

## Chapter 1

# Phases and Phase Transitions

In discussing phase transitions, the first thing that we have to do is to define a phase. This is a concept from thermodynamics and statistical mechanics, where a phase is defined as a homogeneous system. As a simple example, let us consider instant coffee. This consists of coffee powder dissolved in water, and after stirring it we have a homogeneous mixture, i.e., a single phase. If we add to a cup of coffee a spoonful of sugar and stir it well, we still have a single phase — sweet coffee. However, if we add ten spoonfuls of sugar, then the contents of the cup will no longer be homogeneous, but rather a mixture of two homogeneous systems or phases, sweet liquid coffee on top and coffee-flavored wet sugar at the bottom.

In the above example, we obtained two different phases by changing the composition of the system. However, the more usual type of phase transition, and the one that we will consider mostly in this book, is when a single system changes its phase as a result of a change in the external conditions, such as temperature, pressure, or an external magnetic or electric field. The most familiar example from everyday life is water. At room temperature and normal atmospheric pressure this is a liquid, but if its temperature is reduced to below  $0^{\circ}\text{C}$  it will change into ice, a solid, while if its temperature is raised to above  $100^{\circ}\text{C}$  it will change into steam, a gas. As one varies both the temperature and pressure, one finds a line of points in the pressure–temperature diagram, Fig. 1.1, along which two phases can exist in equilibrium, and this is called the coexistence curve.

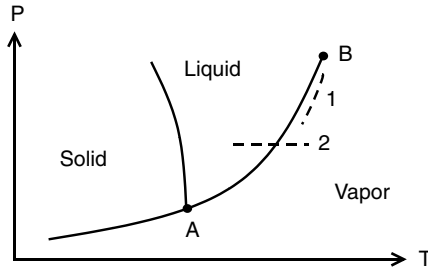


Fig. 1.1 The phase diagram for water.

We now consider in more detail the change of phase when water boils, in order to show how to characterize the different phases, instead of just using the terms solid, liquid or gas. Let us examine the density  $\rho(T)$  of the system as a function of the temperature  $T$ . The type of phase transition that occurs depends on the experimental conditions. If the temperature is raised at a constant pressure of 1 atmosphere (thermodynamic path 2 in Fig. 1.1), then initially the density is close to  $1 \text{ g/cm}^3$ , and when the system reaches the phase transition line (at the temperature of  $100^\circ\text{C}$ ) a second (vapor) phase appears with a much lower density, of order  $0.001 \text{ g/cm}^3$ , and the two phases coexist. After crossing this line, the system fully transforms into the vapor phase. This type of phase transition, with a discontinuity in the density, is called a first order phase transition, because the density is the first derivative of the thermodynamic potential. However, if both the temperature and pressure are changed so that the system remains on the coexistence curve AB (thermodynamic path 1 in Fig. 1.1), one has a two-phase system all along the path until the critical point B ( $T_c = 374^\circ\text{C}$ ,  $p_c = 220 \text{ atm.}$ ) is reached, when the system transforms into a single (“fluid”) phase. The critical point is the end-point of the coexistence curve, and one expects some anomalous behavior at such a point. This type of phase transition is called a second order one, because at the critical point B the density is continuous and only a second derivative of the thermodynamic potential, the thermal expansion coefficient, behaves anomalously. Anomalies in thermodynamical quantities are the hallmarks of a phase transition.

Phase transitions, of which the above is just an everyday example, occur in a wide variety of conditions and systems, including some in fields such as economics and sociology in which they have only recently been recognized as such. The paradigm for such transitions, because of its conceptual simplicity, is the paramagnetic–ferromagnetic transition in magnetic systems. These systems consist of magnetic moments which at high temperatures point in random directions, so that the system has no net magnetic moment. As the system is cooled, a critical temperature is reached at which the moments start to align themselves parallel to each other, so that the system acquires a net magnetic moment (at least in the presence of a weak magnetic field which defines a preferred direction). This can be called an order–disorder phase transition, since below this critical temperature the moments are ordered while above it they are disordered, i.e., the phase transition is accompanied by symmetry breaking. Another example of such a phase transition is provided by binary systems consisting of equal numbers of two types of particle, A and B. For instance, in a binary metal alloy with attractive forces between atoms of different type, the atoms are situated at the sites of a crystal lattice, and at high temperatures the A and B atoms will be randomly distributed among these sites. As the temperature is lowered, a temperature is reached below which the equilibrium state is one in which the positions of these atoms alternate, so that most of the nearest neighbors of an A atom are B atoms and vice versa.

The above transitions occur in real space, i.e., in that of the spatial coordinates. Another type of phase transition, of special importance in quantum systems, occurs in momentum space, which is often referred to as  $k$ -space. Here, the ordering of the particles is not with respect to their position but with respect to their momentum. One example of such a system is superfluidity in liquid helium, which remains a liquid down to 0 K (in contrast to all other liquids, which solidify at sufficiently low temperatures and high pressures) but at around 2.2 K suddenly loses its viscosity and so acquires very unusual flow properties. This is a result of the fact that the particles tend to be in a state with zero momentum,  $k = 0$ , which is an ordering in  $k$ -space. Another well-known example is superconductivity. Here, at

sufficiently low temperatures electrons near the Fermi surface with opposite momentum link up to form pairs which behaves as bosons with zero momentum. Their motion is without any friction, and since the electrons are charged this motion results in an electric current without any external voltage.

Phase transitions occur in nature in a great variety of systems and under a very wide range of conditions. For instance, the paramagnetic–ferromagnetic transition occurs in iron at around 1000 K, the superfluidity transition in liquid helium at 2.2 K, and Bose–Einstein condensation of atoms at  $10^{-7}$  K. In addition to this wide temperature range, phase transitions occur in a wide variety of substances, including solids, classical liquids and quantum fluids. Therefore, phase transitions must be a very general phenomenon, associated with the basic properties of many-body systems. This is one reason why the theory of phase transitions is so interesting and important. Another reason is that thermodynamic functions become singular at phase transition points, and these mathematical singularities lead to many unusual properties of the system which are called “critical phenomena”. These provide us with information about the real nature of the system which is not otherwise apparent, just as the behavior of a poor man who suddenly wins a million-dollar lottery can show much more about his real character than one might deduce from his everyday behavior. A third reason for studying phase transitions is scientific curiosity. For instance, how do the short-range interactions between a magnetic moment and its immediate neighbors lead to a long-range ordering of the moments in a ferromagnet, without any sudden external impetus? A similar question was raised (but not answered) by King Solomon some 3000 years ago, when it was written (Proverbs 30, 27). “The locusts have no king, yet they advance together in ranks”.

## 1.1 Classification of Phase Transitions

The description and analysis of phase transitions requires the use of thermodynamics and statistical physics, and so we will now summarize the thermodynamics of a many-body system [1]. In

thermodynamics each state of a system is defined by some characteristic energy. If the state of the system is defined by its temperature  $T$  and its pressure  $P$  or volume  $V$ , this energy is called the free energy. One part of this energy is the energy  $E$  of the system at zero temperature, while the other part depends on the temperature and the entropy  $S$  of the system. If the independent variables are the temperature and pressure, then the relevant thermodynamic potential is the Gibbs free energy  $G = E - TS + PV$ , while if they are the temperature and volume it is the Helmholtz free energy  $F = E - TS$ . The differentials of these free energies for a simple system are

$$dG = -SdT + VdP, \quad dF = -SdT - PdV. \quad (1.1)$$

If the system has a magnetic moment there is an extra term  $-MdH$  in the above expressions, and if the number  $N$  of particles is variable we must add the term  $\mu dN$ , where  $\mu$  is the chemical potential. Then the first derivatives of the free energy give us the values of physical properties of the system such as the specific volume ( $V/N = [1/N]\partial G/\partial P$ ), entropy ( $S = -\partial G/\partial T$ ) and magnetic moment ( $M = -\partial G/\partial H$ ), while its second partial derivatives give properties such as the specific heat ( $C_p = T\partial S/\partial T = -T\partial^2 G/\partial T^2$ ), the compressibility and the magnetic susceptibility of the system.

Let us now consider the effect on the free energy  $G$  of changing an external parameter, for instance the temperature. Such a change cannot introduce a sudden change in the energy of the system, because of the conservation of energy. Hence, if we consider the free energy per unit volume,  $g$ , of a system with a fixed number of particles and write  $G = gV$ , there are only two possibilities. Either the change  $\delta G$  in  $G$  arises from a change in the free energy density  $g$ ,  $\delta G = V\delta g$ , or it comes from a change in the volume  $V$ ,  $\delta G = g\delta V$ . When the properties of a system change as a result of a phase transition, they can undergo a small change  $\delta g$  all over the system at once or initially only in some parts  $\delta V$  of it, as shown in Fig. 1.2. If the new phase appears as  $\delta G = g\delta V$ , so that it appears only in parts  $\delta V$  of the system, then it requires the formation of stable nuclei, namely of regions of the new phase large enough for them to grow rather than to shrink. Since the energy consists of a negative volume term

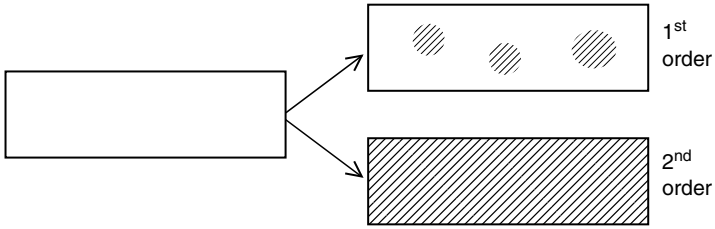


Fig. 1.2 The two different possibilities for the change  $\delta G$  in the free energy associated with 1st order and 2nd order phase transitions.

and a positive surface one, which for a spherical nucleus of radius  $r$  are proportional to  $r^3$  and  $r^2$  respectively, this critical size  $r_c$  is that for which the volume term equals the surface one, so that for  $r > r_c$  growth of the nucleus leads to a decrease in its energy. Because of the need for nucleation, the first phase can coexist with the second phase, in a metastable state, even beyond the critical temperature for the phase transition. This is a first order phase transition. The best known manifestations of such a transition are superheating and supercooling.

In the other case, where the phase transition occurs simultaneously throughout the system,  $\delta G = V\delta g$ . Although the difference  $\delta g$  between the properties of these phases is small, the old phase which occupied the whole volume cannot exist, even as a metastable state, on the other side of the critical point, and it is replaced there by a new phase. These two phases are associated with different symmetries. For instance, in the paramagnetic state of a magnetic system there is no preferred direction, while in the ferromagnetic state there is a preferred direction, that of the total magnetic moment. In this case, the critical point is the end-point of the two phases, and so there must be some sudden change there, i.e., some discontinuity in their properties. This is an example of a second order phase transition.

Phase transitions are classified, as proposed by Ehrenfest, by the order of the derivative of the free energy which becomes discontinuous (or, in modern terms, exhibits a singularity) at the phase transition temperature. In a first order phase transition, a first derivative becomes discontinuous. A common example of this is the transition

from a liquid to a gas when water boils, where the density shows a discontinuity. In a second order phase transition, on the other hand, properties such as the density or magnetic moment of the system are continuous, but their derivatives (which correspond to the second derivatives of the free energy), such as the compressibility or the magnetic susceptibility, are discontinuous. In this book, we will be concerned mainly with second order phase transitions, with which are associated many unusual properties.

## 1.2 Appearance of a Second Order Phase Transition

Before proceeding to a detailed mathematical analysis, it is worthwhile to consider qualitatively an example of how a second order phase transition can occur. Accordingly, we will now discuss the mean field theory of the paramagnetic–ferromagnetic phase transition in magnetic materials, originally proposed by Pierre Weiss some 100 years ago, in 1907 [2]. This consists of the sudden ordering of the magnetic moments in a system as the temperature is lowered to below a critical temperature  $T_c$ . He suggested that these materials consist of particles each of which has a magnetic dipole moment  $\mu$ . For  $N$  such particles, the maximum possible magnetic moment of the system is  $M_0 = N\mu$ , when the moments of all the particles are aligned. Such a state is possible at  $T = 0$  K, when there is no thermal energy to disturb the orientation of the moments. In the presence of a small magnetic field  $\mathbf{H}$ , the energy of a dipole of moment  $\boldsymbol{\mu}$  is  $-\boldsymbol{\mu} \cdot \mathbf{H}$ . For the sake of simplicity, we consider only two possible orientations of the dipoles, parallel and anti-parallel to the field, or up and down, and denote by  $N_+$  and  $N_-$  respectively the number of dipoles in these two orientations at any given temperature. Similar results can be obtained if one allows the moments to adopt arbitrary orientations with respect to the field, but the analysis is slightly more complicated. Then the total magnetic moment of the system in the direction of the field is  $M = (N_+ - N_-)\mu$ , and its energy is  $E = -MH$ . The main assumption of Weiss was that there is some internal magnetic field acting on each of the dipoles, and that this

field is proportional to  $M/M_0$ . This is a very reasonable assumption if the internal field on a given particle is due to the magnetic moments of the surrounding particles. Of course, it is an approximation to assume that each particle experiences the same magnetic field, and we will consider more refined theories later. We therefore write the effective field acting on each dipole (in the absence of an external field) in the form  $H_m = CM/M_0$ . According to Boltzmann's law, which was already known by then, the number of particles  $N_{\pm}$  with moments pointing up and down at temperature  $T$  is proportional to  $\exp(\mp\mu H_m/kT)$ . Here and throughout the book, we denote the Boltzmann constant by  $k$ . It readily follows that

$$\frac{M}{M_0} = \frac{N_+ - N_-}{N_+ + N_-} = \tanh\left(\frac{T_c}{T} \frac{M}{M_0}\right) \quad (1.2)$$

where  $T_c = C\mu/k$ . As can be seen from Fig. 1.3, if  $T_c/T < 1$  then this equation only has the trivial solution  $M = 0$ , since for small arguments  $\tanh(x) \simeq x$ , and so there is no spontaneous magnetic moment if  $T > T_c$ . On the other hand, if  $T < T_c$  then the equation has two solutions. An examination of the effect of a small change in the internal field shows that the solution with  $M > 0$  is the stable one, i.e., the system has a spontaneous magnetic moment and so is ferromagnetic. The critical temperature  $T_c$  at which this transition from paramagnetism to ferromagnetism takes place is given by

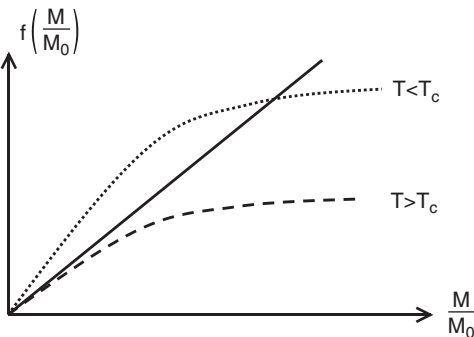


Fig. 1.3 Graphical solution of Eq. (1.2) for the magnetization  $M$  in the Weiss mean-field model

$T_c = C\mu/k$ , the famous Weiss equation. At the time that Weiss wrote his paper, quantum mechanics, electronic spin and exchange effects had not been discovered, and so he could only estimate the strength of the internal field from the known dipole-dipole interactions, and this led to an estimate of  $T_c$  of around 1 K. Weiss knew that for iron  $T_c$  is around 1000 K, and so wrote bravely at the end of his paper [2] that his theory does not agree with experiments but future research will have to explain this discrepancy of three orders of magnitude. In spite of this discrepancy, his paper was accepted for publication, and we now know that his ideas of the nature of the paramagnetic–ferromagnetic phase transition are qualitatively correct.

### 1.3 Correlations

For a second order phase transition, a second derivative of the free energy diverges as the phase transition is approached. For instance, the magnetic susceptibility  $\partial M/\partial H = -\partial^2 G/\partial H^2$  tends to infinity as  $T \rightarrow T_c$ . Now according to the fluctuation–dissipation theorem [1], the magnetic susceptibility is proportional to the integral over all space of the average of the product of the magnetic moment at two points distance  $r$  apart, which describes the correlation between the magnetic moments at these points,

$$\frac{\partial M}{\partial H} \sim \int \langle M(0)M(r) \rangle d\tau. \quad (1.3)$$

In general, the magnetic moment (spin) at any site tends to align the spin at an adjacent site in the same direction as itself, so as to lower the energy. However, this tendency is opposed by that of the entropy, so that far from the critical point there is a finite correlation length  $\xi$  such that

$$\langle M(0)M(r) \rangle \sim \exp(-r/\xi).$$

Here, the correlation length  $\xi$  has the following physical meaning. If one forces a particular spin to be aligned in some specified direction, the correlation length measures how far away from that spin the other spins tend to be aligned in this direction. In the disordered

state, the spin at a given point is influenced mainly by the nearly random spins on the adjacent points, so that the correlation length is very small. As the phase transition is approached, the system has to become “prepared” for a fully ordered state, and so the “order” must extend to larger and larger distances, i.e.,  $\xi$  has to grow. However, the divergence of the integral in Eq. (1.3) as  $T \rightarrow T_c$  implies that at the critical point the correlation function cannot decrease exponentially with distance  $r$ , but rather must decay at best as an inverse power of  $r$ ,

$$\langle M(0)M(r) \rangle \sim r^{-\gamma}, \quad \gamma \leq 3. \quad (1.4)$$

This is a point of great physical significance. It means that near the critical point not only do we not have any small energy parameter, since the critical temperature is of the same order of magnitude as the interaction energy, but also we do not have any typical length scale since the correlation length diverges on approaching the critical point. In other words, all characteristic lengths are equally important near the critical point, which makes this problem extremely complicated. A similar situation of various characteristic lengths arises in the problem of the motion of water in an ocean, but these are associated with different phenomena. The Angstroms–micron length scale is appropriate for studying the interactions between water molecules, but one must take into account lengths of order of meters for studying the tides and the kilometer length scale for studying the ocean streams. This is in contrast to the situation near critical points, where one cannot perform such a separation of different length scales.

We now return to the question raised at the beginning of this chapter, namely how one can obtain long-range correlations from short-range interactions. In mathematical terms, the question is how an exponentially decaying correlation can transfer the mutual influence of different atoms located far away from each other. A qualitative answer to this question has been given by Stanley [3]. The correlations between two particles far apart do indeed decay exponentially. However, the number of paths between these two particles along which the correlations occur increase exponentially. The exponents of these two exponential functions, one positive and one

negative, compensate each other at the critical point, and this leads to the long-range power law correlations. By contrast, for a one-dimensional system the exponential increase corresponding to the number of different paths is replaced by unity, and so the negative exponent leads to the absence of ordering and so to no phase transition for non-zero temperatures.

Curiously enough, in the Red Army of the former Soviet Union the order given by an officer standing in front of the line of soldiers was “Attention! Look at the chest of the fourth man!”. For some unclear reason, they decided that the correlation length is equal to four, and the soldiers will be ordered in a straight line if each one will align with his fourth neighbor in the row.

## 1.4 Conclusion

Phase transitions are very general phenomena which occur in a great variety of systems under very different conditions. They can be divided into first-order and second-order transitions depending on which derivatives of the free energies have anomalies at the transition. The existence of phase transitions, as such, was established a hundred years ago in the framework of the mean field theory. Three major factors which present severe difficulties for the theoretical description of phase transitions are the non-analyticity of the thermodynamic potentials, the absence of small parameters, and the equal importance of all length scales.