$ is a bit more tedious. One has $\psi(\boldsymbol{p}) = (\varepsilon - c_p T)\, v_x$, in which case

$$\Delta(\psi) = \tfrac{1}{2} m \Big[ (\boldsymbol{V} \cdot \boldsymbol{u})\, u_x - (\boldsymbol{V} \cdot \boldsymbol{u}')\, u'_x \Big] \ . \tag{8.199}$$

Ultimately, one obtains the lower bound

$$\kappa \ge \frac{150\, k_{\rm B}\, (k_{\rm B}T)^3}{\pi\, m^3} \bigg/ \big\langle u^5\, R(u) \big\rangle \ . \tag{8.200}$$

Thus, independent of the potential, this variational calculation yields a Prandtl number of

$$\text{Pr} = \frac{\nu}{a} = \frac{\eta\, c_p}{m\,\kappa} = \tfrac{2}{3} \ , \tag{8.201}$$

which is very close to what is observed in dilute monatomic gases (see Tab. 8.1).

While the variational expressions for $\eta$ and $\kappa$ are complicated functions of the potential, for hard sphere scattering the calculation is simple, because $b = d \sin\phi_0 = d \cos(\frac{1}{2}\chi)$, where $d$ is the hard sphere diameter. Thus, the impact parameter $b$ is independent of the relative speed $u$, and one finds $R(u) = \frac{1}{3} d^3$. Then

$$\big\langle u^5\, R(u) \big\rangle = \tfrac{1}{3} d^3 \big\langle u^5 \big\rangle = \frac{128}{\sqrt{\pi}} \bigg(\frac{k_{\rm B}T}{m}\bigg)^{5/2} d^2 \tag{8.202}$$

and one finds

$$\eta \ge \frac{5\,(m k_{\rm B} T)^{1/2}}{16\sqrt{\pi}\, d^2} \qquad , \qquad \kappa \ge \frac{75\, k_{\rm B}}{64\sqrt{\pi}\, d^2} \bigg(\frac{k_{\rm B}T}{m}\bigg)^{1/2} \ . \tag{8.203}$$

## 8.8 The Equations of Hydrodynamics

We now derive the equations governing fluid flow. The equations of mass and momentum balance are

$$\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\!\cdot(\rho\,\boldsymbol{V}) = 0 \tag{8.204}$$

$$\frac{\partial(\rho\,V_\alpha)}{\partial t} + \frac{\partial\Pi_{\alpha\beta}}{\partial x^\beta} = 0\;, \tag{8.205}$$

where

$$\Pi_{\alpha\beta} = \rho\,V_\alpha V_\beta + p\,\delta_{\alpha\beta} - \overbrace{\left\{\eta\left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha} - \tfrac{2}{3}\,\boldsymbol{\nabla}\!\cdot\boldsymbol{V}\,\delta_{\alpha\beta}\right) + \zeta\,\boldsymbol{\nabla}\!\cdot\boldsymbol{V}\,\delta_{\alpha\beta}\right\}}^{\tilde\sigma_{\alpha\beta}}\;. \tag{8.206}$$

Substituting the continuity equation into the momentum balance equation, one arrives at

$$\rho\,\frac{\partial\boldsymbol{V}}{\partial t} + \rho\,(\boldsymbol{V}\!\cdot\boldsymbol{\nabla})\boldsymbol{V} = -\boldsymbol{\nabla}p + \eta\,\nabla^2\boldsymbol{V} + (\zeta + \tfrac{1}{3}\eta)\boldsymbol{\nabla}(\boldsymbol{\nabla}\!\cdot\boldsymbol{V})\;, \tag{8.207}$$

which, together with continuity, are known as the *Navier-Stokes equations*. These equations are supplemented by an equation describing the conservation of energy,

$$T\,\frac{\partial s}{\partial T} + T\,\boldsymbol{\nabla}\!\cdot(s\boldsymbol{V}) = \tilde\sigma_{\alpha\beta}\,\frac{\partial V_\alpha}{\partial x^\beta} + \boldsymbol{\nabla}\!\cdot(\kappa\boldsymbol{\nabla}T)\;. \tag{8.208}$$

Note that the LHS of eqn. 8.207 is $\rho\,D\boldsymbol{V}/Dt$, where $D/Dt$ is the convective derivative. Multiplying by a differential volume, this gives the mass times the acceleration of a differential local fluid element. The RHS, multiplied by the same differential volume, gives the differential force on this fluid element in a frame instantaneously moving with constant velocity $\boldsymbol{V}$. Thus, this is Newton's Second Law for the fluid.

## 8.9 Nonequilibrium Quantum Transport

### 8.9.1 Boltzmann equation for quantum systems

Almost everything we have derived thus far can be applied, *mutatis mutandis*, to quantum systems. The main difference is that the distribution $f^0$ corresponding to local equilibrium is no longer of the Maxwell-Boltzmann form, but rather of the Bose-Einstein or Fermi-Dirac form,

$$f^0(\boldsymbol{r},\boldsymbol{k},t) = \left\{\exp\left(\frac{\varepsilon(\boldsymbol{k}) - \mu(\boldsymbol{r},t)}{k_{\rm B}T(\boldsymbol{r},t)}\right) \mp 1\right\}^{-1}\;, \tag{8.209}$$

where the top sign applies to bosons and the bottom sign to fermions. Here we shift to the more common notation for quantum systems in which we write the distribution in terms of the wavevector $\boldsymbol{k} = \boldsymbol{p}/\hbar$ rather than the momentum $\boldsymbol{p}$. The quantum distributions satisfy detailed balance with respect to the quantum collision integral

$$\left(\frac{\partial f}{\partial t}\right)_{\rm coll} = \int\!\frac{d^3\!k_1}{(2\pi)^3}\!\int\!\frac{d^3\!k'}{(2\pi)^3}\!\int\!\frac{d^3\!k'_1}{(2\pi)^3}\;w\,\Big\{f'f'_1\,(1\pm f)\,(1\pm f_1) - f f_1\,(1\pm f')\,(1\pm f'_1)\Big\} \tag{8.210}$$

where $w = w(\boldsymbol{k},\boldsymbol{k}_1\,|\,\boldsymbol{k}',\boldsymbol{k}'_1)$, $f = f(\boldsymbol{k})$, $f_1 = f(\boldsymbol{k}_1)$, $f' = f(\boldsymbol{k}')$, and $f'_1 = f(\boldsymbol{k}'_1)$, and where we have assumed time-reversal and parity symmetry. Detailed balance requires

$$\frac{f}{1\pm f}\cdot\frac{f_1}{1\pm f_1} = \frac{f'}{1\pm f'}\cdot\frac{f'_1}{1\pm f'_1}\;, \tag{8.211}$$

where $f = f^0$ is the equilibrium distribution. One can check that

$$f = \frac{1}{e^{\beta(\varepsilon-\mu)} \mp 1} \qquad \Longrightarrow \qquad \frac{f}{1 \pm f} = e^{\beta(\mu-\varepsilon)} \ , \tag{8.212}$$

which is the Boltzmann distribution, which we have already shown to satisfy detailed balance. For the streaming term, we have

$$\begin{aligned} df^0 &= k_{\rm B}T \, \frac{\partial f^0}{\partial \varepsilon} \, d\bigg(\frac{\varepsilon-\mu}{k_{\rm B}T}\bigg) \\ &= k_{\rm B}T \, \frac{\partial f^0}{\partial \varepsilon} \left\{ -\frac{d\mu}{k_{\rm B}T} - \frac{(\varepsilon-\mu)\, dT}{k_{\rm B}T^2} + \frac{d\varepsilon}{k_{\rm B}T} \right\} \\ &= -\frac{\partial f^0}{\partial \varepsilon} \left\{ \frac{\partial \mu}{\partial \boldsymbol{r}} \cdot d\boldsymbol{r} + \frac{\varepsilon-\mu}{T} \, \frac{\partial T}{\partial \boldsymbol{r}} \cdot d\boldsymbol{r} - \frac{\partial \varepsilon}{\partial \boldsymbol{k}} \cdot d\boldsymbol{k} \right\} \ , \end{aligned} \tag{8.213}$$

from which we read off

$$\begin{aligned} \frac{\partial f^0}{\partial \boldsymbol{r}} &= -\frac{\partial f^0}{\partial \varepsilon} \left\{ \frac{\partial \mu}{\partial \boldsymbol{r}} + \frac{\varepsilon-\mu}{T} \, \frac{\partial T}{\partial \boldsymbol{r}} \right\} \\ \frac{\partial f^0}{\partial \boldsymbol{k}} &= \hbar \boldsymbol{v} \, \frac{\partial f^0}{\partial \varepsilon} \ . \end{aligned} \tag{8.214}$$

The most important application is to the theory of electron transport in metals and semiconductors, in which case $f^0$ is the Fermi distribution. In this case, the quantum collision integral also receives a contribution from one-body scattering in the presence of an external potential $U(\boldsymbol{r})$, which is given by Fermi's Golden Rule:

$$\begin{aligned} \bigg(\frac{\partial f(\boldsymbol{k})}{\partial t}\bigg)'_{\rm coll} &= \frac{2\pi}{\hbar} \sum_{\boldsymbol{k}' \in \hat{\Omega}} |\langle \, \boldsymbol{k}' \, | \, U \, | \, \boldsymbol{k} \, \rangle|^2 \, \big(f(\boldsymbol{k}') - f(\boldsymbol{k})\big) \, \delta\big(\varepsilon(\boldsymbol{k}) - \varepsilon(\boldsymbol{k}')\big) \\ &= \frac{2\pi}{\hbar V} \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3} \, |\, \hat{U}(\boldsymbol{k}-\boldsymbol{k}')|^2 \, \big(f(\boldsymbol{k}') - f(\boldsymbol{k})\big) \, \delta\big(\varepsilon(\boldsymbol{k}) - \varepsilon(\boldsymbol{k}')\big) \ . \end{aligned} \tag{8.215}$$

The wavevectors are now restricted to the first Brillouin zone, and the dispersion $\varepsilon(\boldsymbol{k})$ is no longer the ballistic form $\varepsilon = \hbar^2\boldsymbol{k}^2/2m$ but rather the dispersion for electrons in a particular energy band (typically the valence band) of a solid[10]. Note that $f = f^0$ satisfies detailed balance with respect to one-body collisions as well[11].

In the presence of a weak electric field $\boldsymbol{E}$ and a (not necessarily weak) magnetic field $\boldsymbol{B}$, we have, within the relaxation time approximation, $f = f^0 + \delta f$ with

$$\frac{\partial\, \delta f}{\partial t} - \frac{e}{\hbar c} \, \boldsymbol{v} \times \boldsymbol{B} \cdot \frac{\partial\, \delta f}{\partial \boldsymbol{k}} - \boldsymbol{v} \cdot \bigg[ e\, \boldsymbol{\mathcal{E}} + \frac{\varepsilon-\mu}{T} \, \boldsymbol{\nabla} T \bigg] \, \frac{\partial f^0}{\partial \varepsilon} = -\frac{\delta f}{\tau} \ , \tag{8.216}$$

where $\boldsymbol{\mathcal{E}} = -\boldsymbol{\nabla}(\phi - \mu/e) = \boldsymbol{E} - e^{-1}\boldsymbol{\nabla}\mu$ is the gradient of the 'electrochemical potential' $\phi - e^{-1}\mu$. In deriving the above equation, we have worked to lowest order in small quantities. This entails dropping terms like $\boldsymbol{v} \cdot \frac{\partial\, \delta f}{\partial \boldsymbol{r}}$ (higher order in spatial derivatives) and $\boldsymbol{E} \cdot \frac{\partial\, \delta f}{\partial \boldsymbol{k}}$ (both $\boldsymbol{E}$ and $\delta f$ are assumed small). Typically $\tau$ is energy-dependent, *i.e.* $\tau = \tau\big(\varepsilon(\boldsymbol{k})\big)$.

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[10] We neglect interband scattering here, which can be important in practical applications, but which is beyond the scope of these notes.

[11] The transition rate from $|\boldsymbol{k}'\rangle$ to $|\boldsymbol{k}\rangle$ is proportional to the matrix element and to the product $f'(1-f)$. The reverse process is proportional to $f(1-f')$. Subtracting these factors, one obtains $f' - f$, and therefore the nonlinear terms felicitously cancel in eqn. 8.215.

We can use eqn. 8.216 to compute the electrical current $\boldsymbol{j}$ and the thermal current $\boldsymbol{j}_q$,

$$\boldsymbol{j} = -2e \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\, \boldsymbol{v}\, \delta f \tag{8.217}$$

$$\boldsymbol{j}_q = 2 \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\, (\varepsilon - \mu)\, \boldsymbol{v}\, \delta f \ . \tag{8.218}$$

Here the factor of 2 is from spin degeneracy of the electrons (we neglect Zeeman splitting).

In the presence of a time-independent temperature gradient and electric field, linearized Boltzmann equation in the relaxation time approximation has the solution

$$\delta f = -\tau(\varepsilon)\, \boldsymbol{v} \cdot \left( e\boldsymbol{\mathcal{E}} + \frac{\varepsilon - \mu}{T}\, \boldsymbol{\nabla} T \right) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \ . \tag{8.219}$$

We now consider both the electrical current[12] $\boldsymbol{j}$ as well as the thermal current density $\boldsymbol{j}_q$. One readily obtains

$$\boldsymbol{j} = -2e \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\ \boldsymbol{v}\, \delta f \equiv L_{11}\, \boldsymbol{\mathcal{E}} - L_{12}\, \boldsymbol{\nabla} T \tag{8.220}$$

$$\boldsymbol{j}_q = 2 \int\limits_{\hat{\Omega}} \frac{d^3k}{(2\pi)^3}\ (\varepsilon - \mu)\, \boldsymbol{v}\, \delta f \equiv L_{21}\, \boldsymbol{\mathcal{E}} - L_{22}\, \boldsymbol{\nabla} T \tag{8.221}$$

where the *transport coefficients* $L^{11}$ *etc.* are matrices:

$$L^{\alpha\beta}_{11} = \frac{e^2}{4\pi^3\hbar} \int\! d\varepsilon\, \tau(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int\! dS_\varepsilon\, \frac{v^\alpha\, v^\beta}{|\boldsymbol{v}|} \tag{8.222}$$

$$L^{\alpha\beta}_{21} = T L^{\alpha\beta}_{12} = -\frac{e}{4\pi^3\hbar} \int\! d\varepsilon\, \tau(\varepsilon)\, (\varepsilon - \mu) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int\! dS_\varepsilon\, \frac{v^\alpha\, v^\beta}{|\boldsymbol{v}|} \tag{8.223}$$

$$L^{\alpha\beta}_{22} = \frac{1}{4\pi^3\hbar T} \int\! d\varepsilon\, \tau(\varepsilon)\, (\varepsilon - \mu)^2 \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int\! dS_\varepsilon\, \frac{v^\alpha\, v^\beta}{|\boldsymbol{v}|} \ . \tag{8.224}$$

If we define the hierarchy of integral expressions

$$\mathcal{J}^{\alpha\beta}_n \equiv \frac{1}{4\pi^3\hbar} \int\! d\varepsilon\, \tau(\varepsilon)\, (\varepsilon - \mu)^n \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int\! dS_\varepsilon\, \frac{v^\alpha\, v^\beta}{|\boldsymbol{v}|} \tag{8.225}$$

then we may write

$$L^{\alpha\beta}_{11} = e^2\, \mathcal{J}^{\alpha\beta}_0 \qquad , \qquad L^{\alpha\beta}_{21} = T L^{\alpha\beta}_{12} = -e\, \mathcal{J}^{\alpha\beta}_1 \qquad , \qquad L^{\alpha\beta}_{22} = \frac{1}{T}\, \mathcal{J}^{\alpha\beta}_2 \ . \tag{8.226}$$

The linear relations in eqn. (8.221) may be recast in the following form:

$$\begin{aligned} \boldsymbol{\mathcal{E}} &= \rho\, \boldsymbol{j} + Q\, \boldsymbol{\nabla} T \\ \boldsymbol{j}_q &= \sqcap\, \boldsymbol{j} - \kappa\, \boldsymbol{\nabla} T \ , \end{aligned} \tag{8.227}$$

where the matrices $\rho$, $Q$, $\sqcap$, and $\kappa$ are given by

$$\rho = L^{-1}_{11} \qquad\qquad Q = L^{-1}_{11}\, L_{12} \tag{8.228}$$

$$\sqcap = L_{21}\, L^{-1}_{11} \qquad\qquad \kappa = L_{22} - L_{21}\, L^{-1}_{11}\, L_{12} \ , \tag{8.229}$$

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[12] In this section we use $\boldsymbol{j}$ to denote electrical current, rather than particle number current as before.

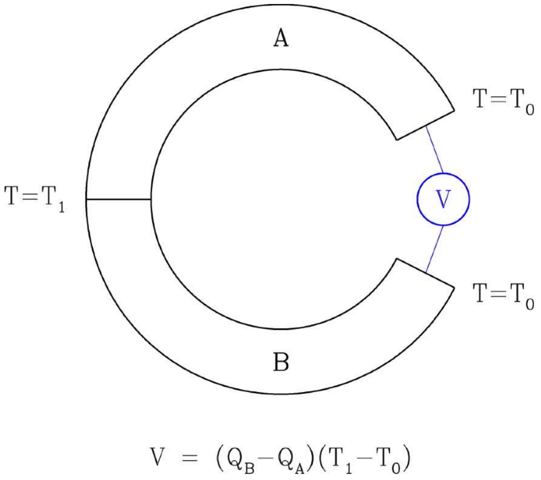

Figure 8.7: A thermocouple is a junction formed of two dissimilar metals. With no electrical current passing, an electric field is generated in the presence of a temperature gradient, resulting in a voltage $V = V_{\rm A} - V_{\rm B}$.

or, in terms of the $\mathcal{J}_n$,

$$\rho = \frac{1}{e^2}\,\mathcal{J}_0^{-1} \qquad\qquad Q = -\frac{1}{e\,T}\,\mathcal{J}_0^{-1}\,\mathcal{J}_1 \tag{8.230}$$

$$\sqcap = -\frac{1}{e}\,\mathcal{J}_1\,\mathcal{J}_0^{-1} \qquad\qquad \kappa = \frac{1}{T}\Big(\mathcal{J}_2 - \mathcal{J}_1\,\mathcal{J}_0^{-1}\,\mathcal{J}_1\Big) \ , \tag{8.231}$$

These equations describe a wealth of transport phenomena:

- Electrical resistance ($\boldsymbol{\nabla} T = \boldsymbol{B} = 0$)
  An electrical current $\boldsymbol{j}$ will generate an electric field $\boldsymbol{\mathcal{E}} = \rho\boldsymbol{j}$, where $\rho$ is the electrical resistivity.
- Peltier effect ($\boldsymbol{\nabla} T = \boldsymbol{B} = 0$)
  An electrical current $\boldsymbol{j}$ will generate an heat current $\boldsymbol{j}_q = \sqcap\boldsymbol{j}$, where $\sqcap$ is the Peltier coefficient.
- Thermal conduction ($\boldsymbol{j} = \boldsymbol{B} = 0$)
  A temperature gradient $\boldsymbol{\nabla} T$ gives rise to a heat current $\boldsymbol{j}_q = -\kappa\boldsymbol{\nabla} T$, where $\kappa$ is the thermal conductivity.
- Seebeck effect ($\boldsymbol{j} = \boldsymbol{B} = 0$)
  A temperature gradient $\boldsymbol{\nabla} T$ gives rise to an electric field $\boldsymbol{\mathcal{E}} = Q\boldsymbol{\nabla} T$, where $Q$ is the Seebeck coefficient.

One practical way to measure the thermopower is to form a junction between two dissimilar metals, A and B. The junction is held at temperature $T_1$ and the other ends of the metals are held at temperature $T_0$. One then measures a voltage difference between the free ends of the metals – this is known as the Seebeck effect. Integrating the electric field from the free end of A to the free end of B gives

$$V_{\rm A} - V_{\rm B} = -\int\limits_{\rm A}^{\rm B} \boldsymbol{\mathcal{E}}\cdot d\boldsymbol{l} = (Q_{\rm B} - Q_{\rm A})(T_1 - T_0)\ . \tag{8.232}$$

What one measures here is really the difference in thermopowers of the two metals. For an absolute measurement of $Q_{\rm A}$, replace B by a superconductor ($Q = 0$ for a superconductor). A device which converts a temperature gradient into an emf is known as a *thermocouple*.

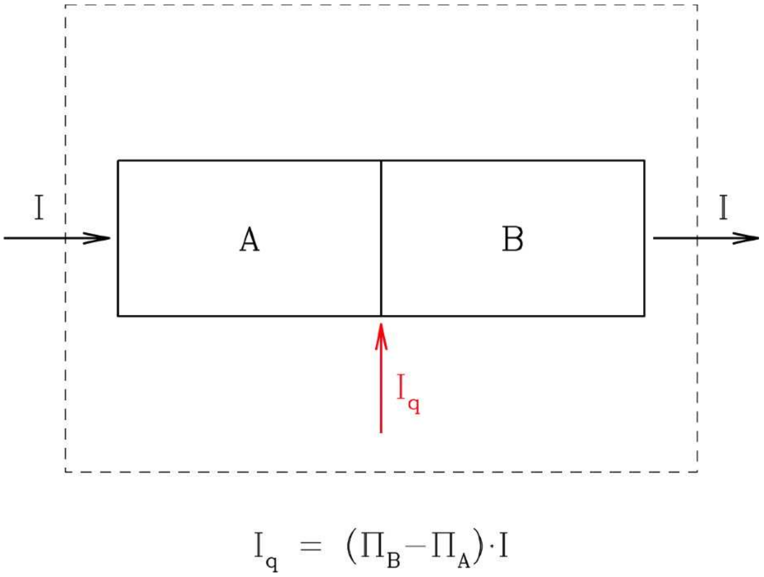

Figure 8.8: A sketch of a Peltier effect refrigerator. An electrical current $I$ is passed through a junction between two dissimilar metals. If the dotted line represents the boundary of a thermally well-insulated body, then the body cools when $\sqcap_{\rm B} > \sqcap_{\rm A}$, in order to maintain a heat current balance at the junction.

The Peltier effect has practical applications in refrigeration technology. Suppose an electrical current $I$ is passed through a junction between two dissimilar metals, A and B. Due to the difference in Peltier coefficients, there will be a net heat current into the junction of $W = (\sqcap_{\rm A} - \sqcap_{\rm B})\, I$. Note that this is proportional to $I$, rather than the familiar $I^2$ result from Joule heating. The sign of $W$ depends on the direction of the current. If a second junction is added, to make an ABA configuration, then heat absorbed at the first junction will be liberated at the second. [13]

### 8.9.2 The Heat Equation

We begin with the continuity equations for charge density $\rho$ and energy density $\varepsilon$:

$$\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j} = 0 \tag{8.233}$$

$$\frac{\partial\varepsilon}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{j}_\varepsilon = \boldsymbol{j}\cdot\boldsymbol{E}\ , \tag{8.234}$$

where $\boldsymbol{E}$ is the electric field[14]. Now we invoke local thermodynamic equilibrium and write

$$\begin{aligned}\frac{\partial\varepsilon}{\partial t} &= \frac{\partial\varepsilon}{\partial n}\,\frac{\partial n}{\partial t} + \frac{\partial\varepsilon}{\partial T}\,\frac{\partial T}{\partial t}\\ &= -\frac{\mu}{e}\,\frac{\partial\rho}{\partial t} + c_V\,\frac{\partial T}{\partial t}\ ,\end{aligned} \tag{8.235}$$

---

[13] To create a refrigerator, stick the cold junction inside a thermally insulated box and the hot junction outside the box.

[14] Note that it is $\boldsymbol{E}\cdot\boldsymbol{j}$ and *not* $\boldsymbol{\mathcal{E}}\cdot\boldsymbol{j}$ which is the source term in the energy continuity equation.

where $n$ is the electron *number density* ($n = -\rho/e$) and $c_V$ is the specific heat. We may now write

$$\begin{aligned} c_V \, \frac{\partial T}{\partial t} &= \frac{\partial \varepsilon}{\partial t} + \frac{\mu}{e} \, \frac{\partial \rho}{\partial t} \\ &= \boldsymbol{j} \cdot \boldsymbol{E} - \boldsymbol{\nabla} \cdot \boldsymbol{j}_\varepsilon - \frac{\mu}{e} \, \boldsymbol{\nabla} \cdot \boldsymbol{j} \\ &= \boldsymbol{j} \cdot \boldsymbol{\mathcal{E}} - \boldsymbol{\nabla} \cdot \boldsymbol{j}_q \; . \end{aligned} \tag{8.236}$$

Invoking $\boldsymbol{j}_q = \sqcap \boldsymbol{j} - \kappa \boldsymbol{\nabla} T$, we see that if there is no electrical current ($\boldsymbol{j} = 0$), we obtain the *heat equation*

$$c_V \, \frac{\partial T}{\partial t} = \kappa_{\alpha\beta} \, \frac{\partial^2 T}{\partial x^\alpha \, \partial x^\beta} \; . \tag{8.237}$$

This results in a time scale $\tau_T$ for temperature diffusion $\tau_T = \mathcal{C} L^2 c_V / \kappa$, where $L$ is a typical length scale and $\mathcal{C}$ is a numerical constant. For a cube of size $L$ subjected to a sudden external temperature change, $L$ is the side length and $\mathcal{C} = 1/3\pi^2$ (solve by separation of variables).

### 8.9.3 Calculation of Transport Coefficients

We will henceforth assume that sufficient crystalline symmetry exists (*e.g.* cubic symmetry) to render all the transport coefficients multiples of the identity matrix. Under such conditions, we may write $\mathcal{J}_n^{\alpha\beta} = \mathcal{J}_n \, \delta_{\alpha\beta}$ with

$$\mathcal{J}_n = \frac{1}{12\pi^3 \hbar} \int \! d\varepsilon \, \tau(\varepsilon) \, (\varepsilon - \mu)^n \left( -\frac{\partial f^0}{\partial \varepsilon} \right) \int \! dS_\varepsilon \, |\boldsymbol{v}| \; . \tag{8.238}$$

The low-temperature behavior is extracted using the Sommerfeld expansion,

$$\mathcal{I} \equiv \int\limits_{-\infty}^{\infty} \! d\varepsilon \, H(\varepsilon) \left( -\frac{\partial f^0}{\partial \varepsilon} \right) = \pi \mathcal{D} \csc(\pi \mathcal{D}) \, H(\varepsilon) \Big|_{\varepsilon = \mu} \tag{8.239}$$

$$= H(\mu) + \frac{\pi^2}{6} (k_{\rm B} T)^2 \, H''(\mu) + \ldots \tag{8.240}$$

where $\mathcal{D} \equiv k_{\rm B} T \, \frac{\partial}{\partial \varepsilon}$ is a dimensionless differential operator.[15]

Let us now perform some explicit calculations in the case of a parabolic band with an energy-independent scattering time $\tau$. In this case, one readily finds

$$\mathcal{J}_n = \frac{\sigma_0}{e^2} \, \mu^{-3/2} \, \pi \mathcal{D} \csc \pi \mathcal{D} \, \varepsilon^{3/2} \, (\varepsilon - \mu)^n \Big|_{\varepsilon = \mu} \; , \tag{8.241}$$

where $\sigma_0 = n e^2 \tau / m^*$. Thus,

$$\begin{aligned} \mathcal{J}_0 &= \frac{\sigma_0}{e^2} \left[ 1 + \frac{\pi^2}{8} \, \frac{(k_{\rm B} T)^2}{\mu^2} + \ldots \right] \\ \mathcal{J}_1 &= \frac{\sigma_0}{e^2} \, \frac{\pi^2}{2} \, \frac{(k_{\rm B} T)^2}{\mu} + \ldots \\ \mathcal{J}_2 &= \frac{\sigma_0}{e^2} \, \frac{\pi^2}{3} (k_{\rm B} T)^2 + \ldots \; , \end{aligned} \tag{8.242}$$

---

[15] Remember that physically the fixed quantities are temperature and total carrier number density (or charge density, in the case of electron and hole bands), and *not* temperature and chemical potential. An equation of state relating $n$, $\mu$, and $T$ is then inverted to obtain $\mu(n, T)$, so that all results ultimately may be expressed in terms of $n$ and $T$.

from which we obtain the low-$T$ results $\rho = \sigma_0^{-1}$,

$$Q = -\frac{\pi^2}{2} \, \frac{k_B^2 T}{e\,\varepsilon_F} \qquad\qquad \kappa = \frac{\pi^2}{3} \, \frac{n\tau}{m^*} \, k_B^2 T \ , \tag{8.243}$$

and of course $\sqcap = TQ$. The predicted universal ratio

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3} \, (k_B/e)^2 = 2.45 \times 10^{-8} \, \mathrm{V}^2 \, \mathrm{K}^{-2} \ , \tag{8.244}$$

is known as the *Wiedemann-Franz law*. Note also that our result for the thermopower is unambiguously negative. In actuality, several nearly free electron metals have positive low-temperature thermopowers (Cs and Li, for example). What went wrong? We have neglected electron-phonon scattering!

### 8.9.4 Onsager Relations

Transport phenomena are described in general by a set of linear relations,

$$J_i = L_{ik} \, F_k \ , \tag{8.245}$$

where the $\{F_k\}$ are *generalized forces* and the $\{J_i\}$ are *generalized currents*. Moreover, to each force $F_i$ corresponds a unique conjugate current $J_i$, such that the rate of internal entropy production is

$$\dot{S} = \sum_i F_i \, J_i \quad \Longrightarrow \quad F_i = \frac{\partial \dot{S}}{\partial J_i} \ . \tag{8.246}$$

The Onsager relations (also known as *Onsager reciprocity*) state that

$$L_{ik}(\boldsymbol{B}) = \eta_i \, \eta_k \, L_{ki}(-\boldsymbol{B}) \ , \tag{8.247}$$

where $\eta_i$ describes the parity of $J_i$ under time reversal:

$$J_i^T = \eta_i \, J_i \ , \tag{8.248}$$

where $J_i^T$ is the time reverse of $J_i$. To justify the Onsager relations requires a microscopic description of our nonequilibrium system.

The Onsager relations have some remarkable consequences. For example, they require, for $\boldsymbol{B} = 0$, that the thermal conductivity tensor $\kappa_{ij}$ of any crystal must be symmetric, independent of the crystal structure. In general,this result does not follow from considerations of crystalline symmetry. It also requires that for every 'off-diagonal' transport phenomenon, *e.g.* the Seebeck effect, there exists a distinct corresponding phenomenon, *e.g.* the Peltier effect.

For the transport coefficients studied, Onsager reciprocity means that in the presence of an external magnetic field,

$$\rho_{\alpha\beta}(\boldsymbol{B}) = \rho_{\beta\alpha}(-\boldsymbol{B}) \tag{8.249}$$

$$\kappa_{\alpha\beta}(\boldsymbol{B}) = \kappa_{\beta\alpha}(-\boldsymbol{B}) \tag{8.250}$$

$$\sqcap_{\alpha\beta}(\boldsymbol{B}) = T \, Q_{\beta\alpha}(-\boldsymbol{B}) \ . \tag{8.251}$$

Let's consider an isotropic system in a weak magnetic field, and expand the transport coefficients to first order in $\boldsymbol{B}$:

$$\rho_{\alpha\beta}(\boldsymbol{B}) = \rho \, \delta_{\alpha\beta} + \nu \, \epsilon_{\alpha\beta\gamma} \, B^\gamma \tag{8.252}$$

$$\kappa_{\alpha\beta}(\boldsymbol{B}) = \kappa \, \delta_{\alpha\beta} + \varpi \, \epsilon_{\alpha\beta\gamma} \, B^\gamma \tag{8.253}$$

$$Q_{\alpha\beta}(\boldsymbol{B}) = Q \, \delta_{\alpha\beta} + \zeta \, \epsilon_{\alpha\beta\gamma} \, B^\gamma \tag{8.254}$$

$$\sqcap_{\alpha\beta}(\boldsymbol{B}) = \sqcap \, \delta_{\alpha\beta} + \theta \, \epsilon_{\alpha\beta\gamma} B^\gamma \ . \tag{8.255}$$

Onsager reciprocity requires $\sqcap = T\,Q$ and $\theta = T\,\zeta$. We can now write

$$\boldsymbol{\mathcal{E}} = \rho\,\boldsymbol{j} + \nu\,\boldsymbol{j}\times\boldsymbol{B} + Q\,\boldsymbol{\nabla}T + \zeta\,\boldsymbol{\nabla}T\times\boldsymbol{B} \tag{8.256}$$

$$\boldsymbol{j}_q = \sqcap\,\boldsymbol{j} + \theta\,\boldsymbol{j}\times\boldsymbol{B} - \kappa\,\boldsymbol{\nabla}T - \varpi\,\boldsymbol{\nabla}T\times\boldsymbol{B}\ . \tag{8.257}$$

There are several new phenomena lurking:

- Hall effect ($\frac{\partial T}{\partial x} = \frac{\partial T}{\partial y} = j_y = 0$)
  An electrical current $\boldsymbol{j} = j_x\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an electric field $\boldsymbol{\mathcal{E}}$. The Hall coefficient is $R_{\rm H} = \mathcal{E}_y / j_x\,B_z = -\nu$.
- Ettingshausen effect ($\frac{\partial T}{\partial x} = j_y = j_{q,y} = 0$)
  An electrical current $\boldsymbol{j} = j_x\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield a temperature gradient $\frac{\partial T}{\partial y}$. The Ettingshausen coefficient is $P = \frac{\partial T}{\partial y} \big/ j_x\,B_z = -\theta/\kappa$.
- Nernst effect ($j_x = j_y = \frac{\partial T}{\partial y} = 0$)
  A temperature gradient $\boldsymbol{\nabla}T = \frac{\partial T}{\partial x}\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an electric field $\boldsymbol{\mathcal{E}}$. The Nernst coefficient is $\Lambda = \mathcal{E}_y \big/ \frac{\partial T}{\partial x}\,B_z = -\zeta$.
- Righi-Leduc effect ($j_x = j_y = \mathcal{E}_y = 0$)
  A temperature gradient $\boldsymbol{\nabla}T = \frac{\partial T}{\partial x}\,\hat{\boldsymbol{x}}$ and a field $\boldsymbol{B} = B_z\,\hat{\boldsymbol{z}}$ yield an orthogonal temperature gradient $\frac{\partial T}{\partial y}$. The Righi-Leduc coefficient is $\mathcal{L} = \frac{\partial T}{\partial y} \big/ \frac{\partial T}{\partial x} B_z = \zeta/Q$.

## 8.10 Stochastic Processes

A *stochastic process* is one which is partially random, *i.e.* it is not wholly deterministic. Typically the randomness is due to phenomena at the microscale, such as the effect of fluid molecules on a small particle, such as a piece of dust in the air. The resulting motion (called *Brownian motion* in the case of particles moving in a fluid) can be described only in a statistical sense. That is, the full motion of the system is a *functional* of one or more independent random variables. The motion is then described by its averages with respect to the various random distributions.

### 8.10.1 Langevin equation and Brownian motion

Consider a particle of mass $M$ subjected to dissipative and random forcing. We'll examine this system in one dimension to gain an understanding of the essential physics. We write

$$\dot{p} + \gamma p = F + \eta(t)\ . \tag{8.258}$$

Here, $\gamma$ is the damping rate due to friction, $F$ is a constant external force, and $\eta(t)$ is a *stochastic random force*. This equation, known as the Langevin equation, describes a ballistic particle being buffeted by random forcing events. Think of a particle of dust as it moves in the atmosphere; $F$ would then represent the external force due to gravity and $\eta(t)$ the random forcing due to interaction with the air molecules. For a sphere of radius $a$ moving with velocity $\boldsymbol{v}$ in a fluid, the *Stokes drag* is given by $\boldsymbol{F}_{\rm drag} = -6\pi\eta a\boldsymbol{v}$, where $a$ is the radius. Thus,

$$\gamma_{\rm Stokes} = \frac{6\pi\eta a}{M}\ , \tag{8.259}$$

where $M$ is the mass of the particle. It is illustrative to compute $\gamma$ in some setting. Consider a micron sized droplet ($a = 10^{-4}$ cm) of some liquid of density $\rho \sim 1.0\,{\rm g/cm^3}$ moving in air at $T = 20^\circ$ C. The viscosity of air is

$\eta = 1.8 \times 10^{-4}\,\mathrm{g/cm\cdot s}$ at this temperature[16]. If the droplet density is constant, then $\gamma = 9\eta/2\rho a^2 = 8.1 \times 10^4\,\mathrm{s}^{-1}$, hence the time scale for viscous relaxation of the particle is $\tau = \gamma^{-1} = 12\,\mu\mathrm{s}$. We should stress that the viscous damping on the particle is of course due to the fluid molecules, in some average 'coarse-grained' sense. The random component to the force $\eta(t)$ would then represent the fluctuations with respect to this average.

We can easily integrate this equation:

$$\begin{aligned}\frac{d}{dt}\big(p\,e^{\gamma t}\big) &= F\,e^{\gamma t} + \eta(t)\,e^{\gamma t}\\ p(t) &= p(0)\,e^{-\gamma t} + \frac{F}{\gamma}\big(1-e^{-\gamma t}\big) + \int\limits_0^t \!ds\;\eta(s)\,e^{\gamma(s-t)}\end{aligned} \tag{8.260}$$

Note that $p(t)$ is indeed a functional of the random function $\eta(t)$. We can therefore only compute averages in order to describe the motion of the system.

The first average we will compute is that of $p$ itself. In so doing, we assume that $\eta(t)$ has zero mean: $\langle\eta(t)\rangle = 0$. Then

$$\langle p(t)\rangle = p(0)\,e^{-\gamma t} + \frac{F}{\gamma}\big(1-e^{-\gamma t}\big)\ . \tag{8.261}$$

On the time scale $\gamma^{-1}$, the initial conditions $p(0)$ are effectively forgotten, and asymptotically for $t \gg \gamma^{-1}$ we have $\langle p(t)\rangle \to F/\gamma$, which is the terminal momentum.

Next, consider

$$\langle p^2(t)\rangle = \langle p(t)\rangle^2 + \int\limits_0^t \!ds_1\!\int\limits_0^t \!ds_2\; e^{\gamma(s_1-t)}\,e^{\gamma(s_2-t)}\,\langle\eta(s_1)\,\eta(s_2)\rangle\ . \tag{8.262}$$

We now need to know the two-time correlator $\langle\eta(s_1)\,\eta(s_2)\rangle$. We assume that the correlator is a function only of the time difference $\Delta s = s_1 - s_2$, so that the random force $\eta(s)$ satisfies

$$\langle\eta(s)\rangle = 0 \tag{8.263}$$

$$\langle\eta(s_1)\,\eta(s_2)\rangle = \phi(s_1-s_2)\ . \tag{8.264}$$

The function $\phi(s)$ is the *autocorrelation function* of the random force. A macroscopic object moving in a fluid is constantly buffeted by fluid particles over its entire perimeter. These different fluid particles are almost completely uncorrelated, hence $\phi(s)$ is basically nonzero except on a very small time scale $\tau_\phi$, which is the time a single fluid particle spends interacting with the object. We can take $\tau_\phi \to 0$ and approximate

$$\phi(s) \approx \varGamma\,\delta(s)\ . \tag{8.265}$$

We shall determine the value of $\varGamma$ from equilibrium thermodynamic considerations below.

With this form for $\phi(s)$, we can easily calculate the equal time momentum autocorrelation:

$$\begin{aligned}\langle p^2(t)\rangle &= \langle p(t)\rangle^2 + \varGamma\int\limits_0^t \!ds\; e^{2\gamma(s-t)}\\ &= \langle p(t)\rangle^2 + \frac{\varGamma}{2\gamma}\big(1-e^{-2\gamma t}\big)\ .\end{aligned} \tag{8.266}$$

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[16] The cgs unit of viscosity is the *Poise* (P). $1\,\mathrm{P} = 1\,\mathrm{g/cm\cdot s}$.

Consider the case where $F = 0$ and the limit $t \gg \gamma^{-1}$. We demand that the object thermalize at temperature $T$. Thus, we impose the condition

$$\bigg\langle \frac{p^2(t)}{2M} \bigg\rangle = \tfrac{1}{2}k_{\rm B}T \qquad \Longrightarrow \qquad \varGamma = 2\gamma M k_{\rm B}T \quad , \tag{8.267}$$

where $M$ is the particle's mass. This determines the value of $\varGamma$.

We can now compute the general momentum autocorrelator:

$$\begin{aligned}\big\langle p(t)\, p(t')\big\rangle - \big\langle p(t)\big\rangle\big\langle p(t')\big\rangle &= \int\limits_0^t\!ds \int\limits_0^{t'}\!ds'\; e^{\gamma(s-t)}\, e^{\gamma(s'-t')}\, \big\langle \eta(s)\, \eta(s')\big\rangle \\ &= M k_{\rm B}T\, e^{-\gamma|t-t'|} \qquad (t, t' \to \infty \;,\; |t-t'| \text{ finite}) \;. \end{aligned}\tag{8.268}$$

The full expressions for this and subsequent expressions, including subleading terms, are contained in an appendix, §8.14.

Let's now compute the position $x(t)$. We find

$$x(t) = \big\langle x(t)\big\rangle + \frac{1}{M}\int\limits_0^t\!ds \int\limits_0^s\!ds_1\; \eta(s_1)\, e^{\gamma(s_1-s)} \;, \tag{8.269}$$

where

$$\big\langle x(t)\big\rangle = x(0) + \frac{Ft}{\gamma M} + \frac{1}{\gamma}\bigg(v(0) - \frac{F}{\gamma M}\bigg)\big(1 - e^{-\gamma t}\big) \;. \tag{8.270}$$

Note that for $\gamma t \ll 1$ we have $\big\langle x(t)\big\rangle = x(0) + v(0)\, t + \frac{1}{2}M^{-1}Ft^2 + \mathcal{O}(t^3)$, as is appropriate for ballistic particles moving under the influence of a constant force. This long time limit of course agrees with our earlier evaluation for the terminal velocity, $v_\infty = \big\langle p(\infty)\big\rangle/M = F/\gamma M$. We next compute the position autocorrelation:

$$\begin{aligned}\big\langle x(t)\, x(t')\big\rangle - \big\langle x(t)\big\rangle\big\langle x(t')\big\rangle &= \frac{1}{M^2}\int\limits_0^t\!ds \int\limits_0^{t'}\!ds'\; e^{-\gamma(s+s')} \int\limits_0^s\!ds_1 \int\limits_0^{s'}\!ds_1'\; e^{\gamma(s_1+s_2)}\, \big\langle \eta(s_1)\, \eta(s_2)\big\rangle \\ &= \frac{2k_{\rm B}T}{\gamma M}\,\mathsf{min}(t,t') + \mathcal{O}(1) \;.\end{aligned}$$

In particular, the equal time autocorrelator is

$$\big\langle x^2(t)\big\rangle - \big\langle x(t)\big\rangle^2 = \frac{2k_{\rm B}T\, t}{\gamma M} \equiv 2D\, t \;, \tag{8.271}$$

at long times, up to terms of order unity. Here,

$$D = \frac{k_{\rm B}T}{\gamma M} \tag{8.272}$$

is the *diffusion constant*. For a liquid droplet of radius $a = 1\,\mu{\rm m}$ moving in air at $T = 293\,{\rm K}$, for which $\eta = 1.8 \times 10^{-4}\,{\rm P}$, we have

$$D = \frac{k_{\rm B}T}{6\pi\eta a} = \frac{(1.38 \times 10^{-16}\,{\rm erg/K})\,(293\,{\rm K})}{6\pi\,(1.8 \times 10^{-4}\,{\rm P})\,(10^{-4}\,{\rm cm})} = 1.19 \times 10^{-7}\,{\rm cm}^2/{\rm s} \;. \tag{8.273}$$

This result presumes that the droplet is large enough compared to the intermolecular distance in the fluid that one can adopt a continuum approach and use the Navier-Stokes equations, and then assuming a laminar flow.

If we consider molecular diffusion, the situation is quite a bit different. As we shall derive below in §8.10.3, the molecular diffusion constant is $D = \ell^2/2\tau$, where $\ell$ is the mean free path and $\tau$ is the collision time. As we found in eqn. 8.91, the mean free path $\ell$, collision time $\tau$, number density $n$, and total scattering cross section $\sigma$ are related by

$$\ell = \bar{v}\tau = \frac{1}{\sqrt{2}\,n\sigma} \ , \tag{8.274}$$

where $\bar{v} = \sqrt{8k_{\rm B}T/\pi m}$ is the average particle speed. Approximating the particles as hard spheres, we have $\sigma = 4\pi a^2$, where $a$ is the hard sphere radius. At $T = 293\,{\rm K}$, and $p = 1\,{\rm atm}$, we have $n = p/k_{\rm B}T = 2.51 \times 10^{19}\,{\rm cm}^{-3}$. Since air is predominantly composed of $N_2$ molecules, we take $a = 1.90 \times 10^{-8}\,$cm and $m = 28.0\,{\rm amu} = 4.65 \times 10^{-23}\,$g, which are appropriate for $N_2$. We find an average speed of $\bar{v} = 471\,{\rm m/s}$ and a mean free path of $\ell = 6.21 \times 10^{-6}\,$cm. Thus, $D = \frac{1}{2}\ell\bar{v} = 0.146\,{\rm cm}^2/{\rm s}$. Though much larger than the diffusion constant for large droplets, this is still too small to explain common experiences. Suppose we set the characteristic distance scale at $d = 10\,{\rm cm}$ and we ask how much time a point source would take to diffuse out to this radius. The answer is $\Delta t = d^2/2D = 343\,{\rm s}$, which is between five and six minutes. Yet if someone in the next seat emits a foul odor, your sense the offending emission in on the order of a second. What this tells us is that diffusion isn't the only transport process involved in these and like phenomena. More important are *convection* currents which distribute the scent much more rapidly.

### 8.10.2 Langevin equation for a particle in a harmonic well

Consider next the equation

$$M\ddot{X} + \gamma M\dot{X} + M\omega_0^2 X = F_0 + \eta(t) \ , \tag{8.275}$$

where $F_0$ is a constant force. We write $X = \frac{F_0}{M\omega_0^2} + x$ and measure $x$ relative to the potential minimum, yielding

$$\ddot{x} + \gamma\,\dot{x} + \omega_0^2\,x = \frac{1}{M}\,\eta(t) \ . \tag{8.276}$$

At this point there are several ways to proceed.

Perhaps the most straightforward is by use of the Laplace transform. Recall:

$$\hat{x}(\nu) = \int\limits_0^\infty \! dt\, e^{-\nu t}\,\eta(\nu) \tag{8.277}$$

$$x(t) = \int\limits_{\mathcal{C}} \frac{d\nu}{2\pi i}\, e^{+\nu t}\,\hat{x}(\nu) \ , \tag{8.278}$$

where the contour $\mathcal{C}$ proceeds from $a - i\infty$ to $a + i\infty$ such that all poles of the integrand lie to the left of $\mathcal{C}$. We then have

$$\begin{aligned} \frac{1}{M}\int\limits_0^\infty \! dt\, e^{-\nu t}\,\eta(t) &= \frac{1}{M}\int\limits_0^\infty \! dt\, e^{-\nu t}\Big(\ddot{x} + \gamma\,\dot{x} + \omega_0^2\,x\Big) \\ &= -(\nu + \gamma)\,x(0) - \dot{x}(0) + \big(\nu^2 + \gamma\nu + \omega_0^2\big)\,\hat{x}(\nu) \ . \end{aligned} \tag{8.279}$$

Thus, we have

$$\hat{x}(\nu) = \frac{(\nu + \gamma)\,x(0) + \dot{x}(0)}{\nu^2 + \gamma\nu + \omega_0^2} + \frac{1}{M} \cdot \frac{1}{\nu^2 + \gamma\nu + \omega_0^2} \int\limits_0^\infty \! dt\, e^{-\nu t}\,\eta(t) \ . \tag{8.280}$$

Now we may write

$$\nu^2 + \gamma\nu + \omega_0^2 = (\nu - \nu_+)(\nu - \nu_-) \ , \tag{8.281}$$

where

$$\nu_\pm = -\tfrac{1}{2}\gamma \pm \sqrt{\tfrac{1}{4}\gamma^2 - \omega_0^2} \ . \tag{8.282}$$

Note that $\mathsf{Re}\,(\nu_\pm) \le 0$ and that $\gamma + \nu_\pm = -\nu_\mp$.

Performing the inverse Laplace transform, we obtain

$$\begin{aligned} x(t) = \frac{x(0)}{\nu_+ - \nu_-}\Big(\nu_+\, e^{\nu_- t} - \nu_-\, e^{\nu_+ t}\Big) + \frac{\dot x(0)}{\nu_+ - \nu_-}\Big(e^{\nu_+ t} - e^{\nu_- t}\Big) \\ + \int\limits_0^\infty \! ds\, K(t-s)\, \eta(s) \ , \end{aligned} \tag{8.283}$$

where

$$K(t-s) = \frac{\Theta(t-s)}{M\,(\nu_+ - \nu_-)}\Big(e^{\nu_+ (t-s)} - e^{\nu_- (t-s)}\Big) \tag{8.284}$$

is the *response kernel* and $\Theta(t-s)$ is the step function which is unity for $t > s$ and zero otherwise. The response is *causal*, *i.e.* $x(t)$ depends on $\eta(s)$ for all previous times $s < t$, but not for future times $s > t$. Note that $K(\tau)$ decays exponentially for $\tau \to \infty$, if $\mathsf{Re}(\nu_\pm) < 0$. The marginal case where $\omega_0 = 0$ and $\nu_+ = 0$ corresponds to the diffusion calculation we performed in the previous section.

### 8.10.3 Discrete random walk

Consider an object moving on a one-dimensional lattice in such a way that every time step it moves either one unit to the right or left, at random. If the lattice spacing is $\ell$, then after $n$ time steps the position will be

$$x_n = \ell \sum_{j=1}^n \sigma_j \ , \tag{8.285}$$

where

$$\sigma_j = \begin{cases} +1 & \text{if motion is one unit to right at time step } j \\ -1 & \text{if motion is one unit to left at time step } j \ . \end{cases} \tag{8.286}$$

Clearly $\langle \sigma_j \rangle = 0$, so $\langle x_n \rangle = 0$. Now let us compute

$$\big\langle x_n^2 \big\rangle = \ell^2 \sum_{j=1}^n \sum_{j'=1}^n \langle \sigma_j \sigma_{j'} \rangle = n\ell^2 \ , \tag{8.287}$$

where we invoke

$$\big\langle \sigma_j \sigma_{j'} \big\rangle = \delta_{jj'} \ . \tag{8.288}$$

If the length of each time step is $\tau$, then we have, with $t = n\tau$,

$$\big\langle x^2(t) \big\rangle = \frac{\ell^2}{\tau}\, t \ , \tag{8.289}$$

and we identify the diffusion constant

$$D = \frac{\ell^2}{2\tau} \ . \tag{8.290}$$

Suppose, however, the random walk is *biased*, so that the probability for each independent step is given by

$$P(\sigma) = p\,\delta_{\sigma,1} + q\,\delta_{\sigma,-1} \ , \tag{8.291}$$

where $p + q = 1$. Then

$$\langle \sigma_j \rangle = p - q = 2p - 1 \tag{8.292}$$

and

$$\begin{aligned} \langle \sigma_j \sigma_{j'} \rangle &= (p-q)^2 \, \big(1 - \delta_{jj'}\big) + \delta_{jj'} \\ &= (2p-1)^2 + 4\,p\,(1-p)\,\delta_{jj'} \ . \end{aligned} \tag{8.293}$$

Then

$$\langle x_n \rangle = (2p-1)\,\ell n \tag{8.294}$$

$$\big\langle x_n^2 \big\rangle - \big\langle x_n \big\rangle^2 = 4\,p\,(1-p)\,\ell^2 n \ . \tag{8.295}$$

### 8.10.4 Fokker-Planck equation

Suppose $x(t)$ is a stochastic variable. We define the quantity

$$\delta x(t) \equiv x(t+\delta t) - x(t) \ , \tag{8.296}$$

and we assume

$$\big\langle \delta x(t) \big\rangle = F_1\big(x(t)\big)\,\delta t \tag{8.297}$$

$$\big\langle \big[\delta x(t)\big]^2 \big\rangle = F_2\big(x(t)\big)\,\delta t \tag{8.298}$$

but $\big\langle \big[\delta x(t)\big]^n \big\rangle = \mathcal{O}\big((\delta t)^2\big)$ for $n > 2$. The $n = 1$ term is due to *drift* and the $n = 2$ term is due to *diffusion*. Now consider the conditional probability density, $P(x, t \,|\, x_0, t_0)$, defined to be the probability distribution for $x \equiv x(t)$ given that $x(t_0) = x_0$. The conditional probability density satisfies the composition rule,

$$P(x_2, t_2 \,|\, x_0, t_0) = \int\limits_{-\infty}^{\infty}\! dx_1 \, P(x_2, t_2 \,|\, x_1, t_1)\, P(x_1, t_1 \,|\, x_0, t_0) \ , \tag{8.299}$$

for any value of $t_1$. This is also known as the *Chapman-Kolmogorov equation*. In words, what it says is that the probability density for a particle being at $x_2$ at time $t_2$, given that it was at $x_0$ at time $t_0$, is given by the product of the probability density for being at $x_2$ at time $t_2$ given that it was at $x_1$ at $t_1$, multiplied by that for being at $x_1$ at $t_1$ given it was at $x_0$ at $t_0$, integrated over $x_1$. This should be intuitively obvious, since if we pick any time $t_1 \in [t_0, t_2]$, then the particle had to be *somewhere* at that time. Indeed, one wonders how Chapman and Kolmogorov got their names attached to a result that is so obvious. At any rate, a picture is worth a thousand words: see fig. 8.9.

Proceeding, we may write

$$P(x, t+\delta t \,|\, x_0, t_0) = \int\limits_{-\infty}^{\infty}\! dx' \, P(x, t+\delta t \,|\, x', t)\, P(x', t \,|\, x_0, t_0) \ . \tag{8.300}$$

Now

$$\begin{aligned} P(x, t+\delta t \,|\, x', t) &= \big\langle \delta\big(x - \delta x(t) - x'\big) \big\rangle \\ &= \bigg\{ 1 + \big\langle \delta x(t) \big\rangle \frac{d}{dx'} + \tfrac{1}{2} \big\langle \big[\delta x(t)\big]^2 \big\rangle \frac{d^2}{dx'^2} + \ldots \bigg\} \, \delta(x - x') \\ &= \delta(x - x') + F_1(x') \, \frac{d\,\delta(x - x')}{dx'} \, \delta t + \tfrac{1}{2} F_2(x') \, \frac{d^2 \delta(x - x')}{dx'^2} \, \delta t + \mathcal{O}\big((\delta t)^2\big) \ , \end{aligned} \tag{8.301}$$

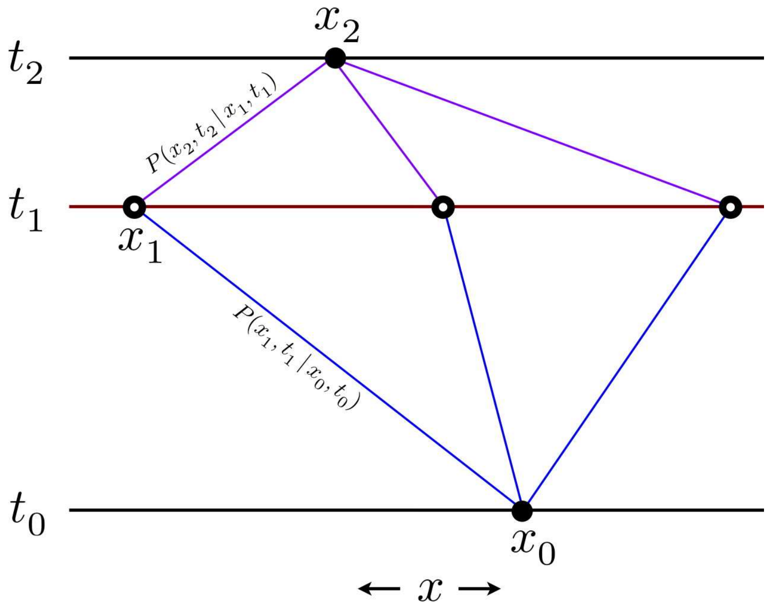

Figure 8.9: Interpretive sketch of the mathematics behind the Chapman-Kolmogorov equation.

where the average is over the random variables. We now insert this result into eqn. 8.300, integrate by parts, divide by $\delta t$, and then take the limit $\delta t \to 0$. The result is the Fokker-Planck equation,

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\big[F_1(x)\,P(x,t)\big] + \frac{1}{2}\,\frac{\partial^2}{\partial x^2}\big[F_2(x)\,P(x,t)\big] \ . \tag{8.302}$$

### 8.10.5 Brownian motion redux

Let's apply our Fokker-Planck equation to a description of Brownian motion. From our earlier results, we have

$$F_1(x) = \frac{F}{\gamma M} \qquad , \qquad F_2(x) = 2D \ . \tag{8.303}$$

A formal proof of these results is left as an exercise for the reader. The Fokker-Planck equation is then

$$\frac{\partial P}{\partial t} = -u\,\frac{\partial P}{\partial x} + D\,\frac{\partial^2 P}{\partial x^2} \ , \tag{8.304}$$

where $u = F/\gamma M$ is the average terminal velocity. If we make a Galilean transformation and define

$$y = x - ut \qquad , \qquad s = t \tag{8.305}$$

then our Fokker-Planck equation takes the form

$$\frac{\partial P}{\partial s} = D\,\frac{\partial^2 P}{\partial y^2} \ . \tag{8.306}$$

This is known as the *diffusion equation*. Eqn. 8.304 is also a diffusion equation, rendered in a moving frame.

While the Galilean transformation is illuminating, we can easily solve eqn. 8.304 without it. Let's take a look at this equation after Fourier transforming from $x$ to $q$:

$$P(x,t) = \int\limits_{-\infty}^{\infty} \frac{dq}{2\pi}\, e^{iqx}\, \hat{P}(q,t) \tag{8.307}$$

$$\hat{P}(q,t) = \int\limits_{-\infty}^{\infty} dx\, e^{-iqx}\, P(x,t)\ . \tag{8.308}$$

Then as should be well known to you by now, we can replace the operator $\frac{\partial}{\partial x}$ with multiplication by $iq$, resulting in

$$\frac{\partial}{\partial t}\,\hat{P}(q,t) = -(Dq^2 + iqu)\,\hat{P}(q,t)\ , \tag{8.309}$$

with solution

$$\hat{P}(q,t) = e^{-Dq^2 t}\, e^{-iqut}\,\hat{P}(q,0)\ . \tag{8.310}$$

We now apply the inverse transform to get back to $x$-space:

$$\begin{aligned} P(x,t) &= \int\limits_{-\infty}^{\infty} \frac{dq}{2\pi}\, e^{iqx}\, e^{-Dq^2 t}\, e^{-iqut} \int\limits_{-\infty}^{\infty} dx'\, e^{-iqx'}\, P(x',0) \\ &= \int\limits_{-\infty}^{\infty} dx'\, P(x',0) \int\limits_{-\infty}^{\infty} \frac{dq}{2\pi}\, e^{-Dq^2 t}\, e^{iq(x-ut-x')} \\ &= \int\limits_{-\infty}^{\infty} dx'\, K(x-x',t)\, P(x',0)\ , \end{aligned} \tag{8.311}$$

where

$$K(x,t) = \frac{1}{\sqrt{4\pi D t}}\, e^{-(x-ut)^2/4Dt} \tag{8.312}$$

is the *diffusion kernel*. We now have a recipe for obtaining $P(x,t)$ given the initial conditions $P(x,0)$. If $P(x,0) = \delta(x)$, describing a particle confined to an infinitesimal region about the origin, then $P(x,t) = K(x,t)$ is the probability distribution for finding the particle at $x$ at time $t$. There are two aspects to $K(x,t)$ which merit comment. The first is that the center of the distribution moves with velocity $u$. This is due to the presence of the external force. The second is that the standard deviation $\sigma = \sqrt{2Dt}$ is increasing in time, so the distribution is not only shifting its center but it is also getting broader as time evolves. This movement of the center and broadening are what we have called *drift* and *diffusion*, respectively.

### 8.10.6 Master Equation

Another way to model stochastic processes is via the *master equation*, which was discussed in chapter 3. Recall that if $P_i(t)$ is the probability for a system to be in state $|\, i\,\rangle$ at time $t$ and $W_{ij}$ is the transition rate from state $|\, j\,\rangle$ to state $|\, i\,\rangle$, then

$$\frac{dP_i}{dt} = \sum_j \big( W_{ij} P_j - W_{ji} P_i \big)\ . \tag{8.313}$$

Consider now a model in which the states $|\, n\,\rangle$ are labeled by nonnegative integers. Let $\alpha_n$ denote the rate of transitions from $|\, n\,\rangle \to |\, n+1\,\rangle$ and let $\beta_n$ denote the rate of transitions from $|\, n\,\rangle \to |\, n-1\,\rangle$. The master equation then takes the form[17]

$$\frac{dP_n}{dt} = \alpha_{n-1} P_{n-1} + \beta_{n+1} P_{n+1} - \big(\alpha_n + \beta_n\big) P_n \ . \tag{8.314}$$

Let us assume we can write $\alpha_n = K\bar{\alpha}(n/K)$ and $\beta_n = K\bar{\beta}(n/K)$, where $K \gg 1$. We assume the distribution $P_n(t)$ has a time-dependent maximum at $n = K\phi(t)$ and a width proportional to $\sqrt{K}$. We expand relative to this maximum, writing

$$n \equiv K\phi(t) + \sqrt{K}\,\xi \ , \tag{8.315}$$

and we define

$$P_n(t) \equiv \varPi(\xi, t) \ . \tag{8.316}$$

We now rewrite the master equation in eqn. 8.314 in terms of $\varPi(\xi,t)$. Since $n$ is an independent variable, we set

$$dn = K\dot{\phi}\,dt + \sqrt{K}\,d\xi \quad \Rightarrow \quad d\xi\big|_n = -\sqrt{K}\,\dot{\phi}\,dt \ . \tag{8.317}$$

Therefore

$$\frac{dP_n}{dt} = -\sqrt{K}\,\dot{\phi}\,\frac{\partial \varPi}{\partial \xi} + \frac{\partial \varPi}{\partial t} \ . \tag{8.318}$$

Next, we write, for any function $f_n$ ,

$$\begin{aligned} f_n &= K f\big(\phi + K^{-1/2}\xi\big) \\ &= K f(\phi) + K^{1/2}\,\xi\, f'(\phi) + \tfrac{1}{2}\,\xi^2\, f''(\phi) + \ldots \ . \end{aligned} \tag{8.319}$$

Similarly,

$$\begin{aligned} f_{n\pm 1} &= K f\big(\phi + K^{-1/2}\xi \pm K^{-1}\big) \\ &= K f(\phi) + K^{1/2}\,\xi\, f'(\phi) \pm f'(\phi) + \tfrac{1}{2}\,\xi^2\, f''(\phi) + \ldots \ . \end{aligned} \tag{8.320}$$

Dividing both sides of eqn. 8.314 by $\sqrt{K}$, we have

$$-\frac{\partial \varPi}{\partial \xi}\,\dot{\phi} + K^{-1/2}\,\frac{\partial \varPi}{\partial t} = (\bar{\beta} - \bar{\alpha})\,\frac{\partial \varPi}{\partial \xi} + K^{-1/2}\bigg\{(\bar{\beta}' - \bar{\alpha}')\,\xi\,\frac{\partial \varPi}{\partial \xi} + \tfrac{1}{2}(\bar{\alpha} + \bar{\beta})\,\frac{\partial^2 \varPi}{\partial \xi^2} + (\bar{\beta}' - \bar{\alpha}')\varPi\bigg\} + \ldots \ . \tag{8.321}$$

Equating terms of order $K^0$ yields the equation

$$\dot{\phi} = \bar{\alpha}(\phi) - \bar{\beta}(\phi) \ . \tag{8.322}$$

Equating terms of order $K^{-1/2}$ yields the Fokker-Planck equation,

$$\frac{\partial \varPi}{\partial t} = \big(\bar{\beta} - \bar{\alpha}\big)\,\frac{\partial}{\partial \xi}\,\big(\xi\,\varPi\big) + \tfrac{1}{2}\big(\bar{\alpha} + \bar{\beta}\big)\,\frac{\partial^2 \varPhi}{\partial \xi^2} \ , \tag{8.323}$$

where $\bar{\alpha} = \bar{\alpha}\big(\phi(t)\big)$ and $\bar{\beta} = \bar{\beta}\big(\phi(t)\big)$ are to be regarded as functions of $t$, *i.e.* $\bar{\alpha}(t)$ and $\bar{\beta}(t)$.

If in the limit $t \to \infty$, eqn. 8.322 evolves to a stable fixed point $\phi^*$, then the stationary solution of the Fokker-Planck eqn. 8.323, $\varPi_{\text{eq}}(\xi) = \varPi(\xi, t=\infty)$ must satisfy

$$\big(\bar{\beta} - \bar{\alpha}\big)\,\frac{\partial}{\partial \xi}\,\big(\xi\,\varPi_{\text{eq}}\big) + \tfrac{1}{2}\big(\bar{\alpha} + \bar{\beta}\big)\,\frac{\partial^2 \varPi_{\text{eq}}}{\partial \xi^2} = 0 \quad \Rightarrow \quad \varPi_{\text{eq}}(\xi) = \frac{1}{\sqrt{2\pi\sigma^2}}\,e^{-\xi^2/2\sigma^2} \ , \tag{8.324}$$

where

$$\sigma^2 = \frac{\beta(\phi^*) + \alpha(\phi^*)}{\beta(\phi^*) - \alpha(\phi^*)} \ . \tag{8.325}$$

---

[17] We further demand $\beta_{n=0} = 0$ and $P_{-1}(t) = 0$ at all times.

## 8.11 Appendix I : Boltzmann Equation and Collisional Invariants

*Problem* : The linearized Boltzmann operator $L\psi$ is a complicated functional. Suppose we replace $L$ by $\mathcal{L}$, where

$$
\begin{aligned}
\mathcal{L}\psi = -\gamma\,\psi(\boldsymbol{v},t) + \gamma\bigg(\frac{m}{2\pi k_{\rm B}T}\bigg)^{3/2} &\int\! d^3\!u \, \exp\bigg(-\frac{m\boldsymbol{u}^2}{2k_{\rm B}T}\bigg) \\
\times \bigg\{ 1 + \frac{m}{k_{\rm B}T}\,\boldsymbol{u}\cdot\boldsymbol{v} + \frac{2}{3}\bigg(\frac{m\boldsymbol{u}^2}{2k_{\rm B}T} - \frac{3}{2}\bigg)&\bigg(\frac{m\boldsymbol{v}^2}{2k_{\rm B}T} - \frac{3}{2}\bigg)\bigg\}\,\psi(\boldsymbol{u},t)\ .
\end{aligned}
\tag{8.326}
$$

Show that $\mathcal{L}$ shares all the important properties of $L$. What is the meaning of $\gamma$? Expand $\psi(\boldsymbol{v},t)$ in spherical harmonics and Sonine polynomials,

$$
\psi(\boldsymbol{v},t) = \sum_{r\ell m} a_{r\ell m}(t)\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y^\ell_m(\hat{\boldsymbol{n}}),
\tag{8.327}
$$

with $x = mv^2/2k_{\rm B}T$, and thus express the action of the linearized Boltzmann operator algebraically on the expansion coefficients $a_{r\ell m}(t)$.

The Sonine polynomials $S^n_\alpha(x)$ are a complete, orthogonal set which are convenient to use in the calculation of transport coefficients. They are defined as

$$
S^n_\alpha(x) = \sum_{m=0}^{n} \frac{\Gamma(\alpha+n+1)\,(-x)^m}{\Gamma(\alpha+m+1)\,(n-m)!\,m!}\ ,
\tag{8.328}
$$

and satisfy the generalized orthogonality relation

$$
\int\limits_0^\infty\! dx\, e^{-x}\, x^\alpha\, S^n_\alpha(x)\, S^{n'}_\alpha(x) = \frac{\Gamma(\alpha+n+1)}{n!}\,\delta_{nn'}\ .
\tag{8.329}
$$

*Solution* : The 'important properties' of $L$ are that it annihilate the five collisional invariants, *i.e.* $1$, $\boldsymbol{v}$, and $v^2$, and that all other eigenvalues are *negative*. That this is true for $\mathcal{L}$ can be verified by an explicit calculation.

Plugging the conveniently parameterized form of $\psi(\boldsymbol{v},t)$ into $\mathcal{L}$, we have

$$
\begin{aligned}
\mathcal{L}\psi = -\gamma \sum_{r\ell m} a_{r\ell m}(t)\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y^\ell_m(\hat{\boldsymbol{n}}) \ + \ &\frac{\gamma}{2\pi^{3/2}} \sum_{r\ell m} a_{r\ell m}(t) \int\limits_0^\infty\! dx_1\, x_1^{1/2}\, e^{-x_1} \\
\times \int\! d\hat{\boldsymbol{n}}_1 \Big[ 1 + 2\,x^{1/2} x_1^{1/2}\, \hat{\boldsymbol{n}}\!\cdot\!\hat{\boldsymbol{n}}_1 + \tfrac{2}{3}\big(x-\tfrac{3}{2}\big)\big(x_1 - \tfrac{3}{2}\big)\Big]&\, S^r_{\ell+\frac{1}{2}}(x_1)\, x_1^{\ell/2}\, Y^\ell_m(\hat{\boldsymbol{n}}_1)\ ,
\end{aligned}
\tag{8.330}
$$

where we've used

$$
u = \sqrt{\frac{2k_{\rm B}T}{m}}\, x_1^{1/2} \qquad , \qquad du = \sqrt{\frac{k_{\rm B}T}{2m}}\, x_1^{-1/2}\, dx_1\ .
\tag{8.331}
$$

Now recall $Y^0_0(\hat{\boldsymbol{n}}) = \frac{1}{\sqrt{4\pi}}$ and

$$
Y^1_1(\hat{\boldsymbol{n}}) = -\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{i\varphi} \qquad\qquad Y^1_0(\hat{\boldsymbol{n}}) = \sqrt{\frac{3}{4\pi}}\,\cos\theta \qquad\qquad Y^1_{-1}(\hat{\boldsymbol{n}}) = +\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{-i\varphi}
$$

$$
S^0_{1/2}(x) = 1 \qquad\qquad S^0_{3/2}(x) = 1 \qquad\qquad S^1_{1/2}(x) = \tfrac{3}{2} - x\ ,
$$

which allows us to write

$$1 = 4\pi\, Y_0^0(\hat{\boldsymbol{n}})\, Y_0^{0\,*}(\hat{\boldsymbol{n}}_1) \tag{8.332}$$

$$\hat{\boldsymbol{n}}\cdot\hat{\boldsymbol{n}}_1 = \frac{4\pi}{3}\Big[\, Y_0^1(\hat{\boldsymbol{n}})\, Y_0^{1\,*}(\hat{\boldsymbol{n}}_1) + Y_1^1(\hat{\boldsymbol{n}})\, Y_1^{1\,*}(\hat{\boldsymbol{n}}_1) + Y_{-1}^1(\hat{\boldsymbol{n}})\, {Y_{-1}^1}^*(\hat{\boldsymbol{n}}_1)\,\Big]\ . \tag{8.333}$$

We can do the integrals by appealing to the orthogonality relations for the spherical harmonics and Sonine polynomials:

$$\int\! d\hat{\boldsymbol{n}}\, Y_m^\ell(\hat{\boldsymbol{n}})\, {Y_{m'}^{l'}}^*(\hat{\boldsymbol{n}}) = \delta_{ll'}\,\delta_{mm'} \tag{8.334}$$

$$\int\limits_0^\infty\! dx\, e^{-x}\, x^\alpha\, S_\alpha^n(x)\, S_\alpha^{n'}(x) = \frac{\Gamma(n+\alpha+1)}{\Gamma(n+1)}\,\delta_{nn'}\ . \tag{8.335}$$

Integrating first over the direction vector $\hat{\boldsymbol{n}}_1$,

$$\begin{aligned}\mathcal{L}\psi = &-\gamma \sum_{r\ell m} a_{r\ell m}(t)\, S_{\ell+\frac{1}{2}}^r(x)\, x^{\ell/2}\, Y_m^\ell(\hat{\boldsymbol{n}}) \\ &+ \frac{2\gamma}{\sqrt{\pi}} \sum_{r\ell m} a_{r\ell m}(t) \int\limits_0^\infty\! dx_1\, x_1^{1/2}\, e^{-x_1} \int\! d\hat{\boldsymbol{n}}_1 \,\Big[ Y_0^0(\hat{\boldsymbol{n}})\, Y_0^{0\,*}(\hat{\boldsymbol{n}}_1)\, S_{1/2}^0(x)\, S_{1/2}^0(x_1) \\ &\qquad + \tfrac{2}{3}\, x^{1/2} x_1^{1/2} \sum_{m'=-1}^{1} Y_{m'}^1(\hat{\boldsymbol{n}})\, {Y_{m'}^1}^*(\hat{\boldsymbol{n}}_1)\, S_{3/2}^0(x)\, S_{3/2}^0(x_1) \\ &\qquad\quad + \tfrac{2}{3}\, Y_0^0(\hat{\boldsymbol{n}})\, Y_0^{0\,*}(\hat{\boldsymbol{n}}_1)\, S_{1/2}^1(x)\, S_{1/2}^1(x_1)\Big]\, S_{\ell+\frac{1}{2}}^r(x_1)\, x_1^{\ell/2}\, Y_m^\ell(\hat{\boldsymbol{n}}_1)\ ,\end{aligned} \tag{8.336}$$

we obtain the intermediate result

$$\begin{aligned}\mathcal{L}\psi = &-\gamma \sum_{r\ell m} a_{r\ell m}(t)\, S_{\ell+\frac{1}{2}}^r(x)\, x^{\ell/2}\, Y_m^\ell(\hat{\boldsymbol{n}}) \\ &+ \frac{2\gamma}{\sqrt{\pi}} \sum_{r\ell m} a_{r\ell m}(t) \int\limits_0^\infty\! dx_1\, x_1^{1/2}\, e^{-x_1} \Big[ Y_0^0(\hat{\boldsymbol{n}})\, \delta_{l0}\, \delta_{m0}\, S_{1/2}^0(x)\, S_{1/2}^0(x_1) \\ &\qquad + \tfrac{2}{3}\, x^{1/2} x_1^{1/2} \sum_{m'=-1}^{1} Y_{m'}^1(\hat{\boldsymbol{n}})\, \delta_{l1}\, \delta_{mm'}\, S_{3/2}^0(x)\, S_{3/2}^0(x_1) \\ &\qquad\quad + \tfrac{2}{3}\, Y_0^0(\hat{\boldsymbol{n}})\, \delta_{l0}\, \delta_{m0}\, S_{1/2}^1(x)\, S_{1/2}^1(x_1)\Big]\, S_{\ell+\frac{1}{2}}^r(x_1)\, x_1^{1/2}.\end{aligned} \tag{8.337}$$

Appealing now to the orthogonality of the Sonine polynomials, and recalling that

$$\Gamma(\tfrac{1}{2}) = \sqrt{\pi} \qquad , \qquad \Gamma(1) = 1 \qquad , \qquad \Gamma(z+1) = z\,\Gamma(z)\ , \tag{8.338}$$

we integrate over $x_1$. For the first term in brackets, we invoke the orthogonality relation with $n = 0$ and $\alpha = \frac{1}{2}$, giving $\Gamma(\frac{3}{2}) = \frac{1}{2}\sqrt{\pi}$. For the second bracketed term, we have $n = 0$ but $\alpha = \frac{3}{2}$, and we obtain $\Gamma(\frac{5}{2}) = \frac{3}{2}\,\Gamma(\frac{3}{2})$, while the third bracketed term involves leads to $n = 1$ and $\alpha = \frac{1}{2}$, also yielding $\Gamma(\frac{5}{2}) = \frac{3}{2}\,\Gamma(\frac{3}{2})$. Thus, we obtain the simple and pleasing result

$$\mathcal{L}\psi = -\gamma {\sum_{r\ell m}}' a_{r\ell m}(t)\, S_{\ell+\frac{1}{2}}^r(x)\, x^{\ell/2}\, Y_m^\ell(\hat{\boldsymbol{n}}) \tag{8.339}$$

where the prime on the sum indicates that the set

$$\mathrm{CI} = \Big\{(0,0,0)\,, \quad (1,0,0)\,, \quad (0,1,1)\,, \quad (0,1,0)\,, \quad (0,1,-1)\Big\} \tag{8.340}$$

are to be excluded from the sum. But these are just the functions which correspond to the five collisional invariants! Thus, we learn that

$$\psi_{r\ell m}(\boldsymbol{v}) = \mathcal{N}_{r\ell m}\, S^r_{\ell+\frac{1}{2}}(x)\, x^{\ell/2}\, Y^\ell_m(\hat{\boldsymbol{n}}), \tag{8.341}$$

is an eigenfunction of $\mathcal{L}$ with eigenvalue $-\gamma$ if $(r,\ell,m)$ does not correspond to one of the five collisional invariants. In the latter case, the eigenvalue is zero. Thus, the algebraic action of $\mathcal{L}$ on the coefficients $a_{r\ell m}$ is

$$(\mathcal{L}a)_{r\ell m} = \begin{cases} -\gamma\, a_{r\ell m} & \text{if } (r,\ell,m) \notin \mathrm{CI} \\ = 0 & \text{if } (r,\ell,m) \in \mathrm{CI} \end{cases} \tag{8.342}$$

The quantity $\tau = \gamma^{-1}$ is the relaxation time.

It is pretty obvious that $\mathcal{L}$ is self-adjoint, since

$$\begin{aligned}
\langle\, \phi \,|\, \mathcal{L}\psi \,\rangle &\equiv \int\! d^3\!v\, f^0(\boldsymbol{v})\, \phi(\boldsymbol{v})\, \mathcal{L}[\psi(\boldsymbol{v})] \\
&= -\gamma\, n \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} \int\! d^3\!v\, \exp\left(-\frac{m\boldsymbol{v}^2}{2k_\mathrm{B}T}\right) \phi(\boldsymbol{v})\, \psi(\boldsymbol{v}) \\
&\quad + \gamma\, n \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3} \int\! d^3\!v \int\! d^3\!u\, \exp\left(-\frac{m\boldsymbol{u}^2}{2k_\mathrm{B}T}\right) \exp\left(-\frac{m\boldsymbol{v}^2}{2k_\mathrm{B}T}\right) \\
&\qquad \times \phi(\boldsymbol{v}) \left[1 + \frac{m}{k_\mathrm{B}T}\, \boldsymbol{u}\cdot\boldsymbol{v} + \frac{2}{3}\left(\frac{m\boldsymbol{u}^2}{2k_\mathrm{B}T} - \frac{3}{2}\right)\left(\frac{m\boldsymbol{v}^2}{2k_\mathrm{B}T} - \frac{3}{2}\right)\right] \psi(\boldsymbol{u}) \\
&= \langle\, \mathcal{L}\phi \,|\, \psi \,\rangle\,,
\end{aligned} \tag{8.343}$$

where $n$ is the bulk number density and $f^0(\boldsymbol{v})$ is the Maxwellian velocity distribution.

## 8.12 Appendix II : Distributions and Functionals

Let $x \in \mathbb{R}$ be a random variable, and $P(x)$ a probability distribution for $x$. The average of any function $\phi(x)$ is then

$$\big\langle \phi(x) \big\rangle = \int\limits_{-\infty}^{\infty}\! dx\, P(x)\, \phi(x) \bigg/ \int\limits_{-\infty}^{\infty}\! dx\, P(x)\,. \tag{8.344}$$

Let $\eta(t)$ be a random *function* of $t$, with $\eta(t) \in \mathbb{R}$, and let $P\big[\eta(t)\big]$ be the probability distribution *functional* for $\eta(t)$. Then if $\varPhi\big[\eta(t)\big]$ is a functional of $\eta(t)$, the average of $\varPhi$ is given by

$$\int\! D\eta\, P\big[\eta(t)\big]\, \varPhi\big[\eta(t)\big] \bigg/ \int\! D\eta\, P\big[\eta(t)\big] \tag{8.345}$$

The expression $\int\! D\eta\, P[\eta]\, \varPhi[\eta]$ is a *functional integral*. A functional integral is a continuum limit of a multivariable integral. Suppose $\eta(t)$ were defined on a set of $t$ values $t_n = n\tau$. A functional of $\eta(t)$ becomes a multivariable function of the values $\eta_n \equiv \eta(t_n)$. The metric then becomes

$$D\eta \longrightarrow \prod_n d\eta_n\,. \tag{8.346}$$

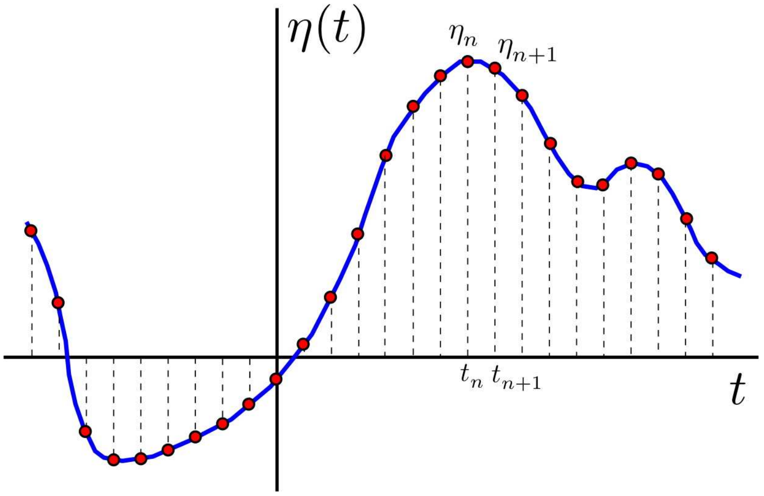

Figure 8.10: Discretization of a continuous function $\eta(t)$. Upon discretization, a functional $\varPhi\big[\eta(t)\big]$ becomes an ordinary multivariable function $\varPhi(\{\eta_j\})$.

In fact, for our purposes we will not need to know any details about the functional measure $D\eta$; we will finesse this delicate issue[18]. Consider the *generating functional*,

$$Z\big[J(t)\big] = \int D\eta\, P[\eta]\, \exp\left(\int\limits_{-\infty}^{\infty} dt\, J(t)\, \eta(t)\right) . \tag{8.347}$$

It is clear that

$$\frac{1}{Z[J]}\, \frac{\delta^n Z[J]}{\delta J(t_1) \cdots \delta J(t_n)}\Bigg|_{J(t)=0} = \big\langle \eta(t_1) \cdots \eta(t_n) \big\rangle . \tag{8.348}$$

The function $J(t)$ is an arbitrary *source function*. We differentiate with respect to it in order to find the $\eta$-field correlators.

Let's compute the generating function for a class of distributions of the Gaussian form,

$$P[\eta] = \exp\left( -\frac{1}{2\varGamma} \int\limits_{-\infty}^{\infty} dt\, \big(\tau^2\, \dot{\eta}^2 + \eta^2\big)\right) \tag{8.349}$$

$$= \exp\left( -\frac{1}{2\varGamma} \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \big(1 + \omega^2 \tau^2\big)\, \big|\hat{\eta}(\omega)\big|^2\right) . \tag{8.350}$$

Then Fourier transforming the source function $J(t)$, it is easy to see that

$$Z[J] = Z[0] \cdot \exp\left( \frac{\varGamma}{2} \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \frac{\big|\hat{J}(\omega)\big|^2}{1 + \omega^2 \tau^2}\right) . \tag{8.351}$$

Note that with $\eta(t) \in \mathbb{R}$ and $J(t) \in \mathbb{R}$ we have $\eta^*(\omega) = \eta(-\omega)$ and $J^*(\omega) = J(-\omega)$. Transforming back to real time,

---

[18] A discussion of measure for functional integrals is found in R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals*.

we have

$$Z[J] = Z[0] \cdot \exp\left(\frac{1}{2}\int\limits_{-\infty}^{\infty}\!dt\int\limits_{-\infty}^{\infty}\!dt'\; J(t)\, G(t-t')\, J(t')\right) , \tag{8.352}$$

where

$$G(s) = \frac{\varGamma}{2\tau}\, e^{-|s|/\tau} \qquad , \qquad \widehat{G}(\omega) = \frac{\varGamma}{1+\omega^2\tau^2} \tag{8.353}$$

is the *Green's function*, in real and Fourier space. Note that

$$\int\limits_{-\infty}^{\infty}\!ds\; G(s) = \widehat{G}(0) = \varGamma \; . \tag{8.354}$$

We can now compute

$$\big\langle \eta(t_1)\,\eta(t_2)\big\rangle = G(t_1-t_2) \tag{8.355}$$

$$\begin{aligned}\big\langle \eta(t_1)\,\eta(t_2)\,\eta(t_3)\,\eta(t_4)\big\rangle &= G(t_1-t_2)\,G(t_3-t_4) + G(t_1-t_3)\,G(t_2-t_4)\\ &\quad + G(t_1-t_4)\,G(t_2-t_3)\; .\end{aligned} \tag{8.356}$$

The generalization is now easy to prove, and is known as *Wick's theorem*:

$$\big\langle \eta(t_1)\cdots\eta(t_{2n})\big\rangle = \sum_{\text{contractions}} G(t_{i_1}-t_{i_2})\cdots G(t_{i_{2n-1}}-t_{i_{2n}}) \; , \tag{8.357}$$

where the sum is over all distinct *contractions* of the sequence $1\text{-}2\cdots 2n$ into products of pairs. How many terms are there? Some simple combinatorics answers this question. Choose the index $1$. There are $(2n-1)$ other time indices with which it can be contracted. Now choose another index. There are $(2n-3)$ indices with which *that* index can be contracted. And so on. We thus obtain

$$C(n) \equiv \begin{array}{c}\text{\# of contractions}\\ \text{of } 1\text{-}2\text{-}3\cdots 2n\end{array} = (2n-1)(2n-3)\cdots 3\cdot 1 = \frac{(2n)!}{2^n\, n!} \; . \tag{8.358}$$

## 8.13 Appendix III : General Linear Autonomous Inhomogeneous ODEs

We can also solve general autonomous linear inhomogeneous ODEs of the form

$$\frac{d^n x}{dt^n} + a_{n-1}\,\frac{d^{n-1}x}{dt^{n-1}} + \ldots + a_1\,\frac{dx}{dt} + a_0\, x = \xi(t) \; . \tag{8.359}$$

We can write this as

$$\mathcal{L}_t\, x(t) = \xi(t) \; , \tag{8.360}$$

where $\mathcal{L}_t$ is the $n^{\text{th}}$ order differential operator

$$\mathcal{L}_t = \frac{d^n}{dt^n} + a_{n-1}\,\frac{d^{n-1}}{dt^{n-1}} + \ldots + a_1\,\frac{d}{dt} + a_0 \; . \tag{8.361}$$

The general solution to the inhomogeneous equation is given by

$$x(t) = x_{\text{h}}(t) + \int\limits_{-\infty}^{\infty}\!dt'\; G(t,t')\,\xi(t') \; , \tag{8.362}$$

where $G(t,t')$ is the Green's function. Note that $\mathcal{L}_t\, x_\mathrm{h}(t) = 0$. Thus, in order for eqns. 8.360 and 8.362 to be true, we must have

$$\mathcal{L}_t\, x(t) = \overbrace{\mathcal{L}_t\, x_\mathrm{h}(t)}^{\text{this vanishes}} + \int\limits_{-\infty}^{\infty}\!dt'\; \mathcal{L}_t\, G(t,t')\, \xi(t') = \xi(t)\ , \tag{8.363}$$

which means that

$$\mathcal{L}_t\, G(t,t') = \delta(t-t')\ , \tag{8.364}$$

where $\delta(t-t')$ is the Dirac $\delta$-function.

If the differential equation $\mathcal{L}_t\, x(t) = \xi(t)$ is defined over some finite or semi-infinite $t$ interval with prescribed boundary conditions on $x(t)$ at the endpoints, then $G(t,t')$ will depend on $t$ and $t'$ separately. For the case we are now considering, let the interval be the entire real line $t \in (-\infty,\infty)$. Then $G(t,t') = G(t-t')$ is a function of the single variable $t-t'$.

Note that $\mathcal{L}_t = \mathcal{L}\big(\frac{d}{dt}\big)$ may be considered a function of the differential operator $\frac{d}{dt}$. If we now Fourier transform the equation $\mathcal{L}_t\, x(t) = \xi(t)$, we obtain

$$\begin{aligned}\int\limits_{-\infty}^{\infty}\!dt\, e^{i\omega t}\, \xi(t) &= \int\limits_{-\infty}^{\infty}\!dt\, e^{i\omega t} \left\{ \frac{d^n}{dt^n} + a_{n-1}\, \frac{d^{n-1}}{dt^{n-1}} + \ldots + a_1\, \frac{d}{dt} + a_0 \right\} x(t) \\ &= \int\limits_{-\infty}^{\infty}\!dt\, e^{i\omega t} \bigg\{ (-i\omega)^n + a_{n-1}\, (-i\omega)^{n-1} + \ldots + a_1\, (-i\omega) + a_0 \bigg\}\, x(t)\ .\end{aligned} \tag{8.365}$$

Thus, if we define

$$\hat{\mathcal{L}}(\omega) = \sum_{k=0}^{n} a_k\, (-i\omega)^k\ , \tag{8.366}$$

then we have

$$\hat{\mathcal{L}}(\omega)\, \hat{x}(\omega) = \hat{\xi}(\omega)\ , \tag{8.367}$$

where $a_n \equiv 1$. According to the Fundamental Theorem of Algebra, the $n^{\text{th}}$ degree polynomial $\hat{\mathcal{L}}(\omega)$ may be uniquely factored over the complex $\omega$ plane into a product over $n$ roots:

$$\hat{\mathcal{L}}(\omega) = (-i)^n\, (\omega-\omega_1)(\omega-\omega_2)\cdots(\omega-\omega_n)\ . \tag{8.368}$$

If the $\{a_k\}$ are all real, then $\big[\hat{\mathcal{L}}(\omega)\big]^* = \hat{\mathcal{L}}(-\omega^*)$, hence if $\Omega$ is a root then so is $-\Omega^*$. Thus, the roots appear in pairs which are symmetric about the imaginary axis. *I.e.* if $\Omega = a + ib$ is a root, then so is $-\Omega^* = -a + ib$.

The general solution to the homogeneous equation is

$$x_\mathrm{h}(t) = \sum_{\sigma=1}^{n} A_\sigma\, e^{-i\omega_\sigma t}\ , \tag{8.369}$$

which involves $n$ arbitrary complex constants $A_i$. The susceptibility, or Green's function in Fourier space, $\hat{G}(\omega)$ is then

$$\hat{G}(\omega) = \frac{1}{\hat{\mathcal{L}}(\omega)} = \frac{i^n}{(\omega-\omega_1)(\omega-\omega_2)\cdots(\omega-\omega_n)}\ , \tag{8.370}$$

Note that $\big[\hat{G}(\omega)\big]^* = \hat{G}(-\omega)$, which is equivalent to the statement that $G(t-t')$ is a real function of its argument. The general solution to the inhomogeneous equation is then

$$x(t) = x_\mathrm{h}(t) + \int\limits_{-\infty}^{\infty}\!dt'\; G(t-t')\, \xi(t')\ , \tag{8.371}$$

where $x_{\mathrm{h}}(t)$ is the solution to the homogeneous equation, *i.e.* with zero forcing, and where

$$\begin{aligned} G(t-t') &= \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, e^{-i\omega(t-t')}\, \hat{G}(\omega) \\ &= i^n \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \frac{e^{-i\omega(t-t')}}{(\omega-\omega_1)(\omega-\omega_2)\cdots(\omega-\omega_n)} \\ &= \sum_{\sigma=1}^{n} \frac{e^{-i\omega_\sigma(t-t')}}{i\,\mathcal{L}'(\omega_\sigma)}\, \Theta(t-t')\ , \end{aligned} \tag{8.372}$$

where we assume that $\mathrm{Im}\,\omega_\sigma < 0$ for all $\sigma$. This guarantees *causality* – the *response* $x(t)$ to the *influence* $\xi(t')$ is nonzero only for $t > t'$.

As an example, consider the familiar case

$$\begin{aligned} \hat{\mathcal{L}}(\omega) &= -\omega^2 - i\gamma\omega + \omega_0^2 \\ &= -(\omega-\omega_+)\,(\omega-\omega_-)\ , \end{aligned} \tag{8.373}$$

with $\omega_\pm = -\frac{i}{2}\gamma \pm \beta$, and $\beta = \sqrt{\omega_0^2 - \frac{1}{4}\gamma^2}$. This yields

$$\mathcal{L}'(\omega_\pm) = \mp(\omega_+ - \omega_-) = \mp 2\beta\ . \tag{8.374}$$

Then according to equation 8.372,

$$\begin{aligned} G(s) &= \left\{ \frac{e^{-i\omega_+ s}}{i\mathcal{L}'(\omega_+)} + \frac{e^{-i\omega_- s}}{i\mathcal{L}'(\omega_-)} \right\} \Theta(s) \\ &= \left\{ \frac{e^{-\gamma s/2}\, e^{-i\beta s}}{-2i\beta} + \frac{e^{-\gamma s/2}\, e^{i\beta s}}{2i\beta} \right\} \Theta(s) \\ &= \beta^{-1}\, e^{-\gamma s/2}\, \sin(\beta s)\, \Theta(s)\ . \end{aligned} \tag{8.375}$$

Now let us evaluate the two-point correlation function $\big\langle x(t)\, x(t')\big\rangle$, assuming the noise is correlated according to $\big\langle \xi(s)\, \xi(s')\big\rangle = \phi(s-s')$. We assume $t, t' \to \infty$ so the transient contribution $x_{\mathrm{h}}$ is negligible. We then have

$$\begin{aligned} \big\langle x(t)\, x(t')\big\rangle &= \int\limits_{-\infty}^{\infty}\! ds \int\limits_{-\infty}^{\infty}\! ds'\ G(t-s)\, G(t'-s')\, \big\langle \xi(s)\, \xi(s')\big\rangle \\ &= \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \hat{\phi}(\omega)\, \big|\hat{G}(\omega)\big|^2\, e^{i\omega(t-t')}\ . \end{aligned} \tag{8.376}$$

### Higher order ODEs

Note that any $n^{\mathrm{th}}$ order ODE, of the general form

$$\frac{d^n x}{dt^n} = F\bigg(x\,,\, \frac{dx}{dt}\,,\, \ldots\,,\, \frac{d^{n-1}x}{dt^{n-1}}\bigg)\ , \tag{8.377}$$

may be represented by the first order system $\dot{\boldsymbol{\varphi}} = \boldsymbol{V}(\boldsymbol{\varphi})$. To see this, define $\varphi_k = d^{k-1}x/dt^{k-1}$, with $k = 1, \ldots, n$. Thus, for $k < n$ we have $\dot{\varphi}_k = \varphi_{k+1}$, and $\dot{\varphi}_n = F$. In other words,

$$\overbrace{\frac{d}{dt}\begin{pmatrix} \varphi_1 \\ \vdots \\ \varphi_{n-1} \\ \varphi_n \end{pmatrix}}^{\dot{\boldsymbol{\varphi}}} = \overbrace{\begin{pmatrix} \varphi_2 \\ \vdots \\ \varphi_n \\ F\big(\varphi_1, \ldots, \varphi_p\big) \end{pmatrix}}^{\boldsymbol{V}(\boldsymbol{\varphi})} . \tag{8.378}$$

An inhomogeneous linear $n^{\text{th}}$ order ODE,

$$\frac{d^n x}{dt^n} + a_{n-1}\,\frac{d^{n-1}x}{dt^{n-1}} + \ldots + a_1\,\frac{dx}{dt} + a_0\,x = \xi(t) \tag{8.379}$$

may be written in matrix form, as

$$\frac{d}{dt}\begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_n \end{pmatrix} = \overbrace{\begin{pmatrix} 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & & \vdots \\ -a_0 & -a_1 & -a_2 & \cdots & -a_{n-1} \end{pmatrix}}^{Q} \begin{pmatrix} \varphi_1 \\ \varphi_2 \\ \vdots \\ \varphi_n \end{pmatrix} + \overbrace{\begin{pmatrix} 0 \\ 0 \\ \vdots \\ \xi(t) \end{pmatrix}}^{\boldsymbol{\xi}} . \tag{8.380}$$

Thus,

$$\dot{\boldsymbol{\varphi}} = Q\,\boldsymbol{\varphi} + \boldsymbol{\xi}\ , \tag{8.381}$$

and if the coefficients $c_k$ are time-independent, *i.e.* the ODE is *autonomous*.

For the homogeneous case where $\xi(t) = 0$, the solution is obtained by exponentiating the constant matrix $Qt$:

$$\boldsymbol{\varphi}(t) = \exp(Qt)\,\boldsymbol{\varphi}(0)\ ; \tag{8.382}$$

the exponential of a matrix may be given meaning by its Taylor series expansion. If the ODE is not autonomous, then $Q = Q(t)$ is time-dependent, and the solution is given by the path-ordered exponential,

$$\boldsymbol{\varphi}(t) = \mathsf{P}\exp\left\{\int\limits_0^t dt'\,Q(t')\right\}\boldsymbol{\varphi}(0)\ , \tag{8.383}$$

where $\mathsf{P}$ is the *path ordering operator* which places earlier times to the right. As defined, the equation $\dot{\boldsymbol{\varphi}} = \boldsymbol{V}(\boldsymbol{\varphi})$ is autonomous, since the $t$-advance mapping $g_t$ depends only on $t$ and on no other time variable. However, by extending the phase space $\mathbb{M} \ni \boldsymbol{\varphi}$ from $\mathbb{M} \to \mathbb{M} \times \mathbb{R}$, which is of dimension $n + 1$, one can describe arbitrary time-dependent ODEs.

In general, path ordered exponentials are difficult to compute analytically. We will henceforth consider the autonomous case where $Q$ is a constant matrix in time. We will assume the matrix $Q$ is real, but other than that it has no helpful symmetries. We can however decompose it into left and right eigenvectors:

$$Q_{ij} = \sum_{\sigma=1}^{n} \nu_\sigma\,R_{\sigma,i}\,L_{\sigma,j}\ . \tag{8.384}$$

Or, in bra-ket notation, $Q = \sum_\sigma \nu_\sigma\,|R_\sigma\rangle\langle L_\sigma|$. The normalization condition we use is

$$\big\langle\, L_\sigma \,\big|\, R_{\sigma'} \,\big\rangle = \delta_{\sigma\sigma'}\ , \tag{8.385}$$

where $\{\nu_\sigma\}$ are the eigenvalues of $Q$. The eigenvalues may be real or imaginary. Since the characteristic polynomial $P(\nu) = \det\,(\nu\,\mathbb{I} - Q)$ has real coefficients, we know that the eigenvalues of $Q$ are either real or come in complex conjugate pairs.

Consider, for example, the $n = 2$ system we studied earlier. Then

$$Q = \begin{pmatrix} 0 & 1 \\ -\omega_0^2 & -\gamma \end{pmatrix} . \tag{8.386}$$

The eigenvalues are as before: $\nu_\pm = -\frac{1}{2}\gamma \pm \sqrt{\frac{1}{4}\gamma^2 - \omega_0^2}$ . The left and right eigenvectors are

$$L_\pm = \frac{\pm 1}{\nu_+ - \nu_-}\begin{pmatrix} -\nu_\mp & 1 \end{pmatrix} \qquad , \qquad R_\pm = \begin{pmatrix} 1 \\ \nu_\pm \end{pmatrix} . \tag{8.387}$$

The utility of working in a left-right eigenbasis is apparent once we reflect upon the result

$$f(Q) = \sum_{\sigma=1}^{n} f(\nu_\sigma)\,\big|\,R_\sigma\,\big\rangle\big\langle\,L_\sigma\,\big| \tag{8.388}$$

for any function $f$. Thus, the solution to the general autonomous homogeneous case is

$$\big|\,\boldsymbol{\varphi}(t)\,\big\rangle = \sum_{\sigma=1}^{n} e^{\nu_\sigma t}\,\big|\,R_\sigma\,\big\rangle\big\langle\,L_\sigma\,\big|\,\boldsymbol{\varphi}(0)\,\big\rangle \tag{8.389}$$

$$\varphi_i(t) = \sum_{\sigma=1}^{n} e^{\nu_\sigma t}\,R_{\sigma,i}\sum_{j=1}^{n} L_{\sigma,j}\,\varphi_j(0) . \tag{8.390}$$

If $\mathrm{Re}\,(\nu_\sigma) \le 0$ for all $\sigma$, then the initial conditions $\boldsymbol{\varphi}(0)$ are forgotten on time scales $\tau_\sigma = \nu_\sigma^{-1}$. Physicality demands that this is the case.

Now let's consider the inhomogeneous case where $\xi(t) \neq 0$. We begin by recasting eqn. 8.381 in the form

$$\frac{d}{dt}\big(e^{-Qt}\,\boldsymbol{\varphi}\big) = e^{-Qt}\,\boldsymbol{\xi}(t) . \tag{8.391}$$

We can integrate this directly:

$$\boldsymbol{\varphi}(t) = e^{Qt}\,\boldsymbol{\varphi}(0) + \int_0^t\! ds\,e^{Q(t-s)}\,\boldsymbol{\xi}(s) . \tag{8.392}$$

In component notation,

$$\varphi_i(t) = \sum_{\sigma=1}^{n} e^{\nu_\sigma t}\,R_{\sigma,i}\,\big\langle\,L_\sigma\,\big|\,\boldsymbol{\varphi}(0)\,\big\rangle + \sum_{\sigma=1}^{n} R_{\sigma,i}\int_0^t\! ds\,e^{\nu_\sigma(t-s)}\,\big\langle\,L_\sigma\,\big|\,\boldsymbol{\xi}(s)\,\big\rangle. \tag{8.393}$$

Note that the first term on the RHS is the solution to the homogeneous equation, as must be the case when $\boldsymbol{\xi}(s) = 0$.

The solution in eqn. 8.393 holds for general $Q$ and $\boldsymbol{\xi}(s)$. For the particular form of $Q$ and $\xi(s)$ in eqn. 8.380, we can proceed further. For starters, $\langle L_\sigma|\boldsymbol{\xi}(s)\rangle = L_{\sigma,n}\,\xi(s)$. We can further exploit a special feature of the $Q$ matrix to analytically determine all its left and right eigenvectors. Applying $Q$ to the right eigenvector $|R_\sigma\rangle$, we obtain

$$R_{\sigma,j} = \nu_\sigma\,R_{\sigma,j-1} \qquad (j > 1) . \tag{8.394}$$

We are free to choose $R_{\sigma,1} = 1$ for all $\sigma$ and defer the issue of normalization to the derivation of the left eigenvectors. Thus, we obtain the pleasingly simple result,

$$R_{\sigma,k} = \nu_\sigma^{k-1} \ . \tag{8.395}$$

Applying $Q$ to the left eigenvector $\langle L_\sigma |$, we obtain

$$-a_0 \, L_{\sigma,n} = \nu_\sigma \, L_{\sigma,1} \tag{8.396}$$

$$L_{\sigma,j-1} - a_{j-1} \, L_{\sigma,n} = \nu_\sigma \, L_{\sigma,j} \qquad (j > 1) \ . \tag{8.397}$$

From these equations we may derive

$$L_{\sigma,k} = -\frac{L_{\sigma,n}}{\nu_\sigma} \sum_{j=0}^{k-1} a_j \, \nu_\sigma^{j-k-1} = \frac{L_{\sigma,n}}{\nu_\sigma} \sum_{j=k}^{n} a_j \, \nu_\sigma^{j-k-1} \ . \tag{8.398}$$

The equality in the above equation is derived using the result $P(\nu_\sigma) = \sum_{j=0}^n a_j \, \nu_\sigma^j = 0$. Recall also that $a_n \equiv 1$. We now impose the normalization condition,

$$\sum_{k=1^n} L_{\sigma,k} \, R_{\sigma,k} = 1 \ . \tag{8.399}$$

This condition determines our last remaining unknown quantity (for a given $\sigma$), $L_{\sigma,p}$ :

$$\big\langle \, L_\sigma \, \big| \, R_\sigma \, \big\rangle = L_{\sigma,n} \sum_{k=1}^{n} k \, a_k \, \nu_\sigma^{k-1} = P'(\nu_\sigma) \, L_{\sigma,n} \ , \tag{8.400}$$

where $P'(\nu)$ is the first derivative of the characteristic polynomial. Thus, we obtain another neat result,

$$L_{\sigma,n} = \frac{1}{P'(\nu_\sigma)} \ . \tag{8.401}$$

Now let us evaluate the general two-point correlation function,

$$C_{jj'}(t,t') \equiv \big\langle \varphi_j(t) \, \varphi_{j'}(t') \big\rangle - \big\langle \varphi_j(t) \big\rangle \, \big\langle \varphi_{j'}(t') \big\rangle \ . \tag{8.402}$$

We write

$$\big\langle \xi(s) \, \xi(s') \big\rangle = \phi(s-s') = \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \hat{\phi}(\omega) \, e^{-i\omega(s-s')} \ . \tag{8.403}$$

When $\hat{\phi}(\omega)$ is constant, we have $\big\langle \xi(s) \, \xi(s') \big\rangle = \hat{\phi}(t) \, \delta(s-s')$. This is the case of so-called *white noise*, when all frequencies contribute equally. The more general case when $\hat{\phi}(\omega)$ is frequency-dependent is known as *colored noise*. Appealing to eqn. 8.393, we have

$$C_{jj'}(t,t') = \sum_{\sigma,\sigma'} \frac{\nu_\sigma^{j-1}}{P'(\nu_\sigma)} \, \frac{\nu_{\sigma'}^{j'-1}}{P'(\nu_{\sigma'})} \int\limits_0^t \! ds \; e^{\nu_\sigma (t-s)} \! \int\limits_0^{t'} \! ds' \; e^{\nu_{\sigma'} (t'-s')} \, \phi(s-s') \tag{8.404}$$

$$= \sum_{\sigma,\sigma'} \frac{\nu_\sigma^{j-1}}{P'(\nu_\sigma)} \, \frac{\nu_{\sigma'}^{j'-1}}{P'(\nu_{\sigma'})} \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \frac{\hat{\phi}(\omega) \, (e^{-i\omega t} - e^{\nu_\sigma t})(e^{i\omega t'} - e^{\nu_{\sigma'} t'})}{(\omega - i\nu_\sigma)(\omega + i\nu_{\sigma'})} \ . \tag{8.405}$$

In the limit $t, t' \to \infty$, assuming $\mathsf{Re}\,(\nu_\sigma) < 0$ for all $\sigma$ (*i.e.* no diffusion), the exponentials $e^{\nu_\sigma t}$ and $e^{\nu_{\sigma'} t'}$ may be neglected, and we then have

$$C_{jj'}(t,t') = \sum_{\sigma,\sigma'} \frac{\nu_\sigma^{j-1}}{P'(\nu_\sigma)} \, \frac{\nu_{\sigma'}^{j'-1}}{P'(\nu_{\sigma'})} \int\limits_{-\infty}^{\infty} \frac{d\omega}{2\pi} \, \frac{\hat{\phi}(\omega) \, e^{-i\omega(t-t')}}{(\omega - i\nu_\sigma)(\omega + i\nu_{\sigma'})} \ . \tag{8.406}$$

## 8.14 Appendix IV : Correlations in the Langevin formalism

As shown above, integrating the Langevin equation $\dot{p} + \gamma p = F + \eta(t)$ yields

$$p(t) = p(0)\, e^{-\gamma t} + \frac{F}{\gamma}\left(1 - e^{-\gamma t}\right) + \int\limits_0^t ds\, \eta(s)\, e^{\gamma(s-t)} \ . \tag{8.407}$$

. Thus, the momentum autocorrelator is

$$\begin{aligned} \big\langle p(t)\, p(t')\big\rangle - \big\langle p(t)\big\rangle\big\langle p(t')\big\rangle &= \int\limits_0^t ds \int\limits_0^{t'} ds'\, e^{\gamma(s-t)}\, e^{\gamma(s'-t')}\, \big\langle \eta(s)\, \eta(s')\big\rangle \\ &= \mathit{\Gamma}\, e^{-\gamma(t+t')} \int\limits_0^{t_{\rm min}} ds\, e^{2\gamma s} = M k_{\rm B} T \left(e^{-\gamma|t-t'|} - e^{-\gamma(t+t')}\right) , \end{aligned} \tag{8.408}$$

where

$$t_{\rm min} = \min(t,t') = \begin{cases} t & \text{if } t < t' \\ t' & \text{if } t' < t \end{cases} \tag{8.409}$$

is the lesser of $t$ and $t'$. Here we have used the result

$$\begin{aligned} \int\limits_0^t ds \int\limits_0^{t'} ds'\, e^{\gamma(s+s')}\, \delta(s-s') &= \int\limits_0^{t_{\rm min}} ds \int\limits_0^{t_{\rm min}} ds'\, e^{\gamma(s+s')}\, \delta(s-s') \\ &= \int\limits_0^{t_{\rm min}} ds\, e^{2\gamma s} = \frac{1}{2\gamma}\Big(e^{2\gamma t_{\rm min}} - 1\Big) \ . \end{aligned} \tag{8.410}$$

One way to intuitively understand this result is as follows. The double integral over $s$ and $s'$ is over a rectangle of dimensions $t \times t'$. Since the $\delta$-function can only be satisfied when $s = s'$, there can be no contribution to the integral from regions where $s > t'$ or $s' > t$. Thus, the only contributions can arise from integration over the square of dimensions $t_{\rm min} \times t_{\rm min}$. Note also

$$t + t' - 2\min(t,t') = |t - t'| \ . \tag{8.411}$$

Let's now compute the position $x(t)$. We have

$$\begin{aligned} x(t) &= x(0) + \frac{1}{M}\int\limits_0^t ds\, p(s) \\ &= x(0) + \int\limits_0^t ds \left[\left(v(0) - \frac{F}{\gamma M}\right) e^{-\gamma s} + \frac{F}{\gamma M}\right] + \frac{1}{M}\int\limits_0^t ds \int\limits_0^s ds_1\, \eta(s_1)\, e^{\gamma(s_1 - s)} \\ &= \big\langle x(t)\big\rangle + \frac{1}{M}\int\limits_0^t ds \int\limits_0^s ds_1\, \eta(s_1)\, e^{\gamma(s_1-s)} \ , \end{aligned} \tag{8.412}$$

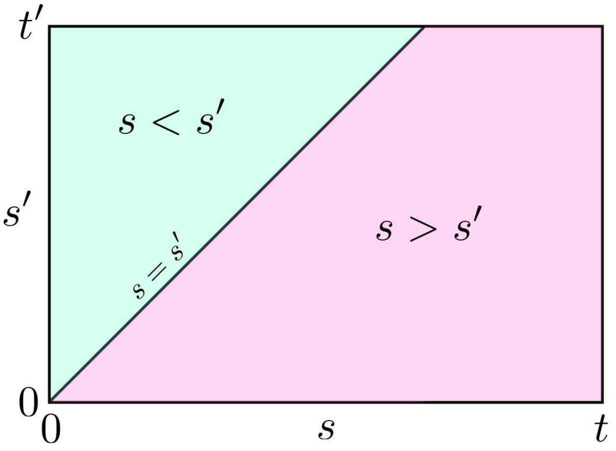

Figure 8.11: Regions for some of the double integrals encountered in the text.

with $v = p/M$. Since $\big\langle \eta(t) \big\rangle = 0$, we have

$$\begin{aligned}\big\langle x(t) \big\rangle &= x(0) + \int\limits_0^t ds \left[\left(v(0) - \frac{F}{\gamma M}\right) e^{-\gamma s} + \frac{F}{\gamma M}\right] \\ &= x(0) + \frac{Ft}{\gamma M} + \frac{1}{\gamma}\left(v(0) - \frac{F}{\gamma M}\right)\big(1 - e^{-\gamma t}\big) \ .\end{aligned} \tag{8.413}$$

Note that for $\gamma t \ll 1$ we have $\big\langle x(t) \big\rangle = x(0) + v(0)\, t + \frac{1}{2} M^{-1} F t^2 + \mathcal{O}(t^3)$, as is appropriate for ballistic particles moving under the influence of a constant force. This long time limit of course agrees with our earlier evaluation for the terminal velocity, $v_\infty = \big\langle p(\infty) \big\rangle / M = F/\gamma M$.

We next compute the position autocorrelation:

$$\begin{aligned}\big\langle x(t)\, x(t') \big\rangle - \big\langle x(t) \big\rangle \big\langle x(t') \big\rangle &= \frac{1}{M^2} \int\limits_0^t ds \int\limits_0^{t'} ds'\, e^{-\gamma(s+s')} \int\limits_0^s ds_1 \int\limits_0^{s'} ds_1'\, e^{\gamma(s_1+s_2)} \big\langle \eta(s_1)\, \eta(s_2) \big\rangle \\ &= \frac{\Gamma}{2\gamma M^2} \int\limits_0^t ds \int\limits_0^{t'} ds' \left(e^{-\gamma|s-s'|} - e^{-\gamma(s+s')}\right)\end{aligned} \tag{8.414}$$

We have to be careful in computing the double integral of the first term in brackets on the RHS. We can assume, without loss of generality, that $t \geq t'$. Then

$$\begin{aligned}\int\limits_0^t ds \int\limits_0^{t'} ds'\, e^{-\gamma|s-s'|} &= \int\limits_0^{t'} ds'\, e^{\gamma s'} \int\limits_{s'}^t ds\ e^{-\gamma s} + \int\limits_0^{t'} ds'\, e^{-\gamma s'} \int\limits_0^{s'} ds\, e^{\gamma s} \\ &= 2\gamma^{-1} t' + \gamma^{-2}\big(e^{-\gamma t} + e^{-\gamma t'} - 1 - e^{-\gamma(t-t')}\big) \ .\end{aligned} \tag{8.415}$$

We then find, for $t > t'$,

$$\big\langle x(t)\, x(t') \big\rangle - \big\langle x(t) \big\rangle \big\langle x(t') \big\rangle = \frac{2k_{\rm B}T}{\gamma M}\, t' + \frac{k_{\rm B}T}{\gamma^2 M}\big(2e^{-\gamma t} + 2e^{-\gamma t'} - 2 - e^{-\gamma(t-t')} - e^{-\gamma(t+t')}\big) \ . \tag{8.416}$$

In particular, the equal time autocorrelator is

$$\big\langle x^2(t)\big\rangle - \big\langle x(t)\big\rangle^2 = \frac{2k_{\rm B}T}{\gamma M}\,t + \frac{k_{\rm B}T}{\gamma^2 M}\,\big(4e^{-\gamma t} - 3 - e^{-2\gamma t}\big)\ . \tag{8.417}$$

We see that for long times

$$\big\langle x^2(t)\big\rangle - \big\langle x(t)\big\rangle^2 \sim 2Dt\ , \tag{8.418}$$

where $D = k_{\rm B}T/\gamma M$ is the diffusion constant.

## 8.15 Appendix V : Kramers-Krönig Relations

Suppose $\hat\chi(\omega) \equiv \hat G(\omega)$ is analytic in the UHP[19]. Then for all $\nu$, we must have

$$\int\limits_{-\infty}^{\infty}\!\frac{d\nu}{2\pi}\,\frac{\hat\chi(\nu)}{\nu - \omega + i\epsilon} = 0\ , \tag{8.419}$$

where $\epsilon$ is a positive infinitesimal. The reason is simple: just close the contour in the UHP, assuming $\hat\chi(\omega)$ vanishes sufficiently rapidly that Jordan's lemma can be applied. Clearly this is an extremely weak restriction on $\hat\chi(\omega)$, given the fact that the denominator already causes the integrand to vanish as $|\omega|^{-1}$.

Let us examine the function

$$\frac{1}{\nu - \omega + i\epsilon} = \frac{\nu-\omega}{(\nu-\omega)^2+\epsilon^2} - \frac{i\epsilon}{(\nu-\omega)^2+\epsilon^2}\ . \tag{8.420}$$

which we have separated into real and imaginary parts. Under an integral sign, the first term, in the limit $\epsilon \to 0$, is equivalent to taking a *principal part* of the integral. That is, for any function $F(\nu)$ which is regular at $\nu = \omega$,

$$\lim_{\epsilon\to 0}\int\limits_{-\infty}^{\infty}\!\frac{d\nu}{2\pi}\,\frac{\nu-\omega}{(\nu-\omega)^2+\epsilon^2}\,F(\nu) \equiv \wp\!\int\limits_{-\infty}^{\infty}\!\frac{d\nu}{2\pi}\,\frac{F(\nu)}{\nu-\omega}\ . \tag{8.421}$$

The *principal part* symbol $\wp$ means that the singularity at $\nu = \omega$ is elided, either by smoothing out the function $1/(\nu - \epsilon)$ as above, or by simply cutting out a region of integration of width $\epsilon$ on either side of $\nu = \omega$.

The imaginary part is more interesting. Let us write

$$h(u) \equiv \frac{\epsilon}{u^2+\epsilon^2}\ . \tag{8.422}$$

For $|u| \gg \epsilon$, $h(u) \simeq \epsilon/u^2$, which vanishes as $\epsilon \to 0$. For $u = 0$, $h(0) = 1/\epsilon$ which diverges as $\epsilon \to 0$. Thus, $h(u)$ has a huge peak at $u = 0$ and rapidly decays to 0 as one moves off the peak in either direction a distance greater that $\epsilon$. Finally, note that

$$\int\limits_{-\infty}^{\infty}\!du\,h(u) = \pi\ , \tag{8.423}$$

a result which itself is easy to show using contour integration. Putting it all together, this tells us that

$$\lim_{\epsilon\to 0}\frac{\epsilon}{u^2+\epsilon^2} = \pi\delta(u)\ . \tag{8.424}$$

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[19] In this section, we use the notation $\hat\chi(\omega)$ for the susceptibility, rather than $\hat G(\omega)$

Thus, for positive infinitesimal $\epsilon$,

$$\frac{1}{u \pm i\epsilon} = \frac{\wp}{u} \mp i\pi\delta(u) \ , \tag{8.425}$$

a most useful result.

We now return to our initial result 8.419, and we separate $\hat{\chi}(\omega)$ into real and imaginary parts:

$$\hat{\chi}(\omega) = \hat{\chi}'(\omega) + i\hat{\chi}''(\omega) \ . \tag{8.426}$$

(In this equation, the primes do not indicate differentiation with respect to argument.) We therefore have, for every real value of $\omega$,

$$0 = \int\limits_{-\infty}^{\infty}\frac{d\nu}{2\pi}\Big[\chi'(\nu) + i\chi''(\nu)\Big]\Big[\frac{\wp}{\nu-\omega} - i\pi\delta(\nu-\omega)\Big] \ . \tag{8.427}$$

Taking the real and imaginary parts of this equation, we derive the *Kramers-Krönig relations*:

$$\chi'(\omega) = +\wp\int\limits_{-\infty}^{\infty}\frac{d\nu}{\pi}\,\frac{\hat{\chi}''(\nu)}{\nu-\omega} \tag{8.428}$$

$$\chi''(\omega) = -\wp\int\limits_{-\infty}^{\infty}\frac{d\nu}{\pi}\,\frac{\hat{\chi}'(\nu)}{\nu-\omega} \ . \tag{8.429}$$