CHAPTER 1

Classical Equilibrium Statistical Mechanics

1.1. The basic axiom

The main aim of statistical mechanics is to derive the thermodynamic properties of macroscopic bodies starting from a description of the motion of the microscopic components (e.g., atoms, electrons, etc.). This would be an impossible and hopeless task if one took the normal approach of mechanics (given the Hamiltonian and the initial conditions, to compute the trajectories), since the number of degrees of freedom is so huge (see, however, Chapter 20): probabilistic methods are mandatory.

The problem can be divided into two parts: (a) Find the probability distribution of the microscopic components in thermal equilibrium, (i.e., after a sufficiently long time). (b) Compute the macroscopic properties of the system from the microscopic probability distribution.

We perform step (a) simply by assuming that the equilibrium probability distribution is given by the Boltzmann formula [see Eq. (1.5)]. While we shall try to justify this hypothesis in the last part of the book, in this chapter we discuss only some general consequences of this hypothesis, mostly notably with reference to elementary thermodynamics. Step (b) will be the main subject of this book. The reader already familiar with the principles of equilibrium statistical mechanics may prefer to skip this chapter.

Let us consider a classical Hamiltonian system with 2N degrees of freedom in a box of volume V: the coordinates qᵢ and the momenta pᵢ satisfy the classical equations of motion.

\[
\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i},
\]

(1.1)

where \( H \) is the Hamiltonian. Let us consider an observable \( A(q, p) \) (we use \( q \) and \( p \) without labels to indicate the set of all \( q \)'s and \( p \)'s), i.e., an arbitrary measurable quantity. The equilibrium average of \( A \) \( \langle A \rangle \) is
defined by

\[ \bar{A} = \lim_{t \to \infty} \frac{1}{t} \int_0^t A[q(t'), p(t')] \, dt' \]
\[ = \int dq \, dp \, A(q, p) P_{eq}(q, p). \quad (1.2) \]

Equation (1.2) defines the equilibrium probability \( P_{eq} \). It is generally believed that for macroscopic systems \((N \to \infty)\) at fixed density \( \rho = N/V \) the expectation values that have a good limit when \( N \to \infty \), i.e., intensive quantities in the thermodynamic language, such as the kinetic energy per particle, satisfy the following relation in most cases:

\[ A[q(t'), p(t')] = \bar{A} + O(N^{-1/2}), \quad (1.3) \]

if the observation time \( t' \) is large enough (so that, for example, thermal diffusion will have eliminated all the initial differences of temperature between different parts of the system).\(^1\)

The function \( P_{eq}(q, p) \) is never negative and satisfies the normalization condition

\[ \int dq \, dp \, P_{eq}(q, p) = 1. \quad (1.4) \]

The fundamental hypothesis of equilibrium statistical mechanics is that \( P_{eq} \) follows the canonical distribution, i.e.

\[ P_{eq}(q, p) = \frac{\exp[-\beta H(q, p)]}{Z}, \quad (1.5) \]

where \( Z \) (the so-called partition function) is fixed by the condition (1.4),

\[ Z = \int dq \, dp \, \exp[-\beta H(q, p)]. \quad (1.6) \]

As we shall see later, \( \beta \) is related to the absolute temperature \( T \) by

\[ \beta = \frac{1}{kT}. \quad (1.7) \]

The Boltzmann coefficient \( k \) relates the empirical scales of temperature and energy; experimentally it is about \( 1.38 \times 10^{-16} \) erg/degree. If we use the same units for both temperature and energy, \( k \) can be set equal to 1, as will be done in most of this book.

It is evident that Eq. (1.5) cannot be true for a finite system; energy is conserved by the equations of motion (1.1). For a given initial condition the energy can take only one value \([P_{eq}(q, p) = \delta(H - E)P_{eq}(q, p)]\), while in Eq. (1.5) configurations with different energies have a nonzero probability. Equation (1.5) can be correct only in the infinite-volume limit \((N \to \infty)\); indeed we shall argue later that the microcanonical distribution \((P_{eq}(q, p) = \text{const.})\) coincides in the infinite-volume limit with the canonical distribution. The reasons for this hope are presented later in the book. However, it is possible to give a physical meaning to Eq. (1.5) for a finite-volume system as well. Let us divide a very large system into two parts and call \( C_1 \) and \( C_2 \) the generalized coordinates of the first and second parts, respectively. We suppose that the total Hamiltonian can be decomposed as

\[ H(C_1, C_2) = H_1(C_1) + H_2(C_2) + \epsilon H_{12}(C_1, C_2), \quad (1.8) \]

where \( \epsilon \) is a small number.

We now consider the case in which the size of system 2 goes to infinity while the size of system 1 remains constant. In this limit, as long as \( \epsilon \) remains different from zero, the large-time probability distribution of the whole system is

\[ P_{eq}(C_1, C_2) = \exp[-\beta H_1(C_1) - \beta H_2(C_2) - \epsilon \beta H_{12}(C_1, C_2)]. \quad (1.9) \]

If we now send \( \epsilon \) to zero but keep the observation time very large (in some cases an explicit computation shows that the time to reach equilibrium for the small system is of order \( e^{-\beta} \); see Chapter 18), the probability distribution (1.9) factors into the product of two independent probability distributions for each of the two subsystems.

Equation (1.5) can therefore be justified for finite systems by considering system 1 to be a part (weakly coupled to the rest) of a nearly infinite system. In other words, the small system is in thermal contact with a thermal reservoir. It is rather important to note that two systems in thermal contact have a distribution probability characterized by the same \( \beta \); from elementary thermodynamics these two systems must have the same temperature. It is thus consistent to assume that there is a universal (system-independent) relation between \( \beta \) and the temperature. We shall see in section 1.3 that \( \beta^{-1} \) is proportional to the absolute temperature.

### 1.2. The entropy

We argued earlier that the probability distribution (1.5) describes a Hamiltonian system at large times; we can now generalize Eq. (1.5). We consider a set of configurations \( C \), with a measure \( d\mu(C) \) and a "Hamilton-
1.2. The Entropy

(1.11) \( S_{\text{eq}} \) and the entropy computed by dividing the phase space into cells of size \( \varepsilon^N \) \( (S_{\text{dis}}) \) are related by a trivial normalization factor when \( \varepsilon \) is very small:

\[
S_{\text{dis}} = S_{\text{eq}} - d \ln \varepsilon .
\]  

(1.13)

We shall see later that the quantum entropy for a system of \( 2N \) degrees of freedom is well approximated by the entropy of the classical system with \( \varepsilon \) equal to the Planck constant.

Let us compute the entropy for a very simple example. The system has \( M \) possible configurations, and only \( L \) configurations (let us say the first \( L \)) have a nonzero equal probability:

\[
P_j = \begin{cases} 
\frac{1}{L} & j \leq L \\
0 & j > L
\end{cases}
\]  

(1.14)

The corresponding entropy is \( \ln L \). From this example we can draw the following general conclusions: If \( S[P] = 0 \), only one configuration has nonzero probability, if \( S[P] = \ln M \), all configurations have the same probability; roughly speaking, we could say that \( \exp[S[P]] \) is the number of configurations in which the system may stay with a not-too-small probability. This last statement can be sharpened by using some concepts from information theory.

Let us consider a system that can stay in \( 2^N \) configurations. If we want to communicate which configuration the system is in, we need to transmit a number between 1 and \( 2^N \), which can be coded as a sequence of \( k \) digits that may be 0 or 1; by definition the message contains \( k \) bits of information. Now if we have \( N \) copies of the same system, we need \( Nk \) bits to transmit the information as to which configuration these \( N \) systems occupy.

Let us suppose that the probability distribution of these \( N \) systems is known; in this case we already have information on the systems, and it is reasonable to assume that we need fewer than \( Nk \) bits to know the configurations of the \( N \) systems. Unfortunately this last statement is not so clear. Our information is probabilistic; if the \( N \) systems stay in a rather unlikely configuration and the message has been coded using fewer than \( Nk \) bits, the message may be interpreted in the wrong way.

A precise way to formulate the problem is the following: If we transmit a message describing the configurations of the \( N \) systems, what is the minimum number of bits \( (B_N) \) that we must communicate to ensure that the probability of misinterpretation of the message (after decoding) goes to zero when \( N \) goes to infinity? The answer is given by Shannon's theorem, and it is very simple:
\[ \frac{\delta Q}{T} = dS_w, \]  

(1.20)

From the second law we know that if \( T \) is the absolute temperature, then \( \delta Q/T \) is an exact differential (this is the definition of the absolute temperature, apart from a multiplicative scale factor):

\[ \frac{\delta Q}{T} = dS_w, \]  

(1.21)

where \( S_w \) is the macroscopic entropy, i.e., the entropy defined in the thermodynamical approach. In other words, \( 1/T \) is the integrating factor of the heat. If we prove that

\[ \beta \delta S = \beta (dU - \delta L) = dS_{eq}, \]  

(1.22)

we find that \( \beta \) is proportional to \( 1/T \) and that \( S_w = S_{eq} \), apart from an additive constant.

Let us prove Eq. (1.22). In order to do work on the system, the Hamiltonian must depend on a control parameter \( \lambda \). We can give energy to the system by changing \( \lambda \). We now consider an infinitesimal variation \( d\lambda \) and \( d\beta \) of \( \lambda \) and \( \beta \). Neglecting higher-order infinitesimals, we have

\[ dS_{eq} = d(\beta U - \beta F) = \beta (dU - \delta L), \]  

(1.25)

which is the desired result; \( \beta \) is therefore \( 1/kT \) (\( k \) can be set equal to 1.
The usual argument runs as follows: after the system has reached equilibrium, if we measure the value of an intensive quantity inside a small region, the output of the measurement will not be the equilibrium value, but thermal fluctuations will be present; when the volume goes to infinity the number of regions in which we can measure $A$ will be proportional to the volume (i.e., to $N$), and fluctuations from different regions will cancel out in the average over the regions. In other words, we divide the volume into $V/N$ parts, $V_0$ being a fixed volume. We have $A = (V/V_0) \sum_i A_i$, where $A_i$ is the observable in the $i$th subvolume. If $V_0$ is not too small, we can assume that the $A_i$'s are independent random variables with a common average $\bar{A}$. (As we shall see in Chapter 7, the assumption of independent fluctuations fails at the phase transition point.) Equation (1.13) follows from the central limit theorem, which states that the probability distribution of the sum of $L$ independent random variables $(A = 1/L \sum_i A_i)$ becomes Gaussian when $L$ goes to infinity:

$$P(A) = \left(\frac{L}{2\pi \delta}\right)^{1/2} \exp\left[-(A - \bar{A})^2 \cdot \frac{L}{(2\delta)}\right].$$

Notes for Chapter 1

2. As an example, we consider the probability distribution

$$P(x) = \frac{1}{(2\pi A)^{1/2}} \exp\left(-\frac{x^2}{2A}\right)$$

for $x$ in the range $-\infty < x < +\infty$. The corresponding entropy is $\int_0^\infty dx P(x) \ln P(x) = -\frac{1}{2} \ln(2\pi A)$, which goes to $-\infty$ when $A$ goes to zero [$P(x)$ becomes a $\delta$ function].

3. Let us check Eq. (1.13) in the case of a one-dimensional distribution: the probability of the system staying in the $i$th cell $x_i < x < x_{i+1}$, $x_i = \epsilon x_i$, is given by $P_i(\epsilon P_i) = \epsilon P(x) = \epsilon P_i$. The entropy is thus

$$S_i = \ln(\epsilon P_i) - \epsilon P_i - \ln \epsilon = -\epsilon \sum_{j=1}^{\infty} \frac{P_j(\ln P_j)}{P_j} - \ln \epsilon.$$

4. There are many books on information theory. One with which I am personally most familiar is A. Kintchin, Mathematical Foundations of Information Theory, Dover, London (1963).

5. The average number of bits we can gain in coding the state of the system is by definition the amount of information contained in the probability distribution.

6. If we want to maximize a function $\Phi(P)$ with the constraint $g(P) = 0$, we can maximize the function $\Phi(P) - \lambda g(P)$, where the so-called Lagrange multiplier $\lambda$ is chosen in such a way that the maximum of $\Phi(P)$ satisfies the constraint. In our case, $g(P) = \sum_i P_j - 1$, we get

$$\frac{\partial}{\partial P_i} \left[ \Phi(P) - \lambda g(P) \right] = H_i + \left( \frac{1}{\beta} + \lambda \right) - \ln P_i = 0,$$

$$P_i = \frac{\exp(-\beta H_i)}{Z}, \quad Z = \sum_j \exp(-\beta H_j).$$

CHAPTER 2

Magnetic Systems

2.1. General Properties

The formalism of the previous chapter can be applied to a very large variety of systems; however, in the next chapters we shall deal mainly with magnetic systems. We have made this choice because magnetic systems offer a very wide spectrum of problems, ranging from very simple to very difficult. Moreover, the physics of magnetic systems has strongies problems that concern other materials and with relativistic field theory. It is, therefore, an ideal starting point.

Let us consider a generic magnetic system; for each configuration of the system we can define the corresponding magnetization \( \mathbf{S}(x) \), \( x \) being a point of the physical space. Microscopically \( \mathbf{S}(x) \) receives contributions both from the motion of the electrons and from the spins of the electrons (and in a very small amount from the nuclei); if the electrons that mainly contribute to \( \mathbf{S}(x) \) are localized near the atoms of a lattice, it may be convenient to define \( \mathbf{S} \) only on the points of the lattice.

From the experimental and theoretical points of view it is interesting to study the response of the system to the action of an external magnetic field \( \mathbf{H}(x) \). Let us therefore consider the following Hamiltonian:

\[
H(C) = H_0(C) - \int_V d^3x \mathbf{H}(x) \cdot \mathbf{S}(x) = H_0(C) - \int_V d^3x \sum_{\mu} h_\mu(x) S_\mu(x),
\]

(2.1)

where \( H_0(C) \) is the Hamiltonian in absence of magnetic field, \( V \) is the volume occupied by the system, and, in order to lighten the notation, we have not indicated explicitly the dependence of \( \mathbf{S} \) on \( C \). As in Sec. 1.2, \( C \) denotes a generic configuration of the system.

Most of the information on the magnetic properties of the system is contained in the free energy \( F[h] \) as a functional of \( h(x) \). If the magnetic field does not depend on \( x \), we can write the free energy as a function of \( h \)

\[
F(h) = \left[ F[h] \right]_{x=0} - k \frac{\delta F[h]}{\delta h} \quad \text{and define a free-energy density} \quad f(h) = F(h)/V. \quad \text{(We shall follow as far as possible the rule of indicating functionals by square brackets and functions by curved brackets.) The expectation values of the local magnetization} \quad (m_\mu(x)) \quad \text{and of the total magnetization} \quad (M_x) \quad \text{are given as}
\]

\[
m_\mu(x) = \langle S_\mu(x) \rangle; \quad M_x = \langle S^T_x \rangle; \quad S^T_x = \int_V d^3x S_\mu(x).
\]

(2.2)

If the Hamiltonian system is spatially homogeneous (i.e., invariant under continuous or discrete translations), and the magnetic field is consequently constant, the magnetization will be an independent (let us neglect the case of antiferromagnets): \( m_\mu(x) = m_\mu \).

It is easy to see that

\[
m_\mu(x) = -\frac{\delta F[h]}{\delta h_\mu(x)}, \quad m_\mu = -\frac{\delta f(h)}{\delta h_\mu}
\]

(2.3)

if we use the definitions

\[
F[h] = -\frac{1}{\beta} m(Z[h]),
\]

\[
Z[h] = \int dC \exp(-\beta H(C)).
\]

(2.4)

There are already nontrivial experimental consequences that follow from Eqs. (2.2), (2.3), and (2.4). Let us start from the relation

\[
u(h) = f(h) - T \frac{\partial f}{\partial T},
\]

(2.5)

where \( u(h) \) is the internal energy density.

If we differentiate Eq. (2.5) with respect to \( h_\mu \) we find

\[
\frac{\partial u(h)}{\partial h_\mu} = \frac{\partial f}{\partial h_\mu} - T \frac{\partial^2 f}{\partial T^2} = -m_\mu + T \frac{\partial m_\mu}{\partial T}.
\]

(2.6)

In the same way, if we define nonmagnetic internal energy \( u_0 = \langle H_0 \rangle = u + \sum_\mu h_\mu m_\mu \), we get

\[
\frac{\partial u_0}{\partial h_\mu} = \sum_\mu h_\mu \frac{\partial m_\mu}{\partial h_\mu} + T \frac{\partial m_\mu}{\partial T}.
\]

(2.7)

Equations (2.6) and (2.7) are consequences of the existence of the free energy (which in a pure thermodynamic treatment follows from the
second law of thermodynamics) and of the equality of cross derivatives; these kinds of relations are normally referred to as Maxwell equations. A very important quantity is the magnetic susceptibility: \( \chi_{\mu\nu} = \delta m_\mu / \delta h_\nu \), in the isotropic case \( \chi_{\mu\nu} = \delta_{\mu\nu} \chi \). We can also consider a point-dependent magnetic susceptibility:

\[
\chi_{\mu\nu}(x, y) = \frac{\delta m_\mu(x)}{\delta h_\nu(y)}.
\]

In a translationally invariant system we have

\[
\chi_{\mu\nu}(x, y) = \chi_{\mu\nu}(x - y), \quad \chi_{\mu\nu} = \frac{1}{V} \int d^3x \chi(x, y).
\] (2.8)

Starting from the relations

\[
\chi_{\mu\nu} = -\frac{\delta^2 F}{\delta h_\mu \delta h_\nu}, \quad \chi_{\mu\nu}(x, y) = \chi_{\mu\nu}(y, x),
\] (2.9)

we get the following symmetry properties of the susceptibility:

\[
\chi_{\mu\nu} = \chi_{\nu\mu}, \quad \chi_{\mu\nu}(x, y) = \chi_{\nu\mu}(y, x).
\] (2.10)

If we perform explicitly the derivatives of Eq. (2.4) we find

\[
\chi_{\mu\nu} = \beta \langle s^\mu s^\nu \rangle_c = \beta \{ \langle s^\mu s^\nu \rangle_c - \langle s^\mu \rangle \langle s^\nu \rangle_c \}
= \beta \{ \langle s^\mu - \langle s^\mu \rangle_c \rangle \langle s^\nu - \langle s^\nu \rangle_c \rangle \}
= \beta \langle (s^\mu - \langle s^\mu \rangle_c) (s^\nu - \langle s^\nu \rangle_c) \rangle_c
= \beta \langle (s^\mu(x) - \langle s^\mu \rangle_c) (s^\nu(y) - \langle s^\nu \rangle_c) \rangle_c
= \beta \langle (s^\mu(x) - \langle s^\mu \rangle_c) (s^\nu(y) - \langle s^\nu \rangle_c) \rangle_c.
\] (2.11)

If the probability distribution \( P(C) \) is concentrated on a single configuration (i.e., if it is a delta function), no thermodynamical fluctuations are present and the right-hand sides of Eqs. (2.10) and (2.11) are zero. If we consider the diagonal elements of the susceptibility, we get \( \chi_{\mu\mu} = \langle (s^\mu - \langle s^\mu \rangle_c)^2 \rangle_c \); in other words, the diagonal elements of the susceptibility tensor are given by the variance of the probability distribution of the quantity \( s^\mu \).

Equation (2.11) is a particular case of the more general theorem, which states that the linear response of a system is proportional to the random thermodynamical fluctuations. If the Hamiltonian is \( H_0 + \lambda H_1 \), we have

\[
- \frac{1}{\beta} \frac{d}{d\lambda} \langle A \rangle = \langle H_1 A \rangle_c = \langle H_1 A \rangle - \langle H_1 \rangle \langle A \rangle.
\] (2.12)

Although the proof of Eq. (2.12) is trivial, there is an extension to the dynamic statistical mechanics that is considerably less trivial. It is often called "the fluctuation-dissipation theorem" and is described in Chapter 17. In this context the word "dissipation" is synonymous with "response." Although this name may sound strange, in many cases the linear response is proportional to the energy dissipated in the presence of an external perturbation; for example, if an electric field \( E \) acts on a conductor, the energy dissipated (\( E_d \)) is given by

\[
E_d = EI = \frac{E^2}{R}.
\] (2.13)

where the electric current \( I \) is fixed by Ohm's law, \( I = E/R \).

2.2. Spontaneous symmetry breaking

Ferromagnetic systems have spontaneous magnetization at low temperatures, i.e., below the Curie temperature. If a system in zero external magnetic field has a magnetization pointing in a given direction, in the absence of an external perturbation (if we stay below the Curie temperature) the magnetization will not change with time; however, when we apply an external magnetic field and then remove it, we can have the same system with a time-independent spontaneous magnetization that is the opposite of the previous one. In other words the systems may stay in two (or more) states characterized by the direction of the magnetization; however, in the presence of an external magnetic field (neglecting possible nonequilibrium effects, e.g., hysteresis) the magnetization will always be oriented in the direction of the external field.

From the microscopic point of view it is clear that for each configuration \( C \) there is another configuration \( C' \) such that \( C \) and \( C' \) have the same energy but opposite magnetization, i.e., \( S(C) = -S(C') \). The configuration \( C' \) can be obtained from the configuration \( C \) by inverting the sign of all the velocities and the spins of all the particles of the system.

When spontaneous magnetization is present, the Hamiltonian of the system is invariant under a transformation that changes the sign of the magnetization; however, the state of the system, i.e., its probability distribution, is not invariant under this transformation. When this happens we say that the symmetry is spontaneously broken (it would be explicitly broken in the presence of an external magnetic field).

At first sight spontaneous symmetry breaking seems to be in conflict with the fundamental principles of statistical mechanics, i.e., Eq. (1.5): if \( H \) is invariant, \( P \) must also be invariant. This argument is absolutely correct for a finite volume, but fails for an infinite system in which Eq. (1.5) is only formal because \( Z \) is infinite. If we start from Eq. (1.5) for
finite systems and we go to the infinite-volume limit with the magnetic field $h$ exactly equal to zero, the magnetization will always be equal to zero (the integral of an odd function is zero).

However, this last result is true only if $h$ is exactly equal to zero; a better insight on the problem may be obtained if we consider the magnetization density and the free energy as functions of $h$ in the infinite-volume limit. The symmetry argument tells us that $f(h) = f(-h)$ and $m(h) = -f(h)/\partial h = -m(-h)$, i.e., $f$ and $m$ are even and odd functions of $h$, respectively. We have two possibilities: either $m(h)$ is continuous at $h = 0$ and $m(0)$ is consequently zero, or $m(h)$ is discontinuous at $h = 0$ and $m(0)$ is not so well defined; this second case corresponds to spontaneous symmetry breaking, as we shall see. More precisely, these two possibilities correspond to

$$f(h) = f(0) + 0(h^\alpha), \quad \alpha > 1$$

(2.14)

$$f(h) = f(0) - m_0|h| + 0(h^\alpha).$$

In case (a), $f$ is differentiable with respect to $h$ and $m(h)$ is continuous. In case (b), $f$ is not differentiable with respect to $h$ at $h = 0$ and $m$ is a discontinuous function;

$$m^+ = \lim_{h \to 0^+} m(h) = m_0, \quad m^- = \lim_{h \to 0^-} m(h) = -m_0. \quad (2.15)$$

The symmetry relation implies only $m^+ = -m^-$. In case (a) the magnetization at $h = 0$ is really zero, whereas in case (b) an infinitesimal magnetic field is enough to produce a nonzero magnetization (see Fig. 3.2). If that happens, we say that the system has a spontaneous magnetization. In the limit $h \to 0$ the Hamiltonian becomes invariant under the transformation $S \to -S$, but the statistical expectation values are not invariant under the same transformation, so we say that the symmetry is spontaneously broken. For most of the ferromagnets, case (b) is realized at low enough temperature (below the Curie temperature), at least in three dimensions.

The nondifferentiability of the free energy with respect to a parameter and the existence of two or more equilibrium states is the distinctive feature of a first-order transition: according to the Ehrenfest classification, if the free energy is differentiable $(k-1)$ times, but not $k$ times, the singularity point is called a transition of order $k$ (notice that the free energy is always continuous). However, it is customary to call any transition of order greater than the first a second-order transition. If a first-order phase transition is induced by changing the temperature, we are in the presence of a latent heat.

2.2. Spontaneous Symmetry Breaking

$$u_+ = \lim_{T \to T_c^+} \left( \frac{\partial \beta f}{\partial \beta} \right), \quad u_- = \lim_{T \to T_c^-} \left( \frac{\partial \beta f}{\partial \beta} \right). \quad (2.16)$$

It is crucial to understand that phase transitions (and by consequence spontaneous symmetry breaking) are possible only if the volume of the system is infinite. Indeed, in a finite volume, if the configuration space is compact, $Z$ is an entire function (we assume that the Hamiltonian is not singular): $|Z(\beta)| = \int dC \exp(-\beta H(C)) \leq V_C \exp(\beta |H|)$ even for complex $\beta$, where $V_C = \int dC$ is the volume of the configuration space and $|H| = \max \{|H(C)|\}$; in the extreme case the configuration space is a finite set of points and $Z$ is a linear combination of exponentials. If the configuration space is not compact but $Z(\beta) = \int dC \exp(-\beta H(C))$ is finite (i.e., the integral is convergent) for any real positive $\beta$, the same integral must exist for any complex $\beta$ such that Re $\beta > 0$ ($|Z(a + ib)| \leq Z(a)$); it is clear, however, that the integral defining $Z$ will be divergent at $\beta = 0$ when the volume of the configuration space is infinite ($\beta H$ is positive).

We have proved that the partition function of a reasonable Hamiltonian $Z$ (such that $Z(\beta)$ is defined for positive $\beta$) is an analytic function in the positive half of the complex $\beta$ plane; a similar result may be obtained for the behavior of $Z$ as a function of the magnetic field.

What happens to the free energy (i.e., $-1/\beta \ln Z(\beta)$)? If $Z$ is analytic, its logarithm may be singular only at the points where $Z = 0$. Now for real values of the parameters (temperature and magnetic field) $Z$ is the sum of positive terms, so it cannot have zeros; consequently the free energy is analytic near the positive real axis for a finite-volume system. However, in the infinite-volume limit a nonanalytic free energy may be produced if the complex zeros of the partition function pinch the real parameter axis. A toy model is given by a system of volume $V$, which can stay in only two states (of equal energy at zero magnetic field) having total magnetization $\pm V$, respectively. We easily obtain for the free energy as a function of the magnetic field $h$

$$Z(h) = 2 \cosh(\beta h V), \quad f(h) = -\frac{1}{\beta V} \ln[2 \cosh(\beta h V)],$$

$$m(h) = \tanh(\beta h V), \quad Z\left(\frac{(2n + 1)\pi i}{2\beta V}\right) = 0. \quad (2.17)$$

When $V$ goes to infinity, the zeros of $Z$ pinch the real $h$ axis at $h = 0$, and the expectation value of the magnetization $\langle m \rangle$ becomes $m = \text{sign}(h)$. In a real macroscopic system of finite extent the internal energy will change a finite amount (in units of $k$) when the temperature changes by $10^{-20}$ Kelvin, and for all practical purposes we are in the presence of a discontinuity. In order to have a mathematical discontinuity we must go
to the infinite-volume limit. This is one of the main reasons why in this book we shall concentrate on infinite-volume systems: in this limiting case sharper statements can be made.

In order to specify the finite system Hamiltonian, we must fix the Hamiltonian of the bulk and the boundary conditions (i.e., the Hamiltonian at the surface); if we do not stay at a first-order phase transition point, by definition there is only one thermodynamic stable phase, and the distribution probability in the infinite-volume limit will not depend on the boundary condition. We shall see later that the effect of the boundary conditions on the expectation values at the center of a box of side \( L \) vanishes as \( \exp(-L/\xi) \) in the generic case (as a power at a second-order phase-transition point). At a first-order transition point there are two or more phases, and the final result will depend on the boundary conditions. For example, in the magnetic case, the expectation value of the magnetization will be \( \pm m \) if we constrain the magnetization on the boundary to be positive or negative, respectively; if we set free our periodic boundary conditions for the magnetization at the surface, the expectation value of the magnetization will be zero by symmetry arguments. In other words the boundary conditions for a nearly infinite system play the same role as an infinitesimal magnetic field for an infinite system: in both cases we produce a difference in energy between the two most likely configurations (characterized by having mostly positive or negative magnetization). This energy difference goes to infinity with the volume or with the surface, so that only one of the two possible configurations dominates the sum in the partition function, when the volume goes to infinity.

If we consider the time evolution\(^6\) of a real system at the first-order phase-transition point inside a box of side \( L \), the large-time behavior strongly depends on the initial conditions: at exactly \( 0^\circ C \) we can have either ice or water. Similarly the spontaneous magnetization of a piece of iron may point in any direction. A detailed computation shows that we need to wait for a time proportional to \( \exp(L^{1/2}) \) (an incredibly large time!) to see the spontaneous reverse of the magnetization.\(^8\) In order to reproduce the experimental situation we must first send the volume to infinity, and only later the observation time to infinity: The two limits do not commute.

If we define

\[
\langle \cdot \rangle_x = \lim_{\hbar \to 0} \langle \cdot \rangle_h
\]

we expect that the large-time behavior of a single large (or infinite-volume) system will be described by \( \langle \cdot \rangle_e \) or \( \langle \cdot \rangle_\perp \) if the \( t=0 \) initial conditions are homogeneous in space (i.e., translationally invariant).\(^9\)

On the contrary, if we average over the possible initial conditions we get

\[
\langle \cdot \rangle = \frac{1}{2} \langle \cdot \rangle_+ + \frac{1}{2} \langle \cdot \rangle_-. 
\]

2.2. Spontaneous Symmetry Breaking

the symmetric \( h = 0 \) state:

\[
\langle \cdot \rangle_0 = \frac{1}{2} \langle \cdot \rangle_+ + \frac{1}{2} \langle \cdot \rangle_- .
\]

(2.19)

From the foregoing discussion it is clear that \( \langle \cdot \rangle_0 \) describes a statistical mixture, and only \( \langle \cdot \rangle_\perp \) can describe the large-time behavior of a single system. The general situation in mathematical terms is the following: let us consider the set of all possible translationally invariant states. This set is convex\(^11\) (e.g., we could obtain the state \( \langle \cdot \rangle_\perp = p \langle \cdot \rangle_+ + (1 - p) \langle \cdot \rangle_- \) by imposing free boundary conditions but adding an external magnetic field equal to \( \text{arctanh}(2p - 1)/(\beta V) \) before sending the volume to infinity). A state that cannot be decomposed as the superposition of two different states \( \langle \cdot \rangle_e = \alpha \langle \cdot \rangle_0 + (1 - \alpha) \langle \cdot \rangle_\perp \) implies \( \langle \cdot \rangle_e = \langle \cdot \rangle_\perp \) if \( 0 < \alpha < 1 \) is said to be pure or extremal. It can be proved that each state can be decomposed in a unique way as the convex combination of pure states.\(^12\) In this language, a symmetry group \( G \) is spontaneously broken if the symmetric state is not pure and it can be decomposed as the convex combination of pure states that transform as a nontrivial representation of \( G \).

The argument for identifying the pure states with large-time behavior of a single, spatially homogeneous system is mainly the following: If we add to the Hamiltonian a small perturbation localized around the point \( x \) \( (\delta H = B(x)) \), we expect on physical grounds that the expectation value of an observable \( A(y) \) localized around the point \( y \) does not change at all when \( |x - y| \) goes to infinity.\(^13\) From the linear response theory this may happen if the connected correlation functions \( \langle B(x)A(y) \rangle_\rho \to 0 \) at large distance for any \( B \) and \( A \). The vanishing of the connected correlation functions at large distances is the clustering property.\(^14\) If it is satisfied, the state is said to be clustering or is said to satisfy the “cluster decomposition property.” Now the stability of the large-time evolution of a single physical system implies that the corresponding state is clustering. Up to now our argument may be described as mere handwaving; however, there is a rigorous theorem which states that pure states are clustering and vice versa. Spontaneous symmetry breaking can be related to the failure of the clustering decomposition in the symmetric state. Indeed, coming back to our magnetic case, it is easy to show that

\[
\langle S(x)S(y) \rangle_{\rho p} = \langle S(x)S(y) \rangle_{\rho} - \langle S(x) \rangle_{\rho} \langle S(y) \rangle_{\rho} = 4p(1 - p)m^2 \quad \text{for } |x - y| \to \infty .
\]

According to the theorem, the only two clustering states are the two extremal states at \( p = 0 \) and \( p = 1 \) (i.e., \( \langle \cdot \rangle_\perp \) and \( \langle \cdot \rangle_\perp \)).
Appendix to Chapter 2

Functional were introduced in the last century by the great Italian mathematician, Vito Volterra. The basic idea behind them is very simple: in the same way that a function \( f(x) \) associates a number \( x \) with another number, \( i.e., f(x) \), a functional \( F[g] \) associates a function \( g(x) \) with a number, \( i.e., F[g] \).

Very elementary examples of functionals are the definite integral (\( I[g] = \int_a^b g(x) \, dx \)) of the value of the function at a given point (\( f[x(0)] = g(0) \)), and the maximum of a function in a given interval (\( M[g] = \max_{x \in [a,b]} g(x) \)). The functional \( S[g] = \int dx \; g(x) \ln g(x) \) is the entropy of \( g(x) \) if the function \( g \) is positive definite and normalized to one \((\int g(x) \, dx = 1)\).

Generally speaking, we must consider when dealing with functionals; very often they may take an infinite value even when the function \( g \) seems to be "well behaved" (\( I[g] = \infty \) if \( g = 1/(1 + x^2)^{1/2} \)). If we do not work within well-defined mathematical framework, paradoxical results may be obtained. However, in most cases it is sufficient to consider the functionals as acting only on a restricted space of functions \( i.e., I[g] \) will be well defined when \( g \) is a bounded measurable function with fast decrease at infinity, \( F[g] \) and \( M[g] \) when \( g \) is a continuous function).

For simplicity we skip all the mathematical details, we can define the functional derivative of a functional by starting from the Taylor expansion. We suppose that

\[
F[g + \varepsilon h] = F[g] + \varepsilon \int dx \; \frac{\delta F}{\delta g(x)} \; h(x) + o(\varepsilon^2)
\]

for any reasonable \( h(x) \), where \( \delta F/\delta g(x) \) is by definition the functional derivative; we stress that the functional derivative is a function of \( x \) and a functional of \( g \). In this book all the functional derivatives we need can be computed by inspection. For example, we easily obtain

\[
\frac{\delta I}{\delta g(x)} = f'(g(x)), \quad \frac{\delta M}{\delta g(x)} = \delta(x), \quad \frac{\delta F}{\delta g(x)} = \delta(x)
\]

This last result was obtained by integration by parts. A slightly less trivial example is

\[
\frac{\delta M}{\delta g(x)} = \delta(x - x_M),
\]

where \( x_M \) is the value of \( x \) at which the function \( g(x) \) reaches its maximum in the interval 0-1; if the function \( g(x) \) has more than one maximum the functional \( M \) is not differentiable at this point.

We recall that the Lagrangian approach to classical mechanics can easily be cast into functional language: The action is a functional of the trajectory \( q(t) \) in the time interval from \( t_0 \) to \( t_1 \); its explicit form is

\[
S[q] = \int_{t_0}^{t_1} L(q, \dot{q}) \, dt,
\]

where \( L \) is the Lagrangian function. The classical equations of motion are \( \delta S/\delta q(t) = 0 \); indeed at \( t \neq t_0 \) and \( t \neq t_1 \) we have

\[
\frac{\delta S}{\delta q(t)} = \frac{\partial}{\partial q(t)} L(q(t), \dot{q}(t)) - \frac{d}{dt} \left[ \frac{\partial}{\partial \dot{q}(t)} L(q(t), \dot{q}(t)) \right].
\]

Most of the techniques used for functions of many variables can also be applied to functionals; for example, the proof in the last chapter of the variational principle [Eq (1.18)] can easily be extended to the case where the configuration space is continuous and \( \Phi[P] \) is defined as

\[
\Phi[P] = \int d\mu \; \left( C \right) P[C] \left[ H(C) + \frac{1}{\beta} \ln P(C) \right].
\]

Sometimes it is convenient to approximate the space of functions, on which the functional is defined, by a finite-dimensional space (of dimension \( L \)); in this way the functional is reduced to a function of many variables, and formal manipulations are much easier. This may be a reasonable way to prove theorems on functionals, when we are able to keep under control the results in the limit \( L \) going to infinity.

Notes for Chapter 2

1. \( \langle AB \rangle_C \) stands for the connected average, \( i.e., \langle AB \rangle_C = \langle AB \rangle - \langle A \rangle \langle B \rangle \). For the definition of the connected average of many functions, see p. 53.
Indeed, we have

\[
\frac{d}{d\lambda} \langle A \rangle = \frac{d}{d\lambda} \left\{ \frac{dC[\exp(-\beta H_0 - \lambda H_1)A]}{dC[\exp(-\beta H_0 - \beta \lambda H_1)A]} \right\} \\
= -\beta \int dC \left\{ \frac{\exp(-\beta H_0 - \beta \lambda H_1)A}{Z} \right\} \\
+ \beta \int dC \exp(-\beta H_0 - \lambda \beta H_1)A \cdot \int dC \\
\frac{\exp(-\beta H_0 - \beta \lambda H_1)H_1}{Z^2}.
\]

\[
Z = \int dC[\exp(-\beta H_0 - \beta \lambda H_1)].
\]

For a nice presentation of what happens in real materials see, for example, C. Kittel, Introduction to Solid State Theory, John Wiley and Sons, New York (1966).

This transformation is called time reversal. The reader should notice that in this chapter, from here on, we suppress the indices of the magnetization; our general rule will be to suppress indices as much as possible unless this suppression creates ambiguities.

A value of \(\alpha\) less than 1 is impossible because this leads to an infinite value of the magnetization at \(h = 0\). In case (b) there is a first-order transition in the magnetic field; in case (a), a higher-order transition or no transition at all (e.g., when \(\alpha = 1\)).

The free energy is a convex function, i.e., \(f(\alpha \beta_1 + (1 - \alpha)\beta_2) \geq \alpha f(\beta_1) + (1 - \alpha)f(\beta_2)\). The proof of this is rather simple: In a finite volume, where \(f(\beta)\) is an analytic function, its second derivative with respect to any parameter is always negative because it can be written as the expectation value of minus a perfect square, e.g., \((d^2/\partial\lambda^2)f(\beta) = -(1/\beta V)(\langle H - \langle H \rangle \rangle^2) = -(1/\beta V)(\langle HH \rangle - \langle H \rangle^2)\). It is well known that a function whose second derivative is never positive is convex. Now the limit of differentiable functions may not be differentiable, but the limit of convex functions must be convex (convexity is written under the form of an inequality). It is also well known that convexity implies continuity.

This observation is mainly due to T. D. Lee and C. N. Yang. An elementary discussion of the subject can be found in K. Huang, Statistical Mechanics, John Wiley and Sons, New York (1963).

8. From a purely logical point of view the discussion of the time evolution of a system undergoing a first-order phase transition is out of place here. It is useful, however, for understanding from a physical point of view the importance of the pure (clustering) states, to be defined soon.

9. This kind of estimate is based on the hypothesis that the time needed to go from configuration \(A\) to configuration \(B\) is proportional to \(\exp(-\beta(F_B - F_A))\), \(F_A\) being the maximal free energy that the system must assume in its trajectory (which is supposed to be continuous) from \(A\) to \(B\). A very nice quantitative application of this idea can be found in J. S. Langer and V. Ambegaokar, Phys. Rev. 164, 498 (1967).

The same approach can be used for obtaining the mean life of a metastable state.

10. We want to exclude a macroscopically inhomogeneous initial condition, e.g., half space with positive magnetization and half space with negative magnetization.

11. A subset of a linear space is convex if, when \(a\) and \(b\) belong to this subset, \(c = \alpha a + (1 - \alpha)b\) belongs to the same subset for \(0 \leq \alpha \leq 1\).


13. This condition is very strong. A similar condition under some restrictive technical hypothesis can be shown to imply the canonical distribution.

14. If we define the intensive quantities \(\bar{A}\) and \(\bar{B}\) as \(\bar{A} = 1/V \int_A dx A(x)\) and \(\bar{B} = 1/V \int_B dx B(x)\), in the infinite-volume limit these intensive quantities do not fluctuate (e.g., \(\langle A\bar{B} \rangle = \langle A \rangle \langle B \rangle\) only if the connected correlations go to zero at infinity).


16. See any book on classical mechanics; for example, H. Goldstein, Classical Mechanics, Addison-Wesley, Reading, MA (1950).
3.1. The Model

It is clear that $H_θ^μ[S]$ will depend on $β$ in an explicit way. Now if we could exactly perform the integration over the other degrees of freedom in Eq. (3.1), the final result would be a terrible mess; the normal procedure consists in postulating a simple model form for the effective Hamiltonian, depending on a few parameters that can be fitted from the experiments or approximately computed in a microscopic way. The art of model building is rather subtle; the model must be simple enough to be investigated analytically and flexible enough to reproduce the essential properties of the systems we want to study. Although in most cases one tries to construct models that are as realistic as possible, for very well-known models this process is inverted: one tries to perform experiments on systems whose effective Hamiltonian is, as close as possible to that of a well-known model.

In many magnetic materials the electrons responsible for magnetic behavior are localized near the atoms of a lattice, and the force, which tends to orient the spins, is the exchange interaction (which is a very short-range force). The most popular models, which describe this situation, are the Ising and Heisenberg models: the magnetization is defined only on the points of the lattice. (For simplicity we shall consider mainly the square lattice in two dimensions, the cubic lattice in three dimensions, and the hypercubic lattice in higher dimensions. $D$ will denote the dimensions of the space.) The magnetization $S_i$ can take only the values $±1$ for the Ising model or belongs to the unit three-dimensional sphere for the Heisenberg model $(∑_iS_i^2 = 1)$. One can also consider a generalized $n$-component Heisenberg model in which $S_i$ belongs to the $n$-dimensional unit sphere; for $n = 1$ and 3 we recover the Ising and the Heisenberg models, respectively. The Hamiltonian in the presence of a site-dependent external magnetic field $h_i$ is, in the Ising and $n$-component Heisenberg cases, respectively,

$$H_i = -J ∑_{i,k} S_i S_k - ∑_i h_i S_i$$

$$H_μ = -J ∑_{i,k} S_i^μ S_k^μ - ∑_i h_i^μ S_i^μ,$$  \(3.3\)

where the sum over $i$ and $k$ runs over all possible nearest-neighbor pairs of the lattice. If the exchange constant $J$ is positive, the system is ferromagnetic, and parallel "spins" are energetically favored; if $J$ is negative, the system is antiferromagnetic and nearby spins tend to stay antiparallel. On square or cubic lattices at zero external magnetic fields, ferromagnetic and antiferromagnetic models, having the same value of $|J|$, have the same partition function (i.e., $Z(J)$ is an even function of $J$); indeed one can switch from the ferromagnetic to the antiferromagnetic...
3.2. The Mean-Field Approximation

In spite of the apparent simplicity of the Ising model and of the efforts of more than one generation of physicists, an exact solution (i.e., evaluation of the free energy and of the correlation functions) is available only in one dimension or in two dimensions at zero magnetic field. In the general case, approximate solutions must be considered. The simplest of these is the mean-field approximation, which we now describe.

The starting point of mean-field theory is the variational principle (1.18). However, we do not look for the true minimum of the free-energy functional, but restrict ourselves to simple forms of the probability distribution; in the simplest approximation, the probability distribution is assumed to be factorized. The most general form is

$$P[S] = \prod_i P_i(S_i)$$

leading to

$$P_i(S_i) = \frac{1 + m_i}{2} \delta_{S_i,1} + \frac{1 - m_i}{2} \delta_{S_i,-1},$$

(3.5)

where $\delta_{\cdot,\cdot}$ is the Kronecker delta.

The probability $P$ is already normalized to one:

$$\sum_{\{S\}} P[S] = \prod_i \left[ \sum_{S_i = \pm 1} P_i(S_i) \right] = 1.$$  

(3.6)

We denote by $\Sigma_{\{S\}}$ the sum over all configurations of the system (in this case their number is $2^N$). The factorization of the probability implies the following rules for the expectation values:

$$\langle g_1(S_1)g_2(S_2) \rangle_p = \langle g_1(S_1) \rangle_p \langle g_2(S_2) \rangle_p,$$

$$\langle g(S_i) \rangle_p = \frac{1 + m_i}{2} g(1) + \frac{1 - m_i}{2} g(-1),$$

(3.7)

where the $g$'s are arbitrary functions. We finally find

$$\langle S_i \rangle = m_i,$$

$$\langle H \rangle = -J \sum_{\langle i,k \rangle} m_i m_k - \sum_i h_i m_i,$$

$$S[P] = -\langle \ln P(S) \rangle_p = -\sum_i \langle \ln P_i(S_i) \rangle_p = \sum_i s(m_i)$$

$$s(m) = \frac{1 + m}{2} \ln \left( \frac{1 + m}{2} \right) + \frac{1 - m}{2} \ln \left( \frac{1 - m}{2} \right),$$

(3.8)

$$\Phi[P] = \langle H \rangle_p - \frac{S[P]}{\beta}.$$

The necessary condition for a minimum, $\partial \Phi / \partial m_i = 0$, becomes here

$$-\sum_k J_{ik} m_k - h_i + \beta \arctanh m_i = 0,$$

$$m_i = \tanh \left[ \beta \left( \sum_k J_{ik} m_k + h_i \right) \right],$$

(3.9)

where we have introduced the matrix $J_{ik}$, this matrix is equal to $J$ if $i$ and $k$ are nearest neighbors and it is zero elsewhere: $H = -\frac{1}{2} \sum_{i,k} J_{ik} S_i S_k - \sum_i h_i S_i$. Equation (3.9) is the starting point of the so-called mean-field approximation, which states that each spin $S_i$ feels on the average an external effective magnetic field equal to $h_i + J_{ik} S_k$. Here we have derived Eq. (3.9) starting from the hypothesis of factorized probabilities in order to stress its variational origin.

An alternative derivation of the mean-field equation starts from the
\[ m = \langle S_i \rangle = \langle \tanh(\beta(S_i + S_j + S_k + S_l)) \rangle \]
\[ = \langle A(S_i + S_j + S_k + S_l) \rangle \]
\[ + B(S_i, S_j, S_k, S_l) \]
\[ = 4m_A + 4B(S_i, S_j) \]

where we have used the fact that the spins can take only values ±1. If now we approximate \( \langle S_i, S_j \rangle \) with \( m^2 \), we get \( m = 4Am + 4Bm^3 \). When we compare the result for the critical temperature in this approximation with the mean-field result (which will be computed in subsection 3.4), we see that we find \( \beta_c = 0.357 \) (i.e., \( A = \frac{1}{4} \)), which agrees better with the exact result \( \beta_c = 0.4404 \) (see next chapter) than does the mean-field theory result \( \beta_c = \frac{1}{4} \).

Many equations similar to Eqs. (3.11) and (3.12) can be obtained for the correlation functions by summing over not one spin, but many. Equations of this kind are normally called Dobushin-Lanford-Ruelle equations and are often used to control the probability distribution in the infinite-volume limit in a rigorous way. These equations imply that a given region (in the previous case one spin) is in thermal equilibrium with its surroundings.

Let us come back to the study of the usual mean-field theory equations, i.e., Eq. (3.9). We consider a ferromagnetic \( J > 0 \) and set \( J = 1 \) for simplicity; if the \( h_i \) 's do not depend on \( i \) (constant magnetic field), it is reasonable to suppose (and it is indeed true) that the minimum of \( \Phi \) corresponds to constant magnetization (the \( m_i \) 's do not depend on \( i \)). In this case all the terms of the sum over \( k \) in Eq. (3.9) give the same contribution and their number is equal to \( 2D \). We finally find

\[ \langle S_i \rangle = m_i = m \]
\[ \langle H \rangle \mid N = u = -Dm^2 - \mu m \]

(3.12)

\[ \varphi(m) = \frac{\Phi(m)}{N} = -Dm^2 - \mu m + \frac{1}{\beta} s(m) \]

\[ m = \tanh((2Dm + \mu)\beta) \]

Of course the condition \( d^2 \varphi/dm^2 = 0 \) is not sufficient. We must also impose the condition \( d^2 \varphi/dm^2 > 0 \) in order to be sure that we have found a local minimum and not a local maximum of \( \varphi \). Finally we must compare all the local minima to find the global one.
Let us first discuss the case $h = 0$. The point $m = 0$ is always a solution of the equation $d\varphi/dm = 0$; an elementary computation shows that $d^2\varphi/dm^2 = \chi^{-1} = -2D + 1/\beta(1 - m^2)$.

In the region $2D\beta < 1$, $d^2\varphi/dm^2$ is always positive in the physical interval $-1 \leq m \leq 1$. Therefore there is only one solution of the equation $d\varphi/dm = 0$, and the solution is a (global) minimum. However, in the region $2D\beta > 1$, $d^2\varphi/dm^2$ is negative for $m$ close to zero (i.e., $m^2 < 1 - \frac{1}{2}D\beta$) and positive elsewhere: the point at $m = 0$ is a local maximum.

There are two symmetric minima at $m = \pm m_s$, where

$$m_s \approx 3^{1/2}(2D\beta - 1)^{1/2} \quad 2D\beta \sim 1$$
$$m_s \approx 1 - 2\exp(-4D\beta) \quad 2D\beta \rightarrow \infty. \quad (3.13)$$

If $|h|$ is small, two minima and one maximum will be present. The minimum at which $m$ has the same sign as $h$ will be the global one; if $|h|$ is large enough, the higher minimum and the maximum coalesce, and the function $\varphi(m)$ has only one minimum. The functions corresponding to the various situations are sketched in Fig. 3.1.

The corresponding behavior of $m(h)$ is shown in Fig. 3.2 in the two regions $\beta \approx \beta_c = \frac{1}{2}D$. For $\beta > \beta_c$, spontaneous magnetization is present,

---

**Figure 3.1.** A qualitative sketch of the free energy $\varphi$ as a function of the magnetization $m$ in various situations: (a) $h = 0$, $T > T_c$; (b) $h = 0$, $T = T_c$; (c) $h = 0$, $T < T_c$; (d) positive small $h$, $T < T_c$; (e) positive large $h$, $T < T_c$ or positive small $h$, $T > T_c$.

---

3.2. The Mean-Field Approximation

![Diagram showing magnetization $m$ as a function of magnetic field $h$.](image)

Figure 3.2. The magnetization $m$ as a function of the magnetic field $h$: (a) $T > T_c$; (b) $T < T_c$. In Fig. 3.2b the solid, dashed, and dotted lines denote the stable, metastable, and unstable states, respectively.

And $T_c = 1/\beta_c$, the Curie temperature. The corresponding curve for the free energy in the low-temperature region is shown in Fig. 3.3. Both in Fig. 3.2b and in Fig. 3.3 we can distinguish three regions: the physical one (solid line), which corresponds to the global minimum, the unphysical one (dotted line), which corresponds to the local maximum (here the susceptibility is negative), and a third intermediate region (dashed line), which corresponds to a local minimum.

Handwaving arguments suggest that if we prepare the state at $t = 0$ in the metastable region, i.e., $m > 0$ but $h < 0$ (this can be done by decreasing the magnetic field adiabatically from positive to negative), the system will remain there (local stability) for a very long time, up to the moment when a thermodynamical fluctuation will allow the system to go
to a more stable state \( m < 0 \). This region is called metastable; the mean life of a metastable state may range from seconds to more than a century.\(^6\) Intuitively we expect that we cannot define with infinite precision the expectation values for a metastable state, the observation time being large but finite; if \( t \) is finite in Eq. (1.2), the expectation values will have a small but nontrivial dependence on the initial condition. That is precisely what happens in a purely static approach, as we shall see in Chapter 10.

To summarize, one finds the following result near \( T_c \) at \( h = 0 \):

\[
\begin{align*}
\text{At } T > T_c : & \quad u = 0, \quad m = 0, \\
\text{At } T < T_c : & \quad m \propto (T_c - T)^\beta, \quad u \propto T - T_c, \\
\chi & \propto |T - T_c|^\gamma; \quad \beta = \frac{1}{2}, \quad \gamma = 1.
\end{align*}
\]

(3.14)

At \( T = T_c \) but \( h \neq 0 \), one finds

\[
m \propto h^{1/\delta}, \quad \delta = 3.
\]

(3.15)

The specific heat is discontinuous, but there is no latent heat at \( T = T_c \); we are in presence of a second-order transition; however, no singularity is present if \( h \) is different from zero.

In this way we have derived a rigorous upper bound to the free energy. We can, however, approximate the free energy with the upper bound; in this case the spins \( S \) are assumed not to be correlated.

We shall soon see how one can compute the correlation functions using the linear response theorem: we can thus obtain the first correction to the mean-field approximation and therefore we can decide in which cases the mean-field approximation is reliable. Before doing this, let us sketch how we can reproduce the results of the mean-field approximation in a slightly different way. The key ingredient is the identity

\[
\int d\mu(C) \exp(-\beta H) \geq \int d\mu(C) \exp(-\beta H_0 - \beta \langle H - H_0 \rangle_{H_0}) ,
\]

(3.16)

where

\[
\langle A \rangle_{H_0} = \frac{\int d\mu(C) \exp(-\beta H_0) A}{\int d\mu(C) \exp(-\beta H_0)}.
\]

(3.17)

3.3. A Soluble Model: Weak Long-Range Forces

Equation (3.16) is essentially a convexity inequality that can easily be proved by considering the function

\[
g(\lambda) = \ln \int d[C] \exp[-\beta H_0 - \beta \lambda (H_1 - H_0)].
\]

(3.18)

Obviously \( d^2g/d\lambda^2 \geq 0 \); therefore

\[
g(\lambda) \geq g(0) + \lambda \frac{dg}{d\lambda} \bigg|_{\lambda = 0}.
\]

(3.19)

Specializing Eq. (3.19) to the case \( \lambda = 1 \), we recover inequality (3.16). Let us look at the case \( h_i = 0 \) and consider a trial Hamiltonian \( H_0 = r \Sigma_i S_i \). One finds for the free-energy density

\[
f \leq -\frac{1}{\beta} \ln(2 \cosh(r\beta)) + D \tanh^2(r\beta) - r \tanh(r\beta),
\]

(3.20)

\[
\langle H - H_0 \rangle_{H_0} = Dm^2 - rm, \quad m = \tanh(r\beta).
\]

Now if we substitute \((1/\beta) \arctanh(m) \) for \( r \), we recover Eq. (3.11). This should not be a surprise: indeed, we define

\[
P_{H_0}(C) = \frac{\exp(-\beta H_0(C))}{\int d\mu(C) \exp(-\beta H_0(C))}.
\]

(3.21)

The convexity inequality reduces to the variational principle, and for the \( H_0 \) we have considered, \( P_{H_0} \) has exactly the form given by Eq. (3.5).

3.3. A soluble model: weak long-range forces

In this subsection, we present an Ising model that is exactly soluble by the mean-field approximation.

The model has the same Hamiltonian as Eq. (3.3), where now the sum on \( i \) and \( k \) runs over all possible pairs of a lattice of \( N \) sites, the variable \( J \) being equal to \( 1/N \). The force among spins is weak and long range; the thermodynamic (i.e., infinite-volume) limit is obtained by sending \( N \) to infinity. The model can be solved using the key identity

\[
\exp(-\beta H) = \exp\left(\frac{\beta}{2N} \sum_{i, k} S_i S_k + \beta h \sum_i S_i\right)
\]

\[
= \left(\frac{N\beta}{2\pi}\right)^{1/2} \int_{-\infty}^{\infty} d\lambda \exp\left[-\frac{N\beta \lambda^2}{2} + \sum_i (\beta \lambda + \beta h) S_i\right].
\]

(3.22)
Indeed, the partition function can be written as

\[ Z = \sum_{\{s\}} \exp(-\beta H) = \left( \frac{N\beta}{2\pi} \right)^{1/2} \times \int_{-\infty}^{\infty} \exp\left(-\beta N(\lambda - \frac{N\beta}{2} \lambda^2)\right) d\lambda \exp\left(-\frac{N\beta}{2} \lambda^2\right) \leq N^{1/2} \int_{-\infty}^{\infty} d\lambda \exp\left(-\frac{N\beta}{2} \lambda^2\right) A(\lambda), \]

where \( A(\lambda) = \alpha^2 - \beta^{-1} \ln(2\cosh(\beta \lambda + \beta \hbar)) \),

(3.23)

where \( \Sigma_{\{s\}} \) stands for the sum over the \( 2^N \) possible configurations of the \( N \) spins. The introduction of the variable \( \lambda \) has allowed us to disentangle the contribution of the various spins and to study independent site problems. In the limit \( N \to \infty \) the integral may be evaluated using the method of steepest descent.\(^7\) One easily finds that

\[ f = \min_{\lambda} A(\lambda) + O\left(\frac{1}{N}\right). \]

(3.24)

The value \( \bar{\lambda} \) for which \( A(\lambda) \) is minimized has the physical meaning of the magnetization density; the minimum condition implies

\[ \frac{dA}{d\lambda} \bigg|_{\lambda=\bar{\lambda}} = 0 \Rightarrow \lambda = \tanh[\beta(\lambda + h)] \]

\[ m = -\frac{\partial f}{\partial h} = -\frac{\partial A}{\partial h} \frac{\partial A}{\partial \lambda} = \tanh[\beta(\lambda + h)] = \lambda. \]

(3.25)

Equation (3.25) can be obtained in the mean-field approximation, as we have seen. In other words, the mean-field approximation becomes exact in the infinite-range model. A simple solution of the model is possible owing to the fact that the connected correlation function \( \langle S_i S_k \rangle_c \) (which is \( i \) and \( k \) independent) is of order \( 1/N \) and vanishes when \( N \) goes to infinity. Indeed, from the linear response theorem, it is given by

\[ \langle S_i S_k \rangle_c = \frac{X}{N\beta} = \frac{1}{N\beta} \frac{d\lambda}{dh}. \]

(3.26)

As we shall see later, the mean-field approximation is also exact for finite-range forces in the limit in which the spatial dimensions \( D \) go to infinity.\(^8\) In this case the connected correlation functions also go to zero.

The existence of this soluble model allows us to rederive the mean-field approximation in the following way. We consider the Hamiltonian

\[ H_a = (1-\alpha) \frac{D}{N-1} \sum_i S_i S_k + \alpha \sum_{i,k} J_{i,k} S_i S_k, \]

(3.27)

where the sum \( \Sigma' \) runs over all \( i \) and \( k \) with the condition \( i \neq k \).

At \( \alpha = 0 \) and \( \alpha = 1 \) we recover, respectively, the infinite-range and short-range models. If we call \( f_a \) the free energy density corresponding to the Hamiltonian \( H_a \), it is evident that

\[ \frac{d}{da} f_a |_{a=0} = -\frac{\langle \delta H_a / \delta a \rangle |_{a=0}}{N} \]

\[ = \sum_{i,k} \left( \frac{D}{N-1} - \frac{J_{i,k}}{2} \right) \frac{\langle S_i S_k \rangle_{a=0}}{N} \]

\[ = \left( m^2 + \frac{X}{\beta N} \right) \sum_{i,k} \left( \frac{D}{N-1} - \frac{J_{i,k}}{2} \right) = 0. \]

(3.28)

Indeed, for fixed \( i \) there are \( N-1 \) and \( 2D \) contributions proportional to \( D/(N-1) \) and to \( -D/2 \), respectively.

The convexity inequality (3.19) tells us that \( f_a \approx f_i \). We have thus recovered the standard inequality of mean-field theory. We shall see later how a similar procedure can be used to derive another soluble model of the mean-field approximation, the hierarchical model, which, however, has a much richer structure.

### 3.4. The Correlation Functions

We now compute the correlation functions in the framework of the mean-field approximation. At first sight this seems impossible. The very first assumption of the mean-field approximation is that spins are uncorrelated; the probability distribution is factorized. This difficulty may be bypassed by using the linear response theorem,

\[ \langle S_i S_k \rangle_{h=0} = \frac{1}{\beta} \frac{\partial}{\partial h_i} \frac{\partial}{\partial h_k} F[h] |_{h=0} = \frac{1}{\beta} \frac{\partial m_i}{\partial h_i} |_{h=0}. \]

(3.29)

We can thus start from the factorized \( F[S] \) to compute \( F[h] \) for general \( h \), as discussed in the previous section, and obtain the correlation function using Eq. (3.29). The reader may find the argument paradoxical—we use a distribution probability that has zero correlation functions to compute...
the correlation functions! The solution is evident: Eq. (3.29) holds only for the true $F$ or if $P = P_{eq}$. If $P \neq P_{eq}$ the correlation function and the response function are no longer equal. Now in order to justify the use of Eq. (3.29) we must argue that the error of the response function is smaller than the error of the correlation function when $P$ is near but not equal to $P_{eq}$. This is true, as can be seen from a quite general argument (which holds for most of the variational problems). If $P_{eq}$ is the approximate distribution probability, we assume that the difference $P_{eq} - P_{ap} = \delta P$ is small in some sense. (If $\delta P$ is not small, the approximation does not make sense. This assumption is quite natural.) Just to compare orders, let us say that $\delta P$ is of order $\epsilon$. It is clear that

$$
\langle S_i S_k \rangle_{eq} = \langle S_i S_k \rangle_{ap} + 0(\epsilon)
$$

$$
\delta \Phi(P_{ap}) = \Phi(P_{eq}) + 0(\epsilon^2).
$$

(3.30)

Indeed, the term proportional to $\epsilon$ vanishes due to the condition $\delta \Phi / \delta P|_{P_{eq}} = 0$. Similarly, in the variational approach to quantum mechanics, if there is an error of order $\epsilon$ on the wave function $\langle \psi | H | \psi \rangle$ of an eigenstate, the error of the corresponding energy $E = \langle \psi | H | \psi \rangle$ is of order $\epsilon^2$. This argument justifies the computation of the correlation functions using Eq. (3.29).

For simplicity let us present the computation only in the region $h = 0$, $T > T_c$. Here $m_0 = 0$.

If we add an infinitesimal point-dependent magnetic field, the $m_k$ will also be infinitesimally small. Neglecting terms of order $m_k^2$, we find that Eq. (3.9) reduces to

$$
\sum_k i_k m_k + m_i / \beta = h_i.
$$

(3.31)

whose solution is in the matrix notation

$$
m_i = \sum_k A_{ik} h_k
$$

$$
A_{ik} = \left( \frac{1}{\beta} - J \right)_{i,k}^{-1} \Leftrightarrow \sum_k \left( \frac{\delta_{ik}}{\beta} - J_{ik} \right) A_{kl} = \delta_{lk}.
$$

(3.32)

In other words, $A$ is the inverse of the matrix $1/\beta - J$.

The solution of Eq. (3.32) can easily be found using the Fourier transform. If the configuration space is a cubic lattice, the Fourier transform is defined in the first Brillouin zone $-\pi \leq p_\nu \leq \pi$, $\nu = 1, \ldots, D$. We obtain

$$
A_{kl} = \frac{\beta}{(2\pi)^D} \int_B d^D p G_0(p) \exp[i(\vec{k} - \vec{l}) \cdot \vec{p}]
$$

$$
G_0(p) = \left(1 - 2\beta \sum_k \cos p_k\right)^{-1}
$$

$$
\int_B d^D p = \prod_{\nu = 1}^D \int_{-\pi}^\pi dp_\nu.
$$

(3.33)

Now it is evident that

$$
\langle S_i S_k \rangle = \langle S_i \rangle \langle S_k \rangle = \frac{\beta}{\beta}.
$$

(3.34)

Using this result for the correlation functions, we can compute the corrections to the mean-field result $u = 0$ for $T > T_c$. We find

$$
u = -\frac{1}{2} \sum_k \langle S_i S_k \rangle J_{ik} = \frac{1}{2} \sum_k A_{ik} I_{ik}.
$$

(3.35)

Using the fact that $J$ connects spins only at distance one, we obtain

$$
u = \frac{-1}{(2\pi)^D} \int_B d^D p \frac{\sum_{\nu} \cos p_\nu}{1 - 2\beta \sum_{\nu} \cos p_\nu}
$$

$$
C = \frac{d^D}{d\beta} = \frac{2\beta^2}{(2\pi)^D} \int_B d^D p \left( \sum_{\nu} \cos p_\nu \right)^2
$$

$$
\left(1 - 2\beta \sum_{\nu} \cos p_\nu\right).
$$

(3.36)

Near the phase transition one finds that $G_0(p)$ develops a pole at $p^2 = 0$:

$$
G_0(p) = \left[ \beta p^2 + (1 - 2\beta) \right]^{-1}
$$

(3.37)

and

$$
A_{k,0} \propto k^{-D+2} \text{ at exactly } 2D\beta = 1.
$$

(3.38)

Now the integration region near $p = 0$ may give a large contribution to the specific heat near the transition. Indeed, we find for small $1 - 2D\beta$:...
3.4. The Correlation Functions

\[ \vec{G}^0(n) = \int_0^\infty d\alpha \exp(-\alpha)I_n\left(\frac{alpha}{D}\right)\left[I_0\left(\frac{alpha}{D}\right)\right]^{D-1} \]

\[ -\left(\frac{beta}{D}\right)^n, \]  

as can be seen using the following property of the Bessel functions:

\[ I_0(\lambda) = 1 - \lambda^2 + O(\lambda^4) \]

\[ I_n(\lambda) = \frac{\lambda^n}{n!} + O(\lambda^{n+1}) \]  

\[ I_n(\lambda) \sim \frac{\exp \lambda}{\lambda^n} \quad \text{for } \lambda \to \infty. \]

Indeed, at fixed \( \tilde{\beta} \) the integral is dominated by the region of integration in \( \alpha \) near \( \alpha = 0 \), when \( D \to \infty \). The possible dangerous region \( \alpha \beta / D \gg 1 \) does not contribute as long as \( \tilde{\beta} \leq 1 \). When \( \tilde{\beta} > 1 \), the \( \alpha \) integral is divergent, but for these values of \( \tilde{\beta} \) we stay in the low-temperature phase and Eq. (3.29) is not valid.

We have already stated that for large \( n \) we have an exponential decay of the correlation functions at distances larger than the correlation length \( \xi \) [Eq. (3.38)]. Although this result may be obtained directly from the integral representation (3.41), it is simpler to use the following theorem: If \( f(p) \) is an analytic function (with period 2\( \pi \)) and the nearest singularity to the real axis is at \( p = ip_s \), we have

\[ \int_{-\pi}^\pi dp f(p) \exp(ipn) = \exp(-np_s). \]  

The proof is very simple, and it is based on the deformation of the integration path in the complex \( p \) plane. Now the function

\[ f(p) = \int_{-\pi}^\pi \prod_{s=1}^D dp_s \left[1 - 2\tilde{\beta} \left(\cos p + \sum_{s=1}^D \cos p_s \right)\right]^{-1} \]  

will be singular at the point where

\[ 1 - 2\beta \cos(ip_s) + D - 1 = 0. \]  

For example, in even dimensions we have

\[ f(p) \sim (p - ip_s)^{D/2 - 3/2} + \text{regular term}. \]

The singular term comes from the integration region where all the \( p_s \),
\( (\nu = 2, \ldots, D) \) are near zero. Equation (3.45) implies
\[
p_{\nu} = \xi^{-1} \sim \text{arccosh} \left[ \frac{1}{2\beta} - D + 1 \right] = \left( \frac{1 - 2DB}{\beta} \right)^{1/2} \quad \text{for } 2DB = 1. \tag{3.47}
\]

The correlation length goes to infinity at the critical temperature. Indeed, we already know that at the critical temperature the correlation function decays like a power, i.e., much slower than an exponential. In principle we could define the correlation length in more general terms: if \( \vec{v} \) is a rational unit vector (i.e., \( \{ 1, \frac{1}{2}, 0, 0, \ldots \} \)) the correlation length in the direction \( \vec{v} \) is defined by
\[
G^0(\nu \vec{v}) = \exp[-n \xi(\vec{v})] \tag{3.48}
\]
when \( n \) goes to infinity (for those \( n \) such that \( n \vec{v} \) has integer components).

Clearly we recover the previous definition of \( \xi \) when \( \vec{v} \) is in the direction of one of the axes of the lattice.

The generalization of the previous argument tells us that
\[
\sum_{\nu} \cosh[\xi^{-1}(\vec{v})\nu] = \frac{1}{2\beta}. \tag{3.49}
\]

Using this definition, we find that the correlation length depends on the direction \( \nu \); fortunately near the transition point we have
\[
\xi^{-1}(\vec{v}) = \left( \frac{1 - 2DB}{\beta} \right)^{1/2} \left[ 1 - \frac{1 - 2DB}{6\beta} \nu^2 \right] \tag{3.50}
\]
\[
\nu^2 = \sum_{\nu} \nu^2
\]
The divergent term of the correlation length is independent of \( \nu \); indeed, near the transition point the correlation function is isotropic at large distances, i.e.,
\[
A_{\rho,k} \approx A(k^2), \quad k^2 = \sum_{\nu} k^2_{\nu} \tag{3.51}
\]
in the region of large \( k \). The dominant integration region is at small \( \rho \), where \( G(p) \) can be approximated as
\[
\beta^{-1} \left[ \frac{1 - 2BD}{\beta} + p^2 + O(p^4) \right]^{-1}. \tag{3.52}
\]

3.5. Second-Order Phase Transitions

As we shall see later in the general case as well, the correlation functions will be isotropic at the transition point. We notice \textit{en passant} that Eq. (3.47) is in apparent contradiction with Eq. (3.41): the latter does not reduce to the former when \( D \) goes to infinity. The reason for this disagreement is clear: The limits \( D \to \infty \) and \( n \to \infty \) do not commute, and it is possible that
\[
\lim_{D \to \infty} \left\{ \lim_{n \to \infty} \frac{1}{n} \ln[G(n)] \right\} \neq \lim_{n \to \infty} \left\{ \frac{1}{n} \ln[\lim_{D \to \infty} G(n)] \right\}. \tag{3.53}
\]
Indeed, Eq. (3.41) has been obtained in the limit \( D \to \infty \) at fixed \( n \). A different formula is obtained if we study the large-\( D \) limit in the region \( n \) much larger than \( D \).

3.5. Second-order phase transitions

We can now use the results we have obtained in the study of the mean-field approximation to get some insight into the general properties of second-order phase transition.\textsuperscript{12}

Near the critical point the correlation function behaves as
\[
\xi^0(n) \sim \exp\left( -\frac{n}{\xi} \right) / \left( n^{(D-1)/2} \xi^{(D-3)/2} \right) \quad \text{for } \frac{n}{\xi} \to \infty
\]
\[
\xi \sim \left( \frac{T - T_c}{T_c} \right)^{-\nu}, \quad \nu = \frac{1}{2} \tag{3.54}
\]
\[
G^0(n) \sim n^{-\nu(D-2+\eta)}, \quad \eta = 0 \text{ for } T \approx T_c.
\]

In other words, the correlation function is exponentially damped at all temperatures but the critical one, where the correlation length \( \xi \) goes to infinity.

Now the correlation function is essentially different from zero at distance \( \xi \) only if the system can have a coherent fluctuation of size \( \xi \). The coherence length has thus the meaning of the maximum radius of likely fluctuations, i.e., fluctuations of radius larger than \( \xi \) have exponentially small probabilities. It is generally believed that at second-order phase transition point the coherence length goes to infinity. The argument is based on the fact that fluctuations which produce an increase of order \( kT = \beta^{-1} \) in free energy are definitely present.

Let us study for simplicity what happens when we reach \( T_c \) from below on the line \( k = 0 \). The critical point \( (T = T_c) \) is the endpoint of a line of first-order transitions.\textsuperscript{13} Now we argue that if the difference between the two phases goes to zero at the critical point (in this case the two phases have a different spontaneous magnetization \( \pm m_s \)), the correlation length
must have gone to infinity. Let us consider the possibility of having a bubble of large radius of phase II (i.e., negative magnetization) while the rest of the system is in phase I (i.e., positive magnetization). See Fig. 3.4 for such a configuration. The only part out of equilibrium would be the surface of the sphere. The contribution to the free energy coming from the interphase is intuitively proportional\(^14\) to \(R^{D-1}m_s^2\). Fluctuations up to a critical radius \(R_c = m_s^{2/(D-1)}\) are allowed. Obviously \(R_c\) goes to infinity when \(m\to 0\).\(^15\)

The argument is compelling from the physical point of view.\(^16\) As we approach the critical point we can have correlated fluctuations on larger and larger scales, just at the critical point the fluctuation radius becomes infinite, and we have correlation functions that decay like powers at large distances.

Collecting together the predictions of the mean-field approximation, Eqs. (3.12)-(3.15), (3.38), and (3.42), we have

\[
\begin{align*}
\xi(T, h)|_{h=0} &= |T - T_c|^{-\nu}, \\
\chi(T, h)|_{h=0} &= |T - T_c|^{-\nu}, \\
\tilde{G}(h)|_{T=T_c, A=0} &= \mu^{-(D-2+\xi)}, \\
C(T, h)|_{h=0} &= |T - T_c|^{-\eta}, \\
m(T, h)|_{h=0} &= |T - T_c|^\beta, \\
m(T, h)|_{T=T_c} &= |h|^{1/\xi}
\end{align*}
\]

(3.55)

where \(\alpha, \beta, \gamma, \delta, \eta, \nu\) are called critical exponents and take the values:

\[
\begin{align*}
\alpha &= D - 4, & \beta &= \frac{1}{\xi}, & \gamma &= 1, \\
\delta &= 3, & \eta &= 0, & \nu &= \frac{1}{\xi}.
\end{align*}
\]

(3.56)

The existence of strong fluctuations makes the predictions of mean-field theory unreliable (they have been derived under the hypothesis of small fluctuations). We shall see later on that Eqs. (3.55) are indeed correct, but for \(D < 4\) the true values of the critical exponents are not given by Eq. (3.56).\(^18\)

There is strong experimental and theoretical evidence that the values of the exponents have a high degree of universality (that is, they are the same for different lattice structures). This result should not be considered too surprising because the exponents give us information about fluctuations on a scale much larger than the lattice spacing and at such large distances that the detailed form of the interaction should be an irrelevant detail.

The problems of understanding precisely the reasons for this remarkable universality, the determination of relations among critical exponents (e.g., \(\gamma = (2 - \eta)\nu\)), and the very computation of the exponents, were the object of very intensive studies in the years 1964–1976. Nowadays, from a physical point of view, the problem is essentially solved, although in most cases only approximate evaluations of the critical exponents are available.

The general strategy for obtaining these results is described in Chapter 7 dedicated to the renormalization group. Before reaching this stage, we must develop tools (e.g., perturbative expansion, diagrammatic techniques) that will allow us to compute the corrections to the mean-field approximation in a systematic way.

### 3.6. The Infinite-Volume Limit

As we have already stressed, we want to compute the free-energy density in the infinite-volume limit. If the problem is well defined, the free-energy density of a system in a finite box must have a limit when the size of the box goes to infinity, and the limit should not depend on the boundary conditions we have used. We now present a rigorous elementary proof of this fact for the Ising model at zero magnetic fields with nearest-neighbor interaction; the extension to an arbitrary finite-range model is trivial.

We first note that the total energy of a system of \(N\) spins satisfies the obvious bounds

\[
-ND < E < ND.
\]

(3.57)

The number of configurations is \(2^N\), so that the partition function \(Z_N\) and the free-energy density \(f_N\) satisfy the bounds

\[
2^N \exp(-\beta ND) \leq Z_N \leq 2^N \exp(\beta ND)
\]

(3.58)

\[
-D + \frac{\ln 2}{\beta} \leq f_N \leq D + \frac{\ln 2}{\beta}.
\]
These bounds are very important. They exclude the most dangerous possibility (i.e., \( f_{\infty} \rightarrow \infty \) when \( N \rightarrow \infty \)). For simplicity, we consider the case of cubic boxes \( N = L^D \) (where \( L \) can take only the values \( 2^n \)) and use free boundary conditions. We denote by \( Z_N^F \) the corresponding partition function.

It is easy to see that

\[
\left( Z_{L^D}^F \right)^D \exp(-D(2L)^{D-1} \beta) \\
\leq Z_{(2L)^D}^F \leq \left( Z_{L^D}^F \right)^D \exp(D(2L)^{D-1} \beta). \tag{3.59}
\]

Indeed, we can glue together \( 2^D \) systems of side \( L \) to give one system of side \( 2L \). (See Fig. 3.5 in two dimensions.) The only difference between \( Z_{L^D}^F \) and \( Z_{(2L)^D}^F \) will come from the contribution to the energy coming from spins near the boundary, but their contribution cannot exceed \( D(2L)^{D-1} \).

Equation (3.47) implies

\[
|f_{(2L)^D} - f_L| \leq \frac{C}{L}, \tag{3.60}
\]

where \( C \) is a constant independent of \( L \). A standard theorem implies the convergence of the sequence \( f_{n^D} \) for \( n \rightarrow \infty \). A similar technique can be used to prove the independence of \( f \) on the boundary conditions in the infinite-volume limit. Indeed, the effect of the boundary conditions on the total free energy is proportional to \( L^{D-1} \) (a surface effect), and it cannot change the value of \( f = F_L/L^D \) in a significant way.

A more elegant proof of the existence of the infinite-volume limit for the Ising system may be obtained by proving that the free-energy density...

9. For the Fourier transform of functions defined on a lattice and the related definition of Brillouin zones, see C. Kittel, op. cit.

10. The \( L \) are integer order Bessel functions of imaginary arguments; here (and in the rest of the book) we follow for special functions the notation of I. S. Gradshteyn and I. M. Ryzhik, Table of Integrals, Series and Products, Academic Press, New York (1965).

11. See, for example, P. M. Morse and H. Feshbach, Methods of Theoretical Physics, McGraw-Hill, New York (1953), Chapter 4.


13. The critical point of the liquid-gas transition is very similar to the Curie point in this respect.

14. The actual power of \( m^2 \) is not important; we require only that it vanish at the Curie point.

15. This approach may be pushed further. A first attempt in the sixties was not fully successful in obtaining quantitative predictions for the critical exponents. For a review see M. F. Fisher, Physica 3, 255 (1967). Nowadays it is understood that this approach may become quantitative for the Ising case in \( 1 + \varepsilon \) dimensions \( (\varepsilon \) being a small number); for more details see the review of D. Wallace in Proceedings of the 1982 Les Houches Summer School, ed. by J. B. Zuber and R. Stora, North-Holland, Amsterdam (1984), p. 173.

16. We remark that this result is automatic if \( m \) can be found by solving an equation of the form \( \varphi(m, T) = 0 \), where \( \varphi(m, T) \) is a sufficient smooth function. Indeed, the coalescence of the two solutions, that for \( m \) different from zero with that for \( m = 0 \), implies that \( \varphi(0, T_c) = 0 \). The magnetic susceptibility \( \chi = \langle \delta \varphi / \delta m \rangle^{-1} \) is thus infinite. This can happen only if the fluctuations go to zero slowly at large distances [each term in Eq. (2.11) is bounded].

17. We have added the corrections to the mean-field theory coming from fluctuations [Eq. (3.38)], which gives the leading contribution for \( D \leq 4 \). The specific heat of mean-field theory without corrections would only be discontinuous. (The case \( \alpha = 0 \) is normally interpreted as a logarithmic singularity.)

18. Quite often the values of the exponents predicted by Eq. (3.44) are called the classical exponents.

19. The argument is quite general; for an application to other systems see K. Huang, Statistical Mechanics, John Wiley and Sons, New York (1963).

20. In a box of side \( L \) (the \( D \) coordinates satisfy the bounds \( 1 \leq i_j \leq L \)), the points of would-be coordinates \( 0 \) and \( L + 1 \) are identified with those of coordinates \( L \) and \( 1 \), respectively. The system has the geometry of a \( D \)-dimensional torus; the box does not have a surface (i.e., a boundary), and no point is privileged with respect to the other points.

21. If free boundary conditions are used, those terms in the Hamiltonian that connect spins inside and outside the box are omitted, or equivalently, the spins outside the box are set to zero.

22. The increase of the free energy with the size of the box for periodic boundary conditions can be easily proven for systems with a positive transfer matrix (see Chapter 12). The decrease of the free energy for free boundary conditions is a consequence of the so-called Griffith's inequalities for ferromagnetic systems [R. R. Griffiths, J. Math. Phys. 8, 478 (1967)].
CHAPTER 4

The Low-Temperature and High-Temperature Expansions

4.1. The low-temperature expansion

The low- and high-temperature expansions make it possible for us to study the free energy systematically, as a function of the temperature and of the magnetic field; for a long time they have been the main tools for investigating the critical properties of a spin system. We consider the low-temperature expansion first.

In the Ising model at low temperature most of the spins are oriented in one direction (let us say conventionally the positive one); only a few spins will be oriented in the negative direction. While at exactly zero temperature all the spins are positive, at a very low temperature we can compute the partition functions in a finite volume by including only those configurations that have up to \( k \) reversed spins. For large \( k \) the computation is long, but accurate; for small \( k \) it is simpler, but less accurate.

Let us see how it works. We consider the partition function of \( N \) spins with periodic boundary conditions in a cubic box of side \( L \) (\( N = L^d \)). At the end we shall send \( L \) to infinity.

We begin by doing the computation for \( k = 2 \); the combinatorics are simple enough if \( L > k \): there is only one configuration with all the spins up (positive), \( N \) configurations with one spin down, \( \binom{N}{2} = N(N-1)/2 \) configurations with two spins down, and \( DN \) configurations with two nearest-neighbor down spins. When all the spins are up, the energy of the configuration is \( E_0 = -ND \); if only one spin is down, the energy gap is given by \( E - E_0 = 4D \); if two spins are down and if they are nearest neighbors \( E - E_0 = 8D - 4 \); and if they are not nearest neighbors, \( E - E_0 = 8D \).

We finally obtain \( Z \),

\[
Z = \exp \beta E_0 \left[ 1 + N t^D + ND t^{D - 1} + \frac{N(N-1-2D)}{2} t^{2D} + \ldots \right]
\]

\( t = \exp -4\beta \) .

In the limit \( \beta \to \infty \) (\( t \to 0 \)) all the terms with two spins down are much smaller (for \( D > 1 \)) than those having only one spin down. This observation is crucial. Indeed, Eq. (4.1) tells us that

\[
f = -D + \frac{1}{\beta N} \ln \left[ 1 + \sum_{k} \frac{C_k}{C_1} \right]
\]

(4.2)

where the \( C_k \), i.e., the contribution from \( k \) flipped spins) are of order \( N^k \). Now in order to avoid a trivial zero on the r.h.s. of Eq. (4.2), we first expand the finite volume \( f \) in powers of \( t \), and only at the end do we take the \( N \to \infty \) limit. In other words, we consider the \( C_k \) to be of order \( \epsilon^k \), and we collect in \( f \) all terms of order \( \epsilon^k \), using the Taylor expansion for the logarithm.

Using this prescription we would get for \( k = 2 \) or \( k = 3 \), respectively,

\[
f = -D + \frac{1}{\beta N} \left[ C_1 + C_2 - \frac{C_1^2}{2} \right]
\]

\[
f = -D + \frac{1}{\beta N} \left[ C_1 + C_2 - \frac{C_1^2}{2} + C_3 + \frac{C_1^3}{3} - C_1 C_2 \right].
\]

(4.3)

Similar formulae hold for higher \( k \)'s. If we compute the \( C_k \)'s, we discover that all terms proportional to \( N \) cancel in Eq. (4.3), and \( f \) is \( N \) independent (strictly this happens only if we stick to boxes such that \( L > k \)). This phenomenon is quite general: if the interaction is short range, the low-temperature expansion for the free-energy density never contains terms proportional to the volume for a ferromagnetic Ising model. Before presenting the general argument, it is useful to consider the following simplified problems. We suppose that the energies of configurations of \( k \) down spins are given by \( E_k - E_0 = 4kD \) (we forget that the energy changes when two down spins are in contact) and that their number is exactly given by \( N^k / k! \) (we neglect excluded volume effects). If these hypotheses we find

\[
f = -D + \frac{1}{\beta N} \ln \sum_{k} \frac{N^k}{k!} = -D + \frac{1}{\beta} \ln \frac{1}{t^D} .
\]

(4.4)

Similarly, if we use the same form for the energies but take care of the excluded volume effects, i.e., instead of \( N^k / k! \) we write \( \binom{N}{k} k! \), we find

\[
f = -D + \frac{1}{\beta N} \ln \left[ \sum_{k} \binom{N}{k} t^k \right] = -D + \frac{1}{\beta N} \ln(1 + t^D)^N
\]

\[
= -D + \frac{1}{\beta} \ln(1 + t^D) .
\]

(4.5)