

PX439/CO904: Statistical Mechanics of Complex Systems

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Preface

This course can be viewed as a masters level course in statistical mechanics viewed from an interdisciplinary perspective and with examples coming from a range of disciplines outside of the usual physics or chemistry setting. I inherited the course from Ellák Somfai and have retained the choice of topics that Ellák covered, but have tried to do so in my own way, and have updated the choice of examples to cover, to give greater overlap with topics that I myself am familiar with.

These notes contain, in general, more material than I will be able to cover in the lectures. This extra material is intended to provide additional clarification and is included for your interest. Only material explicitly covered in lectures, or the problem sets, will be examinable.

I apologise for the current lack of figures, which I hope to add in due course. If anyone would like to assist me, I would be glad to receive files, preferably in pdf format.

The module is given in two forms: as the Complexity module CO904, and as the Physics module PX439. The lectures for both modules are the same, but there are differences in other areas and particularly in the way that the module is examined.

Please make careful note of the following schedule for the course. Lectures will be held from 1300-1500 on Mondays and from 1100-1300 on Thursdays of weeks 6-10 in the Complexity Seminar Room, D1.07, Zeeman Building.

Those taking the Complexity module CO904 are required to attend classes. These will be held from 1000-1200 on Mondays and from 1400-1600 on Thursdays of weeks 6-10 in the Complexity Seminar Room, D1.07. The classes will introduce numerical techniques for doing statistical mechanics that are intended to complement and augment the lectures. They will be led by Charo del Genio. Please bring your laptops with you. Two problem sets accompany the CO904 module and each contribute 25% to your final grade, with the end of term viva making up the remaining 50%. Vivas for all students taking the CO904 module will be held on Monday of week 11 (10th December 2012).

Physics students taking the PX439 module will sit a summer examination in May (or June). Past exam papers are available from the Physics department website. You are also welcome to attempt the problem sets for the CO904 module, although I will not collect or mark solutions from students not enrolled on the CO904 module.

I will not have any ‘office hours’. You are most strongly encouraged to ask questions during the classes, but you are also welcome to come and speak to me at any time – my office door is open when I am in.

Books and other reading

There are many good books. You are encouraged to read as many as you can. Some with particular relevance to the course are listed below.

1. J. Sethna, *Statistical Mechanics: Entropy, Order Parameters, and Complexity*, Oxford University Press, Oxford, 2004.
2. M. Kardar, *Statistical Physics of Particles*, and *Statistical Physics of Fields*, Cambridge University Press, Cambridge, 2008.
3. J. L. Cardy, *Scaling and Renormalization in Statistical Physics*, Cambridge University Press, Cambridge, 1995.
4. P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge University Press, Cambridge, 1995.
5. G. Mussardo, *Statistical Field Theory*, Oxford University Press, Oxford, 2010.

Several original articles, or research reviews, are also well worth reading. Please let me know of any not on the list that you have found particularly interesting.

1. E. T. Jaynes, *Information Theory and Statistical Mechanics*, *Phys. Rev.* **106**, 620–630 (1957).
2. E. T. Jaynes, *Information Theory and Statistical Mechanics. II*, *Phys. Rev.* **108**, 171–190 (1957).
3. C. E. Shannon, *A Mathematical Theory of Communication*, *Bell System Technical Journal* **27**, 379–423 (1948); **27**, 623–656 (1948).
4. K. Maruyama, F. Nori, and V. Vedral, *The physics of Maxwell’s demon and information*, *Rev. Mod. Phys.* **81**, 1–23 (2009).

Chapter 1

What is statistical mechanics?

Statistical mechanics tries to explain why things that are made out of large numbers of constituents behave the way they do and to relate the collective behaviour they exhibit, and the transitions they undergo, to the properties of individual particles. Traditionally, this has included the phases of water, the crystalline structure of solids, the ordering of alloys, the onset of ferromagnetism and the wealth of liquid crystalline phases, but more recently it has also extended to new phenomena such as the flocking of birds, swarming of bacteria, and the flow of traffic along our road systems, on the internet, or of molecular motors walking along microtubules in our cells.

To take the phases of water as an example, it is well known that large collections of water molecules can exist in different states; as water vapour, as liquid water, and as solid ice. They are all made of the same water molecules with the same interactions between the molecules, so where does this multiplicity in macroscopic form come from, and how do we describe the transitions between them, or predict when they will occur? Moreover, lots of materials exist in solid, liquid and gas phases, and there is nothing special about water molecules in this regard. This behaviour is universal and so are the transitions between phases. The macroscopic properties of a system derive from its microscopic constituents, but often they do not depend sensitively on them. It is possible to give a canonical description of *the* liquid-gas transition, or *the* liquid-solid transition, such that it applies equally to all sorts of systems, instead of having to describe each material individually and uniquely. This suggests that simple models will suffice to capture the germaine features and hints at a sort of universality.

Indeed the development and analysis of minimal models for different types of macroscopic behaviour preoccupies much of statistical mechanics. For instance, considerable insight into the liquid-solid and glass, or jamming, transitions can be gained from the study of packing problems, particularly of hard discs in a box. The idea is simple. At low densities, or small packing fractions, the discs have lots of room to move and behave as a fluid, but as the density increases they pack more tightly and their motion becomes restricted by the presence of their neighbours. Eventually they solidify, or become jammed. This solid state may consist of an ordered arrangement of particles, say at the sites of a face centred cubic lattice, and then it describes a crystal. But it may also consist of a random or disordered arrangement of particles that have just become ‘stuck’, which is known as a glass. In either case, the macroscopic behaviour depends only on the fact that the particles cannot overlap and is controlled by a single parameter, the packing fraction or density. Thus disc packings offer universal insight into a wide range of systems displaying jamming or glassy behaviour.

Of course, there are many variants of this type of packing model. Perhaps the most important is the replacement of hard discs with long thin rods. Surprisingly, although this makes the constituents more complicated, the description of their macroscopic behaviour is in some sense simpler. In this case, before forming a solid, the rods undergo an alignment transition, spon-

taneously selecting a common direction in which to point. The basic reason why they do this is because their elongated shape makes it easier for them all to pack this way at high enough densities. Again, the fine details of the molecule are relatively unimportant and all that matters is that they are long and thin, and cannot overlap. The aligned state that forms in this way is known as a *nematic liquid crystal* and has turned out to be tremendously useful, supplying as it does the material for all modern flat panel displays.

How is it that statistical mechanics describes such things? In short, statistical mechanics is about *states*. There are macroscopic states; the orientations of the rods may be random, corresponding to an isotropic state, or they may be aligned along a common direction, corresponding to a nematic state. In the nematic state, the direction of alignment is a free variable. And then there are microscopic states; a detailed list of the positions and orientations of every rod in the system, such as one might get from a computer simulation. Of course, as we have said, the exact state of any particular molecule is not important when we want to know how the system as a whole behaves. Correspondingly, for any macroscopic state there will be a large number of specific configurations of all of the constituent molecules that are consistent with the macroscopic properties of the whole. Rotating a few rods by a little bit does not change the bulk alignment. What does turn out to be important, however, is how *many* microscopic states there are for any given macrostate, and how *likely* each of them is to occur. This is the *entropy* as embodied by Boltzmann's famous formula

$$S = k_B \ln(\Omega), \quad (1.0.1)$$

where Ω is the number of microstates. Statistical mechanics is built upon these two things: an enumeration of every possible microscopic state of the system, and an associated probability distribution giving the likelihoods that each would be found if the microstate was determined precisely.

To illustrate, the isotropic-nematic transition is concerned with the alignment of rods along a common direction. Thus it suffices to label the microstates by the positions and orientations of every rod. In the isotropic phase no particular orientation is preferred and the probability distribution for rod orientations reflects this. On the other hand, in the nematic phase the rods align along a common direction and the probability distribution is peaked around one particular direction. The issue is to specify exactly what the probability distribution should be.

To get a feeling for what we are after, consider the isotropic phase where there is no average orientation for the rods. It is natural to assume that then any orientation of an individual rod is as likely as any other and that the probability distribution for rod orientations should simply be uniform, $p(\boldsymbol{\nu}) = (4\pi)^{-1}$. However, this is not the only distribution consistent with our macroscopic knowledge. It is easy to check that the distribution

$$p(\boldsymbol{\nu}) = \sum_{i=1}^3 \frac{1}{6} (\delta(\boldsymbol{\nu} - \mathbf{e}_i) + \delta(\boldsymbol{\nu} + \mathbf{e}_i)), \quad (1.0.2)$$

in which the rods can point only along the principal Cartesian directions, works just as well. But this distribution, although compatible with our macroscopic observation of the average orientation, puts rather more constraints on the possible microstates than the uniform distribution does, or than we can support on the basis of what we know. Is there a way of measuring this and quantifying the difference between the two distributions?

1.1 Entropy and Information

A solution to this problem was provided by Claude Shannon in 1948. It came, not in the arena of statistical mechanics, but in information theory. Information theory might seem abstract and

unrelated, *a priori*, to physics. Strings of 0s and 1s encoding messages, images, television signals, monetary transfers and so on are not the usual domain of what is considered to be physics. But, of course, this information must be encoded in *something*, and likewise must be stored in *something*. For instance, as the magnetisation of spins in a solid state hard drive, pits on a CD or DVD, grooves on a record, the polarisation state of photons, and so on. Thus information, especially at its most fundamental level, and physics are more closely connected than they might first seem. In particular, the amount of information that can be stored using the magnetic moments of a solid state hard drive is clearly closely analogous to the number of distinct microstates that the spins can be put into. The more microstates available, the more information can be stored.

Shannon constructed a quantitative measure of the information content of any probability distribution for a random variable, which we now call the *Shannon information entropy* and will denote $H(\{p_\alpha\})$. It is a function only of the probabilities and is based upon the following three natural requirements:

- (i) It should be a continuous function of each of the probabilities p_α .
- (ii) If all states are equally likely, it should be a continuous, monotonically increasing function of the number of such possible states. Denoting by $A(n) = H(\frac{1}{n}, \dots, \frac{1}{n})$ the value of the Shannon entropy when each of the n possibilities takes the same probability, $p_\alpha = \frac{1}{n}$, this means

$$A(n) < A(n+1), \quad \text{for all } n.$$

- (iii) If the possibilities are grouped into larger collections, then the same value of the entropy should be obtained from the entropy of this new set plus a weighted average of the entropies of each of its constituent collections. What this means is as follows. Suppose the original set $\mathcal{A}$ of n possibilities $\{a_\alpha\}_{\alpha=1}^n$ is grouped into a new set $\mathcal{B}$ of m possibilities $\{b_\beta\}_{\beta=1}^m$, with b_β containing r_β of the original possibilities. The probability w_β associated to entire set b_β is the sum of the probabilities p_α of the original possibilities a_α contained in the group b_β , and the entropy of this group is $H(b_\beta) = H(\{\frac{p_\alpha}{w_\beta}\}_{a_\alpha \in b_\beta})$. Then the original entropy can be calculated from the new partition according to

$$H(\mathcal{A}) = H(\mathcal{B}) + \sum_{\beta=1}^m w_\beta H(b_\beta).$$

Before presenting Shannon's theorem, let us consider what these three conditions mean for some particular system, using our model of hard rods as an example. Recall the two distributions ('uniform' and 'discrete')

$$p_u(\boldsymbol{\nu}) = \frac{1}{4\pi}, \quad \text{and} \quad p_d(\boldsymbol{\nu}) = \sum_{i=1}^3 \frac{1}{6} (\delta(\boldsymbol{\nu} - \mathbf{e}_i) + \delta(\boldsymbol{\nu} + \mathbf{e}_i)), \quad (1.1.1)$$

for the rod orientations corresponding to a macroscopically isotropic state. The second of these places severe constraints on the possible orientations that the rods might be in and so offers far fewer potential microstates. Thus the Shannon entropy of this distribution should be less than that of the uniform distribution. This is not simply a matter of the second distribution allowing only discrete orientations, for we could equally consider the distribution

$$p_{d,\epsilon}(\boldsymbol{\nu}) = \frac{\epsilon}{4\pi} + \sum_{i=1}^3 \frac{1-\epsilon}{6} (\delta(\boldsymbol{\nu} - \mathbf{e}_i) + \delta(\boldsymbol{\nu} + \mathbf{e}_i)), \quad (1.1.2)$$

for any ϵ and do not wish to think it fundamentally different to the discrete distribution ($\epsilon = 0$) for vanishingly small values of ϵ . What this means is that whatever measure we come up with should be a continuous function of the probabilities.

Returning to the Shannon entropy and the number of microstates, we see from this continuity property that the information entropy cannot simply be the number of microstates, for surely there are as many microstates in $p_{d,\epsilon}$ as there are in p_u , it is just that only a small number of them have any significant probability in the former. However, if each microstate has the same probability then only their number matters and we expect that when more are available the information content will be greater.

Finally, suppose we were to group the possibilities in the discrete distribution $p_d(\nu)$, for instance combining the two orientations $\pm \mathbf{e}_i$ into a single option ‘aligned along axis i ’, which would occur with probability $\frac{1}{6} + \frac{1}{6} = \frac{1}{3}$. The two sub-possibilities in each group each have probability $\frac{1/6}{1/3} = \frac{1}{2}$. As this is merely labelling, it will not have altered the information content of the system. However, the total information is not simply the Shannon entropy of the probability distribution for the combined possibilities, since some of the original microstates are now contained within the groups. A consistent value for the Shannon entropy can be obtained by adding to the Shannon entropy of the combined probability distribution a weighted average of the Shannon entropies for each of the groups, the weighting reflecting how likely each is to come up

$$H\left(\frac{1}{6}, \dots, \frac{1}{6}\right) = H\left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right) + \sum_{i=1}^3 \frac{1}{3} H_i\left(\frac{1}{2}, \frac{1}{2}\right) = H\left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3}\right) + H\left(\frac{1}{2}, \frac{1}{2}\right). \quad (1.1.3)$$

With these motivations in place we are ready to state the Shannon theorem. This result lays the foundations of information theory and links it with the foundations of statistical mechanics.

Theorem 1.1.1. (*Shannon, 1948*) *There is a unique function*

$$H(\{p_\alpha\}) = -k \sum_{\alpha=1}^n p_\alpha \ln(p_\alpha), \quad (1.1.4)$$

that satisfies these three conditions, where k is an arbitrary positive constant that sets the units of H .

PROOF: Let $\mathcal{A}$ be a set of s^m equally probable possibilities and consider a grouping into a new set $\mathcal{B}$ of s combined possibilities, each equally likely, and each containing s^{m-1} of the possibilities of $\mathcal{A}$. Then, from (iii) we have

$$A(s^m) = A(s) + A(s^{m-1}), \quad (1.1.5)$$

and iterating the process we find $A(s^m) = mA(s)$. Similarly $A(t^n) = nA(t)$. Choosing m such that $s^m \leq t^n < s^{m+1}$ the monotonicity property (ii) gives

$$\begin{aligned} A(s^m) &\leq A(t^n) < A(s^{m+1}), \\ mA(s) &\leq nA(t) < (m+1)A(s), \end{aligned} \quad (1.1.6)$$

and dividing by $nA(s)$ we find

$$\frac{m}{n} \leq \frac{A(t)}{A(s)} < \frac{m}{n} + \frac{1}{n}, \quad \text{or} \quad \left| \frac{A(t)}{A(s)} - \frac{m}{n} \right| < \frac{1}{n}. \quad (1.1.7)$$

Since we may choose n as large as we please we can make this quantity as small as we like. Now, from the inequality $s^m \leq t^n < s^{m+1}$, by taking logarithms and dividing by $n \ln(s)$, we find

$$\left| \frac{\ln(t)}{\ln(s)} - \frac{m}{n} \right| < \frac{1}{n}, \quad (1.1.8)$$

which we may use to obtain

$$\left| \frac{A(t)}{A(s)} - \frac{\ln(t)}{\ln(s)} \right| < \frac{2}{n} \quad \Rightarrow \quad A(s) = k \ln(s), \quad (1.1.9)$$

for some positive constant k .

This establishes Shannon's theorem for sets of equiprobable events. To extend to the general case we use property (iii) and consider a set $\mathcal{A}$ of n equiprobable events that we subsequently group into a new set of possibilities $\mathcal{B}$ consisting of m possible outcomes b_β made up by grouping together r_β of the events from $\mathcal{A}$. Any set $\mathcal{B}$ with any rational probabilities can be constructed in this way from some $\mathcal{A}$. Then from (iii) we have

$$k \ln(n) = H(\mathcal{B}) + \sum_{\beta=1}^m \frac{r_\beta}{n} k \ln(r_\beta), \quad (1.1.10)$$

$$\Rightarrow \quad H(\mathcal{B}) = -k \sum_{\beta=1}^m \frac{r_\beta}{n} \ln\left(\frac{r_\beta}{n}\right). \quad (1.1.11)$$

As r_β/n is just the probability p_β of the β^{th} possible outcome of the set $\mathcal{B}$, this establishes Shannon's theorem for rational probabilities. If some, or all, of the probabilities are irrational then we may approximate them by rationals and obtain the same result in the limit by the continuity assumption (i). $\square$

REMARK: The Shannon entropy provides us with a precise measure of how many microstates are compatible with our knowledge of the macrostate, accounting for the probabilities of each microstate. For this reason it is often said to characterise how much we *don't* know, or to reflect our ignorance about the microscopic details of the system. If we wish to commit only to things that we know, then we should choose a probability distribution that maximises our ignorance, as measured by the Shannon entropy.

1.2 Joint events and correlations

We digress from the development of statistical mechanics to consider some general properties of the Shannon entropy. In many systems it naturally happens that we can measure several properties of the same system. For instance, if both Alice and Bob are rolling dice we can record both of their results. There will be probability distributions for each of them, ignoring the other altogether, but also probabilities for combined results such as Alice gets 3 and Bob gets 5. This is a *joint probability* $p(\{\mathcal{A} = 3\} \cap \{\mathcal{B} = 5\})$ and a list of all the joint probabilities for all possible pairs of outcomes is a joint probability distribution $p(\mathcal{A} \cap \mathcal{B})$. The probability distributions for either individual is recovered by summing over all possible outcomes that the other might get, e.g.,

$$p(\mathcal{A} = a) = \sum_b p(\{\mathcal{A} = a\} \cap \{\mathcal{B} = b\}), \quad (1.2.1)$$

$$\text{or} \quad p(\mathcal{A}) = \sum_{\mathcal{B}} p(\mathcal{A} \cap \mathcal{B}). \quad (1.2.2)$$

In probability theory these are usually referred to as *marginal probabilities*, while in physics one often talks about reduced probability distributions (density matrices) and partial traces. If the joint probability distribution factors into a product of the two marginals

$$p(\mathcal{A} \cap \mathcal{B}) = p(\mathcal{A})p(\mathcal{B}), \quad (1.2.3)$$

then the two random variables are said to be *independent*, or *uncorrelated*.

The Shannon entropy of the joint probability distribution is the *joint entropy*

$$H(\mathcal{A} \cap \mathcal{B}) = -k \sum_{\mathcal{A} \cap \mathcal{B}} p(\mathcal{A} \cap \mathcal{B}) \ln(p(\mathcal{A} \cap \mathcal{B})), \quad (1.2.4)$$

and reduces to the sum of the Shannon entropies of the two marginals

$$H(\mathcal{A} \cap \mathcal{B}) = H(\mathcal{A}) + H(\mathcal{B}), \quad (1.2.5)$$

when Alice and Bob's results are uncorrelated, as can easily be checked. In this sense the entropy of independent random variables is an *extensive* quantity, directly proportional to the number of random variables. In the case where the random variables we are interested in are the positions and momenta of gas molecules (non-interacting particles in a box), the entropy is proportional to the number of particles, or, if the density is constant, to the volume of the box.

A second type of combined quantity that we might ask about is the probability distribution for Alice's results given that Bob gets a 5. This is a *conditional probability distribution* $p(\mathcal{A}|\{\mathcal{B} = 5\})$ and is related to the joint distribution and the marginal for Bob in a natural way

$$p(\mathcal{A}|\{\mathcal{B} = 5\})p(\mathcal{B} = 5) = p(\mathcal{A} \cap \{\mathcal{B} = 5\}), \quad (1.2.6)$$

$$\Rightarrow \quad p(\mathcal{A}|\mathcal{B}) = \frac{p(\mathcal{A} \cap \mathcal{B})}{p(\mathcal{B})}. \quad (1.2.7)$$

The Shannon entropy of the conditional probability distribution is defined as usual as

$$H(\mathcal{A}|\{\mathcal{B} = b\}) = -k \sum_a p(\{\mathcal{A} = a\}|\{\mathcal{B} = b\}) \ln(p(\{\mathcal{A} = a\}|\{\mathcal{B} = b\})). \quad (1.2.8)$$

The *conditional information entropy* of the two random variables is obtained by averaging these conditional entropies against the marginal for Bob

$$H(\mathcal{A}|\mathcal{B}) := \sum_b p(\mathcal{B} = b)H(\mathcal{A}|\{\mathcal{B} = b\}). \quad (1.2.9)$$

It is not difficult to show from this that the conditional entropy is the difference between the joint entropy and the marginal entropy for Bob

$$H(\mathcal{A}|\mathcal{B}) = H(\mathcal{A} \cap \mathcal{B}) - H(\mathcal{B}), \quad (1.2.10)$$

which we leave as an exercise.

Finally, the *mutual information* of a pair of random variables is the excess of the entropy of the two marginals over that of the joint distribution

$$I(\mathcal{A}, \mathcal{B}) := H(\mathcal{A}) + H(\mathcal{B}) - H(\mathcal{A} \cap \mathcal{B}), \quad (1.2.11)$$

so that it provides a measure of the extent to which the two random variables are related, or correlated. Using equation (1.2.10) we see that the mutual information can also be expressed as

$$I(\mathcal{A}, \mathcal{B}) = H(\mathcal{A}) - H(\mathcal{A}|\mathcal{B}), \quad (1.2.12)$$

leading to an interpretation as the reduction in the uncertainty in the random variable $\mathcal{A}$ obtained by gaining knowledge of the random variable $\mathcal{B}$, or how much $\mathcal{B}$ tells you about $\mathcal{A}$.

1.3 Maximum entropy statistical mechanics

With Shannon's theorem in place to provide a characterisation of probability distributions for the microstates compatible with a given macrostate, we are in a position to give a protocol for doing statistical mechanics. This was first described by Edwin Jaynes in 1957 and firmly ties together the subjects of statistical mechanics and information theory¹. The fundamental assertion of Jaynes's approach to statistical mechanics is that the Shannon entropy associated to a probability distribution p_α is equal to the thermodynamic entropy of Boltzmann and Gibbs

$$H_n(\{p_\alpha\}) = -k_B \sum_\alpha p_\alpha \ln(p_\alpha) = S, \quad (1.3.1)$$

provided the constant k in Shannon's formula is chosen to be the Boltzmann constant k_B . Furthermore, the probability distribution that best reflects the macroscopic properties that we know without committing us to unfounded assumptions is the one that maximises the Shannon entropy. This method of selecting probability distributions is known as *maximum entropy inference*, or *maxent*. As it does not take any input from microscopic equations of motion – Newton's laws, Hamilton's equations, the Schrödinger equation – it is entirely complementary to any such description, which can make some people feel uneasy.

REMARK: A word about notation is in order. From now on we will exclusively use the symbol S to denote the entropy, whether it be the thermodynamic entropy or the information entropy, as is usual in physics. In information theory the symbol H is frequently used because this is what Shannon chose in his landmark paper, however in physics H is traditionally reserved for the Hamiltonian, a convention that we shall now adopt. Hopefully any potential for confusion will be minimised by restricting the duplicity in notation to this initial discussion.

1.3.1 Microcanonical ensemble

Although there is a strong sense in which this exercise is tautological let us go through the motions nonetheless and demonstrate that the maximum entropy probability distribution associated with a complete lack of macroscopic information is the one in which every possible state is assigned the same probability. That is we wish to maximise the Shannon entropy (1.3.1) subject only to the condition that the probabilities sum to unity. Using a Lagrange multiplier² for the constraint we find

$$0 = \delta \left(-k_B \sum_\alpha p_\alpha \ln(p_\alpha) - k_B \lambda_0 \left[\sum_\alpha p_\alpha - 1 \right] \right), \quad (1.3.2)$$

$$= -k_B \sum_\alpha \left(\delta p_\alpha \ln(p_\alpha) + \delta p_\alpha \right) - k_B \lambda_0 \sum_\alpha \delta p_\alpha, \quad (1.3.3)$$

$$= -k_B \sum_\alpha \left[\ln(p_\alpha) + 1 + \lambda_0 \right] \delta p_\alpha, \quad (1.3.4)$$

and hence the probability distribution is

$$p_\alpha = e^{-1-\lambda_0}. \quad (1.3.5)$$

¹Of course, there are other approaches to statistical mechanics that do not give such a fundamental role to information theory.

²Here, and throughout, we will find it convenient to define all Lagrange multipliers with an explicit factor of k_B . This convention is not universal, but I feel it has sufficient merits to adopt it here.

The Lagrange multiplier λ_0 can be determined through the constraint that the probability distribution is normalised, leading to $\lambda_0 = \ln(\Omega) - 1$ or

$$p_\alpha = \frac{1}{\Omega}, \quad (1.3.6)$$

where Ω is the total number of possible states. In statistical physics this distribution, (1.3.6), is known as the *microcanonical ensemble*.

With the expression (1.3.6) for the probabilities the Shannon entropy becomes

$$S = -k_B \sum_\alpha p_\alpha \ln(p_\alpha) = -k_B \sum_\alpha \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = k_B \ln(\Omega), \quad (1.3.7)$$

and is precisely Boltzmann's famous formula.

1.3.2 The canonical ensemble

In the canonical ensemble we increase our macroscopic knowledge by one unit, asserting that while the microstates α can have different energies E_α , the average energy $\langle E_\alpha \rangle = E$ is fixed. Again, the assignment of probabilities p_α that best reflects this information whilst being least committal about everything else is obtained through maximising the entropy, subject to our known constraints

$$0 = \delta \left(-k_B \sum_\alpha p_\alpha \ln(p_\alpha) - k_B \lambda_0 \left[\sum_\alpha p_\alpha - 1 \right] - k_B \beta \left[\sum_\alpha p_\alpha E_\alpha - E \right] \right), \quad (1.3.8)$$

$$= -k_B \sum_\alpha \left(\ln(p_\alpha) + 1 + \lambda_0 + \beta E_\alpha \right) \delta p_\alpha. \quad (1.3.9)$$

This gives the probability distribution

$$p_\alpha = e^{-1-\lambda_0-\beta E_\alpha}, \quad (1.3.10)$$

with the Lagrange multipliers λ_0 and β again determined by the constraints

$$\sum_\alpha p_\alpha = 1, \quad \Rightarrow \quad e^{1+\lambda_0} = \sum_\alpha e^{-\beta E_\alpha}, \quad (1.3.11)$$

$$\sum_\alpha p_\alpha E_\alpha = E \quad \Rightarrow \quad \sum_\alpha (E_\alpha - E) e^{-\beta E_\alpha} = 0. \quad (1.3.12)$$

These equations introduce two of the most important concepts in statistical physics. The latter equation, (1.3.12), is an implicit relation for β and is taken as a statistical definition of *temperature*. That is, what we mean when we say that a physical system is in equilibrium with a well-defined temperature T is that equation (1.3.12) is satisfied with

$$\beta = \frac{1}{k_B T}. \quad (1.3.13)$$

Even more important is the first equation, (1.3.11), which introduces for the first time the *partition function*

$$Z := \sum_\alpha e^{-\beta E_\alpha}. \quad (1.3.14)$$

It is fair to say that the partition function is the single most important object in statistical physics and that most problems in statistical physics revolve around attempts at calculating the partition function.

1.3.3 The grand canonical ensemble

Beyond the canonical ensemble, the next situation to consider is one where we are also provided with information about the average number of particles in the system. That is, we consider a situation in which the state α is a state of n_α particles and where the average number of particles $\langle n_\alpha \rangle = N$ is known and fixed. Then the maximum entropy formalism tells us that the probability that best represents this information is the one that maximises the entropy (1.3.1) subject to constraints on the average energy and the number of particles, in addition to the normalisation of the probability distribution

$$0 = \delta \left(-k_B \sum_{\alpha} p_{\alpha} \ln(p_{\alpha}) - k_B \lambda_0 \left[\sum_{\alpha} p_{\alpha} - 1 \right] - k_B \beta \left[\sum_{\alpha} p_{\alpha} E_{\alpha} - E \right] - k_B \gamma \left[\sum_{\alpha} p_{\alpha} n_{\alpha} - N \right] \right), \quad (1.3.15)$$

$$= -k_B \sum_{\alpha} \left(\ln(p_{\alpha}) + 1 + \lambda_0 + \beta E_{\alpha} + \gamma n_{\alpha} \right) \delta p_{\alpha}. \quad (1.3.16)$$

It is conventional to write the Lagrange multiplier γ as $\gamma = -\beta\mu$ and refer to the new parameter μ as the *chemical potential*. Running through the same sort of arguments as we did for the canonical ensemble, we then find that the probability distribution is given by (EXERCISE: show this)

$$p_{\alpha} = \frac{e^{-\beta(E_{\alpha} - \mu n_{\alpha})}}{\mathcal{Z}}, \quad \mathcal{Z} = \sum_{\alpha} e^{-\beta(E_{\alpha} - \mu n_{\alpha})}, \quad (1.3.17)$$

where $\mathcal{Z}$ is known as the *grand canonical partition function*.

1.3.4 A general constraint problem

Finally, let us consider a more general situation in which we are tasked with finding the probability distribution that best reflects the known information, or set of constraints,

$$f_i(\{p_{\alpha}\}) = C_i, \quad \text{for } i = 1, \dots, M, \quad (1.3.18)$$

while making the fewest possible assumptions about anything else. As usual, this is provided by the maximum entropy prescription

$$0 = \delta \left(-k_B \sum_{\alpha} p_{\alpha} \ln(p_{\alpha}) - k_B \lambda_0 \left[\sum_{\alpha} p_{\alpha} - 1 \right] - \sum_{i=1}^M k_B \lambda_i \left[f_i(\{p_{\alpha}\}) - C_i \right] \right), \quad (1.3.19)$$

$$= -k_B \sum_{\alpha} \left(\ln(p_{\alpha}) + 1 + \lambda_0 + \sum_{i=1}^M \lambda_i \frac{\partial f_i}{\partial p_{\alpha}} \right) \delta p_{\alpha}, \quad (1.3.20)$$

and the probability distribution is, at least in principle, determined from the equations

$$\ln(p_{\alpha}) + 1 + \lambda_0 + \sum_{i=1}^M \lambda_i \frac{\partial f_i}{\partial p_{\alpha}} = 0, \quad (1.3.21)$$

for each α , together with the constraint equations (1.3.18) and the condition that the sum of the probabilities be unity $\sum_{\alpha} p_{\alpha} = 1$. We see that a general solution of Gibbs type is only possible if the constraints (1.3.18) are linear in the probabilities, in other words when they are averages

or expectation values. However, when they are linear then the partial derivatives are constants – let us call them ϕ_i^α – and the probabilities are given by

$$p_\alpha = e^{-1-\lambda_0-\sum_i \lambda_i \phi_i^\alpha} = \frac{1}{\mathcal{Z}} e^{-\sum_i \lambda_i \phi_i^\alpha}, \quad (1.3.22)$$

where, as usual

$$\mathcal{Z} = \sum_\alpha e^{-\sum_i \lambda_i \phi_i^\alpha}, \quad (1.3.23)$$

is the partition function.

REMARK: In the literature you will often see the canonical ensemble referred to as a *Gibbs ensemble* in recognition of Josiah Willard Gibbs' contributions to statistical mechanics. The general constraint problem we have described here, including the grand canonical ensemble which is the simplest case, is then referred to as a *generalised Gibbs ensemble*. Generalised Gibbs ensembles are characteristic of integrable systems, which possess a large (infinite) number of conserved quantities.

Chapter 2

Thermodynamics, fluctuations and correlations

The description and understanding of macroscopic quantities and the relations between them is called *thermodynamics*. Of course, in principle, thermodynamic behaviour should be understandable in terms of the microscopic constituents and statistical mechanics supplies the means of doing this. Here we survey the general methods by which the correspondence between statistical mechanics and thermodynamics is obtained and introduce the important concepts of fluctuations and correlations.

2.1 Macroscopic variables from microstates

Having determined the probability distribution we may now use its expression in terms of the Lagrange multipliers $\{\lambda_i\}$ to rewrite all macroscopic quantities in terms of the partition function and the constraints. As we shall see this eventually leads to the usual relations of thermodynamics between macroscopic observables. The first quantities to treat this way, the constraints C_i , may seem a little funny, for we know what they are already, but the exercise is still a useful one;

$$C_j = \sum_{\alpha} p_{\alpha} \phi_j^{\alpha} = \frac{1}{Z} \sum_{\alpha} \phi_j^{\alpha} e^{-\sum_i \lambda_i \phi_i^{\alpha}} = -\frac{\partial \ln(Z)}{\partial \lambda_j}. \quad (2.1.1)$$

For instance, in the canonical ensemble the only constraint is on the average energy of the system $E = \langle H \rangle$ and its Lagrange multiplier is the inverse temperature $\beta = 1/k_B T$

$$E = -\frac{\partial \ln(Z)}{\partial \beta}. \quad (2.1.2)$$

Apart from an interpretation of the logarithm of the partition function, this is now expressed in terms of thermodynamic quantities.

The next important quantity to reexpress in this way is the entropy, for which we find

$$S(\{C_i\}) = -k_B \sum_{\alpha} p_{\alpha} \ln(p_{\alpha}), \quad (2.1.3)$$

$$= k_B \sum_{\alpha} p_{\alpha} \left(1 + \lambda_0 + \sum_{i=1}^M \lambda_i \phi_i^{\alpha} \right), \quad (2.1.4)$$

$$= k_B \ln(Z(\{\lambda_i\})) + k_B \sum_{i=1}^M \lambda_i C_i. \quad (2.1.5)$$

Thus we see that the entropy $S(\{C_i\})$ and the logarithm of the partition function $-k_B \ln(\mathcal{Z}(\{\lambda_i\}))$ are a Legendre transform pair. Consider again the canonical ensemble where there is a single constraint, the expectation value of the energy, and the Lagrange multiplier is $\beta = (k_B T)^{-1}$. Then the general expression for the entropy gives

$$S(E) = k_B \ln(\mathcal{Z}(\beta)) + \frac{1}{T} E, \quad (2.1.6)$$

$$\Rightarrow E - TS = -k_B T \ln(\mathcal{Z}) =: F, \quad (2.1.7)$$

and introduces the important *Helmholtz free energy* F , which is the Legendre transform of the (internal) energy E . In many calculations the Helmholtz free energy provides the most convenient way of relating statistical mechanics to thermodynamics so that it is especially useful to remember its relation to the partition function.

There is an analogous story for the grand canonical ensemble for which we have

$$S(E, N) = k_B \ln(\mathcal{Z}(\beta, \mu)) + \frac{1}{T} E - \frac{1}{T} \mu N, \quad (2.1.8)$$

$$\Rightarrow E - TS - \mu N = -k_B T \ln(\mathcal{Z}) =: A. \quad (2.1.9)$$

The thermodynamic potential A is known as the *grand potential* and, like the Helmholtz free energy in the canonical ensemble, often provides the most convenient connection between statistical mechanics and thermodynamics in calculations.

Whereas derivatives of the logarithm of the partition function gave the constraints, derivatives of the entropy with respect to the constraints yield the Lagrange multipliers

$$\frac{\partial S(\{C_i\})}{\partial C_j} = k_B \sum_{k=1}^M \frac{\partial \ln(\mathcal{Z}(\{\lambda_i\}))}{\partial \lambda_k} \frac{\partial \lambda_k}{\partial C_j} + k_B \sum_{k=1}^M \frac{\partial \lambda_k}{\partial C_j} C_k + k_B \lambda_j = k_B \lambda_j. \quad (2.1.10)$$

Again for the canonical ensemble this reduces to a familiar result

$$\frac{\partial S}{\partial E} = k_B \beta = \frac{1}{T}. \quad (2.1.11)$$

In other words the temperature is given by the rate of change of the entropy for a change in energy. Our default assumption so far is that this change is occurring in an otherwise closed system contained in a box of fixed size, so that the energy change is due to a flow of heat. In differential notation then equation (2.1.11) is equivalent to $dS = \frac{1}{T} dQ$, which is one of the canonical expressions for entropy in thermodynamics.

The second derivatives produce interesting results known as the *reciprocity relations*. For instance, the second derivatives of the entropy are

$$k_B \frac{\partial \lambda_j}{\partial C_k} = \frac{\partial^2 S(\{C_i\})}{\partial C_j \partial C_k} = k_B \frac{\partial \lambda_k}{\partial C_j}, \quad (2.1.12)$$

on account of the symmetry of mixed second derivatives. Likewise, the second derivatives of the logarithm of the partition function are

$$\frac{\partial C_j}{\partial \lambda_k} = -\frac{\partial^2 \ln(\mathcal{Z}(\{\lambda_i\}))}{\partial \lambda_j \partial \lambda_k} = \frac{\partial C_k}{\partial \lambda_j}. \quad (2.1.13)$$

As the matrices $\frac{\partial \lambda_j}{\partial C_k}$ and $\frac{\partial C_j}{\partial \lambda_k}$ are inverses of each other this leads to the relation

$$-\frac{\partial^2 \ln(\mathcal{Z}(\{\lambda_i\}))}{\partial \lambda_j \partial \lambda_k} = k_B \left(\frac{\partial^2 S(\{C_i\})}{\partial C_j \partial C_k} \right)^{-1}, \quad (2.1.14)$$

between the Hessians.

Let us think about what these derivatives mean. For instance, in the canonical ensemble where the constraint is the average energy $E = \langle H \rangle$ and the Lagrange multiplier is the inverse temperature $\beta = \frac{1}{k_B T}$ the derivative is

$$\frac{\partial E}{\partial \beta} = -k_B T^2 \frac{\partial E}{\partial T} = -k_B T^2 C_V, \quad (2.1.15)$$

where C_V is the *heat capacity* at constant volume. The heat capacity is an example of a *response function*, the increase in the average energy of the system in response to an increase in the temperature.

There is also another way of thinking about the derivatives $\frac{\partial C_j}{\partial \lambda_k}$ that comes from the microscopic underpinnings. C_j is the expectation value of the quantity ϕ_j^α and so its derivative is

$$\frac{\partial C_j}{\partial \lambda_k} = \frac{\partial}{\partial \lambda_k} \left(\frac{1}{Z} \sum_{\alpha} \phi_j^\alpha e^{-\sum_i \lambda_i \phi_i^\alpha} \right), \quad (2.1.16)$$

$$= -\frac{1}{Z} \sum_{\alpha} \phi_j^\alpha \phi_k^\alpha e^{-\sum_i \lambda_i \phi_i^\alpha} + \left(\frac{1}{Z} \sum_{\alpha} \phi_j^\alpha e^{-\sum_i \lambda_i \phi_i^\alpha} \right) \left(\frac{1}{Z} \sum_{\alpha} \phi_k^\alpha e^{-\sum_i \lambda_i \phi_i^\alpha} \right), \quad (2.1.17)$$

$$= -\langle \phi_j^\alpha \phi_k^\alpha \rangle + \langle \phi_j^\alpha \rangle \langle \phi_k^\alpha \rangle. \quad (2.1.18)$$

Thus these derivatives are related to *correlations* in the values, or measurements, of ϕ_i^α . The expectation value of the product $\phi_j^\alpha \phi_k^\alpha$ is known as the *correlation function*, $\langle \phi_j^\alpha \phi_k^\alpha \rangle$. The derivative $-\frac{\partial C_j}{\partial \lambda_k}$ is the correlation function of the fluctuations $\phi_j^\alpha - \langle \phi_j^\alpha \rangle$ of the ϕ_j^α from their expected values

$$-\frac{\partial C_j}{\partial \lambda_k} = \langle (\phi_j^\alpha - \langle \phi_j^\alpha \rangle) (\phi_k^\alpha - \langle \phi_k^\alpha \rangle) \rangle, \quad (2.1.19)$$

and is known as a *connected correlation function*, or in probability as a *covariance*. The *variance* of a random variable ϕ_j^α is the connected correlation function of the variable with itself.

What this shows us is that fluctuations in observables are important and are directly related to thermodynamic response functions. For instance in the canonical ensemble the fluctuations in the energy, i.e., its variance, are proportional to the heat capacity

$$\text{var}(H) = \langle (H - E)^2 \rangle = -\frac{\partial E}{\partial \beta} = k_B T^2 C_V. \quad (2.1.20)$$

The relative size of fluctuations are also important. These are characterised by the ratio of the standard deviation (square root of the variance) to the mean value, which for fluctuations of the energy in the canonical ensemble is

$$\frac{\sigma_E}{E} = \frac{\sqrt{k_B T^2 \frac{\partial E}{\partial T}}}{E} \sim \frac{1}{\sqrt{E}}. \quad (2.1.21)$$

Since the energy is an extensive quantity the relative size of the fluctuations decreases as we increase the size of the system. This behaviour of the relative fluctuations in the energy, and the characteristic exponent $-\frac{1}{2}$, is common across many quantities. For instance the number fluctuations in the grand canonical ensemble satisfy

$$\frac{\sigma_N}{N} = \frac{\sqrt{k_B T \frac{\partial N}{\partial \mu}}}{N} \sim \frac{1}{\sqrt{N}}. \quad (2.1.22)$$

2.2 Spatial correlations

What we have seen in the previous section illustrates a key technique for calculating correlation functions of any observable. Suppose, for definitiveness, that we are interested in the correlation function of an observable ϕ and that we are working in the canonical ensemble. Consider a generalised partition function (or *generating function*)

$$Z(\beta, h) = \sum_{\alpha} e^{-\beta E_{\alpha} + h \phi_{\alpha}}, \quad (2.2.1)$$

where ϕ_{α} is the value of the observable ϕ in the state α . The expectation value of ϕ is given by the derivative of the logarithm of $Z(\beta, h)$ with respect to h evaluated at $h = 0$

$$\langle \phi \rangle = \frac{1}{Z} \sum_{\alpha} \phi_{\alpha} e^{-\beta E_{\alpha}} = \left. \frac{\partial \ln(Z(\beta, h))}{\partial h} \right|_{h=0}. \quad (2.2.2)$$

Likewise, the connected correlation function is given by the second derivative

$$\langle \phi^2 \rangle - \langle \phi \rangle^2 = \left. \frac{\partial^2 \ln(Z(\beta, h))}{\partial h^2} \right|_{h=0}. \quad (2.2.3)$$

This approach can be used for all sorts of observables, including for *local* observables $\phi(r)$. Here r is a label for spatial positions within the system, for instance it may range over the sites of a regular crystalline lattice that we expect to find atoms located at in a solid material. Then if we consider the generating function

$$Z(\beta, \{h(r)\}) = \sum_{\alpha} e^{-\beta E_{\alpha} + \sum_r h(r) \phi_{\alpha}(r)}, \quad (2.2.4)$$

we can calculate correlation functions in exactly the same way as before

$$\langle \phi(r) \phi(r') \rangle - \langle \phi(r) \rangle \langle \phi(r') \rangle = \left. \frac{\partial^2 \ln(Z(\beta, \{h(r)\}))}{\partial h(r) \partial h(r')} \right|_{h(r)=0}. \quad (2.2.5)$$

These spatial correlation functions are of considerable importance in many problems in statistical mechanics, both because they provide a measure of the degree of order in the system and also because they are directly measurable in many types of scattering experiments. Generically, their behaviour with the separation $|r - r'|$ may be separated into three types. In the high temperature phase the system is disordered and correlations exist only over short distances. The correlation function correspondingly decays exponentially with distance with the general form (here we assume $\langle \phi \rangle = 0$ as is often the case)

$$\langle \phi(r) \phi(r') \rangle \sim e^{-|r-r'|/\xi}, \quad \text{as } |r - r'| \rightarrow \infty, \quad (2.2.6)$$

where the lengthscale ξ is known as the *correlation length*. This is the characteristic behaviour of *short range order*. In contrast, in the ordered phase the spins align over large distances and the asymptotic behaviour of the correlation function is

$$\langle \phi(r) \phi(r') \rangle \sim \text{const.} \neq 0, \quad \text{as } |r - r'| \rightarrow \infty, \quad (2.2.7)$$

corresponding to *long range order*. Finally, exactly at the critical point, or in the low temperature phase of certain models, the behaviour of the system is intermediate between these two types and the correlation function takes the algebraic form

$$\langle \phi(r) \phi(r') \rangle \sim |r - r'|^{-(d-2)-\eta}, \quad \text{as } |r - r'| \rightarrow \infty, \quad (2.2.8)$$

known as *quasi long range order*. The exponent η is an example of a *critical exponent* and is a universal characteristic of the model.

Legendre transforms

There are many variables and potentials in statistical mechanics and thermodynamics that are related to each other through Legendre transforms. For instance, we saw in § 2.1 that the entropy S and $-k_B \ln(Z)$ are related in this way, and similar relations exist between the thermodynamic potentials. Here, for completeness, we recap the definition and some elementary properties of Legendre transforms.

We will consider only the Legendre transforms of convex functions. A function $\phi : \mathbb{R} \rightarrow (-\infty, \infty]$ is said to be convex if $\phi(tx + (1-t)y) \leq t\phi(x) + (1-t)\phi(y)$ for every $x, y \in \mathbb{R}$ and all $t \in [0, 1]$. If ϕ is a convex function then we define its Legendre transform¹ ϕ^* to be

$$\phi^*(p) = \sup_{x \in \mathbb{R}} (px - \phi(x)). \quad (2.2.9)$$

In physics we always assume that the functions we deal with are differentiable, unless we are forced to admit otherwise, and this is the approach we shall adopt here. The location of the supremum (maximum) can be found by the usual methods of calculus

$$0 = \frac{d}{dx}(px - \phi(x)) = p - \frac{d\phi}{dx}, \quad (2.2.10)$$

giving an implicit relation for the value $x(p)$ at which the maximum occurs. Using this to replace x with $x(p)$ in equation (2.2.9) gives an ‘explicit’ expression for the Legendre transform

$$\phi^*(p) = px(p) - \phi(x(p)). \quad (2.2.11)$$

There is a nice graphical interpretation of the Legendre transform based on equation (2.2.10). $d\phi/dx$ is the gradient of the graph of ϕ and so the supremum occurs at that value of x where the gradient of ϕ is equal to p . Moreover, $px - \phi(x)$ is simply the vertical distance between the straight line px and the graph of ϕ , so that the value of the Legendre transform is just the maximum of this distance. For convex functions this occurs where the gradient of ϕ is equal to p .

The Legendre transform $\phi^*(p)$ is itself a convex function (check!) and so we may also consider its Legendre transform

$$\phi^{**}(x) = \sup_{p \in \mathbb{R}} (xp - \phi^*(p)). \quad (2.2.12)$$

Again, assuming ϕ^* is differentiable the location of the supremum is given implicitly by the relation $x = d\phi^*/dp$, leading to the analogous relation

$$\phi^{**}(x) = xp(x) - \phi^*(p(x)), \quad (2.2.13)$$

for this double Legendre transform. It is tempting to use equation (2.2.11) to rewrite this as

$$\phi^{**}(x) = xp - (px - \phi(x)) = \phi(x), \quad (2.2.14)$$

and conclude that the Legendre transform of ϕ^* is simply ϕ . That this is correct follows if everything is differentiable² since then the locations of the two maxima $x(p)$ and $p(x)$ are inverse functions

$$x = \left. \frac{d\phi^*}{dp} \right|_{p=p(x)} = \left[x(p) + p \frac{dx(p)}{dp} - \frac{dx(p)}{dp} \frac{d\phi}{dx} \right]_{x=x(p)} \Big|_{p=p(x)} = x(p(x)), \quad (2.2.15)$$

¹More properly we should call this the Legendre-Fenchel transform, although Fenchel’s name is often skipped in the physics literature.

²More general conditions are given by the Fenchel-Moreau theorem.

which we used in writing equation (2.2.14).

The idea of Legendre transforms extend naturally in a couple of directions. First, we may treat concave functions by simply replacing supremum with infimum in the definition. And second, we can treat functions of several variables in an obvious way

$$\phi^*(p_1, \dots, p_n) = \sup_{\mathbf{x} \in \mathbb{R}^n} \left(\sum_{i=1}^n p_i x_i - \phi(x_1, \dots, x_n) \right). \quad (2.2.16)$$

Indeed this extends in exactly the same way to the case where $\mathbf{x}$ belongs to any vector space and $\mathbf{p}$ to its dual.

Chapter 3

Models

Models play a crucial part in statistical physics, providing highly simplified descriptions of physical phenomena and interacting systems stripped to their bare essentials. This allows for considerable insight into what exactly is important in any particular problem and also reveals deep connections and similarities between seemingly unrelated systems. Here we consider very briefly a few important models as a means to illustrate some central ideas in statistical physics.

3.1 The Ising model

Far and away the simplest, and most influential, model in statistical physics is the *Ising model*. The exact determination of the partition function for the two-dimensional Ising model by Lars Onsager in 1944 is widely considered to be one of the most seminal results in statistical mechanics.

In its canonical formulation the Ising model is a model of two-state spins $s_i = \pm 1$ on a lattice interacting via nearest neighbour only interactions with Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} s_i s_j - h \sum_i s_i, \quad (3.1.1)$$

where the angled brackets $\langle i, j \rangle$ denote the restriction to nearest neighbour sites, J is an *exchange constant* describing the strength of the nearest neighbour interaction, and h is an applied external magnetic field.

The Ising model provides a minimal description of several systems. Originally it was introduced to provide a model of (uniaxial) ferromagnetism, the idea being that the spins would be randomly ± 1 at high temperatures, and thus correspond to a paramagnetic phase, but would all adopt the same value (either all $+1$ or all -1) at sufficiently low temperatures, corresponding to a ferromagnet. A second application is to ordering transitions in alloys, such as β -brass, which is an alloy of copper and zinc. If we think of the copper atoms as corresponding to plus spins and the zinc atoms to minus spins, then we can describe the alloy using the Ising model, with the coupling constant J giving a highly simplified description of the interactions between atoms. At high temperatures the copper and zinc are arranged randomly, but below the ordering temperature they adopt a ‘checkerboard’ structure in which copper atoms have zinc atoms for their neighbours and vice-versa. This is the ground state of the Hamiltonian (3.1.1) if J is negative, corresponding to the *antiferromagnetic* Ising model.

In one dimension the Ising model can be solved in a variety of ways. Perhaps the most useful and widely encountered is the transfer matrix approach, however, this is not the strategy we will follow. Instead we will present a graphical method, which provides a nice contrast and reveals the connections between statistical mechanics and combinatorial problems on lattices. We restrict our attention to zero magnetic field, $h = 0$, for a one-dimensional chain of N sites with periodic

boundary conditions $s_{i+N} = s_i$. The graphical method is introduced by writing the partition function in the form

$$Z_N = \sum_{\{s_i\}} e^{\beta J \sum_i s_i s_{i+1}}, \quad (3.1.2)$$

$$= \sum_{\{s_i\}} \prod_i \left(\cosh(\beta J) + s_i s_{i+1} \sinh(\beta J) \right), \quad (3.1.3)$$

$$= \cosh^N(\beta J) \sum_{\{s_i\}} \prod_i \left(1 + x s_i s_{i+1} \right), \quad (3.1.4)$$

where $x := \tanh(\beta J)$. Expanding out the product over sites we obtain 2^N terms that we may group according to powers of x . When x is small we might hope that only the first couple of terms are important, which gives the basis for a *high temperature expansion* of the partition function. But for any value of x this way of writing the partition function affords a convenient graphical representation and means of computing it. For each term $s_i s_{i+1}$ we draw a line connecting the sites i and $i+1$. The partition function is then given by a weighted sum of all possible ways of placing bonds on the lattice. Empty sites have no factors of the spin variable s_i at that site, internal sites come with two factors of s_i and sites at the ends of the line segments come with a single factor of s_i . When we take the sum over the possible values of the spin at these ‘free ends’ we get two equal and opposite terms that cancel, otherwise we get a factor of 2 from each spin, since each can take the two values ± 1 . So configurations with ‘free ends’ make no contribution to the partition function and only two terms survive: one in which no bonds are present, and the other where all bonds are present

$$Z_N = \cosh^N(\beta J) \left(2^N + 2^N x^N \right), \quad (3.1.5)$$

$$= \left(2 \cosh(\beta J) \right)^N (1 + \tanh^N(\beta J)). \quad (3.1.6)$$

With the partition function we can calculate all the thermodynamic properties of the Ising chain, as well as the response functions and fluctuations. But our interest in the model is in its ability to describe ordering transitions, for instance in (uniaxial) ferromagnets or β -brass. A generic measure of the order in the system is given by the spin-spin correlation function

$$\langle s_k s_{k+r} \rangle = \frac{1}{Z_N} \sum_{\{s_i\}} \prod_i s_k s_{k+r} e^{\beta J s_i s_{i+1}}, \quad (3.1.7)$$

$$= \frac{1}{Z_N} \cosh^N(\beta J) \sum_{\{s_i\}} \prod_i s_k s_{k+r} \left(1 + x s_i s_{i+1} \right), \quad (3.1.8)$$

which again can be easily computed using a graphical method. This time the only terms in the expansion that survive the trace over the spins are those that connect the sites k and $k+r$. Since the chain is periodic there are two such terms, joining together the two sites in opposite directions around the chain. Remembering that the trace over the possible values of the spins gives a factor of 2 from each spin we find that the correlation function is

$$\langle s_k s_{k+r} \rangle = \frac{x^r + x^{N-r}}{1 + x^N} \xrightarrow{N \rightarrow \infty} \tanh^r(\beta J). \quad (3.1.9)$$

Thus the two-point function decays exponentially as $\sim e^{-r/\xi}$ with a correlation length

$$\xi = \frac{1}{\ln(\coth(\beta J))}. \quad (3.1.10)$$

This reflects the absence of a phase transition at non-zero temperature in the one-dimensional Ising model. However, there *is* a transition at $T = 0$, an indication for which is given by the divergence of the correlation length as $T \rightarrow 0$.

3.1.1 Duality in the two-dimensional Ising model

The lack of a transition at non-zero temperature in the one-dimensional model meant that for some years after it was first introduced the model was not considered particularly interesting. However, all that changed when it was realised that the two-dimensional model *does* undergo a transition. This was shown by Rudolf Peierls using a scaling argument for the free energy change associated to reversing a block of spins in an otherwise aligned state. There is an energy cost associated with the flipped spins at the interface. If the length of the interface is L then this energy cost will be $\Delta E = 2JL$. The trick is then to argue that the entropy also scales linearly with the interface length. The entropy of the interface comes from the number of different configurations it can adopt and we can estimate these by thinking about a random walk on the square lattice. At each step there are three possible directions for the walk to go in (we exclude the possibility of backtracking). This gives of order 3^L random walks. Since in two dimensions the return probability for a random walk tends to unity as $L \rightarrow \infty$ this will also be a good estimate of the number of configurations for the boundary of a domain of reversed spins when the length of the interface is large. Thus we can estimate the free energy change of introducing a domain of flipped spins as $\Delta F \approx 2JL - T k_B \ln(3^L) = L(2J - k_B T \ln(3))$. When the temperature is high such reversals are favourable and the system is disordered, but for sufficiently low temperatures the free energy change is positive and the aligned ferromagnetic state is stable.

Peierls' argument establishes the existence of a transition, but it does not solve the model as was possible in one dimension, or offer a strategy for doing so. As already mentioned, Onsager's exact solution of the two-dimensional Ising model¹ is one of the seminal results in statistical physics. His solution, based on transfer matrices, is long and technical. The analysis of the Ising model has been central to a very substantial fraction of the significant developments in statistical physics and so it seems appropriate to cover at least a small part of it. An important, and accessible, property is the exact determination of the transition temperature, due to Kramers and Wannier². The key observation is that the partition function can be organised in two different, but related, ways, one adapted to high temperatures and the other to low temperatures.

We will work with a square lattice having N sites. Neglecting any boundary effects there are then also N horizontal nearest neighbour interactions and N vertical ones. Taking different couplings J_h and J_v for these, the partition function is given by

$$Z(\beta J_h, \beta J_v) = \sum_{\{s_i\}} \exp \left\{ \beta J_h \sum_{\text{horizontal}} s_i s_j + \beta J_v \sum_{\text{vertical}} s_i s_k \right\}, \quad (3.1.11)$$

with the sums extending over all horizontal and vertical nearest neighbour interactions. Our first approach to organising the partition function makes use of the same identity $e^{K s_i s_j} = \cosh(K) + \sinh(K) s_i s_j$ as we exploited in one dimension. The partition function then becomes

$$Z(\beta J_h, \beta J_v) = (\cosh(\beta J_h) \cosh(\beta J_v))^N \sum_{\{s_i\}} \prod_{\text{horizontal}} (1 + x s_i s_j) \prod_{\text{vertical}} (1 + y s_i s_k), \quad (3.1.12)$$

where $x := \tanh(\beta J_h)$ and $y := \tanh(\beta J_v)$. Expanding out the products over horizontal and vertical interactions we can see that the general term takes the form

$$x^r y^s \times \{ \text{product of neighbouring spins} \}. \quad (3.1.13)$$

¹L. Onsager, *Phys. Rev.* **65**, 117–149 (1944).

²H. A. Kramers and G. H. Wannier, *Phys. Rev.* **60**, 252–262 (1941); *ibid* 263–276 (1941).

Precisely as in one dimension, each term can be represented graphically by drawing a line connecting the spins appearing in the product. The only terms that survive the sum over possible spin configurations are those where each spin appears an even number of times, corresponding to diagrams containing only *closed polygons*. Each of these collects a factor of 2^N from the sum over spin configurations, so that the partition function may be written

$$Z(\beta J_h, \beta J_v) = (2 \cosh(\beta J_h) \cosh(\beta J_v))^N \sum_{\text{closed polygons}} x^r y^s, \quad (3.1.14)$$

where r is the number of horizontal links in the polygon and s the number of vertical links.

This form of the partition function forms the basis of a *high temperature expansion* since at high temperatures both x and y are small and the sum over closed polygons can be well approximated by just the first few terms

$$\sum_{\text{closed polygons}} x^r y^s = 1 + N x^2 y^2 + N (x^4 y^2 + x^2 y^4) + \dots \quad (3.1.15)$$

When the temperature is not so high this will no longer be a good approximation to the partition function. Indeed, we expect that at low temperatures the spins will be mostly aligned so that such configurations should dominate the partition function. We can use this intuition as the basis for a second way of organising our calculation. In any configuration, let s and r denote the number of anti-aligned horizontal and vertical nearest neighbour spins, respectively. As there are then $N - s$ and $N - r$ aligned horizontal and vertical nearest neighbour spins, the Boltzmann weight for this configuration is simply

$$\exp\{\beta J_h(N - 2s) + \beta J_v(N - 2r)\}. \quad (3.1.16)$$

Moreover, the spin configuration gives us directly a graphical representation of every term. Each pair of neighbouring sites on the square lattice can be connected by an edge shared between two adjacent square plaquettes. For every anti-aligned pair of neighbouring spins we draw a line between the centres of the two plaquettes whose common edge connects the neighbouring spins. In this way any spin configuration is mapped to a closed polygon on the *dual lattice*, which will have r horizontal edges and s vertical edges. This mapping is two to one since reversing the signs of all the spins yields the same closed polygon but any other change gives a different polygon. Thus the partition function can be written

$$Z(\beta J_h, \beta J_v) = 2 e^{N(\beta J_h + \beta J_v)} \sum'_{\text{closed polygons}} u^r v^s, \quad (3.1.17)$$

where $u := \exp\{-2\beta J_v\}$ and $v := \exp\{-2\beta J_h\}$ and the prime on the sum reminds us that these are closed polygons on the dual lattice.

The key point is that the square lattice is *self-dual*, i.e., the dual lattice is again the square lattice, and so the sum over closed polygons appearing in equation (3.1.17) is the *same* as that in equation (3.1.14), just in terms of different variables. The upshot of this is that we obtain a duality mapping relating the partition function at high and low temperatures

$$\frac{Z(\beta J_h, \beta J_v)}{(2 \cosh(\beta J_h) \cosh(\beta J_v))^N} = \frac{Z(\widetilde{\beta J_h}, \widetilde{\beta J_v})}{2 e^{N(\widetilde{\beta J_h} + \widetilde{\beta J_v})}}, \quad (3.1.18)$$

where the parameters satisfy the relations

$$\tanh(\beta J_h) = e^{-2\widetilde{\beta J_v}}, \quad \text{and} \quad \tanh(\beta J_v) = e^{-2\widetilde{\beta J_h}}, \quad (3.1.19)$$

although it is traditional to write them in the equivalent symmetrical form

$$\sinh(2\beta J_h) \sinh(2\widetilde{\beta J_v}) = 1, \quad \text{and} \quad \sinh(2\widetilde{\beta J_h}) \sinh(2\beta J_v) = 1. \quad (3.1.20)$$

This mapping relates the high temperature behaviour of the two-dimensional Ising model to its behaviour at low temperatures. The transition between the disordered and ordered phases corresponds to a fixed point of the mapping and so occurs when

$$\sinh(2\beta_c J_h) \sinh(2\beta_c J_v) = 1, \quad (3.1.21)$$

which identifies the exact value of the critical temperature of the two-dimensional Ising model.

3.2 The Potts model

The Ising model has inspired a plethora of variants; here, and in the next section, we mention just two of them.

The Potts model is again a model of interacting ‘spins’ on a lattice with the interactions restricted to just nearest neighbours like in the Ising model. There are two differences, however. First, we allow the spins to take any of q distinct values. And second, the interaction is chosen such that there is a contribution $-J$ to the energy if two adjacent spins take the same value, but no contribution if they take different values. In other words the Hamiltonian is

$$H = -J \sum_{\langle i,j \rangle} \delta_{s_i, s_j}. \quad (3.2.1)$$

The partition function can again be given a graphical expansion

$$Z = \sum_{\{s_i\}} e^{\beta J \sum_{\langle i,j \rangle} \delta_{s_i, s_j}}, \quad (3.2.2)$$

$$= \sum_{\{s_i\}} \prod_{\langle i,j \rangle} \left(1 + (e^{\beta J} - 1) \delta_{s_i, s_j} \right), \quad (3.2.3)$$

$$= e^{N\beta J} \sum_{\{s_i\}} \prod_{\langle i,j \rangle} \left((1 - p) + p \delta_{s_i, s_j} \right), \quad (3.2.4)$$

where $p := 1 - e^{-\beta J}$. Expanding out the product gives a sum over all graphs $\mathcal{G}$ that can be drawn on the lattice. The weighting is composed of a factor of p for each edge in the graph, a factor of $(1 - p)$ for each edge in the complement, and a factor of q from the sum over the different values the spin can take. The Kronecker delta imposes the same value for the spins in each connected component of the graph, so we get a factor of q from each connected component. Thus the partition function may be written as

$$Z = e^{N\beta J} \sum_{\text{graphs}} p^{|\mathcal{G}|} (1 - p)^{|\overline{\mathcal{G}}|} q^{||\mathcal{G}||}, \quad (3.2.5)$$

where $|\mathcal{G}|$ is the number of edges in the graph, $|\overline{\mathcal{G}}|$ is the number of edges in the complement and $||\mathcal{G}||$ is the number of connected components.

This is the random cluster representation of the Potts model. Unlike the original spin formulation, it can be interpreted for any value of q , not just when q is an integer.

3.3 The $O(n)$ model

An important family of models that generalise the Ising model is the $O(n)$ model. The partition function is the same as that of the Ising model except that the spins are taken to be vectors and have n components, $\mathbf{s}_i = [s_1^i, \dots, s_n^i]^T$, whose values are constrained only by the normalisation of the spins. The Hamiltonian for the model is

$$H = -J \sum_{\langle i,j \rangle} \mathbf{s}_i \cdot \mathbf{s}_j, \quad (3.3.1)$$

and is invariant under $O(n)$ transformations of all the spins, which is the origin of the name of the model. Several special cases are worth mentioning: the case $n = 1$ recovers the Ising model, $n = 2$ is called the XY model, and $n = 3$ is the Heisenberg model.

The partition function again gives rise to an interesting graphical interpretation. As usual we write

$$Z = \sum_{\{\mathbf{s}_i\}} e^{\beta J \sum_{\langle i,j \rangle} \mathbf{s}_i \cdot \mathbf{s}_j}, \quad (3.3.2)$$

$$\propto \sum_{\{\mathbf{s}_i\}} \prod_{\langle i,j \rangle} (1 + x \mathbf{s}_i \cdot \mathbf{s}_j). \quad (3.3.3)$$

After expanding out the product we can perform the trace over the possible values each spin can take. If we choose to normalise according to $\sum_{\mathbf{s}_i} s_a^i s_b^i = \delta_{ab}$ (and $\sum_{\mathbf{s}_i} \mathbf{s}_i = 0$) then only closed loops will contribute to the partition function, like in the Ising model, and each loop will be weighted by a factor of n . Thus the partition function for the $O(n)$ model can be written

$$Z \propto \sum_{\text{loops}} x^{\text{length}} n^{\text{number of loops}}. \quad (3.3.4)$$

As in the Potts model, this way of writing the partition function gives a general definition of the $O(n)$ model valid for any value of n and not just integer values. The limit $n \rightarrow 0$, for instance, provides a method for calculating the statistics of self avoiding random walks, or polymers.

3.4 The restricted solid-on-solid model

The graphical representation of the $O(n)$ model as a collection of closed loops on the lattice suggests a dual model whose partition function is given by precisely the same set of configurations. This duality exists for the XY model, $n = 1$, and is known as the *restricted solid-on-solid* model. It is defined by specifying a set of height variables h_i on the sites of the dual lattice. The heights can take any integer values, but heights on neighbouring sites are restricted to differing by at most ± 1 . The Hamiltonian simply assigns an energetic cost to neighbouring heights taking different values

$$H = K \sum_{\langle i,j \rangle} |h_i - h_j|. \quad (3.4.1)$$

This gives a basic description of surface growth or interface profiles, with the h_i s representing the local surface height³. The model exhibits a *roughening transition* from a state where the surface is flat and all the h_i s take the same value, to a state where the h_i s vary considerably and the surface is rough.

³In Monge gauge.

Let us demonstrate the duality with the XY model. Expressing the model in terms of the differences $n_{ij} = h_i - h_j$ in height between nearest neighbour sites i and j , the partition function for the restricted solid-on-solid model can be written as

$$Z = \sum'_{\{n_{ij}\}} e^{-\beta K \sum_{\langle i,j \rangle} |n_{ij}|}. \quad (3.4.2)$$

However, as indicated by the prime, this is not a free sum over the variables n_{ij} . Since in going around any closed path we always return to the same height it must be that the sum of the changes n_{ij} around any closed path gives zero. This can be ensured by demanding that the sum of the n_{ij} around every *plaquette* of the lattice be equal to zero. Putting this constraint directly into the partition function we have

$$Z = \sum_{\{n_{ij}\}} \prod_{\text{plaquettes}} \delta_{\sum n_{ij}, 0} e^{-\beta K \sum_{\langle i,j \rangle} |n_{ij}|}, \quad (3.4.3)$$

$$= \sum_{\{n_{ij}\}} \prod_{\text{plaquettes}} \int_0^{2\pi} \frac{d\theta_P}{2\pi} e^{i\theta_P \sum n_{ij}} e^{-\beta K \sum_{\langle i,j \rangle} |n_{ij}|}. \quad (3.4.4)$$

The dual variables θ_P , that enforce the constraints, are associated to each plaquette and can be thought of as living on the sites of the dual lattice. Reexpressing the sum over nearest neighbour bonds $\langle i, j \rangle$ as a sum over the neighbouring plaquettes $\langle P, P' \rangle$ that are separated by this bond the partition function becomes

$$Z = \left(\prod_{\text{plaquettes}} \int_0^{2\pi} \frac{d\theta_P}{2\pi} \right) \sum_{\{n_{ij}\}} e^{\sum_{\langle P, P' \rangle} (i(\theta_P - \theta_{P'}) n_{ij} - \beta K |n_{ij}|)}. \quad (3.4.5)$$

It is then easy to perform the sum over the variables n_{ij} to get

$$Z = \left(\prod_{\text{plaquettes}} \int_0^{2\pi} \frac{d\theta_P}{2\pi} \right) \prod_{\langle P, P' \rangle} \left(1 + 2e^{-\beta K} \cos(\theta_P - \theta_{P'}) \right), \quad (3.4.6)$$

which is the graphical representation, equation (3.3.3), of the partition function for the XY model. This shows that the dual of the restricted solid-on-solid model is the XY model with coupling $x = 2e^{-\beta K}$. Just as in the Kramers-Wannier duality of the Ising model this relates the low temperature behaviour of one model with the high temperature behaviour of its dual.

3.5 The Tonks gas: excluded volume

The final model we will consider is a packing model that captures some of the essential features of excluded volume interactions and leads to a minimal description of the isotropic-nematic transition. As we did with the Ising model we will start with a one-dimensional example that can be solved exactly and use the insights that we gain to direct approximate calculations in two dimensions.

The model we consider is the *Tonks gas*; a one-dimensional collection of impenetrable rods of length $2R$ confined to a line of length L . The interaction between rods is simple excluded volume with an infinite energy cost if any two rods overlap and zero energy otherwise. The partition function just calculates the number of allowed configurations, since any arrangement of rods with no overlaps is counted with unit weight and any arrangement in which two, or

more, rods overlap carries zero weight. Considering the k^{th} rod we note that its position satisfies $(2k-1)R \leq x_k \leq x_{k+1} - 2R$, so that the partition function is

$$Z = \int_{(2N-1)R}^{L-R} dx_N \cdots \int_{(2k-1)R}^{x_{k+1}-2R} dx_k \cdots \int_R^{x_2-2R} dx_1. \quad (3.5.1)$$

Introducing the change of variables $y_k = x_k - (2k-1)R$ this becomes

$$Z = \int_0^{L-2NR} dy_N \cdots \int_0^{y_{k+1}} dy_k \cdots \int_0^{y_2} dy_1, \quad (3.5.2)$$

$$= \frac{(L-2NR)^N}{N!}, \quad (3.5.3)$$

$$= \frac{L^N}{N!} \left(1 - \frac{1}{2}l_0 n\right)^N, \quad (3.5.4)$$

where $n = N/L$ is the number density and $l_0 = 4R$ is the *excluded length* - the length of the line surrounding the position of any given rod that is excluded to all the others. The free energy is thus

$$F = -k_B T \ln(Z) = k_B T N (\ln(n) - 1) - k_B T N \ln\left(1 - \frac{1}{2}l_0 n\right), \quad (3.5.5)$$

where we have made use of Stirling's formula $\ln(N!) \approx N \ln(N) - N$ to simplify the factorial. The first term here is the usual expression for an *ideal gas* - that is, a gas of non-interacting particles - while the second term reveals the effect of the excluded volume interactions.

The pressure of the Tonks gas is captured by the derivative of the free energy with respect to the size of the confining box

$$p = -\frac{\partial F}{\partial L} = k_B T n + k_B T \frac{\frac{1}{2}l_0 n^2}{1 - \frac{1}{2}l_0 n}. \quad (3.5.6)$$

This expression for the pressure as a function of the number density is known as the *equation of state*. It is singular when the number density takes the critical value $n_c = 2l_0^{-1}$ corresponding to close packing of the rods. Singularities in thermodynamic quantities, like the pressure, are the hallmark of phase transitions. In this case the transition is from a state in which the rods have the freedom to move, a *gas* (or liquid) phase, to one in which their positions are sharply defined and the rods are immobile, a *solid* phase.

Although it is not so simple to determine the partition function exactly in higher dimensions, nonetheless we can use the insights provided by the Tonks gas to obtain an approximate method of calculation. One problem that can be treated this way is the isotropic-nematic transition of a collection of impenetrable rods that are long and thin. The partition function for this problem, considering rods that can point in any direction in three dimensions, was first calculated by Onsager in 1949⁴. Like his calculation of the partition function for the two-dimensional Ising model this is long and technical and we will be satisfied with a simpler calculation that still captures the germaine features.

The model we consider is one of rods of length L and width D in two dimensions with the constraint that they can only have one of two orientations; vertical or horizontal. Naturally, this is an extreme simplification of the continuum of possible orientations but it still captures the essential idea. If there are equal numbers of vertically and horizontally oriented rods the system is isotropic, but if there are more with one orientation than the other then the system has spontaneously aligned and is nematic.

⁴L. Onsager, *Ann. New York Acad. Sci.* **51**, 627-659 (1949).

We do not do any calculations whatsoever and simply write down an approximation for the partition function by direct analogy with the result for the Tonks gas. Indeed, recall that the free energy of the Tonks gas is

$$F = k_B T N (\ln(n) - 1) - k_B T N \ln\left(1 - \frac{1}{2} l_0 n\right), \quad (3.5.7)$$

$$= k_B T N (\ln(n) - 1) + k_B T \frac{1}{2} l_0 N n + \dots \quad (3.5.8)$$

where the two terms have the natural interpretation as the ideal gas entropy and a first correction due to excluded volume interactions between two rods. Viewed this way we see that the free energy can be thought of as an expansion in powers of the number density n with coefficients that capture the excluded volume interactions between rods. The first such term $\sim \frac{1}{2} l_0 n$ describes interactions between a pair of rods and so is proportional to the number density, with the coefficient being simply one-half the excluded length. This structure should describe the general problem too and so by analogy we can write the free energy of our two-dimensional rod system as

$$F = k_B T f N (\ln(fn) - 1) + k_B T (1 - f) N (\ln((1 - f)n) - 1) \\ + k_B T \frac{1}{2} a_{VV} f^2 N n + k_B T a_{VH} f(1 - f) N n + k_B T \frac{1}{2} a_{HH} (1 - f)^2 N n, \quad (3.5.9)$$

where f is the fraction of rods that are aligned vertically. The first two terms are the ideal gas entropies for the vertical and horizontal rods, respectively, and the remaining terms correspond to the two-particle excluded area interactions. There are three types of these interactions: between two vertically aligned rods, between two horizontally aligned rods, and between one vertically aligned and one horizontally aligned rod. The factor of two associated to this last type is just a combinatorial factor. From simple geometry we can estimate these excluded areas as

$$a_{VV} = a_{HH} = 2L \times 2D, \quad (3.5.10)$$

$$a_{VH} = (L + D)^2, \quad (3.5.11)$$

so that the free energy becomes

$$F = k_B T f N (\ln(fn) - 1) + k_B T (1 - f) N (\ln((1 - f)n) - 1) \\ + k_B T 2LD N n + k_B T (L - D)^2 f(1 - f) N n. \quad (3.5.12)$$

Now the fraction of vertical rods can be determined from the condition that the system wants to minimise its free energy. In other words

$$\frac{\partial F}{\partial f} = 0 \quad \Rightarrow \quad \ln\left(\frac{f}{1 - f}\right) + (L - D)^2 (1 - 2f)n = 0. \quad (3.5.13)$$

This has the solution $f = \frac{1}{2}$, corresponding to the isotropic phase, for any value of the number density and shape anisotropy. But there are also non-trivial solutions. To see this, let $s = 2f - 1$ and expand the logarithm to get

$$2s + \frac{2}{3}s^3 + \dots - (L - D)^2 ns = 0. \quad (3.5.14)$$

From this we find that when the number density of the rods exceeds the critical value

$$n_c = \frac{2}{(L - D)^2}, \quad (3.5.15)$$

the isotropic phase becomes unstable with respect to an imbalance in the populations, or the onset of the nematic phase. Above this critical number density the order increases as

$$s = \pm \sqrt{\frac{3(n - n_c)}{2n_c}}, \quad (3.5.16)$$

so that we predict a continuous transition between the nematic and isotropic phases.

Chapter 4

Phase transitions

Phase transitions are perhaps the most dramatic and important macroscopic phenomena to emerge from a system of interacting particles. Many examples are familiar; the liquid-gas transition in boiling water, or the liquid-solid transition in freezing, the ferromagnetic transition, and the superconducting transition. But there are many more besides; a plethora of liquid crystalline phase transitions, percolation, the roughening transition for interfaces or growing surfaces, and the glass transition to give only a few. The importance of phase transitions is that they facilitate significant, or wholesale, changes to the bulk characteristics of a system and allow its properties to be completely redefined. Much of statistical mechanics is devoted to their study.

4.1 Minimising the free energy

Although the macroscopic behaviour of a large number of interacting constituents is determined from knowledge of the partition function, an exact calculation of Z is usually only available in limited cases and, apart from the simple one-dimensional cases we considered, these are typically long and technical. For cases where exact calculations are not yet available, and also for cases where they are, it is useful to be able to give an approximate calculation of the partition function that can still be enough to capture the macroscopic behaviour. The simplest of these is a *saddle point approximation*; the idea is to retain only the most relevant microscopic configurations in the partition function sum.

The basic idea behind the saddle point approximation of the partition function is to reexpress the sum over states as a sum over energies

$$Z = \sum_{\text{states}, \alpha} e^{-\beta E_\alpha} = \sum_{\text{energy}, \mathcal{E}} \Omega(\mathcal{E}) e^{-\beta \mathcal{E}} = \sum_{\text{energy}, \mathcal{E}} e^{-\beta(\mathcal{E} - k_B T \ln(\Omega))}, \quad (4.1.1)$$

where $\Omega(\mathcal{E})$ is the number of states with energy $\mathcal{E}$. In the exponent we can recognise $k_B \ln(\Omega)$ as the entropy of a microcanonical ensemble of states all with fixed energy $\mathcal{E}$ (Boltzmann's formula), so that the exponent is the free energy $\mathcal{F} = \mathcal{E} - TS$ of the microstates with energy $\mathcal{E}$. Now, both the energy $\mathcal{E}$ and the entropy S are extensive variables, increasing proportionately to the number of number of particles N (or to the volume), so that we may write $\mathcal{E} = N\varepsilon$ and $S = Ns$ with ε and s the energy and entropy per particle, respectively

$$Z = \sum_{\text{energy}, \mathcal{E}} e^{-\beta N(\varepsilon - Ts)}. \quad (4.1.2)$$

In the thermodynamic limit where the number of particles is very large ($N \sim 10^{23}$) this sum will be exponentially dominated by that term with the lowest free energy. Retaining only this term

should give a good estimate of the partition function in the thermodynamic limit and is called the saddle point approximation

$$Z \approx e^{-\beta N f_0}, \quad f_0 = \inf_{\varepsilon} (\varepsilon - Ts). \quad (4.1.3)$$

Thus we find that the partition function can be approximated by $e^{-\beta N f_0}$ where f_0 is chosen so as to minimise the free energy per particle. In other words, in the thermodynamic limit the system minimises the free energy.

4.2 Landau theory

Armed with this strategy for approximating the partition function we can give a general method, due to Landau, for describing the macroscopic behaviour of interacting systems and treating phase transitions: we minimise the free energy.

But what is the free energy? From what we have seen so far the free energy is just the logarithm of the partition function. But the problem is that we do not know the partition function then this does not help. Landau's insight was to realise that a parameterised expression for the free energy can be written down on entirely general grounds, appealing to symmetries and invariances. This can then be minimised with respect to the parameters to find the expected behaviour of the system. Before describing Landau theory in general let us revisit our simplified calculation of the isotropic-nematic transition to get a feeling for how it works.

We found earlier that the free energy of a collection of hard rods that can align only horizontally or vertically is

$$F = k_B T N f (\ln(fn) - 1) + k_B T N (1 - f) (\ln((1 - f)n) - 1) + k_B T N 2LDn + k_B T N (L - D)^2 f(1 - f)n, \quad (4.2.1)$$

and that the transition was characterised by $s = 2f - 1$ becoming non-zero. In other words s is a macroscopic measure of the alignment of the rods, which vanishes in the isotropic phase and becomes non-zero in the nematic phase. Any quantity with this property is called an *order parameter*. If we rewrite the free energy in terms of s , and expand about $s = 0$ ¹, it becomes (EXERCISE)

$$F = k_B T N \left(\text{const.} + \frac{1}{2}s^2 + \frac{1}{12}s^4 + \dots - \frac{n(L - D)^2}{4}s^2 + \mathcal{O}(ns^4, n^2s^2) \right), \quad (4.2.2)$$

where the constant term depends on the number density n but does not depend on s . All that is needed to describe the transition is the simple dependence on s : (i) only even powers of s appear in the free energy due to the symmetry between the horizontal and vertical orientations, and (ii) by increasing the number density we can change the sign of the lowest order term ($\sim s^2$). When this term changes sign there is a qualitative change in the macroscopic properties of the system; a phase transition.

The essence of Landau theory is contained in this example. We identify an *order parameter* – any physical quantity that vanishes in the one phase and becomes non-zero in the other – and then write a phenomenological expression for the free energy as an expansion in terms of all invariants of the order parameter consistent with the symmetries of the system and truncated at lowest non-trivial order². The art in Landau theory is in doing this well.

¹Recall that s grows continuously from zero, equation (3.5.16).

²We will not delve too deeply into what “lowest non-trivial order” means, but remark only that this is fully explained with the framework of the renormalisation group.

4.2.1 The liquid-gas transition

In the liquid-gas transition it is the density that distinguishes between the two phases, and so the density difference $\delta\rho = \rho - \rho_{\text{gas}}$ makes a natural choice for the order parameter; vanishing in the gas phase and becoming non-zero in the liquid phase. The density is a scalar and so the invariants that can enter into an expansion for the free energy are simply all powers of the density

$$F = \frac{A}{2}\delta\rho^2 - \frac{B}{3}\delta\rho^3 + \frac{C}{4}\delta\rho^4 + \dots \quad (4.2.3)$$

where A, B and C are phenomenological parameters and there is no term linear in $\delta\rho$ since we are expanding about equilibrium. This free energy then describes a *first order*, or *discontinuous*, transition from the gas $\delta\rho = 0$ to the liquid phase $\delta\rho \neq 0$ as the parameter A is varied. We will not study the properties of the transition here because we will see it shortly.

4.2.2 The ferromagnetic transition

Similarly, in the paramagnet-ferromagnet transition, the magnetisation $\mathbf{m}$, i.e., the average spin $\langle \mathbf{s}_i \rangle = \mathbf{m}$, serves as the order parameter. This time the order parameter is a vector and the free energy, which is a scalar, is constructed out of the available invariants, $m^2 = \mathbf{m} \cdot \mathbf{m}$. The Landau expansion for the free energy is

$$F = \frac{A}{2}m^2 + \frac{C}{4}(m^2)^2 + \dots \quad (4.2.4)$$

and describes a *continuous* transition from the paramagnetic phase with $m = 0$ to the ferromagnetic phase with $m \neq 0$ as the parameter A changes sign. Indeed, the saddle point approximation tells us that we should minimise F and the minimum is given by

$$Am + Cm^3 = 0. \quad (4.2.5)$$

When A is negative there is a solution with $m = \pm\sqrt{-A/C}$, corresponding to the ferromagnetic phase and indicating a phase transition at $A = 0$. Because A is the parameter that needs to be tuned to get the system through the phase transition, and in this case it is the temperature that we are varying, A is referred to as a *relevant thermal scaling variable*. It is explained in texts on the renormalisation group (e.g., Cardy, p.44) that relevant scaling variables are analytic close to the critical surface, so that we may write $A = a(T - T_c)$ with a a positive phenomenological constant.

4.2.3 The isotropic-nematic transition

Although it is typical to illustrate Landau theory with either the liquid-gas or ferromagnet transitions, we will not follow this well-trodden path but instead take as our primary illustration the isotropic-nematic transition. We will see that the discussion of Landau theory for the isotropic-nematic transition, which was first given by de Gennes³, reproduces the canonical presentation of both continuous and discontinuous transitions.

The first important issue is the identification of a suitable order parameter. The key point is that the order in the nematic phase is not vectorial, as it is in a magnet, but rather is a line field. The rods of our two-dimensional mini Onsager theory may align vertically, but whether they point up or down is immaterial. How are we to encode this in an expansion for the free energy? Recall that any physical quantity which distinguishes the nematic phase from the isotropic liquid can serve as an order parameter. Surely the most characteristic feature of nematics is that they are

³P. G. de Gennes, *Phys. Lett. A* **30**, 454-455 (1969); *J. Phys. France Colloq.* **32** (C5), 3-9 (1971).

optically active; after all this is why they are used to make displays! Now, the optical behaviour of continuous media is captured by the dielectric tensor ϵ , which relates the field inside a dielectric medium to the external field that has been applied, $\mathbf{D} = \epsilon \mathbf{E}$. The dielectric tensor, like any second rank tensor, can be decomposed into irreducible pieces that transform amongst themselves under rotations, namely

$$\epsilon = \frac{1}{3} \text{tr}(\epsilon) \mathbf{1} + \frac{1}{2}(\epsilon - \epsilon^T) + \left[\frac{1}{2}(\epsilon + \epsilon^T) - \frac{1}{3} \text{tr}(\epsilon) \mathbf{1} \right]. \quad (4.2.6)$$

The first term is isotropic and so appears in both the nematic and isotropic liquids. Also, under static conditions, the dielectric tensor is symmetric so that the skew component vanishes identically. Thus the distinction between the isotropic and nematic phases is captured by the *deviatoric* part of the dielectric tensor – the traceless symmetric part. As this is a quantity that distinguishes between the two phases, it serves as an order parameter⁴ and it is traditional in the literature to denote it by the symbol $\mathbf{Q}$.

The free energy density is then constructed as an expansion in terms of the invariants of the order parameter $\mathbf{Q}$, leading to the Landau-de Gennes free energy⁵

$$F = \frac{a(T - T_c)}{2} \text{tr}(\mathbf{Q}^2) - \frac{B}{3} \text{tr}(\mathbf{Q}^3) + \frac{C}{4} (\text{tr}(\mathbf{Q}^2))^2. \quad (4.2.7)$$

Dimensionality is important here, for it can swiftly be verified that in two dimensions the cubic invariant $\text{tr}(\mathbf{Q}^3)$ vanishes identically with profound effect on the nature of the transition. But first let us consider the most relevant case of three dimensions.

As the $\mathbf{Q}$ -tensor is symmetric it can be diagonalised, so that in the basis where it is diagonal we have

$$\mathbf{Q} = \begin{bmatrix} s & 0 & 0 \\ 0 & -\frac{1}{2}(s - b) & 0 \\ 0 & 0 & -\frac{1}{2}(s + b) \end{bmatrix}, \quad (4.2.8)$$

where s is called the *scalar order parameter* and b is known as the *biaxial order parameter*. The existence of a biaxial nematic, with $b \neq 0$, has long been anticipated theoretically but such materials have only recently been confirmed experimentally, and even then the biaxiality is weak. The vast majority of experimental systems find a nematic phase with *uniaxial* symmetry corresponding to $b = 0$ ⁶. Restricting to this case the free energy assumes the simple form

$$F = \frac{3a(T - T_c)}{4} s^2 - \frac{B}{4} s^3 + \frac{9C}{16} s^4, \quad (4.2.9)$$

with a non-zero cubic term, as in (4.2.3) for the liquid-gas system, implying that the transition is *first order*. Minimising to find the value for the order parameter we obtain

$$\partial_s F = \frac{9C}{4} s \left[s^2 - \frac{B}{3C} s + \frac{2a(T - T_c)}{3C} \right], \quad (4.2.10)$$

so that there are equilibrium solutions with $s = 0$, corresponding to the isotropic phase, and

$$s = \frac{B}{6C} \left(1 \pm \left[1 - \frac{24aC(T - T_c)}{B^2} \right]^{1/2} \right), \quad (4.2.11)$$

⁴Of course, there are other quantities that perform the same service, for instance the deviatoric part of the magnetic susceptibility tensor. See the book by de Gennes & Prost for more details.

⁵This contains all the independent invariants since, e.g., $\det(\mathbf{Q}) = \frac{1}{3} \text{tr}(\mathbf{Q}^3)$ and $\text{tr}(\mathbf{Q}^4) = \frac{1}{2} (\text{tr}(\mathbf{Q}^2))^2$.

⁶The Landau theory predicts just such a transition (with $b = 0$) for any free energy truncated at fourth order, as in (4.2.7).

where only the positive square root turns out to be relevant and describes the nematic phase.

Since the transition is first order it no longer takes place at the temperature $T = T_c$ where the coefficient of the quadratic term changes sign. Rather, the transition temperature is a little higher and corresponds to the point where the isotropic and nematic phases both have the same free energy. Writing the free energy as

$$F = \frac{9C}{16}s^2 \left[s^2 - \frac{4B}{9C}s + \frac{4a(T - T_c)}{3C} \right], \quad (4.2.12)$$

$$= \frac{9C}{16}s^2 \left[\left(s - \frac{2B}{9C} \right)^2 + \frac{4a(T - T_c)}{3C} - \frac{4B^2}{81C^2} \right], \quad (4.2.13)$$

allows us to identify the isotropic-nematic transition temperature as

$$T_{\text{IN}} - T_c = \frac{B^2}{27aC}, \quad (4.2.14)$$

as well as the jump $2B/9C$ in the scalar order parameter right at the transition.

Finally, it is a feature of discontinuous transitions that the transition shows some hysteresis, with each phase remaining metastable over a small range of temperatures upon either heating or cooling. The lowest temperature to which the isotropic phase can be cooled before it becomes linearly unstable is called the *limit of supercooling*. Similarly, the highest temperature at which the nematic is metastable is known as the *limit of superheating*. We may determine both by examining the Hessian

$$\partial_{ss}F = \frac{3a(T - T_c)}{2} - \frac{3B}{2}s + \frac{27C}{4}s^2. \quad (4.2.15)$$

Evaluating the Hessian at $s = 0$ determines the limit of supercooling of the isotropic phase to be $T = T_c$. Similarly, evaluating at the nematic minimum leads to an expression for the limit of superheating of

$$T_{\text{SH}} - T_c = \frac{B^2}{24aC}. \quad (4.2.16)$$

4.3 Continuous transitions and critical exponents

While the isotropic-nematic transition in three dimensions provides an illustration of first order phase transitions, the two-dimensional version serves as an example of a continuous transition.

In a basis where the $\mathbf{Q}$ -tensor is diagonal it takes the form

$$\mathbf{Q} = \begin{bmatrix} s & 0 \\ 0 & -s \end{bmatrix}, \quad (4.3.1)$$

where s is the scalar order parameter, and the free energy becomes

$$F = a(T - T_c)s^2 + Cs^4, \quad (4.3.2)$$

in perfect analogy to what we found from our simplified calculation of the partition function for a system of impenetrable rods, equation (4.2.2). The equilibrium state is the one with minimum free energy, so

$$\frac{\partial F}{\partial s} = 0 = 2a(T - T_c)s + 4Cs^3, \quad (4.3.3)$$

$$\Rightarrow \quad s = \begin{cases} 0 & T > T_c, \\ \pm \sqrt{\frac{a(T_c - T)}{2C}} & T \leq T_c. \end{cases} \quad (4.3.4)$$

Table 4.1: Summary of the conventional equilibrium critical exponents for a continuous phase transition. ϕ denotes the order parameter, h a relevant field to which it couples and d is the spatial dimension.

exponent	definition	observable
α	$C_V \sim T - T_c ^{-\alpha}$	heat capacity
β	$\phi \sim T - T_c ^\beta$	order parameter (temperature)
γ	$\chi \sim T - T_c ^{-\gamma}$	susceptibility
δ	$\phi \sim h ^{1/\delta}$ at $T = T_c$	order parameter (field)
ν	$\xi \sim T - T_c ^{-\nu}$	correlation length
η	$\langle \phi(r)\phi(r') \rangle \sim r - r' ^{-(d-2)-\eta}$	correlation function

There is no order at high temperature, $T > T_c$, and the material is in the isotropic phase, but at low temperatures, $T < T_c$, the equilibrium state is the nematic phase. The order parameter grows continuously from zero as a power law $s \sim |T_c - T|^\beta$ with a characteristic exponent $\beta = \frac{1}{2}$ according to this mean field description. Such continuous onset of order is characteristic of *continuous phase transitions*, of which we might consider the two-dimensional isotropic-nematic transition to be a prototypical example. The exponent β is the first of a series of power law exponents, called *critical exponents*, that are fundamental, and universal, attributes of continuous transitions.

For transitions like the isotropic-nematic transition or the paramagnet-ferromagnet transition there are six conventional equilibrium critical exponents, whose definitions we summarise in Table 4.1. The first of these describes the behaviour of the heat capacity close to the critical point (transition temperature $T = T_c$). In the present case, since $s \sim |T - T_c|^{1/2}$ the free energy has the temperature dependence $F \sim -(T_c - T)^2$ just below the transition and the heat capacity behaves like

$$C_V = -k_B T \frac{\partial^2 F}{\partial T^2} \sim 2k_B T_c. \quad (4.3.5)$$

Thus the heat capacity is finite at T_c (although it does have a discontinuity – EXERCISE) and the critical exponent is $\alpha = 0$.

The coupling of a magnetic field to the liquid crystal can be accounted for by a term $-\Delta\chi \mathbf{H} \cdot \mathbf{Q} \cdot \mathbf{H}$ in the free energy density, where $\Delta\chi$ is (proportional to) the difference in the magnetic susceptibility parallel and perpendicular to the director. If we assume this is positive then the molecules will align parallel to the field so that the contribution to the free energy density becomes $-\Delta\chi H^2 s$. The quantity $\Delta\chi H^2$ that couples linearly to the order parameter is known as the *conjugate field*. We shall denote it by the symbol h . Minimising the energy in the presence of the field we now find

$$\frac{\partial F}{\partial s} = 0 = 2a(T - T_c)s + 4Cs^3 - h, \quad (4.3.6)$$

and precisely at the transition $T = T_c$ we have the scaling $s \sim h^{1/\delta}$ with the critical exponent $\delta = 3$. Away from T_c we see paramagnetic response with $s \sim h|T_c - T|^{-1}$ so that the susceptibility $\chi = \frac{\partial s}{\partial h} \sim |T_c - T|^{-1}$ giving the critical exponent $\gamma = 1$.

Finally we may record for completeness that within this mean field calculation the correlation exponents are $\nu = \frac{1}{2}$ and $\eta = 0$, although we do not quite have the tools to demonstrate this at present.

4.4 Orientational order and gradient energy

So far we have only given an explicit description of the magnitude of the order, s , and we have not yet made mention of the orientational order that is the real characteristic feature of nematics, or ferromagnets. This is a major shortcoming and it is hard to imagine that the orientational degrees of freedom are unimportant to the thermodynamics. Likewise, the foregoing description of Landau theory was restricted to *homogeneous* systems without any spatial variations. This might be appropriate when the spatial variations are small, or energetically suppressed, but this is not always so as we will now illustrate. We use the nematic liquid crystal for continuity, but the description applies generally to any systems that spontaneously break a continuous symmetry.

The orientational degrees of freedom of the nematic phase are captured by the order parameter, $\mathbf{Q}$. Considering the two-dimensional case for definitiveness, the general form of the $\mathbf{Q}$ -tensor is

$$\mathbf{Q} = \begin{bmatrix} Q_{xx} & Q_{xy} \\ Q_{xy} & -Q_{xx} \end{bmatrix}, \quad (4.4.1)$$

and a comparison to the diagonal form reveals that

$$\det(\mathbf{Q}) = -Q_{xx}^2 - Q_{xy}^2 = -s^2. \quad (4.4.2)$$

Thus a natural parameterisation is to write the $\mathbf{Q}$ -tensor in the form

$$\mathbf{Q} = s \begin{bmatrix} \cos(2\theta) & \sin(2\theta) \\ \sin(2\theta) & -\cos(2\theta) \end{bmatrix}, \quad (4.4.3)$$

where θ is the angle the molecules make relative to some reference direction, the x -axis in this case. One may check that the vector

$$\mathbf{n} = \begin{bmatrix} \cos(\theta) \\ \sin(\theta) \end{bmatrix}, \quad (4.4.4)$$

is an eigenvector of $\mathbf{Q}$ with eigenvalue s . It is called the *director field* and it gives the direction along which the molecules align in the nematic phase. In fact, the $\mathbf{Q}$ -tensor only determines this direction up to a sign – $-\mathbf{n}$ is as good a choice as $+\mathbf{n}$ – so that really we should be talking about the pair $\{\mathbf{n}, -\mathbf{n}\}$ or the line field (element of $\mathbb{RP}^1$) that they define. Nonetheless, the universal convention in the literature is to simply use the vector $\mathbf{n}$ and to impose the equivalence $\mathbf{n} \sim -\mathbf{n}$ by hand whenever necessary. In terms of the director, the $\mathbf{Q}$ -tensor takes the general form

$$\mathbf{Q} = 2s \left(\mathbf{n} \otimes \mathbf{n} - \frac{1}{2} \mathbf{1} \right). \quad (4.4.5)$$

This makes explicit that the order parameter captures both the magnitude of the order s and the direction of alignment $\mathbf{n}$. However, the free energy, equation (4.3.2), is insensitive to this alignment, being independent of $\mathbf{n}$ or of the angle θ . This is as it should be: there is no reason why the molecules should align along one direction in preference to any other, so there is no reason for the free energy density to depend on the angle θ . The orientational order emerges spontaneously.

But there is a consequence to this. If I rotate all the molecules to point in some other direction θ' the free energy will not change. In other words a *uniform* rotation (or change in θ) costs *no* energy. This should be contrasted with making a uniform change in the magnitude of the order s , which does cost energy. (EXERCISE: calculate this energetic cost.) This gives rise to a serious issue: if it costs no energy to change the alignment of all of the rods then why is the direction that they point in well defined? To answer this question it is important to consider fluctuations in the alignment and configurations where the order is not perfectly homogeneous.

Consider a configuration in which the orientation varies with position, $\theta = \theta(\mathbf{x})$. Since uniform changes in θ cost no energy we can expect that *slow* variations will carry only a modest energy cost and, moreover, that this energy cost will vanish as the lengthscale over which the variation occurs gets ever larger. This is captured by a dependence of the energy on gradients $\nabla\theta$ and the simplest form for such a *gradient energy* is

$$F_{\text{gradient}} = \int_{\Omega} \frac{1}{2} K |\nabla\theta|^2. \quad (4.4.6)$$

Combined with equation (4.2.7) or (4.3.2) for the magnitude of the order this provides the basis for the description of ordered materials, taking into account slow spatial variations.

Similar gradient energies can be constructed to account for spatial variations in any phase transition; for instance, in the liquid-gas transition we have

$$F_{\text{liquid-gas}} = \int_{\Omega} \frac{1}{2} K |\nabla\delta\rho|^2 + \frac{a(T - T_c)}{2} \delta\rho^2 - \frac{B}{3} \delta\rho^3 + \frac{C}{4} \delta\rho^4, \quad (4.4.7)$$

and for the ferromagnet transition the appropriate free energy is

$$F_{\text{ferromagnet}} = \int_{\Omega} \frac{1}{2} K |\nabla\mathbf{m}|^2 + \frac{a(T - T_c)}{2} |\mathbf{m}|^2 + \frac{C}{4} |\mathbf{m}|^4. \quad (4.4.8)$$

4.5 Fluctuations and quasi-long-range order in the XY model

The foregoing discussion of spatial variations in the orientation and the associated gradient energy allow us to give a terse description of an intriguing and influential transition, the *Berezinskii-Kosterlitz-Thouless* transition⁷ of the XY model. This transition illustrates two important general concepts. First, that spatial variations qualitatively alter the nature of a phase transition below a certain dimension. And second, the appearance of topological defects in ordered phases. We start with how slow variations in the order affect the orientational correlation function.

In the XY model the order parameter is a vector $\mathbf{m}$. The foregoing discussion considered its magnitude $s = |\mathbf{m}|$ and we saw that at a special temperature s changes from being zero to being non-zero through a continuous transition. Now we want to consider the orientational order. Let us denote by $\mathbf{n}$ a unit vector pointing in the direction of the local magnetisation, i.e., $\mathbf{m} = s\mathbf{n}$. We have just argued that if $\mathbf{n}$ varies very slowly from one point to another that should cost a vanishingly small energy, since uniform rotations cost no energy. So what we would like to know is; if we include these slowly varying configurations in our estimate for the partition function how will they effect the orientational correlation function $\langle \mathbf{n}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{y}) \rangle$? Said more plainly, do the spins point in the same direction at different places?

Recall our simple expectation. In the high temperature phase we expect the orientation to be correlated only over a modest length scale ξ and thereafter to become random. In this case the correlation function decays exponentially, $\sim e^{-|\mathbf{x}-\mathbf{y}|/\xi}$, and we have short range order. But at low temperatures, if there is a non-zero magnetisation because the spins point in a common direction, then the correlation function will tend to a non-zero limit for large separations and we have a state of long range order.

Let us now calculate the correlation function explicitly, using the gradient energy (4.4.6) to provide the Boltzmann weight for configurations with slow spatial variations about a supposed

⁷V. L. Berezinskii, Sov. Phys. JETP **32**, 493–500 (1971) [ZhETF **59**, 907–920 (1970)]; Sov. Phys. JETP **34**, 610 (1972) [ZhETF **61**, 1144–1156 (1971)]. J. M. Kosterlitz and D. J. Thouless, J. Phys. C: Solid State Phys. **5**, L124–L126 (1972); J. Phys. C: Solid State Phys. **6**, 1181–1203 (1973).

uniformly aligned state. This is given by

$$\langle \mathbf{n}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{y}) \rangle = \langle \cos(\theta(\mathbf{x}) - \theta(\mathbf{y})) \rangle = \Re \langle e^{i(\theta(\mathbf{x}) - \theta(\mathbf{y}))} \rangle = \frac{1}{Z} \sum_{\{\theta(\mathbf{r})\}} e^{i(\theta(\mathbf{x}) - \theta(\mathbf{y}))} e^{-\beta \int d^d r \frac{K}{2} |\nabla \theta|^2}, \quad (4.5.1)$$

where the sum is over all field configurations. This is an example of a statistical field theory, but we do not need any of the formal machinery of that subject for our purposes. Indeed it is sufficient to work only with the exponent in the sum over states. Introducing a Fourier decomposition

$$\theta(\mathbf{r}) = \int \frac{d^d q}{(2\pi)^d} e^{i\mathbf{q} \cdot \mathbf{r}} \tilde{\theta}(\mathbf{q}), \quad (4.5.2)$$

the exponent can be written as (EXERCISE)

$$-\frac{1}{2} \int \frac{d^d q}{(2\pi)^d} \tilde{\theta}(-\mathbf{q}) [\beta K q^2] \tilde{\theta}(\mathbf{q}) + i \int \frac{d^d q}{(2\pi)^d} [e^{-i\mathbf{q} \cdot \mathbf{x}} - e^{-i\mathbf{q} \cdot \mathbf{y}}] \tilde{\theta}(\mathbf{q}). \quad (4.5.3)$$

By completing the square we can rewrite this in the form (EXERCISE)

$$-\frac{1}{2} \int \frac{d^d q}{(2\pi)^d} \tilde{\vartheta}(-\mathbf{q}) [\beta K q^2] \tilde{\vartheta}(\mathbf{q}) - \frac{1}{2} \int \frac{d^d q}{(2\pi)^d} [e^{-i\mathbf{q} \cdot \mathbf{x}} - e^{-i\mathbf{q} \cdot \mathbf{y}}] \frac{k_B T}{K q^2} [e^{i\mathbf{q} \cdot \mathbf{x}} - e^{i\mathbf{q} \cdot \mathbf{y}}], \quad (4.5.4)$$

where we have defined a new variable $\tilde{\vartheta}(\mathbf{q}) = \tilde{\theta}(\mathbf{q}) - i[e^{i\mathbf{q} \cdot \mathbf{x}} - e^{i\mathbf{q} \cdot \mathbf{y}}] \frac{k_B T}{K q^2}$. As this is just a relabelling of the variables describing our configurations⁸ the sum over $\tilde{\vartheta}$ is the same as the sum over $\tilde{\theta}$ and the first term simply gives the partition function Z . Thus we find that the orientational correlation function is

$$\langle \mathbf{n}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{y}) \rangle = \exp \left\{ -\frac{k_B T}{K} \int \frac{d^d q}{(2\pi)^d} \frac{1 - \cos(\mathbf{q} \cdot (\mathbf{x} - \mathbf{y}))}{q^2} \right\}. \quad (4.5.5)$$

The integral is an interesting one. In principle we should regularise its behaviour at both small and large q . The small q limit is $2\pi/L$ where L is the linear size of the system and turns out to be unimportant, i.e., we can set $L \rightarrow \infty$ without difficulty. The large q cut-off $2\pi/a$ is associated with the typical molecular size (or lattice constant) a and is important – the integral is ultraviolet divergent without it. Most importantly the behaviour of the integral depends on the dimension, which is why we have left it unspecified at this stage. We will consider explicitly only the case of two dimensions, $d = 2$, leaving the three-dimensional version as an exercise.

In two dimensions the integral is

$$\int \frac{d^2 q}{(2\pi)^2} \frac{1 - \cos(\mathbf{q} \cdot (\mathbf{x} - \mathbf{y}))}{q^2} = \Re \frac{1}{(2\pi)^2} \int_0^{2\pi/a} q^{-1} dq \int_0^{2\pi} d\alpha [1 - e^{iq|\mathbf{x}-\mathbf{y}|\cos(\alpha)}], \quad (4.5.6)$$

$$= \frac{1}{2\pi} \int_0^{2\pi|\mathbf{x}-\mathbf{y}|/a} dq \frac{1 - J_0(q)}{q}, \quad (4.5.7)$$

where J_0 is the Bessel function of the first kind. The asymptotic behaviour of the integral can be extracted by splitting the range of integration as

$$\begin{aligned} \int_0^{2\pi|\mathbf{x}-\mathbf{y}|/a} dq \frac{1 - J_0(q)}{q} &= \int_0^1 dq \frac{1 - J_0(q)}{q} - \int_1^{2\pi|\mathbf{x}-\mathbf{y}|/a} q^{-1} J_0(q) dq \\ &\quad + \int_1^{2\pi|\mathbf{x}-\mathbf{y}|/a} q^{-1} dq. \end{aligned} \quad (4.5.8)$$

⁸The Jacobian for this transformation is unity.

Here, the first two integrals are both finite even as we take away the cut-off and only the third term contains a divergence. Thus we have

$$\int_0^{2\pi|\mathbf{x}-\mathbf{y}|/a} dq \frac{1 - J_0(q)}{q} = \ln\left(\frac{2\pi|\mathbf{x}-\mathbf{y}|}{a}\right) + \gamma, \quad (4.5.9)$$

where γ denotes the regular part, and the correlation function is

$$\begin{aligned} \langle \mathbf{n}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{y}) \rangle &= \exp\left\{-\frac{k_B T}{2\pi K} \ln\left(\frac{2\pi|\mathbf{x}-\mathbf{y}|e^\gamma}{a}\right)\right\}, \\ &= \left(\frac{a}{2\pi e^\gamma |\mathbf{x}-\mathbf{y}|}\right)^{k_B T / 2\pi K}. \end{aligned} \quad (4.5.10)$$

Thus the correlation function decays to zero at large separations but it does so only algebraically, which is a signifier of *quasi long range order*. What we have found is that (in sufficiently low spatial dimension) allowing for fluctuations in the alignment about a putative preferred direction can lead to a situation where at very large distances the fluctuations are so severe as to destroy any global alignment in the system. This phenomenon goes by the name of *fluctuation induced destruction of long range order* and the dimension in which this happens, $d = 2$ in this case, is known as the *lower critical dimension*.

4.5.1 Vortices and the Berezinskii-Kosterlitz-Thouless transition

The nature of the low temperature phase in the XY model, and of the transition between exponential decay of correlation functions (short range order) at high temperatures and the algebraic decay at low temperatures found in the previous section, was first described by Berezinskii and, independently, by Kosterlitz and Thouless. We record only a very coarse description of the transition, going no further than an estimate of the transition temperature.

The key idea in understanding the behaviour is the realisation that there are configurations in which the spins vary slowly from place to place, but which are fundamentally different from the uniform state. These are known as *vortices*. They are configurations in which the orientation rotates about a point of singularity, or *topological defect*. Representative configurations are given by the functions⁹

$$\theta(\mathbf{x}) = s \operatorname{Im} \ln(z) + \theta_0 = s\phi + \theta_0, \quad (4.5.11)$$

where $z = x + iy$ is a complex coordinate, θ_0 is a constant offset, and ϕ is the usual polar angle in an equivalent representation. The number s is an integer, known as the *winding number* of the vortex, which we will describe more fully in the next section. (EXERCISE: sketch some vortex configurations for different values of s .)

With this idea for the relevant configurations, we can give an argument due to Kosterlitz and Thouless for the transition temperature of the XY model. The argument is based on giving an estimate of the free energy of an isolated vortex. Using (4.5.11) we can calculate the energy of a vortex

$$E_{\text{vortex}} = \int d^2x \frac{K}{2} |\nabla \theta|^2 = \int_0^{2\pi} d\phi \int_a^L dr \frac{K}{2} \frac{s^2}{r^2} = \pi K s^2 \ln\left(\frac{L}{a}\right), \quad (4.5.12)$$

where a is a short length scale cutoff comparable to the molecular size (or the size of the vortex core) and L is the linear size of the system. On the other hand, such a vortex can be placed at any of $(L/a)^2$ sites and so has an entropy $S = 2k_B \ln(L/a)$. It follows that the free energy of the vortex is

$$F_{\text{vortex}} = E - TS = \left[\pi K s^2 - 2k_B T\right] \ln\left(\frac{L}{a}\right). \quad (4.5.13)$$

⁹Recall $\mathbf{n} = [\cos(\theta), \sin(\theta)]^T$.

We can think about this as follows: At high temperature F_{vortex} will be negative so that there is a benefit to creating free vortices. The typical configuration is one in which vortices are abundant and their presence disorders the spins so that the material is paramagnetic. At low temperatures, however, F_{vortex} is positive and vortices are suppressed. This is not quite the right way to think about it since we have seen from the correlation function (4.5.10) that the spins are not simply aligned. Rather, we might say that at low temperatures the vortices are held together tightly in vortex-antivortex pairs. As the temperature is raised the typical separation between the vortices in these dipoles increases until at some critical temperature there is an ‘*unbinding transition*’ and vortices are able to move freely. Our estimate for the free energy predicts that the transition temperature is (the $s = \pm 1$ vortices unbind first)

$$T_{\text{BKT}} = \frac{\pi K}{2k_B}. \quad (4.5.14)$$

This is the Berezinskii-Kosterlitz-Thouless transition.

4.6 Topological defects

The vortices in the XY model are the first example of one of the most ubiquitous, distinctive and dramatic properties to emerge in the collective behaviour of systems of large numbers of interacting components. These are *topological defects*. A topological defect is a point, or line (or set), at which the order is discontinuous, or ill-defined, and which is preserved under any continuous deformation of the system. In addition to the role they play in determining the nature of the transition in the XY model, they exert a fundamental influence over a wide variety of phenomena, including fracture and the strength of solids, type II superconductivity, coarsening of ordered media, and a plethora of textures in liquid crystalline phases.

The classification of the topological defects that any particular system can possess is exemplified by the vortices of the XY model. It is based on measuring the variation of the order parameter on a *Burgers circuit* encircling the defect. This is just any simple loop around the defect point on which we take a measurement. At each point of the Burgers circuit we record the local orientation of the spins (or value of the order parameter). Moving around the circuit the orientation changes and the full record of this change constitutes a map from the points of the measuring loop (S^1) to the space of possible orientations of the spins (S^1)

$$\begin{array}{ccc} \left\{ \begin{array}{c} \text{points of the} \\ \text{measuring circuit} \end{array} \right\} & \longrightarrow & \left\{ \begin{array}{c} \text{possible spin} \\ \text{orientations} \end{array} \right\} \\ S^1 & \longrightarrow & S^1 \end{array}$$

Since a complete traversal of the Burgers circuit brings us back to where we started, the spin orientation (or local value of the order parameter) must also return to its initial value. What this means is that the total rotation must be an integer multiple of 2π . This integer is known as the *winding number* and is a unique, and complete, descriptor of the defect type. Because it is an integer, it is preserved under any continuous deformation, which gives the defect its topological nature.

At a more formal level, the classification of configurations up to continuous deformations leads to their identification with the distinct *homotopy classes* of continuous maps and bring the mathematical subject of *homotopy theory* into the remit of statistical physics. In the case of vortices, the measurement of the local orientation at each point of a Burgers circuit is equivalent to a continuous map $S^1 \rightarrow S^1$, so that the vortices are labelled by the homotopy classes of these maps. This set of homotopy classes is known as the *fundamental group* of the space of possible spin

orientations, denoted $\pi_1(S^1)$, and our simple notions about integer winding numbers corresponds to the well-known result $\pi_1(S^1) \cong \mathbb{Z}$.

What about other systems? Are there topological defects in other ordered phases? And if so, how are they classified? Perhaps the simplest case is the two-dimensional nematic, which is similar to the magnetisation of the XY model in all regards, except that the order is characterised by a line element rather than a vector so that $\mathbf{n} \sim -\mathbf{n}$. It is not hard to see that there are topological defects here too – they are known as *disclinations* rather than vortices, but this is just jargon – and that they have the same appearance as those of the XY model. They too can be classified by taking measurements on any Burgers circuit encircling the defect, and again this provides us with a map from the points of the measuring loop (S^1) to the space of possible orientations of the line elements (this is the *real projective line* $\mathbb{RP}^1$)

$$\begin{array}{ccc} \left\{ \begin{array}{c} \text{points of the} \\ \text{measuring circuit} \end{array} \right\} & \longrightarrow & \left\{ \begin{array}{c} \text{possible line} \\ \text{orientations} \end{array} \right\} \\ S^1 & \longrightarrow & \mathbb{RP}^1 \end{array}$$

The only difference is that we recover the initial orientation after a rotation of any multiple of π not 2π because of the symmetry under $\mathbf{n} \sim -\mathbf{n}$. Thus the allowed winding numbers are any *half-integer*¹⁰. This is a striking prediction for experiment: in two-dimensional nematic liquid crystals there are topological defects with *half-integer* winding numbers, whereas in magnetic systems there are only integer strength defects. Indeed, precisely this feature is readily seen in any ordinary liquid crystal in the laboratory.

However, the distinction is even more dramatic in three dimensions. A naive extension of the two-dimensional vortices into three dimensions is simply to ‘cross them with an interval’ to give a *line defect* along the z -axis whose orientation at any value of z is just equation (4.5.11). This is naive because it can be removed by a continuous rotation of all the spins. Simply give them all a component in the $+z$ -direction. At zero rotation we have the apparent singular vortex line. But after a $\pi/2$ rotation they spins simply all point along the z -direction and there is no defect. This can be done continuously, for instance through the family of configurations

$$\mathbf{n} = \left[\cos\left(\frac{\pi}{2}t\right) \cos(s\phi), \cos\left(\frac{\pi}{2}t\right) \sin(s\phi), \sin\left(\frac{\pi}{2}t\right) \right]^T, \quad (4.6.1)$$

where t is a parameter ranging from 0 to 1¹¹. We may also see this in terms of the orientations recorded on any Burgers circuit. This measurement corresponds, much as before, to a continuous map from the points of the measuring loop (S^1) to the space of possible orientations of the spins in three-dimensions (this is the two-sphere S^2)

$$\begin{array}{ccc} \left\{ \begin{array}{c} \text{points of the} \\ \text{measuring circuit} \end{array} \right\} & \longrightarrow & \left\{ \begin{array}{c} \text{possible spin} \\ \text{orientations} \end{array} \right\} \\ S^1 & \longrightarrow & S^2 \end{array}$$

This is nothing more nor less than a closed loop on the surface of a sphere, the shape of which we may freely change, provided we do so continuously, as this just corresponds to a continuous deformation of the spins. The uniform configuration where the spins all point in the same direction corresponds to a constant loop on the sphere that simply remains at a single point. Non-trivial line defects correspond to loops on the surface of the sphere that cannot be converted

¹⁰At the formal level this corresponds to the result $\pi_1(\mathbb{RP}^1) \cong \frac{1}{2}\mathbb{Z}$.

¹¹Such a continuous transformation is called a *homotopy*.

into this constant one. But there are none¹²! In the words of Sidney Coleman; you “can’t lasso a basketball”. There are *no* line defects in a three-dimensional magnet.

What about in a nematic liquid crystal? As in two dimensions, the only change is that the order is that of a line element rather than a vector, so that we have the equivalence relation $\mathbf{n} \sim -\mathbf{n}$. Thinking about measurements on a Burgers circuit in the usual way we obtain a continuous map from the points of the measuring loop (S^1) to the space of possible orientations of a line element in three-dimensions (this is the *real projective plane* $\mathbb{RP}^2$)

$$\begin{array}{ccc} \left\{ \begin{array}{c} \text{points of the} \\ \text{measuring circuit} \end{array} \right\} & \longrightarrow & \left\{ \begin{array}{c} \text{possible line} \\ \text{orientations} \end{array} \right\} \\ S^1 & \longrightarrow & \mathbb{RP}^2 \end{array}$$

It is easiest to think in terms of what the image of this map looks like on $\mathbb{RP}^2$. It is a closed loop. As in the magnetic case, a uniform configuration of the nematic corresponds to a closed loop that just sits motionless at a single point on $\mathbb{RP}^2$. The question is; are there any loops that can *not* be continuously twisted, turned and shrunk to become equivalent to this one? It turns out that there are! The real projective plane may be imagined as the usual two-sphere with antipodal points ($\mathbf{n}$ and $-\mathbf{n}$) identified. The loop that connects antipodal points on S^2 cannot be shrunk to a single point no matter how hard you try. Thus there is at least one topological line defect in nematics. And it turns out that this is all there is (EXERCISE: see if you can convince yourself that this is true)¹³. The formal statement is that $\pi_1(\mathbb{RP}^2) \cong \mathbb{Z}/2\mathbb{Z}$. Again, this is a remarkable and profound prediction for experiment; there are *no* line defects in three-dimensional magnets, but there *are* in three-dimensional nematic liquid crystals. Needless to say, it is amply verified.

Several other ordered materials exhibit line defects in three-dimensions – for instance, superconductors, superfluids, crystals, and smectic liquid crystals – while others do not – for instance, uniaxial magnets (as in the Ising model) – but we leave it to the interested reader to pursue the details further.

Finally, as a last comment, we can’t help but mention that although there are no *line* defects in a three-dimensional magnet, there *are* defects. These are *point defects*, often known colloquially as *hedgehogs*. The simplest example is the radial configuration $\mathbf{n} = \mathbf{e}_r$ that just points radially outwards from the singular point. These point defects are classified in an entirely analogous manner to the line defects we have just discussed, or the vortices we started out with, by taking a measurement of the orientation on some measuring circuit surrounding the defect. Of course a point cannot be surrounded by a loop in three dimensions; you need a sphere to do that. Thus for point defects we take our measurements on a sphere surrounding the point¹⁴ and by doing so obtain a continuous map from the points of the measuring surface (S^2) to the space of possible orientations of a unit vector in three-dimensions (S^2)

$$\begin{array}{ccc} \left\{ \begin{array}{c} \text{points of the} \\ \text{measuring surface} \end{array} \right\} & \longrightarrow & \left\{ \begin{array}{c} \text{possible spin} \\ \text{orientations} \end{array} \right\} \\ S^2 & \longrightarrow & S^2 \end{array}$$

¹²Hopefully drawing a few pictures here will convince you that the result is true, although of course this is a long way short of a proof. The formal result is that $\pi_1(S^2) \cong 1$.

¹³For the physicists: this is not unrelated to the fact that there are physical objects which behave non-trivially under 2π rotations, but a 4π rotation is always trivial. The difference is that this case concerns the rotation group $SO(3)$ instead of the space of distinct line elements in three dimensions. But as a space $SO(3)$ is the same as $\mathbb{RP}^3$ – the three-sphere with antipodal points identified –, which is why they are similar.

¹⁴Again for the physicists, think about the use of Gaussian surfaces to measure enclosed charges in electrostatics. It is exactly the same.

The point defects are classified by the *distinct* measurements that can be made. As before, two measurements are considered equivalent if one can be converted to the other by a continuous deformation of the spins, and are distinct if no such continuous conversion is possible. At a formal level they correspond to the homotopy classes of maps $S^2 \rightarrow S^2$, which collectively form the *second homotopy group* $\pi_2(S^2)$. The result, which we will not explain in any detail, is that there are an infinite number of distinct point defects¹⁵, which may be labelled by a generalisation of the winding number, known simply as the *degree* of the map. The simple radial configuration $\mathbf{n} = \mathbf{e}_r$ has degree 1.

¹⁵In homotopy theory this is the result $\pi_2(S^2) \cong \mathbb{Z}$.

Chapter 5

Scaling

Scaling is the name given to the set of ideas that arise in response to attempts to understand the behaviour of materials in the vicinity of continuous phase transitions. Its aim is to provide a framework for describing, and understanding, the following general observations:

- (i) Many quantities that are measured in experiments show *power law* dependence on control variables. For instance this is true for the dependence of the order parameter on both the temperature deviation $T - T_c$ and the strength of an applied field, the dependence of the heat capacity on $T - T_c$, or the dependence of the susceptibility on $T - T_c$.
- (ii) The exponents of these power laws – the critical exponents – are *universal*, meaning they depend on the nature of the transition but not on the specific material.
- (iii) The power law behaviour does not depend on $T - T_c$ and $|h|$ separately, but only on a particular ratio of them. For instance the order parameter has the behaviour

$$s(T - T_c, h) \sim |T - T_c|^\beta f\left(\frac{|h|}{|T - T_c|^\Delta}\right),$$

where f is a universal function known as a *scaling function*. This means that a *two* parameter family of measurements, covering different values of both $T - T_c$ and h can, if plotted in the correct way, be collapsed onto a *single* curve. This is known as *scaling collapse*.

- (iv) The conventional critical exponents $(\alpha, \beta, \gamma, \delta, \dots)$ are not independent, but satisfy non-trivial relations. For instance, $\alpha + 2\beta + \gamma = 2$ or $\gamma = \beta(\delta - 1)$.

It is one of the major triumphs of statistical physics that an understanding of these general observations was developed in the 1960s and developed into a sophisticated set of tools (known as the renormalisation group) in the early 1970s. But it has grown and expanded considerably since then and today the ideas of scaling and power law behaviour are applied to all sorts of problems, such as surface growth processes, general non-equilibrium phenomena, earthquake statistics, stock market crashes, major social changes, and flocking, swarming and other forms of collective motion. In these cases, the quantities considered and variables they depend on are different, and the foundation upon which they are based is not as solid as the original problems of continuous phase transitions, but the idea and the strategy of analysis is the same. We want to predict the values of critical exponents, determine any relations between them and establish the existence and consequences of a suitable scaling function. As an illustration, we are going to focus on the particular problem of surface growth, or fluctuating interfaces, to give an example of time-dependent, non-equilibrium processes. But first, to provide some insight and a guide to phenomenology, we describe the swelling of a collapsed polymer, or the behaviour of a random walk of fixed length.

Suppose we have a polymer chain of length L that is initially squeezed into a very tight ball¹. If we release the chain and let it expand, how will the size of the polymer depend on the time from the release? A standard measure of the size is the *radius of gyration* or root mean square of the position of the chain relative to its centre of mass. In the simplest case of a Gaussian chain, the conformations of the polymer just correspond to ordinary random walks, and so its size can be taken from the statistics of random walks. At short times the polymer will swell freely, by which we mean that its size (or radius of gyration) should be independent of the length of the chain. However, it will depend on the time since it was released. Since the root mean square displacement of a random walk grows diffusively with time $\Delta x \sim t^{1/2}$, we expect that the size of the polymer will also show this early time behaviour, $R_g(L, t) \sim t^{1/2}$. On the other hand, this sort of growth cannot continue forever, since at very late times the size of the polymer will ultimately be limited by the length of the chain. Indeed, from the same random walk statistics we expect the late time scaling $R_g(L, t) \sim L^{1/2}$. The switch between these behaviours occurs at a time $t_\times$ known as the *crossover time*, which depends on the length of the chain. A *scaling relation* asserts that the crossover time depends on system size as a power law $t_\times \sim L^z$ where z is known as the *dynamic exponent*. The growth of the polymer can be captured for all times and all chain lengths in a single *scaling form*

$$R_g(L, t) \sim L^{1/2} f\left(\frac{t}{L^z}\right), \quad (5.0.1)$$

where f is a scaling function. The late time behaviour is recovered if the function f becomes asymptotically constant for large values of its argument. The short time behaviour is also recovered if for small values of the argument $f(x) \sim x^{1/2}$ since then we will have $R_g(L, t) \sim L^{1/2-z/2}t^{1/2}$. This is independent of the system size only if the dynamic exponent is $z = 1$, giving a definite prediction for experiment.

In summary, what we have seen is that if the radius of gyration is divided by the length of the chain to the $\frac{1}{2}$ power and plotted against the time divided by L^z then all of the data for all chain lengths and all times will fall on a single universal curve – the scaling function $f(t/L^z)$. This is an example of *data collapse through scaling*, or simply *scaling collapse*.

The determination of scaling collapse, and in particular the values of critical exponents that achieve it, is a major industry both in the original setting of statistical mechanics and more broadly in complexity science.

5.1 Surface growth and interfaces

One of the simplest examples of dynamic, non-equilibrium, processes that can be described using the ideas of scaling is the growth of a surface, or evolution of an interface. Examples include the advance of a burning front in a fire, the growth of a colony of bacteria, or the simple deposition of material onto a substrate such as occurs in snowfalls or molecular beam epitaxy. There are several different minimal models for these: simple random deposition in which the deposited material simply sticks where it lands, or deposition with relaxation where the deposited material can subsequently move over the growing surface, and the restricted solid-on-solid model we described earlier. Here we will think mostly about random deposition with relaxation, but some of our first statements will apply more generally.

There are many properties of the growth process that we might be interested in: the full probability distribution for the height profile, the two-point correlation function $\langle h(\mathbf{x}, t)h(\mathbf{x}', t') \rangle$, and so on. One of the simplest, and the one we shall focus on, is the *surface roughness* or *mean width* of the interface $w(L, t)$. This is a function of the system size L and the time t that the

¹Say by being in a poor solvent.

surface has been growing from. This is defined as the square root of the average of the fluctuations in the height

$$w(L, t) = \sqrt{\left\langle \left(h(\mathbf{x}, t) - \langle h(\mathbf{x}', t') \rangle_{\eta', \mathbf{x}'} \right)^2 \right\rangle_{\eta, \mathbf{x}}}, \quad (5.1.1)$$

where the average is over both the noise η and the points $\mathbf{x}$ of the substrate. The average over $\mathbf{x}$ of a quantity $A(\mathbf{x}, t)$ is defined as

$$\langle A(\mathbf{x}, t) \rangle_{\mathbf{x}} = \frac{1}{L^d} \int d^d x A(\mathbf{x}, t), \quad (5.1.2)$$

where d is the dimension of the *surface*, or *interface*.

What general behaviour can we expect for the mean width? At short times, the effects of the finite size confinement will not be apparent and the mean width should depend only on the time t that the surface has been growing for. Much like the diffusive spread of a random walk, we can expect the mean width of the surface to scale with a power of the time, giving the scaling behaviour

$$w(L, t) \sim t^\beta, \quad \text{early times} \quad (5.1.3)$$

where β is the *growth exponent*.

On the other hand, at very long times, the growth will be restricted by the finite system size and the mean width should depend only on the size L . This is captured by the late time scaling form

$$w(L, t) \sim L^\chi, \quad \text{late times} \quad (5.1.4)$$

where χ is called the *roughness exponent*. The crossover between the early and late behaviour takes place at the *crossover time* $t_\times$. This crossover time itself depends non-trivially on the system size, characterised by the scaling relation

$$t_\times \sim L^z, \quad \text{crossover time} \quad (5.1.5)$$

where z is known as the *dynamic exponent*.

The behaviour at all times can be captured by a single type of scaling behaviour

$$w(L, t) \sim L^\chi f\left(\frac{t}{L^z}\right), \quad (5.1.6)$$

with f a universal function, known as the *Family-Vicsek scaling relation*. The late time behaviour $w \sim L^\chi$ is recovered if the function f becomes asymptotically a finite constant for large values of its argument (when $t \gg t_\times \sim L^z$). But likewise the early time behaviour will be recovered if $f(x)$ behaves as x^β for small x since then we will have

$$w(L, t) \sim L^\chi \left(\frac{t}{L^z}\right)^\beta \sim L^{\chi - \beta z} t^\beta. \quad (5.1.7)$$

This has the correct time dependence, but it is only independent of the system size as we expect if the exponents satisfy the relation $\chi = \beta z$. Thus a consistent scaling behaviour describes the mean width for all times and all system sizes only if the critical exponents are related in a particular way, giving a precise prediction that can be tested in experiments.

5.1.1 The Edwards-Wilkinson model

The Edwards-Wilkinson model is a continuum evolution equation – perhaps the simplest – that captures some of the general features of surface growth. It is an equation for the rate of change of the surface height function $h(\mathbf{x}, t)$ that includes three features. A linear drift term that corresponds to the advancement of the surface due to continual deposition of material. A surface diffusion term corresponding to the movement of material within the surface after it has landed on it. This has the effect of smoothing the surface profile. And finally there is a stochastic noise term, capturing the inherent randomness of the growth process.

The Edwards-Wilkinson equation for surface growth is

$$\frac{\partial h(\mathbf{x}, t)}{\partial t} = v_0 + \nu \nabla^2 h + \eta(\mathbf{x}, t). \quad (5.1.8)$$

The linear drift term v_0 can be removed by the simple shift $h \rightarrow h + v_0 t$, corresponding to transforming to the comoving frame. We will assume this to have been done in what follows and neglect the term v_0 . The noise $\eta(\mathbf{x}, t)$ is taken to be *delta correlated* in both space and time

$$\langle \eta(\mathbf{x}, t) \rangle = 0, \quad (5.1.9)$$

$$\langle \eta(\mathbf{x}, t) \eta(\mathbf{x}', t') \rangle = 2D \delta(\mathbf{x} - \mathbf{x}') \delta(t - t'). \quad (5.1.10)$$

The analysis of the Edwards-Wilkinson equation is greatly simplified by virtue of the fact that it is linear and invariant under translations, since this makes it amenable to solution via Fourier transform². We take the Fourier transform with respect to space only and obtain

$$\frac{\partial \tilde{h}(\mathbf{k}, t)}{\partial t} + \nu k^2 \tilde{h} = \tilde{\eta}(\mathbf{k}, t), \quad (5.1.11)$$

where $k = |\mathbf{k}|$. The solution, with initial condition $\tilde{h}(\mathbf{k}, 0) = 0$, is

$$\tilde{h}(\mathbf{k}, t) = e^{-\nu k^2 t} \int_0^t ds e^{\nu k^2 s} \tilde{\eta}(\mathbf{k}, s). \quad (5.1.12)$$

Let us calculate the mean width within the Edwards-Wilkinson model and show that the scaling form of Family and Vicsek is indeed obtained. The mean square width is

$$w^2(L, t) = \frac{1}{L^d} \int d^d x \langle h(\mathbf{x}, t) h(\mathbf{x}, t) \rangle_\eta, \quad (5.1.13)$$

$$\begin{aligned} &= \frac{1}{L^d} \int d^d x \int \frac{d^d k}{(2\pi)^d} \int \frac{d^d k'}{(2\pi)^d} e^{i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{x}} e^{-\nu(k^2 + k'^2)t} \\ &\quad \times \int_0^t ds \int_0^t ds' e^{\nu(k^2 s + k'^2 s')} \langle \tilde{\eta}(\mathbf{k}, s) \tilde{\eta}(\mathbf{k}', s') \rangle. \end{aligned} \quad (5.1.14)$$

$$= 2D \int \frac{d^d k}{(2\pi)^d} e^{-2\nu k^2 t} \int_0^t ds e^{2\nu k^2 s}, \quad (5.1.15)$$

$$= \frac{D \Omega_{d-1}}{(2\pi)^d \nu} \int_{2\pi/L}^\infty dk k^{d-3} [1 - e^{-2\nu k^2 t}], \quad (5.1.16)$$

$$= \frac{D \Omega_{d-1}}{8\pi^2 \nu} L^{2-d} \left(\frac{8\pi^2 \nu t}{L^2} \right)^{1-d/2} \int_{8\pi^2 \nu t/L^2}^\infty dy y^{d/2-2} [1 - e^{-y}], \quad (5.1.17)$$

²It is true that this is not strictly correct for systems of a finite size L . For these we should really be looking at Fourier series rather than transforms, but the calculation still proceeds in an entirely analogous manner and leads to the same scaling form.

where Ω_{d-1} is the solid angle of a $(d-1)$ -dimensional sphere³. The calculation so far applies in general dimension, and is enough to see that a scaling form of the Family-Vicsek type does indeed arise for the mean width in the Edwards-Wilkinson model. In particular, we can see immediately that the dynamic scaling exponent is $z = 2$. We might even go further and identify the roughness exponent as $\chi = \frac{2-d}{2}$ and the growth exponent as $\beta = \frac{2-d}{4}$, however, before reaching this conclusion we should really consider the asymptotic behaviour of the integral a little more carefully.

The Edwards-Wilkinson model has the appealing feature of being sufficiently simple that many properties can be calculated explicitly. We have particularly exploited its linearity. But there are other general features too. We record two of them. First, the equation has a symmetry under the simultaneous change of sign of the height $h(\mathbf{x}, t)$ and the noise $\eta(\mathbf{x}, t)$; $h \rightarrow -h$, $\eta \rightarrow -\eta$. What this means is that the surface (or interface) looks the same from both sides. Just from the properties of the surface (or interface) you cannot tell which side you are on. This might be appropriate for some growth problems, but it will not be for all. Second, the equation is gradient descent of an energy function

$$\frac{\partial h}{\partial t} = -\nu \frac{\delta H}{\delta h} + \eta, \quad (5.1.18)$$

$$\text{with} \quad H = \int d^d x \frac{1}{2} (\nabla h)^2. \quad (5.1.19)$$

This energy function is the linearised expression for the difference in the area of the surface over that of a flat profile ($h = 0$) and so has a physical interpretation in terms of surface tension. Whilst there is nothing wrong with equations that are derivable from equilibrium energy functions, there is a sense in which this makes the model close to equilibrium behaviour so that it may not capture generic non-equilibrium phenomena.

5.1.2 The Kardar-Parisi-Zhang equation

A different continuum equation for growth processes was introduced by Kardar, Parisi and Zhang with the aim of removing the $h \rightarrow -h$ symmetry of the Edwards-Wilkinson model and including the simplest type of non-linearity. It can be viewed as the simplest stochastic continuum equation that incorporates the following general features:

- (i) There is translational symmetry under constant shifts in the surface position, $h \rightarrow h + \text{const.}$ This has the implication that the growth only depends on gradients of h .
- (ii) The growth is *isotropic*, meaning that there are no preferred directions within the substrate, or only isotropic gradients enter the equation of motion.
- (iii) There is no inversion symmetry under $h \rightarrow -h$.
- (iv) The growth equation does not have to be derivable from any microscopic conservation law, or from an equilibrium energy functional.

Based on these considerations, the simplest equation of motion for the surface is⁴

$$\frac{\partial h(\mathbf{x}, t)}{\partial t} = \nu \nabla^2 h + \frac{\lambda}{2} (\nabla h)^2 + \eta(\mathbf{x}, t), \quad (5.1.20)$$

³ $\Omega_0 = 2$, $\Omega_1 = 2\pi$, $\Omega_2 = 4\pi$, $\Omega_{d-1} = 2\pi^{d/2}/\Gamma(d/2)$.

⁴As in the Edwards-Wilkinson model, there could be a linear drift term v_0 on the right-hand-side, but as this can be eliminated through a simple shift $h \rightarrow h + v_0 t$ we neglect it by transforming to the comoving frame.

and is known as the Kardar-Parisi-Zhang, or KPZ, equation. The first term is the same as that of the Edwards-Wilkinson equation and captures the diffusion of particles within the surface so as to smooth the profile. The second term is the simplest allowed non-linear contribution and breaks the inversion symmetry $h \rightarrow -h$. It may be viewed as capturing the fact that surface growth proceeds through motion of the surface along its normal since, for small slopes, the component of the surface normal vector in the vertical direction is $N_z \approx 1 - \frac{1}{2}(\nabla h)^2$. An important feature is that this term in the equation of motion cannot be generated from gradient descent of an equilibrium energy function, so the term differs in two fundamental ways from the general features of the Edwards-Wilkinson equation. Finally, η is a random noise term as before.

A remarkable feature of the KPZ equation is that it can be linearised with the help of the Cole-Hopf transformation. Defining $W := \exp\{\frac{\lambda}{2\nu}h\}$ the KPZ equation is equivalent to

$$\frac{\partial W}{\partial t} = \nu \nabla^2 W + \frac{\lambda}{2\nu} W \eta, \quad (5.1.21)$$

which is a stochastic diffusion equation with *multiplicative noise*. This can be solved using the Feynman-Kac path integral but some simpler insight comes from first solving the deterministic equation with the noise neglected. Then the solution is

$$W(\mathbf{x}, t) = \int d^d x' \frac{1}{(4\pi\nu t)^{d/2}} e^{-|\mathbf{x} - \mathbf{x}'|^2/4\nu t} W_0(\mathbf{x}'), \quad (5.1.22)$$

where $W_0(\mathbf{x}) = W(\mathbf{x}, 0)$ is the initial profile. Reverting to the height of the surface $h(\mathbf{x}, t)$ this becomes

$$h(\mathbf{x}, t) = \frac{2\nu}{\lambda} \ln \left[\frac{1}{(4\pi\nu t)^{d/2}} \int d^d x' \exp \left\{ \frac{\lambda}{2\nu} h_0(\mathbf{x}') - \frac{|\mathbf{x} - \mathbf{x}'|^2}{4\nu t} \right\} \right]. \quad (5.1.23)$$

In the inviscid limit $\nu \rightarrow 0$ the integral can be estimated using saddle point techniques leading to the solution

$$h(\mathbf{x}, t) = \max_{\mathbf{x}'} \left(h_0(\mathbf{x}') - \frac{|\mathbf{x} - \mathbf{x}'|^2}{2\lambda t} \right), \quad (5.1.24)$$

$$= h_0(\mathbf{x}) + \max_{\mathbf{x}'} \left(h_0(\mathbf{x}') - h_0(\mathbf{x}) - \frac{|\mathbf{x} - \mathbf{x}'|^2}{2\lambda t} \right). \quad (5.1.25)$$

This form for the interface profile allows us to extract a scaling form for self-similar growth, i.e., when $h(\mathbf{x}, t)$ is, at least statistically, just a translate of the profile $h_0(\mathbf{x})$. This will occur when $h_0(\mathbf{x}') - h_0(\mathbf{x}) \approx |\mathbf{x} - \mathbf{x}'|^2/2\lambda t$ (at least on average). If we further assume that the profile $h_0(\mathbf{x})$ corresponds to a *self-affine fractal*

$$\langle |h_0(\mathbf{x}) - h_0(\mathbf{x}')| \rangle \sim |\mathbf{x} - \mathbf{x}'|^\chi, \quad (5.1.26)$$

where χ is the roughness exponent, we have the scaling balance for large separations and late times

$$L^\chi \sim \frac{L^2}{t}, \quad \Rightarrow \quad t \sim L^{2-\chi}, \quad (5.1.27)$$

leading to the identity between exponents $\chi + z = 2$. In $d = 1$, if the surface is like a random walk we can expect $\chi = \frac{1}{2}$ and this relation then predicts $z = \frac{3}{2}$. And then the Family-Vicsek scaling relation gives the growth exponent as $\beta = \frac{1}{3}$.

Finally, let us mention briefly that a useful transformation is to consider the *slope* of the interface rather than the height. To this end, we define $\mathbf{v} := -\lambda \nabla h$ and, by acting on the KPZ equation with $-\lambda \nabla$, find that the slope satisfies

$$\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} = \nu \nabla^2 \mathbf{v} - \lambda \nabla \eta. \quad (5.1.28)$$

In other words the slope of the growing interface satisfies the stochastic viscous Burgers equation. This helps to explain why the KPZ equation is linearised by the Cole-Hopf transformation. A feature of the Burgers equation not shared by the original KPZ equation, is that it is *Galilean invariant*. As usual, the presence of a symmetry has consequences for the properties of the system and in this case it turns out that Galilean invariance implies a relation between the scaling exponents, $\chi + z = 2$, the same relation that we saw before.