PX3A7: Statistical Physics

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Preface

PX3A7 replaces the module PX366 for the academic year 2023-2024, which it also extends from 7.5 to 15 CATS. The syllabus remains the same but topics will be covered in greater detail and developed further. As the additional material naturally involves more advanced topics, the increase in the size of these lectures notes, and of the total content in the course, is somewhat less than a factor of two. The exam is anticipated for the Summer period and will consist of three questions and have a two hour duration. The previous exam papers for PX366 remain an excellent resource for preparation.

This is a third year course in statistical physics that may be seen as building on the content of PX265 Thermal Physics II. The module is more of a 'topics' course than it is a 'definitive' account of the foundations of statistical physics and there is only a brief review of those foundational notions that we will make most use of. The choice of topics is fairly classical, albeit influenced by my interests (or, rather, limited knowledge), although it is geared towards the 'soft' side of things rather than the 'hard' side and in particular there is no coverage of quantum topics.

These notes cover the entire content of the course, however, the delivery in lectures may differ slightly, including in the order of topics. The problem sets form an integral part of the course, both reviewing material from the notes and lectures and expanding upon it.

As always, I will be grateful to receive comments, corrections, or general feedback, and especially suggestions for improvement.

Books and other reading

There are lots of good books. You are encouraged to read as many as you can. There is no single book I know of that covers all aspects of this course, but some with particular relevance to the topics we cover are listed below.

1. J.M. Yeomans, *Statistical Mechanics of Phase Transitions*, Clarendon Press, Oxford, 1992.

   An excellent and accessible account of the physics of phase transitions from a traditional perspective. This covers all of the topics on the Ising model and Landau theory in more detail than we go into.

2. Richard A.L. Jones, *Soft Condensed Matter*, Oxford University Press, Oxford, 2002.

   General coverage of statistical physics applied to soft matter at a similar level to this course. Particularly useful for the material on phase separation and polymers.

3. M. Doi, *Soft Matter Physics*, Oxford University Press, Oxford, 2013. doi:10.1093/acprof:oso/9780199652952.001.0001

   General coverage of statistical physics in soft matter in theoretical style at a level similar to the course but also going beyond it. Particularly useful for rubber elasticity and Brownian motion, but also with useful coverage of phase separation and liquid crystals.

4. J. Cardy, *Scaling and Renormalization in Statistical Physics*, Cambridge University Press, Cambridge, 1996. doi:10.1017/CBO9781316036440

   Incredible and authoritative insights into the modern theory of phase transitions. Although mostly focused on material going beyond our course, the first three chapters cover the basic ideas of phase transitions and mean field theory.

5. Mehran Kardar, *Statistical Physics of Particles* and *Statistical Physics of Fields*, Cambridge University Press, Cambridge, 2007.

   Two companion books coming from a graduate course at MIT. They give an excellent up to date account that contains careful explanations and many helpful insights. Covers more than this course, including at a higher level, but where there is overlap you should find Kardar's books an excellent reference.

6. M. Doi and S.F. Edwards, *The Theory of Polymer Dynamics*, Oxford University Press, Oxford, 1986.

   A classic monograph on polymer physics. The material that we cover is treated in chapter 2. Chapter 3 includes a treatment of Brownian motion at a level going beyond what we do.

7. James P. Sethna, *Statistical Mechanics: Entropy, Order Parameters, and Complexity*, Oxford University Press, Oxford, 2006.

   General coverage of all the core aspects of statistical mechanics at a level more suited to a masters course. Well written and highly insightful.

8. P.M. Chaikin and T.C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge University Press, Cambridge, 1995.

   A benchmark graduate level text in the United States. Highly authoritative treatment of general thermodynamics, Landau theory of phase transitions, liquid crystals and much more. Bedtime reading for Onslow.

9. L.D. Landau and E.M. Lifshitz, *Statistical Physics: Volume 5 of the Course of Theoretical Physics*, 3rd edition, Butterworth-Heinemann, Oxford, 1980.

   A wonderful account with the highest standard of theoretical physics.

Chapter 1

Statistical Mechanics, Ideal Gases and Liquids

Statistical mechanics is many things to many people but at its core it is about describing the properties and behaviour of systems containing a large number of particles or fundamental constituents. We begin, as everyone always seems to, with a qualitative description of water and its three principal phases: solid (ice), liquid (water, or liquid water), and gas (steam, or water vapour). Everyone knows that water freezes at about 0° Celsius and boils at about 100° Celsius; these are examples of **phase transitions**. The **transition temperature** depends on the pressure and these are the values at standard atmospheric pressure at sea level. A **phase diagram** maps out the state of the system as a function of the **control variables**, here the temperature and pressure: A schematic phase diagram for water is shown in Fig. 2.1. The lines mark the phase transitions corresponding to freezing (or melting), boiling (or condensing) and sublimation. These three transitions meet at the **triple point** where all three phases coexist.

There may be some features that you are not as familiar with. For instance, the diagram indicates that it is possible to vary the temperature and pressure so as to pass between the gas and liquid phases without any transition at all. Indeed, this is correct. The end point of the liquid–gas transition line is called a **critical end point** and the state of water at that critical point is its own phase, called the **critical phase**, as distinct from the solid, liquid and gas phases as they are from each other. One of the characteristic properties of this critical state is that it scatters light strongly, a phenomenon known as **critical opalescence**.

Water provides one example of a system displaying different phases and phase transitions. There are many others. A substantial part of statistical physics centres on trying to understand phases and phase transitions in general. Away from phase transitions, the understanding of phases involves trying to account for their macroscopic properties, for instance the speed of sound, the viscosity of water, or the elasticity of rubber.
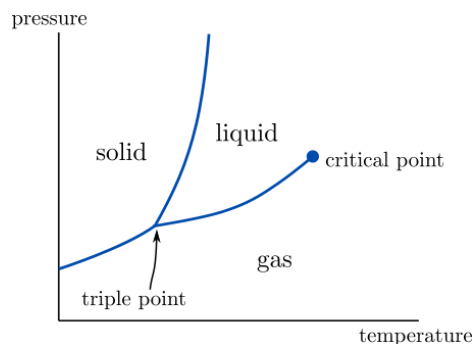

Figure 1.1: Schematic phase diagram for a simple fluid such as water showing the phase behaviour as a function of temperature and pressure.

1.1 Entropy, Partition Function, Free Energy

We provide a very brief review of how classical statistical mechanics captures thermodynamic properties. Loosely, the idea is that the macroscopic properties of a system can be obtained from knowledge of the possible microscopic states. Often, this is organised into different **ensembles**, called microcanonical, canonical and grand canonical. In the **microcanonical ensemble** the principal exercise is simply to count the number Ω of possible microstates; this is connected to thermodynamic quantities through Boltzmann's famous formula for the **entropy**

$$S = k_\mathrm{B} \ln \Omega. \tag{1.1}$$

An equivalent, but more general, expression gives the entropy in terms of the probabilities p_α of each microstate, labelled by α,

$$S = -k_\mathrm{B} \sum_{\text{states } \alpha} p_\alpha \ln p_\alpha. \tag{1.2}$$

To see the connection we need only note that $p_\alpha = 1/\Omega$ in the microcanonical ensemble, for then

$$S = -k_\mathrm{B} \sum_{\text{states } \alpha} p_\alpha \ln \frac{1}{\Omega} = k_\mathrm{B} \sum_{\text{states } \alpha} p_\alpha \ln \Omega = k_\mathrm{B} \ln \Omega, \tag{1.3}$$

using that the sum of the probabilities equals 1. The general expression for the entropy was found by Gibbs and put on the much broader context of information theory by Claude Shannon and is commonly referred to as the **Shannon entropy**.

In the **canonical ensemble** the different possible microstates can have different energies E_α and are connected to a heat bath at temperature T. The probabilities of the microstates are no longer all equal, as they are in the microcanonical ensemble, and are given by the **Boltzmann weights** $\mathrm{e}^{-\beta E_\alpha}$, where $\beta \equiv (k_\mathrm{B}T)^{-1}$ is the inverse temperature. More precisely the probabilities are

$$p_\alpha = \frac{\mathrm{e}^{-\beta E_\alpha}}{Z}, \tag{1.4}$$

where the normalising factor Z is the **partition function**

$$Z = \sum_{\text{states } \alpha} \mathrm{e}^{-\beta E_\alpha}. \tag{1.5}$$

Let us see what this means for the entropy. From the Shannon formula (1.2) we have

$$
\begin{aligned}
S &= -k_\mathrm{B} \sum_{\text{states } \alpha} p_\alpha \ln p_\alpha = -k_\mathrm{B} \sum_{\text{states } \alpha} p_\alpha \big[-\beta E_\alpha - \ln Z \big], \\
&= \frac{1}{T} \sum_{\text{states } \alpha} p_\alpha E_\alpha + k_\mathrm{B} \ln Z.
\end{aligned}
\tag{1.6}
$$

Recognising the sum as giving the average energy (or expectation value for the energy), which we write as $\langle E \rangle$, or simply as E, we rearrange this formula into the form

$$-k_\mathrm{B} T \ln Z = E - TS \equiv F. \tag{1.7}$$

Here, F is the **Helmholtz free energy**, although we will often simply call it the free energy.

Often it is said that calculating the partition function is the key objective of statistical mechanics, since it facilitates the determination of all macroscopic properties. For instance, the (thermodynamic) energy E is

$$E = \sum_{\text{states } \alpha} E_\alpha p_\alpha = \sum_{\text{states } \alpha} E_\alpha \frac{\mathrm{e}^{-\beta E_\alpha}}{Z} = \frac{-1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}, \tag{1.8}$$

and the heat capacity is

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T}\left(-\frac{\partial \ln Z}{\partial \beta}\right) = \frac{1}{k_B T^2}\frac{\partial^2 \ln Z}{\partial \beta^2}. \tag{1.9}$$

We will find that there is not a 'one size fits all' approach to statistical physics and that the three main quantities – the entropy S, partition function Z and free energy F – each take centre stage at different times.

1.1.1 Grand Canonical Ensemble

The canonical ensemble describes a system that is connected to a **heat bath**, with which it can exchange heat – hence the energies of the microstates are not all equal – in order to maintain a fixed temperature T. Two such systems are in equilibrium if they have the same temperature; if the temperatures are different heat will flow between them until they equilibrate.

The **grand canonical ensemble** describes a system that is connected to a heat bath and also a particle reservoir, with which it can exchange particles to maintain a fixed **chemical potential** μ. Two such systems are in equilibrium if they have the same temperature and chemical potential; if the chemical potentials are different then particles will flow between them until they equilibrate.

The microstates of the grand canonical ensemble are labelled by their energy E_α and number of particles n_α. These are both variable through connection with the reservoir. The Boltzmann weights are given by $e^{-\beta(E_\alpha - \mu n_\alpha)}$ and the (grand canonical) partition function is

$$Z = \sum_{\text{states } \alpha} e^{-\beta(E_\alpha - \mu n_\alpha)}. \tag{1.10}$$

We calculate the entropy using the Shannon forumula (1.2)

$$S = -k_B \sum_{\text{states } \alpha} p_\alpha \ln p_\alpha = -k_B \sum_{\text{states } \alpha} p_\alpha \left[-\beta(E_\alpha - \mu n_\alpha) - \ln Z\right],$$

$$= \frac{1}{T}(E - \mu N) + k_B \ln Z. \tag{1.11}$$

Rearranging this gives the free energy as

$$-k_B T \ln Z = E - TS - \mu N. \tag{1.12}$$

Strictly, this is not the Helmholtz free energy and is often given the unimaginative name 'grand canonical free energy', or 'grand thermodynamic potential', although often we will not be so careful in distinguishing between the different thermodynamic free energies.

1.1.2 Information Theory and Shannon's Theorem

The origins of entropy in thermodynamics are contained in the behaviour of heat engines and other tangible physical properties like the speed of sound in air[1]. The great insights of Boltzmann and Gibbs are that the entropy is given by the probability distribution for the microstates, *i.e.* the values of the p_α. What should these be? One answer is that they are the steady state values obtained by solving Newton's equation (or Hamilton's equation or the Schrödinger equation) for the motion of every particle. More correctly, you obtain them from long time averages over the dynamics, after any initial transients have disappeared. This can be done in computer simulation for numbers of particles that are modestly large but still small compared to Avagadro's number. It is a basic premise of statistical mechanics (ergodic hypothesis) that such time averages over the dynamics give the same results as ensemble averages.

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[1]Famously, Newton's prediction for the speed of sound in air was about 50 m s^{-1} too slow because he treated sound vibrations as isothermal rather than isentropic.

However, there is another answer that does not involve solving any dynamics and on the face of it may seem to be a different conception of the steady state probability distribution. It comes from the information content of probability distributions. In 1948 Claude Shannon laid the foundations for information theory in his landmark paper

C.E. Shannon, A Mathematical Theory of Communication, The Bell System Technical Journal **27**, 379–423 (1948). doi:10.1002/j.1538-7305.1948.tb01338.x

In it, Shannon proved that there is exists a unique function, satisfying a few basic assumptions, that characterises the information content in any probability distribution. This is the Shannon entropy

$$S = -k \sum_\alpha p_\alpha \ln p_\alpha, \tag{1.13}$$

where k is a positive constant that sets the units. For bit string messages it tells you how many bits of information are needed in order to transmit the message precisely. It provides a means for statistical inference, assigning likelihoods to different possible outcomes on the basis of known information and with as little bias as possible. For a given set of probabilities the Shannon entropy measures how much more you need to know to identify the exact state, so in order to avoid making unsupported assertions you should maximise the entropy. This approach is called **maximum entropy inference**.

The same philosophy can be applied to choosing the probabilities p_α of microstates in statistical physics. Maximising the Shannon entropy subject to the known information (*e.g.* average energy, average particle number, etc.) provides the least biased estimate for the probabilites. Identifying the Shannon entropy with the thermodynamic entropy (and setting $k = k_B$) this method reproduces the usual ensembles and Gibbs distribution. This approach to statistical mechanics was first presented by Edwin Jaynes. The fundamental connection it makes between the foundations of information theory and physics has been influential in both directions.

Let us see how the maximum entropy approach describes the canonical ensemble. In the canonical ensemble the information we know about the microstates is that their average energy is fixed (by contact with a heat bath)

$$\sum_\alpha p_\alpha E_\alpha = E, \tag{1.14}$$

where p_α is the probability of finding the system in microstate α, which has energy E_α. To determine the probabilities we maximise the Shannon entropy subject to this constraint and that the total probabilities sum to unity

$$\Rightarrow \qquad -k_B\big(\ln p_\alpha + 1\big) - \lambda_1 E_\alpha - \lambda_2 = 0, \tag{1.15}$$

where λ_1, λ_2 are the two Lagrange multipliers. Solving for the probabilities we obtain

$$p_\alpha = e^{-1-\lambda_2/k_B - \lambda_1 E_\alpha/k_B} = \frac{1}{Z} e^{-\beta E_\alpha}, \tag{1.16}$$

where we define $Z = \exp\{1 + \lambda_2/k_B\}$ and $\beta = \lambda_1/k_B$ as more conventional symbols. Thus the application of maximum entropy inference to determine the probabilities reproduces the ensembles of statistical mechanics.

The interested reader may like to take a look at Jaynes' original paper

E.T. Jaynes, Information Theory and Statistical Mechanics, Phys. Rev. **106**, 620 (1957). doi:10.1103/PhysRev.106.620

1.2 Ideal Gas

Perhaps the simplest description of a single component gas (or liquid) is a collection of non-interacting point particles in a container of volume V. It is not without its merits – it recovers Boyle's law for the equation of state of ideal gases – but it does not begin to capture the phase behaviour of water, for example. The most obvious thing that is missing is any form of interaction between the particles. These turn out to be difficult to account for, at least analytically. Basically, this is because there are many possibilities for the nature of the interactions and this in turn gives rise to the tremendous diversity in macroscopic behaviour and phases that even simple systems can exhibit.

Consider a gas of N identical particles in a box of volume V. The (positional) configurations of the gas are given by listing the positions $\{\mathbf{x}_i\}$, $i = 1, \ldots, N$, of all N particles and the partition function is

$$Z = \frac{1}{N!} \int_V \cdots \int_V d^3x_1 \cdots d^3x_N = \frac{V^N}{N!}, \tag{1.17}$$

where the factor of $N!$ accounts for the fact that the particles are indistinguishable. The free energy is

$$F = -k_\mathrm{B}T \ln Z \approx -k_\mathrm{B}T \big[N \ln V - \big(N \ln N - N\big)\big] \approx N k_\mathrm{B}T \ln \frac{N}{V}, \tag{1.18}$$

using Stirling's approximation $\ln N! \approx N \ln N - N$. The pressure in the ideal gas is given by

$$p = -\frac{\partial F}{\partial V} = \frac{N k_\mathrm{B}T}{V}, \tag{1.19}$$

and is known as the **ideal gas law**; it is the equation of state for a gas (or liquid) of non-interacting particles.

1.3 Hard Core Interactions: Excluded Volume

Now suppose we think of each particle as a sphere of radius a and the confining volume as a cubic box of side L. The configurations consist of the possible positions for the centres of each spherical particle. For a single particle, this is no longer the total volume of the box, $V = L^3$, but rather the smaller size $(L-2a)^3$ since the centre of the particle must always be at least a distance a away from any wall. This is an example of an **excluded volume**, a volume of space that the particle cannot occupy because of its **hard-core interactions** with the confining surfaces. If the same excluded volume, hard-core interactions are imposed between any two particles then we have a simple model of an interacting system, the **hard-core gas**. The partition function, as before, is just the integral over all possible configurations, *i.e.* positions for the centres of the N particles. The difficulty is in correctly accounting for the constraints, *i.e.* ensuring that no particles overlap; this can be done in one dimension but not in general. Nonetheless, some
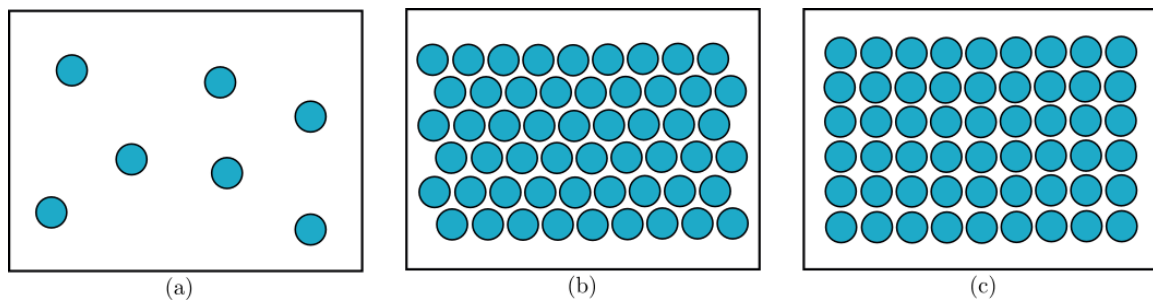

Figure 1.2: The hard-core gas model. (a) A gas (or liquid) phase at low density. (b) At high density the particles adopt a crystalline arrangement to avoid any overlaps; the highest density is achieved for a hexagonal lattice. (c) A square lattice arrangement.

basic conceptions are fairly intuitive, as illustrated in Fig. 1.2. When the density is low, the configurations are hardly constrained at all and the behaviour should be the same as that of the ideal gas. However, when the density is high, the particles have to be placed carefully into the box in order that they all fit with no overlaps. It is relatively easy to speculate that the best way of achieving this is to place them regularly in a crystal structure (although it is not so easy to prove). You might even be able to convince yourself that in two dimensions hexagonal packing is better than square. Thus we expect that even this simple model will capture a phase transition between gas (or liquid) and solid phases. This is indeed observed in numerical simulations.

1.3.1 Perturbative Expansions in the Density

Let's see how to incorporate roughly the effects of two-body excluded volume interactions. It is easy to see that the volume that a particle excludes from the position of any one other is

$$V_{\text{ex}} = \frac{4\pi}{3}(2a)^3, \tag{1.20}$$

because their centres cannot come closer than $2a$ apart. A rough estimate for the total reduction in accessible volume for a single particle is therefore

$$V \to V - N\frac{V_{\text{ex}}}{2}, \tag{1.21}$$

where the factor of $\frac{1}{2}$ accounts for the fact that the excluded volume is a two-body effect and so shared between two particles, *i.e.* it keeps track of double counting. This gives an approximation for the free energy of the interacting gas

$$F = Nk_{\text{B}}T\left[\ln\frac{N}{V - NV_{\text{ex}}/2} - 1\right] \approx Nk_{\text{B}}T\left[\ln\frac{N}{V} + \frac{N}{V}\frac{V_{\text{ex}}}{2} + \cdots\right]. \tag{1.22}$$

The second form hints at a useful interpretation of our rough approximation, namely it gives the first term in a perturbative expansion of the free energy in powers of the density, N/V. This is the basis of 'cluster expansion' methods that formalise what we have done. For the pressure (equation of state) we find

$$p = -\frac{\partial F}{\partial V} = k_{\text{B}}T\left[\frac{N}{V} + \frac{V_{\text{ex}}}{2}\left(\frac{N}{V}\right)^2 + \cdots\right], \tag{1.23}$$

which again represents a series expansion in powers of the density and is known as the **virial expansion**. The excluded volume divided by 2 is the coefficient of the quadratic term, which is called the second virial coefficient.

1.3.2 Depletion Interaction

As a simple, but important, application of excluded volume interactions, suppose a larger spherical particle of radius R is placed in a non-interacting gas. Larger particles, with sizes of order a micron are typically called **colloids**. The volume that the colloid excludes from the possible positions of the centre of a single gas particle is (see Fig. 1.3(a))

$$V_{\text{ex}} = \frac{4\pi}{3}(R + a)^3. \tag{1.24}$$

The remaining volume available to the gas is $V - V_{\text{ex}}$. The concept of excluded volume gives rise to an attractive force between two colloidal particles, as shown in Fig. 1.3(b), that acts whenever their separation h is less than $2a$ and the 'excluded volumes' of the two colloids overlap. The volume excluded to the centres of the gas particles by the two colloids is then a little less than
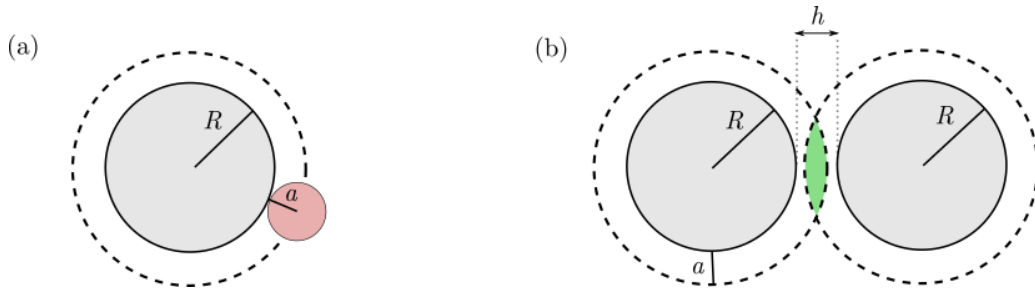
Figure 1.3: (a) Excluded volume around a colloidal particle: a large colloid (grey) excludes gas particles (red) from a region surrounding it, indicated by the dashed line. (b) Depletion interaction between two colloids induced by an overlap of their excluded volumes (green).

the sum of their individual excluded volumes and, in particular, a function of their separation h, i.e. $V_{\mathrm{ex}} = V_{\mathrm{ex}}(h)$. The free energy for the gas is then approximately

$$F \approx N k_{\mathrm{B}} T \ln \frac{N}{V - V_{\mathrm{ex}}(h)} \approx N k_{\mathrm{B}} T \ln \frac{N}{V} + \frac{N}{V} k_{\mathrm{B}} T \, V_{\mathrm{ex}}(h). \qquad (1.25)$$

The second term has the structural form of the pressure in the ideal gas times the excluded volume, in other words it represents the work done in excluding the gas from the volume taken up by the colloids. This is minimised by minimising the excluded volume, or by maximising the *overlap* of the individual excluded volumes from each colloid. From either point of view we see that there is a free energy gain in pushing the colloids together, or an effective short-range attractive force between them. This is known as the **depletion interaction**, or the Asakura-Oosawa theory after its discoverers. In actual colloidal systems it is commonly controlled by adding a gas of polymer particles, whose size is small compared to the colloid and can be controlled to tune the range (and strength) of the depletion interaction.

1.4   Virial Expansion

We now turn to a slightly more formal presentation of the statistical mechanics of interacting particles, that also includes more general interactions. Let us approximate the interactions between particles by pairwise potentials $U_{ij} = U(\mathbf{r}_i - \mathbf{r}_j)$ depending only on the particle separation. Then the partition function is

$$Z = \frac{1}{N!} \int e^{-\beta \sum_{i<j} U_{ij}} \prod_{a=1}^{N} d^3 r_a = \frac{1}{N!} \int \prod_{i<j} e^{-\beta U_{ij}} \prod_{a=1}^{N} d^3 r_a. \qquad (1.26)$$

Now if the interactions are short-ranged (*e.g.* contact interactions) and the density is low then for most positions of particles i and j the interaction will be small and $\exp\{-\beta U_{ij}\} \approx 1$. This would then reproduce the ideal gas law. To go beyond it we use the fact that $\exp\{-\beta U_{ij}\}$ is almost always close to 1 and write

$$e^{-\beta U_{ij}} = 1 + \left(e^{-\beta U_{ij}} - 1\right) \equiv 1 + f_{ij}. \qquad (1.27)$$

The functions f_{ij} defined in this way are called the Mayer f functions. They are numerically small and we use this to develop a perturbative expansion of the partition function

$$Z = \frac{1}{N!} \int \prod_{i<j}(1 + f_{ij}) \prod_{a=1}^{N} d^3 r_a = \frac{1}{N!} \int \left(1 + \sum_{i<j} f_{ij} + \sum_{i<j,k<l} f_{ij} f_{kl} + \cdots \right) \prod_{a=1}^{N} d^3 r_a. \qquad (1.28)$$

The leading term gives $V^N/N!$ as for the ideal gas. The first correction involves the terms with a single f_{ij} and since the interaction potential is the same for every pair (choice of i and j) the

contribution will be that for any one pair (say $i = 1$ and $j = 2$) multiplied by the number of pairs. Thus we can evaluate the partition function as

$$Z = \frac{1}{N!}\left[V^N + V^{N-2} \cdot \binom{N}{2} \int f_{12} \, d^3 r_1 d^3 r_2 + \cdots \right]. \tag{1.29}$$

For the integral we change variables to the centre-of-mass $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and relative $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ coordinates, which gives

$$\int f_{12} \, d^3 r_1 d^3 r_2 = V \int f_{12}(\mathbf{r}) \, d^3 r. \tag{1.30}$$

We can then write the free energy as

$$F = -k_B T \ln Z = -k_B T \left[N \ln V - \left(N \ln N - N \right) + \frac{N(N-1)}{2V} \int f_{12}(\mathbf{r}) \, d^3 r + \cdots \right], \tag{1.31}$$

and hence the pressure is given by

$$p = -\frac{\partial F}{\partial V} = k_B T \left[\frac{N}{V} - \frac{N(N-1)}{2V^2} \int f_{12}(\mathbf{r}) \, d^3 r + \cdots \right]. \tag{1.32}$$

Now N is of order Avagadro's number so $N - 1 \approx N$ and writing $n = N/V$ for the number density we see that we have obtained an expansion for the pressure in powers of the density of the general form

$$p = k_B T \left[n + \sum_{k \geq 2} B_k \, n^k \right]. \tag{1.33}$$

This is known as the **virial expansion** and the coefficients B_k are called the **virial coefficients**. We have calculated the second virial coefficient and shown that it is given by

$$B_2 = -\frac{1}{2} \int f_{ij}(\mathbf{r}) \, d^3 r. \tag{1.34}$$

The systematic calculation of the higher virial coefficients is usually facilitated by working with the grand canonical ensemble, which streamlines and simplifies the organisation and counting of all n-body ($n = 3, 4, \dots$) interactions. We do not cover this here and leave the interested reader to consult the books, *e.g.* Kardar's.

1.4.1 Van der Waals Equation of State

You should be able to verify that for hard-core interactions $B_2 = \frac{1}{2} V_{\text{ex}}$, confirming the informal arguments we gave in §1.3.1. Let us see how the value changes if we also include an attractive part of the interaction for separations outside of the hard core. Such interactions arise generally from electrostatics: fluctuations in the electronic charge density around any particle induce a small dipole moment and the induced dipole moment of one particle interacts with that of any other giving rise to dipole-dipole interactions, which decay with separation as $1/r^6$. A widely used interaction of this form is the **Lennard-Jones potential**

$$U_{\text{LJ}}(\mathbf{r}) = 4\epsilon \left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right), \tag{1.35}$$

where ϵ is an energy scale and σ is a length-scale. The repulsive term in r^{-12} mimics a short-range (hard-core) repulsion and is phenomenological. One can check that the potential vanishes at $r = \sigma$ and takes the value $-\epsilon$ at its minimum at $r = 2^{1/6}\sigma$. If we focus only on the attractive part of the interaction we can approximate the contribution it makes to the virial coefficient by

$$\int_{r > \sigma} f_{ij}(\mathbf{r}) \, d^3 r \approx \int_{r > \sigma} \left(e^{4\beta\epsilon\sigma^6/r^6} - 1 \right) 4\pi r^2 \, dr \approx 4\pi \int_{r > \sigma} \frac{4\beta\epsilon\sigma^6}{r^6} r^2 \, dr, \tag{1.36}$$
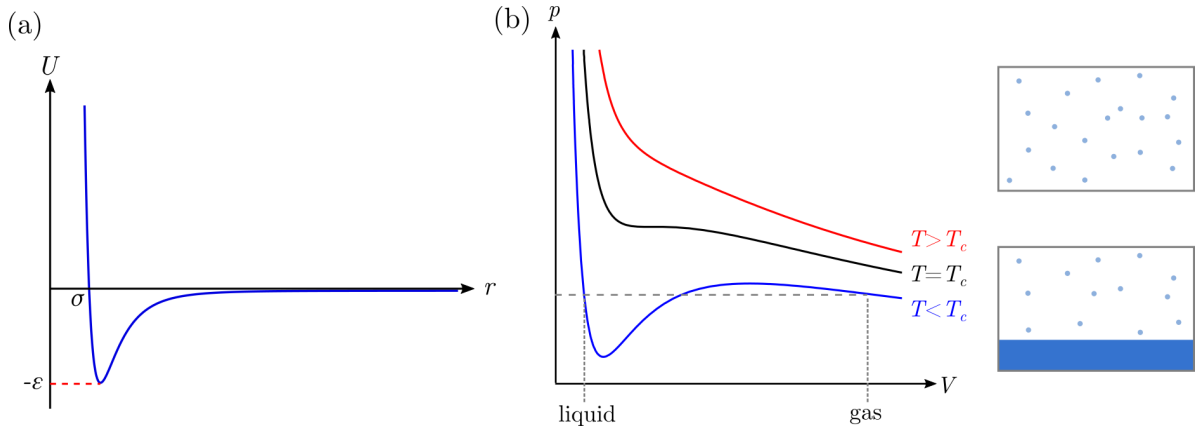
Figure 1.4: (a) The Lennard-Jones potential. (b) Isotherms of the van der Waals equation of state. The attractive interactions lead to condensation of the liquid phase, which coexists with its less dense vapour.

where in the last step we used a Taylor expansion. Performing the integral we find the second virial coefficient is modified to

$$B_2 \approx \frac{1}{2} V_{\text{ex}} - \frac{8 \pi \epsilon \sigma^3}{3 k_{\text{B}} T}. \tag{1.37}$$

The attractive part of the interaction reduces the value of the second virial coefficient by an amount that depends on the strength of the attraction (ϵ) and on the temperature. To keep things simple, let's take $\sigma = 2a$ to be the hard-core separation so that we have

$$B_2 \approx \frac{1}{2} V_{\text{ex}} - \frac{2 \epsilon V_{\text{ex}}}{k_{\text{B}} T}, \tag{1.38}$$

and the equation of state can be written

$$p = k_{\text{B}} T \left(n + B_2 n^2 + \cdots \right) = n \, k_{\text{B}} T \left(1 + \frac{V_{\text{ex}}}{2} n \right) - 2 \epsilon V_{\text{ex}} n^2 + \cdots . \tag{1.39}$$

Rearranging, and using the approximation $1 + n \, V_{\text{ex}}/2 \approx (1 - n V_{\text{ex}}/2)^{-1}$, we can put this into the form

$$\left(p + 2 \epsilon V_{\text{ex}} \frac{N^2}{V^2} \right) \left(V - \frac{N V_{\text{ex}}}{2} \right) = N \, k_{\text{B}} T. \tag{1.40}$$

The result of doing all this is that we have reproduced the **van der Waals equation of state**. Like Boyle's ideal gas law, the van der Waals equation was originally obtained from empirical observations; statistical mechanics has provided an explanation for how such an equation of state arises.

To get a rough idea of what the van der Waals equation of state tells us about interacting particle systems it is useful to plot a few of the isotherms – the relationship between pressure and volume for different values of the temperature. In Fig. 1.4(b) we show three of them that convey the basic phenomenology. At high temperatures the situation is similar to the ideal gas, which is to say the isotherm has the same general shape as it does in the ideal case ($pV = Nk_{\text{B}}T$) and there is a single value of the volume (density) for each value of the pressure. However, at low enough temperatures the situation is different, the isotherm develops a 'minimum' and, for a certain range of pressures, there are three values of the volume for a given pressure. The smallest value corresponds to a dense phase, or liquid, while the largest value represents a less dense gas, the liquid's vapour; the intermediate value is unstable. Thus the van der Waals equation of state predicts that at low enough temperatures, and the right pressure, the system can co-exist in two phases – a condensed liquid together with its vapour. This is exactly what is observed for many liquid-gas systems.
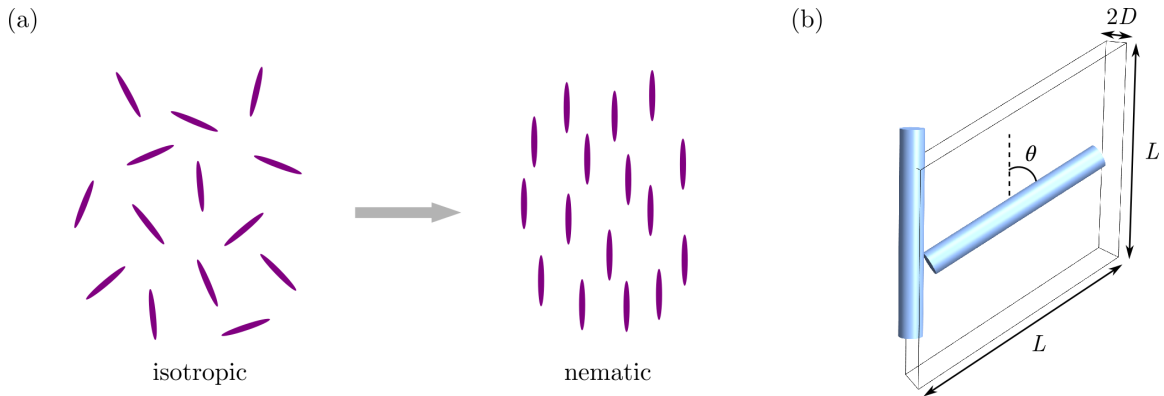
9

Figure 1.5: (a) Schematic of the isotropic and nematic phases of hard rods. In the nematic phase the molecules all align along a common direction. A phase transition occurs by changing density, or temperature. (b) The excluded volume of two hard rods depends on their relative orientation. This figure indicates how to estimate it when the rods are very slender, $L \gg D$.

1.5 Hard Rods

There are a huge number of extensions and embellishments to the simple hard-sphere fluid. We mention briefly just one, the replacement of hard spheres with hard rods, representing molecules that are long and thin, with a length L much greater than their diameter D. The microscopic states of the system now involve specifying the positions and orientations of all of the rods; see the cartoons of Fig. 1.5. The interesting new feature is how the orientations are constrained, or coordinated, by the hard core interactions. The excluded volume for a pair of rods depends on their relative orientations and is larger when the rods are perpendicular ($\sim L^2 D$) compared to when they are parallel ($\sim L D^2$). This difference drives an alignment transition from a state where the rods are oriented randomly, the **isotropic phase**, to one where they all adopt the same orientation, which is known as a **nematic liquid crystal** and illustrated schematically in Fig. 1.5(a). This is the material that underpins all of our flat panel displays. An important feature is that it is only the orientations of the molecules that become ordered and not their positions as in the formation of a crystal; the nematic state is still fluid. This is a state of matter intermediate between simple isotropic liquids and crystalline solids. There are literally dozens of them, known collectively as the mesomorphic phases.

From Fig.1.5(b) we can see that the excluded volume for two rods with an angle θ between them is approximately

$$V_{\text{ex}} \simeq L^2 \sin\theta \,.\, 2D, \tag{1.41}$$

when the rods are very slender. If we let $f(\theta, \phi)$ be the distribution function for rod orientations then the number of rods with a given orientation is Nf and (1.22) becomes

$$
\begin{aligned}
F = Nk_{\text{B}}T\Bigg[&\int f(\theta, \phi) \ln \frac{f(\theta, \phi)N}{V} \, \sin\theta \, d\theta \, d\phi \\
&+ \frac{N}{V} \int f(\theta_1, \phi_1) f(\theta_2, \phi_2) \frac{1}{2} V_{\text{ex}}(\theta) \, \sin\theta_1 \, d\theta_1 \, d\phi_2 \, \sin\theta_2 \, d\theta_2 \, d\phi_2 + \cdots \Bigg],
\end{aligned}
\tag{1.42}
$$

integrating over orientations. The problem now is to determine the distribution f so as to minimise F. This approach to the isotropic–nematic transition was first presented by Lars Onsager in 1949, using a variational method to estimate f. Onsager found that he was able to compute all the integrals for the trial form

$$f(\theta, \phi) = \frac{\alpha}{4\pi \sinh\alpha} \cosh\big(\alpha \cos\theta\big), \tag{1.43}$$

where α is a free parameter. $\alpha = 0$ corresponds to the isotropic distribution $f = \frac{1}{4\pi}$, while large values of α give a distribution peaked around $\theta = 0, \pi$. The free energy can then be minimised

with respect to α to determine the state of the system. The result predicts a (first order) phase transition to fairly large values of $\alpha \approx 20$ at modest densities provided the rods are sufficiently slender ($L \gg D$). In § 4.2.2 we will reproduce this result from a different approach.

Direct variation of (1.42) with respect to $f(\theta, \phi)$, subject to the constraint that the probability distribution is normalised, leads to the condition

$$\ln f(\theta_1, \phi_1) + 1 + \frac{N}{V} \int f(\theta_2, \phi_2) V_{\text{ex}}(\theta) \sin \theta_2 \, d\theta_2 \, d\phi_2 - \lambda = 0, \tag{1.44}$$

where λ is a Lagrange multiplier enforcing the constraint. This can be written in the form

$$f(\theta_1, \phi_1) = \frac{1}{Z} \exp \left\{ -\frac{N}{V} \int f(\theta_2, \phi_2) V_{\text{ex}}(\theta) \sin \theta_2 \, d\theta_2 \, d\phi_2 \right\}, \tag{1.45}$$

where Z is a normalisation factor, and self-consistent solutions developed numerically. With minor modification the self-consistent form also provides the basis for a mean field theory treatment of the isotropic-nematic transition that is covered in one of the problems.

1.5.1 Measure of Alignment: Nematic Order

The degree of alignment of the rods is fully encoded in the probability distribution $f(\theta, \phi)$, however, it is useful to have simpler measures, such as the average orientation, or first moment of the distribution. We will find it convenient to denote the orientation of a rod by a unit vector $\boldsymbol{\nu}$. It is clear that when the distribution is isotropic, $f(\theta, \phi) = \frac{1}{4\pi}$, the average orientation vanishes

$$\langle \nu_x \rangle = \langle \nu_y \rangle = \langle \nu_z \rangle = 0. \tag{1.46}$$

In statistical physics it is traditional to use an angle bracket notation for statistical averages, i.e. $\langle \nu_x \rangle = \int \nu_x f(\theta, \phi) \sin \theta \, d\theta d\phi$. It turns out that the same is true for the probability distribution (1.43); the average orientation vanishes. This is a fundamental property of nematic order. The probability distribution is invariant under the **nematic symmetry** $\boldsymbol{\nu} \to -\boldsymbol{\nu}$. Thus to distinguish the nematic and isotropic phases we have to go to the second moments $\langle \nu_i \nu_j \rangle$. For an isotropic distribution we can compute these from symmetry; they vanish if $i \neq j$ and if they are equal

$$\langle \nu_x \nu_x \rangle = \langle \nu_y \nu_y \rangle = \langle \nu_z \nu_z \rangle = \frac{1}{3} \langle \nu_x \nu_x + \nu_y \nu_y + \nu_z \nu_z \rangle = \frac{1}{3}. \tag{1.47}$$

We can summarise this by saying that for an isotropic distribution

$$Q_{ij} = \left\langle \nu_i \nu_j - \frac{1}{3} \delta_{ij} \right\rangle, \tag{1.48}$$

vanishes for all i and j. On the other hand, for a probability distribution strongly peaked around $\theta = 0, \pi$, such as (1.43) for large α, this average does not vanish. For instance

$$Q_{zz} = \frac{2}{\alpha^2} \left(1 - \frac{\alpha \cosh \alpha}{\sinh \alpha} + \frac{\alpha^2}{3} \right). \tag{1.49}$$

Thus the measure Q_{ij} – the second moment of the probability distribution – serves to distinguish the nematic phase from the isotropic one. It is conventional to write it as

$$Q_{ij} = \left\langle \nu_i \nu_j - \frac{1}{3} \delta_{ij} \right\rangle = s \left(n_i n_j - \frac{1}{3} \delta_{ij} \right). \tag{1.50}$$

Here, s is a scalar measure of the degree of order that vanishes in the isotropic phase and is non-zero in the nematic; it is called the **scalar order parameter**. The average direction of alignment in the nematic is captured by the unit vector **n**, which is called the **nematic director**.

Chapter 2

Phase Separation

In this chapter we begin our description of phases and phase transitions by discussion of an idealised model example: the **phase separation** of a binary fluid mixture, also called the *AB fluid*. Two fluids that are brought together may mix thoroughly, or remain separated, as is the case for oil and water. Transitions between mixed and unmixed states can be induced by varying the interactions between the two fluids or the temperature.

2.1 Entropy of Mixing and Interaction Energy

The tendency for two fluids to mix is entropic. A simple model that captures this is to break space up into a large number of boxes each of which can be assigned to either fluid A or B. If each box (or site) is occupied independently then the probabilities are

$$p_A = \frac{V_A}{V} \equiv \phi_A, \qquad\qquad p_B = \frac{V_B}{V} \equiv \phi_B, \qquad (2.1)$$

where V_A, V_B are the total volumes of each fluid, and obviously $V = V_A + V_B$. ϕ_A and ϕ_B are the called the **volume fractions**. As each box is treated independently there are only two possibilities – either it contains fluid A or fluid B – and the entropy per site is

$$S_{\text{site}} = -k_{\text{B}}\big[\phi_A \ln \phi_A + \phi_B \ln \phi_B\big]. \qquad (2.2)$$

Often this is written in the form

$$S_{\text{site}} = -k_{\text{B}}\big[\phi \ln \phi + (1 - \phi) \ln(1 - \phi)\big], \qquad (2.3)$$

making use of the fact that $\phi_A + \phi_B = 1$ and slightly streamlining the notation.

What causes the fluids to separate are repulsive interactions between them. It is clear that the important term is going to be proportional to $\phi_A \phi_B$, but let us arrive at this a little more carefully. We assume that the interactions are short ranged and only with the immediately neighbouring molecules; this is a good approximation in many cases. The expectation value of the interaction energy between any single box and its neighbours is

$$\phi_A \sum_{\text{neighbours}} \big(\epsilon_{AA}\phi_A + \epsilon_{AB}\phi_B\big) + \phi_B \sum_{\text{neighbours}} \big(\epsilon_{AB}\phi_A + \epsilon_{BB}\phi_B\big), \qquad (2.4)$$

where the first term accounts for the interactions when the box contains fluid A, which it does with probability ϕ_A, and the second when it contains fluid B, and $\epsilon_{AA}, \epsilon_{BB}, \epsilon_{AB}$ are the three interaction energies. If there are z nearest neighbours then the expectation value for the total interaction energy per site is

$$E_{\text{site}} = \frac{z}{2}\big[\epsilon_{AA}\phi_A^2 + \epsilon_{BB}\phi_B^2 + 2\epsilon_{AB}\phi_A\phi_B\big], \qquad (2.5)$$

where the factor of $\frac{1}{2}$ accounts for the fact that each interaction is counted *twice* in summing over all sites – once when it is the 'central' site and once when it is a 'neighbour'. We reexpress the interaction energy in the form

$$
\begin{aligned}
E_{\text{site}} &= \frac{z}{2}\Big[\epsilon_{AA}\phi_A\big(1-\phi_B\big) + \epsilon_{BB}\phi_B(1-\phi_A) + 2\epsilon_{AB}\phi_A\phi_B\Big], \\
&= \frac{z}{2}\big[2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}\big]\phi_A\phi_B + \frac{z}{2}\big(\phi_A\epsilon_{AA} + \phi_B\epsilon_{BB}\big).
\end{aligned}
\tag{2.6}
$$

The last term is the expectation value for the interaction energy when the two fluids are completely separated, so that the energy associated to mixing is indeed a term proportional to $\phi_A\phi_B$. For synergy with our subsequent topics we choose to write this interaction energy as $\Delta\,\phi_A\phi_B$, although in the literature it is far more common to see it written as $\chi\,k_{\text{B}}T\,\phi_A\phi_B$.

2.2   Phase Diagram for the AB Fluid

Combining this expression for the interaction energy with the entropy calculated previously we obtain the free energy per site of mixing for an AB fluid

$$
F_{\text{site}} \equiv f\,v_0 = \Delta\,\phi(1-\phi) + k_{\text{B}}T\Big[\phi\ln\phi + (1-\phi)\ln(1-\phi)\Big].
\tag{2.7}
$$

It is common to denote the free energy per volume (free energy density) by the lower case f as we do from here on. v_0 is the 'volume of a site' making sure the dimensions are correct; you can think of it as the volume of a molecule. Now, consider how the free energy varies with the volume fraction. When Δ is negative, the interactions favour mixing and the energy is lowest when $\phi = \frac{1}{2}$. The same value maximises the entropy and so overall the free energy is at its minimum. When Δ is positive the interaction energy is minimised by taking $\phi = 0$ or 1 but this comes at the expense of reducing the entropy to zero and so will only be favoured when Δ is sufficiently large, or T sufficiently small. This is the essence of phase separation. But how does it actually work? And what is the critical value of Δ, or T?

We answer the second question first. There are many ways in which we might do this, however, it is somewhat convenient for our subsequent development to work directly with the expression for the free energy. We write $\phi = (1+s)/2$ and treat s as small, using the Taylor series

$$
\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \frac{1}{4}x^4 + \cdots,
\tag{2.8}
$$

to arrive at

$$
fv_0 = \frac{\Delta}{4} - k_{\text{B}}T\ln 2 + \frac{(2k_{\text{B}}T - \Delta)}{4}\,s^2 + \frac{k_{\text{B}}T}{12}\,s^4 + \cdots.
\tag{2.9}
$$

The free energy has a single minimum at $s = 0$ when $T > \Delta/2k_{\text{B}}$ but when T is less than this – equivalently $\Delta > \Delta_c = 2k_{\text{B}}T$ – then $s = 0$ becomes a local maximum for the free energy and the minimum is instead at the non-zero values

$$
s \approx \pm\left(\frac{3(\Delta - 2k_{\text{B}}T)}{2k_{\text{B}}T}\right)^{1/2}.
\tag{2.10}
$$

Now suppose we have a mixture that would like to separate. How should it do so? Suppose we split the mixture into two parts, with a volume V_a having the composition ϕ_a (A rich) and a volume V_b having the composition ϕ_b (B rich). We need

$$
V_a\phi_a + V_b\phi_b = V\Phi, \qquad \text{and} \qquad V_a + V_b = V,
\tag{2.11}
$$

so that overall the total composition (fraction of liquid A and liquid B) and total volume remain correct. The total free energy of this separated state is $V_a f(\phi_a) + V_b f(\phi_b)$ and so long as this is less than the total free energy $V f(\Phi)$ of the mixed state it will be favourable to separate in
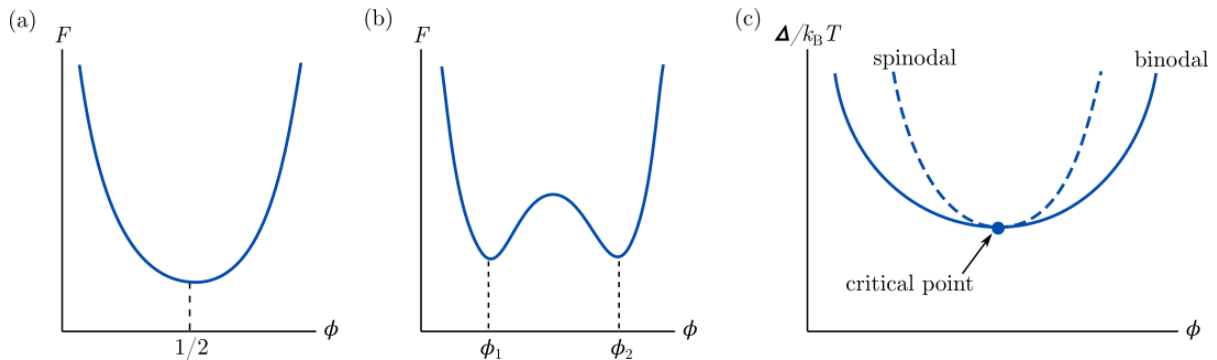
Figure 2.1: Free energy for a binary mixture with (a) $\Delta < 2k_{\mathrm{B}}T$ and (b) $\Delta > 2k_{\mathrm{B}}T$. (c) Schematic phase diagram for the binary fluid; the mixture is stable outside the binodal but inside it prefers to separate. Between the binodal and spinodal the mixture is metastable, while within the spinodal it is linearly unstable.

this way. To determine the compositions ϕ_a, ϕ_b and volumes V_a, V_b we minimise the free energy subject to the two constraints, which gives the conditions

$$f'(\phi_a) = f'(\phi_b) = \frac{f(\phi_a) - f(\phi_b)}{\phi_a - \phi_b}. \tag{2.12}$$

The slope of the free energy density at the two separated compositions is equal and given by the chord between them; this is **Maxwell's common tangent construction**. For symmetric free energy functions (invariant under $\phi \to 1 - \phi$), as we are considering, the common tangent construction gives ϕ_a and ϕ_b as the two minima ϕ_1, ϕ_2 of the free energy density.

We summarise the situation with the phase diagram for a two fluid mixture, Fig. 2.1. Mixtures are characterised by the volume fractions $\phi_A = \phi$ and $\phi_B = 1 - \phi$ of the two liquids and the interaction parameter $\Delta - 2k_{\mathrm{B}}T$. Not all homogeneous mixtures are unstable and demix: the two volumes V_a, V_b of A rich and B rich liquid are both positive only when $\phi_1 < \Phi < \phi_2$ and it is only mixtures within this range that separate; those outside it remain stably mixed. The boundary between the stable and unstable regions is called the **binodal**; it is the locus of the minima ϕ_1, ϕ_2 of the free energy. Inside the binodal the mixture favours phase separation because the linear combination $V_a f(\phi_a) + V_b f(\phi_b)$ of energies of the A rich and B rich portions is less than the energy $V f(\Phi)$ of the homogeneous mixture; this happens because the free energy density is **non-convex** between ϕ_1 and ϕ_2. The loss of convexity is a signifier of the instability. Within the binodal the free energy curve can be further separated into a region where it is *locally* convex and an inner region where it is locally concave. The crossover between these regions is called the **spinodal**. Inside the spinodal the homogeneous mixture is linearly unstable and demixing happens spontaneously; this is known as **spinodal decomposition**. In contrast, outside the spinodal (but still inside the binodal) the homogeneous mixture is linearly stable to small fluctuations despite not being the lowest energy state.

2.3   Solutions and Osmotic Pressure

The model of the AB fluid applies also to solutions, a material dissolved in a liquid; for instance, this may be as simple as salt in water. ϕ is then the volume fraction of the solute and $1 - \phi$ that of the solvent. Suppose we add to a solution a small volume dV of pure solvent. This will lead to a change in free energy $dF = -p_{\mathrm{osm}} \, dV$ where p_{osm} is the **osmotic pressure**. To calculate it we first note that we have not added any more solute so that its total volume (initially ϕV) remains constant

$$d(\phi V) = d\phi \, V + \phi \, dV = 0, \qquad \Rightarrow \qquad d\phi = -\frac{\phi}{V} \, dV. \tag{2.13}$$

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This then gives the change in free energy as

$$dF = d\big(f(\phi)V\big) = \left(\frac{df}{d\phi}\,d\phi\right)V + f(\phi)\,dV, \tag{2.14}$$

$$= -\big[\phi f'(\phi) - f(\phi)\big]dV, \tag{2.15}$$

and we can read off the expression $p_{\mathrm{osm}} = \phi f'(\phi) - f(\phi)$ for the osmotic pressure. For the free energy density (2.7) this becomes

$$p_{\mathrm{osm}} = \frac{1}{v_0}\left[-\Delta\phi^2 - k_{\mathrm{B}}T\ln(1-\phi)\right]. \tag{2.16}$$

Often the addition of solvent is taken to come from a reservoir that the solution is in contact with via a semi-permeable membrane, *i.e.* one that allows the solvent molecules to pass but not the solute. The osmotic pressure is then the force per unit area that the solution exerts on this semi-permeable membrane. If we consider that the reservoir has a fixed volume then the process of transferring an amount dV from the reservoir to the solution will change its free energy by an amount $-f(0)\,dV$. Including this contribution in the total free energy change modifies the osmotic pressure by a constant[1] to give $p_{\mathrm{osm}} = \phi f'(\phi) - f(\phi) + f(0)$.

Let's expand the expression for the osmotic pressure (2.16) as a Taylor series in ϕ

$$p_{\mathrm{osm}} = \frac{k_{\mathrm{B}}T}{v_0}\phi + \frac{1}{v_0}\left(\frac{k_{\mathrm{B}}T}{2} - \Delta\right)\phi^2 + \cdots . \tag{2.17}$$

This has the form of a virial expansion. To connect it more explicitly note that $V_A = N_A v_0$ so that the osmotic pressure is

$$p_{\mathrm{osm}} = k_{\mathrm{B}}T\left[\frac{N_A}{V} + \left(\frac{1}{2} - \frac{\Delta}{k_{\mathrm{B}}T}\right)v_0\left(\frac{N_A}{V}\right)^2 + \cdots\right], \tag{2.18}$$

and we can identify $(\frac{1}{2} - \frac{\Delta}{k_{\mathrm{B}}T})v_0$ as the second virial coefficient. It has the same basic form as we found for the van der Waals equation of state in §1.4.1.

2.4 Interfacial Tension

When the two fluids demix there is an interface between the A rich phase and the B rich phase. The statistical properties of interfaces reflect the same competition between interaction energies and entropy. When the interaction energy dominates the interface is sharp and as small as possible to minimise the unfavourable interactions between the two liquids. By contrast, when the interaction energy is weak entropy dominates and the interface may expand so as to explore many more microstates and increase its entropy. In general the interface may be described by a free energy per unit area, known as a **surface tension**.

To say more, we need to recognise that the composition ϕ is spatially varying since it takes different values in the A rich and B rich regions; in other words it is a function $\phi(\mathbf{x})$. What sort of function is it? Locally, within any separated region it is constant, taking the values ϕ_1, ϕ_2 corresponding to the minima of the free energy. At the interface it has to interpolate between these values. A simple functional form which captures this (and turns out to be the correct function for certain simplified models) is the sigmoid

$$\phi(x) = \frac{\phi_1 + \phi_2}{2} + \frac{\phi_2 - \phi_1}{2}\tanh(x/\xi). \tag{2.19}$$

Here, we are taking the interface to be the plane $x = 0$ so that ϕ only depends on the x-coordinate and ξ is a length scale that characterises the width of the interface. Regardless of

---

[1]More correctly $f(0)$ may depend on temperature (and pressure) but is only a property of the solvent. For the free energy density (2.7) $f(0) = 0$.

the precise form, the gradients, $d\phi/dx$ or $\nabla\phi$, are localised around the interface. This allows a simple **gradient** contribution to the free energy density

$$f_{\text{gradient}} = \frac{\kappa}{2}(\nabla\phi)^2, \tag{2.20}$$

to capture the physics of a surface tension. The coefficient κ controls the strength of the surface tension, which turns out to be proportional to $\sqrt{\kappa}$.

Let us argue for this on dimensional grounds: Combining the gradient term with the free energy in the form (2.9) gives

$$f = \frac{\kappa}{8}(\nabla s)^2 + \frac{(2k_{\text{B}}T - \Delta)}{4}s^2 + \frac{k_{\text{B}}T}{12}s^4 + \cdots, \tag{2.21}$$

and if the length scale of the interface is ξ then comparing the first and second terms gives the dimensional balance

$$\frac{\kappa}{\xi^2} \sim \Delta - 2k_{\text{B}}T, \qquad \text{or} \quad \xi \sim \sqrt{\frac{\kappa}{\Delta - 2k_{\text{B}}T}}. \tag{2.22}$$

The width of the interface is proportional to $\sqrt{\kappa}$. In addition, close to the critical temperature $T_c = \Delta/2k_{\text{B}}$, this length scale diverges as $|T_c - T|^{-1/2}$ which turns out to be a characteristic feature of critical phase transitions. What about the surface tension? To get the energy per unit area of the interface we integrate the gradient contribution across the width of the interface

$$\sigma = \int \frac{\kappa}{2}\left(\frac{d\phi}{dx}\right)^2 dx \approx \frac{\kappa}{2}\left(\frac{\phi_2 - \phi_1}{\xi}\right)^2 \xi \sim \frac{\kappa}{\xi}, \tag{2.23}$$

making reasonable estimates. We see that the surface tension σ is proportional to $\sqrt{\kappa}$ as claimed.

2.5 Cahn-Hilliard Equation

How does the composition $\phi(\mathbf{x}, t)$ evolve in time? Because it represents the volume fractions of the two fluids ($\phi_A = \phi$, $\phi_B = 1 - \phi$) and neither fluid is created nor destroyed, it must be conserved so we require a continuity equation

$$\partial_t \phi = -\nabla \cdot \mathbf{J}, \tag{2.24}$$

where $\mathbf{J}$ is the current, or flux – ϕ may be transported but it must be conserved because the total quantity of each fluid is fixed. The current represents a flow of molecules from the liquid A rich phase to the liquid B rich phase, or *vice-versa*, and such particle flows are controlled by the chemical potential. When the chemical potential is constant (the same in both phases) there is no flow, so the current should be $\mathbf{J} = -M\nabla\mu$, where M is a positive material dependent constant. Finally, the chemical potential is given by[2]

$$\mu = \frac{\partial f}{\partial \phi} - \kappa\nabla^2\phi, \tag{2.25}$$

with contributions both from the gradient of the bulk free energy (the desire to minimise the free energy) and the curvature of interfaces. Putting all the pieces together we obtain the **Cahn-Hilliard equation**

$$\partial_t \phi = M\nabla^2\frac{\partial f}{\partial \phi} - \kappa M\nabla^4\phi. \tag{2.26}$$

Consider again the instability of the homogeneous mixture with $\phi = \frac{1}{2}$. We linearise the Cahn-Hilliard equation for small fluctuations around this state, setting $\phi = (1 + s)/2$ as we did previously and using (2.9) for the bulk free energy

$$\partial_t s = 2M(2k_{\text{B}}T - \Delta)\nabla^2 s - \kappa M\nabla^4 s. \tag{2.27}$$

---

[2]Those familiar with the calculus of variations will be able to recognise this as the functional derivative of the free energy, $\mu = \delta F/\delta\phi$.

Taking the Fourier transform in space we find solutions

$$\tilde{s}(\mathbf{k}, t) = \tilde{s}_0(\mathbf{k}) \, e^{-Mk^2[2(2k_{\mathrm{B}}T - \Delta) + \kappa k^2]t}. \tag{2.28}$$

These decay provided $2(2k_{\mathrm{B}}T - \Delta) + \kappa k^2 > 0$, which would imply stability for those modes. However, whenever Δ is large enough (or T is below the critical temperature $T_c = \Delta/2k_{\mathrm{B}}$) the modes with small enough wavevector k are unstable and grow exponentially. One can show that the modes that grow fastest have wavevectors with

$$k^2 = \frac{\Delta - 2k_{\mathrm{B}}T}{\kappa}, \tag{2.29}$$

and this selects the length scale that first appears in the initial stages of phase separation. A more general analysis identifies the spinodal and the initial growth rates for unstable homogeneous mixtures with other values of $\phi_1 < \phi < \phi_2$ within the binodal.

2.6 Droplet Equilibrium and Ostwald Ripening

In the late stages of phase separation there will be round droplets of the minority phase (A, say) in the majority phase (B). They are round because of the surface tension. We consider the condition of equilibrium of an A-rich droplet of radius R. Let ϕ_a denote the volume fraction of the droplet and ϕ_b that of the surrounding B-rich majority phase. Then the free energy is

$$F = \left(V - \frac{4\pi R^3}{3}\right) f(\phi_b) + \frac{4\pi R^3}{3} f(\phi_a) + 4\pi R^2 \sigma, \tag{2.30}$$

where the first two terms represent the bulk phases and the last is the surface tension contribution from the interface. The volume fractions ϕ_a, ϕ_b and droplet size R are not independent since we must still satisfy

$$\left(V - \frac{4\pi R^3}{3}\right)\phi_b + \frac{4\pi R^3}{3} \phi_a = V\Phi, \tag{2.31}$$

to conserve the total amount of A fluid. Minimisation of the free energy subject to this constraint gives

$$f'(\phi_a) = f'(\phi_b) = \frac{f(\phi_a) - f(\phi_b) + 2\sigma/R}{\phi_a - \phi_b}. \tag{2.32}$$

This entails two conditions: The first is an 'equal tangent' condition; the two volume fractions have the same slope in the free energy density. The second is the value of this slope. First suppose the droplet is very large so that we may treat the radius as effectively infinite. Then (2.32) reproduces Maxwell's common tangent construction. It will be enough to consider the case of a symmetric potential with $f(\phi_a) = f(\phi_b)$ where the equilibrium condition simplifies to $f'(\phi_a) = f'(\phi_b) = 0$.

When the droplet radius is finite its effect, through the surface tension term in (2.32), is to modify the values of ϕ_a, ϕ_b (from the infinite radius limit) by small amounts such that $f'(\phi_a) = f'(\phi_b) \neq 0$. What is important is that the magnitude of this effect is larger for smaller droplets. To say a little more, consider the chemical potential of the droplet, which is

$$\mu_{\mathrm{droplet}} = f'(\phi) - \kappa\nabla^2\phi \, \bigg|_{\mathrm{droplet}} \approx f'(\phi_a) = \frac{1}{\phi_a - \phi_b} \frac{2\sigma}{R}. \tag{2.33}$$

Thus the chemical potential is a function of droplet size and is larger for smaller droplets. This means that if we have two droplets of different size, the smaller one will be at higher chemical potential than the larger setting a gradient between them. The flow of particles in response to this gradient is from the small droplet to the large. The large droplet grows through the evaporation of the small droplet, diffusion of its molecules through the surrounding majority phase, and condensation onto the larger droplet. This process is called **Ostwald ripening**.

Chapter 3

Ising Model

The Ising model is undoubtedly the great landmark of statistical mechanics. At its base it is a model of ferromagnetism but its significance far exceeds these origins. Its tremendous utility resides in the facts that (i) the partition function can be evaluated exactly (in one and two dimensions), and (ii) the result is non-trivial and therefore instructive.

3.1 Definition of the Ising Model

The **Ising model** is a collection of spins s_i on the sites i of a (regular) lattice. Each spin can take one of two values $s_i = \pm 1$ and interacts with its nearest neighbours through an **exchange interaction** $-Js_i s_j$, where J is the **exchange coupling**; when it is positive the interaction is ferromagnetic, favouring alignment of spins, whereas when it is negative the interaction is antiferromagnetic. The energy of the configuration of spins is

$$E = -\sum_{\langle i,j \rangle} Js_i s_j, \tag{3.1}$$

where the sum is taken over all nearest neighbouring sites i and j, denoted by the symbol $\langle i,j \rangle$. The partition function is therefore

$$Z = \sum_{\{s_i\}} e^{\beta J \sum_{\langle i,j \rangle} s_i s_j}. \tag{3.2}$$

The model is defined for any number of spatial dimensions and for any lattice type. It is most commonly studied in one dimension – a linear chain of spins – or on a square lattice in two dimensions, as illustrated in Fig. 3.1.
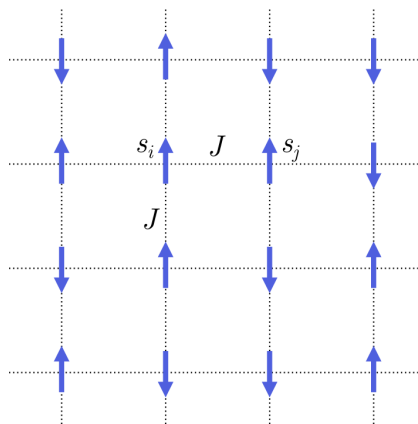

Figure 3.1: Schematic illustration of the Ising model on a two-dimensional square lattice. Each site has a spin s_i, depicted as an arrow pointing up ($s_i = +1$) or down ($s_i = -1$), and spins on neighbouring sites interact via an exchange coupling $-Js_i s_j$.

3.2 Mean Field Theory

The basic idea in the Ising model is that the interactions favour alignment of spins, while temperature (or entropy) acts to randomise them. We might expect that at high temperatures $(k_\mathrm{B}T \gg J)$ the interactions would be largely irrelevant and the spins random with no net magnetisation. The phase is then **paramagnetic**. On the other hand at low temperatures $(k_\mathrm{B}T \lesssim J)$ the interactions will align the spins and the phase will become **ferromagnetic**. Exactly this behaviour is found by an approximate analysis of the model known as **mean field theory**.

The idea can be introduced as follows. Suppose the state is characterised by a well-defined average magnetisation, *i.e.* $\langle s_i \rangle = m$. In the paramagnetic phase $m = 0$, while in the ferromagnetic phase $m \neq 0$ (and tends towards ± 1). We write the exchange interaction as

$$-Js_i s_j = -J\big(m + (s_i - m)\big)\big(m + (s_j - m)\big),$$
$$= Jm^2 - Jm(s_i + s_j) - J(s_i - m)(s_j - m). \tag{3.3}$$

The idea is that the final term is small; it is proportional to the *product* of the fluctuations $(s_i - m)$ of the individual spins from the average value. The mean field approximation consists in neglecting this quadratic term. Thus the mean field energy can be written

$$E_\mathrm{mf} = \sum_{\langle i,j \rangle}\big[Jm^2 - Jm(s_i + s_j)\big] = N\frac{Jzm^2}{2} - Jzm\sum_i s_i, \tag{3.4}$$

where z is the number of nearest neighbours for any lattice site ($z = 2d$ for a cubic lattice in d dimensions) and the mean field partition function evaluates to

$$Z_\mathrm{mf} = \sum_{\{s_i\}} e^{-\beta E_\mathrm{mf}} = e^{-N\beta Jzm^2/2} \sum_{\{s_i\}} \prod_i e^{\beta Jzms_i}, \tag{3.5}$$

$$= e^{-N\beta Jzm^2/2}\left(\sum_{s_i = \pm 1} e^{\beta Jzms_i}\right)^N, \tag{3.6}$$

$$= e^{-\frac{1}{2}N\beta Jzm^2 + N\ln(2\cosh\beta Jzm)}. \tag{3.7}$$

We can read off the mean field free energy per site

$$F_\mathrm{mf}/N = f = \frac{Jzm^2}{2} - k_\mathrm{B}T\ln\Big(2\cosh\beta Jzm\Big). \tag{3.8}$$

The equilibrium phase should be given by the condition of minimising the free energy, so we determine m by exactly this criterion, $\partial f/\partial m = 0$. This yields the self-consistent equation

$$m = \tanh\beta Jzm. \tag{3.9}$$

At high temperature the only solution is $m = 0$ and there is no net magnetisation; the state is paramagnetic. However, below a **critical temperature** $T_c = Jz/k_\mathrm{B}$ additional solutions at non-zero values of m emerge and are the stable solutions; the state is ferromagnetic with macroscopic (partial) alignment of all the spins.

3.2.1 Phase Behaviour

The phase behaviour of the Ising model is given as a function of the temperature and an applied external magnetic field H. Such an applied magnetic field contributes a term $-H\sum_i s_i$ to the energy, favouring alignment of the spins with the applied field. Repeating the mean field analysis as above leads to an expression for the free energy per site of

$$F_\mathrm{mf}/N = f = \frac{Jzm^2}{2} - k_\mathrm{B}T\ln\Big(2\cosh\beta(Jzm + H)\Big), \tag{3.10}$$

and as before the state of the system (value of m) is determined by minimising this free energy.

There are numerous ways of pursuing the analysis but it will be convenient for our subsequent development to take the approach of a Taylor series of the free energy density

$$f = f_0 + \frac{Jz(1 - \beta Jz)}{2} m^2 + \frac{\beta^3 (Jz)^4}{12} m^4 - \beta Jz m \, H + \cdots . \tag{3.11}$$

Here, f_0 denotes terms independent of the magnetisation m and we have explicitly written only those terms that are 'relevant'[1], leaving those that are 'irrelevant' to the dot-dot-dots. What this means is that the expression (3.11) correctly captures the form and behaviour of the full expression (3.10); the higher order terms do not alter the qualitative structure.

When $\beta Jz < 1$ the free energy has a single minimum given approximately by

$$m \approx \frac{\beta H}{1 - \beta Jz} = \frac{1}{k_{\mathrm{B}}T - Jz} H. \tag{3.12}$$

The magnetisation is proportional to the applied field and is only non-zero when the applied field is non-zero; the phase is **paramagnetic**. The magnetic response to the field is characterised by the **susceptibility**

$$\chi = \frac{\partial m}{\partial H} \approx \frac{1}{k_{\mathrm{B}}T - Jz}. \tag{3.13}$$

We note that this *diverges* as $T \to T_c \equiv Jz/k_{\mathrm{B}}$ with the power law form $\chi \sim |T - T_c|^{-1}$. The exponent of -1 is an example of a **critical exponent**.

When $T < T_c = Jz/k_{\mathrm{B}}$ the behaviour is different and the free energy is minimised by a non-zero magnetisation even in zero applied field. Indeed, we find

$$m \approx \pm \left(\frac{3(\beta Jz - 1)}{(\beta Jz)^3} \right)^{1/2} . \tag{3.14}$$

This non-zero spontaneous magnetisation without external field indicates a **ferromagnetic** phase; the temperature $T_c = Jz/k_{\mathrm{B}}$ at which the state switches (in zero field) from paramagnetic to ferromagnetic is called the **critical temperature**. We comment particularly that the onset of the magnetisation has a power law form $m \sim |T - T_c|^{1/2}$; the exponent $\frac{1}{2}$ is another example of a critical exponent.

3.3 Exact Solution in One Dimension

The Ising model in one dimension is exactly solvable. This provides further insight into the model and also a check on the mean field analysis.

We consider a one-dimensional chain of N sites with periodic boundary conditions ($s_N \equiv s_0$) – so that sites $i = 0$ and $i = N - 1$ also interact via an exchange interaction $-Js_0 s_{N-1}$ and there are no 'end effects'. The partition function is

$$Z = \sum_{\{s_i\}} \mathrm{e}^{\beta J \sum_{i=0}^{N-1} s_i s_{i+1}} = \sum_{\{s_i\}} \prod_{i=0}^{N-1} \mathrm{e}^{\beta J s_i s_{i+1}} . \tag{3.15}$$

To understand this expression we introduce the **transfer matrix T**: This is a 2×2 matrix

$$\mathbf{T} = \begin{bmatrix} \mathrm{e}^{\beta J} & \mathrm{e}^{-\beta J} \\ \mathrm{e}^{-\beta J} & \mathrm{e}^{\beta J} \end{bmatrix} , \tag{3.16}$$

whose entries are the possible values of the Boltzmann weight $\mathrm{e}^{\beta J s_i s_{i+1}}$ according to the different configurations of spins on neighbouring sites

$$(s_i, s_{i+1}) \in \big\{ (1, 1), \ (1, -1), \ (-1, 1), \ (-1, -1) \big\} . \tag{3.17}$$

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[1]The proper explanation of these terms forms part of the set of ideas known as the **renormalisation group**; see, particularly, Cardy's book for an excellent account.

The rows correspond to different values of s_i and the columns to different values of s_{i+1}. For instance, the (12)-entry T_{12} corresponds to $s_i = +1$ and $s_{i+1} = -1$. Now write out the partition function in full and focus on the terms involving the particular spin s_k

$$Z = \sum_{s_0 = \pm 1} \cdots \sum_{s_k = \pm 1} \cdots \sum_{s_{N-1} = \pm 1} e^{\beta J s_0 s_1} \times \cdots \times e^{\beta J s_{k-1} s_k} \, e^{\beta J s_k s_{k+1}} \times \cdots \times e^{\beta J s_{N-1} s_0}. \qquad (3.18)$$

One then needs to recognise that summing over the possible values of s_k, with all other spins held fixed, amounts to matrix multiplication, giving the $(s_{k-1} s_{k+1})$-element of $\mathbf{T}^2$, i.e. $[\mathbf{T}^2]_{s_{k-1} s_{k+1}}$. Continuing to sum over all of the spins in this way we obtain

$$Z = \sum_{s_0 = \pm 1} \left[\mathbf{T}^N\right]_{s_0 s_0} = \text{tr } \mathbf{T}^N = \lambda_1^N + \lambda_2^N, \qquad (3.19)$$

where λ_1, λ_2 are the two eigenvalues of the transfer matrix. Calculating the eigenvalues we find $\lambda_1 = 2 \cosh \beta J$ and $\lambda_2 = 2 \sinh \beta J$, so that the exact expression for the partition function is

$$Z = \left(2 \cosh \beta J\right)^N + \left(2 \sinh \beta J\right)^N = \left(2 \cosh \beta J\right)^N \left[1 + \tanh^N \beta J\right]. \qquad (3.20)$$

Finally, the free energy per site is

$$f = F/N = -k_{\mathrm{B}} T \ln 2 \cosh \beta J - \frac{k_{\mathrm{B}} T}{N} \ln \left[1 + \tanh^N \beta J\right]. \qquad (3.21)$$

In the thermodynamic limit, $N \to \infty$, only the first term survives. The free energy per spin is an unremarkable function of βJ, with no structural transformation at any finite value of the temperature, and there is no phase transition (for $T \neq 0$).

3.3.1 Correlation Function

To develop this a little further, we calculate the **correlation function** $\langle s_0 s_r \rangle$ between the spins on sites r apart[2]. If the spins are all aligned – either all $+1$ or all -1 – then this will take the value $+1$ no matter the separation r; but if on large enough scales the spins are independently aligned then the values of s_0 and s_r will be uncorrelated and $\langle s_0 s_r \rangle \approx 0$. Thus this correlation function tells us about the order in the system. We have

$$\langle s_0 s_r \rangle = \sum_{\{s_i\}} s_0 s_r \frac{1}{Z} e^{\beta J \sum_i s_i s_{i+1}} = \frac{1}{Z} \sum_{\{s_i\}} s_0 s_r \prod_i e^{\beta J s_i s_{i+1}}. \qquad (3.22)$$

Next, we use the fact that $s_i^2 = +1$ to write

$$s_0 s_r = s_0 s_1 \, s_1 s_2 \, \cdots \, s_{r-1} s_r, \qquad (3.23)$$

which allows us to express the correlation function as

$$\langle s_0 s_r \rangle = \frac{1}{Z} \sum_{\{s_i\}} \prod_{i=0}^{r-1} s_i s_{i+1} \, e^{\beta J s_i s_{i+1}} \prod_{i=r}^{N-1} e^{\beta J s_i s_{i+1}} = \frac{1}{Z} \text{ tr } \mathbf{C}^r \mathbf{T}^{N-r}, \qquad (3.24)$$

introducing the transfer matrix again, and where

$$\mathbf{C} = \begin{bmatrix} e^{\beta J} & -e^{-\beta J} \\ -e^{-\beta J} & e^{\beta J} \end{bmatrix}. \qquad (3.25)$$

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[2] We are using the periodicity to choose one of the spins to be site 0.

Now the key algebraic fact is that the matrix $\mathbf{C}$ commutes with the transfer matrix, $[\mathbf{C}, \mathbf{T}] = 0$, and consequently they can be simultaneously diagonalised. This allows the trace to be calculated and gives an exact expression for the correlation function

$$\langle s_0 s_r \rangle = \frac{(2 \sinh \beta J)^r (2 \cosh \beta J)^{N-r} + (2 \cosh \beta J)^r (2 \sinh \beta J)^{N-r}}{(2 \cosh \beta J)^N + (2 \sinh \beta J)^N}. \tag{3.26}$$

In the thermodynamic limit $N \to \infty$ this becomes

$$\langle s_0 s_r \rangle = \left(\tanh \beta J \right)^r, \tag{3.27}$$

and we see that it vanishes for large enough r no matter what the value of βJ. At large (enough) separations the spins are always uncorrelated and there is no long range ferromagnetic alignment in the one-dimensional Ising model. It is common to convey this by writing the correlation function in the general form

$$\langle s_0 s_r \rangle = \mathrm{e}^{-r/\xi} \qquad \text{with} \qquad \xi = \frac{1}{\ln \coth \beta J}. \tag{3.28}$$

The length scale ξ characterises the distance over which the correlation between spins decays; it is called the **correlation length**.

3.4 Loops and Transition Temperature in Two Dimensions

The exact solution of the one-dimensional Ising model shows that it does not, in fact, have a phase transition (at non-zero temperature). It turns out that in two dimensions the model does have a phase transition at non-zero temperature. In this section, we try to describe this by considering expansions for the partition function at both low and high temperatures.

The partition function for the two-dimensional Ising model on the square lattice is

$$Z = \sum_{\{s_i\}} \mathrm{e}^{\beta J \sum_{\langle i,j \rangle} s_i s_j}. \tag{3.29}$$

We begin at low temperature where the idea is to think about the nature of configurations that are closest in energy to the ground state where all spins align. Clearly, the first excited state involves just one flipped spin. In the energy all nearest neighbour pairs contribute $-J$ except for the four interactions between the flipped spin and each of its nearest neighbours, where the energy is $+J$. The difference in energy between the first excited state and the ground state is therefore $4 \times 2J$ and the expansion for the partition function begins

$$Z = 2 \, \mathrm{e}^{2N\beta J} \left(1 + N \left(\mathrm{e}^{-2\beta J} \right)^4 + \cdots \right). \tag{3.30}$$

For the next term we need to identify the second excited state. These are configurations where two neighbouring spins are both flipped, see Fig. 3.2. One can see that the count of unfavourable interactions is now six, so the energy (compared to the ground state) is $6 \times 2J$ and the partition function is

$$Z = 2 \, \mathrm{e}^{2N\beta J} \left(1 + N \left(\mathrm{e}^{-2\beta J} \right)^4 + 2N \left(\mathrm{e}^{-2\beta J} \right)^6 + \cdots \right). \tag{3.31}$$

One can continue in this way adding in more and more excited states limited only by your perseverance. To organise things it is convenient to represent the emerging partition function as a 'graphical expansion' with the terms represented by diagrams of little loops encircling the flipped spins

$$Z = 2 \, \mathrm{e}^{2N\beta J} \sum_{\text{loops}} \mathcal{N}_\ell \left(\mathrm{e}^{-2\beta J} \right)^\ell, \tag{3.32}$$

where $\mathcal{N}_\ell$ is the number of loops of length ℓ.

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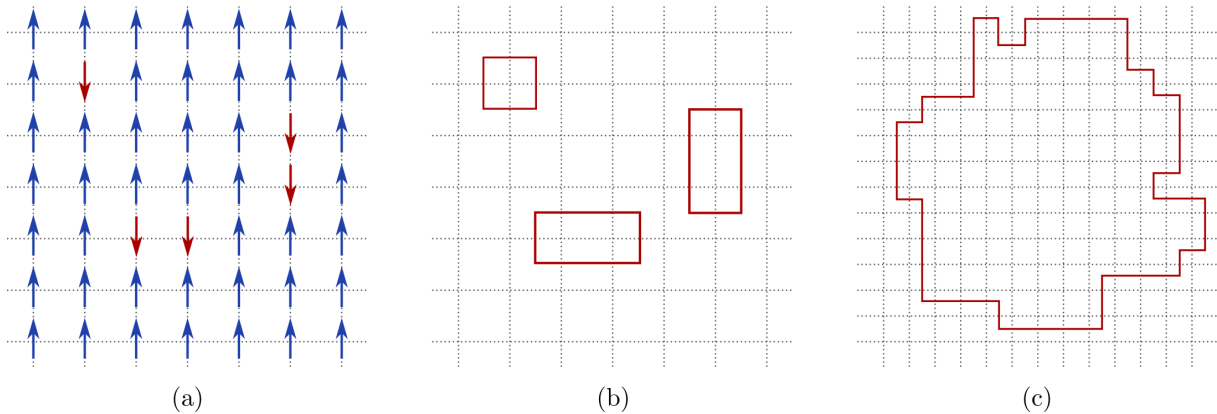(a)   (b)   (c)

Figure 3.2: (a) Configurations of spins with some flipped (red). There is an isolated flipped spin (lowest energy excitation) and both of the pairs of flipped spins (next lowest excitation). (b) Equivalent pictorial representation in terms of loops on the square lattice. (c) An example of a larger domain of flipped spins. Such domains have an entropy associated with the number of configurations of the boundary that is exponential in the boundary length.

The sum that appears here has the form of a partition function for loops

$$Z_{\text{loops}} = \sum_{\text{loops}} e^{-\beta\left(2J\ell - k_{\text{B}}T \ln \mathcal{N}_\ell\right)}, \tag{3.33}$$

with a free energy

$$F_{\text{loop}} = 2J\ell - k_{\text{B}}T \ln \mathcal{N}_\ell = 2J\ell - TS_\ell, \tag{3.34}$$

where S_ℓ is the entropy of a loop of length ℓ, see Fig. 3.2(c). To estimate the entropy we estimate the number of ways of forming a closed loop of length ℓ. When ℓ is large the requirement that the loop has to close is not so constraining and we may estimate the number from just counting the number of paths of length ℓ. Imposing that you cannot double back, at each step you can choose to go in one of three directions: ahead, left, or right. This gives an estimate of 3^ℓ for the number of paths. The number of (large) closed loops will be similar, albeit smaller, and we might estimate it as c^ℓ where c is a number slightly less than 3. The free energy is therefore approximately

$$F_{\text{loop}} = \left(2J - k_{\text{B}}T \ln c\right)\ell. \tag{3.35}$$

So if T is higher than $2J/k_{\text{B}} \ln c$ the free energy is lowered by having the loop, whereas when T is smaller than this the energy cost wins out and the loop is suppressed. This suggests a transition temperature

$$T_c = \frac{2J}{k_{\text{B}} \ln c}, \tag{3.36}$$

between paramagnetic and ferromagnetic states in the two-dimensional Ising model. The argument we have just described is due to Rudolf Peierls and is called the **Peierls argument**.

In fact it is possible to obtain the exact value of the transition from the 'loop picture' of the partition function. This comes from also studying a suitable expansion at high temperature. One of the problems shows that the high temperature expansion is

$$Z = 2^N \left(\cosh \beta J\right)^{2N} \sum_{\text{loops}} \mathcal{N}_\ell \, x^\ell, \tag{3.37}$$

where $x = \tanh \beta J$. The fact that both the low and high temperature expansions for the partition function involve the same graphical representation as a sum over loops implies a general correspondence between the partition function at low (β_{low}) and high (β_{high}) temperatures, related to each other by

$$e^{-2\beta_{\text{low}}J} = \tanh \beta_{\text{high}}J. \tag{3.38}$$

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This result is known as Kramers-Wannier duality. The critical temperature of the two-dimensional Ising model is identified with the fixed point of the duality and turns out to be given exactly by

$$T_c = \frac{2J}{k_\mathrm{B} \ln(1 + \sqrt{2})}. \tag{3.39}$$

3.5 Onsager's Solution in Two Dimensions – *off syllabus*

In 1944 Lars Onsager produced the exact solution of the Ising model on the two-dimensional square lattice. For a long time afterwards, and perhaps even still, this was seen as the most significant result in statistical mechanics. The approach is an extension of the transfer matrix method we used for the one-dimensional model. To describe it in any meaningful way would require an entire lecture course in itself. Let us record only that there is a continuous phase transition from a paramagnetic state to a ferromagnetic one at a critical value of the temperature, as was the case for the mean field analysis. The exact transition temperature can be given as

$$\frac{J}{k_\mathrm{B} T_c} = \frac{1}{2} \ln \cot \frac{\pi}{8}, \tag{3.40}$$

and is not the same as that predicted by mean field theory ($J/k_\mathrm{B}T_c = 1/4$). Other aspects of the mean field analysis also turn out to be incorrect, for example the behaviour of the specific heat at the transition (which is logarithmically divergent) or the exponent in the power law growth of the magnetisation, $m \sim |T - T_c|^\beta$ – the correct value is $\beta = 1/8$. The reasons for the shortcomings of mean field theory, and a way of salvaging it, would come approximately 25 years later with the work of Kenneth Wilson, and others, on the foundations of the renormalisation group. Wilson received the Nobel Prize for this work in 1982.

Onsager gave several equivalent expressions for the free energy density, for example

$$f = -k_\mathrm{B}T \ln 2 \cosh 2\beta J - \frac{k_\mathrm{B}T}{2\pi^2} \int_0^\pi \int_0^\pi \ln\left[1 - 2\,\mathrm{sech}\,2\beta J \tanh 2\beta J \cos \omega_1 \cos \omega_2\right] d\omega_1 \, d\omega_2. \tag{3.41}$$

In principle this allows for the determination of the thermodynamic phase behaviour, however, there is still quite some analysis involved in actually doing this. Those who are sufficiently motivated may consider looking at Onsager's original paper for an idea of what is involved:

L. Onsager, Crystal Statistics. I. A Two-Dimensional Model with an Order-Disorder Transition, Phys. Rev. **65**, 117 (1944). doi:10.1103/PhysRev.65.117

Onsager's exact solution of the two-dimensional Ising model prompted the development of an entire field of research on exactly solvable models; the classic reference in this area is Rodney Baxter's book *"Exactly Solvable Models in Statistical Mechanics"*.

3.6 Monte Carlo Simulation

The calculation of thermodynamic averages, or the partition function, analytically is generally very difficult. In many cases the statistical averages can be approximated by numerical methods. For an observable quantity A the average we want to compute is the ensemble average

$$\langle A \rangle = \sum_{\text{states } \alpha} p_\alpha A_\alpha. \tag{3.42}$$

The enormous number of microstates makes computing this directly unfeasible with current computers. What is possible to compute directly with a computer is the mean of a set of sampled values

$$\overline{A} = \frac{1}{N_s} \sum_{\text{sampled states } \alpha} A_\alpha, \tag{3.43}$$

where N_s is the number of samples. If we choose our samples to reflect the underlying probability distribution, and use enough samples, then this will be a good approximation to the actual statistical average, $\overline{A} \approx \langle A \rangle$.

So how do we choose our samples so that we are drawing values of A from the correct probability distribution? The way we will generate samples is from a (Markov) process for moving from one state to another. If we set up the process correctly, *i.e.* with the right properties, then (after an initial transient) it will move through the space of states in a way that reflects the equilibrium probability distribution and allows us to compute good averages. Let $\Pi_{\alpha \to \beta}$ denote the probability of moving from state α to state β. If we focus on a particular state (α, say) there will be transitions into it and transitions out of it such that the change in the probability of that state is

$$dp_\alpha = \sum_{\beta \neq \alpha} \Big(p_\beta \Pi_{\beta \to \alpha} - p_\alpha \Pi_{\alpha \to \beta} \Big). \tag{3.44}$$

In steady state, if our process is moving around the space of states without changing the probabilities, this has to vanish. We impose this condition by requiring each term in the sum to vanish separately

$$p_\beta \Pi_{\beta \to \alpha} - p_\alpha \Pi_{\alpha \to \beta} = 0. \tag{3.45}$$

This is known as **detailed balance**. It will be implemented by any algorithm with transition probabilities $\Pi_{\beta \to \alpha}$ satisfying

$$\frac{\Pi_{\beta \to \alpha}}{\Pi_{\alpha \to \beta}} = \frac{p_\alpha}{p_\beta} = e^{-\beta(E_\alpha - E_\beta)}, \tag{3.46}$$

where we have used that the probabilities are given by the Gibbs distribution.

A popular algorithm for simulation of the Ising model is the **Metropolis algorithm**, which consists of repeating the following three basic steps:

(i) Pick a spin (lattice site) at random.

(ii) Calculate the change in energy ΔE associated with flipping that spin.

(iii) If $\Delta E < 0$ flip the spin, while if $\Delta E > 0$ flip it with probability $\exp\{-\beta \Delta E\}$.

It is clear that the algorithm implements detailed balance and so will correctly sample from the equilibrium distribution. Part of its simplicity is that the only state transitions it considers are flips of individual spins, which can make it slow for large system sizes.

Chapter 4

Phase Transitions

General education identifies three distinct phases of matter: solids, liquids and gases. This trichotomy has certain useful features, particularly in drawing commonalities. For example oil and water are both liquids; they are the same phase despite being chemically distinct. That they are the same phase means they exhibit common properties and can be described by unified physical theories. Liquids flow; their flow is resisted by viscosity and described by the Navier-Stokes equations. Gases are also described by the Navier-Stokes equations (unless they are very rarefied). The distinction from liquids is that the density is much lower and they are much more easily compressed; in fluid dynamics gases are typically modelled as compressible fluids and liquids as incompressible. Solids do not flow; they stretch (are elastic) but are able to resist shear.

The different phases – solids, liquids and gases – are distinguished by the different physical properties they exhibit, but they are also distinguished by **phase transitions** between them. This is a sharp, or dramatic, change at special values of the temperature and pressure. It is marked by a 'singularity' in some thermodynamic property, by which I mean here either a discontinuity or a divergence. We would like to understand what is happening and describe it in a unified physical theory. However, any systematic study of phase transitions makes it clear that there are many more phases than just three. We give a few examples.

4.1   Short Survey of Phases

Liquid Crystals

Liquid crystals are beautiful and mysterious; discovered in 1888 they remained an esoteric curiosity until about 1970 when the basic designs for liquid crystal based displays were worked out and patented. You are almost surely reading this on just such a display. They exhibit properties intermediate between those of simple liquids and crystalline solids. There are many different liquid crystal phases, the main ones being the nematic, cholesteric, smectic, and columnar phases, although there are literally dozens more.

The **nematic** is the simplest of the liquid crystalline phases. The molecules are rod-like and display orientational order, all pointing along a common direction, but there is no ordering of the molecular positions and they flow like a liquid. **Cholesterics** are chiral nematics; the alignment of molecules exhibits a helical rotation and the phase has a handedness (there are right- and left-handed versions).

In **smectic** phases, in addition to the orientational order there is also partial ordering of molecular positions, along only one spatial direction. They behave like a solid along that direction but remain fluid in the two orthogonal directions. It is often described as a one-dimensional stack of fluid layers. Several different smectic phases can be defined depending on how the 'layering' direction relates to the orientational order; when they are the same the phase is smectic A while when there is an angle between them the phase is smectic C.

The **columnar** phase is a counterpart of smectics that has two-dimensional positional order and is fluid along just one direction. They are typically formed from flat, disc-shaped molecules, which stack into one-dimensional fluid columns that then arrange themselves in a hexagonal lattice. Highly concentrated solutions of DNA exhibit this phase[1].

Amphiphiles

An **amphiphilic** molecule is one with both hydrophilic (water liking) and hydrophobic (water fearing) parts. Common examples are provided by **lipids**, which have a hydrophilic head group (typically having charge or dipole moment) and one or two hydrophobic hydrocarbon tails. Lipids are used as surfactants and are also the primary constituent of cell walls and membranes. In solution, they form a variety of different self-organised structures to satisfy the conflicting desires of the head groups to be in contact with the water and the tail groups to avoid contact, with a series of phase transitions as a function of concentration. At low concentration they form spherical **micelles** with the hydrophilic head groups in contact with the water and the hydrophobic tails shielded inside the micelle. As the concentration increases cylindrical micelles with hexagonal packing (a columnar phase) form and then planar bilayers with lamellar stacking (a smectic phase). Increasing the concentration further there are inverted (with the water on the inside and the oily tails outside) hexagonal columnar and spherical micelle phases.

Magnets

A **paramagnet** develops a field in response to an applied one, whereas a **ferromagnet** maintains its own field. In ferromagnets the exchange coupling is positive and the spins all align along the same direction. When the exchange coupling is negative anti-alignment of neighbouring spins is favoured and the material is an **antiferromagnet**. There are other types of spatially varying magnetic order (helical, canted) corresponding to further phases and also there can be frozen disordered, or amorphously ordered, spin configurations, which are called **spin glasses**.

Superfluids

At low enough temperatures most materials solidify, however helium remains a quantum liquid. Below a certain critical temperature this liquid loses its viscosity and flows without resistance. The **superfluid** state was identified by Pyotr Kapitza in 1937 and the theory worked out shortly afterwards by Lev Landau.

Superconductors

In 1911 Kammerlingh Onnes discovered that mercury had a sudden change of properties at 4.2 K, including the loss of all electrical resistance. This new phase was called a **superconductor**. Many elements are superconducting (*e.g.* Al, Zn, Ga, Sn, Pb, Nb, etc.) at similarly low temperatures but some layered materials, such as the cuprate superconductors, have transition temperatures even above 100 K. The transition is associated with the state of electrons, *i.e.* changes to their eigenstates and energy levels, or band structure, and is characterised by both the loss of resistance and the expulsion of magnetic fields.

Metals and insulators

Depending on their band structure some materials conduct and are metals while others do not and are insulators. There are also materials that change from metallic to insulating behaviour as some control parameters are varied, *e.g.* temperature, pressure or composition. This is the **metal-insulator** transition. Some early examples were found in magnetite and NiO. A basic model for the transition was developed by Neville Mott and is called the **Mott transition**.

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[1]At lower concentrations DNA also exhibits cholesteric phases.

There are many other transitions involving resistance, or conductance, properties. One of the most influential is the **quantum Hall effect** discovered by Klaus von Klitzing in 1980, which was subsequently shown to be associated to topological properties of the band structure and has developed into the broader research topic of topological insulators and topological phase transitions.

4.2 Landau Theory

A general framework for describing phase transitions and studying ordered phases was introduced by Lev Landau. It is an expression for the free energy in terms of a quantity characterising the ordered state. We have seen two examples of this already; the demixing of a binary fluid and the paramagnet-to-ferromagnet transition described by the Ising model. In both cases the transition could be described by giving a suitable Taylor series for the free energy density

$$f = \frac{\Delta}{4} - k_{\mathrm{B}}T \ln 2 + \frac{2k_{\mathrm{B}}T - \Delta}{4}\, s^2 + \frac{k_{\mathrm{B}}T}{12}\, s^4 + \cdots, \tag{2.9}$$

$$f = f_0 + \frac{Jz(1 - \beta Jz)}{2}\, m^2 + \frac{\beta^3(Jz)^4}{12}\, m^4 - \beta JzH\, m + \cdots, \tag{3.11}$$

parameterised by a quantity (s or m) that is zero in one phase and becomes non-zero after the transition. The general formalism that Landau developed follows the same structure. The idea of **Landau theory** can be summarised as follows:

i. Identify an **order parameter**. This is any (macroscopic) physical quantity that serves to distinguish between the two phases.

ii. Construct all ways in which the order parameter can contribute to the free energy. These are all the **scalar invariants** of the order parameter.

iii. Write a Taylor series for the free energy using the available invariants, stopping once all relevant[2] terms have been included.

iv. The phase transition is described by selecting the value of the order parameter with the condition that it minimise the free energy.

It is conventional to choose the order parameter to take the value zero in the high temperature phase and acquire a non-zero value in the low temperature phase. There are two ways this can happen: the order parameter can jump discontinuously to its new value – this is called a **discontinuous** or **first order** phase transition – or it can grow continuously from zero, which is then called a **continuous phase transition**. This represents the basic dichotomy of phase transitions; we will see examples of both. The terminology 'first order' originates from an older classification of phase transitions based on the lowest order of derivative of f where a discontinuity is observed. The modern understanding is that the main distinction is on whether or not there is a finite correlation length at the transition; for first order transitions there is, while for continuous transitions the correlation length diverges.

4.2.1 Ferromagnetism

We have already seen that the Ising model describes the transition between a paramagnet and a ferromagnet. However, the Ising model is a simplification in the following sense: the spins are simple scalars taking only the values ± 1, whereas magnetisation (and spin) is really a vector

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[2]As with the previous footnote on this term, we do not explain it formally. The essence is that higher order terms in the Taylor series do not alter the description of the transition.

quantity. A mild generalisation of the Ising model takes care of this: We let the spins be vectors $\mathbf{S}_i$ and take the energy to be

$$E = -\sum_{\langle i,j \rangle} J\,\mathbf{S}_i \cdot \mathbf{S}_j. \tag{4.1}$$

The spins can be classical vectors with a fixed length, $|\mathbf{S}| = S$, or even quantum operators satisfying the usual commutation relations for spin. In a fully general situation, the number of components n of the vector $\mathbf{S}$ need not be the same as the spatial dimension d. This general case is called the $O(n)$ **model** since the energy (4.1) is invariant under the action of the rotation group $O(n)$ on the spins $\mathbf{S}_i$. The most important cases are $n = 2$ and $n = 3$; the former is more commonly called the XY **model** and the latter is called the **Heisenberg model**. The Ising model is the case $n = 1$.

Now we develop the Landau theory for the transition. The basic idea is the same as for the mean field treatment of the Ising model. The order parameter is the magnetisation, the expectation value of the spins. This is a (n-component) vector $\mathbf{m}$. It vanishes in the paramagnetic phase and is non-zero in the ferromagnet. The scalar invariants that we can construct from it alone is simply the magnitude squared $|\mathbf{m}|^2 = \mathbf{m} \cdot \mathbf{m}$ and powers thereof. With an applied magnetic field $\mathbf{H}$ there is also the scalar product $\mathbf{m} \cdot \mathbf{H}$ (and powers thereof). This identifies those quantities involving the order parameter that can contribute to the free energy. It is given by writing a Taylor series using these invariants

$$f = f_0 + \frac{a(T - T_c)}{2}\,(\mathbf{m} \cdot \mathbf{m}) + \frac{u}{4}\,(\mathbf{m} \cdot \mathbf{m})^2 - \chi_0 \mathbf{H} \cdot \mathbf{m} + \cdots. \tag{4.2}$$

The coefficients are phenomenological; a, u and χ_0 are positive constants, T is the temperature and T_c is the critical temperature. f_0 represents a constant contribution to the free energy (independent of $\mathbf{m}$); such contributions will be neglected from now on as they do not affect the phase transition. Writing $\mathbf{m} \cdot \mathbf{m} = m^2$ and $\mathbf{H} \cdot \mathbf{m} = Hm$ reduces (4.2) to the same form as the mean field analysis of the Ising model. The analysis of the phase transition is then the same as it was there; we cover it in §4.3.

4.2.2 Nematic Liquid Crystal

As a second illustration of Landau's theory we consider the example of liquid crystals. This is, to begin with, slightly more involved than the example of ferromagnetism, but it offers greater depth of insight into the full remit of Landau's theory.

What is the order parameter for the liquid crystal phase? A defining feature of the liquid crystalline state is its optical properties; after all this is why they find uses in displays. Macroscopic optical properties of materials are described by their dielectric tensor, $\boldsymbol{\epsilon}$ or ϵ_{ij} in index notation. Liquid crystals exhibit different dielectric responses – different refractive indices – parallel ($\epsilon_\parallel$) and perpendicular ($\epsilon_\perp$) to a preferred **optic axis**; this is known as **birefringence**. Within the material the dielectric tensor is therefore of the form

$$\boldsymbol{\epsilon} = \begin{bmatrix} \epsilon_0 \epsilon_\parallel & 0 & 0 \\ 0 & \epsilon_0 \epsilon_\perp & 0 \\ 0 & 0 & \epsilon_0 \epsilon_\perp \end{bmatrix} = \frac{\epsilon_0(\epsilon_\parallel + 2\epsilon_\perp)}{3} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \frac{\epsilon_0(\epsilon_\parallel - \epsilon_\perp)}{3} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \tag{4.3}$$

where in the second equality the first term represents a simple isotropic material and the second is non-zero in the (nematic) liquid crystal state. This is the order parameter for the isotropic–nematic transition: we write it as

$$\mathbf{Q} = \frac{s}{3} \begin{bmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \tag{4.4}$$

where $s \propto \epsilon_\parallel - \epsilon_\perp$ represents the magnitude of the order and is called the **scalar order parameter**. The order parameter is a traceless, symmetric rank 2 tensor that is conventionally called the **Q tensor**.

Next, we need to identify all the scalar quantities we can form using $\mathbf{Q}$ that can appear in the free energy. These are the traces of powers of $\mathbf{Q}$, namely $\operatorname{tr}\mathbf{Q} = 0$, $\operatorname{tr}\mathbf{Q}^2$ and $\operatorname{tr}\mathbf{Q}^3$. Other possibilities, for instance $\operatorname{tr}\mathbf{Q}^4$ or $\det\mathbf{Q}$, can all be expressed in terms of the traces already given. One way to see this is to note that a symmetric matrix can be diagonalised and its eigenvalues are (effectively) the independent scalar quantities characterising it. Any scalar invariant is expressible as some combination of the eigenvalues and so there are the same number of independent scalar invariants as there are eigenvalues. The identification of the set of independent scalar invariants from which to construct the free energy is a major component of Landau theory that is more fully illustrated by the liquid crystal example than in the case of ferromagnetism.

Having identified the independent scalar quantities, the Landau free energy density for the isotropic–nematic transition

$$f = \frac{a(T - T_c)}{2}\operatorname{tr}\mathbf{Q}^2 - \frac{B}{3}\operatorname{tr}\mathbf{Q}^3 + \frac{C}{4}\left(\operatorname{tr}\mathbf{Q}^2\right)^2, \tag{4.5}$$

is a Taylor series built from the scalar invariants with arbitrary (material dependent) coefficients a, B and C that are all positive. As usual, T is the temperature and T_c is a constant temperature where the coefficient of the quadratic term changes sign. This description of the liquid crystal isotropic–nematic phase transition was first given by Pierre-Gilles de Gennes.

4.3 Discontinuous Transitions

The isotropic–nematic transition described by (4.5) provides a canonical example of a **discontinuous**, or **first order**, **transition**. We develop the analysis of the transition here.

Calculating the free energy density (4.5) for the form (4.4) we find

$$f = \frac{a(T - T_c)}{3}\, s^2 - \frac{2B}{27}\, s^3 + \frac{C}{9}\, s^4. \tag{4.6}$$

This differs from both (2.9) and (3.11) in having a term cubic in the (scalar) order parameter. The presence of a cubic order term in the free energy is a signature of a **discontinuous** phase transition. The cleanest way to see what happens is to sketch the form of the free energy and how it changes as the temperature is lowered, which is shown in Fig. 4.1. At high temperatures the free energy has a single minimum at $s = 0$, corresponding to the isotropic phase. As the temperature is lowered, the first thing that happens is the appearance of a secondary minimum at positive s; this is the minimum corresponding to the nematic phase. When it first appears, at $T - T_c = B^2/24aC$, the value of the free energy at this secondary minimum is higher than the value of the free energy in the isotropic phase; the ordered state is a **superheated** nematic. It is only at a lower temperature, given by $T - T_c = B^2/27aC$, that the nematic minimum becomes the global free energy minimum and the energetically preferred state; this identifies the isotropic–nematic transition temperature. At the transition the order parameter s jumps discontinuously from zero to a finite non-zero value, which is characteristic of first order, or discontinuous, phase transitions. Finally, at the lower temperature $T = T_c$ the isotropic state ($s = 0$) ceases to be a minimum; this is the limit of **supercooling** of the isotropic phase.

Let us explain how to calculate these things. First the transition temperature. From Fig. 4.1 we see that the transition occurs when the minimum in the free energy at non-zero s has the same value as the minimum at $s = 0$. Since $f(0) = 0$ this is a non-zero s for which $f(s) = 0$ and, moreover, is a degenerate double root. The roots of f are given by

$$f = \frac{C}{9}\, s^2\left(s^2 - \frac{2B}{3C}\, s + \frac{3a(T - T_c)}{C}\right) = 0, \tag{4.7}$$

and the condition for a non-zero double root is that the discriminant of the second factor vanishes

$$\frac{4B^2}{9C^2} - \frac{12a(T - T_c)}{C} = 0, \quad \Rightarrow \quad T - T_c = \frac{B^2}{27aC}. \tag{4.8}$$
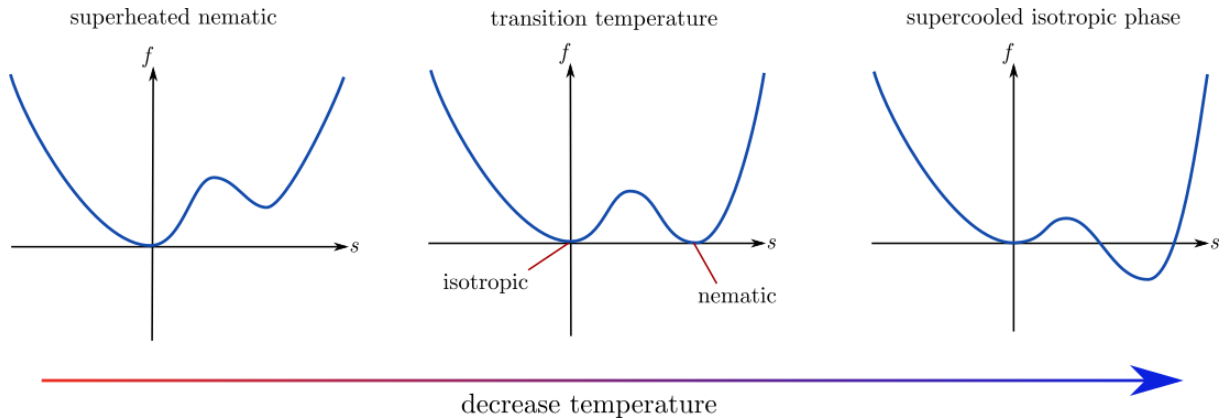
Figure 4.1: Isotropic–nematic transition in three dimensions as an exemplar of a discontinuous or first order phase transition: As the temperature is lowered the nematic phase first becomes metastable in superheated form; at the transition the value of the free energy in the two minima is the same; at lower temperatures the isotropic phase remains metastable until a limit of supercooling is reached.

The value of the scalar order parameter corresponding to the non-zero minimum at the transition is $s = B/3C$. Thus at the isotropic-nematic transition the scalar order parameter jumps discontinuously from $s = 0$ (isotropic phase) to $s = B/3C$ (nematic phase).

To determine how it develops below the transition temperature we consider the extrema of the free energy density

$$0 = \frac{df}{ds} = \frac{2a(T - T_c)}{3} s - \frac{2B}{9} s^2 + \frac{4C}{9} s^3 = \frac{4C}{9} s \left(s^2 - \frac{B}{2C} s + \frac{3a(T - T_c)}{2C} \right). \tag{4.9}$$

We see that the isotropic state ($s = 0$) is always an extremum; its nature comes from the value of the second derivative at $s = 0$, $d^2 f/ds^2|_{s=0} = 2a(T - T_c)/3$, and so it is a minimum for $T > T_c$ but becomes a maximum for $T < T_c$, which identifies T_c as the limit of supercooling of the isotropic phase. The other extrema, when they exist, are given by

$$s = \frac{B}{4C} \pm \left[\frac{B^2}{16C^2} - \frac{3a(T - T_c)}{2C} \right]^{1/2}. \tag{4.10}$$

The plus sign is associated with the nematic minimum and the negative sign with an unstable local maximum in the free energy density. Thus the degree of nematic alignment increases as the temperature is reduced further, as we would expect.

4.4 Continuous Transitions

As a prototype for continuous transitions we take the ferromagnetic transition that we have studied previously. We reproduce (4.2)

$$f = f_0 + \frac{a(T - T_c)}{2} (\mathbf{m} \cdot \mathbf{m}) + \frac{u}{4} (\mathbf{m} \cdot \mathbf{m})^2 - \chi_0 \mathbf{H} \cdot \mathbf{m} + \cdots. \tag{4.11}$$

Writing $\mathbf{m} \cdot \mathbf{m} = m^2$ and $\mathbf{H} \cdot \mathbf{m} = Hm$ this reduces to

$$f = f_0 + \frac{a(T - T_c)}{2} m^2 + \frac{u}{4} m^4 - \chi_0 Hm, \tag{4.12}$$

and the condition that m minimise the free energy reads

$$0 = \frac{df}{dm} = a(T - T_c)m + um^3 - \chi_0 H. \tag{4.13}$$

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When $H = 0$ we have solutions

$$m = 0, \qquad \text{or} \qquad m = \left(\frac{a|T - T_c|}{u} \right)^{1/2}, \tag{4.14}$$

with the latter only for $T < T_c$. This describes a continuous transition at a **critical tempera-ture** $T = T_c$ with onset of the magnetisation showing the power law scaling $m \sim |T - T_c|^\beta$ with **critical exponent** $\beta = \frac{1}{2}$. This exponent is a pure number, independent of any microscopic details, whose value is a prediction of Landau theory.

Now we consider the response to the magnetic field. For $T > T_c$ we are in the paramagnetic state where without the field $m = 0$; the leading balance is therefore

$$m = \frac{\chi_0}{a|T - T_c|} H. \tag{4.15}$$

On the other hand, for $T < T_c$ we are in the ferromagnetic state and m is close to $(a|T - T_c|/u)^{1/2}$. We write

$$m = \left(\frac{a|T - T_c|}{u} \right)^{1/2} + \delta m, \tag{4.16}$$

and extract the leading order balance to find

$$\delta m = \frac{\chi_0}{2a|T - T_c|} H. \tag{4.17}$$

The magnetisation again increases linearly with the applied field, and in almost exactly the same way. We can summarise both responses by giving the susceptibility

$$\chi = \frac{\partial m}{\partial H} = \begin{cases} \frac{\chi_0}{a|T - T_c|} & T > T_c, \\ \frac{\chi_0}{2a|T - T_c|} & T < T_c. \end{cases} \tag{4.18}$$

We see here that the susceptibility shows a power law divergence $\chi \sim |T - T_c|^{-\gamma}$ with the same critical exponent $\gamma = 1$ on both sides of the transition temperature. The prefactor differs on either side but only by a factor of 2. Both the exponent and the ratio of prefactors are pure numbers that do not depend on any microscopic details and whose values are predictions of Landau theory. Exactly at the critical temperature the response to the applied field is different; the Landau theory predicts

$$m = \left| \frac{\chi_0 H}{u} \right|^{1/3}, \tag{4.19}$$

so that we have the power law dependence $m \sim |H|^{1/\delta}$ with critical exponent $\delta = 3$.

Finally, we consider the heat capacity (for $H = 0$), which is obtained from the second derivative of the free energy (chapter 3 problem set)

$$C = -T \frac{\partial^2 f}{\partial T^2}. \tag{4.20}$$

Above T_c we can set $m = 0$ and the heat capacity is $C = -T(\partial^2 f_0 / \partial T^2)$; the only important point is that this contribution is regular through the critical temperature $T = T_c$. Below T_c we set $m = (a|T - T_c|/u)^{1/2}$, which gives

$$f = f_0 - \frac{a^2|T - T_c|^2}{4u}, \tag{4.21}$$

and hence an additional contribution to the heat capacity of $a^2 T/2u = a^2 T_c/2u$, plus contri-butions regular in $T - T_c$. Thus, the Landau theory prediction is that the heat capacity does not diverge like the susceptibility, but rather displays a jump discontinuity at T_c (by an amount that depends on the material parameters). Nonetheless, it is common to present the behaviour of the heat capacity as a power law $C \sim |T - T_c|^{-\alpha}$ with a critical exponent α. The Landau theory predicts the value $\alpha = 0$.
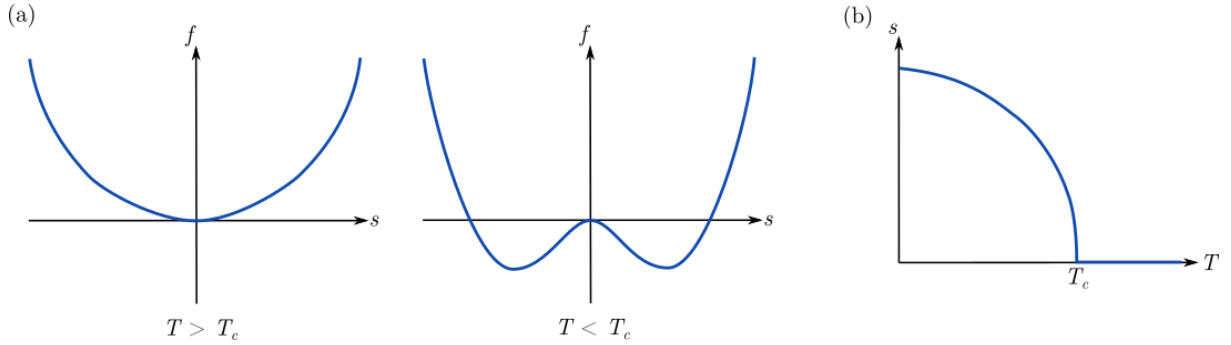
Figure 4.2: Isotropic–nematic transition in two dimensions as an exemplar of a continuous phase transition: (a) Structural transformation of the free energy on passing through the transition temperature $T = T_c$. (b) The scalar order parameter evolves continuously from zero at the transition with a power law onset, $s \sim |T - T_c|^\beta$, characteristic of continuous transitions.

4.4.1 Isotropic–Nematic Transition in Two Dimensions

The isotropic–nematic transition in two spatial dimensions gives another example of a continuous phase transition, as we now describe. Paralleling what we did in §4.2.2 we write the dielectric tensor in two dimensions as

$$\boldsymbol{\epsilon} = \begin{bmatrix} \epsilon_0 \epsilon_\parallel & 0 \\ 0 & \epsilon_0 \epsilon_\perp \end{bmatrix} = \frac{\epsilon_0(\epsilon_\parallel + \epsilon_\perp)}{2} \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \frac{\epsilon_0(\epsilon_\parallel - \epsilon_\perp)}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{4.22}$$

and read off the form of the Q tensor order parameter, $\mathbf{Q} = \frac{s}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$. As a 2×2 matrix there are only independent two scalar invariants, which we take to be $\operatorname{tr} \mathbf{Q} = 0$ and $\operatorname{tr} \mathbf{Q}^2 = \frac{s^2}{2}$. The Landau-de Gennes free energy is therefore

$$f = \frac{a(T - T_c)}{2} \operatorname{tr} \mathbf{Q}^2 + \frac{C}{4}\left(\operatorname{tr} \mathbf{Q}^2\right)^2 = \frac{a(T - T_c)}{4} s^2 + \frac{C}{16} s^4. \tag{4.23}$$

In particular, you should verify that there is no longer a cubic order term since, for example, $\operatorname{tr} \mathbf{Q}^3 = 0$. We conclude from the *absence* of the cubic term that the transition is continuous. Indeed, the form of the free energy density in terms of the scalar order parameter s is identical to that of the ferromagnet in terms of the magnetisation m. As a result all of the same predictions can be made for the transition, including the power law behaviour of thermodynamic quantities (magnitude of order, susceptibility, heat capacity) and values for the critical exponents. The fact that different, and *a priori* unrelated, physical systems should show the same quantitative behaviour at a continuous phase transition is known as **universality**. We say that the two-dimensional isotropic–nematic transition is in the same universality class as a (two-dimensional) magnet.

4.4.2 Superfluid Helium

The superfluid state is a coherent quantum state of low temperature helium atoms in which they flow without viscosity. The proper characterisation of the quantum state is a bit technical but for our purposes it is enough to identify that it is something about the quantum wavefunction that distinguishes the superfluid from the normal phase. A suitable order parameter is therefore a complex scalar field ψ (which need not be normalised to unity). The scalar invariant that can be used in the free energy is $|\psi|^2 = \bar{\psi}\psi$ and it follows that a Landau theory for the transition is

$$f = \frac{a(T - T_c)}{2} |\psi|^2 + \frac{u}{4} |\psi|^4. \tag{4.24}$$

Writing the complex wavefunction in polar form $\psi = \psi_0\, e^{i\theta}$ this reduces to

$$f = \frac{a(T - T_c)}{2} \psi_0^2 + \frac{u}{4} \psi_0^4, \tag{4.25}$$

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and so has the same form as the two-dimensional ferromagnetic and isotropic–nematic transitions. This is another example of universality.

4.4.3 Multicritical Points

The continuous transitions we have seen so far have all come down to essentially the same form for the free energy. This is essentially a property of the genericity of the Taylor series expansion for the free energy. However, there are different classes of transitions, known as **multicritical points**. One way of obtaining them is to have another parameter that allows you to tune the nature of the transition.

We give one example that applies to the superfluid transition in mixtures of ^{4}He and ^{3}He. The Landau free energy density for the transition is

$$f = \frac{a\big(T - T_c(x)\big)}{2}\,\psi_0^2 + \frac{u(x)}{4}\,\psi_0^4 + \frac{g}{6}\,\psi_0^6, \tag{4.26}$$

where we have emphasised that the critical temperature T_c and, more importantly, the coefficient of the fourth order term u depend on the volume fraction x of ^{3}He atoms. In particular, at a critical volume fraction $x = x_c$ this coefficient vanishes and then subsequently becomes negative. So long as u is positive the transition is as described in §4.4.2. When $u = 0$ the transition is still continuous but with different values for the critical exponents. This transition is an example of a **tricritical point**[3]. The magnitude of the order ψ_0 is given by minimising the free energy

$$0 = \frac{\partial f}{\partial \psi_0} = a(T - T_c)\,\psi_0 + g\,\psi_0^5, \qquad \Rightarrow \qquad \psi_0 = \left(\frac{a|T - T_c|}{g}\right)^{1/4}. \tag{4.27}$$

Thus at the tricritical point we find the critical exponent $\beta = \frac{1}{4}$. Similarly, we can calculate the heat capacity below the transition temperature by substituting the temperature dependence of ψ_0 back into the free energy to obtain

$$f = -\frac{a^{3/2}|T - T_c|^{3/2}}{3g^{1/2}} + \text{regular}. \tag{4.28}$$

Since $C = -T\partial^2 f/\partial T^2$, the heat capacity exhibits a power law divergence $C \sim |T - T_c|^{-\alpha}$ with critical exponent $\alpha = \frac{1}{2}$.

When u is negative the transition becomes discontinuous. Perhaps the easiest way to see this is from a graph of the form of f. The value of the transition temperature and the magnitude of the discontinuity in the order parameter can be obtained using the same method as in §4.3.

This phase transition in mixtures of ^{4}He and ^{3}He is also well-described by a spin 1 variant of the Ising model called the Blume-Emery-Griffiths model, whose analysis is covered in simplified form in the Chapter 3 Problems. It is shown in that problem that the mean field free energy has the form (4.26) and that the quartic coefficient u vanishes at a special value of the couplings in the Hamiltonian, corresponding to $x_c = \frac{2}{3}$. This transition is an example of one where mean field theory gives an accurate description of the experimental observations.

4.5 Critical Exponents and Scaling

A feature that mean field theory correctly captures is that close to the transition thermodynamic quantities display power law dependence on the distance from the critical point. For example, the magnetisation $m \sim |T - T_c|^{1/2}$ and the susceptibility $\chi \sim |T - T_c|^{-1}$ both follow simple power laws and the same is observed for other properties such as the heat capacity, correlation length, etc. The values of the exponents in the power laws obtained by mean field theory are not

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[3]The terminology derives from a more detailed analysis which shows that there are three lines of Ising-like critical transitions that intersect at the tricritical point.

always correct but the power law behaviour is. The study of these **critical exponents** became a major part of understanding continuous phase transitions. We summarise below the standard definitions for the main exponents (within the Ising model):

$$\text{heat capacity, } \alpha \qquad\qquad\qquad C \sim |t|^{-\alpha}, \qquad\qquad (4.29)$$

$$\text{order parameter, } \beta \qquad\qquad\qquad m \sim |t|^{\beta}, \qquad\qquad (4.30)$$

$$\text{susceptibility, } \gamma \qquad\qquad\qquad \chi \sim |t|^{-\gamma}, \qquad\qquad (4.31)$$

$$\text{order parameter with field, } \delta \qquad\qquad m \sim |h|^{1/\delta}, \qquad\qquad (4.32)$$

$$\text{correlation length, } \nu \qquad\qquad\qquad \xi \sim |t|^{-\nu}, \qquad\qquad (4.33)$$

$$\text{correlation function, } \eta \qquad\qquad \langle s(\mathbf{0})s(\mathbf{r})\rangle \sim |\mathbf{r}|^{2-d-\eta}. \qquad\qquad (4.34)$$

Here, $t = (T - T_c)/T_c$ is the reduced temperature and similarly h is a dimensionless version of the applied field.

Consider the magnetisation $m = m(t, h)$. An experiment might measure the magnetisation as a function of applied field for a range of different temperatures, giving a collection of magnetisation curves for each value of the temperature studied. We would like to understand the structure of such data. We have seen $m \sim |h|^{1/\delta}$ at $t = 0$ and also $m \sim |t|^{\beta}$ at $h = 0$. Both of these are captured by the form

$$m = |h|^{1/\delta}\,\Phi_1\!\left(\frac{|t|^{\beta}}{|h|^{1/\delta}}\right) \qquad \text{or} \qquad m = |t|^{\beta}\,\Phi_2\!\left(\frac{|h|^{1/\delta}}{|t|^{\beta}}\right), \qquad\qquad (4.35)$$

for functions Φ_1, Φ_2 that take constant vales at 0 and then become linear, $\Phi(x) \approx a + bx$. What this means is that if you plot the magnetisation against magnetic field using $m/|t|^{\beta}$ and $h/|t|^{\beta\delta}$ as coordinate axes the data at different values of the temperature will all fall on a single curve

$$\frac{m}{|t|^{\beta}} = \Phi\!\left(\frac{h}{|t|^{\beta\delta}}\right). \qquad\qquad (4.36)$$

This is known as **scaling collapse** and Φ as a **scaling function**. You plot the magnetisation curves with the magnetisation scaled by a power of the reduced temperature $(m/|t|^{\beta})$ and the applied field scaled by another power of the reduced temperature $(h/|t|^{\Delta})$ and find values of the exponents β, Δ such that the data all collapses on a single curve. The scaling function Φ shows power law behaviour $\Phi(x) \sim x^{1/\delta}$ that can also be obtained from the fit to the experimental data; in doing so we obtain the relation $\Delta = \beta\delta$, known as an exponent identity – not all of the power laws are independent. We would like to understand how this scaling form (and the same for other properties, or other transitions) arises from properties of the free energy. The set of ideas that does this is known as **scaling theory**.

The idea is to consider how the theory looks at different scales, or different levels of coarse-graining. This is a general and fundamental idea. We are used to aggregating properties over regions that contain several fundamental degrees of freedom but are still small compared to the system size or size of interest. Atoms are collections of protons, neutrons and electrons; protons and neutrons are collections of quarks and gluons; molecules are collections of atoms; cells are fundamental units in biology but composed of many molecules; in fluid dynamics a fluid element contains many molecules but is small compared to all other scales; thermodynamics is the ultimate coarse-graining of statistical mechanics. It is remarkable that that you can use this idea as the basis for a general quantitative understanding of continuous phase transitions.

The partition function is a sum over all states in the system. We can think of organising the states by their energy, or as normal modes by their mode number or wavevector. If we do the sum over the high energy modes first the remaining partition function will be for some modified theory with only lower energy modes. We are after what this modified theory is. Because high energies are associated to short length scales we can equally view this a coarse-graining process where we have removed the fine detail (atomic level resolution) and are now focused

on larger things (molecular scale, 10 nm, micron-scale, *etc.*). The next key idea is that at the critical point the correlation length diverges. The system then behaves as if it is **scale free** and displays statistically the same properties on all length scales. For the partition function, this means that the modified theory, represented by the remaining part after we have done the sum over the highest energy modes, is the same as the one we started with. Close to the critical point the change will be 'small'. The scaling hypothesis is that it amounts to multiplicative scaling of the reduced temperature t and applied field h by factors related to the level of coarse-graining.

We let a represent the microscopic scale in the theory; for lattice models it is the **lattice constant**. The scaling hypothesis is that the process of coarse-graining is given by the transformation

$$a \mapsto ba, \tag{4.37}$$
$$t \mapsto b^{y_t}t, \tag{4.38}$$
$$h \mapsto b^{y_h}h, \tag{4.39}$$

where b is the scale factor. The scaling of the reduced temperature and external field is described by two exponents, y_t and y_h, called the **scaling dimensions**. These two exponents determine all of the critical behaviour at the transition.

The scaling behaviour implies for the singular part of free energy density the transformation

$$f_s(t,h) \mapsto b^{-d}f_s\big(b^{y_t}t, b^{y_h}h\big). \tag{4.40}$$

The prefactor b^{-d} accounts for the scaling of volume. As the transformation does not change the partition function we can equate these two expressions. The idea now is to choose the rescaling so that after it the thermal variable t takes some standard value t_0 (which you may take to be 1). This amounts to choosing $b = |t_0/t|^{1/y_t}$. For the singular part of the free energy we then have

$$f_s(t,h) \mapsto |t/t_0|^{d/y_t}f_s\big(t_0, |t/t_0|^{-y_h/y_t}h\big) = |t/t_0|^{d/y_t}\varphi\big(|t/t_0|^{-y_h/y_t}h\big), \tag{4.41}$$

where φ is a scaling function.

Let us see what it implies for the critical exponents. First, when $h = 0$ we have $f_s \sim |t/t_0|^{d/y_t}$ and then find for the heat capacity ($C = -T\,\partial^2 F/\partial T^2$)

$$C \sim \partial_{tt}f_s \sim |t/t_0|^{d/y_t-2}, \qquad \Rightarrow \quad \alpha = 2 - \frac{d}{y_t}. \tag{4.42}$$

For the magnetisation we start from the thermodynamic relation $m = \partial f/\partial h$, which gives the scaling form

$$m \sim \partial_h f_s \sim |t/t_0|^{d/y_t}.|t/t_0|^{-y_h/y_t}\varphi'\big(|t/t_0|^{-y_h/y_t}h\big). \tag{4.43}$$

Comparing with (4.36) we find that $\beta = (d - y_h)/y_t$ and $\beta\delta = y_h/y_t$, or $\delta = y_h/(d - y_h)$. Calculating also the susceptibility we find

$$\chi \sim \frac{\partial m}{\partial h} \sim |t/t_0|^{(d-2y_h)/y_t}\,\varphi''\big(|t/t_0|^{-y_h/y_t}h\big), \qquad \Rightarrow \quad \gamma = \frac{2y_h - d}{y_t}. \tag{4.44}$$

Since all of the critical exponents are determined by the scaling dimensions y_t and y_h only two of them can be independent and there must exist relations between any three critical exponents. Some examples are

$$\alpha + 2\beta + \gamma = 2, \tag{4.45}$$
$$\gamma = \beta(\delta - 1). \tag{4.46}$$

Their derivation is a matter of piecing together the results we have developed and is requested in the problems. Historically the relations between critical exponents was discovered first and only later explained through the scaling theory for the free energy. This was a major part of its early success.

The critical behaviour of continuous phase transitions is understood by identifying the relevant scaling variables (t and h) and studying how their scaling behaviour affects the form of the free energy near the transition (4.40). All that remains is to determine the values of the scaling dimensions (y_t and y_h) for any given transition.

4.5.1 Critical Exponents in the Gaussian Theory

In this section we will find values for the scaling dimensions y_t, y_h of the Ising model and hence for all of the critical exponents. Ultimately, this will follow from little more than dimensional analysis. However, in order to get there we need to recast the lattice model with spins on discrete lattice sites as a continuous field theory. This process is easy enough to motivate roughly, and hence produce results to compare with experiment. A rigorous mathematical treatment is analogous to that of quantum field theory and is only available in some special cases; the proper formalism is still to be fully developed by the analysts. There are many presentations of this material with different styles and conventions; I am following Cardy's book in which factors of the lattice spacing are kept explicit and coupling constants are dimensionless.

We consider a lattice model with lattice spacing a and argue for its corresponding continuum limit. This will involve replacing the lattice spins s_i with a continuous field $s(\mathbf{r})$, while the sum over lattice sites will become an integral

$$\sum_i \to \int \frac{d^d r}{a^d}. \tag{4.47}$$

To motivate the continuum form of the nearest neighbour interaction $s_i s_j$ we write $s_j = s_i + (s_j - s_i)$ and then interpret the nearest neighbour difference as a discrete derivative[4]. This leads to

$$s_i s_j \to s(\mathbf{r})^2 + s(\mathbf{r}) \Big(a \partial_{(i \to j)} s(\mathbf{r}) + \frac{a^2}{2} \partial^2_{(i \to j)} s(\mathbf{r}) + \cdots \Big), \tag{4.48}$$

where the notation $\partial_{(i \to j)}$ indicates the derivative in the direction between sites i and j. In the sum over nearest neighbours $\langle i, j \rangle$ the first derivative terms will cancel out but the second derivative ones will not; the leading part will be the Laplacian $\nabla^2 s$ and up to an integration by parts this results in a term in the energy of the form $|\nabla s|^2$. Thus the continuum description of the Ising model takes the form

$$\beta \Big(-J \sum_{\langle i, j \rangle} s_i s_j \Big) \to \int \frac{K}{2} a^2 |\nabla s|^2 + \frac{A}{2} s^2 \frac{d^d r}{a^d}, \tag{4.49}$$

where $K \sim \beta J$ and $A \sim -\beta J z$ but it is convenient to introduce new – albeit temporary! – symbols for them. Finally, it is traditional to rescale the field $s \to K^{-1/2} a^{d/2-1} s$ so as to standardise the prefactor of the gradient term to $1/2$. With this done the continuum version of the Ising model is described by a free energy

$$\beta F = \int \frac{1}{2} |\nabla s|^2 + \frac{t a^{-2}}{2} s^2 \, d^d r, \tag{4.50}$$

where $t = A/K$ is the dimensionless thermal scaling variable. This is known as the **Gaussian theory**.

We can now use the Gaussian theory to determine the scaling dimension y_t. Under a rescaling of the lattice spacing $a \to ba$, the continuum theory is preserved by the rescaling $t \to b^2 t$, so $y_t = 2$. We can also determine the magnetic scaling dimension y_h. The coupling to a magnetic field adds a term $-h a^{-1-d/2} s$ to the integrand in (4.50). The factors of the lattice spacing a are those needed so that h is dimensionless. Considering the same rescaling $a \to ba$ gives $y_h = 1 + d/2$. This determines values for all of the critical exponents.

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[4]You could equally just consider Taylor series.

Unfortunately, since what we have done is really little more than dimensional analysis it is too simple and the exponents obtained in this way from the Gaussian theory are still not correct, except in dimension 4. The essence of the issue is that when t is negative the energy in the Gaussian theory (and hence statistical weight) for configurations with constant non-zero s is unbounded from below. To fix this, we should add to the integrand a positive term in s^4 such that the energy is minimised by a non-zero value of $s \sim |-t/u|^{1/2}$ (like in mean field theory). That is, we consider the free energy

$$\beta F = \int \frac{1}{2}\left|\nabla s\right|^2 + \frac{ta^{-2}}{2}s^2 + \frac{ua^{d-4}}{4}s^4 - ha^{-1-d/2}s \, d^dr, \qquad (4.51)$$

where u is a new dimensionless coupling. It is easy to see that its scaling dimension (in the Gaussian theory) is $y_u = 4-d$ so that under rescalings it gets smaller, and hence less important, in dimensions $d > 4$ but becomes larger, and hence more important, when $d < 4$. The special dimension $d = 4$ where its behaviour changes is called the **upper critical dimension** of the Ising model. The remaining task is to properly account for the effects that a non-zero u has on the scaling dimensions y_t and y_h for $d < 4$. Doing so requires a bit more formalism than we currently have at hand. It was provided by Kenneth Wilson in his development of the **renormalisation group**, for which he received the Nobel Prize in 1982. The exponents in the Ising model were first calculated in one of the most famous papers in statistical physics, whose title conveys the methodology:

K.G. Wilson and M.E. Fisher, Critical Exponents in 3.99 Dimensions, Phys. Rev. Lett. **28**, 240 (1972). doi:10.1103/PhysRevLett.28.240

There are many excellent accounts of the renormalisation group; for instance I learned about it from John Cardy's book *"Scaling and Renormalization in Statistical Physics"*; in addition Michael Fisher's early review article continues to be recommended widely:

M.E. Fisher, The renormalization group in the theory of critical behavior, Rev. Mod. Phys. **46**, 597 (1974). doi:10.1103/RevModPhys.46.597

4.6 Gradient Energy

In our discussion of phase separation we saw that the volume fraction ϕ is in general a function, $\phi = \phi(\mathbf{x})$, taking different values in different places according to whether the point $\mathbf{x}$ is in an A rich domain or a B rich domain. This spatial variation was associated with a gradient contribution $\frac{1}{2}\kappa|\nabla\phi|^2$ to the free energy. We have just seen that a term of the same form arises naturally in the continuum limit of the Ising model. The same considerations can be made in general; spatial variations on macroscopic scales are a generic feature of all phases. One can return to the example of liquid crystals and their use in displays to illustrate this: If the order parameter did not vary with position the screen you are looking at would be filled homogeneously with a single colour and different pixels would not show different parts of the full screen image.

How is this spatial variation accounted for in general? For definitiveness, let us take the case of the XY model, where the magnetisation is a two component vector $\mathbf{m} = [m_x, m_y] = m[\cos\theta, \sin\theta]$. We will focus on the second of these forms where we represent the vector by it magnitude m and direction θ, the angle it makes with the Cartesian x-direction. Spatial variation in the order parameter $\mathbf{m}(\mathbf{x})$ allows for a contribution to the free energy from gradients $\nabla\mathbf{m} = [\nabla m_x, \nabla m_y]$. The free energy can only depend on scalars constructed from these gradients, the simplest of which is

$$\left|\nabla\mathbf{m}\right|^2 = \left|\nabla m_x\right|^2 + \left|\nabla m_y\right|^2 = |\nabla m|^2 + m^2|\nabla\theta|^2. \qquad (4.52)$$

Including this gradient contribution yields the free energy density

$$f = \frac{a(T - T_c)}{2}(\mathbf{m} \cdot \mathbf{m}) + \frac{u}{4}(\mathbf{m} \cdot \mathbf{m})^2 + \frac{K}{2}|\nabla \mathbf{m}|^2, \qquad (4.53)$$

$$= \frac{a(T - T_c)}{2}m^2 + \frac{u}{4}m^4 + \frac{K}{2}|\nabla m|^2 + \frac{Km^2}{2}|\nabla \theta|^2, \qquad (4.54)$$

where K is an energy scale associated with the gradients, usually called an **elastic constant**. Precisely the same free energy, just with m replaced by s and up to some numerical factors, applies for the two-dimensional nematic liquid crystal. Although this should be clear conceptually – the direction of the optic axis is the analogue of the direction of the magnetisation –, we defer the calculational details to the problems.

The free energy (4.54) depends only on gradients of θ and is independent of its value. Consequently, the orientation is *not* determined by the condition of free energy minimisation, as the magnitude of the order is, but instead is chosen *spontaneously*; this is known as **spontaneous symmetry breaking**. Inexorably tied to this is the fact that *uniform* changes in θ do not cost any energy, while *non-uniform* changes can be made to have an arbitrarily low energy cost by making the change slowly enough. These low energy excitations are a hallmark of spontaneous symmetry breaking phase transitions and are amongst the most important properties of the ordered phase. In the case of ferromagnetism they are called **spin waves**; more generally they are known as **Goldstone modes**.

4.7   Dynamics: Fast and Slow Variables

What are the dynamics of small perturbations of the order and its relaxation to equilibrium? In the case of phase separation, the most important consideration was that the total amount of each fluid species was conserved. However, the orientation of a nematic liquid crystal is not subject to any such conservation law; the total number of molecules pointing along some direction is not conserved. Thus the dynamics in this case is simpler and the order just relaxes to equilibrium. The general form of such relaxation is that the gradient of the free energy provides a thermodynamic force that restores the order parameter to its equilibrium value. In two dimensions the isotropic–nematic transition is continuous and has the same structure as the XY model, so we use (4.54) with m replaced by s to follow prevailing notational convention. The relaxation of the magnitude s and orientation θ is given by[5]

$$\frac{\partial s}{\partial t} = -\Gamma\Big(a(T - T_c)s + Cs^3 + Ks|\nabla \theta|^2 - K\nabla^2 s\Big), \qquad (4.55)$$

$$\frac{\partial \theta}{\partial t} = \Gamma_s K \nabla \cdot \Big(s^2 \nabla \theta\Big), \qquad (4.56)$$

where Γ and Γ_s are relaxational constants for the magnitude and orientation, respectively.

The dynamics of s and θ are fundamentally different. Consider first a homogeneous departure of the magnitude s from its equilibrium value s_{eq}. We write $s = s_{\mathrm{eq}} + \delta s$ and linearise in δs. One then finds that this perturbation decays exponentially as

$$\delta s(t) = \delta s(0)\, e^{-\Gamma(a(T - T_c) + 3Cs_{\mathrm{eq}}^2)t} \equiv \delta s(0)\, e^{-t/\tau_s}. \qquad (4.57)$$

In other words, the magnitude s relaxes to its equilibrium value exponentially with a time constant τ_s; we say that it is a **fast** degree of freedom.

In contrast, the orientation θ is a **slow variable**. To see this, let $s = s_{\mathrm{eq}}$ take its equilibrium value and note that θ does not decay at all for homogeneous perturbations from its initial value. To find the behaviour when it is slowly varying take a spatial Fourier transform to get

$$\frac{\partial \tilde{\theta}(\mathbf{q}, t)}{\partial t} = -\Gamma_s K s_{\mathrm{eq}}^2 q^2\, \tilde{\theta}(\mathbf{q}, t), \qquad \Rightarrow \qquad \tilde{\theta}(\mathbf{q}, t) = \tilde{\theta}_0(\mathbf{q})\, e^{-\Gamma K s_{\mathrm{eq}}^2 q^2 t}. \qquad (4.58)$$

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[5]The form of this equation will be recognisable to those familiar with the calculus of variations: $\partial s/\partial t = -\Gamma\, \delta F/\delta s$ and $\partial \theta/\partial t = -\Gamma_s\, \delta F/\delta \theta$.

Although each Fourier mode decays exponentially, the time constants diverge as the magnitude of the wavevector q goes to zero. Choosing an initial perturbation $\theta_0(\mathbf{x}) = \theta_0 \exp\{-|\mathbf{x}|^2/2\sigma^2\}$ that is a Gaussian of width σ and height θ_0, we find, after inverse Fourier transform, that the perturbation decays as (d is the spatial dimension)

$$\theta(\mathbf{x}, t) = \theta_0 \left(\frac{\sigma^2}{\sigma^2 + 2\Gamma K s_{\text{eq}}^2 t} \right)^{d/2} e^{-\frac{|\mathbf{x}|^2}{2(\sigma^2 + 2\Gamma K s_{\text{eq}}^2 t)}}. \tag{4.59}$$

The maximum at $\mathbf{x} = 0$ decays algebraically as $\sim t^{-d/2}$ at late times, illustrating that the orientation evolves much more slowly than the magnitude of the order, s.

This separation of timescales between the dynamics of s and θ further emphasises the fundamental significance of the low energy excitations (spin waves or Goldstone modes) associated to a spontaneously broken continuous symmetry. They completely dominate the description of the phase and phase behaviour on long length and timescales. On timescales long compared to τ_s we can simply take the magnitude of the order to be its equilibrium value $s = s_{\text{eq}}$ (everywhere) and the system is described solely in terms of the slow orientation degree of freedom

$$f = f_{\text{eq}} + \frac{K s_{\text{eq}}^2}{2} |\nabla\theta|^2, \qquad\qquad \frac{\partial\theta}{\partial t} = \Gamma_s K s_{\text{eq}}^2 \nabla^2\theta. \tag{4.60}$$

4.8 Topological Defects

The extreme softness and long timescales of slow degrees of freedom bring fundamentally new physics that impacts even the nature of the phase transition. There is a lot that can be said but I mention only one aspect. Equation (4.60) identifies any states with $\nabla^2\theta = 0$ as stationary configurations. In addition to the uniform solutions $\theta = $ const. there are also *non-uniform* stationary states. The most important of these are the class of **vortices**

$$\theta(\mathbf{x}) = w \arctan \frac{y}{x} = w\,\phi, \tag{4.61}$$

where ϕ is the azimuthal angle of polar coordinates in two dimensions and w is an integer, called the **winding number**, or **charge**, of the vortex. These vortices in the two-dimensional XY model are examples of **topological defects**, which are general features of ordered phases that dominate and control many of their properties. In fact, there is a difference between the defects in a magnet and in a nematic liquid crystal. In the latter case there is nematic symmetry $\mathbf{n} \sim -\mathbf{n}$, which translates to $\theta \sim \theta + \pi$. As a result w is allowed to be a half-integer in the liquid crystal case and the fundamental defects have windings $w = \pm\frac{1}{2}$. These are readily identifiable in experimental images and are one of the easiest ways of telling that alignment is nematic rather than vectorial. The same defects also arise in a superfluid (with integer winding): Writing the order parameter in polar form $\psi = \psi_0 \exp\{i\theta\}$ separates the fast amplitude (ψ) from the slow phase (θ) degree of freedom. The phase, and through it the superfluid velocity $\mathbf{v} \sim \nabla\theta$, possesses the same vortices, which is where the name originates from.

Let us calculate the energy of a defect. There are several methods for this but for us a simple direct calculation will do. The gradients in orientation are $\nabla\theta = \frac{w}{r}\mathbf{e}_\phi$, where r is the radial distance in the plane. The energy of the defect is then

$$F_{\text{defect}} = \int \frac{K s_{\text{eq}}^2}{2} \frac{w^2}{r^2} r\,dr\,d\phi = \int_{r_c}^{R} \pi K s_{\text{eq}}^2 \frac{w^2}{r}\,dr = \pi K s_{\text{eq}}^2 w^2 \ln \frac{R}{r_c}. \tag{4.62}$$

The energy is logarithmically divergent both at large distances ($r = R$) and small distances ($r = r_c$) so the integral needs to be restricted in both limits. At short distances we know that ultimately we will encounter the finite size of the molecules when a description in terms of a continuous variable averaging over many molecules is no longer appropriate. However, even before getting that small we can say that we will reach a distance where the energy cost

associated with the gradients of orientation exceeds the energy gain from forming the ordered phase (i.e. $s \neq 0$); this distance defines a core radius r_c within which the order melts to the isotropic phase ($s = 0$). In typical situations (away from the transition temperature) this distance is of molecular scale. The large length-scale cut-off ($r = R$) corresponds either to the size of the sample (experimental container) or to the distance between defects.

For a pair of defects it can be shown that

$$F \simeq \pi K s_{\text{eq}}^2 \left((w_1 + w_2)^2 \ln \frac{R}{r_c} - 2 w_1 w_2 \ln \frac{d}{r_c} \right), \tag{4.63}$$

where d is their separation. The term divergent with system size is eliminated by a 'neutral' configuration, where the defects have equal and opposite winding numbers. Their energy is then logarithmic in their separation so that they (each) experience an attractive force of magnitude

$$\frac{\partial F}{\partial d} = \frac{2 \pi K s_{\text{eq}}^2 w^2}{d}, \tag{4.64}$$

inversely proportional to their separation. This is Coulomb's law for charged particles in two dimensions.

Individual defects have no dynamics. Pairs of defects have long range interactions and slow dynamics. In fact they behave exactly like electric charges in two dimensions; this is because they satisfy Laplace's equation $\nabla^2 \theta = 0$ which also governs the electrostatic potential. Defects with the same winding number repel, while those with opposite winding attract[6]. Because of this analogy, states of the XY model with multiple defects are referred to as a **Coulomb gas**. They completely dominate the phase transition, as was discovered by Mike Kosterlitz and David Thouless, and independently Vadim Berezinskii, in the early 1970s. This example has become a cornerstone for many subsequent developments and in 2016 Kosterlitz and Thouless shared the Nobel Prize for their work. You can watch (or read) Kosterlitz's Nobel Lecture here:

J. Michael Kosterlitz, Nobel Prize Lecture: *Topological Defects and Phase Transitions*, (2016). https://www.nobelprize.org/prizes/physics/2016/kosterlitz/lecture/.

If you are interested in getting a slightly more complete overview of the set of ideas for describing phases and phase transitions introduced here, then I can recommend an engaging article by James Sethna:

James P. Sethna, Order Parameters, Broken Symmetry, and Topology, https://arxiv.org/pdf/cond-mat/9204009.pdf.

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[6]And the force varies with the inverse first power of separation; Coulomb's law in two dimensions.

Chapter 5

Polymers

Polymers are an important class of material used in plastics, fibres, resins, coatings and glues, and occur naturally in egg white, dough, chewing gum, DNA, proteins and many other biopolymers. A polymer is a long chain molecule consisting of fundamental units, or monomers, joined together by chemical bonds. There is great variety in the chemical molecules and complexes that can be used as monomers, allowing for control and functionalisation of their properties. This is a part of the art of polymer chemistry, but for the most basic physical characteristics of polymers the actual chemical composition is unimportant and we can treat the monomers simply as idealised beads. Similarly, there is great variety in polymer architectures – there are linear polymers, branched polymers, star polymers, dendrimers, ring polymers and many more – but we will limit ourselves to the simplest: the **linear polymer**.

linear polymer   branched polymer   star polymer   dendrimer   ring polymer
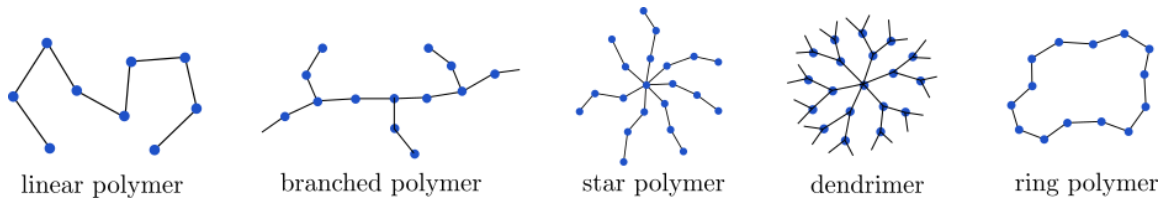
5.1 Statistical Models of Linear Polymer Chains

There are many simple models that describe the macroscopic properties of polymer chains; here we briefly introduce three models of linear polymers. In the **freely jointed chain**, the polymer is modelled as a chain of $N+1$ monomers with neighbouring monomers connected by N **bonds** of fixed length but arbitrary orientation. If the positions of the monomers are $\mathbf{r}_i$, for $i = 0, \ldots, N$, then the bonds are the vectors $\mathbf{b}_i = \mathbf{r}_i - \mathbf{r}_{i-1}$, which all have the same magnitude $|\mathbf{b}_i| = b$. Since the orientation is arbitrary we have $\langle \mathbf{b}_i \rangle = 0$ and in the freely jointed chain the bonds are taken to be independent so that we also have

$$\langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = b^2 \, \delta_{ij}. \tag{5.1}$$

A quantity of interest is the typical size of a polymer chain; not only is this relevant to several physical properties but it is directly accessible in scattering experiments. One measure of the polymer size is the length of the **end-to-end vector**

$$\mathbf{R}_{\mathrm{ee}} = \mathbf{r}_N - \mathbf{r}_0 = \sum_{i=1}^{N} \mathbf{b}_i. \tag{5.2}$$

Evidently $\langle \mathbf{R}_{\mathrm{ee}} \rangle = 0$ since $\langle \mathbf{b}_i \rangle = 0$, but this tells us only that there is no preferred direction for the end-to-end vector and not its preferred length. For the latter, we calculate

$$\left\langle |\mathbf{R}_{\mathrm{ee}}|^2 \right\rangle = \left\langle \sum_{i,j=1}^{N} \mathbf{b}_i \cdot \mathbf{b}_j \right\rangle = \sum_{i,j=1}^{N} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = Nb^2. \tag{5.3}$$

Hence the root mean square of the end-to-end vector is $R_{\mathrm{ee}} = \sqrt{N}\,b$ and increases with the degree of polymerisation as $N^{1/2}$.

The same scaling $R \sim N^{1/2}$ is found for other measures of the size of the polymer; a common measure is the **radius of gyration**, R_{g}, which is the root mean square of the separation of each monomer from the centre of mass

$$R_{\mathrm{g}}^2 = \frac{1}{N+1}\sum_{i=0}^{N}\left\langle \left| \mathbf{r}_i - \mathbf{r}_{\mathrm{cm}} \right|^2 \right\rangle. \tag{5.4}$$

In one of the problems we will calculate that, for large N, $R_{\mathrm{g}}^2 \approx Nb^2/6$. Thus the radius of gyration and end-to-end vector do not measure exactly the same length scale but they do have the same scaling with N for simple linear polymers. In general situations, R_{g} can give a more appropriate measure of the polymer size since its definition carries over also to branched polymers or star polymers, for instance.

An essentially identical description but with discrete bond orientations is provided by lattice models of polymer chains. A **lattice polymer** is simply a polymer chain constrained to a lattice, say a square lattice in two dimensions or a cubic lattice in three dimensions; the monomers sit at lattice sites and the bonds are restricted to only connect nearest neighbour sites. It should be clear that the discreteness inherent to lattice models will affect some properties quantitatively but that the basic scaling $R_{\mathrm{ee}} \sim N^{1/2}$ will not be altered, at least for large N, so long as the bonds continue to be chosen independently.

As a final example of a model for capturing the macroscopic properties of polymer chains we mention the **Gaussian chain**. The freely jointed chain draws individual bonds from a distribution of fixed length b with uniformly arbitrary direction. The Gaussian chain instead draws each polymer bond – a step $\mathbf{r}$ – from the Gaussian distribution

$$P_{\mathrm{bond}}(\mathbf{r}) = \left(\frac{3}{2\pi b^2} \right)^{3/2} \mathrm{e}^{-\frac{3|\mathbf{r}|^2}{2b^2}}. \tag{5.5}$$

This has the same first and second moments

$$\langle \mathbf{r} \rangle = 0, \qquad\qquad \langle \mathbf{r} \cdot \mathbf{r} \rangle = b^2, \tag{5.6}$$

as the freely jointed chain and so the Gaussian chain gives rise to the same expression for the end-to-end separation ($R_{\mathrm{ee}} = N^{1/2}\,b$) of a polymer chain made from N independent bonds. The Gaussian model gives us further a simple expression for the full probability distribution of the end-to-end vector (here I continue to simply use $\mathbf{r}$ for this vector), namely the Gaussian distribution

$$P_{\mathrm{ee}}(\mathbf{r}) = \left(\frac{3}{2\pi N b^2} \right)^{3/2} \mathrm{e}^{-\frac{3|\mathbf{r}|^2}{2Nb^2}}, \tag{5.7}$$

where here $\mathbf{r}$ is the end-to-end vector of the entire chain. To see this, note that the end-to-end probability for N bonds, $P_{\mathrm{ee},\,N}(\mathbf{r})$, can be expressed as the convolution of that for $N-1$ bonds with the probability distribution for a single bond

$$P_{\mathrm{ee},\,N}(\mathbf{r}) = \int P_{\mathrm{ee},\,N-1}(\mathbf{r}-\mathbf{x})P_{\mathrm{bond}}(\mathbf{x})\,d^3x = P_{\mathrm{ee},\,N-1} * P_{\mathrm{bond}}(\mathbf{r}). \tag{5.8}$$

Taking Fourier transforms we then obtain

$$\tilde{P}_{\mathrm{ee},\,N}(\mathbf{q}) = \tilde{P}_{\mathrm{ee},\,N-1}(\mathbf{q})\tilde{P}_{\mathrm{bond}}(\mathbf{q}) = \left(\tilde{P}_{\mathrm{bond}}(\mathbf{q}) \right)^N, \tag{5.9}$$

where the second equality comes from iteration. The probability distribution (5.7) then follows from inverse Fourier transform. By the central limit theorem the probability distribution for any other model, for instance the freely jointed chain, is asymptotically the same as this for large enough N and hence the Gaussian model gives, for long polymers, a universal description

of chain statistics. Note that although the freely jointed and Gaussian chains have the same first and second moments they do not give the same results for all properties. For example, in the freely jointed chain the end-to-end vector has a maximum length of Nb, corresponding to a fully extended chain, whereas in the Gaussian model there is no maximum extension but only the Gaussian distribution (5.7).

5.1.1   Persistence Length

Some polymers are very flexible, while others are stiff. This difference originates in an energetic cost for bending polymer bonds and gives rise to another characteristic length scale for a polymer; the **persistence length**. As a simple model, consider the freely jointed chain model and write $\mathbf{u}_i = \mathbf{b}_i/b$ for the unit vector specifying the orientation of each bond. Then we can take a bending energy for the polymer chain of[1]

$$E = -\kappa \sum_{i=1}^{N-1} \mathbf{u}_i \cdot \mathbf{u}_{i+1} = -\kappa \sum_{i=1}^{N-1} \cos \theta_i, \tag{5.10}$$

that penalises any angle θ between neighbouring bonds by a **bending stiffness** κ. If we treat the angles θ_i as the degrees of freedom then we can compute the partition function (for the bond angle degrees of freedom) as

$$Z = \sum_{\{\theta_i\}} e^{\beta\kappa \sum_{i=1}^{N-1} \cos \theta_i} = \sum_{\{\theta_i\}} \prod_{i=1}^{N-1} e^{\beta\kappa \cos \theta_i} = \left(\sum_{\{\theta\}} e^{\beta\kappa \cos \theta} \right)^{N-1}. \tag{5.11}$$

Now, of course, the bond angle θ is a continuous variable so the sum is really an integral; its exact form depends on the number of spatial dimensions, but in three dimensions it is

$$Z = \left(\int_{\theta=0}^{\pi} e^{\beta\kappa \cos \theta} \sin \theta \, d\theta \right)^{N-1} = \left(\frac{2 \sinh \beta\kappa}{\beta\kappa} \right)^{N-1}. \tag{5.12}$$

Finally, we can calculate the expectation value for the bond angle as

$$\langle \cos \theta \rangle = \frac{\int_0^{\pi} \cos \theta \, e^{\beta\kappa \cos \theta} \sin \theta \, d\theta}{\int_0^{\pi} e^{\beta\kappa \cos \theta} \sin \theta \, d\theta} = \frac{\partial \ln Z}{\partial (\beta\kappa)} = \coth \beta\kappa - \frac{1}{\beta\kappa}. \tag{5.13}$$

When the bending stiffness is small, $\beta\kappa \ll 1$, we have $\langle \cos \theta \rangle \approx \beta\kappa/3$ and the orientations of neighbouring segments are essentially uncorrelated. Whereas, when the stiffness is large, $\beta\kappa \gg 1$, we get $\langle \cos \theta \rangle \approx 1 - (\beta\kappa)^{-1}$ and neighbouring segments are approximately parallel.

How does this extend along the chain? We consider the expectation value $\langle \mathbf{u}_i \cdot \mathbf{u}_{i+n} \rangle$ of bonds n apart. Now, from our preceding calculation we can say that on average

$$\mathbf{u}_{i+1} = \langle \cos \theta \rangle \mathbf{u}_i + \langle \sin \theta \rangle \mathbf{u}_i^{\perp}, \tag{5.14}$$

where $\mathbf{u}_i^{\perp}$ is a vector orthogonal to $\mathbf{u}_i$. This then suggests

$$\langle \mathbf{u}_i \cdot \mathbf{u}_{i+n} \rangle = \langle \cos \theta \rangle \langle \mathbf{u}_i \cdot \mathbf{u}_{i+n-1} \rangle + \langle \sin \theta \rangle \langle \mathbf{u}_i \cdot \mathbf{u}_{i+n-1}^{\perp} \rangle, \tag{5.15}$$

and if the polymer is relatively stiff $\langle \sin \theta \rangle$ will be small and we can drop the second term. Upon recursion, this gives the result

$$\langle \mathbf{u}_i \cdot \mathbf{u}_{i+n} \rangle \approx \langle \cos \theta \rangle^n = e^{n \ln \langle \cos \theta \rangle} \approx e^{-\frac{n}{\beta\kappa}}. \tag{5.16}$$

The alignment of bonds decays exponentially along the polymer. The length scale over which it does so is $\ell_{\mathrm{p}} \approx \beta\kappa b$ and is called the **persistence length**. Flexible polymers are long compared

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[1]We remark that this is the same energy as the one-dimensional (classical spin) Heisenberg chain.

to their persistence length, while stiff polymers have a length comparable to, or smaller than, their persistence length.

The idea of a persistence length and that polymers are flexible on scales large compared to this suggests a coarse-graining of the description of semi-flexible polymers back to the freely jointed chain. The idea is to introduce a new 'effective' (or renormalised) bond length b_r and consider this to be the new fundamental unit, or effective monomer. Since there are b_r/b monomers per effective monomer, there are $N_r = Nb/b_r$ effective monomers in the coarse-grained description. The idea is to choose b_r such that the end-to-end vector statistics recovers the expression for the freely jointed chain

$$\langle |\mathbf{R}_{\text{ee}}|^2 \rangle = N_r b_r^2 = Nb^2 \left(\frac{b_r}{b} \right). \tag{5.17}$$

The length scale determined by this is known as the **Kuhn length**. The relationship between the Kuhn length and the persistence length depends on the particular model used to describe the stiffness; when the scales are all well separated one finds $b_r \approx 2\ell_{\text{p}}$. This mapping indicates a universality in the properties of polymers; provided they are long compared to their persistence length they can all be described by an effective freely jointed chain.

5.2 Elasticity

Suppose we pull on a polymer so as to separate the ends by an amount $\mathbf{r}$. This stretches the polymer out and restricts its available configurations, reducing the entropy. As such it increases the free energy and we can say that we have done work against a force seeking to return the polymer to its preferred configuration where on average the end-to-end vector is zero. Equivalently, in order to hold the end-to-end vector at the non-zero displacement $\mathbf{r}$ (on average) we have to supply a force. The force–extension relationship characterises the elasticity of a polymer chain. It is worth emphasising that the origin of this elasticity is purely entropic and does not come from interactions between the monomers, which here we are neglecting. We should also say that polymers are very stretchy; as we have seen, the end-to-end separation scales as $N^{1/2}$ whereas for a fully stretched polymer this end-to-end separation would be proportional to N. When N is large this increase in length is very considerable.

We will present two descriptions of polymer elasticity, using both the freely jointed chain and Gaussian chain models. First, the freely jointed chain: If we apply a force $\mathbf{f}$ to maintain an end-to-end vector $\mathbf{r}$ then the polymer configuration will have an energy

$$E = -\mathbf{f} \cdot \mathbf{r} = -\sum_{i=1}^{N} \mathbf{f} \cdot \mathbf{b}_i = -fb \sum_{i=1}^{N} \cos \theta_i, \tag{5.18}$$

where $f = |\mathbf{f}|$ and θ_i is the angle between the ith polymer bond and the direction of the force. The partition function is

$$Z = \sum_{\{\mathbf{b}_i\}} \mathrm{e}^{-\beta E} = \sum_{\{\mathbf{b}_i\}} \prod_{i=1}^{N} \mathrm{e}^{\beta fb \cos \theta_i} = \left(\sum_{|\mathbf{b}|=b} \mathrm{e}^{\beta fb \cos \theta} \right)^N. \tag{5.19}$$

What we mean in the final expression is the sum over all bond vectors $\mathbf{b}$ with magnitude b. The set of all such vectors is clearly the sphere of radius b and we may parameterise them by polar angles (θ, ϕ) for points of the sphere. Thus, really, we have an integral

$$Z = \left(\int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \mathrm{e}^{\beta fb \cos \theta} \sin \theta \, d\theta d\phi \right)^N = \left(\frac{4\pi k_{\text{B}} T}{fb} \sinh \beta fb \right)^N. \tag{5.20}$$

From the partition function we can calculate the average extension in the usual way

$$\langle r \rangle = \frac{1}{Z} \sum_{\{\mathbf{b}_i\}} \left(b \sum_{i=1}^{N} \cos \theta_i \right) \mathrm{e}^{\beta fb \sum_i \cos \theta_i} = k_{\text{B}} T \frac{d \ln Z}{df} = Nb \left[\coth \frac{fb}{k_{\text{B}} T} - \frac{k_{\text{B}} T}{fb} \right]. \tag{5.21}$$

This is a force-extension relation, telling us the extension that results from applying a given force, or the force that is required to produced a particular extension. It is useful to consider the limiting behaviour for large and small forces. When $fb/k_\mathrm{B}T$ is small we find

$$\langle r \rangle = \frac{Nfb^2}{3k_\mathrm{B}T}, \qquad \Rightarrow \quad f = \frac{3k_\mathrm{B}T}{Nb^2}\langle r \rangle, \tag{5.22}$$

a **linear** force–extension relation as you would have for a standard Hookean spring with spring constant $3k_\mathrm{B}T/Nb^2$. Polymers resist stretching with standard linear elasticity for small forces; the fact that the spring constant is proportional to the temperature reflects the entropic origin of this elasticity. On the other hand, when $fb/k_\mathrm{B}T$ is large we have the limiting behaviour

$$\langle r \rangle \approx Nb\left[1 - \frac{k_\mathrm{B}T}{fb}\right], \qquad \Rightarrow \quad f = \frac{Nk_\mathrm{B}T}{Nb - \langle r \rangle}. \tag{5.23}$$

The polymer extension asymptotes to its maximum value Nb of a fully stretched chain and the force that is needed to achieve this diverges.

The analysis is in many respects simpler and more direct for the Gaussian chain. The probabilities (5.7) of a polymer chain with end-to-end separation $\mathbf{r}$ have the form $\mathrm{e}^{-\beta E}$ of a Boltzmann weight with 'energy' $E = k_\mathrm{B}T\frac{3|\mathbf{r}|^2}{2Nb^2}$. Of course, this is not a fundamental interaction but rather an entropic one (so it is really a free energy), arising from the fact that there are many more configurations with a small end-to-end separation that there are for a highly extended chain. It corresponds to the same Hookean elasticity as we found for the freely jointed chain at small extensions, with the same spring constant $3k_\mathrm{B}T/Nb^2$. But in the Gaussian chain the elasticity is purely Hookean, so that for large extensions the elasticity deviates from that of the freely jointed chain in that it remains purely harmonic and there is no maximal extension.

5.2.1 Rubber Elasticity

A rubber is a network of polymer chains with cross-links connecting them. The segment of polymer chain between any two cross-links can be viewed as a subchain; we will consider that it has length N (variable); its end-to-end vector is, of course, the separation $\mathbf{r}$ between the two cross-links that it connects. When the rubber is stretched the cross-links will move, their separations will change and the polymer subchains connecting them will resist this by their elasticity. If we treat each subchain as a Gaussian chain then it will contribute a free energy $k_\mathrm{B}T\frac{3|\mathbf{r}|^2}{2Nb^2}$ from the separation of its ends. The total free energy will be the sum of the contributions from each subchain; we write this as a free energy density

$$f = n_c \sum_N \int P(\mathbf{r}, N)\frac{3k_\mathrm{B}T|\mathbf{r}|^2}{2Nb^2}\, d^3r, \tag{5.24}$$

where n_c is the number density of subchains and $P(\mathbf{r}, N)$ is the probability that a subchain has end-to-end vector $\mathbf{r}$ and length N. This probability will depend on the details of the polymer network and how it is cross-linked but in the simplest approximation we can take

$$P(\mathbf{r}, N) = P(N)P_\mathrm{ee}(\mathbf{r}) = P(N)\left(\frac{3}{2\pi Nb^2}\right)^{3/2}\mathrm{e}^{-\frac{3|\mathbf{r}|^2}{2Nb^2}}, \tag{5.25}$$

as the product of the probability distribution for the end-to-end vector of the Gaussian chain with N bonds and the probability $P(N)$ that the subchain has N bonds.

Now suppose that the rubber is stretched so that the separation between cross-links becomes $\mathbf{r}'$. The resulting change in free energy is the elastic free energy of the rubber

$$f_\mathrm{elastic} = n_c \sum_N \int P(\mathbf{r}, N)\frac{3k_\mathrm{B}T}{2Nb^2}(|\mathbf{r}'|^2 - |\mathbf{r}|^2)\, d^3r. \tag{5.26}$$

In simple (affine) elasticity the separations $\mathbf{r}'$ in the stretched state are related to those in the undeformed state by a linear transformation $\mathbf{r}' = \boldsymbol{\Lambda}\mathbf{r}$, where $\boldsymbol{\Lambda}$ is a 3×3 matrix, the deformation tensor. Switching to an index notation we can write the elastic free energy density as

$$f_{\text{elastic}} = n_c \sum_N \int P(\mathbf{r}, N) \frac{3k_{\text{B}}T}{2Nb^2} \left(\Lambda_{ij}\Lambda_{ik}\, r_j r_k - r_i r_i \right) d^3r, \tag{5.27}$$

$$= \frac{n_c k_{\text{B}}T}{2} \left(\Lambda_{ij}\Lambda_{ij} - 3 \right). \tag{5.28}$$

Finally, if the deformation tensor takes the form

$$\boldsymbol{\Lambda} = \begin{bmatrix} \lambda_x & 0 & 0 \\ 0 & \lambda_y & 0 \\ 0 & 0 & \lambda_z \end{bmatrix}, \tag{5.29}$$

corresponding to stretching the rubber by a factor λ_x along the x-axis, and similarly for y and z, then we can write the elastic energy density as

$$f_{\text{elastic}} = \frac{n_c k_{\text{B}}T}{2} \left[\left(\lambda_x^2 - 1 \right) + \left(\lambda_y^2 - 1 \right) + \left(\lambda_z^2 - 1 \right) \right]. \tag{5.30}$$

For a material that is incompressible the deformation must preserve its volume so that $\lambda_x \lambda_y \lambda_z = 1$. In this case, if we stretch along one direction (say x) by a factor λ the material will contract in the other directions (y and z) such that they scale by a factor $1/\sqrt{\lambda}$. The elastic energy for such stretching of an incompressible rubber is

$$f_{\text{elastic}} = \frac{n_c k_{\text{B}}T}{2} \left(\lambda^2 + \frac{2}{\lambda} - 3 \right), \tag{5.31}$$

and the work done in stretching it is

$$df_{\text{elastic}} = n_c k_{\text{B}}T \left(\lambda - \frac{1}{\lambda^2} \right) d\lambda, \tag{5.32}$$

corresponding to a non-Hookean force $n_c k_{\text{B}}T(\lambda - \lambda^{-2})$. Finally, linearising for λ close to 1 identifies the **Young's modulus** of the rubber as $3n_c k_{\text{B}}T$.

5.3 Flory Theory: Size of a Polymer with Interactions

What is the typical size R of a polymer chain of length N? We have seen, for the freely jointed chain and Gaussian chain models, that $R \sim N^{1/2}$, whether we take for R the end-to-end separation or radius of gyration. This can be contrasted with the scalings for a tightly packed ball – a collapsed polymer, or globule –, whose size grows as $R \sim N^{1/3}$, or a perfectly stiff rod – where all the bond vectors point in the same direction $\mathbf{b}_i = \mathbf{b}$ for all i – for which $R \sim N$. These behaviours would arise if there were very strong interactions between the monomers, respectively attractive and repulsive, and the scaling $R \sim N^{1/2}$ of the freely jointed chain reflects the complete omission of any interactions from the description.

The following simple argument of Flory gives a prediction for the polymer size when (weak, repulsive) interactions are accounted for. Let Δ be the interaction energy between two monomers. Each monomer will, on average, interact with a number of others given by the concentration N/R^3 of monomers in the polymer chain. Hence we estimate the total interaction energy to be

$$E_{\text{interact}} = \frac{1}{2} \Delta N \frac{N}{R^3}, \tag{5.33}$$

the factor of $1/2$ allowing for double counting (as usual), and combining with the entropic energy of stretching the chain to a size R this gives an overall free energy

$$F = \frac{3k_{\text{B}}T R^2}{2Nb^2} + \frac{\Delta N^2}{2R^3}. \tag{5.34}$$

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We minimise the free energy with respect to the size R and find

$$0 = \frac{3k_\mathrm{B}TR}{Nb^2} - \frac{3\Delta N^2}{2R^4}, \qquad \Rightarrow \quad R \sim N^{3/5}. \tag{5.35}$$

The result, $R \sim N^{3/5}$, is known as **Flory scaling**. The typical size of the interacting chain is larger than that of the non-interacting one, which certainly makes sense.

In general, the dependence of the polymer size on chain length is described by a scaling form $R \sim N^\nu$ where ν is the scaling exponent. A non-interacting chain has the 'Gaussian' exponent $\nu = 1/2$, while a fully collapsed polymer with very strong attractive interactions has $\nu = 1/3$. It turns out that the Flory exponent, $\nu = 3/5$, for a chain with repulsive interactions is very close to, but not exactly, the correct value for a polymer chain with hard core excluded volume interactions between the monomers. The basic model for such excluded volume interactions is the **self-avoiding random walk** and the scaling exponent for them is $\nu = 0.588$, as was discovered by an ingenious argument of Pierre-Gilles de Gennes[2].

5.3.1 Polymer Brush

The extension of poylmers due to interactions finds numerous uses. One such involves physically, or chemically, grafting polymers to surfaces, creating a type of polymer coating. A single polymer will be stretched away from the surface, since it finds many more available configurations away from the surface where it can move more freely. When there are many polymers forming a dense coating the interactions between polymer chains greatly enhance this stretching as each chain seeks to avoid too much overlap with its neighbours. This effect can be estimated from an adaptation of Flory theory and predicts that the end-to-end extension of such a polymer coating scales linearly with N. Thus the polymers are almost fully stretched and form a stiff **polymer brush**. These coatings can be used to control repulsive interactions between colloidal particles and thereby stabilise them in solution. It is fascinating that the entropy of polymers can be used both to aggregrate colloids through the depletion interaction and also to stabilise colloidal dispersions through the repulsive interactions from a grafted polymer brush.

5.3.2 Flory Scaling and Elasticity

The Flory scaling for polymer size $R_\mathrm{F} \sim N^{3/5}$ has implications for its elastic response at both weak and strong stretching. These can be obtained using scaling arguments, mimicked on those used in describing phase transitions, which emphasises their generality and independence from specific microscopic details.

We consider the scaling form for the extension x of a polymer subject to a force f pulling its ends apart. The extension is a length and should depend on the natural length scale of the polymer R_F and on the length scale $k_\mathrm{B}T/f$ obtained by comparing the (work done by the) force to the thermal energy scale (as the only relevant energy scale). Thus the extension can be written in the scaling form

$$x = R_\mathrm{F}\, \Phi\!\left(\frac{fR_\mathrm{F}}{k_\mathrm{B}T}\right), \tag{5.36}$$

where Φ is a 'scaling function'. For weak forces we expect a linear relation between force and extension, *i.e.* $\Phi(y) \sim y$ for small y. This gives

$$x \sim \frac{fR_\mathrm{F}^2}{k_\mathrm{B}T} \sim \frac{fb^2}{k_\mathrm{B}T}\, N^{6/5} \qquad \text{or} \qquad f \sim \frac{k_\mathrm{B}T}{N^{6/5}b^2}\, x,$$

with the result that the spring constant decreases more rapidly with degree of polymerisation ($N^{-6/5}$) than in an ideal chain (N^{-1}); self-avoiding chains are 'softer' than ideal chains.

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[2]De Gennes' argument involves taking the $n \to 0$ limit of the $O(n)$ model of ferromagnetism! This result formed part of de Gennes' Nobel citation when he was awarded the Nobel Prize in 1991.

The ideal scaling, $x \sim N$, reflects that the force is transmitted along the polymer chain through a constant tension in the chemical bonds between neighbouring monomers. The different scaling of the self-avoiding chain arises from excluded volume interactions between monomers that are widely separated along the chain contour length, *i.e.* from distant parts of the chain coming close together. For large forces when the chain is strongly stretched these distant monomer interactions are largely suppressed and the self-avoiding chain exhibits the scaling $x \sim N$ expected for a constant tension transmitted along its contour length. Since $R_F \sim N^{3/5}$ this requires the scaling $\Phi(y) \sim y^{2/3}$ and translates into a force–extension relation

$$ x \sim Nb \left(\frac{fb}{k_B T} \right)^{2/3} \qquad \text{or} \qquad f \sim x^{3/2}, $$

that differs from Hookean elasticity.

5.4 Polymer Solutions

We consider briefly the description of polymer solutions. Recall from Chapter 2 that the free energy density for a mixture can be written

$$ f = \frac{k_B T}{v_0} \left(\chi \phi (1 - \phi) + \phi \ln \phi + (1 - \phi) \ln(1 - \phi) \right), \tag{5.37} $$

where ϕ is the volume fraction of A fluid molecules. The first term $\chi \phi(1 - \phi)$ represents the interactions between A and B molecules, while the last two terms represent the entropy associated with their mixing. The same form can be adopted for a polymer solution with a minor modification to account for the long chain-like structure of a polymer. We let ϕ denote the volume fraction of *monomers*; then $1 - \phi$ is the volume fraction of solvent molecules. The interactions are between solvent molecules and monomers so this term is unchanged. Similarly, the entropy for the solvent $(1 - \phi) \ln(1 - \phi)$ remains unchanged. However, the entropy for the polymer should be reduced by a factor N because in each polymer N monomers are chemically bonded together. This leads to the Flory-Huggins theory for polymer solutions

$$ f = \frac{k_B T}{v_0} \left(\chi \phi (1 - \phi) + \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) \right). \tag{5.38} $$

Minimisation of this free energy density gives the condition

$$ \chi (1 - 2\phi) + \frac{1}{N} \ln \phi + \frac{1}{N} - \ln(1 - \phi) - 1 = 0, \tag{5.39} $$

which identifies the binodal in the phase diagram. It is a bit easier to obtain the structure of the phase diagram from the spinodal, given by the loss of convexity in the free energy density

$$ \frac{\partial^2 f}{\partial \phi^2} = -2\chi + \frac{1}{N\phi} + \frac{1}{1 - \phi} = 0, \qquad \text{or} \qquad \frac{1}{N\phi} + \frac{1}{1 - \phi} = 2\chi. \tag{5.40} $$

The critical point is the smallest value of χ for which this has a solution and is given by

$$ \phi_c = \frac{1}{1 + \sqrt{N}}, \qquad\qquad \chi_c = \frac{1}{2} \left(1 + \frac{1}{\sqrt{N}} \right)^2. \tag{5.41} $$

When $N = 1$ this recovers the critical point $\phi_c = \frac{1}{2}$, $\chi_c = 2$ of the AB fluid model of Chapter 2. When N is large the critical value of the interaction parameter reduces to close to $\frac{1}{2}$ and the critical concentration is $\phi_c \approx \frac{1}{\sqrt{N}}$, which can be very small.

It is also insightful to consider the osmotic pressure of the polymer solution. This is

$$p_{\text{osm}} = \frac{k_{\text{B}}T}{v_0}\left(-\chi\phi^2 + \frac{\phi}{N} - \ln(1-\phi) - \phi\right), \tag{5.42}$$

$$= \frac{k_{\text{B}}T}{v_0}\left(\frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2 + \frac{1}{3}\phi^3 + \cdots\right), \tag{5.43}$$

where the second form represents a virial expansion at low polymer concentration. We see that the second virial coefficient is

$$B_2 = \frac{k_{\text{B}}T}{v_0}\left(\frac{1}{2} - \chi\right), \tag{5.44}$$

and the condition for it to vanish, $\chi = \frac{1}{2}$, marks a cancellation of the excluded volume interactions of the self-avoiding chain with the repulsive interactions between polymer and solvent. This is the θ-**condition** at which the behaviour of the polymer is the same as that of an ideal chain. When $\chi < \frac{1}{2}$ the polymer chains are swollen and we observe the Flory scaling $R \sim N^{3/5}$. This is referred to as a "good solvent". In a "poor solvent", $\chi > \frac{1}{2}$, we observe phase separation into a dense component where chains overlap and a dilute component where the polymers collapse to a globule. At the crossover $\chi = \frac{1}{2}$ we have a "θ-solvent" and observe the ideal scaling $R \sim N^{1/2}$.

5.5 Polymer in a Box

The problem of a particle in a box is a cornerstone of quantum mechanics; and in statistical mechanics, as we reviewed, it reproduces Boyle's law for ideal gases. Here, we consider the polymer cousin of this basic problem, a Gaussian polymer chain in a cubic box of side L. The concept is simple enough: when a polymer is close to one of the walls its configurations are restricted since it must stay inside the box and this reduction in entropy leads to an entropic preference to stay away from the walls. The challenge is to quantify the reduction in allowed configurations, and the resulting thermodynamic properties of the polymer in a box, which we do by recasting the problem as a differential equation.

For the Gaussian chain model the probability $P(\mathbf{r}, \mathbf{r}_0)$ that a polymer with one end at $\mathbf{r}_0$ has its other end at $\mathbf{r}$ is the Gaussian distribution

$$P(\mathbf{r}, \mathbf{r}_0) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-\frac{3|\mathbf{r}-\mathbf{r}_0|^2}{2Nb^2}} \equiv G(\mathbf{r}, \mathbf{r}_0). \tag{5.45}$$

The notation $G(\mathbf{r}, \mathbf{r}_0)$ is commonly used here because this is also the Green function of the diffusion equation (with diffusion constant $D = b^2/6$)

$$\frac{\partial G}{\partial N} = \frac{b^2}{6}\nabla^2 G. \tag{5.46}$$

It may seem weird to differentiate with respect to N, since this is supposed to be the fixed, integer number of bonds in the polymer. So in a sense this is just a purely mathematical observation. However, it affords the following interpretation: In the usual diffusion equation N is the time t and one thinks of the solution describing how an initial source spreads out by random motion. The Gaussian polymer chain can be thought of as being built up step-by-step, starting at an initial point $\mathbf{r}_0$ and taking N random steps, each of size b on average. This is the same as diffusing randomly for time $t = N$ with root-mean-square displacement b. Consistent with this (5.45) is the solution of (5.46) satisfying $G(\mathbf{r}, \mathbf{r}_0) = \delta(\mathbf{r}-\mathbf{r}_0)$ at $N = 0$. The tremendous utility of the differential equation is that we can use it to find the probability distribution for a polymer chain in different spaces, thereby gaining insight into polymer confinement.

We take this up for a polymer confined to a cubic box of side L. The statistical weight $G(\mathbf{r}, \mathbf{r}_0)$ for a chain of length N, starting at $\mathbf{r}_0$ and ending at $\mathbf{r}$ is given by the solution of

the diffusion equation (5.46) that vanishes on the boundaries and reduces to the delta function $\delta(\mathbf{r} - \mathbf{r}_0)$ when $N = 0$. This solution is (see problems)

$$G(\mathbf{r}, \mathbf{r}_0) = g(x, x_0)g(y, y_0)g(z, z_0), \tag{5.47}$$

with

$$g(x, x_0) = \frac{2}{L}\sum_{n=1}^{\infty} \sin\frac{n\pi x}{L}\sin\frac{n\pi x_0}{L}\, e^{-n^2\pi^2 Nb^2/6L^2}. \tag{5.48}$$

The partition function for the polymer in the box is the sum of these statistical weights for all configurations of the polymer, *i.e.* for all choices of $\mathbf{r}$ and $\mathbf{r}_0$ within the box,

$$Z = \iint_{\text{box}} G(\mathbf{r}, \mathbf{r}_0)\, d^3r\, d^3r_0 = Z_x^3, \tag{5.49}$$

where

$$Z_x = \int_0^L\int_0^L g(x, x_0)\, dx\, dx_0 = \frac{8L}{\pi^2}\sum_{n,\text{ odd}}\frac{1}{n^2}\, e^{-n^2\pi^2 Nb^2/6L^2}. \tag{5.50}$$

Let us first suppose that the box is large compared to the polymer, *i.e.* $L \gg R_{\mathrm{g}} = \sqrt{Nb^2/6}$. Then the exponential is approximately unity (for every n) and it is known, *e.g.* from a course on Fourier series, that

$$\sum_{n,\text{ odd}}\frac{1}{n^2} = \frac{\pi^2}{8}, \tag{5.51}$$

so that $Z_x \approx L$ and $Z \approx L^3 = V$, the volume of the box. The free energy of the polymer is therefore $F = -k_{\mathrm{B}}T\ln Z \approx -k_{\mathrm{B}}T\ln V$ and if we calculate the pressure, $p = -\partial F/\partial V$, we recover the ideal gas law

$$p = \frac{k_{\mathrm{B}}T}{V}. \tag{5.52}$$

This result is both reassuring and interesting. A gas of polymers behaves just like an ideal gas of simple, formless point particles; the fact that the polymer has internal structure and many, many internal degrees of freedom and conformations does not matter for the macroscopic behaviour, at least whenever the box is large compared to the polymer size.

Now we consider the opposite limit of tight confinement. When $L \lesssim R_{\mathrm{g}} = \sqrt{Nb^2/6}$ we can approximate the infinite sum in (5.50) by just retaining the first term, since the others are all exponentially smaller. This gives

$$Z \approx e^{3\ln(8L/\pi^2) - \pi^2 Nb^2/2L^2}, \tag{5.53}$$

and a free energy

$$F \approx -k_{\mathrm{B}}T\ln\frac{8^3 V}{\pi^6} + k_{\mathrm{B}}T\frac{\pi^2 Nb^2}{2V^{2/3}}, \tag{5.54}$$

so that the pressure is now given by

$$p = -\frac{\partial F}{\partial V} \approx \frac{k_{\mathrm{B}}T}{V} + \frac{k_{\mathrm{B}}T\,\pi^2 Nb^2}{3V^{5/3}} \approx \frac{k_{\mathrm{B}}T\,\pi^2 Nb^2}{3V^{5/3}}. \tag{5.55}$$

This expression differs from that of a simple ideal gas with a stronger dependence on the volume, or degree of confinement. Polymers that are packed very tightly into small spaces are stored at high pressure; or equivalently, if you were to open a small hole in the side of the box to let the polymer out there would be a strong entropic drive for it to escape.

Chapter 6

Brownian Motion

Particles that are in equilibrium are not at rest; rather they have a mean square velocity given by the temperature $\langle |\mathbf{v}|^2 \rangle = 3k_{\mathrm{B}}T/m$, where m is the particle's mass; this is an example of the equipartition theorem. Now the mass of a particle is its density times its volume, or $m \sim \rho a^3$, where a is (say) the radius. Particles in equilibrium have typical squared velocities $\langle v^2 \rangle \sim k_{\mathrm{B}}T/\rho a^3$ that increase sharply as the size gets smaller and smaller. The typical squared velocities of a micron sized particle are nine orders of magnitude larger than those of a millimetre sized particle made from the same material. It is inevitable[1] that for some particle size these velocities will become directly observable using microscopy. Precisely these molecular motions were observed by Robert Brown in 1827; they are now known as **Brownian motion**. The basic statistical description of Brownian motion as a consequence of the interactions of colloidal particles with individual water molecules was first given by Albert Einstein in one of his *annus mirabilis* papers of 1905.

6.1 Thermal Motion: Equipartition

Let us review briefly the **equipartition theorem**. The kinetic energy of a particle of mass m is $E = |\mathbf{p}|^2/2m$, where $\mathbf{p}$ is the momentum. Hence, the partition function associated with the momentum degrees of freedom is[2]

$$Z = \int \mathrm{e}^{-\beta \frac{|\mathbf{p}|^2}{2m}} \, d^3 p = \left(\frac{2\pi m}{\beta} \right)^{3/2},$$

(6.1)

and from the partition function we recover the energy as

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_{\mathrm{B}}T,$$

(6.2)

establishing the equipartition theorem. Exactly the same analysis holds for any degree of freedom that contributes quadratically to the energy.

6.2 Motion of a Brownian Particle

Consider a single Brownian particle, moving erratically due to random collisions with water molecules. We would like to describe both its velocity $\mathbf{v}(t)$ and position $\mathbf{x}(t)$ and in particular their statistical averages. Each component of the velocity and position are independent, so it is enough to describe any one of the components and since this streamlines the notation a bit that

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[1]Another option is that statistical mechanics ceases to apply.

[2]You will note that I am not careful here about dividing by appropriate factors of Planck's constant to get the dimensions right; I trust you have seen this story in another course.

is how we will present it. Now, the basic description of the motion of any particle is Newton's second law; for a Brownian particle this is called the **Langevin equation**

$$m\frac{d^2x}{dt^2} = -\gamma\frac{dx}{dt} + \xi, \tag{6.3}$$

where m is the mass of the particle, γ is a frictional damping coefficient and $\xi(t)$ is a random forcing, or noise, coming from the thermal motions of water molecules. Note that the frictional damping also comes from interactions of the Brownian particle with the water molecules and as a result the friction γ and noise ξ are related, since they share a common origin. Establishing this relation will be our first major result. We take the random force to have mean zero $\langle\xi(t)\rangle = 0$ and to be delta correlated in time

$$\langle\xi(t)\xi(t')\rangle = 2\Gamma\delta(t-t'). \tag{6.4}$$

This is known as white noise. The strength of the noise Γ is not a 'free' parameter and we will see that its value can be determined by consistency with the equipartition theorem.

Let us develop the formal solution of (6.3). First, we let $v = dx/dt$ denote the velocity of the particle and find for it the solution

$$v(t) = v(0)\,e^{-t/\tau} + \frac{1}{m}\,e^{-t/\tau}\int_0^t e^{t'/\tau}\xi(t')\,dt', \tag{6.5}$$

where $\tau = m/\gamma$ is a relaxational timescale. We can say that it is the characteristic timescale over which the particle loses memory of its initial velocity. It is useful to estimate its magnitude. For a small particle moving in a fluid the friction coefficient is $\gamma = 6\pi\mu a$, where μ is the fluid viscosity and a the particle radius; this is a classic result in fluid dynamics known as **Stokes' drag**. Taking a spherical particle of density ρ we have $\tau = (2\rho/9\mu)a^2$. The density of water is $\rho \sim 1$ g cm^{-3} and its viscosity is $\mu \sim 1$ mPa s at room temperatures (1 Pa ~ 10 g cm^{-1} s^{-2}). So, for a micron sized particle ($a \sim 10^{-4}$ cm) we have $\tau \sim 2 \times 10^{-7}$ s. When we observe at our normal timescales, say video rate of 30 fps (or even 60 fps), we are observing times that are very much longer than this characteristic time for thermalisation of velocity, i.e. $t \gg \tau$.

Note that the average velocity quickly decays to zero. This is to be expected since the motion is random and as likely to be in one direction as any other; there is only a short timescale $t \lesssim \tau$ memory of the initial velocity. Now we consider the mean square velocity

$$\begin{aligned}
\langle v(t)^2\rangle &= v(0)^2\,e^{-2t/\tau} + \frac{2}{m}\,v(0)\,e^{-2t/\tau}\int_0^t e^{t'/\tau}\langle\xi(t')\rangle\,dt' \\
&\quad + \frac{1}{m^2}\,e^{-2t/\tau}\int_0^t\int_0^t e^{(t'+t'')/\tau}\langle\xi(t')\xi(t'')\rangle\,dt'dt''.
\end{aligned} \tag{6.6}$$

Using the noise statistics $\langle\xi(t')\rangle = 0$ and $\langle\xi(t')\xi(t'')\rangle = 2\Gamma\,\delta(t'-t'')$ this simplifies to

$$\langle v(t)^2\rangle = v(0)^2\,e^{-2t/\tau} + \frac{\Gamma\tau}{m^2}\Big[1 - e^{-2t/\tau}\Big]. \tag{6.7}$$

Finally, taking the long time limit $t \gg \tau$ to let the velocity equilibrate, and recalling that $\tau = m/\gamma$, we find that in equilibrium

$$\langle v^2\rangle = \frac{\Gamma}{m\gamma}, \qquad \Rightarrow \qquad \left\langle\frac{1}{2}mv^2\right\rangle = \frac{1}{2}\frac{\Gamma}{\gamma}, \tag{6.8}$$

and comparing with the equipartition theorem we conclude that $\Gamma = \gamma\,k_{\rm B}T$. This is an important result; it establishes that the correlations in the noise are determined by the frictional coefficient that resists, or dissipates, the motion. It is the first example of what are known as **fluctuation-dissipation relations**.

6.2.1   Mean Square Displacement and Einstein Relation

Having described the velocity of the Brownian particle we now turn to its position. To start, we largely repeat what we said above about timescales, but with a slightly different presentation: The ratio of the inertial and drag forces is

$$\frac{m\,d^2x/dt^2}{\gamma\,dx/dt} \sim \frac{mv/T}{\gamma v} = \frac{\tau}{T}, \tag{6.9}$$

where T is a typical timescale for the motion and v a typical velocity. Thus, if we are interested in describing motions that take place over milliseconds or seconds, or longer, then the inertial term is essentially negligible compared to the drag and we can simplify the Langevin equation to the purely relaxational form

$$\gamma\frac{dx}{dt} = \xi. \tag{6.10}$$

The formal solution is

$$x(t) - x(0) = \frac{1}{\gamma}\int_0^t \xi(t')\,dt'. \tag{6.11}$$

It follows that the average position of the particle $\langle x(t)\rangle$ is just its initial position $x(0)$. More interesting is how far it 'spreads', which is captured by the **mean square displacement**

$$\left\langle |x(t) - x(0)|^2 \right\rangle = \frac{1}{\gamma^2}\int_0^t\int_0^t \left\langle \xi(t')\xi(t'') \right\rangle dt'\,dt'' = \frac{2k_{\mathrm{B}}T}{\gamma}\,t. \tag{6.12}$$

The mean square displacement of a particle is known to be related to the diffusion constant D by $\langle |x(t) - x(0)|^2 \rangle = 2Dt$, so this result establishes the celebrated **Einstein relation**

$$D = \frac{k_{\mathrm{B}}T}{\gamma}, \tag{6.13}$$

between the diffusion constant and the frictional damping.

6.2.2   Motion in a Harmonic Potential

Returning now to the Langevin description of the motion of a Brownian particle, suppose the particle is moving in a potential $V(x)$ so that it experiences a force $-dV/dx$. The Langevin equation in this case reads

$$\gamma\frac{dx}{dt} = -\frac{dV}{dx} + \xi. \tag{6.14}$$

For concreteness, we will focus on the case of a harmonic potential $V = \frac{1}{2}Kx^2$ with spring constant K. Not only does this reflect the generic situation near a potential minimum but it gives a good description of the important experimental technique of trapping particles in laser tweezers. The formal solution of the Langevin equation is

$$x(t) = x(0)\,\mathrm{e}^{-Kt/\gamma} + \frac{1}{\gamma}\,\mathrm{e}^{-Kt/\gamma}\int_0^t \mathrm{e}^{Kt'/\gamma}\xi(t')\,dt', \tag{6.15}$$

and we find, by the same calculational steps as for the velocity before,

$$\left\langle |x(t)|^2 \right\rangle = |x(0)|^2\,\mathrm{e}^{-2Kt/\gamma} + \frac{k_{\mathrm{B}}T}{K}\left[1 - \mathrm{e}^{-2Kt/\gamma}\right]. \tag{6.16}$$

Taking the long time limit ($t \gg \gamma/K$) to lose memory of the initial condition and equilibrate we recover the expected result from equipartition

$$\left\langle \frac{1}{2}Kx^2 \right\rangle = \frac{1}{2}k_{\mathrm{B}}T. \tag{6.17}$$

6.3 Diffusion, Smoluchowski and Fokker-Planck Equations

The motion of Brownian particles is closely related to the diffusive spread of solute particles from an initial concentrated source. We try to bring out this connection briefly. The diffusion equation for the concentration $c(\mathbf{x}, t)$ of solute is

$$\frac{\partial c}{\partial t} = D\nabla^2 c. \tag{6.18}$$

The basic solution due to a source initially localised at the origin, $c(\mathbf{x}, 0) = \delta(\mathbf{x})$, is

$$c(\mathbf{x}, t) = \frac{1}{(4\pi Dt)^{3/2}}\, \mathrm{e}^{-\frac{|\mathbf{x}|^2}{4Dt}}. \tag{6.19}$$

The distribution of the solute is such that its average position is $\langle \mathbf{x} \rangle = 0$, while the amount that it is spread out over time is $\langle |\mathbf{x}|^2 \rangle = 6Dt$; this is a contribution $2Dt$ for each of the x, y and z directions so that the 'mean-square displacement' of the solute particles from where they started is exactly the same as that of a Brownian particle.

The diffusion equation has the form of a continuity equation

$$\frac{\partial c}{\partial t} + \nabla \cdot \mathbf{J} = 0, \tag{6.20}$$

where the current $\mathbf{J}$ is given by Fick's law $\mathbf{J} = -D\nabla c$. More generally, if the solute is also moving in response to a potential $V(\mathbf{x})$ then this will contribute a velocity $\gamma^{-1}\nabla V$ to the current

$$\mathbf{J} = -D\nabla c - c\frac{1}{\gamma}\nabla V. \tag{6.21}$$

When the current vanishes the solute concentration is given by

$$c(\mathbf{x}) = c_0\, \mathrm{e}^{-V(\mathbf{x})/\gamma D}. \tag{6.22}$$

Now, since in equilibrium we would have a Boltzmann distribution $c \sim \exp\{-V(\mathbf{x})/k_{\mathrm{B}}T\}$ this gives another approach to the Einstein relation $D = k_{\mathrm{B}}T/\gamma$. Using the Einstein equation we can rewrite the diffusion equation in this more general context as

$$\frac{\partial c}{\partial t} = \frac{1}{\gamma}\nabla \cdot \left[k_{\mathrm{B}}T\nabla c + c\nabla V \right], \tag{6.23}$$

which is known as the **Smoluchowski equation**.

Now the concentration may be viewed as a probability density for the positions of the solute particles, multiplied by the total number of solute particles, so we may view the Smoluchowski equation as an evolution equation for the probability density $\Psi(\mathbf{x}, t)$

$$\frac{\partial \Psi}{\partial t} = \frac{1}{\gamma}\nabla \cdot \left[k_{\mathrm{B}}T\,\nabla\Psi + \nabla V\,\Psi \right]. \tag{6.24}$$

As this is just a statement of conservation of probability, where the flux of probability consists of thermal effects acting to spread it out evenly and flows in response to potential gradients, the same equation should hold for any probability distribution and not only that for particle positions. With this more general probabilistic interpretation it is called the **Fokker-Planck equation**.

6.3.1 Steady State Probability Distribution

The evolution of the probability distribution under the Fokker-Planck equation produces a flow in which the free energy steadily decreases, except when the system is at equilibrium. To see this consider the function

$$\mathcal{F}[\psi] = \int_\Omega V\psi + k_\mathrm{B}T\psi \ln \psi \, d^d x, \tag{6.25}$$

and compute directly its time derivative

$$\partial_t \mathcal{F} = \int_\Omega \left[V + k_\mathrm{B}T \ln \psi + k_\mathrm{B}T \right] \partial_t \psi \, d^d x. \tag{6.26}$$

We use the Fokker-Planck equation, $\partial_t \psi + \nabla \cdot \mathbf{J} = 0$, and integrate by parts to find

$$\partial_t \mathcal{F} = -\int_\Omega \left[V + k_\mathrm{B}T \ln \psi + k_\mathrm{B}T \right] \nabla \cdot \mathbf{J} \, d^d x, \tag{6.27}$$

$$= -\int_{\partial\Omega} \left[V + k_\mathrm{B}T \ln \psi + k_\mathrm{B}T \right] \mathbf{J} \cdot d\mathbf{S} + \int_\Omega \mathbf{J} \cdot \nabla \left[V + k_\mathrm{B}T \ln \psi + k_\mathrm{B}T \right] d^d x, \tag{6.28}$$

$$= -\int_{\partial\Omega} \left[V + k_\mathrm{B}T \ln \psi + k_\mathrm{B}T \right] \mathbf{J} \cdot d\mathbf{S} - \int_\Omega \frac{1}{\psi} |\mathbf{J}|^2 \, d^d x, \tag{6.29}$$

where in the last line we have used that $-\nabla V \, \psi - k_\mathrm{B}T\nabla\psi = \mathbf{J}$. Now, if the current $\mathbf{J}$ either vanishes on the boundary, or is purely tangential, then the first term vanishes and we are left with

$$\partial_t \mathcal{F} = -\int_\Omega \frac{1}{\psi} |\mathbf{J}|^2 \, d^d x \leq 0, \tag{6.30}$$

where the equality holds if and only if $\mathbf{J} = 0$. In other words, the free energy is non-increasing and stationary only when the current vanishes identically. Setting $\mathbf{J} = 0$ we obtain the equilibrium probability distribution

$$-\nabla V \, \psi - k_\mathrm{B}T\nabla\psi = 0, \qquad \Rightarrow \quad \psi = \frac{1}{Z}\, \mathrm{e}^{-V/k_\mathrm{B}T}, \tag{6.31}$$

where $Z = \int_\Omega \mathrm{e}^{-V/k_\mathrm{B}T} \, d^d x$. The equilibrium state is the Boltzmann distribution.

6.4 Correlation Functions

A **correlation function** is an expectation value of the product of two observable quantities. Some examples include $\langle v(t)v(0)\rangle$, $\langle x(t_1)x(t_2)\rangle$ and $\langle v(t)x(t)\rangle$. For instance, for a Brownian particle in a harmonic potential, such as a laser trap, we find

$$\langle x(t_1)x(t_2)\rangle = x(0)^2\, \mathrm{e}^{-K(t_1+t_2)/\gamma} + \frac{k_\mathrm{B}T}{K}\left[\mathrm{e}^{-K|t_1-t_2|/\gamma} - \mathrm{e}^{-K(t_1+t_2)/\gamma} \right],$$
$$\simeq \frac{k_\mathrm{B}T}{K}\, \mathrm{e}^{-K|t_1-t_2|/\gamma}. \tag{6.32}$$

Thus measurements of the position of the particle within the trap at different times, t_1, t_2, decay exponentially with the difference in times; the positions at widely separated times are uncorrelated and the exponential decay of the correlation function is characteristic of this. Correlation functions like $\langle x(t_1)x(t_2)\rangle$ of the same quantity at different times are called **autocorrelation functions**. As in this example, they typically depend only on the difference in times, *i.e.* $\langle x(t_1)x(t_2)\rangle = \langle x(t_1-t_2)x(0)\rangle$.

As a second example, consider the velocity autocorrelation function $\langle v(t)v(0)\rangle$ for a free particle. We have from (6.5)

$$\langle v(t)v(0)\rangle = v(0)^2\, \mathrm{e}^{-t/\tau}, \tag{6.33}$$

and again the autocorrelation function decays exponentially with time reflecting the random, uncorrelated nature of the motion. Next, note that

$$\int_0^\infty \langle v(t)v(0) \rangle \, dt = v(0)^2 \, \tau = \frac{mv(0)^2}{\gamma}, \tag{6.34}$$

so that averaging also over initial conditions gives

$$\int_0^\infty \langle v(t)v(0) \rangle \, dt = \frac{\langle mv^2 \rangle}{\gamma} = \frac{k_{\mathrm{B}}T}{\gamma} = D. \tag{6.35}$$

This is an important result: the integral of the velocity autocorrelation function is the diffusion constant. It is an example of a **Green-Kubo relation** and holds more generally for all transport properties. Often the diffusion constant is defined by the Green-Kubo formula (6.35).

6.4.1   Linear Response and Fluctuation-Dissipation

There is a general relationship between correlation functions and the linear response when a system is forced or driven by an external field. This exists both for equilibrium correlation functions and for time correlation functions. We present two simplified descriptions of this to convey the basic idea and generality, starting with equilibrium correlations. Consider a particle in a harmonic trap, centred at $x = 0$. The equilibrium probability distribution for the position x of the particle is

$$\Psi_{\mathrm{eq}} = \left(\frac{K}{2\pi k_{\mathrm{B}}T} \right)^{1/2} e^{-\frac{Kx^2}{2k_{\mathrm{B}}T}}. \tag{6.36}$$

The expectation value for the position of the particle is $\langle x \rangle = 0$ and the equilibrium correlation function for the position is $\langle x^2 \rangle = k_{\mathrm{B}}T/K$. Now suppose we pull on the particle with a force f then the particle responds to this force by acquiring a non-zero expectation value for its position

$$\langle x \rangle = \frac{1}{K} f \equiv x_0. \tag{6.37}$$

This is an example of a **response function**: the coefficient relating the response to the force is a susceptibility. Now, when equilibrium with the force is re-established the probability distribution will be

$$\Psi_{\mathrm{eq},f} = \left(\frac{K}{2\pi k_{\mathrm{B}}T} \right)^{1/2} e^{-\frac{K(x-x_0)^2}{2k_{\mathrm{B}}T}}, \tag{6.38}$$

and we can clearly use this probability distribution to calculate the expectation value of the position $\langle x \rangle_f = \int x \Psi_{\mathrm{eq},f} \, dx$ but if we consider that f is small then we may expand $\Psi_{\mathrm{eq},f}$ about the equilibrium distribution in the absence of the force and find

$$\langle x \rangle_f = \int x \Psi_{\mathrm{eq},f} \, dx = \int x \Psi_{\mathrm{eq}} \, e^{-\frac{K(x_0^2 - 2xx_0)}{2k_{\mathrm{B}}T}} \, dx, \tag{6.39}$$

$$= \int x \Psi_{\mathrm{eq}} \left(1 + \frac{Kxx_0}{k_{\mathrm{B}}T} + \cdots \right) dx, \tag{6.40}$$

$$= 0 + \frac{Kx_0}{k_{\mathrm{B}}T} \langle x^2 \rangle + \cdots. \tag{6.41}$$

Recalling that $Kx_0 = f$ is the force this demonstrates an equivalence between the (linear) response function and the equilibrium correlation function. This equivalence is known as the **fluctuation-dissipation theorem**. It is the same as we found in §6.2; there we were also considering the application of a force but the response was different, namely a velocity of motion through the fluid. Nonetheless, we found the same result: the velocity response in the presence of the force ($\langle v \rangle_f = \frac{1}{\gamma} f$) was related to the velocity correlations in the absence of the force ($\langle v^2 \rangle = k_{\mathrm{B}}T/m$).

For the free Brownian particle we can also express the relation between response and correlation in terms of the time-dependence of its position, making connection, once again, with the mean square displacement and diffusion constant. The probability distribution[3] for the position of the free Brownian particle is

$$\Psi(x,t) = \frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{(x-x_0)}{4Dt}}. \tag{6.42}$$

Here the particle is at x_0 at time $t = 0$. If we drag the particle with a force f so that it moves with some velocity v then the probability distribution will become

$$\Psi_f(x,t) = \frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{(x-x_0-vt)}{4Dt}} = \frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{(x-x_0)}{4Dt}}\left(1 + \frac{v(x-x_0)}{2D} + \cdots\right), \tag{6.43}$$

and if we calculate the expectation value of the position at time t we have

$$\langle x(t)\rangle_f = \left\langle x + \frac{v}{2D}\,x(x-x_0) + \cdots \right\rangle = x_0 + \frac{v}{2D}\left\langle (x-x_0)^2 \right\rangle + \cdots. \tag{6.44}$$

Using that the mean square displacement (in the absence of the force) is $\langle (x-x_0)^2 \rangle = 2Dt$ we obtain the expected response for the particle position when it is dragged, $\langle x(t)\rangle_f = \langle x \rangle + vt$. Again, we see that linear responses are determined by equilibrium fluctuations.

6.5 Fluctuations in Statistical Physics

In this closing section we describe in outline how the Langevin equation for the motion of Brownian particles extends to describe the fluctuating dynamics of any thermodynamic quantity. For this purpose we illustrate using the Landau theory of ferromagnetism. In §4.4.1 we gave the Landau free energy for a two-dimensional nematic, which we reproduce here in the form

$$f = \frac{a(T-T_c)}{2}\,s^2 + \frac{u}{4}\,s^4. \tag{6.45}$$

In the ordered phase the equilibrium value for the scalar order parameter is $s_{\text{eq}} = (a|T-T_c|/u)^{1/2}$. If we consider fluctuations in the free energy about this equilibrium value then they are described by a Taylor expansion of f about $s = s_{\text{eq}}$

$$f = f(s_{\text{eq}}) + \frac{1}{2}\,2a|T-T_c|^2\,\delta s^2 + \cdots, \tag{6.46}$$

where $\delta s = s - s_{\text{eq}}$. This is a quadratic energy like a harmonic spring with spring constant $2a|T-T_c|$. Applying the equipartition theorem we expect

$$\langle \delta s^2 \rangle = \frac{k_{\text{B}} T}{2a|T-T_c|}. \tag{6.47}$$

Let us see how to capture this result in a Langevin equation. In §4.7 we introduced the relaxation equation for the nematic order, which we reproduce here with an additional random noise term

$$\frac{\partial s}{\partial t} = -\Gamma\,\frac{\partial f}{\partial s} + \xi = -\Gamma\left[a(T-T_c)s + us^3\right] + \xi. \tag{6.48}$$

Linearising about the equilibrium state gives an equation for the fluctuations δs

$$\frac{\partial \delta s}{\partial t} = -\Gamma\,2a|T-T_c|\,\delta s + \xi. \tag{6.49}$$

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[3]Note that this is not an equilibrium probability distribution.

The formal solution is

$$\delta s(t) = \delta s(0)\, \mathrm{e}^{-t/\tau_s} + \mathrm{e}^{-t/\tau_s} \int_0^t \mathrm{e}^{t'/\tau_s}\, \xi(t')\, dt', \tag{6.50}$$

where $\tau_s = (\Gamma\, 2a|T - T_c|)^{-1}$ is a relaxational timescale for the order fluctuations, as in §4.7. By following the same calculation as we did in §6.2 we find that the Langevin equation reproduces the equipartition result for $\langle \delta s^2 \rangle$ if the statistics for the noise are

$$\langle \xi(t) \rangle = 0, \qquad\qquad \langle \xi(t)\xi(t') \rangle = 2\Gamma k_{\mathrm{B}}T\, \delta(t - t'). \tag{6.51}$$

We can see here also an example of the fluctuation-dissipation theorem. The equilibrium correlation function (6.47) should be related to the response to an external field (as in the magnetic case), that is to the susceptibility. The linear response to applying a field H is to change the magnitude of the order according to

$$s = s_{\mathrm{eq}} + \frac{1}{2a|T - T_c|}\, H, \tag{6.52}$$

which identifies the susceptibility as $\chi = 1/2a|T - T_c|$ and reveals the same general relationship $\langle (s - s_{\mathrm{eq}})^2 \rangle = k_{\mathrm{B}}T\, \chi$ between responses and fluctuations.

This one example is generic and representative of a general framework for including thermal fluctuations in all aspects of statistical physics. In what we have outlined here we have neglected spatial variation, thinking of the order as time-dependent $s(t)$ but not also position dependent $s(\mathbf{x}, t)$. Simiarly, we have not described the orientation $\theta(\mathbf{x}, t)$, which we do briefly as a conclusion. Recall that the orientation dominates the behaviour on large scales and over long times, because the magnitude of the order reduces to its equilibrium value quickly. This is described by the free energy and deterministic dynamical relaxation

$$F = \int \frac{K}{2}|\nabla\theta|^2\, d^d x, \qquad\qquad \frac{\partial\theta}{\partial t} = \Gamma_\theta K\nabla^2\theta. \tag{6.53}$$

To deal with the gradients it is convenient to work with a Fourier decomposition, which we give as a discrete Fourier series[4]

$$\theta(\mathbf{x}, t) = \sum_{\mathbf{q}} \tilde{\theta}_{\mathbf{q}}(t)\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{x}}, \tag{6.54}$$

in terms of which the energy is

$$F = \sum_{\mathbf{q}} \frac{K}{2}\, q^2 |\tilde{\theta}_{\mathbf{q}}|^2, \tag{6.55}$$

and is a sum of quadratic 'normal modes' with 'frequencies' Kq^2. The analysis in terms of these normal modes of the orientation is then the same as before. The equipartition theorem gives

$$\left\langle |\tilde{\theta}_{\mathbf{q}}|^2 \right\rangle = \frac{k_{\mathrm{B}}T}{Kq^2}, \tag{6.56}$$

which we can also obtain from a Langevin equation

$$\frac{\partial\tilde{\theta}_{\mathbf{q}}}{\partial t} = -\Gamma_\theta Kq^2\tilde{\theta}_{\mathbf{q}} + \tilde{\xi}_{\mathbf{q}}(t), \tag{6.57}$$

where the $\xi_{\mathbf{q}}$ are white noises with correlation

$$\left\langle \overline{\tilde{\xi}_{\mathbf{q}'}(t')}\tilde{\xi}_{\mathbf{q}}(t) \right\rangle = 2\delta_{\mathbf{q},\mathbf{q}'}\Gamma_\theta\, k_{\mathrm{B}}T\, \delta(t - t'). \tag{6.58}$$

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[4]The continuous treatment using Fourier transforms is not really conceptually different but we leave it to the books, or another course.

We close with a short look at the total fluctuation in all the normal modes

$$\langle|\theta|^2\rangle = \sum_{\mathbf{q}}\langle|\tilde{\theta}_{\mathbf{q}}|^2\rangle = \sum_{\mathbf{q}} \frac{k_{\mathrm{B}}T}{Kq^2}. \tag{6.59}$$

To do the sum we can approximate it by an integral

$$\langle|\theta|^2\rangle = \int \frac{k_{\mathrm{B}}T}{Kq^2} \frac{d^d q}{(2\pi)^d} = \frac{k_{\mathrm{B}}T}{K} \frac{\omega_{d-1}}{(2\pi)^d} \int \frac{1}{q^2} q^{d-1} dq, \tag{6.60}$$

where we have switched to polar coordinates and ω_{d-1} is the total angle (volume) of a $(d-1)$-dimensional unit sphere[5]. The upper limit on the integral should be roughly $2\pi/a$ corresponding to wavevectors probing the smallest scales of the lattice size (or molecular size). The lower limit corresponds to wavevectors probing the largest length scales and so should be about $2\pi/L$, where L is the linear system size. The integral is convergent as $L \to \infty$ only in dimensions above $d = 2$. In two dimensions it diverges logarithmically as $\ln(L/a)$ and the total fluctuations in the orientation are unbounded in the thermodynamic limit. This is the **Mermin-Wagner theorem**. It shows that there is no phase transition to a long-range aligned state in two dimensions, *i.e.* no nematic or ferromagnetic transition. What replaces it is the topological defect transition of Berezinskii-Kosterlitz-Thouless that we mentioned in §4.8.

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[5]$\omega_{d-1} = 2\pi^{d/2}/\Gamma(d/2)$.

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