Chapter 10

Overview of Phase Transitions

10.1   Thermodynamic Phases

In this chapter, we develop the beginnings of a description of thermodynamic phases and the transitions that occurs as the system changes from one phase to another. Before the beginning of science, people classified the materials in the world about them according to their properties. They saw gases, and liquids, and solids and their distinct behaviors. More recently, scientists have distinguished normal materials from superfluids, and studied a whole variety of magnetic materials, of liquid crystals, of ferroelectrics, and many additional phases of matter. One can make the distinction between the phases in question by observing the qualitative difference among the phases or alternatively by observing the *phase transition* which takes the system from one phase to another. Our prototype system, the Ising model, shows several distinct thermodynamic phases. Some of these are depicted in Fig. 10.1. On the left, we see a paramagnetic phase. There is a considerable randomness to the arrangement of spins and no long-ranged order appears. In contrast, in the right hand panel we see a system with the long-ranged order characteristic of the ferromagnetic phase. Through the entire system the spins tend to point upward with only a few islands of 'wrong' behavior, caused by fluctuations. The center panel depicts a situation intermediate between the ferromagnetic and the paramagnetic. In this so-called 'critical phase' there are
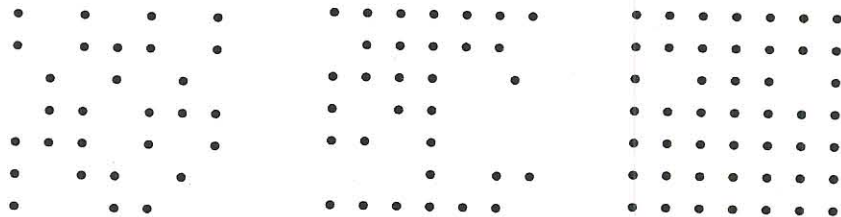

Fig. 10.1. Three different phases for an Ising model. The pictures show spins on a lattice. Spins pointing up are indicated by dots; those pointing down by blanks. The left hand picture shows a paramagnetic phase, the middle one a critical phase, and the right hand picture shows a ferromagnetic phase.

correlations among the different spins. Over large regions of the system, like spins tend to group together. However, one spin direction does not predominate over the other as in the ferromagnetic case. In the following chapters, we shall have much more to say about this critical phase.

10.2   Phase Transitions

The world would indeed be a dull place if there were no distinction among the different phases of matter. No separation of oil and water, no distinction between stream-bed and stream, none between sky and earth, no difference between airy snowflake and sitting water. But it is far from obvious why such distinctions and changes between phases should exist. If a phase transition is to occur, it must be true that two different thermodynamic phases can both exist under the same external thermodynamic conditions. Thus for example a dilute fluid, water vapor, and a dense fluid, liquid water, can be in contact with one another under identical conditions of temperature and pressure. Here the phases are different in character. Each phase of water has its own free energy which depends on number, volume, and temperature. When the free energies of the different phases are different, then the phase with the smaller free energy is the more stable. (This is part of a general rule which states that the relative probability of observing configurations of the system with different free energies is proportional to an exponential of the free energy difference divided by $k_\mathrm{B}T$. Thus when two configurations differ by a macroscopic energy difference, in a situation of thermodynamic equilibrium, only the phase with the lower free energy will be observed.)

Thus if two phases are in equilibrium, they must have the same free energy per particle. So coexisting water vapor and liquid water have equal free energy per particle. In fact, the line of coexistence is computed by calculating the free energy as a function of density and temperature in each phase, and then finding the density in which the free energy per particle is equal in the two phases. In this case, the equality of the free energy is viewed as just an accidental occurrence.

But, sometimes there is some symmetry relation which defines the behavior of the system. In that case, there will often be some kind of symmetry connecting the coexisting phases. In a magnetic material, for example, the magnetism is produced by spins and other magnetic moments which can line up spontaneously to produce a natural magnetism. A magnetic moment is a special kind of vector, one which changes sign under the operation of time reversal. (Change the direction of every velocity in a system. The electromagnetic currents will all change sign, and with them all magnetic moments and magnetic fields.) In the absence of a magnetic field applied from outside the material, the system will always have a natural degeneracy: If there is a state in which the average magnetization points in a given direction, then there will be an equivalent state in which it will point is exactly the opposite direction. In the simplest kind of magnetic material there is one 'easy axis' and the natural magnetism will occur with the spins lining up parallel or antiparallel to that axis. Call the spin in the direction of that axis σ or σ_z. Then phase transition involves a magnetization density, m, proportional to the average of this spin $\langle \sigma \rangle$. Notice that at the

first order phase transition, the system thus has to choose between two thermodynamically equivalent states, with different values of the magnetization density, m. The two phases have values of m's which differ by a sign. Furthermore, the value of the magnetization density is same throughout a very large region of the sample, one containing many, many spins.[1] The system spontaneously chooses a particular phase, based upon its history or some weak residual magnetic fields. And after this choice is made and the system has a single thermodynamic phase, then $\langle \sigma \rangle$ will have the same sign and the same value throughout the material. One of the most interesting question about this situation is: How can a huge number of atoms, perhaps 10^{23} of them, can chooses one of the possible phases, and apply the choice across the entire system?

10.3 Two Kinds of Transitions

In nature there are two different kinds of phase transitions. The first kind, observed when we boil water at home, involves a discontinuous change in some intensive thermodynamic quantity. This discontinuity is observed, for example, in the density expressed as a function of pressure and temperature. In a magnet, the direction of magnetization might suddenly change so that the magnetization density vector will change discontinuously. These changes are called *discontinuous* phase transition or *first order* phase transitions. Thermodynamic variables, like this density or magnetization, which exhibit the discontinuity, are called *order parameters*, since their value reflects the strength and kind of ordering in the system. Our two examples of first order transitions are the boiling of water or having a domain of iron jump from one direction of magnetization to another. In either case, if we increase the temperature the jump or discontinuity will become smaller. In the fluid, the vapor density will approach the liquid density. In the magnet, the magnitude of the magnetization will get closer to zero. In both cases, at some critical temperature, T_c, the discontinuity will vanish and the phase transition will change its character. At this special point, we say there is a *continuous* or *second order* phase transition.

All of this is illustrated in Figs. 10.2 and 10.3. These figures plot the magnetization density as it is determined by an approximate theory of the ferromagnetic behavior, called mean field theory. We describe this theory in this chapter and the next. For now, we wish to look at results. Figure 10.2 plots dimensionless magnetization, $\langle \sigma \rangle$ versus dimensionless magnetic field, h, for various values of the temperature. Notice how there is a discontinuity in $\langle \sigma \rangle$ at zero values of the field for $T < T_c$ — reflecting a first-order transition. This $h = 0$ discontinuity disappears at $T = T_c$ — producing a second order transition at that point. This discontinuity in m as we pass through vanishing values of h reflects one kind

---

[1]In what is called a single-domain ferromagnet, the magnetization is uniform throughout the same. But most ferromagnets actually have a tendency to split up into different domains, each with its own direction of the magnetization. This splitting occurs because of weak but long ranged magnetic forces. Magnetic energies are minimized by the splitting into different domains. The domains are usually quite large, containing many atoms. So the ferromagnet is well-represented as a system with long-ranged order over wide regions. In other kinds of ordered phases, the domains can be even larger — extending sometimes over microns or even centimeters.
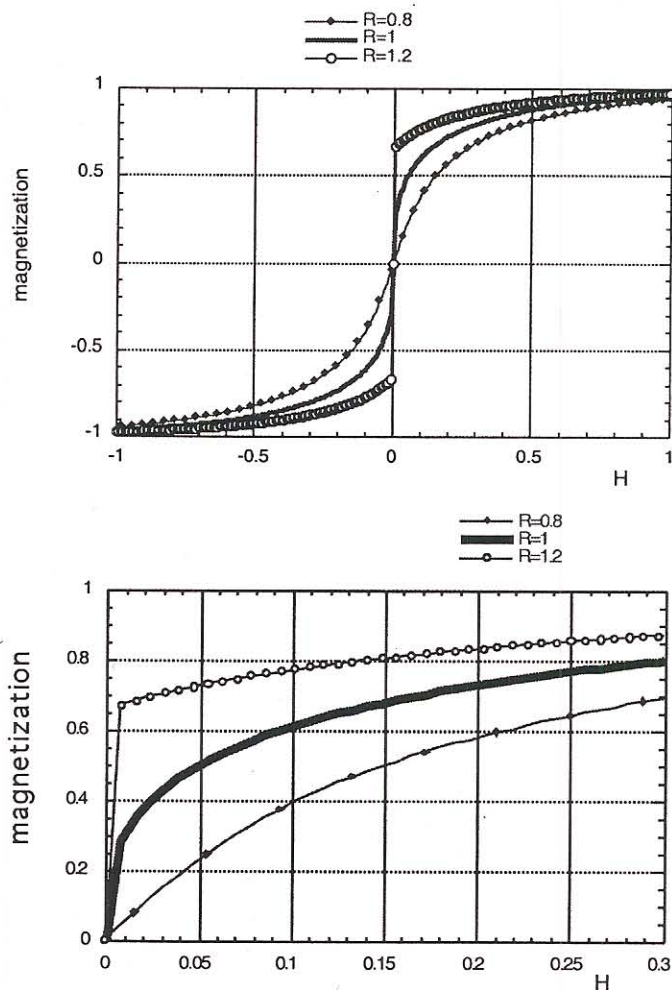
Fig. 10.2. Magnetization plotted as a function of magnetic field. The curves are plotted for three values of $R = T_c/T$, corresponding to above, at, and below the critical temperature. Notice how the curve for $T > T_c$ appears smooth while the one for $T < T_c$ shows a discontinuity at zero field. For $T = T_c$, the discontinuity disappears and is replace by an infinite slope in the magnetization versus field curve. The upper part shows a larger region of field, the lower is a blowup for small values of the magnetic field.

of singularity in this system. This singularity disappears if $T > T_c$, where magnetization is a smooth function of field. Exactly at the critical temperature, we see an infinite slope of m versus h, showing us that the mathematical singularity remains present at this second order transition.

This same data is plotted in a different way in Fig. 10.3. Here we look at m as a function of T. This figure contains several curves each for a different value of the applied magnetic field. The most interesting is the curve marked '$h = 0$' which shows a magnetization which is zero for $T > T_c$. In contrast, for $T < T_c$, m has two branches, one positive-one negative.

There is an exact symmetry which involves flipping the sign of both m and h. Thus if the function $m(h, T)$ gives the magnetization as a function of temperature and magnetic field,
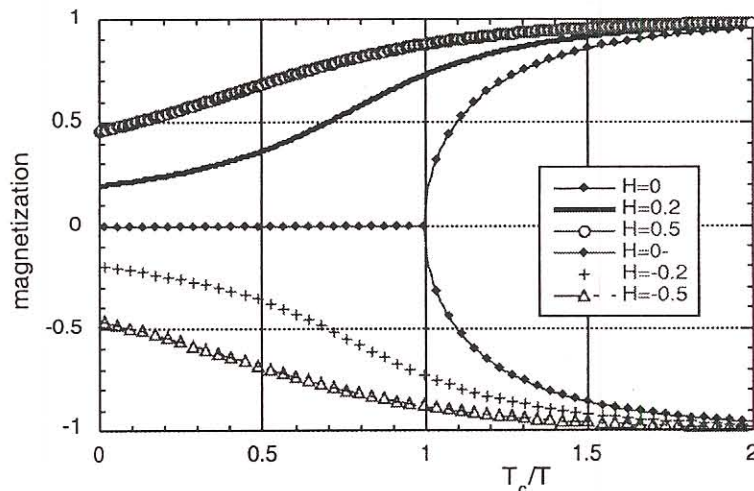
Fig. 10.3. Magnetization plotted as a function of the ratio, R of critical temperature to actual temperature for different values of the magnetic field. Notice the jump in the zero field magnetization for temperatures below the critical temperature.

another equally good solution is $-m(-h, T)$. Each curve with $h > 0$ has a corresponding curve — with oppositely signed m — that applies for the magnetic field with flipped sign. The symmetry is also realized at zero field. At high temperatures, the magnetization is zero for $h = 0$. Then the symmetry is trivially realized since changing the sign of the magnetization changes nothing. However, at low temperatures, for each value of the temperature, the magnetization can take on either of two possible values. The symmetry under flipping the sign of the magnetic field is here reflected in the equality of the magnitude of $\langle \sigma \rangle$ in each of these zero-field phases.

Sometimes we see phase transitions which do not easily fit into the framework given above. There is an interesting phase transition which involves the dissociation of uncharged atoms into charged components. When the charges are tightly bound together we call the material a dielectric. It is an insulator, which may polarize in an electric field but certainly does not conduct electricity. When the atoms dissociate, the charged components may move in opposite directions in response to an electric field. This kind of matter is called a plasma, and can conduct electricity. In general, one does not know whether this *metal to insulator* transition is first order or higher. There is a realization of this transition in three-dimensional condensed matter systems.[2] A very similar transition occurs in the early universe in which quarks bind together to form the hadrons and mesons we see today. In the Chapters 15 and 16, we shall discuss the two-dimensional version of this phase transition. Of course this transition also occurs in three-dimensional systems.

Transitions into and out of the glassy state, provides other examples in which the basic nature of the transition is unknown. A ordinary glass is a liquid in which some of the molecular motions are very substantially slowed down. The phase transitions become hard

---

[2]For a discussion of this transition see the several papers in P. W. Anderson *A Career in Theoretical Physics* (World Scientific, Singapore, 1994).

to see because one has to wait too long. We would like to extrapolate to the phase transition. But we are not quite sure how that might work.

10.4   Back to the Ising Model

We have already discussed in Chapter 4 the setup of an Ising problem which describes the simplest ferromagnets. Recall the previous discussion. We can set up a Hamiltonian which contains a set of spins $\sigma_{\mathbf{r}}$, where $\mathbf{r}$ is the lattice site defining the location of the spin. Each $\sigma_{\mathbf{r}}$ takes on two values: plus one and minus one. As in Chapters 2 and 3, we work with a simple hypercubic lattice

$$\mathbf{r} = a(n_1, n_2, \ldots, n_\mu, \ldots, n_d),\tag{10.1}$$

where a is the lattice constant and each of the n's is an integer. To produce a ferromagnetic phase transition there must be an interaction between neighboring spins which gives a lower energy to spin configurations in which spins are aligned. An external magnetic field is taken into account by saying that there is a lower energy when a spin is aligned along the magnetic field than opposite to it. This kind of situation can be represented by a Hamiltonian with two terms

$$\mathcal{H} = -\sum_{\mathbf{r}} \sigma_{\mathbf{r}} B(\mathbf{r})\mu - J\sum_{\langle \mathbf{r},\mathbf{r}'\rangle} \sigma_{\mathbf{r}}\sigma_{\mathbf{r}'}.\tag{10.2}$$

Here $2J$ is the energy cost for moving a pair of neighboring spins from an aligned configuration to an anti-aligned one while $2B(\mathbf{r})\mu$ is the energy cost of moving the spin at $\mathbf{r}$ from being lined up with the field to the opposite. The first sum says that the latter energy applies to all spins. The notation $\langle \mathbf{r}, \mathbf{r}'\rangle$ means include all pairs of nearest neighboring spins. The number of nearest neighbors of a given lattice site is generally denoted by z. For the simple hypercubic lattice, $z = 2d$. We take both J and $B\mu$ to be positive. The partition function is obtained by summing an exponential of $-\beta\mathcal{H}$, which we write as

$$W[\sigma] = -\beta\mathcal{H} = \sum_{\mathbf{r}} h(\mathbf{r})\sigma_{\mathbf{r}} + K\sum_{\langle \mathbf{r},\mathbf{r}'\rangle} \sigma_{\mathbf{r}}\sigma_{\mathbf{r}'}.\tag{10.3}$$

Here $h(\mathbf{r})$ is a dimensionless rendition of the magnetic field and K is a dimensionless version of the coupling strength. Both of these go to zero at infinite temperature and to infinity at zero temperature. In most of our calculations we shall let the field $h(\mathbf{r})$ be independent of position. In that case, we shall write it as simply h.

Notice that the Hamiltonian is left invariant if we change the sign of both the magnetic field, h, and also of each of the spins, $\sigma_{\mathbf{r}}$.

We have already talked about the possibility (and difficulties) of calculating the consequences of the Hamiltonian (10.3) for statistical systems. The calculation can be carried out for one dimension and at zero field for two dimensions. (See Chapter 4.) Beyond that, little can be done exactly; it is just too hard. However there is one special case which is

quite easy: the one in which the coupling among the spins is zero. Then, as we have already seen, the spin is determined by a single particle Hamiltonian, ϵ, with

$$-\beta H = h\sigma_{\mathbf{r}}, \tag{10.4}$$

a simple calculation gives the average magnetization as

$$\langle \sigma_{\mathbf{r}} \rangle = \tanh h. \tag{10.5}$$

But Eq. (10.5) tells us nothing very direct about the phase transition.

10.5   Mean Field Theory of Magnets

But we can get some of the qualitative properties of the phase transition by examining an approximate theory called 'mean field theory'. The many variants of this theory work reasonably well and, in fact, often provide a qualitatively correct theory of phase transitions and other physical properties. The idea behind this theory is to make the approximation that each spin behaves as if it were an independent spin sitting in the mean field produced by all the other spins. To reflect this idea we focus upon the particular spin at $\mathbf{r}$ and consider how the Hamiltonian depends upon that spin alone. We see that

$$-\beta\mathcal{H} = h\sigma_{\mathbf{r}} + K\sigma_{\mathbf{r}} \sum_{\mathbf{r}' \text{ nn to } \mathbf{r}} \sigma_{\mathbf{r}'} + \text{constant}. \tag{10.6}$$

The last sum is over all $\mathbf{r}'$ which are nearest neighbors to $\mathbf{r}$. The 'constant' represents all terms which do not depend upon the spin $\sigma_{\mathbf{r}}$. Now here comes the approximation. Assume that one can replace the fluctuating sum in Eq. (10.6) by a sum of the averages values of all the neighboring spins. Thus, Eq. (10.6) becomes

$$-\beta H = \sigma_{\mathbf{r}} \left(h + K \sum_{\mathbf{r}' \text{ nn to } \mathbf{r}} \langle \sigma_{\mathbf{r}'} \rangle \right) + \text{constant} \tag{10.7a}$$

which can be equally well represented as

$$-\beta H = \sigma_{\mathbf{r}} h_{\text{eff}}(\mathbf{r}) + \text{const}, \tag{10.7b}$$

where the effective field has the value

$$h_{\text{eff}}(\mathbf{r}) = h(\mathbf{r}) + K \sum_{\mathbf{r}' \text{ nn to } \mathbf{r}} \langle \sigma_{\mathbf{r}'} \rangle. \tag{10.8}$$

As we see, the mean field, h_{eff}, is composed of two parts, first the externally applied field h, and second the internally generated field. Since the spin at $\mathbf{r}$ has its probabilities determined by this effective field, its average is given by equation in this approximation the

average is given by Eq. (10.5) with h replaced by h_{eff}. Thus, the mean field theory implies that

$$\langle \sigma_{\mathbf{r}} \rangle = \tanh h_{\text{eff}}(\mathbf{r})\,. \tag{10.9}$$

In the special case in which the system is translationally invariant, we write $\langle \sigma \rangle$ for $\langle \sigma_{\mathbf{r}} \rangle$ and find that Eq. (10.9) is the statement:

$$\langle \sigma \rangle = \tanh h_{\text{eff}} \tag{10.10}$$

where h_{eff} is given by Eq. (10.8) as

$$h_{\text{eff}} = h + Kz\langle \sigma \rangle\,. \tag{10.11}$$

In this expression, z is, as we have mentioned, the number of nearest neighbors of a given site. In the hypercubic lattice, $z = 2d$, where d is the dimension of the system.

   We might expect Eq. (10.10) to be accurate in the limit as z becomes very large. For, when z is large, we have an effective field which is a sum of many terms. The fluctuation in this field gets smaller and smaller as z gets larger and larger. In the limit, the spin in question sees the summed effects of many, many different spins and one might expect to replace the sum by its average. Thus, in particular, we might expect the mean field theory to be particularly accurate for systems in very high dimensions. Notice that K is inversely proportional to the temperature. Therefore, Kz can be thought of as T_{c}/T, which T_{c} is some kind of characteristic temperature for the problem. As we shall see that temperature is, in fact, the critical temperature at which we have a continuous transition. We thus can write the effective field for the problem as

$$h_{\text{eff}} = h + \langle \sigma \rangle \frac{T_{\text{c}}}{T}\,. \tag{10.12}$$

10.6   The Phases

Equations (10.10) and (10.11) constitute the mean field theory for the equilibrium properties of this Ising model. Now we are ready to get the thermodynamic properties of the system by solving Eq. (10.10). Take first the case in which h and $\langle \sigma \rangle$ are both quite small. Then we can expand Eq. (10.10) in a series in both. To first order we find

$$\langle \sigma \rangle = h_{\text{eff}} = h + \langle \sigma \rangle Kz\,. \tag{10.13}$$

Here z is a symbol for the number of nearest neighbors, which is $2d$ for a hypercubic lattice. Since Kz is inversely proportional to the temperature, we can write it as T_{c}/T and solve Eq. (10.13) to find

$$\langle \sigma \rangle = \frac{h}{1 - T_{\text{c}}/T}\,. \tag{10.14}$$

Equation (10.14) shows a singularity at $T = T_c$. Therefore we interpret $T_c = TKz$ as the critical temperature.

From Eq. (10.14), so long as the temperature is above T_c, $\langle \sigma \rangle$ and h point in the same direction while, according to Eq. (10.14), when the temperature is below the critical temperature, $\langle \sigma \rangle$ and h are antiparallel. However the latter is an impossible result. To see its impossibility use Eq. (10.14) to find that the magnetic susceptibility, which is the derivative of magnetization with respect to field, has the value

$$\chi = \left. \frac{\partial \langle \sigma \rangle}{\partial h} \right|_T = \frac{1}{1 - T_c/T} \, . \tag{10.15}$$

Equation (10.15) was derived from the mean field theory (10.10) using as the sole assumption that $\langle \sigma \rangle$ and h were both sufficiently small so that one can do an expansion in them.

However for $T < T_c$ Eq. (10.15) must be nonsense. Recall our discussion of operators and field in Chapter 7. The total magnetization operator $M = \sum_{\mathbf{r}} \sigma_{\mathbf{r}}$ is the operator conjugate to the field h. As a result, we know that

$$\langle M \rangle = \frac{\partial}{\partial h} \ln Z = N \langle \sigma_{\mathbf{r}} \rangle \, . \tag{10.16a}$$

Here the derivative is to be calculated at fixed coupling, K and constant number of sites, N. A higher order calculation is done in which the same way. We see that the derivative of the average spin is exactly the susceptibility

$$\chi = \frac{\partial}{\partial h} \langle \sigma_{\mathbf{r}} \rangle = \frac{\langle (M - \langle M \rangle)^2 \rangle}{N} \, .$$

Since the last expression is certainly positive, so is the susceptibility. Equation (10.15), then, must fail as soon as T falls below the critical temperature, T_c — since it then gives the wrong sign of the susceptibility. We thus derive a wrong result in this region.

This incorrectness should not be a great surprise to us. If T is far enough below T_c, the magnetization and $\langle \sigma \rangle$ are never very small. Hence one can never expand in them. To see the difficulty, let us try to solve Eq. (10.10) for $\langle \sigma \rangle$ at $h = 0$. To do this, we use a graphical method. We generate graphs for two functions of $\langle \sigma \rangle = x$. The first is just $f(x) = x$. This will represent the left hand side of Eq. (10.10). The second is $g(x) = \tanh(xT_c/T)$. This will be the right hand side. When f crosses g we have a solution for the magnetization. Figures 10.4 and 10.5 show this graphical calculation. The first one, Fig. 10.4, is for $T > T_c$ and shows the one expected root at $x = \langle \sigma \rangle = 0$. The second panel, Fig. 10.5, is for $T < T_c$ and shows three roots! One of these is $\langle \sigma \rangle = 0$ — which has given us trouble. We might suspect that this root is not physically realized. There are two additional roots at nonzero values of the spontaneous magnetization. Because the problem is symmetric under the operation of changing the sign of both σ and h, the two roots are equal in magnitude and opposite in sign.

Somehow the system must choose one of these roots. Which one? We shall see.

A graphical understanding is a beginning. But analytical work often gives us a richer understanding than can be obtained from pure numerics. Therefore, we now turn to obtaining an analytical understanding of the mean field theory for low temperatures.
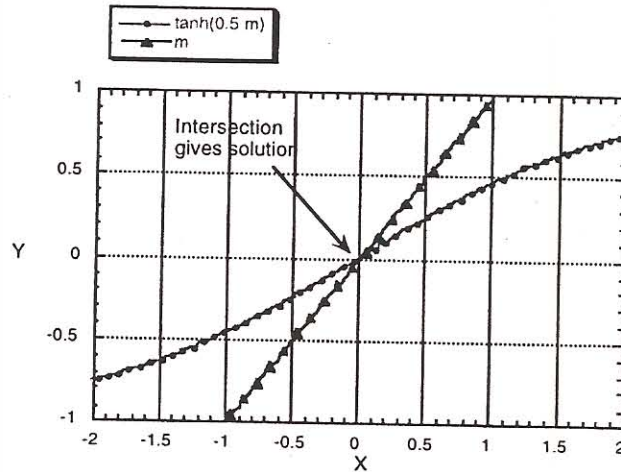
Fig. 10.4. Graphical method of equation solving. Two curves give respectively the left and right hand sides of Eq. (10.9), We calculate the magnetization for zero magnetic field and $T_c/T = 0.5$, using Eq. (10.9). The X-value is $\langle\sigma\rangle$. We draw two curves as a function of X. In one curve, the Y-value is the right hand side of Eq. (10.9) expressed as a function of $\langle\sigma\rangle$ for fixed values of K. For the other it is $\langle\sigma\rangle$ itself. Where these cross we have solutions to Eq. (10.9).
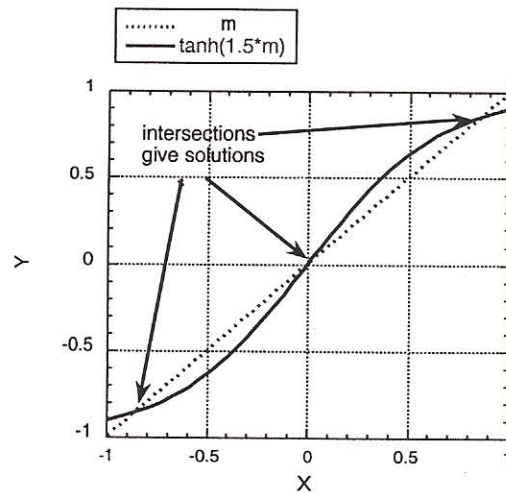

Fig. 10.5. Another graphical calculation of magnetization. Just like Fig. 10.4, except that T is one half of T_c. We follow the same method of equation solving. As in the last figure, the X-axis represents $\langle\sigma\rangle$ while the Y-axis plots $\langle\sigma\rangle$ and the mean field approximation to that quantity. Now there are three solutions: zero magnetization, and the two values of the spontaneous magnetization.

10.7   Low Temperature Result

The quantity $\langle\sigma\rangle T_c/T$ as the interpretation of being the portion of the effective magnetic field induced by the interaction among the spins. For low temperatures, this induced field tends to be very large in magnitude. Let us assume that both this field and the usual magnetic field h, are positive. Thus the induced field is lined up with the applied field. In

this case, the argument of the hyperbolic tangent in Eq. (10.10) is very large and one can use the expression:

$$\tanh x = 1 - 2e^{-2x}, \tag{10.17}$$

which is true for large x. Then Eq. (10.10) becomes:

$$\langle \sigma \rangle = 1 - 2\exp\left[-2\left(h + \frac{\langle \sigma \rangle T_c}{T}\right)\right].$$

To lowest order in an expansion appropriate for low temperatures, one can replace the $\langle \sigma \rangle$ on the right hand side of this expression by unity and find:

$$\langle \sigma \rangle = 1 - 2\exp\left[-2\left(h + \frac{T_c}{T}\right)\right], \qquad \text{(phase +)}. \tag{10.18a}$$

When one calculates the susceptibility from this expression one finds a perfectly positive (and small) value consistent with everything we know from thermodynamics and statistical mechanics. We label this phase as $+$ since it has a positive value of the magnetization. Equation (10.18a) looks like a perfectly acceptable solution even for negative values of h. There is another solution which is constructed from the approximation $\langle \sigma \rangle \approx -1$, which we call phase $-$. Its magnetization has the form:

$$\langle \sigma \rangle \approx -1 + 2\exp\left[-2\left(-h + \frac{T_c}{T}\right)\right], \qquad \text{(phase --)}, \tag{10.18b}$$

and yet a third solution, which we obtained before as Eq. (10.14)

$$\langle \sigma \rangle = \frac{-hT}{T_c - T}, \qquad \text{(phase 0)}. \tag{10.18c}$$

All three solutions look OK. In the next section, we shall argue that only one solution at a time is acceptable. The conclusion as the temperature goes to zero (10.18a) is an acceptable solution only for $h \geq 0$, while (10.18b) is acceptable only for $h \leq 0$, and (10.18c) is never true for low temperatures. This last phase is labeled phase zero since it will have zero magnetization at zero field.

10.8   Free Energy Selection Argument

Equation (10.18) give us three presumably possible thermodynamic states for the system when h is small and the temperature is low. Which one(s) of these situation represents a possible behavior of the real system? To make the right selection we follow a principle that whatever the thermodynamic state achieved by the system is the one which produces the minimum of the free energy, F, or the maximum of the quantity

$$\exp(-\beta F) = \text{Tr}\, \exp(-\beta H). \tag{10.19}$$

In writing this expression, we use our convention that the quantum sum over states and the classical sum over phase space will be represented by the symbol Tr. To find the free energy we notice that the derivative of the free energy with respect to β is given in terms of the average value of the energy:

$$-\frac{\partial \beta F}{\partial \beta} = \langle H \rangle . \tag{10.20}$$

In mean field theory, to calculate the average energy we start with H and replace each spin in the Hamiltonian by its average. Thus, Eq. (10.20) becomes

$$-\beta \frac{\partial (\beta F)}{\partial \beta} = h \sum_{\mathbf{r}} \langle \sigma \rangle + K \sum_{\langle \mathbf{r}, \mathbf{r}' \rangle} \langle \sigma \rangle^2 = N \langle \sigma \rangle \left[h + \frac{Kz \langle \sigma \rangle}{2} \right] . \tag{10.21}$$

Here, N is the number of lattice sites while Kz has the physical interpretation of being the ratio T_c/T. Now consider the case $h = 0$. We wish to know how the free energy depends upon our choice of state. For $T > T_c$, there is no choice. For $T < T_c$, in the unmagnetized state $\langle \sigma \rangle$ is and remains zero. Then if F_c is the value of the free energy at the critical point, Eq. (10.21) reads

$$F = F_c \quad \text{for } h = 0 \text{ and all } T \qquad \text{(phase 0)} . \tag{10.22}$$

Then the free energy is F_c for this configuration. In the magnetized configuration, Eq. (10.21) reads

$$T \left(\frac{\partial (\beta F)}{\partial T} \right)_h = N \frac{T_c}{T} \frac{\langle \sigma \rangle^2}{2} . \tag{10.23}$$

All factors in this expression are non-negative.

Notice that Eq. (10.23) describes all three phases at once. To get the actual free energy at $T < T_c$, one integrates this equation downward in temperature starting at T_c, using the boundary condition that $\beta F = \beta_c F_c$ at the critical temperature. One visualizes doing the integral separately in each of the three phases, in each case stopping the integration at some temperature, T, below the critical temperature. Then one finds that in phase zero the right hand side is zero so that βF remains at the critical value $\beta_c F_c$. On the other hand, in the other two phases, the right hand side of Eq. (10.23) is positive and thus gives a negative contribution to the downward integral, so that

$$\beta F < \beta_c F_c \text{ for } h = 0 \text{ and } T < T_c \qquad \text{(phase + and phase $-$)} . \tag{10.24}$$

The general rule is that configurations of lower free energy are more likely. In big systems, in which the number of degrees of freedom is approaching infinity, a small difference in free energy per site can results in vastly different probabilities. Here, for $T < T_c$, we have a lower free energy for the two magnetized phases. The system will pick one of these two, and not the unmagnetized phase. A similar argument shows that in a system with a very

large number of lattice sites, N, if h is positive only the positive magnetization phase will be realized. Conversely for negative h only phase — will be achieved. There two phases will be cleanly separated for sufficiently large values of $|h|$. In homework Problem 10.3 we ask you to show that the condition '$|h|$ is sufficiently large' gets weaker and weaker as the number of sites gets larger. Thus, in an infinite system all nonzero values of $|h|$ give us only one thermodynamically stable phase.

So far, we have not emphasized one essential fact about all these phase transitions. *Phase transitions only occur in infinitely large systems.* Phase transitions are signaled by qualitative differences between two phases of a thermodynamic system. They occur when there is some kind of mathematical discontinuity in the behavior of the system as a function of parameters like K and h. For example, in our Ising example as N goes to infinity the magnetization jumps discontinuously as a function of h. However, it is easy enough to prove mathematically that such a jump cannot occur for a finite system.[3] Thus, somehow, phase transitions must be linked to the fact that there are an effectively infinite number of particles in the system. So they are not just a result of mechanics. They are reflections of the mechanics of large systems.

10.9 Behaviors of Different Phases

It is tautological to say that different phases behave differently. A crystalline solid is different from a liquid, which is different from a superfluid, and that is different from a ferromagnet. There is a direct, but deep, reason for the difference. In many, but not all phase transitions, one or more of the phases has a nontrivial set of symmetry properties. In this case 'nontrivial' means that the configuration of the system has less than the full symmetry of the Hamiltonian. For example, a crystalline solid has a Hamiltonian which displays both a rotational and a translational invariance. However, the produced lattice shows neither symmetry. Each lattice picks out a set of directions for its crystalline axes. A rotation of the crystal produces another, equivalent, but different configuration. Similarly every lattice picks out preferred positions, which are the equilibrium position of the constituents. Displace the entire lattice a little, and you have other equilibrium positions. Thus, the full translational symmetry is broken. One can often see the broken rotational order. Crystalline solids produce *crystals*, that is pieces of material with surfaces arranged in facets along directions set by the crystal axes. The translational order cannot be seen with the naked eye. Nonetheless these ordering priorities have consequences which are immediately apparent. In contrast to a fluid, a solid is resistant to a shear. It holds its shape. The difference between the disorder of a fluid and the order of a solid is particularly evident in its dynamical behavior. A fluid will propagate only one kind of sound, a longitudinal wave.

---

[3]The magnetization is the logarithmic derivative of the partition function. Such a derivative can never show a discontinuity in any region in which Z is analytic in h. But, for a finite system, Z is a finite sum of exponentials of h. It is analytic. Therefore no discontinuities. Indeed, finite-but-large systems can show changes which appear quite abrupt. But, in each case, a close examination of the 'jump' region will show a continuous behavior. The abrupt jumps only occur for infinite N.

Typically, a solid will respond to a transient shear by producing a transverse sound wave. This kind of excitation is directly produced because the shear tries to break the produced order and then the system responds dynamically to restore the order. It is generically true that interesting phases show some kind of broken symmetry, by producing a kind of ordering. It is further true that when this ordering is locally disturbed, the system will produce a dynamical response characteristic of the phase in question.

The Bose condensed system provides another example. The superfluid ordering is achieved by having a macroscopic number of particles fall into a single quantum state. This state is defined by a complex wave function. The ordering determines the wave function of this state, defining its magnitude but not its phase angle.[4] In the Bose condensed system, the condensate wave function has a phase angle, which defines the thermodynamic phase, and takes on all possible values between 0 and 2π. Thus the thermodynamic phase has a symmetry under the rotation of the phase angle. This symmetry is called a 'U(1)' symmetry.

In equilibrium the phase angle does not vary in space. The system responds to variations in the phase angle in two different ways. If there is a fixed spatial variation produced by external forces, then the system will produce a 'supercurrent' in which there is a mass-flow along the gradient of the phase. This current is entirely different from ordinary mass flow in that this kind of flow can occur without friction, and without energy losses from heating. In contrast, if we apply no forces, but start the system in a situation with a spatially varying phase angle, then it will produce a new characteristic form of sound wave called 'second sound'. We should not be surprised if a U(1) symmetry can produce waves, after all photons are produced in much the same fashion.

One almost always finds that a broken symmetry produces an ordering and that disturbing that ordering produces some characteristic type of dynamical response. This response is called a 'Goldstone–Nambu Boson'. Jeffrey Goldstone, now at MIT, and Yoshiro Nambu from Chicago first made this general argument. The word 'boson' appears in the argument because one important application of the argument is to broken symmetry states in particle physics. The reader has been prepared, specifically in Chapter 4, for the fact that there is an intimate connection between statistical physics and particle physics. We shall see more of this connection in the next few chapters. We start here. The particle physicist is often interested in understanding the connection between the more 'fundamental' short-ranged and high energy interactions and the more accessible lower energy and longer-ranged behavior. The statistical physicist is also interested in relating microscopic interactions to macroscopic behavior. Most of the richness provided by microscopic interactions are really present only at the micro scale. However a few effects persist out to the macro scale. These are:

(1) The effects of inherently long-ranged forces like electromagnetic interactions or gravity.

---

[4]Notice that we are in the process of using two different meanings of the word 'phase'. There is a phase of a thermodynamic system, e.g. liquid or gaseous. To be more precise, we use the words 'thermodynamic phase' to specify this meaning. But, there is also the phase of a complex number. We refer to the latter as a 'phase angle'.

(2) The special effects of long-ranged correlation produced near the critical point. The theory of critical behavior, which develops this class of application is the subject of succeeding chapters.

(3) Long-ranged interaction which occur in broken symmetry states.[5]

The treatment of long-ranged forces are almost identical in particle physics and statistical physics. Thus, in recent years, the paths of statistical theory and particle theory have often run parallel. The discussion of the Higgs particle in high energy physics followed the lines of the treatment of the Anderson mode in superconductors.[6] The critical state has formed the basis for the calculation of the masses and interactions which occur in particle physics.

This chapter has been concerned with the mean field theory of first order phase transitions. This theory neglects fluctuations in the ordering which drives the phase transition. Of course, in an finite-range, finite-system the fluctuations are always there. Thus, our analysis has left something out. The neglected fluctuations are important. Sometimes the system is in the 'wrong' phase — that is it is a liquid when, by free energy considerations, it should be a solid. In another case, its magnetization points opposite to the magnetic field. In these situations the real system will undergo a dynamical process which will bring it to the 'right' phase. The process starts with a fluctuation. In a transitory process, the system produces a region within the 'wrong' phase that is essentially a small piece of the 'right' phase. If that region is large enough it will tend to grow and bring the entire system into the equilibrium phase. Naturally, in order to understand, the process, we must understand fluctuations and it is precisely these fluctuations which are left out in mean field theory. One must go beyond mean field theory to understand some of the most interesting problems in first order phase transitions: the long-lived existence of states of the wrong phase (termed *metastability*), the particularly long-lived metastable states called glasses, and the dynamical processes by which equilibrium is restored. These issues are not fully understood to this day. So we go on, to the somewhat easier problem of second order phase transitions.

Homework

Problem 10.1 (Magnetization versus T_c/T). Draw plots of the solutions to the mean field equation for the magnetization as a function of T_c/T for $h = 0$, $h = 0.1$, $h = 0.2$, and $h = 1.0$.

Problem 10.2 (Anti-ferromagnetism). An anti-ferromagnetic has spins at different sites lined up in opposite directions, so that the total magnetization is zero. Mean field theory gives a description of anti-ferromagnetism directly analogous to the ferromagnetism we discussed. It arises for negative values of the coupling J and hence negative values of K.

---

[5] Particle physics is much concerned with showing that long-ranged forces can always be understood in terms of microscopic mechanism like #2 and #3. The first point is that there are some inherently long-ranged forces in nature. Statistical physics uses these forces; particle physics must try to explain them, perhaps in terms of #2 and #3.

[6] P. W. Anderson, Phys. Rev. **130**, 62 (1962).

(1) Find the appropriate mean field theory for antiferromagnetism.

(2) Calculate the magnetic susceptibility for this system.

Problem 10.3 (Phase Probabilities). Below Eq. (10.24) we discussed a free energy evaluation for the relative probabilities for the different phases of the system. Imagine a system with N particles, at $h = 0$ with a temperature a little below the critical temperature. Using mean field theory, estimate the probability that the system will be in the unmagnetized phase for $N = 100$ and $N = 10^{20}$.

   Now apply a small positive magnetic field. For $T < T_c$, what is the condition that makes the phase with negative magnetization have a probability of being observed greater than one part in 10^5.

Problem 10.4 (Magnetic Susceptibility for $T < T_c$). Calculate an expression for the magnetic susceptibility in mean field theory for $T < T_c$ and $h = 0$. Evaluate this expression more explicitly for low temperatures and for temperatures close to the critical temperature.