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Statistical physics and probability theory

One of the greatest achievements of science has been to realize that matter is made out of a small number of simple elementary components. This result seems to be in striking contrast to our experience. Both at a simply perceptual level and with more refined scientific experience, we come into touch with an ever-growing variety of states of matter with disparate properties. The ambitious purpose of statistical physics (and, more generally, of a large branch of condensed matter physics) is to understand this variety. It aims at explaining how complex behaviours can emerge when large numbers of identical elementary components are allowed to interact.

We have, for instance, experience of water in three different states (solid, liquid and gaseous). Water molecules and their interactions do not change when passing from one state to the other. Understanding how the same interactions can result in qualitatively different macroscopic states, and what governs the change of state, is a central topic of statistical physics.

The foundations of statistical physics rely on two important steps. The first one consists in passing from the deterministic laws of physics, such as Newton's laws, to a probabilistic description. The idea is that a precise knowledge of the motion of each molecule in a macroscopic system is inessential to an understanding of the system as a whole: instead, one can postulate that the microscopic dynamics, because of its chaoticity, allows a purely probabilistic description. The detailed justification of this basic step has been achieved in only a small number of concrete cases. Here we shall bypass any attempt at such a justification: we directly adopt a purely probabilistic point of view, as a basic postulate of statistical physics.

The second step starts from the probabilistic description and recovers determinism at a macroscopic level by some sort of law of large numbers. We all know that water boils at 100°C (at atmospheric pressure) and that its density (at 25°C and atmospheric pressure) is 1 g/cm^3 . The regularity of these phenomena is not related to the deterministic laws which rule the motions of water molecules. It is instead a consequence of the fact that, because of the large number of particles involved in any macroscopic system, fluctuations are 'averaged out'. We shall discuss this kind of phenomenon in Section 2.4 and, more mathematically, in Chapter 4.

The purpose of this chapter is to introduce the most basic concepts of this discipline for an audience of non-physicists with a mathematical background. We adopt a somewhat restrictive point of view, which keeps to classical (as opposed to quantum) statistical physics, and basically describes it as a branch of probability the-

ory (Sections 2.1–2.3). In Section 2.4 we focus on large systems, and stress that the statistical-physics approach becomes particularly meaningful in this regime. Theoretical statistical physics often deals with highly idealized mathematical models of real materials. The most interesting (and challenging) task is in fact to understand the *qualitative* behaviour of such systems. With this aim, one can discard any ‘irrelevant’ microscopic detail from the mathematical description of the model. In Section 2.5, the study of ferromagnetism through the introduction of the Ising model gives an example of this modelling procedure. Compared with the case of Ising ferromagnets, the theoretical understanding of spin glasses is much less developed. Section 2.6 presents a rapid preview of this fascinating subject.

2.1 The Boltzmann distribution

The basic ingredients for a probabilistic description of a physical system are:

- A **space of configurations** \mathcal{X} . One should think of $x \in \mathcal{X}$ as giving a complete microscopic determination of the state of the system under consideration. We are not interested in defining the most general mathematical structure for \mathcal{X} such that a statistical-physics formalism can be constructed. Throughout this book we shall in fact consider only two very simple types of configuration spaces: (i) finite sets, and (ii) smooth, compact, finite-dimensional manifolds. If the system contains N ‘particles’, the configuration space is a product space:

$$\mathcal{X}_N = \underbrace{\mathcal{X} \times \cdots \times \mathcal{X}}_N. \quad (2.1)$$

The configuration of the system has the form $\underline{x} = (x_1, \dots, x_N)$. Each coordinate $x_i \in \mathcal{X}$ is meant to represent the state (position, orientation, etc.) of one of the particles. Except for a few examples, we shall focus on configuration spaces of type (i). We shall therefore adopt a discrete-space notation for \mathcal{X} . The generalization to continuous configuration spaces is in most cases intuitively clear (although it may present some technical difficulties).

- A set of **observables**, which are real-valued functions on the configuration space $\mathcal{O} : x \mapsto \mathcal{O}(x)$. If \mathcal{X} is a manifold, we shall limit ourselves to observables which are smooth functions of the configuration x . Observables are physical quantities which can be measured through an experiment (at least in principle).
- Out of all the observables, a special role is played by the **energy function** $E(x)$. When the system is an N -particle system, the energy function generally takes the form of sums of terms involving few particles. An energy function of the form

$$E(\underline{x}) = \sum_{i=1}^N E_i(x_i) \quad (2.2)$$

corresponds to a **non-interacting** system. An energy of the form

$$E(\underline{x}) = \sum_{i_1, \dots, i_k} E_{i_1, \dots, i_k}(x_{i_1}, \dots, x_{i_k}) \quad (2.3)$$

is called a **k -body** interaction. In general, the energy will contain some pieces involving k -body interactions, with $k \in \{1, 2, \dots, K\}$. An important feature of

real physical systems is that K is never a large number (usually $K = 2$ or 3), even when the number of particles N is very large. The same property holds for all measurable observables. However, for the general mathematical formulation which we shall use here, the energy can be any real-valued function on \mathcal{X} .

Once the configuration space \mathcal{X} and the energy function are fixed, the probability $\mu_\beta(x)$ for the system to be found in the configuration x is given by the **Boltzmann distribution**:

$$\mu_\beta(x) = \frac{1}{Z(\beta)} e^{-\beta E(x)}, \quad Z(\beta) = \sum_{x \in \mathcal{X}} e^{-\beta E(x)}. \quad (2.4)$$

The real parameter $T = 1/\beta$ is the **temperature** (and β is referred to as the inverse temperature). Note that the temperature is usually defined as $T = 1/(k_B\beta)$, where the value of k_B , Boltzmann's constant, depends on the unit of measure for the temperature. Here we adopt the simple choice $k_B = 1$. The normalization constant $Z(\beta)$ is called the **partition function**. Notice that eqn (2.4) indeed defines the density of the Boltzmann distribution with respect to some reference measure. The reference measure is usually the counting measure if \mathcal{X} is discrete or the Lebesgue measure if \mathcal{X} is continuous. It is customary to denote the expectation value with respect to the Boltzmann measure by angle brackets: the expectation value $\langle \mathcal{O}(x) \rangle$ of an observable $\mathcal{O}(x)$, also called its **Boltzmann average**, is given by

$$\langle \mathcal{O} \rangle = \sum_{x \in \mathcal{X}} \mu_\beta(x) \mathcal{O}(x) = \frac{1}{Z(\beta)} \sum_{x \in \mathcal{X}} e^{-\beta E(x)} \mathcal{O}(x). \quad (2.5)$$

Example 2.1 One intrinsic property of elementary particles is their spin. For ‘spin-1/2’ particles, the spin σ takes only two values: $\sigma = \pm 1$. A localized spin-1/2 particle, whose only degree of freedom is the spin, is described by $\mathcal{X} = \{+1, -1\}$, and is called an **Ising spin**. The energy of the spin in a state $\sigma \in \mathcal{X}$ in a magnetic field B is

$$E(\sigma) = -B\sigma. \quad (2.6)$$

The Boltzmann probability of finding the spin in the state σ is

$$\mu_\beta(\sigma) = \frac{1}{Z(\beta)} e^{-\beta E(\sigma)} \quad Z(\beta) = e^{-\beta B} + e^{\beta B} = 2 \cosh(\beta B). \quad (2.7)$$

The average value of the spin, called the **magnetization**, is

$$\langle \sigma \rangle = \sum_{\sigma \in \{1, -1\}} \mu_\beta(\sigma) \sigma = \tanh(\beta B). \quad (2.8)$$

At high temperatures, $T \gg |B|$, the magnetization is small. At low temperatures, the magnetization is close to its maximal value: $\langle \sigma \rangle = 1$ if $B > 0$. Section 2.5 will discuss the behaviour of many Ising spins, with some more complicated energy functions.

Example 2.2 Some spin variables can have a larger space of possible values. For instance, a **Potts spin** with q states takes values in $\mathcal{X} = \{1, 2, \dots, q\}$. In the presence of a magnetic field of intensity h pointing in the direction $r \in \{1, \dots, q\}$, the energy of the Potts spin is

$$E(\sigma) = -B \mathbb{I}(\sigma = r) . \quad (2.9)$$

In this case, the average value of the spin in the direction of the field is

$$\langle \mathbb{I}(\sigma = r) \rangle = \frac{\exp(\beta B)}{\exp(\beta B) + (q - 1)} . \quad (2.10)$$

Example 2.3 Let us consider a single water molecule inside a closed container: for instance, inside a bottle. A water molecule H_2O is already a complicated object, but in a first approximation, we can neglect its structure and model the molecule as a point inside the bottle. The space of configurations then reduces to

$$\mathcal{X} = \text{BOTTLE} \subset \mathbb{R}^3 , \quad (2.11)$$

where we have denoted by **BOTTLE** the region of \mathbb{R}^3 delimited by the container. Note that this description is not very accurate at a microscopic level.

The description of the precise form of the bottle can be quite complex. On the other hand, it is a good approximation to assume that all positions of the molecule are equiprobable: the energy is independent of the particle's position $x \in \text{BOTTLE}$. One then has:

$$\mu(x) = \frac{1}{Z} , \quad Z = |\mathcal{X}| , \quad (2.12)$$

and the Boltzmann average of the particle's position, $\langle x \rangle$, is the barycentre of the bottle.

Example 2.4 In assuming that all the configurations in the previous example are equiprobable, we neglected the effect of gravity on the water molecule. In the presence of gravity our water molecule at position x has an energy

$$E(x) = w h(x) , \quad (2.13)$$

where $h(x)$ is the height corresponding to the position x and w is a positive constant, determined by terrestrial attraction, which is proportional to the mass of the molecule. Given two positions x and y in the bottle, the ratio of the probabilities to find the particle at these positions is

$$\frac{\mu_\beta(x)}{\mu_\beta(y)} = \exp\{-\beta w[h(x) - h(y)]\}. \quad (2.14)$$

For a water molecule at a room temperature of 20° C ($T = 293$ K), one has $\beta w \approx 7 \times 10^{-5} \text{ m}^{-1}$. Given a point x at the bottom of the bottle and y at a height of 20 cm, the probability to find a water molecule ‘near’ x is approximately 1.000014 times larger than the probability to find it ‘near’ y . For a tobacco-mosaic virus, which is about 2×10^6 times heavier than a water molecule, the ratio is $\mu_\beta(x)/\mu_\beta(y) \approx 1.4 \times 10^{12}$, which is very large. For a grain of sand, the ratio is so large that one never observes the grain floating at around y . Note that, while these ratios of probability densities are easy to compute, the partition function and therefore the absolute values of the probability densities can be much more complicated to estimate, and depend on the shape of the bottle.

Example 2.5 In many important cases, we are given the space of configurations \mathcal{X} and a stochastic dynamics defined on it. The most interesting probability distribution for such a system is the stationary state $\mu_{\text{st}}(x)$ (we assume that it is unique). For the sake of simplicity, we can consider a finite space \mathcal{X} and a discrete-time Markov chain with transition probabilities $\{w(x \rightarrow y)\}$ (in Chapter 4 we shall recall some basic definitions concerning Markov chains). It happens sometimes that the transition rates satisfy, for any pair of configurations $x, y \in \mathcal{X}$, the relation

$$f(x)w(x \rightarrow y) = f(y)w(y \rightarrow x), \quad (2.15)$$

for some positive function $f(x)$. As we shall see in Chapter 4, when this condition, called **detailed balance**, is satisfied (together with a few other technical conditions), the stationary state has the Boltzmann form (2.4) with $e^{-\beta E(x)} = f(x)$.

Exercise 2.1 As a particular realization of the above example, consider an 8×8 chessboard and a special piece sitting on it. At any time step, the piece will stay still (with probability $1/2$) or move randomly to one of the neighbouring positions (with probability $1/2$). Does this process satisfy the condition (2.15)? Which positions on the chessboard have lower and higher ‘energy’? Compute the partition function.

From a purely probabilistic point of view, one can wonder why one bothers to decompose the distribution $\mu_\beta(x)$ into the two factors $e^{-\beta E(x)}$ and $1/Z(\beta)$. Of course the motivations for writing the Boltzmann factor $e^{-\beta E(x)}$ in exponential form come essentially from physics, where one knows (either exactly or to within some level

of approximation) the form of the energy. This also justifies the use of the inverse temperature β (after all, one could always redefine the energy function in such a way as to set $\beta = 1$).

However, even if we adopt a mathematical viewpoint, and if we are interested in only a particular distribution $\mu(x)$ which corresponds to a particular value of the temperature, it is often illuminating to embed it into a one-parameter family as is done in the Boltzmann expression (2.4). Indeed, eqn (2.4) interpolates smoothly between several interesting situations. As $\beta \rightarrow 0$ (**high-temperature limit**), one recovers the uniform probability distribution

$$\lim_{\beta \rightarrow 0} \mu_\beta(x) = \frac{1}{|\mathcal{X}|}. \quad (2.16)$$

Both the probabilities $\mu_\beta(x)$ and the expectation values $\langle \mathcal{O}(x) \rangle$ of the observables can be expressed as convergent Taylor expansions around $\beta = 0$. For small β the Boltzmann distribution can be seen as a ‘softening’ of the original distribution.

In the limit $\beta \rightarrow \infty$ (**low-temperature limit**), the Boltzmann distribution concentrates on the global maxima of the original distribution. More precisely, a configuration $x_0 \in \mathcal{X}$ such that $E(x) \geq E(x_0)$ for any $x \in \mathcal{X}$ is called a **ground state**. The minimum value of the energy $E_0 = E(x_0)$ is called the **ground state energy**. We shall denote the set of ground states by \mathcal{X}_0 . It is elementary to show that, for a discrete configuration space,

$$\lim_{\beta \rightarrow \infty} \mu_\beta(x) = \frac{1}{|\mathcal{X}_0|} \mathbb{I}(x \in \mathcal{X}_0), \quad (2.17)$$

where $\mathbb{I}(x \in \mathcal{X}_0) = 1$ if $x \in \mathcal{X}_0$ and $\mathbb{I}(x \in \mathcal{X}_0) = 0$ otherwise. The above behaviour is summarized in physicists’ jargon by saying that, at low temperature, ‘low energy configurations dominate’ the behaviour of the system.

2.2 Thermodynamic potentials

Several properties of the Boltzmann distribution (eqn (2.4)) are conveniently summarized through the thermodynamic potentials. These are functions of the temperature $1/\beta$ and of the various parameters defining the energy $E(x)$. The most important thermodynamic potential is the **free energy**

$$F(\beta) = -\frac{1}{\beta} \log Z(\beta), \quad (2.18)$$

where $Z(\beta)$ is the partition function already defined in eqn (2.4). The factor $-1/\beta$ in eqn (2.18) is due essentially to historical reasons. In calculations, it is often more convenient to use the **free entropy**¹ $\Phi(\beta) = -\beta F(\beta) = \log Z(\beta)$.

¹Unlike the other potentials, there is no universally accepted name for $\Phi(\beta)$; however, because this potential is very useful, we have adopted the name ‘free entropy’ for it.

Two more thermodynamic potentials are derived from the free energy: the **internal energy** $U(\beta)$ and the **canonical entropy** $S(\beta)$:

$$U(\beta) = \frac{\partial}{\partial \beta}(\beta F(\beta)), \quad S(\beta) = \beta^2 \frac{\partial F(\beta)}{\partial \beta}. \quad (2.19)$$

By direct computation, one obtains the following identities concerning the potentials defined so far:

$$F(\beta) = U(\beta) - \frac{1}{\beta} S(\beta) = -\frac{1}{\beta} \Phi(\beta), \quad (2.20)$$

$$U(\beta) = \langle E(x) \rangle, \quad (2.21)$$

$$S(\beta) = - \sum_x \mu_\beta(x) \log \mu_\beta(x), \quad (2.22)$$

$$-\frac{\partial^2}{\partial \beta^2}(\beta F(\beta)) = \langle E(x)^2 \rangle - \langle E(x) \rangle^2. \quad (2.23)$$

For discrete \mathcal{X} , eqn (2.22) can be rephrased by saying that the canonical entropy is the Shannon entropy of the Boltzmann distribution, as we defined it in Chapter 1. This implies that $S(\beta) \geq 0$. Equation (2.23) implies that the free entropy is a convex function of the temperature. Finally, eqn (2.21) justifies the name ‘internal energy’ for $U(\beta)$.

In order to have some intuition of the content of these definitions, let us reconsider the high- and low-temperature limits already treated in the previous section. In the high-temperature limit, $\beta \rightarrow 0$, one finds

$$F(\beta) = -\frac{1}{\beta} \log |\mathcal{X}| + \langle E(x) \rangle_0 + \Theta(\beta), \quad (2.24)$$

$$U(\beta) = \langle E(x) \rangle_0 + \Theta(\beta), \quad (2.25)$$

$$S(\beta) = \log |\mathcal{X}| + \Theta(\beta). \quad (2.26)$$

(Recall that Θ stands for ‘of the order of-’; see Appendix A.) The interpretation of these formulae is straightforward. At high temperature, the system can be found in any possible configuration with similar probabilities (the probabilities being exactly equal when $\beta = 0$). The entropy counts the number of possible configurations. The internal energy is just the average value of the energy over the configurations with uniform probability.

While the high-temperature expansions (2.24)–(2.26) have the same form for both a discrete and a continuous configuration space \mathcal{X} , in the low-temperature case we must be more careful. If \mathcal{X} is finite, we can meaningfully define the **energy gap** $\Delta E > 0$ as follows (recall that we have denoted by E_0 the ground-state energy):

$$\Delta E = \min\{E(y) - E_0 : y \in \mathcal{X} \setminus \mathcal{X}_0\}. \quad (2.27)$$

With this definition, we get

$$F(\beta) = E_0 - \frac{1}{\beta} \log |\mathcal{X}_0| + \Theta(e^{-\beta \Delta E}), \quad (2.28)$$

$$U(\beta) = E_0 + \Theta(e^{-\beta \Delta E}), \quad (2.29)$$

$$S(\beta) = \log |\mathcal{X}_0| + \Theta(e^{-\beta \Delta E}). \quad (2.30)$$

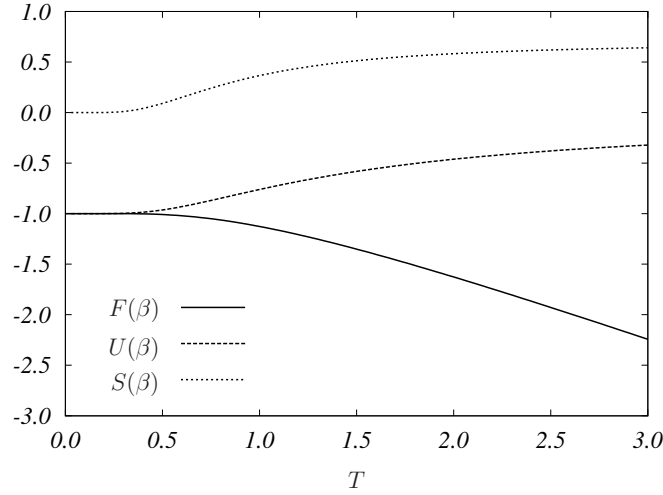


Fig. 2.1 Thermodynamic potentials for a two-level system with $\epsilon_1 = -1$ and $\epsilon_2 = +1$ as a function of the temperature $T = 1/\beta$.

The interpretation is that, at low temperature, the system is found with equal probability in any of the ground states, and nowhere else. Once again, the entropy counts the number of available configurations, and the internal energy is the average of their energies (which coincide with that of the ground state).

Exercise 2.2 *A two-level system.* This is the simplest non-trivial example: $\mathcal{X} = \{1, 2\}$, $E(1) = \epsilon_1$, $E(2) = \epsilon_2$. Without loss of generality, we assume $\epsilon_1 < \epsilon_2$. This example can be used as a mathematical model for many physical systems, such as the spin-1/2 particle discussed above.

Derive the following results for the thermodynamic potentials (where $\Delta = \epsilon_2 - \epsilon_1$ is the energy gap):

$$F(\beta) = \epsilon_1 - \frac{1}{\beta} \log(1 + e^{-\beta\Delta}), \quad (2.31)$$

$$U(\beta) = \epsilon_1 + \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \Delta, \quad (2.32)$$

$$S(\beta) = \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} \beta\Delta + \log(1 + e^{-\beta\Delta}). \quad (2.33)$$

The behaviour of these functions is presented in Fig. 2.1. The reader can work out the asymptotics, and check the general high- and low-temperature behaviour given above.

Exercise 2.3 We return to the example of the previous section: one water molecule, modelled as a point, in a bottle. We consider the case of a cylindrical bottle of base $B \subset \mathbb{R}^2$ (surface area $|B|$) and height d .

Using the energy function in eqn (2.13), derive the following explicit expressions for the thermodynamic potentials:

$$F(\beta) = -\frac{1}{\beta} \log |B| - \frac{1}{\beta} \log \frac{1 - e^{-\beta w d}}{\beta w}, \quad (2.34)$$

$$U(\beta) = \frac{1}{\beta} - \frac{w d}{e^{\beta w d} - 1}, \quad (2.35)$$

$$S(\beta) = \log |B d| + 1 - \frac{\beta w d}{e^{\beta w d} - 1} - \log \left(\frac{\beta w d}{1 - e^{-\beta w d}} \right). \quad (2.36)$$

Note that the internal-energy formula can be used to compute the average height of the molecule $\langle h(x) \rangle = U(\beta)/w$. This is a consequence of the definition of the energy (see eqn (2.13)) and of eqn (2.21). If we plug in the correct constant w , we can find that the average height falls below 49.99% of the height of the bottle $d = 20$ cm only when the temperature is below 3.2 K.

Exercise 2.4 Using eqns (2.34)–(2.36), derive the low-temperature expansions

$$F(\beta) = -\frac{1}{\beta} \log \left(\frac{|B|}{\beta w} \right) + \Theta(e^{-\beta w d}), \quad (2.37)$$

$$U(\beta) = \frac{1}{\beta} + \Theta(e^{-\beta w d}), \quad (2.38)$$

$$S(\beta) = \log \left(\frac{|B|e}{\beta w} \right) + \Theta(e^{-\beta w d}). \quad (2.39)$$

In this case \mathcal{X} is continuous, and the energy has no gap. Nevertheless, these results can be understood as follows: at low temperature, the molecule is confined to a layer of height of order $1/(\beta w)$ above the bottom of the bottle. It therefore occupies a volume of size $|B|/(\beta w)$. Its entropy is approximately given by the logarithm of such a volume.

Exercise 2.5 Let us reconsider the above example and assume the bottle to have a different shape, for instance a sphere of radius R . In this case it is difficult to compute explicit expressions for the thermodynamic potentials, but one can easily compute the low-temperature expansions. For the entropy, one gets at large β

$$S(\beta) = \log \left(\frac{2\pi e^2 R}{\beta^2 w^2} \right) + \Theta(1/\beta). \quad (2.40)$$

The reader should try to understand the difference between this result and eqn (2.39) and provide an intuitive explanation, as in the previous example. Physicists say that the low-temperature thermodynamic potentials reveal the ‘low-energy structure’ of the system.

2.3 The fluctuation–dissipation relations

It often happens that the energy function depends smoothly upon some real parameters. These can be related to the experimental conditions under which a physical system is studied, or to some fundamental physical quantity. For instance, the energy of a water molecule in a gravitational field (see eqn (2.13)) depends upon the weight w of the molecule itself. Although this is a constant number in the physical world, it is useful, in the theoretical treatment, to consider it as an adjustable parameter.

It is therefore interesting to consider an energy function $E_\lambda(x)$ which depends smoothly upon some parameter λ and admits the following Taylor expansion in the neighbourhood of $\lambda = \lambda_0$:

$$E_\lambda(x) = E_{\lambda_0}(x) + (\lambda - \lambda_0) \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda_0}(x) + O((\lambda - \lambda_0)^2). \quad (2.41)$$

The dependence of the free energy and of other thermodynamic potentials upon λ in the neighbourhood of λ_0 is easily related to the explicit dependence of the energy function itself. Let us consider the partition function, and expand it to first order in $\lambda - \lambda_0$:

$$\begin{aligned} Z(\lambda) &= \sum_x \exp \left(-\beta \left[E_{\lambda_0}(x) + (\lambda - \lambda_0) \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda_0}(x) + O((\lambda - \lambda_0)^2) \right] \right) \\ &= Z(\lambda_0) \left[1 - \beta(\lambda - \lambda_0) \left\langle \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda_0} \right\rangle_0 + O((\lambda - \lambda_0)^2) \right], \end{aligned} \quad (2.42)$$

where we have denoted by $\langle \cdot \rangle_0$ the expectation with respect to the Boltzmann distribution at $\lambda = \lambda_0$.

This shows that the free entropy behaves as

$$\left. \frac{\partial \Phi}{\partial \lambda} \right|_{\lambda_0} = -\beta \left\langle \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda_0} \right\rangle_0, \quad (2.43)$$

One can also consider the λ dependence of the expectation value of a generic observable $A(x)$. Using again the Taylor expansion, one finds that

$$\left. \frac{\partial \langle A \rangle_\lambda}{\partial \lambda} \right|_{\lambda_0} = -\beta \left\langle A ; \left. \frac{\partial E}{\partial \lambda} \right|_{\lambda_0} \right\rangle_0. \quad (2.44)$$

where we have denoted by $\langle A; B \rangle$ the **connected correlation function**: $\langle A; B \rangle = \langle AB \rangle - \langle A \rangle \langle B \rangle$. A particular example of this relation was given in eqn (2.23).

The result (2.44) has important practical consequences and many generalizations. Imagine you have an experimental apparatus that allows you to tune some parameter λ (for instance the pressure of a gas, or the magnetic or electric field acting on some material) and to monitor the value of an observable $A(x)$ (the volume of the gas, or the polarization or magnetization of the material). The quantity on the left-hand

side of eqn (2.44) is the response of the system to an infinitesimal variation of the tunable parameter. On the right-hand side, we find some correlation function within the ‘unperturbed’ system. One possible application is to measure correlations within a system by monitoring its response to an external perturbation. The relation (2.44) between a correlation and a response is called the **fluctuation–dissipation theorem**.

2.4 The thermodynamic limit

The main purpose of statistical physics is to understand the macroscopic behaviour of a large number, $N \gg 1$, of simple components (atoms, molecules, etc.) when they are brought together.

To be concrete, let us consider a few drops of water in a bottle. A configuration of the system is given by the positions and orientations of all the H_2O molecules inside the bottle. In this case \mathcal{X} is the set of positions and orientations of a single molecule, and N is typically of order 10^{23} (more precisely, 18 g of water contains approximately 6×10^{23} molecules). The sheer magnitude of such a number leads physicists to focus on the $N \rightarrow \infty$ limit, also called the **thermodynamic limit**.

As shown by the examples below, for large N , the thermodynamic potentials are often proportional to N . One is thus led to introduce the **intensive thermodynamic potentials** as follows. Let us denote by $F_N(\beta)$, $U_N(\beta)$, and $S_N(\beta)$ the free energy, internal energy, and canonical entropy, respectively, for a system with N ‘particles’. The **free energy density** is defined by

$$f(\beta) = \lim_{N \rightarrow \infty} F_N(\beta)/N, \quad (2.45)$$

if the limit exists, which is usually the case (at least if the forces between particles decrease fast enough at large distance). One defines analogously the **energy density** $u(\beta)$ and the **entropy density** $s(\beta)$.

The free energy $F_N(\beta)$, is, quite generally, an analytic function of β in a neighbourhood of the real β axis. This is a consequence of the fact that $Z(\beta)$ is analytic throughout the entire β plane, and strictly positive for real β ’s. A question of great interest is whether analyticity is preserved in the thermodynamic limit (2.45), under the assumption that the limit exists. Whenever the free energy density $f(\beta)$ is non-analytic, one says that a **phase transition** occurs. Since the free entropy density $\phi(\beta) = -\beta f(\beta)$ is convex, the free energy density is necessarily continuous whenever it exists.

In the simplest cases, the non-analyticities occur at isolated points. Let β_c be such a point. Two particular types of singularities occur frequently:

- The free energy density is continuous, but its derivative with respect to β is discontinuous at β_c . This singularity is called a **first-order phase transition**.
- The free energy and its first derivative are continuous, but the second derivative is discontinuous at β_c . This is called a **second-order phase transition**.

Higher-order phase transitions can be defined as well, along the same lines.

Apart from being interesting mathematical phenomena, phase transitions correspond to *qualitative* changes in the underlying physical system. For instance, the

transition from water to vapor at 100°C at normal atmospheric pressure is modelled mathematically as a first-order phase transition in the above sense. A great part of this book will be devoted to the study of phase transitions in many different systems, where the interacting ‘particles’ can be very diverse objects such as bits of information or occupation numbers on the vertices of a graph.

When N grows, the volume of the configuration space increases exponentially: $|\mathcal{X}_N| = |\mathcal{X}|^N$. Of course, not all of the configurations are equally important under the Boltzmann distribution: the lowest-energy configurations have greater probability. What is important is therefore the number of configurations at a given energy. This information is encoded in the **energy spectrum** of the system,

$$\mathcal{N}_\Delta(E) = |\Omega_\Delta(E)|, \quad \Omega_\Delta(E) \equiv \{x \in \mathcal{X}_N : E \leq E(x) < E + \Delta\}. \quad (2.46)$$

In many systems of interest, the energy spectrum diverges exponentially as $N \rightarrow \infty$, if the energy is scaled linearly with N . More precisely, there exists a function $s(e)$ such that, given two numbers e and $\delta > 0$,

$$\lim_{N \rightarrow \infty} \frac{1}{N} \log \mathcal{N}_{N\delta}(Ne) = \sup_{e' \in [e, e+\delta]} s(e'). \quad (2.47)$$

The function $s(e)$ is called the **microcanonical entropy density**. The statement (2.47) is often rewritten in the more compact form

$$\mathcal{N}_\Delta(E) \doteq_N \exp \left[N s \left(\frac{E}{N} \right) \right]. \quad (2.48)$$

The notation $A_N \doteq_N B_N$ will be used throughout the book to denote that two quantities A_N and B_N (which behave exponentially in N) are equal **to leading exponential order**, meaning $\lim_{N \rightarrow \infty} (1/N) \log(A_N/B_N) = 0$. We shall often use \doteq without an index when there is no ambiguity about the large variable N .

The microcanonical entropy density $s(e)$ conveys a great amount of information about the system. Furthermore, it is directly related to the intensive thermodynamic potentials through a fundamental relation

Proposition 2.6 *If the microcanonical entropy density (2.47) exists for any e and if the limit in eqn (2.47) is uniform in e , then the free entropy density (2.45) exists and is given by*

$$\phi(\beta) = \max_e [s(e) - \beta e]. \quad (2.49)$$

If the maximum of $s(e) - \beta e$ is unique, then the internal-energy density equals $\arg \max [s(e) - \beta e]$.

Proof The basic idea is to write the partition function as

$$Z_N(\beta) \doteq \sum_{k=-\infty}^{\infty} \mathcal{N}_\Delta(k\Delta) e^{-\beta k\Delta} \doteq \int \exp\{Ns(e) - N\beta e\} de, \quad (2.50)$$

and to evaluate the last integral by the saddle point method. The reader will find references in the Notes section at the end of this chapter. \square

Example 2.7 Let us consider N identical two-level systems, i.e. $\mathcal{X}_N = \mathcal{X} \times \cdots \times \mathcal{X}$, with $\mathcal{X} = \{1, 2\}$. We take the energy to be the sum of the single-system energies: $E(x) = E_{\text{single}}(x_1) + \cdots + E_{\text{single}}(x_N)$, with $x_i \in \mathcal{X}$. As in the previous section, we set $E_{\text{single}}(1) = \epsilon_1$, $E_{\text{single}}(2) = \epsilon_2 > \epsilon_1$, and $\Delta = \epsilon_2 - \epsilon_1$.

The energy spectrum of this model is quite simple. For any energy $E = N\epsilon_1 + n\Delta$, there are $\binom{N}{n}$ configurations x with $E(x) = E$. Therefore, using the definition (2.47), we get

$$s(e) = \mathcal{H} \left(\frac{e - \epsilon_1}{\Delta} \right). \quad (2.51)$$

Equation (2.49) can now be used to get

$$f(\beta) = \epsilon_1 - \frac{1}{\beta} \log(1 + e^{-\beta\Delta}), \quad (2.52)$$

which agrees with the result obtained directly from the definition (2.18).

The great attention paid by physicists to the thermodynamic limit is extremely well justified by the huge number of degrees of freedom involved in a macroscopic piece of matter. Let us stress that the interest of the thermodynamic limit is more general than these huge numbers might suggest. First of all, it often happens that fairly small systems are well approximated by the thermodynamic limit. This is extremely important for numerical simulations of physical systems: one cannot, of course, simulate 10^{23} molecules on a computer! Even the cases in which the thermodynamic limit *is not* a good approximation are often fruitfully analysed as *violations* of this limit. Finally, the insight gained from analysing the $N \rightarrow \infty$ limit is always crucial in understanding moderate-size systems.

2.5 Ferromagnets and Ising models

Magnetic materials contain molecules with a magnetic moment, a three-dimensional vector which tends to align with the magnetic field felt by the molecule. Moreover, the magnetic moments of two different molecules interact with each other. Quantum mechanics plays an important role in magnetism. Because of quantum effects, the space of possible configurations of a magnetic moment becomes discrete. Quantum effects are also the origin of the ‘exchange interaction’ between magnetic moments. In many materials, the effect of the exchange interaction is such that the energy is lower when two moments align. While the behaviour of a single magnetic moment in an external field is qualitatively simple, when we consider a bunch of interacting moments, the problem is much richer, and exhibits remarkable collective phenomena.

A simple mathematical model for such materials is the Ising model. This describes the magnetic moments by Ising spins localized at the vertices of a certain region of a d -dimensional cubic lattice. To keep things simple, let us consider a region \mathbb{L} which is a cube of side L : $\mathbb{L} = \{1, \dots, L\}^d$. On each site $i \in \mathbb{L}$, there is an Ising spin $\sigma_i \in \{+1, -1\}$ (see Fig. 2.2).

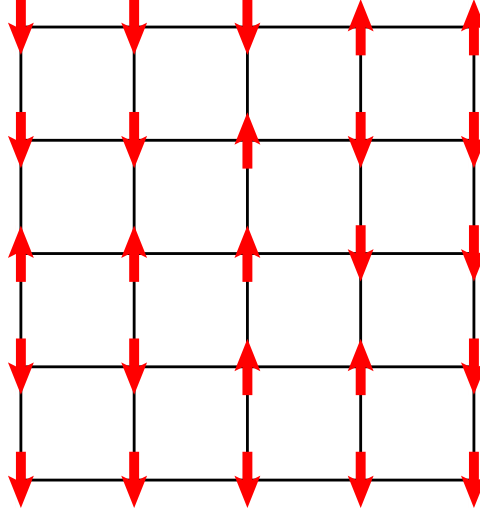


Fig. 2.2 A configuration of a two-dimensional Ising model with $L = 5$. There is an Ising spin σ_i on each vertex i , shown by an arrow pointing up if $\sigma_i = +1$ and pointing down if $\sigma_i = -1$. The energy (2.53) is given by the sum of two types of contributions: (i) a term $-\sigma_i\sigma_j$ for each edge (ij) of the graph, such that the energy is minimized when the two neighbouring spins σ_i and σ_j point in the same direction; and (ii) a term $-B\sigma_i$ for each site i , due to the coupling to an external magnetic field. The configuration depicted here has an energy $-8 + 9B$.

A configuration $\underline{\sigma} = (\sigma_1 \dots \sigma_N)$ of the system is given by assigning the values of all the spins in the system. Therefore, the space of configurations $\mathcal{X}_N = \{+1, -1\}^{\mathbb{L}}$ has the form (2.1), with $\mathcal{X} = \{+1, -1\}$ and $N = L^d$.

The definition of a ferromagnetic Ising model is completed by the definition of the energy function. A configuration $\underline{\sigma}$ has an energy

$$E(\underline{\sigma}) = - \sum_{(ij)} \sigma_i \sigma_j - B \sum_{i \in \mathbb{L}} \sigma_i, \quad (2.53)$$

where the sum over (ij) runs over all the (unordered) pairs of sites $i, j \in \mathbb{L}$ which are nearest neighbours. The real number B measures the applied external magnetic field.

Determining the free energy density $f(\beta)$ in the thermodynamic limit for this model is a non-trivial task. The model was invented by Wilhem Lenz in the early 1920s, who assigned the task of analysing it to his student Ernst Ising. In his thesis of 1924, Ising solved the $d = 1$ case and showed the absence of phase transitions. In 1948, Lars Onsager brilliantly solved the $d = 2$ case, exhibiting the first soluble ‘finite-dimensional’ model with a second-order phase transition. In higher dimensions, the problem is unsolved, although many important features of the solution are well understood.

Before embarking on any calculations, let us discuss some qualitative properties of this model. Two limiting cases are easily understood. At infinite temperature, $\beta = 0$, the energy (2.53) no longer matters and the Boltzmann distribution weights all the configurations with the same factor 2^{-N} . We have therefore an assembly of completely independent spins. At zero temperature, $\beta \rightarrow \infty$, the Boltzmann distribution concen-

trates onto the ground state(s). If there is no magnetic field, i.e. $B = 0$, there are two degenerate ground states: the configuration $\underline{\sigma}^{(+)}$ with all the spins pointing up, $\sigma_i = +1$, and the configuration $\underline{\sigma}^{(-)}$ with all the spins pointing down, $\sigma_i = -1$. If the magnetic field is set to some non-zero value, one of the two configuration dominates: $\underline{\sigma}^{(+)}$ if $B > 0$ and $\underline{\sigma}^{(-)}$ if $B < 0$.

Notice that the reaction of the system to the external magnetic field B is quite different in the two cases. To see this fact, define a ‘rescaled’ magnetic field $x = \beta B$ and take the limits $\beta \rightarrow 0$ and $\beta \rightarrow \infty$ keeping x fixed. The expected value of any spin in \mathbb{L} , in the two limits, is

$$\langle \sigma_i \rangle = \begin{cases} \tanh(x) & \text{for } \beta \rightarrow 0, \\ \tanh(Nx) & \text{for } \beta \rightarrow \infty. \end{cases} \quad (2.54)$$

Each spin reacts independently for $\beta \rightarrow 0$. In contrast, they react as a whole as $\beta \rightarrow \infty$: one says that the response is cooperative.

A useful quantity for describing the response of the system to the external field is the **average magnetization**,

$$M_N(\beta, B) = \frac{1}{N} \sum_{i \in \mathbb{L}} \langle \sigma_i \rangle. \quad (2.55)$$

Because of the symmetry between the up and down directions, $M_N(\beta, B)$ is an odd function of B . In particular, $M_N(\beta, 0) = 0$. A cooperative response can be emphasized by considering the **spontaneous magnetization**

$$M_+(\beta) = \lim_{B \rightarrow 0+} \lim_{N \rightarrow \infty} M_N(\beta, B). \quad (2.56)$$

It is important to understand that a non-zero spontaneous magnetization can appear only in an infinite system: the order of the limits in eqn (2.56) is crucial. Our analysis so far has shown that a spontaneous magnetization exists at $\beta = \infty$: $M_+(\infty) = 1$. On the other hand, $M_+(0) = 0$. It can be shown that the spontaneous magnetization $M_+(\beta)$ is always zero in a high temperature phase defined by $\beta < \beta_c(d)$ (such a phase is called **paramagnetic**). In one dimension ($d = 1$), we shall show below that $\beta_c(1) = \infty$. The spontaneous magnetization is always zero, except at zero temperature ($\beta = \infty$): one speaks of a zero-temperature phase transition. In dimensions $d \geq 2$, $\beta_c(d)$ is finite, and $M_+(\beta)$ becomes non-zero in the **ferromagnetic phase**, i.e. for $\beta > \beta_c$: a phase transition takes place at $\beta = \beta_c$. The temperature $T_c = 1/\beta_c$ is called the **critical temperature**. In the following, we shall discuss the $d = 1$ case, and a variant of the model, called the Curie–Weiss model, where each spin interacts with all the other ones: this is the simplest model which exhibits a finite-temperature phase transition.

2.5.1 The one-dimensional case

The $d = 1$ case has the advantage of being simple to solve. We want to compute the partition function (2.4) for a system of N spins with energy $E(\underline{\sigma}) = -\sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} - B \sum_{i=1}^N \sigma_i$. We shall use the **transfer matrix method**, which belongs to the general dynamic programming strategy familiar to computer scientists.

We introduce a partial partition function, where the configurations of all spins $\sigma_1, \dots, \sigma_p$ have been summed over, at fixed σ_{p+1} :

$$z_p(\beta, B, \sigma_{p+1}) \equiv \sum_{\sigma_1, \dots, \sigma_p} \exp \left[\beta \sum_{i=1}^p \sigma_i \sigma_{i+1} + \beta B \sum_{i=1}^p \sigma_i \right]. \quad (2.57)$$

The partition function (2.4) is given by $Z_N(\beta, B) = \sum_{\sigma_N} z_{N-1}(\beta, B, \sigma_N) \exp(\beta B \sigma_N)$. Obviously, z_p satisfies the recursion relation

$$z_p(\beta, B, \sigma_{p+1}) = \sum_{\sigma_p = \pm 1} T(\sigma_{p+1}, \sigma_p) z_{p-1}(\beta, B, \sigma_p) \quad (2.58)$$

where we have defined the **transfer matrix** $T(\sigma, \sigma') = \exp[\beta \sigma \sigma' + \beta B \sigma']$. This is the 2×2 matrix

$$T = \begin{pmatrix} e^{\beta + \beta B} & e^{-\beta - \beta B} \\ e^{-\beta + \beta B} & e^{\beta - \beta B} \end{pmatrix} \quad (2.59)$$

Introducing the two-component vectors $\psi_L = \begin{pmatrix} \exp(\beta B) \\ \exp(-\beta B) \end{pmatrix}$ and $\psi_R = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$, and the standard scalar product between vectors $(a, b) = a_1 b_1 + a_2 b_2$, the partition function can be written in matrix form:

$$Z_N(\beta, B) = (\psi_L, T^{N-1} \psi_R). \quad (2.60)$$

Let us call the eigenvalues of T λ_1, λ_2 , and the corresponding eigenvectors ψ_1, ψ_2 . It is easy to realize that ψ_1, ψ_2 can be chosen to be linearly independent, and hence ψ_R can be decomposed as $\psi_R = u_1 \psi_1 + u_2 \psi_2$. The partition function is then expressed as

$$Z_N(\beta, B) = u_1 (\psi_L, \psi_1) \lambda_1^{N-1} + u_2 (\psi_L, \psi_2) \lambda_2^{N-1}. \quad (2.61)$$

The diagonalization of the matrix T gives

$$\lambda_{1,2} = e^\beta \cosh(\beta B) \pm \sqrt{e^{2\beta} \sinh^2 \beta B + e^{-2\beta}}. \quad (2.62)$$

For β finite, in the large- N limit, the partition function is dominated by the largest eigenvalue λ_1 , and the free-entropy density is given by $\phi = \log \lambda_1$:

$$\phi(\beta, B) = \log \left[e^\beta \cosh(\beta B) + \sqrt{e^{2\beta} \sinh^2 \beta B + e^{-2\beta}} \right]. \quad (2.63)$$

Using the same transfer matrix technique, we can compute expectation values of observables. For instance, the expected value of a given spin is

$$\langle \sigma_i \rangle = \frac{1}{Z_N(\beta, B)} (\psi_L, T^{i-1} \hat{\sigma} T^{N-i} \psi_R), \quad (2.64)$$

where $\hat{\sigma}$ is the following matrix:

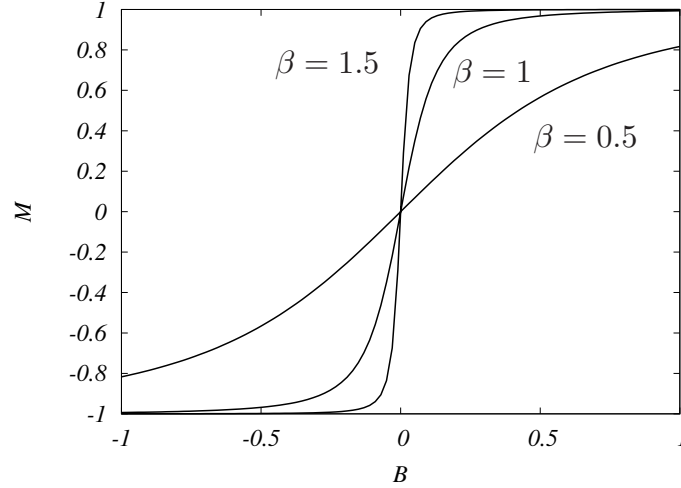


Fig. 2.3 The average magnetization of the one-dimensional Ising model, as a function of the magnetic field B , at inverse temperatures $\beta = 0.5, 1, 1.5$.

$$\hat{\sigma} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (2.65)$$

Averaging over the position i , one can compute the average magnetization $M_N(\beta, B)$. In the thermodynamic limit, we get

$$\lim_{N \rightarrow \infty} M_N(\beta, B) = \frac{\sinh \beta B}{\sqrt{\sinh^2 \beta h + e^{-4\beta}}} = \frac{1}{\beta} \frac{\partial \phi}{\partial B}(\beta, B). \quad (2.66)$$

Both the free energy and the average magnetization turn out to be analytic functions of β and B for $\beta < \infty$. In particular the spontaneous magnetization vanishes at any non-zero temperature:

$$M_+(\beta) = 0, \quad \forall \beta < \infty. \quad (2.67)$$

In Fig. 2.3, we plot the average magnetization $M(\beta, B) \equiv \lim_{N \rightarrow \infty} M_N(\beta, B)$ as a function of the applied magnetic field B for various values of the temperature β . The curves become steeper and steeper as β increases. This statement can be made more quantitative by computing the **susceptibility** associated with the average magnetization,

$$\chi_M(\beta) = \frac{\partial M}{\partial h}(\beta, 0) = \beta e^{2\beta}. \quad (2.68)$$

This result can be interpreted as follows. A single spin in a field has a susceptibility $\chi(\beta) = \beta$. If we consider N spins constrained to take the same value, the corresponding susceptibility will be $N\beta$, as in eqn (2.54). In the present case, the system behaves as if the spins were grouped into blocks of $\chi_M(\beta)/\beta$ spins each. The spins in each group are constrained to take the same value, while spins belonging to different blocks are independent.

This qualitative interpretation can be given further support by computing a **correlation function**.

Exercise 2.6 Consider the one-dimensional Ising model in zero field, $B = 0$. Show that when $\delta N < i < j < (1 - \delta)N$, the correlation function $\langle \sigma_i \sigma_j \rangle$ is, in the large- N limit,

$$\langle \sigma_i \sigma_j \rangle = e^{-|i-j|/\xi(\beta)} + \Theta(e^{-\alpha N}), \quad (2.69)$$

where $\xi(\beta) = -1/\log \tanh \beta$.

[Hint: You can either use the general transfer matrix formalism or, more simply, use the identity $e^{\beta \sigma_i \sigma_{i+1}} = \cosh \beta (1 + \sigma_i \sigma_{i+1} \tanh \beta)$.]

Note that, in eqn (2.69), $\xi(\beta)$ gives the typical distance below which two spins in the system are well correlated. For this reason, it is usually called the **correlation length** of the model. This correlation length increases as the temperature decreases: spins become correlated at larger and larger distances. The result (2.69) is clearly consistent with our interpretation of the susceptibility. In particular, as $\beta \rightarrow \infty$, $\xi(\beta) \approx e^{2\beta}/2$ and $\chi_M(\beta) \approx 2\beta\xi(\beta)$.

The connection between correlation length and susceptibility is very general and can be understood as a consequence of the fluctuation–dissipation theorem (2.44):

$$\begin{aligned} \chi_M(\beta) &= \beta N \left\langle \left(\frac{1}{N} \sum_{i=1}^N \sigma_i \right); \left(\frac{1}{N} \sum_{i=1}^N \sigma_i \right) \right\rangle \\ &= \frac{\beta}{N} \sum_{i,j=1}^N \langle \sigma_i; \sigma_j \rangle = \frac{\beta}{N} \sum_{i,j=1}^N \langle \sigma_i \sigma_j \rangle, \end{aligned} \quad (2.70)$$

where the last equality comes from the fact that $\langle \sigma_i \rangle = 0$ when $B = 0$. Using eqn (2.69), we get

$$\chi_M(\beta) = \beta \sum_{i=-\infty}^{+\infty} e^{-|i|/\xi(\beta)} + \Theta(e^{-\alpha N}). \quad (2.71)$$

It is therefore evident that a large susceptibility must correspond to a large correlation length.

2.5.2 The Curie–Weiss model

The exact solution of the one-dimensional model led Ising to think that there could not be a phase transition for any dimension. Some thirty years earlier, a qualitative theory of ferromagnetism had been put forward by Pierre Curie. Such a theory assumed the existence of a phase transition at a non-zero temperature T_c (the ‘Curie point’) and a non-vanishing spontaneous magnetization for $T < T_c$. The dilemma was eventually solved by Onsager’s solution of the two-dimensional model.

Curie’s theory is realized exactly within a rather abstract model: the **Curie–Weiss model**. We shall present it here as one of the simplest solvable models with a finite-temperature phase transition. Once again, we have N Ising spins $\sigma_i \in \{\pm 1\}$, and a

configuration is given by $\underline{\sigma} = (\sigma_1, \dots, \sigma_N)$. However, the spins no longer sit on a d -dimensional lattice: they all interact in pairs. The energy function, in the presence of a magnetic field B , is given by

$$E(\underline{\sigma}) = -\frac{1}{N} \sum_{(ij)} \sigma_i \sigma_j - B \sum_{i=1}^N \sigma_i, \quad (2.72)$$

where the sum over (ij) runs over all of the $N(N-1)/2$ couples of spins. Notice the peculiar $1/N$ scaling in front of the exchange term. The exact solution presented below shows that this is the only choice which yields a non-trivial free energy density in the thermodynamic limit. This can be easily understood intuitively as follows. The sum over (ij) involves $\Theta(N^2)$ terms of order $\Theta(1)$. In order to get an energy function that scales as N , we need to put a coefficient $1/N$ in front.

In adopting the energy function (2.72), we gave up an attempt to describe any finite-dimensional geometrical structure. This is a severe simplification, but has the advantage of making the model exactly soluble. The Curie–Weiss model is the first example of a large family: the **mean-field models**. We shall explore many instances of this family throughout the book.

A possible approach to the computation of the partition function consists in observing that the energy function can be written in terms of a simple observable, the **instantaneous (or empirical) magnetization**,

$$m(\underline{\sigma}) = \frac{1}{N} \sum_{i=1}^N \sigma_i. \quad (2.73)$$

Notice that this is a function of the configuration $\underline{\sigma}$, and should not be confused with its expected value, the average magnetization (see eqn (2.55)). It is a ‘simple’ observable because it is equal to a sum of observables depending upon a single spin.

We can write the energy of a configuration in terms of its instantaneous magnetization:

$$E(\underline{\sigma}) = \frac{1}{2}N - \frac{1}{2}Nm(\underline{\sigma})^2 - NBm(\underline{\sigma}). \quad (2.74)$$

This implies the following formula for the partition function:

$$Z_N(\beta, B) = e^{-N\beta/2} \sum_m \mathcal{N}_N(m) \exp \left\{ \frac{N\beta}{2}m^2 + N\beta Bm \right\}, \quad (2.75)$$

where the sum over m runs over all of the possible instantaneous magnetizations of N Ising spins: $m = -1 + 2k/N$ with $0 \leq k \leq N$, where k is an integer number, and $\mathcal{N}_N(m)$ is the number of configurations that have a given instantaneous magnetization m . This is a binomial coefficient whose large- N behaviour can be expressed in terms of the entropy function of Bernoulli variables:

$$\mathcal{N}_N(m) = \binom{N}{N(1+m)/2} \doteq \exp \left[N \mathcal{H} \left(\frac{1+m}{2} \right) \right]. \quad (2.76)$$

To leading exponential order in N , the partition function can thus be written as

$$Z_N(\beta, B) \doteq \int_{-1}^{+1} e^{N\phi_{\text{mf}}(m; \beta, B)} dm, \quad (2.77)$$

where we have defined

$$\phi_{\text{mf}}(m; \beta, B) = -\frac{\beta}{2}(1 - m^2) + \beta Bm + \mathcal{H}\left(\frac{1+m}{2}\right). \quad (2.78)$$

The integral in eqn (2.77) is easily evaluated by the Laplace method, to get the final result for the free energy density

$$\phi(\beta, B) = \max_{m \in [-1, +1]} \phi_{\text{mf}}(m; \beta, B). \quad (2.79)$$

One can see that the maximum is obtained away from the boundary points, so that the corresponding m must be a stationary point of $\phi_{\text{mf}}(m; \beta, B)$, which satisfies the **saddle point equation** $\partial\phi_{\text{mf}}(m; \beta, B)/\partial m = 0$:

$$m_* = \tanh(\beta m_* + \beta B). \quad (2.80)$$

In the above derivation, we were slightly sloppy in two steps: substituting the binomial coefficient by its asymptotic form, and changing the sum over m into an integral. The mathematically minded reader is invited to show that these passages are indeed correct.

With a little more work, the above method can be extended to expectation values of observables. Let us consider, for instance, the average magnetization $M(\beta, B)$. It can be easily shown that, whenever the maximum of $\phi_{\text{mf}}(m; \beta, B)$ over m is non-degenerate,

$$M(\beta, B) \equiv \lim_{N \rightarrow \infty} \langle m(\underline{\sigma}) \rangle = m_*(\beta, B) \equiv \arg \max_m \phi_{\text{mf}}(m; \beta, B). \quad (2.81)$$

We can now examine the implications that can be drawn from Eqs. (2.79) and (2.80). Let us consider first the $B = 0$ case (see Fig. 2.4). The function $\phi_{\text{mf}}(m; \beta, 0)$ is symmetric in m . For $0 \leq \beta \leq 1 \equiv \beta_c$, it is also concave and achieves its unique maximum at $m_*(\beta) = 0$. For $\beta > 1$, $m = 0$ remains a stationary point but becomes a local minimum, and the function develops two degenerate global maxima at $m_{\pm}(\beta)$, with $m_+(\beta) = -m_-(\beta) > 0$. These two maxima bifurcate continuously from $m = 0$ at $\beta = \beta_c$.

A phase transition takes place at β_c . Its meaning can be understood by computing the expectation value of the spins. Notice that the energy function (2.72) is symmetric under a spin-flip transformation which maps $\sigma_i \rightarrow -\sigma_i$ for all i . Therefore $\langle \sigma_i \rangle = \langle (-\sigma_i) \rangle = 0$, and the average magnetization vanishes, i.e. $M(\beta, 0) = 0$. On the other hand, the spontaneous magnetization, defined in eqn (2.56), is zero in the paramagnetic phase, i.e. for $\beta < \beta_c$, and equal to $m_+(\beta)$ in the ferromagnetic phase for $\beta > \beta_c$. The physical interpretation of this phase is the following: for any finite N , the pdf of the instantaneous magnetization $m(\underline{\sigma})$ has two symmetric peaks, at $m_{\pm}(\beta)$,

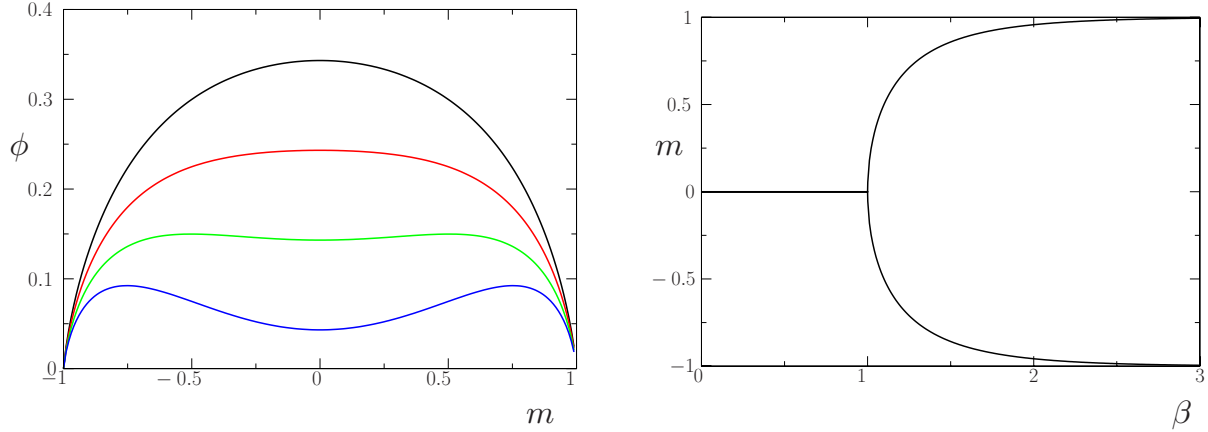


Fig. 2.4 *Left:* the function $\phi_{\text{mf}}(m; \beta, B = 0)$ plotted versus m , for $\beta = 0.7, 0.9, 1.1, 1.3$ (from top to bottom). For $\beta < \beta_c = 1$, there is a unique maximum at $m = 0$; for $\beta > \beta_c = 1$, there are two degenerate maxima at two symmetric values $\pm m_+(\beta)$. *Right:* the values of m which maximize $\phi_{\text{mf}}(m; \beta, B = 0)$, plotted versus β . The phase transition at $\beta_c = 1$ is signalled by a bifurcation.

which become sharper and sharper as N increases. Any external perturbation which breaks the symmetry between the peaks, for instance a small positive magnetic field B , favours one peak with respect to the other one, and therefore the system develops a spontaneous magnetization. Let us stress that the occurrence of a phase transition is a property of systems in the thermodynamic limit $N \rightarrow \infty$.

In physical magnets, symmetry breaking can arise, for instance, from impurities, subtle effects of dipolar interactions together with the shape of the magnet, or an external magnetic field. The result is that at low enough temperatures some systems, the ferromagnets, develop a spontaneous magnetization. If a magnet made of iron is heated, its magnetization disappears at a critical temperature $T_c = 1/\beta_c \approx 770^\circ \text{C}$. The Curie Weiss model is a simple solvable case exhibiting this phase transition.

Exercise 2.7 Compute the expansions of $m_+(\beta)$ and of $\phi(\beta, B = 0)$ near $\beta = \beta_c$, and show that the transition is of second order. Compute the low-temperature behaviour of the spontaneous magnetization.

Exercise 2.8 *Inhomogeneous Ising chain.* The one-dimensional Ising problem does not have a finite-temperature phase transition, as long as the interactions are short-range and translationally invariant. On the other hand, if the couplings in the Ising chain grow fast enough at large distance, one can have a phase transition. This is not a very realistic model from the point of view of physics, but it is useful as a solvable example of a phase transition.

Consider a chain of Ising spins $\sigma_0, \sigma_1, \dots, \sigma_N$ with energy $E(\underline{\sigma}) = -\sum_{n=0}^{N-1} J_n \sigma_n \sigma_{n+1}$. Suppose that the coupling constants J_n form a positive, monotonically increasing sequence, growing logarithmically. More precisely, we assume that $\lim_{n \rightarrow \infty} J_n / \log n = 1$. Denote by $\langle \cdot \rangle_+$ and $\langle \cdot \rangle_-$ the expectation value with respect to the Boltzmann probability distribution when the spin σ_N is fixed at $\sigma_N = +1$ and -1 , respectively.

- (a) Show that, for any $n \in \{0, \dots, N-1\}$, the magnetization is $\langle \sigma_n \rangle_{\pm} = \prod_{p=n}^{N-1} \tanh(\beta J_p)$
- (b) Show that the critical inverse temperature $\beta_c = 1/2$ separates two regimes, such that for $\beta < \beta_c$, one has $\lim_{N \rightarrow \infty} \langle \sigma_n \rangle_+ = \lim_{N \rightarrow \infty} \langle \sigma_n \rangle_- = 0$, and for $\beta > \beta_c$, one has $\lim_{N \rightarrow \infty} \langle \sigma_n \rangle_{\pm} = \pm M(\beta)$, with $M(\beta) > 0$.

Notice that in this case, the role of the symmetry-breaking field is played by the choice of boundary condition.

2.6 The Ising spin glass

In real magnetic materials, localized magnetic moments are subject to several sources of interaction. Apart from the exchange interaction mentioned in the previous section, they may interact through intermediate conduction electrons, for instance. As a result, depending on the material considered, their interaction can be either ferromagnetic (their energy is minimized when they are parallel) or **antiferromagnetic** (their energy is minimized when they point *opposite* to each other). **Spin glasses** are a family of materials whose magnetic properties are particularly complex. They can be produced by diluting a small fraction of a magnetic transition metal such as manganese into a noble metal such as copper in a ratio, say, of 1 : 100. In such an alloy, magnetic moments are localized at manganese atoms, which are placed at random positions in a copper background. Depending on the distance between two manganese atoms, the net interaction between their magnetic moments can be either ferromagnetic or antiferromagnetic.

The **Edwards–Anderson model** is a widely accepted mathematical abstraction of these physical systems. Once again, the basic degrees of freedom are Ising spins $\sigma_i \in \{-1, +1\}$ sitting on the vertices of a d -dimensional cubic lattice $\mathbb{L} = \{1, \dots, L\}^d$, $i \in \mathbb{L}$. The configuration space is therefore $\{-1, +1\}^{\mathbb{L}}$. As in the ferromagnetic Ising model, the energy function reads

$$E(\underline{\sigma}) = - \sum_{(ij)} J_{ij} \sigma_i \sigma_j - B \sum_{i \in \mathbb{L}} \sigma_i, \quad (2.82)$$

where $\sum_{(ij)}$ runs over each edge of the lattice. Unlike the case of the Ising ferromagnet, however, a different coupling constant J_{ij} is now associated with each edge (ij) , and its sign can be positive or negative. The interaction between spins σ_i and σ_j is ferromagnetic if $J_{ij} > 0$ and antiferromagnetic if $J_{ij} < 0$.

A pictorial representation of this energy function is given in Fig. 2.5. The Boltzmann distribution is given by

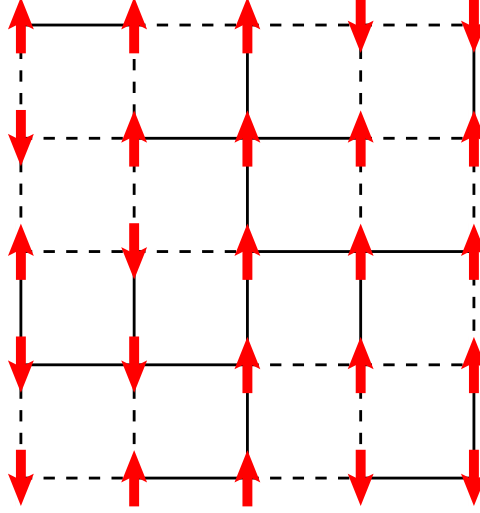


Fig. 2.5 A configuration of a two-dimensional Edwards–Anderson model with $L = 5$. Spins are coupled by two types of interactions: ferromagnetic ($J_{ij} = +1$), indicated by a continuous line, and antiferromagnetic ($J_{ij} = -1$), indicated by a dashed line. The energy of the configuration shown here is $-14 - 7h$.

$$\mu_{\beta}(\underline{\sigma}) = \frac{1}{Z(\beta)} \exp \left\{ \beta \sum_{(ij)} J_{ij} \sigma_i \sigma_j + \beta B \sum_{i \in \mathbb{L}} \sigma_i \right\}, \quad (2.83)$$

$$Z(\beta) = \sum_{\underline{\sigma}} \exp \left\{ \beta \sum_{(ij)} J_{ij} \sigma_i \sigma_j + \beta B \sum_{i \in \mathbb{L}} \sigma_i \right\}. \quad (2.84)$$

It is important to notice that the couplings $\{J_{ij}\}$ play a completely different role from the spins $\{\sigma_i\}$. The couplings are just parameters involved in the definition of the energy function, like the magnetic field B , and they are not summed over when computing the partition function. In principle, for any particular sample of a magnetic material, one should estimate experimentally the values of the J_{ij} 's and then compute the partition function. We could have made explicit the dependence of the partition function and of Boltzmann distribution on the couplings by using notation such as $Z(\beta, B; \{J_{ij}\})$, $\mu_{\beta, B; \{J_{ij}\}}(\underline{\sigma})$. However, when these explicit mentions are not necessary, we prefer to keep to lighter notation.

The present understanding of the Edwards–Anderson model is much poorer than for the ferromagnetic models introduced in the previous section. The basic reason for this difference is **frustration**, which is illustrated in Fig. 2.6 for an $L = 2$, $d = 2$ model (a model consisting of just four spins).

A spin glass is frustrated whenever there exist local constraints that are in conflict, meaning that it is not possible to satisfy all of them simultaneously. In the Edwards–Anderson model, a plaquette is the name given to a group of four neighbouring spins forming a square (i.e. a cycle of length four). A plaquette is frustrated if and only if the product of the J_{ij} 's along all four edges of the plaquette is negative. As shown in Fig. 2.6, it is then impossible to minimize simultaneously all of the four local energy

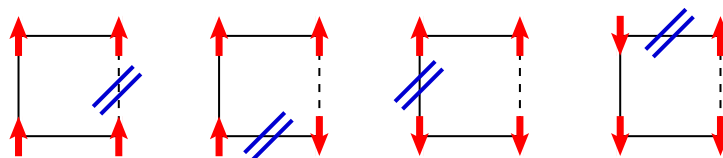


Fig. 2.6 Four configurations of a small Edwards–Anderson model: continuous lines indicate ferromagnetic interactions ($J_{ij} = +1$), and dashed lines indicate antiferromagnetic interactions ($J_{ij} = -1$). In zero magnetic field ($B = 0$), the four configurations are degenerate and have energy $E = -2$. The double bar indicates an unsatisfied interaction. Notice that there is no configuration with a lower energy. This system is frustrated since it is impossible to satisfy simultaneously all constraints.

terms associated with each edge. In a spin glass, the presence of a finite density of frustrated plaquettes generates a very complicated energy landscape. The resulting effect of all the interactions is not obtained by ‘summing’ the effects of each of them separately, but is the outcome of a complex interplay. The ground state spin configuration (the one satisfying the largest possible number of interactions) is difficult to find: it cannot be guessed on symmetry grounds. It is also frequent to find in a spin glass a configuration which is very different from the ground state but has an energy very close to the ground state energy. We shall explore these and related issues throughout the book.

Notes

There are many good introductory textbooks on statistical physics and thermodynamics, for instance Reif (1965) and Huang (1987). Going towards more advanced texts, we can suggest the books by Ma (1985) and Parisi (1988). A more mathematically minded presentation can be found in the books by Gallavotti (1999) and Ruelle (1999). The reader will find there a proof of Proposition 2.6.

The two-dimensional Ising model in a vanishing external field can also be solved by a transfer matrix technique: see for instance Baxter (1982). The transfer matrix, which links one column of the lattice to the next, is a $2^L \times 2^L$ matrix, and its dimension diverges exponentially with the lattice size L . Finding its largest eigenvalue is therefore a complicated task. No one has found the solution so far for $B \neq 0$.

Spin glasses will be a recurring theme in this book, and more will be said about them in the following chapters. An introduction to this subject from a physicist’s point of view is provided by the book by Fischer and Hertz (1993) and the review by Binder and Young (1986). The concept of frustration was introduced by Toulouse (1977).