

Chapter 4

Phase Transitions

4.1 Phenomenology

4.1.1 Basic ideas

In Chapter 3 we saw how interactions can affect the behaviour of systems, modifying properties from those of the corresponding ideal (non-interacting) system. Nevertheless a gas was still recognisable as a gas, albeit with somewhat altered properties; the interactions did not change the fundamental nature of the system. There is, however, another consequence of interactions when, by altering a thermodynamic variable such as temperature, pressure etc. there can suddenly occur a dramatic change in the system's properties; there is a transition to a qualitatively different state. We refer to this as a phase transition.

Phase transitions present a challenge to statistical mechanics. At the transition point the system exhibits, by definition, singular behaviour. As one passes through the transition the system moves between analytically distinct parts of the phase diagram. But how can this be? The thermodynamic behaviour is embodied in the partition function. Thus the partition function must contain the details of any phase transition; it should exhibit the singular behaviour. But the partition function is merely a sum of Boltzmann factors—exponentials of the energy, which must therefore be analytic. There is a paradox: *does* the partition function contain the description of a phase transition or does it not? This question was a source of worry to physicists. And it was debated at the van der Waals Centenary Conference in November 1937. When a vote was taken it transpired that opinion was approximately equally divided between those who believed the partition function did contain details of a sharp transition and those who believed it did not!

The paradox was resolved by H. Kramers. He suggested that the singu-

lar behaviour only appears when the *thermodynamic limit* is taken – that is, when N and V go to infinity while the density N/V remains constant. This view was vindicated through the work of T. D. Lee and C. N. Yang published in 1952 [1, 2] and the discussion in Huang’s book *Statistical Mechanics* [3]). Subsequently there was an elegant reformulation by Fisher [?]; see also Jones [?].

Fisher considered the partition function Z as a function of a *complex* inverse temperature β . For a finite system there are zeros in Z for certain complex values of β . Fisher showed that as the size of the system increases these zeros shift in the complex β plane. And as the thermodynamic is approached, one or more of these zeros moves to the real β axis. It is this that causes a zero in the partition function, resulting in its singular behaviour, indicating a phase transition.

Interactions are responsible for phase transitions. (The Bose-Einstein condensation is the only exception to this; there a phase transition occurs in the absence of interactions.) As a very rough “rule of thumb”, often the temperature of the phase transition is approximately related to the interaction energy by $kT \approx E_{\text{int}}$. Thus the exchange interaction between electronic spins $-\hbar J \mathbf{S}_1 \cdot \mathbf{S}_2$ leads to a ferromagnetic transition at the Curie temperature $T_c \approx \hbar J/k$. However in some cases it might not be immediately clear how to quantify the “interaction”. In the BCS theory of superconductivity it is interactions between lattice vibrations and the electrons that result in the superconducting transition. The transition temperature is given by $kT = 1.14 \hbar \omega_D e^{-1/\rho(0)V}$ where ω_D is the Debye frequency characterizing the phonons, $\rho(0)$ is the density of electron states at the Fermi surface and V is the volume. Here $\hbar \omega_D$ may be regarded as the characteristic energy, but the effect of the exponential is to shift the naïvely expected transition temperature by orders of magnitude; the rule of thumb is thus useless in this case.

From the reductionist perspective the first question one might ask about phase transitions is: “given the hamiltonian for a system, can we predict whether there will be a phase transition?” The answer to this is: “probably in general no”, for reasons that should become apparent. The second question might then be: “knowing that there is a transition and knowing the nature of that transition, can we predict the temperature of the transition from the hamiltonian?” The answer to this question is that we can usually apply the rule above; often we can find a better approximation to the temperature of the transition; very occasionally we can find it exactly (analytically). The key point is the *nature* of the transition; *that* is difficult to predict.

Working against this reductionist view of phase transitions where the hamiltonian is regarded as the all-important descriptor of the system, we have

the observed phenomena of *universality*. It is found that many properties of systems in the vicinity of phase transitions do *not* depend on microscopic details, but are shared by dissimilar systems. The ultimate explanation for this is found through use of the renormalization group, sadly outside the scope of this book. However the scaling arguments of Section 4.1.9 support this idea. The Landau picture of phase transitions in Section 4.5 provides a common language and mathematical description for the phenomena.

4.1.2 Phase diagrams

Let us start with a very familiar example. The general behaviour of a $p - V$ system is shown in Fig. 4.1. The variables of the thermodynamic configuration space are pressure p and volume V together with temperature T . A number of general observations can be made. There are regions where three distinct phases exist: solid, liquid and gas. And there are regions of two-phase coexistence.

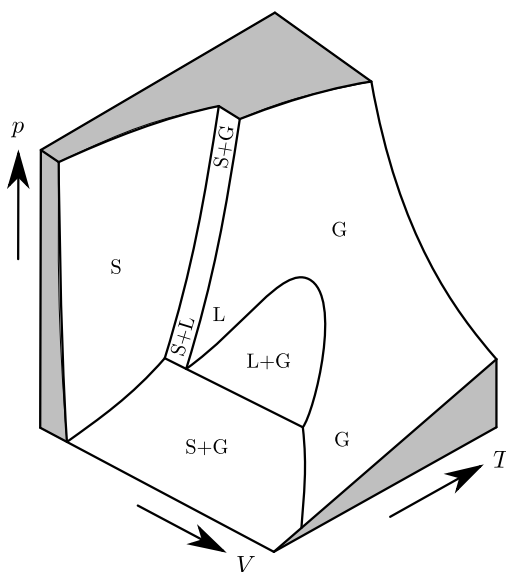
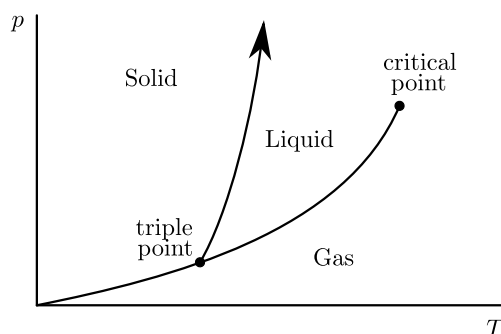


Figure 4.1: Thermodynamic configuration diagram of a $p - V$ system, S – solid, L – liquid, G – gas.

If we project the configuration diagram onto the $p - T$ plane then the surfaces of coexistence become lines (why?). Such a phase diagram is shown in Fig. 4.2. Solid, liquid and gas regions are seen, separated by the coexistence lines. All three phases coexist at the *triple point* and the liquid-gas line terminates at the *critical point*. At the critical point the distinction between the gas phase and the liquid phase disappears.

Figure 4.2: Phase diagram of a $p - V$ system.

Many phase transitions involve a symmetry change. Often it is quite clear what symmetry is involved. Thus the liquid–solid and the gas–solid transitions both involve the breaking of translational symmetry. In the case of superfluids and superconductors it took many years until the appropriate symmetry was identified – gauge symmetry. However in the case of the liquid–gas transition there is no symmetry broken. We will see what symmetries are broken in some different types of phase transition in the next section.

The corresponding configuration diagram for a ferromagnetic magnetic system is shown in Fig. 4.3. The phase diagram for the system is the pro-

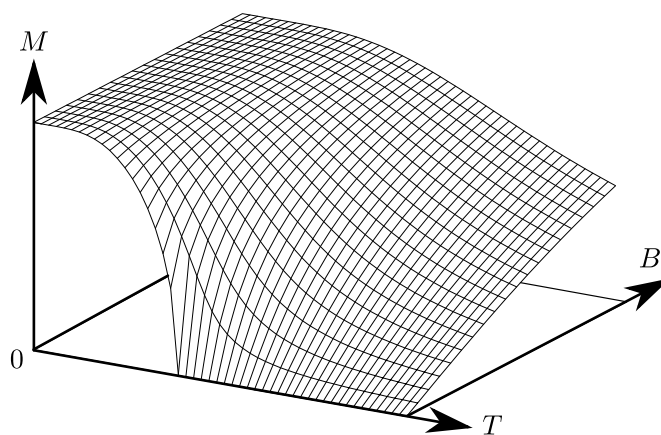


Figure 4.3: Thermodynamic configuration diagram of a magnetic system.

jection of this diagram onto the $B - T$ plane. This is shown in Fig. 4.4.

When the magnetic field is positive the magnetization is pointing up. When the magnetic field is negative the magnetization is pointing down. Above the critical temperature there is no magnetization when B is zero, so

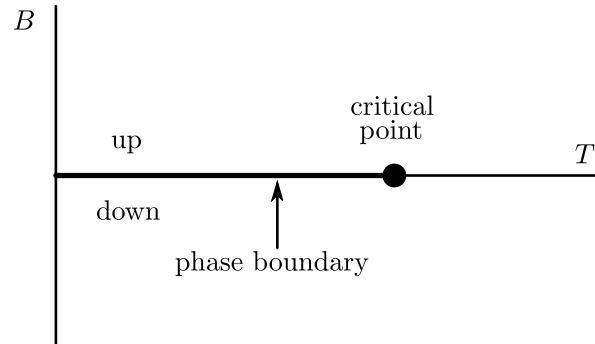


Figure 4.4: Phase diagram for a magnetic system.

one moves smoothly from the up state to the down state. But below the critical temperature there is a magnetization in the absence of a magnetic field. Then as B decreases through zero the magnetization flips from up to down.

4.1.3 Symmetry

At the highest temperatures a system will be at its most disordered. It will have the highest symmetry possible, and this will be the symmetry of the system's hamiltonian. As the temperature is lowered, when there is a phase transition, that symmetry is frequently broken; the resultant system will have a lower symmetry. Consider an isotropic magnet in zero magnetic field. The hamiltonian contains $\mathbf{S}_1 \cdot \mathbf{S}_2$ which is rotationally invariant. Above the transition temperature there is no magnetization and the system has *rotational symmetry*. But when cooled through the ferromagnetic transition a magnetization appears spontaneously. This defines a direction and the rotational symmetry is broken. Other systems have other symmetries broken:

<i>System</i>	<i>Symmetry broken</i>
Crystal	Translational symmetry
Ferromagnet	Rotational symmetry
Ferroelectric	Inversion symmetry
Superfluid	Gauge symmetry

In general the ordered phase will possess a symmetry *lower* (i.e. less symmetric) than that of the system hamiltonian.

Note, however, that the liquid-gas transition does not involve a change of symmetry; not all transitions involve symmetry breaking. But we might say that in this case “homogeneity” is broken.

4.1.4 Order of phase transitions

Historically the first stage in discussing phase transitions from a general perspective was the introduction, by Ehrenfest, of the idea of the *order* of the transition [4]; this was the first step in classifying the nature of the non-analytic behaviour at the transition. When two phases coexist they have a common temperature and a common pressure (magnetic field). Thus the phases will each have the same Gibbs free energy.

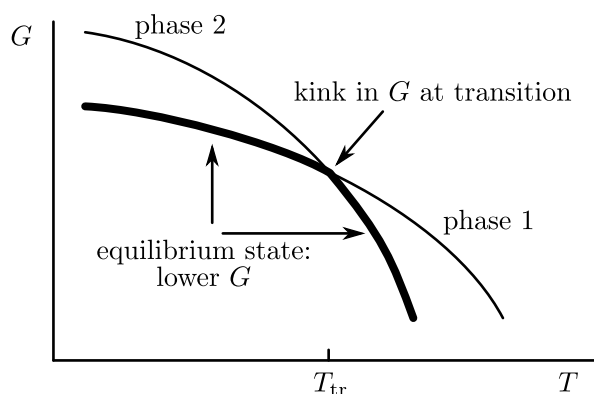


Figure 4.5: Variation of Gibbs free energy for two phases.

In Fig. 4.5 we show the variation of the Gibbs free energy G for two different phases of a system – say solid and fluid, where the curves intersect. The equilibrium state will correspond to the lower G , so we see that the phase transition occurs at the point where the Gibbs free energy is the same for both phases. The observed G will thus display a “kink” at the phase transition.

Traditionally phase transitions were characterized, by Paul Ehrenfest, on the basis of the nature of the kink in G . If the n^{th} derivative of G with respect to T (keeping other intensive variables constant) is the first discontinuous one, then it was said that the transition was n^{th} order. Now since $\partial G/\partial T|_p = -S$ we see that the discontinuity in $\partial G/\partial T$ is the change in entropy between the two phases. Thus at a first order transition the entropy changes discontinuously, while at second and higher order transitions the entropy varies continuously. And since the latent heat, the heat absorbed, is given by $T\Delta S$ it follows that there *is* latent heat involved with a first order transition, but not with higher orders.

Nowadays the classification scheme is not used in quite this way; there are only first and second order transitions. First order transitions are defined as above. And all transitions which are not first order are called second order. So if there is latent heat involved in a phase transition then it is first order,

otherwise it is second order. Following the entropy considerations above, first order transitions are also called discontinuous transitions, while so-called second order transitions are also referred to as continuous transitions. A different way of specifying the distinction will be seen in the following section.

4.1.5 The order parameter

The modern general theory of phase transitions started with the work of Landau and others in the 1930's. In developing a *general* treatment of phase transition phenomena we must use a language applicable to all systems. On warming a ferromagnet (in zero field) the magnetization goes to zero at the critical point. On warming a fluid along the coexistence curve the difference between the liquid and gas densities goes to zero at the critical point. And on warming a superfluid the superfluid density goes to zero at the critical point. The general feature is that there is *some quantity* which goes to zero at the critical point. When there is a symmetry broken on cooling through the critical point, this special quantity will be related to that symmetry.

The special quantity is a measure of the order present in the system; it is called the *order parameter*. Felix Bloch introduced the concept of the order parameter in 1932 and it was developed subsequently by Landau. In the general case we will use φ to denote the order parameter. For convenience we will sometimes normalise φ to be unity in the fully-ordered state.

The nature of the order parameter is important; the magnetization of a ferromagnet is a vector; the fluid density is a scalar. The order parameter for superfluid ^4He is a complex variable; those for liquid crystals and for superfluid ^3He are tensors. We use n to indicate the dimensionality of the order parameter.

<i>System</i>	<i>Order parameter</i>	φ		n
Ferromagnet	magnetization	\mathbf{M}	vector	3
Ferroelectric	polarization along axis	P	real scalar	1
Fluid	density difference	$n - n_c$	real scalar	1
Superfluid ^4He	ground state wavefunction	Ψ_0	complex scalar	2
Superconductor	pair wavefunction	Ψ_s	complex scalar	2
Ising	Ising "magnetization"	m	real scalar	1

We note that a complex scalar may, equivalently, be represented as a two-component (real) vector.

The ferromagnet will be treated in Section 4.3 and again in Section 4.5.2. The ferroelectric is treated in Section 4.6. The fluid is covered in Section 4.2.

Superfluids and superconductors are beyond the scope of this book. The Ising model is treated in Section 4.4. This is a magnet model where the interaction is restricted to the z direction. Its order parameter is a scalar ($n = 1$). And there is a further magnet model where the interaction is restricted to the $x-y$ plane. This is called the XY model; its order parameter is two-dimensional (or a complex scalar) so $n = 2$. It is mentioned briefly in Section 4.4.6.

The behaviour of the order parameter at the transition point gives a way to distinguish the order of the phase transition. As with the entropy, the order parameter changes discontinuously in a first order transition, but continuously in a second order transition; this reinforces the designation *discontinuous* and *continuous* transition. This behaviour is indicated in Fig. 4.6.

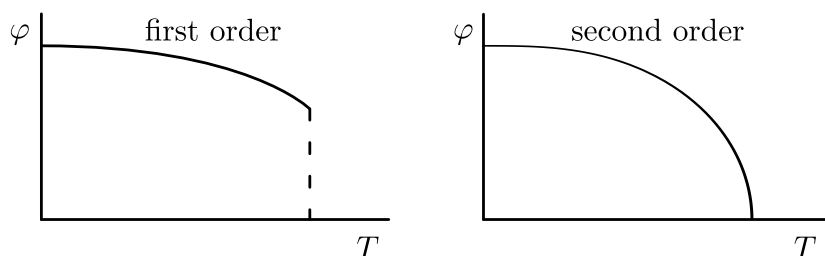


Figure 4.6: Order parameter in first and second order transitions.

Note that the apparent order of the transition may depend on the way the phase boundary is crossed. Thus while in general the liquid–gas transition is first order, it is second order when crossing the critical point from along the coexistence curve. Similarly, in the ferromagnet below T_c , if the field is varied through zero the magnetization changes discontinuously, while it varies continuously when the field is zero and the transition effected by varying the temperature. Furthermore, in the ferromagnet the magnetization can vary continuously from a positive to a negative value by going *around* the critical point – just as in a fluid.

Returning to the first question posed in Section 4.1.1 about predicting transitions from the system hamiltonian, we stated in that section that the difficulty was in knowing the nature of the transition. This can now be reinterpreted as saying the difficulty is in identifying what the order parameter might be in the ordered phase.

Sometimes the order parameter will be one of the usual thermodynamic variables: magnetization for the ferromagnet, polarization for the ferroelectric and density for the fluid. However it may be that the order parameter is some other – possibly unfamiliar – quantity such as the ground state wave function for superfluid ^4He or the pair wave function in superconductors.

A further important quantity is the thermodynamic variable *conjugate* to the order parameter. For the ferromagnet this is the magnetic field while for the ferroelectric it is the electric field. In the case of the fluid the conjugate variable is the chemical potential. The conjugate variable is important since it is by varying this quantity that we can couple to the order parameter in order to study the transition experimentally.

4.1.6 Conserved and non-conserved order parameters

A new concept we must introduce at this stage is that of *conserved* and *non-conserved* order parameters. In the magnetic transition, as we have seen, below the transition there is a spontaneously occurring magnetization. This is the order parameter for that system. The value of the order parameter is determined from thermodynamic arguments by minimising the appropriate free energy.

In the case of the gas–liquid transition the order parameter is essentially the density (more precisely the difference between the density and its value at the critical point). Above the transition the density of the system is determined by external constraints: the volume and the number of atoms. Below the transition the system separates into liquid and gas components. The liquid has a high density while the gas has a low density. However the *mean* density is still a fixed quantity; it is determined by the external constraints and not by minimising a free energy. The fluid system is thus said to have a *conserved order parameter*. We shall see that the binary mixture is another such system. The magnet, by contrast, has a *non-conserved* order parameter.

For a full treatment of systems with a conserved order parameter we must allow the order parameter to vary from place to place by introducing a position-dependent *order parameter density* [5]. It is then the integral of the order parameter density over the system’s volume, which is the conserved quantity. The solution to this problem then gives the spatial dependence of the order parameter – in particular it gives the variation at the interface between the different phases. There is a simpler approach, due to Gibbs [6], that ignores the energy associated with the interface and simply considers coexisting regions with two different (uniform) values of the order parameter.

4.1.7 Critical exponents

In Section 4.1.1 we stated that many properties of systems in the vicinity of phase transitions do not depend on microscopic details, but are shared by dissimilar systems. In using a common description of phase transition

phenomena, it is customary and convenient to specify the nature of the singular behaviour of quantities at the critical point. This is achieved through the introduction of *critical exponents* (and critical amplitudes). One of the successes of the modern theories of critical phenomena is in finding relations between the various critical exponents; this is achieved using scaling arguments, as we shall see in the next section.

The first members of the critical exponent family are denoted by α , β , γ and δ . These describe the singularity of the heat capacity, order parameter, susceptibility and equation of state respectively. In terms of the reduced temperature

$$t = \frac{T - T_c}{T_c} \quad (4.1.1)$$

they are defined (using the ferromagnet variables, for example) through

$$\begin{array}{llll} \text{heat capacity} & C & \sim & |t|^{-\alpha} \\ \text{order parameter} & m & \sim & |t|^\beta \\ \text{susceptibility} & \chi & \sim & |t|^{-\gamma} \\ \text{equation of state at } T_c & m & \sim & |B|^{1/\delta} \end{array}$$

Here the order parameter is the magnetization density, the magnetic moment per unit volume.

There are two more critical exponents, which are connected with the spatial variation of fluctuations in the order as the critical point is approached. For this, we need to introduce the spatial correlation function for the order parameter. We define the correlation function

$$g(\mathbf{r}) = \langle m(\mathbf{r})m(0) \rangle \quad (4.1.2)$$

where $m(\mathbf{r})$ is the magnetization density at position \mathbf{r} . The physical significance of correlation functions such as these is explained in Chapter 5 in Sections 5.1.2 and 5.1.3.

In the vicinity of the critical point the behaviour of the order parameter spatial correlation function is written as

$$g(\mathbf{r}) \sim r^{-p} e^{-r/l}. \quad (4.1.3)$$

And from this we obtain two more exponents, ν and η . These describe the divergence in the correlation length l and the power law decay p that remains at $t = 0$, when l has diverged. The exponents are defined through

$$\begin{array}{llll} \text{correlation length} & l & \sim & |t|^{-\nu} \\ \text{power law decay at } T_c & p & = & d - 2 + \eta \end{array}$$

where d is the dimensionality of the system (it will turn out to be of interest to consider systems of dimension other than three).

A comprehensive theory of critical phenomena will give values for the critical exponents. However it turns out that there are fundamental relations between the critical exponents, so that of the six exponents only two are independent. This is understood from *scaling theory*, which we will encounter in the next section.

4.1.8 The scaling hypothesis

Scaling theory involves the application of *dimensional analysis* to the study of the critical point. Near the critical point there are large fluctuations in the order parameter of the system. A dramatic example of this is the critical opalescence observed in fluids. This is a consequence of the density fluctuations that become very large at the critical point. As the critical point is approached the fluctuations occur over longer and longer distances; this is the correlation length l referred to in the previous section.

Now l is an important length parameter in the system, and it becomes of macroscopic magnitude near the critical point. Since this length is macroscopic, it implies that microscopic details of the system become unimportant close to the critical point. *Thus* there is universality in critical phenomena.

Scaling theory relies on the hypothesis that close to the critical point the anomalous part of all quantities with the dimension of length will be proportional to the characteristic length l . And quantities of the dimension $[\text{length}]^n$ will correspondingly be proportional to l^n . We use the notation $[\dots]$ to denote the dimensions of a quantity. We consider the dimensions of some of the quantities that appear in, or lead to, the critical exponent definitions. A clear account of scaling theory is given in Huang's *Statistical Mechanics* [3]; we have drawn heavily on that discussion.

(a) Thermal capacity critical exponent α

Let us start with the Gibbs free energy G , which, by differentiating twice with respect to temperature, will give the thermal capacity. Now G/kT is dimensionless, although extensive, so that $g = G/kTV$, which is finite in the thermodynamic limit, has the dimensions of inverse volume:

$$[g] = L^{-d} \quad (4.1.4)$$

where d is the dimensionality of the system.

The scaling hypothesis is that L is proportional to the critical length l , whose critical exponent is defined to be ν :

$$l \sim |t|^{-\nu} \quad (4.1.5)$$

so that in the vicinity of the critical point we expect

$$g \sim |t|^{\nu d}. \quad (4.1.6)$$

Now thermal capacity is the second derivative of the Gibbs free energy with respect to temperature. So the definition of the exponent α :

$$C \sim |t|^{-\alpha} \quad (4.1.7)$$

implies the critical behaviour of g can also be written as

$$g \sim |t|^{2-\alpha}. \quad (4.1.8)$$

Equating these two forms for the exponent of g then gives

$$\alpha = 2 - \nu d, \quad (4.1.9)$$

showing how the heat capacity critical exponent relates to the critical length exponent and the system dimensionality.

(b) Order parameter critical exponent β

Now consider the order parameter—in the ferromagnet case this is the magnetization per unit volume. The critical exponent β is defined through

$$m \sim |t|^\beta. \quad (4.1.10)$$

But we can also express the dimensionality of the order parameter from the spatial correlation function (correlation functions and their significance will be discussed in Chapter 5)

$$g(\mathbf{r}) = \langle m(\mathbf{r})m(0) \rangle \sim r^{-p}e^{-r/l}. \quad (4.1.11)$$

Thus

$$\begin{aligned} [m^2] &= L^{-p} \\ &= L^{-(d-2+\eta)} \end{aligned} \quad (4.1.12)$$

so that

$$[m] = L^{(2-d-\eta)/2}. \quad (4.1.13)$$

Now according to the scaling hypothesis, that $L \sim |t|^{-\nu}$, we then have

$$m \sim |t|^{-\nu(2-d-\eta)/2}. \quad (4.1.14)$$

Equating these two forms for the exponent of m then gives

$$\beta = -\nu(2-d-\eta)/2, \quad (4.1.15)$$

showing how the order parameter critical exponent relates to the critical length exponent, the power law decay exponent and the system dimensionality.

(c) Susceptibility critical exponent γ

Next we consider the susceptibility, which gives the critical exponent γ defined by

$$\chi \sim |t|^{-\gamma}. \quad (4.1.16)$$

Now the susceptibility is related to the order parameter's spatial correlation function $g(\mathbf{r})$ defined above. This may be seen from the fluctuation expression for the susceptibility obtained at the end of Section 2.9.2, Eq. (2.9.19):

$$\chi = \mu_0 \frac{1}{VkT} \langle M^2 \rangle. \quad (4.1.17)$$

The magnetization M is given by the integral over the magnetization density m . Thus in n dimensions

$$M = \int m(\mathbf{r}) d^n r \quad (4.1.18)$$

and then

$$\langle M^2 \rangle = \int d^n r_1 \int d^n r_2 \langle m(\mathbf{r}_1) m(\mathbf{r}_2) \rangle. \quad (4.1.19)$$

On the assumption of translational invariance we can arbitrarily fix \mathbf{r}_1 to be at the origin and remove the first integral by simply multiplying by V , the n -dimensional volume

$$\langle M^2 \rangle = V \int \langle m(0) m(\mathbf{r}) \rangle d^n r. \quad (4.1.20)$$

And then the susceptibility is given by

$$\chi = \mu_0 \frac{1}{kT} \int \langle m(0) m(\mathbf{r}) \rangle d^n r. \quad (4.1.21)$$

This is a most important result. Our “derivation” relies on results of Chapter 2 for non-interacting particles. But the result is more general than that; thus our treatment should be regarded as no more than a plausibility argument.

The critical behaviour of the correlation function is given by

$$\langle m(\mathbf{r}) m(0) \rangle \sim r^{-p} e^{-r/l} \quad (4.1.22)$$

then it follows that

$$\begin{aligned} [kT\chi] &= L^{-p} \times L^d \\ &= L^{2-\eta} \end{aligned} \quad (4.1.23)$$

from the definition of p : $p = d - 2 + \eta$. So using the scaling hypothesis $L \sim |t|^{-\nu}$ we then have

$$kT\chi \sim |t|^{\nu(2-\eta)}. \quad (4.1.24)$$

Equating these two forms for the exponent of γ then gives

$$\gamma = \nu(2 - \eta), \quad (4.1.25)$$

showing how the susceptibility critical exponent relates to the critical length exponent and the power law decay exponent.

(d) Equation of state critical exponent δ

Finally we look at the equation of state. From the definitions of β and δ we can write

$$m \sim |t|^{-\beta} \quad \text{and} \quad m \sim B^{1/\delta} \quad (4.1.26)$$

so then we have

$$B \sim |t|^{\beta\delta}. \quad (4.1.27)$$

Now B is related to the Gibbs free energy through

$$m = -\frac{\partial g}{\partial B} \quad (4.1.28)$$

so that

$$[B] = [g]/[m]. \quad (4.1.29)$$

We have already found that $[g] = L^{-d}$ and $[m] = L^{(2-d-\eta)/2}$ so that

$$[B] = [g]/[m] = L^{-(2+d-\eta)/2}. \quad (4.1.30)$$

Using the scaling hypothesis $L \sim |t|^{-\nu}$ we then have

$$B \sim |t|^{\nu(2+d-\eta)}. \quad (4.1.31)$$

Equating these two forms for the exponent of B then gives

$$\delta = \nu(2 + d - \eta)/2\beta, \quad (4.1.32)$$

for the equation of state critical exponent.

By taking linear combinations of the above results we express the relations in the traditional manner as

$$\begin{aligned} \gamma &= \nu(2 - \eta) && \text{Fisher law} \\ \alpha + 2\beta + \gamma &= 2 && \text{Rushbrooke law} \\ \gamma &= \beta(\delta - 1) && \text{Widom law} \\ \nu d &= 2 - \alpha && \text{Josephson law.} \end{aligned}$$

The experimental demonstration of these results is strong evidence in favour of the scaling hypothesis. Thus it would appear that the correlation length *is* the only length of importance in the vicinity of the critical point. A consequence of the hypothesis is that only two critical exponents need be calculated for a specific system. Note the Josephson law is the only one to make explicit mention of the spatial dimensionality d .

4.1.9 Scaling of the free energy

The scaling hypothesis has important consequences for the free energy of systems in the vicinity of the critical point. In particular it has important consequences for the *singular* part of the free energy. Following Fisher [7] we shall define the reduced free energy $f(T, B)$ as

$$f = \frac{-\Delta F}{kTV} \quad (4.1.33)$$

where ΔF is the deviation of the singular part of the free energy from its value at the critical point. We have divided by kT to make the quotient dimensionless. However it is still extensive, so we divide by the volume to produce an intensive quantity, with dimensions of inverse volume.

The scaling hypothesis is equivalent to the assumption that in the vicinity of the critical point the reduced free energy has the functional structure:

$$f(T, B) = A |t|^{2-\alpha} Y \left(D \frac{B}{|t|^\Delta} \right). \quad (4.1.34)$$

Here A and D are non-universal parameters that depend on the particular system. Essentially A sets the energy scale and D sets the magnetic field scale. The quantities α and Δ are the two universal exponents – recall the discussion of the previous section that there are only two independent exponents. Here α is the heat capacity exponent and Δ is related to the familiar critical exponents through $\Delta = 2 - \alpha - \beta$. The universal function $Y(y)$ is defined so that $Y(0) = 1$; thus the need for the A prefactor. There are two branches to Y , one for $t > 0$ and one for $t < 0$. And as $y \rightarrow \infty$ the two branches must meet as t goes through zero.

From the above free energy function, all the scaling laws of the previous section may be derived; see Problems 4.9 and 4.10. Thus we may regard the assumption that the free energy has the above form to be equivalent to the scaling hypothesis of the previous section.

4.2 First order transition – an example

In this section we shall consider the liquid–gas transition in a fluid. This is an example of a first order transition with a conserved order parameter. The order parameter for this system is the density. The system has a conserved order parameter since its mean density is fixed (the volume is regarded as fixed).

4.2.1 Coexistence

In transitions involving a conserved order parameter the ordered phase can only evolve through spatial variation of the order parameter density – so that its integral over all space remains constant. Now a full solution of such a system would determine this spatial variation. However there is an approximation due to Gibbs [6] that sidesteps this complexity. The approximation must be justified *a posteriori*, but its basic assumption is that the system evolves into regions with two distinct values for the order parameter: two coexisting phases. At the boundary between the phases the order parameter will vary between that of the two distinct phases. The change will not be abrupt, as that is energetically costly, but the Gibbs approach is a “thin wall” approximation where the fraction of particles in the intermediate regions is assumed to be extremely small.

When two phases coexist, then adding a small quantity of heat energy will result in the conversion of a small amount of the ordered phase to the disordered phase; there will be latent heat involved. Similarly, changing the volume at constant temperature will alter the proportions of the two phases. The coexistence region for a liquid–gas system is shown in Fig. 4.7. Clearly, during coexistence the pressure remains constant; the pressure depends only on the temperature.

A system will separate into two phases if it energetically favourable to do so. Let us consider a fluid system held at constant temperature and volume. Then the appropriate thermodynamic potential is the Helmholtz free energy $F(T, V)$. This free energy will be minimised when a constraint on the system is removed. In this case the “constraint” is the requirement that the system be uniform or homogeneous. We now remove this constraint and ask whether the free energy could be reduced through the system becoming inhomogeneous.

Fig. 4.8 shows the Helmholtz free energy of a system at a given temperature as a function of *volume per particle* or specific volume v . The solid curve in this figure shows the free energy that a homogeneous system would have. The system comprises N atoms or molecules occupying a volume V .

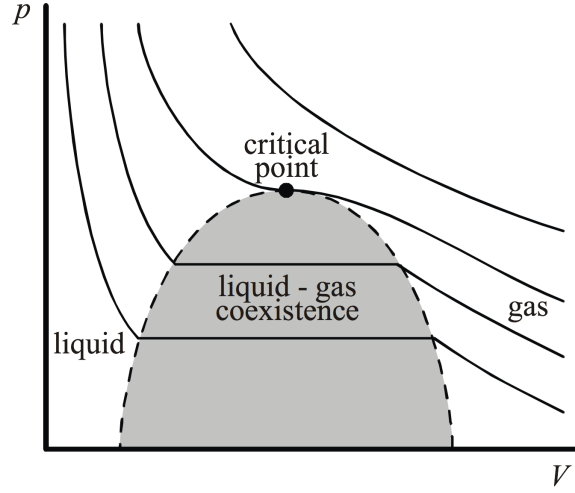


Figure 4.7: Coexistence region, showing $p - V$ isotherms for liquid–gas system.

The volume per particle of the homogeneous system is $v_0 = V/N$. We now ask if the system could lower its free energy by becoming inhomogeneous. In particular we explore the possibility that it segregates into regions of specific volume v_1 and v_2 .

If this happens, it will be subject to the constraint that the total number of particles is fixed. Thus if a fraction α_1 of the particles is in regions of specific volume v_1 and a fraction $\alpha_2 = 1 - \alpha_1$ in regions of specific volume v_2 then

$$v_1\alpha_1 + v_2\alpha_2 = v_0 \quad (4.2.1)$$

so that the fractions are given by

$$\alpha_1 = \frac{v_2 - v_0}{v_2 - v_1}, \quad \alpha_2 = \frac{v_0 - v_1}{v_2 - v_1}. \quad (4.2.2)$$

Then the free energy of the inhomogeneous system will be given by

$$\begin{aligned} F &= \alpha_1 F_1 + \alpha_2 F_2 \\ &= \frac{v_2 F_1 - v_1 F_2}{v_2 - v_1} - \frac{F_1 - F_2}{v_2 - v_1} v_0. \end{aligned} \quad (4.2.3)$$

This expression is linear in v_0 . It is a linear interpolation between points (v_1, F_1) and (v_2, F_2) . Thus the free energy of this inhomogeneous system will be given by the chord in Fig. 4.8, where it intersects the line $v = v_0$; this is indicated as F' in the figure.

We now have the condition for the system to remain homogeneous or to segregate. This depends upon whether F' is below F_0 or not; whenever

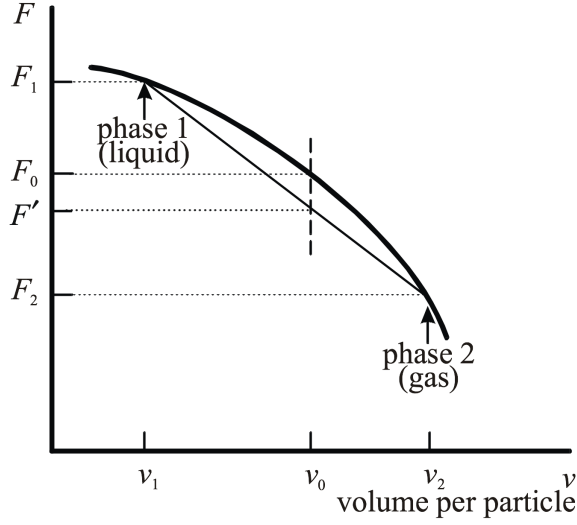


Figure 4.8: Helmholtz free energy curve.

F' falls below F_0 it will be favourable to separate into regions of different specific volume, or density. Thus if the free energy curve is concave, as in Fig. 4.2, phase separation will occur, while if the curve is convex then it is favourable to remain homogeneous.

The lowest free energy is achieved when the straight line becomes takes its lowest possible position, as shown in Fig. 4.9. This determines the equilibrium state: that having the lowest possible free energy for a given overall particle density. For obvious reasons it is referred to as the double tangent construction.

The two coexisting phases have a common tangent in the $F - V$ plane. In other words $\partial F / \partial V|_T$ is the same for both phases. Now the differential relation for the Helmholtz free energy is

$$dF = -SdT - pdV \quad (4.2.4)$$

so that

$$p = - \left. \frac{\partial F}{\partial V} \right|_T; \quad (4.2.5)$$

the derivative is simply (minus) the pressure. Thus we conclude that in equilibrium the coexisting phases will have a common pressure – as expected.

4.2.2 Van der Waals fluid

We encountered the van der Waals equation of state in the previous chapter. We saw there how it provided a way of approximating the effects of inter-

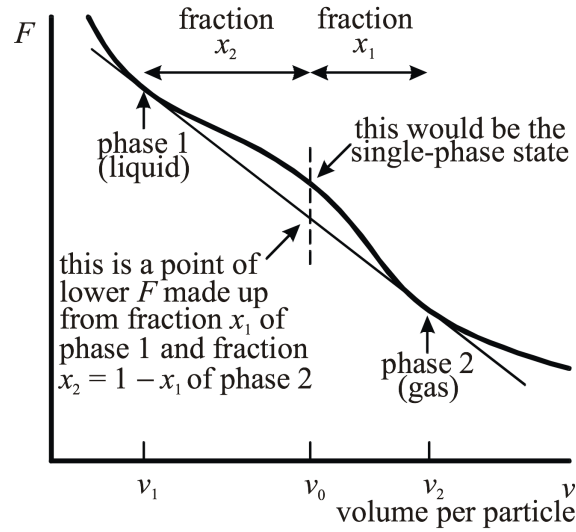


Figure 4.9: Double tangent construction for phase coexistence.

particle interactions in a mean-field manner. At low densities it provided a good description of gas-like behaviour while at high densities it provided a good description of liquid-like behaviour. We shall now see how this equation, when correctly interpreted, is also capable of providing a simple description for the gas–liquid transition. If we plot the equation of state

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = NkT \quad (4.2.6)$$

we obtain the following curves for different temperatures $T_1 < T_2 < T_3$ in Fig. 4.10.

Below the critical point, the curve in the gas–liquid region appears strange. We know from the considerations of the previous section that it is preferable for phase separation to occur and the flat line is the usual behaviour. However, the curve represents the behaviour which would occur *if* the system remained homogeneous. There is a region of superheating and a region of supercooling. Although energetically unfavourable, it is possible in very clean systems that the new phase is not immediately nucleated. Then one can move down an isotherm from the liquid phase into the superheated region. Similarly one can move from the gas, up the isotherm, into the supercooled region. But when the curve changes direction you *have* to go to the two-phase state since the homogeneous phase is unstable if $\partial p/\partial V$ is positive. That would mean the pressure increasing when the volume increased!

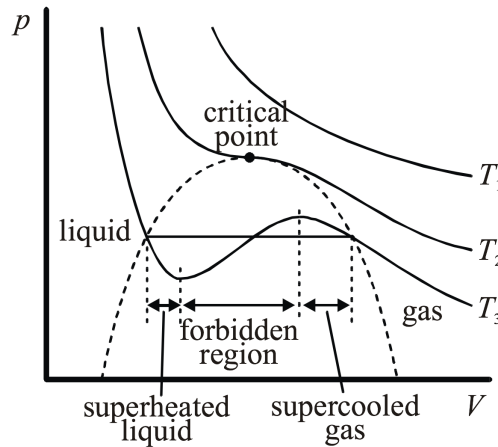


Figure 4.10: Isotherms of the van der Waals equation.

4.2.3 The Maxwell construction

A van der Waals *isotherm* is a $p - V$ curve, given by the van der Waals equation at a given temperature. However in the coexistence region the real isotherm must be a horizontal line: the pressure is a constant. Thus between points A and B of Fig. 4.11 the van der Waals curve is replaced by a straight line. The question is where to position the line; what is the constant pressure during coexistence?

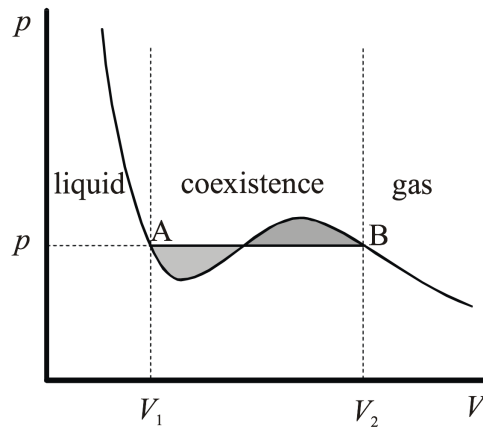


Figure 4.11: Maxwell construction on an isotherm.

Since $p = -\partial F/\partial V|_T$ it follows that the $p - V$ curve is essentially (minus) the derivative of the free energy graph of Fig. 4.9. In particular the curved $p - V$ isotherm comes from the derivative of the homogeneous system free energy curve, while the constant pressure coexistence isotherm comes from

the derivative of the double tangent line. From this the coexistence pressure may be determined in the following way.

The difference in the free energy between the pure liquid and the pure gas, $F_1 - F_2$ may be found by integrating p with respect to V along the isotherm:

$$F_1 - F_2 = \int_{V_2}^{V_1} p \, dV. \quad (4.2.7)$$

Now we may integrate either along the straight line or along the curve between points A and B of Fig. 4.11. If we integrate along the straight line the free energy difference is the area under the straight line joining A and B. And if we integrate along the curve the free energy difference is then the area under the van der Waals curve joining A and B. The free energy must be the same either way and thus the area of the curve above the straight line must be equal to the area below the line. This is known as the *Maxwell construction*. It permits determination of the pressure of the coexisting phases.

When the two phases coexist they have equal temperature, pressure and chemical potential. We have accommodated temperature equality since we are talking about an isotherm. We have also accommodated pressure equality since this followed directly from the double tangent construction. It remains to consider the equality of chemical potentials of the two phases; this means that particles do not wish to flow from one phase to the other. We shall examine the consequence of requiring that the chemical potential at point A be equal to that at point B, in Fig. 4.11. This will give a further insight into the Maxwell construction.

The chemical potential is the Gibbs free energy per particle, $\mu = G/N$. So let us find the change in chemical potential between points A and B and set this to zero. The differential expression for G is given by

$$dG = -SdT + Vdp. \quad (4.2.8)$$

So at constant temperature we then have

$$\Delta G = \int_{\text{point A}}^{\text{point B}} Vdp. \quad (4.2.9)$$

It is convenient to re-express this through an integration by parts:

$$\begin{aligned} \Delta G &= pV \Big|_{p, V_A}^{p, V_B} - \int_{V_A}^{V_B} p dV \\ &= p(V_A - V_B) - \int_{V_A}^{V_B} p dV. \end{aligned} \quad (4.2.10)$$

The first term is the area below the straight line joining A and B. The second term is the area below the van der Waals curve joining A and B. Thus ΔG is the difference between these two areas. And so the requirement that the chemical potentials are equal at points A and B again gives the requirement that the area of the shaded part of the curve must be zero; we recover the Maxwell construction.

The book by Mazenko [8] treats the Maxwell construction for the van der Waals fluid quite extensively.

4.2.4 The critical point

At the critical point the distinction between the liquid and the gas disappears; the two phases become equivalent. This means that at the critical point the discontinuity in $\partial G/\partial T$ vanishes and thus the transition becomes second order. In other words the first order transition becomes second order at the critical point. For the liquid–gas case if the density is fixed to be equal to that at the critical point, then as the system is cooled it will pass through the critical point to a state of two-phase coexistence.

Professionals in the business of phase transitions usually restrict their attention to what is happening in the vicinity of the critical point—and to the universality of the behaviour that emerges there. Thus the concentration on critical exponents etc.

The critical point for the liquid–gas system is the point of inflection, where

$$\left. \frac{\partial p}{\partial V} \right|_T = 0 \quad \text{and} \quad \left. \frac{\partial^2 p}{\partial V^2} \right|_V = 0. \quad (4.2.11)$$

The volume, pressure and temperature at this point are found, in terms of the van der Waals parameters a and b , to be

$$V_c = 3Nb, \quad p_c = \frac{a}{27b^2}, \quad kT_c = \frac{8a}{27b}. \quad (4.2.12)$$

(There is a beautiful calculus-free derivation of this result in Stanley’s book [9]).

4.2.5 Corresponding states

If we define reduced dimensionless variables v , π and t^1 by

$$v = \frac{V}{V_c}, \quad \pi = \frac{p}{p_c}, \quad t = \frac{T}{T_c} \quad (4.2.13)$$

then the van der Waals equation takes on the *universal* form:

$$\left(\pi + \frac{3}{v^2} \right) \left(v - \frac{1}{3} \right) = \frac{8t}{3}. \quad (4.2.14)$$

This is universal in that there are no system-specific quantities. In other words, when the critical volume, temperature and pressure of a system are known then in terms of the reduced variables all fluids should obey the same equation. This is known as the *Law of corresponding states*. Furthermore,

¹Note that the t defined here is different from the reduced temperature defined in Section 4.1.7.

the quantity $p_c V_c / N k T_c$ is predicted to have the universal value $3/8 = 0.375$ for all liquid–gas systems.

As a demonstration of Corresponding States, Fig. 4.12 shows liquid–gas coexistence data for a number of substances plotted in reduced form, originally by Guggenheim [10] and see also [11, 12]. The points do indeed fall reasonably well onto a universal curve. However this is not the curve predicted from the van der Waals equation, the grey curve in the figure.

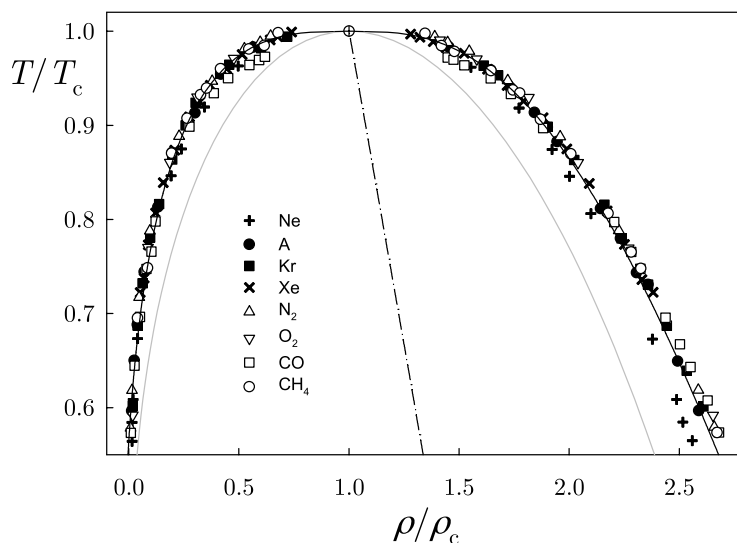


Figure 4.12: Liquid–gas coexistence.

We conclude that the law of corresponding states *does* seem to be followed, but the van der Waals equation does not give a good description of the universal behaviour.

The explanation of this is that the law of corresponding states is not reliant on the precise details of the van der Waals equation. It follows solely from the assumption that the energy of interaction between the particles is of the form

$$U(r) = \varepsilon u(r/\sigma) \quad (4.2.15)$$

where the energy parameter ε and the distance parameter σ are different for different substances, but the functional form of u is the same. In other words, the assumption is that the interaction is of a universal form with a scaling *energy* and a scaling *length* characterizing the substance. So everything which follows from this interaction, such as the equation of state, the critical quantities, etc. must be functions only of these two parameters. Thus the universality when working in terms of the reduced variables, even if this is not precisely in accordance with the predictions of the van der Waals

equation. Furthermore, since p_c , V_c and T_c are simply functions of ε and σ we can eliminate the two variables from the three equations so that the critical compressibility factor $z_c = p_c V_c / NkT_c$ is independent of ε and σ . While the van der Waals equation gives 0.375 for this quantity, experimental measurements give a value of 0.292 ± 0.002 for many substances.

Table 4.1: critical compressibility factor $z_c = p_c V_c / NkT_c$

	⁴ He	Ne	A	Kr	Xe	N ₂	O ₂	CO	CH ₄
z_c	0.308	0.305	0.290	0.291	0.290	0.291	0.292	0.294	0.290

We note that the Lennard-Jones 6 – 12 potential, gives gives $z_c = 0.281$ [13].

4.2.6 Dieterici's equation

We encountered the Dieterici equation in Section 3.5.1. This is a purely phenomenological equation with far less microscopic justification than the van der Waals equation. However, as stated in Chapter 3, the Dieterici equation gives a better description of behaviour near the critical point than does the van der Waals equation. We write the equation in the form

$$p(V - Nb) = NkTe^{-Na/kTV} \quad (4.2.16)$$

where, as we saw, the parameters a and b have precisely the same interpretation as in the van der Waals equation.

The critical point for the liquid–gas system is the point of inflection, where

$$\left. \frac{\partial p}{\partial V} \right|_T = 0 \quad \text{and} \quad \left. \frac{\partial^2 p}{\partial V^2} \right|_T = 0. \quad (4.2.17)$$

The volume, pressure and temperature at this point are found to be

$$V_c = 2Nb, \quad p_c = \frac{a}{4b^2}e^{-2}, \quad kT_c = \frac{a}{4b}. \quad (4.2.18)$$

Then in terms of the reduced dimensionless variables v , π and t

$$v = \frac{V}{V_c}, \quad \pi = \frac{p}{p_c}, \quad t = \frac{T}{T_c} \quad (4.2.19)$$

the Dieterici equation takes on the universal form:

$$\pi \left(v - \frac{1}{2} \right) = \frac{t}{2} e^2 e^{-2/tv}. \quad (4.2.20)$$

As with the reduced van der Waals equation, this is universal in that there are no system-specific quantities. In other words, when the critical volume, temperature and pressure of a system are known then in terms of the reduced variables all fluids should obey the same equation.

For the Dieterici equation the critical compressibility factor is given by

$$z_c = \frac{p_c V_c}{NkT_c} = 2e^{-2} = 0.271. \quad (4.2.21)$$

This is closer to the experimental value around 0.29 than is the van der Waals value of 0.375. It is for this reason that it is claimed the Dieterici equation gives a better description of a fluid's behaviour in the vicinity of the critical point.

Tabulation of fluid models

hhnnnnnnnnnn

	van der Waals	Dieterici	Berthelot	Redlich-Kwong
equation	$(p + \frac{a}{V^2})(V - Nb) = NkT$	$p(V - Nb) = NkTe^{-\frac{Na}{kTV}}$	$(p + \frac{aN^2}{kTV^2})(V - Nb) = NkT$	$p = \frac{NkT}{V - Nb} - \frac{aN^2}{\sqrt{kT}V(V + Nb)}$
p_c	$a/27b^2$	$a/4b^2e^2$	$\sqrt{a/b^3}/6\sqrt{6}$	$0.0299a^{2/3}/b^{5/3}$
kT_c	$8a/27b$	$a/4b$	$(2/3)^{3/2}\sqrt{a/b}$	$0.345(a/b)^{2/3}$
V_c	$3Nb$	$2Nb$	$3Nb$	$3.847Nb$
reduced equation	$(\pi + \frac{3}{t^2})(v - \frac{1}{3}) = \frac{8}{3}t$	$\pi(v - \frac{1}{2}) = \frac{1}{2}te^2e^{-2/tv}$	$(\pi + \frac{3}{t^2})(v - \frac{1}{3}) = \frac{8}{3}t$	aaaaaaaa
z_c	$3/8 = 0.375$	$2/e^2 = 0.271$	$3/8 = 0.375$	$1/3 = 0.333$
kT_B	a/b	a/b	$\sqrt{a/b}$	$(a/b)^{2/3}$
kT_i	$2a/b$	$2a/b$	$\sqrt{3a/b}$	$(5a/2b)^{2/3}$
T_c/T_B	$8/27 = 0.296$	$1/4 = 0.250$	$(2/3)^{3/2} = 0.544$	0.345
T_i/T_B	2	2	$\sqrt{3} = 1.73$	$(5/2)^{2/3} = 1.84$

Experimentally, for non-polar gases $z_c \approx 0.272$, so the Dieterici is best (in this respect).

For the L-J gas: $kT_c/\varepsilon = 1.326$, $\rho_c\sigma^3 = 0.316$, $z_c = 0.281$, $kT_B/\varepsilon = 3.418$, $kT_i/\varepsilon = 6.431$, $T_c/T_B = 0.388$, $T_i/T_B = 1.881$.

4.2.7 Quantum mechanical effects

The observant reader will notice in Fig. 4.12 that the data points for *liquid* neon show a small but consistent deviation from the universal line. Neon is the lightest molecule shown in the figure and its mass is the key. This may be seen even more dramatically in the behaviour of helium, which is significantly lighter. In Fig. 4.13 we show the Guggenheim plot coexistence data again, this time augmented by points from the two helium isotopes [14, 15].

The breakdown of Corresponding States occurs as a consequence of quantum effects; this happens when the de Broglie wavelength λ becomes larger

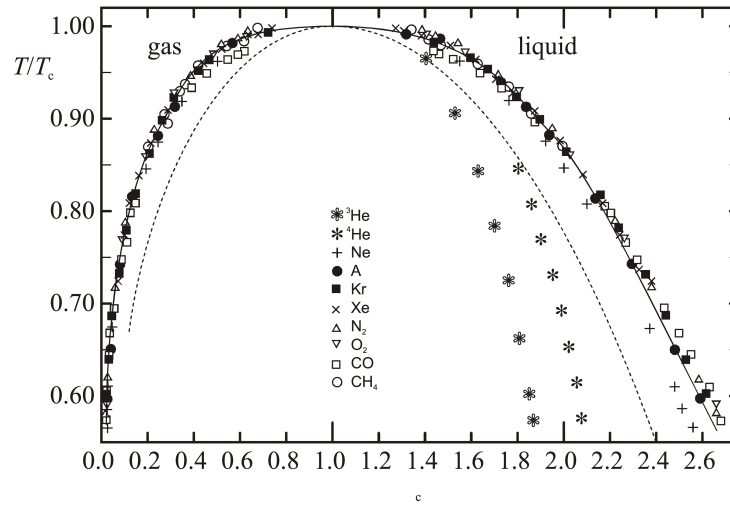


Figure 4.13: Liquid – gas coexistence including data for helium.

than the size of the particles. Then it is no longer appropriate to treat the particles as classical objects since their “extent” is determined by quantum mechanics. *****

A particle of mass m and energy ε has a momentum $p = \sqrt{2m\varepsilon}$ and a de Broglie wavelength $\lambda = h/\sqrt{2m\varepsilon}$. This is compared with the particle’s σ . The ratio (apart from a factor of $\sqrt{2}$)² is known as the de Boer parameter Λ^* :

$$\Lambda^* = \frac{h}{\sigma\sqrt{m\varepsilon}}. \quad (4.2.22)$$

So whenever Λ^* is less than one we may regard the particles as being classical. But if Λ^* is greater than one then quantum effects will be important. We may take the energy and size parameters to be those of the Lennard-Jones interaction. Then the values of Λ^* for the inert gases are shown in Table 4.2.

Table 4.2: de Boer parameters for the inert gases

	³ He	⁴ He	Ne	Ar	Kr	Xe
Λ^*	2.889	2.510	0.544	0.173	0.095	0.058

For most substances we see that Λ^* is small; the de Broglie wavelength is significantly less than the particle size and the particles therefore behave

²Some authors use different numerical factors in the definition of Λ^* ; we follow de Boer’s original expression.

classically. Neon is marginal; here the de Broglie wavelength is beginning to become significant. And the classical picture is entirely inappropriate in the case of helium; there quantum effects become crucial. We should also note that a full quantum treatment would include the effect of statistics; recall that ^4He obeys Bose-Einstein statistics whereas ^3He obeys Fermi-Dirac statistics. There is a quantum extension of the law of corresponding states, introduced by de Boer [16] in 1948.

4.3 Second order transition – an example

4.3.1 The ferromagnet

The essential phenomenon associated with the ferromagnet is that below a certain temperature a magnetization will spontaneously appear in the absence of an applied magnetic field. It is understood that the interaction responsible for ferromagnetism is the exchange interaction between electron spins. The origin of the exchange interaction is the necessity to antisymmetrise the electronic wavefunction, together with the Coulomb repulsion between electrons. Then the symmetric and the antisymmetric wavefunctions have different energies and this may be written as an *effective* spin-dependent Hamiltonian:

$$\mathcal{H}_x = -\hbar J \sum_{i,j}^{\text{nn}} \mathbf{S}_i \cdot \mathbf{S}_j \quad (4.3.1)$$

called the *Heisenberg* hamiltonian. You should be familiar with this from your Atomic Physics studies. The essential feature of this interaction is that when J is positive the energy is minimised when the spins are parallel; this is the energetically favourable state. When J is negative the favourable state occurs when neighbouring spins are antiparallel; this is an antiferromagnet. Note that the exchange interaction is rotationally invariant. The sum is over nearest neighbours and J is called the exchange frequency.

As written above, the sum counts each pair twice since both i and j vary freely. For this reason we will sometimes use the alternate way of expressing the same thing:

$$\mathcal{H}_x = -2\hbar J \sum_{i < j}^{\text{nn}} \mathbf{S}_i \cdot \mathbf{S}_j \quad (4.3.2)$$

since in this case the restriction $i < j$ avoids the double counting.

The phase diagram for a ferromagnet is shown in Fig. 4.14. The system is restricted to the surface, and there is a second, lower surface at negative B and M . The surface is symmetric under $M \rightarrow -M$, $B \rightarrow -B$. Note that

there is a smooth variation between positive and negative magnetization only at $B = 0$ and for $T > T_c$. Otherwise the change is discontinuous.

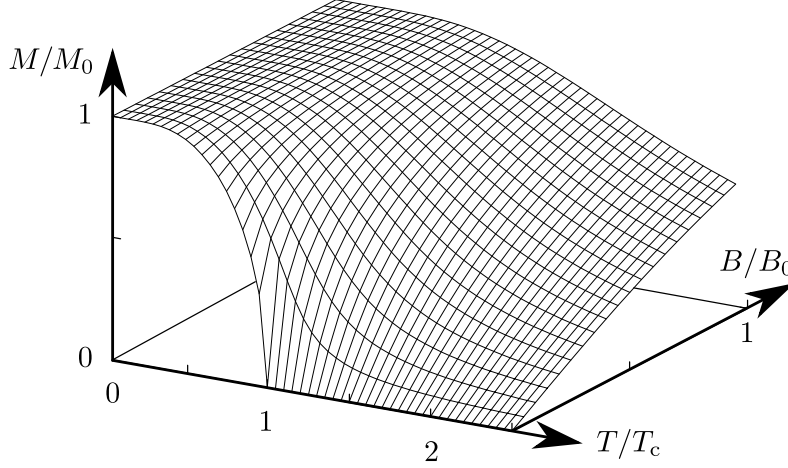


Figure 4.14: Phase diagram for a magnetic system.

For temperatures below the critical temperature a magnetization isotherm is shown in Fig. 4.15. Since $B = 0$ when the magnetization inverts, there is no cost in energy.

4.3.2 The Weiss model

The behaviour of the ferromagnet is contained in its hamiltonian. In the presence of a magnetic field \mathbf{B} , assumed to point in the z direction the hamiltonian is

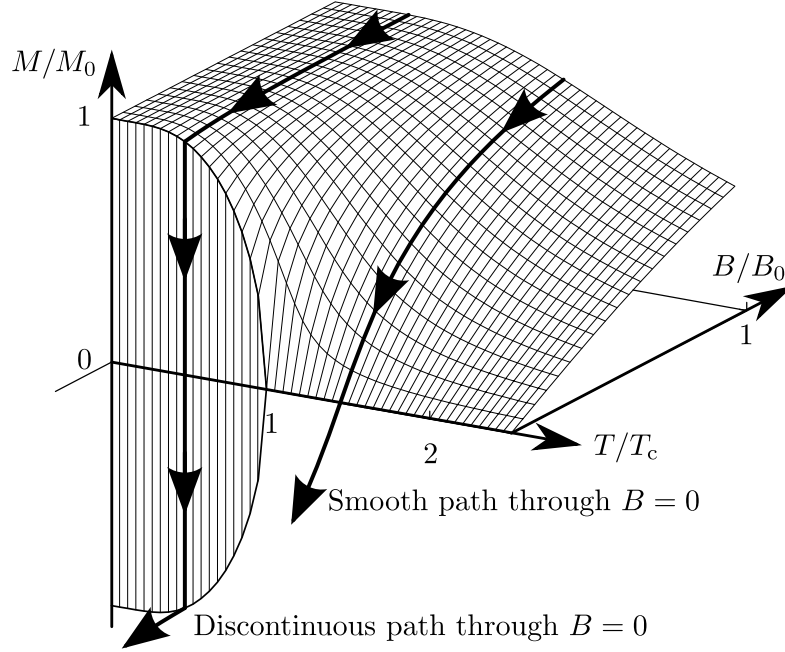
$$\mathcal{H} = -\hbar\gamma\mathbf{B} \cdot \sum_i \mathbf{S}_i - \hbar J \sum_{i,j}^{\text{nn}} \mathbf{S}_i \cdot \mathbf{S}_j \quad (4.3.3)$$

where the first term is the usual $\mathbf{M} \cdot \mathbf{B}$ term for the Zeeman interaction between magnetic moments and a magnetic field; γ is the magnetogyric ratio of the electron. Writing this hamiltonian as

$$\mathcal{H} = -\hbar\gamma \left\{ \mathbf{B} + \frac{J}{\gamma} \sum_j^{\text{nn}} \mathbf{S}_j \right\} \cdot \sum_i \mathbf{S}_i \quad (4.3.4)$$

we see that the effect of the exchange term is to contribute some extra magnetic field at the site of each spin due to its neighbours.

The extra field at each site is different; it is a result of the particular disposition of the site's neighbours. Furthermore the field at a site will vary

Figure 4.15: Variation of M as B goes through zero.

because of the time evolution of the neighbouring moments induced by the hamiltonian. However the time-averaged field at different sites will be expected to be the same. In the model introduced by Pierre Weiss in 1907 the extra field is taken to be the same, and constant, throughout the specimen. The Weiss model is thus a mean field model. The mean extra magnetic field is then

$$\begin{aligned} \mathbf{b} &= \frac{J}{\gamma} \left\langle \sum_j^{\text{nn}} \mathbf{S}_j \right\rangle \\ &= \frac{nJ}{\gamma} \langle \mathbf{S} \rangle \end{aligned} \quad (4.3.5)$$

where n is the number of nearest neighbours of a site.

We have, then, a single-particle effective hamiltonian. The properties of this system may be found from the paramagnet model treated in Chapter 2. There we found the magnetization (total magnetic moment) of an assembly of N spins of magnitude $\hbar/2$ is given by

$$\mathbf{M} = N\gamma\hbar \langle \mathbf{S} \rangle \quad (4.3.6)$$

where the magnitude is

$$M = N \frac{\gamma\hbar}{2} \tanh \frac{\gamma\hbar B}{2kT}, \quad (4.3.7)$$

and pointing in the direction of \mathbf{B} .

Now we must add the mean extra field

$$\mathbf{b} = \frac{nJ}{\gamma} \langle \mathbf{S} \rangle = \frac{nJ}{N\gamma^2\hbar} \mathbf{M} \quad (4.3.8)$$

so that the magnetization is then

$$M = N \frac{\gamma\hbar}{2} \tanh \frac{\gamma\hbar}{2kT} \left\{ B + \frac{nJ}{N\gamma^2\hbar} M \right\}. \quad (4.3.9)$$

This is an implicit equation relating magnetization, magnetic field and temperature. It provides a mathematical representation of the phase diagram shown in the previous section. The equation is, however, non-linear and impossible to solve analytically. But we can find the spontaneous magnetization and the critical temperature; we do this in the next section.

4.3.3 Spontaneous magnetization

In zero applied magnetic field a magnetization will spontaneously appear when the temperature falls below the critical temperature. This may be seen from the equation for magnetization. When $B = 0$, this becomes

$$M = N \frac{\gamma\hbar}{2} \tanh \left\{ \frac{nJ}{2kTN\gamma} M \right\}. \quad (4.3.10)$$

This is still a nonlinear and implicit equation that is difficult to solve analytically. But we can adopt a graphical method, which is highly instructive. We define the auxiliary quantity X by

$$X = \frac{nJ}{2kTN\gamma} M \quad (4.3.11)$$

and then we have two simultaneous equations in two unknowns. The solution corresponds to the intersection of the curves representing the two equations:

$$\begin{aligned} M &= N \frac{\gamma\hbar}{2} \tanh X \\ M &= \frac{2kTN\gamma}{nJ} X. \end{aligned} \quad (4.3.12)$$

These equations are plotted for three different temperatures in Fig. 4.16 below.

We observe there is always a solution at $M = 0$. At high temperatures, as expected, this is the only solution. At low temperatures, however, there is a

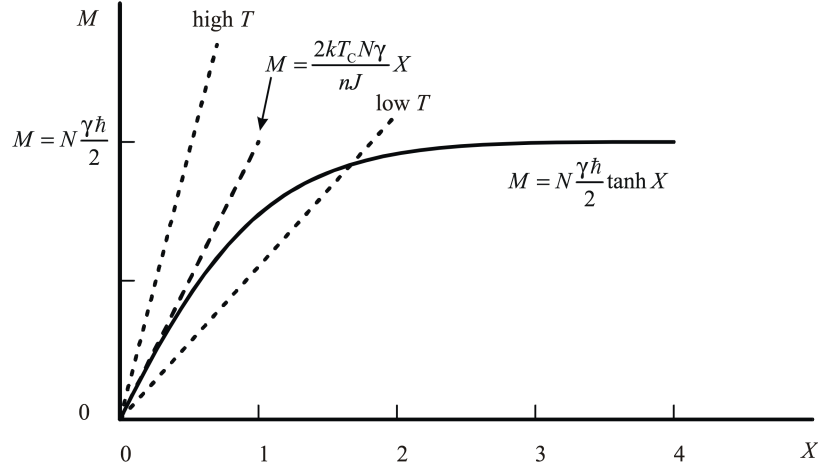


Figure 4.16: Graphical solution for spontaneous magnetization.

second solution where the line intersects the curve at a non-zero value of M . We shall see below in Section 4.5.2 that this corresponds to the energetically favourable solution. Thus for temperatures below a critical value there will be a non-zero magnetization. The critical temperature is that for which the straight line is tangential with the tanh at the origin, when

$$N \frac{\gamma \hbar}{2} = \frac{2kTN\gamma}{nJ}, \quad (4.3.13)$$

that is,

$$T_c = \frac{\hbar n}{4k} J. \quad (4.3.14)$$

In the case of a 2d square lattice, for which $n = 4$, one then has

$$kT_c = \hbar J \quad (4.3.15)$$

an example of our “rule of thumb” for the transition temperature mentioned in Section 4.1.1.

Although an analytic solution for M in terms of T is not possible, we can solve for T in terms of M . We note that the implicit equation for the spontaneous magnetization, Eq. (4.3.10), can be written in the elegant form

$$\frac{M}{M_0} = \tanh \left\{ \frac{M}{M_0} \frac{T_c}{T} \right\} \quad (4.3.16)$$

relating the two (reduced) variables M/M_0 and T/T_c , where $M_0 = N\gamma\hbar/2$, the saturation magnetization, and $T_c = \hbar nJ/4k$, the critical temperature.

This equation may be inverted and solved in the following way. We write it as

$$\begin{aligned} \frac{M}{M_0} \frac{T_c}{T} &= \tanh^{-1} \left(\frac{M}{M_0} \right) \\ &= \frac{1}{2} \ln \left(\frac{1 + M/M_0}{1 - M/M_0} \right), \end{aligned} \quad (4.3.17)$$

so that

$$\begin{aligned} \frac{T}{T_c} &= \frac{M}{M_0} \bigg/ \tanh^{-1} \left(\frac{M}{M_0} \right) \\ &= \frac{2M/M_0}{\ln[(1 + M/M_0)/(1 - M/M_0)]} \end{aligned} \quad (4.3.18)$$

Admittedly, this gives the temperature in terms of the magnetization rather than *vice versa*, but it is an explicit expression. When plotted, this gives the form for the variation of spontaneous magnetization with temperature. This solution is shown in Fig. 4.17.

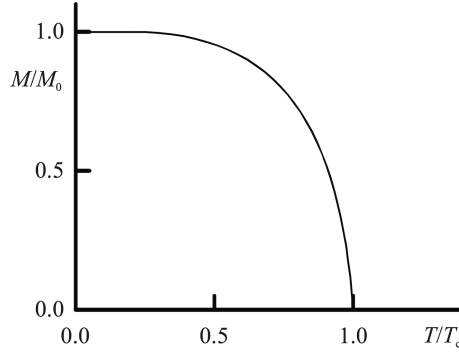


Figure 4.17: Spontaneous magnetization of a ferromagnet.

4.3.4 Critical behaviour

In the vicinity of the critical point the magnetization will be very small. In that case we may expand Eq. (4.3.18) as

$$1 - \frac{T}{T_c} = \frac{1}{3} \left(\frac{M}{M_0} \right)^2 + \frac{4}{45} \left(\frac{M}{M_0} \right)^4 + \frac{44}{945} \left(\frac{M}{M_0} \right)^6 + \dots \quad (4.3.19)$$

and this series may be inverted, giving

$$\frac{M}{M_0} = \sqrt{3} \left(1 - \frac{T}{T_c} \right)^{1/2} - \frac{2\sqrt{3}}{5} \left(1 - \frac{T}{T_c} \right)^{3/2} + \dots \quad (4.3.20)$$

So in the vicinity of the critical point

$$\frac{M}{M_0} \sim \sqrt{3} \left(1 - \frac{T}{T_c}\right)^{1/2}. \quad (4.3.21)$$

This shows the initial growth of the magnetization as the temperature is decreased through the critical point.

The dominant, singular, part of this behaviour is contained in the factor $(1 - T/T_c)^{1/2}$. In particular, it is the exponent $1/2$ which characterizes how M “takes off” from zero. This is the critical exponent β introduced in Section 4.1.7. Our conclusion is thus that the Weiss mean field model gives a value of $1/2$ for β .

The coefficient of the dominant singular temperature behaviour, here the coefficient of $(1 - T/T_c)^{1/2}$, is called the *critical amplitude*. For the Weiss mean field model the magnetization critical amplitude is thus seen to be $\sqrt{3}$.

4.3.5 Magnetic susceptibility

The equation of state for the non-interacting paramagnet is given, from Chapter 2, by

$$M = N \frac{\gamma \hbar}{2} \tanh \frac{\gamma \hbar B}{2kT} \quad (4.3.22)$$

or, in terms of the saturation magnetization $M_0 = N\gamma\hbar/2$:

$$M = M_0 \tanh \frac{M_0 B}{NkT}. \quad (4.3.23)$$

At high temperatures/low polarization the tanh is expanded to leading order, resulting in a linear relation between M and B

$$M = \frac{M_0^2}{NkT} B = \frac{C}{T} B \quad (4.3.24)$$

in terms of the Curie constant C . And in this case we defined the *magnetic susceptibility* χ

$$\chi = \frac{\mu_0}{V} \frac{M}{B}. \quad (4.3.25)$$

The susceptibility of the non-interacting paramagnet is then

$$\chi = \frac{\mu_0 M_0^2}{V N k} \frac{1}{T} = \frac{\mu_0 C}{V T} \quad (4.3.26)$$

noting, particularly, the $1/T$ dependence of the susceptibility – Curie’s law.

We now include the effect of the mean field, which can be written (in terms of T_c) as

$$b = \frac{Nk}{M_0^2} T_c M \quad (4.3.27)$$

so that now the magnetization is

$$\begin{aligned} M &= \frac{M_0^2}{NkT} \left(B + \frac{Nk}{M_0^2} T_c M \right) \\ &= \frac{M_0^2}{NkT} B + M \frac{T_c}{T}. \end{aligned} \quad (4.3.28)$$

This may be solved to give

$$M = \frac{M_0^2}{Nk(T - T_c)} B = \frac{C}{T - T_c} B \quad (4.3.29)$$

so that the susceptibility is now

$$\chi = \frac{M_0^2}{\mu_0 V Nk (T - T_c)} = \frac{\mu_0}{V} \frac{C}{T - T_c}. \quad (4.3.30)$$

This is similar to Curie's law except that the temperature T is replaced by $T - T_c$. By contrast to Curie's law this is referred to as the Curie-Weiss law.

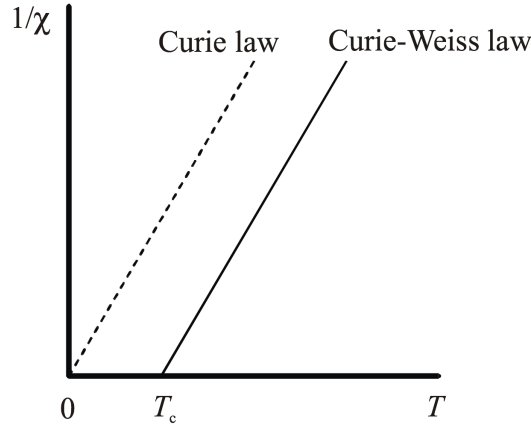


Figure 4.18: Curie and Curie-Weiss laws.

The Curie-Weiss susceptibility exhibits divergent behaviour as the critical point is approached. The exponent of $(T - T_c)^{-1}$ is 1. This is the critical exponent γ . Thus we conclude that the Weiss mean field model gives a value of 1 for the exponent γ .

We see that by plotting the inverse susceptibility as a function of temperature, the transition temperature may be estimated by extrapolating high temperature measurements to zero. Linear extrapolation corresponds to mean field behaviour. In Problem 4.12 you will see that for realistic values of γ above unity, the actual transition temperature will be slightly lower than the mean field estimate.

4.3.6 The ground state and Goldstone modes

The essential feature of the ferromagnetic transition is that below a critical temperature a spontaneous magnetization appears. This happens in the absence of an applied magnetic field. The magnetization appears in a completely arbitrary direction; the interaction responsible for the transition is the Heisenberg exchange hamiltonian and this is rotationally invariant. Nevertheless the vector magnetization must point in some direction. And thus the transition breaks the symmetry of the hamiltonian.

There is, of course, also the $M = 0$ solution and this *does* respect the symmetry of the hamiltonian. But the non-zero M solution, the symmetry-breaking solution, is energetically favourable. This means that the ground state of the system is highly degenerate. We may denote the set of degenerate states by $|\hat{\mathbf{r}}\rangle$, where $\hat{\mathbf{r}}$ is the unit vector pointing in the direction of the magnetization.

It is an observed fact that the ground state of this system is always one of the $|\hat{\mathbf{r}}\rangle$ states; one never observes a linear superposition of such states, even though this is allowed by the laws of quantum mechanics. This puzzle is essentially the classic paradox of Schrödinger's cat, which goes to the very heart of quantum theory.

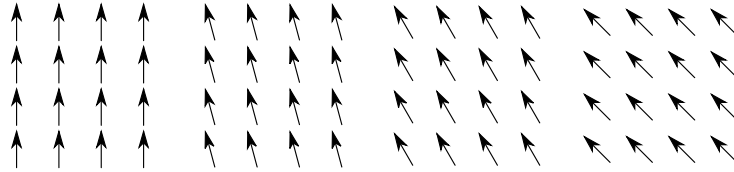


Figure 4.19: Different possible ground states.

The ground state corresponds to a uniform order parameter; the magnetization points in the same direction throughout the specimen. Now it costs energy to deform the order parameter. So if we consider a sinusoidal spatially varying order parameter $\mathbf{M}(\mathbf{r})$:

$$\mathbf{M}(\mathbf{r}) = M_0 \{ \cos(\mathbf{k} \cdot \mathbf{r}) \hat{\mathbf{x}} + \sin(\mathbf{k} \cdot \mathbf{r}) \hat{\mathbf{y}} \} \quad (4.3.31)$$

then this will have an energy above that of the ground state. This expression for $\mathbf{M}(\mathbf{r})$ is the spatial part of a spin wave with wave-vector \mathbf{k} . In the limit $\mathbf{k} \rightarrow 0$ the expression reduces to the uniform ground state with the magnetization pointing in the x direction. Thus the energy of the spin wave goes to zero continuously as k goes to zero.

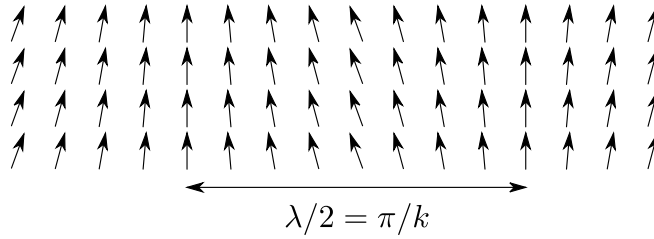


Figure 4.20: Spatial variation of the order parameter.

This is the physical content of Goldstone's theorem which states that when a continuous symmetry is broken there will be excitations involving variations in the order parameter and the dispersion relation for these excitations, $\varepsilon(k)$, satisfies

$$\varepsilon(k) \rightarrow 0 \quad \text{as} \quad k \rightarrow 0. \quad (4.3.32)$$

These excitations are known as Goldstone modes or, when quantised, as Goldstone bosons. They are the low temperature excitations and thus they determine the low temperature thermal properties of the system.

The fact that $\varepsilon(k)$ goes to zero continuously means that there is no energy gap between the ground state and the excitations. This may also be interpreted as saying that the Goldstone bosons have zero mass. And this property follows only when the interaction responsible for the symmetry breaking, here the exchange hamiltonian, is of short range. We may contrast this with the superconducting transition. There the long range of the Coulomb force results in a gap in the plasmon excitation spectrum; then the bosons have mass. This is the condensed matter analogue of the Higgs mechanism of quantum field theory whereby elementary particles acquire mass.

Note that Goldstone modes only appear when a continuous symmetry is broken. The order parameter cannot vary continuously in space when it is a discrete symmetry that is broken, such as that for the Ising model treated in the next section.

4.4 The Ising and other models

4.4.1 Ubiquity of the Ising model

The Ising model is a simple hamiltonian model introduced to treat ferromagnetism. It was originally proposed in the early 1920's by Wilhelm Lenz in an attempt to explain ferromagnetism from microscopic first principles. This was after Weiss had introduced the mean field model of ferromagnetism, but before the advent of the quantum Heisenberg exchange hamiltonian (which we had used to motivate the Weiss mean field). This pre-quantum model comprises an assembly of magnetic moments each of which can point either parallel or antiparallel to a given direction. It was Lenz's hope that this very simplest of interacting systems would exhibit a ferromagnetic transition. Lenz set this as a problem to his student Ernst Ising. Ising was able to solve only the one-dimensional case and he was disappointed to discover that there was no phase transition. It was then not until the 1940's that the two-dimensional case was solved by Lars Onsager, giving a ferromagnetic transition at a finite temperature. However, the three-dimensional Ising model is still not solved; probably it does not admit an analytic solution. A very readable account of the history of the Ising model is given in the review by Brush [17].

Note that the (Weiss) mean field model and its predictions make no mention of the spatial dimension. Within that context the discovery of the difference between the one- and two-dimensional case of the Ising model was rather surprising.

The Ising model is one of the simplest descriptions of a system that leads to a phase transition. It is important furthermore because, notwithstanding its magnetic origin, it can be applied to a variety of dissimilar physical systems. This is an example of the phenomenon of *universality* in phase transitions. Perhaps of even more importance is the fact that the Ising model in two dimensions has been solved analytically. This is one of the very few microscopic models of interacting systems that have been solved exactly, to exhibit a phase transition.

The Ising model is specified in terms of a hamiltonian, so it is a complete microscopic description – but it keeps this description as simple as possible. It is a lattice model; the moments are fixed on sites. Often interactions are permitted only between nearest neighbours. The order parameter is a scalar: the expectation value of the Ising “spin”. The insight of Lenz was in stripping away all superfluous aspects of the ferromagnet while keeping the essence of the system that leads to a transition.

We will write the Ising hamiltonian down in the next section. For the

present we simply note that this involves the energies of neighbouring pairs of the magnetic moments. We shall denote the directions in which the moments can point as up and down. Parallel neighbours have one energy, $\varepsilon_{\uparrow\uparrow}$, while antiparallel neighbours have another, $\varepsilon_{\uparrow\downarrow}$. In the case that

$$\varepsilon_{\uparrow\uparrow} < \varepsilon_{\uparrow\downarrow}, \quad (4.4.1)$$

the parallel state is energetically favourable and the ordered phase will thus be ferromagnetic. But when

$$\varepsilon_{\uparrow\uparrow} > \varepsilon_{\uparrow\downarrow}, \quad (4.4.2)$$

the antiparallel state is favoured and the ordered phase will be antiferromagnetic.

The Ising description need not, however, be restricted to real magnetic moments. For example consider a binary mixture of A atoms and B atoms, as we shall do in Section 4.7. Here again the interaction energies depend upon neighbouring particles. We can imagine that an A atom is represented by an “up moment” and a B atom by a “down moment”. The analogue of the ferromagnetic state is phase-separation, when the A atoms coalesce together as do the B atoms. However if it is favourable for unlike atoms to be neighbours, then we have the analogue of the antiferromagnet and the ordered phase will be a superlattice structure.

Finally, consider a fluid system modelled as a lattice gas. We interpret an up moment as a molecule on the site, while a down moment indicates an empty site: a hole. Adsorption on a surface is an example of this model in two dimensions.

We see how, by interpreting the parameters appropriately, the Ising model may be used to describe a variety of physical systems. In most of the following we will use the language of the magnetic case, but the generalisation to other systems is straightforward. However one should note the distinction between conserved and non-conserved order parameters. For the binary mixture the order parameter is conserved; the numbers of A and B atoms is fixed. However in the magnetic case the order parameter is not conserved as spins may flip. The lattice gas model has a fixed number of molecules. If the number of available sites is fixed then the order parameter is conserved. But if the number of available sites is unlimited then the order parameter is not conserved. In the magnetic description we may imagine applying a magnetic field to the system; this will determine the fraction of up and down moments. In the case of the non-conserved order parameter this field is a free parameter. But for the conserved order parameter case this field is a “chemical potential” whose value is determined by the conserved quantity; it fixes the number of A and B atoms in the binary mixture or the number of molecules in the lattice gas model.

4.4.2 Magnetic case of the Ising model

In the magnetic Ising model we have a magnetic moment on each lattice site which may point either “up” or “down”. As there are only two states, this is reminiscent of a spin $\frac{1}{2}$ problem. It is thus appropriate to utilise a spin operator description, taking the up direction as pointing along the z axis. We then assign to each site a spin with eigenvalue $S^z = +\frac{1}{2}$ if it carries an “up” moment and $S^z = -\frac{1}{2}$ if it carries a “down” moment.³ We must count the number of parallel and antiparallel neighbour pairs. This may be effected through consideration of the product of two neighbouring spins’ eigenvalues; it will have magnitude $+\frac{1}{4}$ if the neighbours are parallel and $-\frac{1}{4}$ if they are antiparallel:

$$\begin{aligned} S_i^z S_j^z &= +\frac{1}{4} \quad \text{for parallel spins} \\ &= -\frac{1}{4} \quad \text{for antiparallel spins.} \end{aligned}$$

It then follows that

$$\begin{aligned} 2S_i^z S_j^z - \frac{1}{2} &= 0 \quad \text{for parallel spins} \\ &= -1 \quad \text{for antiparallel spins} \end{aligned}$$

so that the quantity $-(2S_i^z S_j^z - \frac{1}{2})$ can be used to count the number of antiparallel spins. Similarly

$$\begin{aligned} 2S_i^z S_j^z + \frac{1}{2} &= 1 \quad \text{for parallel spins} \\ &= 0 \quad \text{for antiparallel spins} \end{aligned}$$

so the quantity $2S_i^z S_j^z + \frac{1}{2}$ can be used to count the number of parallel spins.

Thus we have

$$\begin{aligned} N_{\uparrow\downarrow} &= - \sum_{i>j \text{ nn}} (2S_i^z S_j^z - \frac{1}{2}) \\ N_{\uparrow\uparrow} &= \sum_{i>j \text{ nn}} (2S_i^z S_j^z + \frac{1}{2}) \end{aligned} \tag{4.4.3}$$

where $\uparrow\uparrow$ indicates parallel spins of either orientation. In terms of the interaction energies $\varepsilon_{\uparrow\uparrow}$ and $\varepsilon_{\uparrow\downarrow}$ introduced in the previous section the energy of the system is then

$$\begin{aligned} E &= N_{\uparrow\uparrow}\varepsilon_{\uparrow\uparrow} + N_{\uparrow\downarrow}\varepsilon_{\uparrow\downarrow} \\ &= -2(\varepsilon_{\uparrow\downarrow} - \varepsilon_{\uparrow\uparrow}) \sum_{i>j \text{ nn}} 2S_i^z S_j^z + \text{const.} \end{aligned} \tag{4.4.4}$$

³Traditional treatment of the Ising model ascribes the values $+1$ and -1 to the two values of the Ising “spin”. We adopt a different convention that makes better connection with the spin $\frac{1}{2}$ quantum mechanical description of the Heisenberg magnet.

The constant term may be ignored. And then the expression for the Ising hamiltonian may be written as

$$\mathcal{H} = -2\hbar J \sum_{i>j \text{ nn}} S_i^z S_j^z \quad (4.4.5)$$

where $\hbar J = \varepsilon_{\uparrow\downarrow} - \varepsilon_{\uparrow\uparrow}$. Note that the definition of J in our treatment of the Ising model is a factor of four greater than that used in conventional treatments. This has been done purposely to maintain consistency with the J used in the Heisenberg model (footnote 3 on page 228).

We can see from the expression for \mathcal{H} that this is just a *part of* the Heisenberg hamiltonian considered previously. The Heisenberg interaction $\mathbf{S}_i \cdot \mathbf{S}_j$ is here replaced by the product $S_i^z S_j^z$; essentially we are taking only the $z - z$ part of the dot product.

If we include an external magnetic field B parallel to the up direction then the hamiltonian is

$$\mathcal{H} = -2\hbar J \sum_{i>j \text{ nn}} S_i^z S_j^z - \gamma \hbar B \sum_i S_i^z. \quad (4.4.6)$$

The absence of any x or y spin operators is of vital importance. There are only z spin operators and these will therefore all commute. This means that while we have used the quantum-mechanical language of spin $\frac{1}{2}$ and spin operators this is simply a convenient mathematical device and the model is really classical; there are no quantum aspects to the system.

We should also point out that the Weiss mean field treatment of the Heisenberg ferromagnet is equally appropriate for the Ising model. Thus most of the results of Section 4.3 carry over to the Ising case. The only difference is that the order parameter for the Heisenberg magnet can point in any direction while the Ising magnetization can only point “up” or “down”. The Heisenberg magnet breaks a continuous symmetry while the Ising transition breaks a discrete symmetry.

4.4.3 Ising model in one dimension

As Ising discovered, in one dimension the model exhibits no phase transition. This is an important deviation from the mean field prediction, indicating that the spatial dimension is important. The absence of a transition in 1d may be seen in the following elegant argument, due to Landau [18].

The essence of Landau’s argument is to show that at any non-zero temperature the ordered phase is energetically unfavourable. Let us assume that there is an ordered phase below some critical temperature and let us examine

the stability of this phase. We are considering a chain of N ordered spins. Now let us introduce a small element of disorder by reversing all spins from the n^{th} site onwards.



Figure 4.21: Chain with spins reversed from one point onwards.

This will increase the energy by $\hbar J$ (there is no applied magnetic field), the contribution coming from the opposite-pointing pair. The entropy of the system will also increase. Since there is a choice of N sites, after which spins are flipped, the reversal will increase the entropy by $k \ln N$. The effect of the reversal is thus to increase the free energy $F = E - TS$ by

$$\Delta F = \hbar J - kT \ln N. \quad (4.4.7)$$

The equilibrium state of the system is that for which F is a minimum. In the thermodynamic limit ($N \rightarrow \infty$) the second term of ΔF will always dominate so that the reversal operation results in a reduction of the free energy. And further reversal operations will further reduce the free energy. Thus for all non-zero temperatures the entropy term wins out over the energy term and the equilibrium configuration for the system is the disordered state. So only at $T = 0$ can the ordered state exist; at all finite temperatures it is unstable. There is no finite-temperature phase transition in an infinite one-dimensional lattice.

This behaviour is shown from a full microscopic calculation. In the presence of a magnetic field B the fractional magnetization of the one-dimensional Ising system is given (see Plische and Bergersen [19] for details) by

$$m = \frac{\sinh \gamma \hbar B / kT}{(\sinh^2 \gamma \hbar B / kT + e^{-\hbar J / kT})^{1/2}} \quad (4.4.8)$$

As expected, we see that when $B = 0$ there is no spontaneous magnetization at any temperature except $T = 0$. Nevertheless at low temperatures such that

$$\sinh^2 \gamma \hbar B / kT \gg e^{-\hbar J / kT}, \quad (4.4.9)$$

for any field B , however small, there will occur the saturation magnetization.

4.4.4 Ising model in two dimensions

The literature on the 2d Ising model is vast; there are even entire books devoted to the subject. There are various methods for calculating the partition function and the transition temperature. However all are complicated,

requiring more space than we can reasonably devote in this book. We thus content ourselves with quoting the main results. For further details we refer the reader to Landau and Lifshitz [18].

In two dimensions the Ising model exhibits a phase transition. The analytic expression for the transition temperature was derived by Onsager in 1944. The free energy was found, somewhat later, to be

$$F = -Nk \ln (2 \cosh \hbar J / 2kT) - \frac{Nk}{2\pi} \int_0^\pi \ln \frac{1}{2} \left(1 + \sqrt{1 - \kappa^2 \sin^2 \varphi} \right) d\varphi \quad (4.4.10)$$

where

$$\kappa = \frac{2}{\cosh \hbar J / 2kT \coth \hbar J / 2kT}. \quad (4.4.11)$$

The transition occurs at the singularity in F , at a critical temperature of

$$T_c = 0.567 \hbar J / k, \quad (4.4.12)$$

the solution of the equation

$$2 \tanh^2 \hbar J / 2kT_c = 1 \quad \text{or} \quad \sinh \hbar J / 2kT_c = 1. \quad (4.4.13)$$

The spontaneous (reduced) magnetization, the order parameter, is given by

$$m = \left\{ 1 - (\sinh \hbar J / 2kT)^{-4} \right\}^{1/8}. \quad (4.4.14)$$

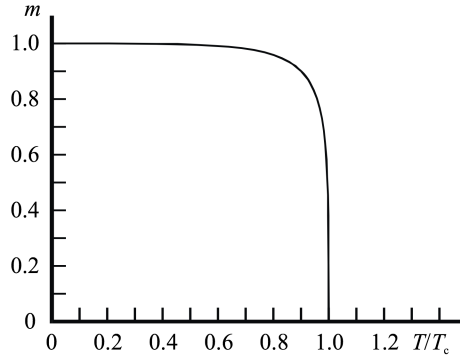


Figure 4.22: Order parameter for 2d Ising model.

The critical exponents for the 2d Ising model may be calculated. We compare these with the two we obtained from the mean field model:

2d Ising model	β	γ
mean field	$\frac{1}{2}$	1
exact calc.	$\frac{1}{8}$	$\frac{7}{4}$

The thermal capacity of the Ising system in the vicinity of the phase transition is shown in Fig. 4.23, together with that calculated from two approximate models.

The mean field calculation gives the simplest behaviour. Note that as the temperature is reduced from above the transition there is no “precursor” of the impending critical behaviour. The Bethe-Peirls approximation is an attempt to do rather better than the mean field calculation. It considers the effects of nearest neighbour interactions exactly, while the spins further away are treated in mean field. Here the predicted critical temperature is somewhat better and there is a small increase in the thermal capacity before the transition occurs.

The precursor in the thermal capacity is an indication that something is “going on” before the transition actually occurs. This is evidence of the importance of fluctuations in the vicinity of the critical point. In Section 4.5.2 we shall see how the mean field/Landau approach indicates, through the dramatic flattening of the free energy at the critical point, that large fluctuations in the order parameter can occur at negligible cost. However mean field theories takes no account of the effects of such fluctuations. The initial assumption that all particles experience the same constant “mean field”, precludes the incorporation of such fluctuations. **Fisher’s comment about fluctuations “feeling out” the new phase.**

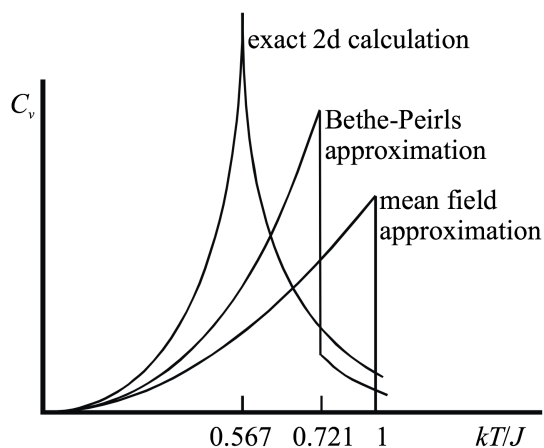


Figure 4.23: Heat capacity of 2d Ising model.

4.4.5 Mean field critical exponents

In treating the Weiss model of the ferromagnet we obtained values for two of the critical exponents. In that mean field treatment no mention was made of

the dimensionality of the order parameter or of the dimensionality of space. Thus mean field arguments will apply equally to the ferromagnet and the Ising model. Note, however, that in contrast to the results of the above two sections, the mean field treatment gives results independent of the spatial dimension.

Recall we found $\beta = 1/2$ for the order parameter exponent and $\gamma = 1$ for the susceptibility exponent. In this section we will use general mean field arguments to extend that discussion, to obtain α , the thermal capacity exponent and δ the equation of state exponent.

a) Thermal capacity critical exponent α The thermal capacity is found from the internal energy of the system by differentiating with respect to temperature. Now the internal energy is given by

$$E = -MB \quad (4.4.15)$$

where B is the sum of the external and internal fields.

So in the absence of an external field we have

$$\begin{aligned} E &\sim M^2 & T < T_c \\ E &= 0 & T > T_c. \end{aligned} \quad (4.4.16)$$

But we know that $M \sim (T - T_c)^{1/2}$; that is the order parameter critical behaviour. Thus we have

$$\begin{aligned} E &\sim T - T_c & T < T_c \\ E &= 0 & T > T_c. \end{aligned} \quad (4.4.17)$$

And differentiating to find the thermal capacity, this gives

$$\begin{aligned} C &= \text{const} & T < T_c \\ &= 0 & T > T_c. \end{aligned} \quad (4.4.18)$$

The result is that the thermal capacity is *discontinuous* at the critical point. Observe this in the mean field curve of Fig. 4.23. Such behaviour is observed in the superconducting transition, but not for real ferromagnets.

In terms of a critical exponent, a discontinuity is understood as a power-law behaviour

$$C \sim \frac{1}{x} (T - T_c)^x \quad (4.4.19)$$

as the quantity x tends to zero. Thus we have the conclusion that the thermal capacity critical exponent α is zero in the mean field model.

b) Equation of state critical exponent δ We now turn to the critical exponent connected with the equation of state at $T = T_c$. Recall that δ is defined by

$$M \sim B^{1/\delta} \quad (4.4.20)$$

evaluated at the critical point. We have to consider here the behaviour of the magnet in the presence of a magnetic field. The equation of state is conveniently written as

$$\frac{M}{M_0} = \tanh \left\{ \frac{M_0 B}{NkT} + \frac{M}{M_0} \frac{T_c}{T} \right\}. \quad (4.4.21)$$

Now in the vicinity of the critical point M is small and if we restrict the discussion to small values of B then we may expand the tanh. Thus we expand as far as

$$\frac{M}{M_0} = \frac{M_0 B}{NkT} + \frac{M}{M_0} \frac{T_c}{T} - \frac{1}{3} \left\{ \frac{M_0 B}{NkT} + \frac{M}{M_0} \frac{T_c}{T} \right\}^3 + \dots \quad (4.4.22)$$

Since we are considering the relation between M and B at the critical point, we set $T = T_c$, giving

$$\frac{M}{M_0} = \frac{M_0 B}{NkT_c} + \frac{M}{M_0} - \frac{1}{3} \left\{ \frac{M_0 B}{NkT_c} + \frac{M}{M_0} \right\}^3, \quad (4.4.23)$$

or

$$\frac{M_0 B}{NkT_c} = \frac{1}{3} \left\{ \frac{M_0 B}{NkT_c} + \frac{M}{M_0} \right\}^3. \quad (4.4.24)$$

This can be rearranged as

$$\frac{M}{M_0} = \left\{ \frac{3M_0 B}{NkT_c} \right\}^{1/3} - \frac{M_0 B}{NkT_c}. \quad (4.4.25)$$

Now when B is small it is the first term on the right hand side that will dominate. Thus we find that at the critical point

$$M \sim B^{1/3} \quad (4.4.26)$$

and so we identify the critical exponent δ as 3 in the mean field approximation.

We are unable to derive the mean field results $\nu = 1/2$ and $\eta = 0$ here as the calculations are rather more complicated. See Huang [3] for details.

We give below the critical exponents for the three-dimensional Heisenberg ferromagnet, comparing values calculated from the mean field theory with those measured experimentally [9].

3-d ferromagnet	α	β	γ	δ	ν	η
mean field	0	$\frac{1}{2}$	1	3	$\frac{1}{2}$	0
experiment	-0.14	0.3	1.4	4.8	0.7	0.04

In the case of the two-dimensional Ising model we can compare the true calculated critical exponents with those from the mean field approximation.

2-d Ising	α	β	γ	δ	ν	η
mean field	0	$\frac{1}{2}$	1	3	$\frac{1}{2}$	0
exact calculation	0	$\frac{1}{8}$	$\frac{7}{4}$	15	1	$\frac{1}{4}$

From these results we must conclude that while the mean field theory provides a good *qualitative* model for behaviour at the critical point, quantitatively it leaves something to be desired. This is because of the limitations imposed by the fundamental assumption of the mean field model; using a *mean* field involved neglecting the variation in the actual field from site to site. It is precisely these fluctuations, which are neglected, that determine the behaviour in the vicinity of the critical point.

4.4.6 The XY model

The interaction hamiltonian for the XY model is given by

$$\mathcal{H} = -2\hbar J \sum_{i>j \text{ nn}} (S_i^x S_j^x + S_i^y S_j^y). \quad (4.4.27)$$

This is an extension of the Ising hamiltonian, but not the full Heisenberg hamiltonian. The order parameter for this model is the magnetization in the x-y plane; it is a vector of dimension $n = 2$. Thus the order parameter is two-dimensional. Since the magnetization can point in any direction in the x-y plane, it can vary continuously; the XY transition thus breaks a continuous symmetry. This model is regarded as a good description for the superfluid transition in liquid ^4He , since the order parameter in this case is a two component vector (or a complex scalar). Estimates for critical exponents for the XY model in three spatial dimensions are $\gamma = 4/3$ and $\alpha = 0$.
?????????

4.4.7 The spherical model

The spherical model was proposed by Mark Kac (pronounced Cats), in 1952. The specification of the original model is probably not so intuitively appealing! But subsequently it was realized that it was equivalent to the limiting

case of the n -vector model as $n \rightarrow \infty$. In other words one takes spin variables of dimension n , with an interaction of the form

$$\mathcal{H} = -2\hbar J \sum_{i>j \text{ nn}} \left(S_i^\alpha S_j^\alpha + S_i^\beta S_j^\beta + S_i^\gamma S_j^\gamma + \dots + S_i^n S_j^n \right), \quad (4.4.28)$$

in the limit of infinite n . Written in this way we can interpret the model as an extension of the Heisenberg model in a direction opposite to that of the Ising (or XY) model.

In 1952 Theodore Berlin obtained the analytic solution of this model for spatial dimension $d = 1, 2$ and 3 and this was subsequently extended to *continuous* n [20]. Berlin found that in one and two dimensions there was no transition to an ordered phase, but there was a transition at finite temperature in three dimensions. For a three-dimensional simple cubic lattice the critical temperature is found to be

$$kT_c = 0.989\hbar J. \quad (4.4.29)$$

So unlike the Ising model, there is no transition in two dimensions.

Another important result is that $d > 4$ the behaviour is independent of d and equivalent to that of the mean field model.

4.4.8 Universality classes

Put the table here??????????

a	d	n	α	β	γ	δ	ν	η
2d Ising	2	1	0	1/8	7/4	15	1	1/4
3d Ising	3	1	0.11	0.33	1.24	4.79	0.63	0.04
3d XY	3	2	-0.01	0.35	1.32	4.78	0.67	0.04
3d Heisenberg	3	3	-0.12	0.37	1.40	4.8	0.71	0.04
3d spherical	3	∞	-1	1/2	2	5	1	0
Mean field	any	any	0	1/2	1	3	1/2	0

4.5 Landau theory of phase transitions

4.5.1 Landau free energy

In order to develop a general theory of phase transitions it is necessary to extend the concept of the free energy. For definiteness we will, in this section, consider the case of a ferromagnet, but it should be appreciated that the ideas introduced apply more generally.

The (magnetic) Helmholtz free energy has proper variables T and B . In differential form

$$dF = -SdT - MdB \quad (4.5.1)$$

and the entropy and magnetization are thus given by

$$S = - \left. \frac{\partial F}{\partial T} \right|_B, \quad M = - \left. \frac{\partial F}{\partial B} \right|_T. \quad (4.5.2)$$

When the temperature and magnetic field are specified the magnetization (the order parameter in this system) is determined – from the second of the above differential relations. It is possible however, perhaps because of some constraint, that the system may be in a *quasi-equilibrium* state with a different value for its magnetization. Then the Helmholtz free energy corresponding to that state will be greater than its equilibrium value; it will be a minimum when M takes its equilibrium value. This is equivalent to the law of entropy increase discussed in Chapter 1 and extended in Appendix 2 on thermodynamic potentials

The conventional Helmholtz free energy applies to systems in thermal equilibrium, as do all thermodynamic potentials. The above discussion leads us to the introduction of a “constrained” Helmholtz free energy for quasi-equilibrium states, which we shall write as

$$F(T, B : M). \quad (4.5.3)$$

The conventional Helmholtz free energy is a mathematical function of T and B ; when T and B are specified then the equilibrium state of the system has Helmholtz free energy $F(T, B)$. The system we are considering here is prevented from achieving its full equilibrium state since its magnetization is constrained to take a certain value. The full equilibrium state of the system is that for which $F(T, B : M)$ is minimised with respect to variations in M , i.e.

$$\frac{\partial F(T, B : M)}{\partial M} = 0. \quad (4.5.4)$$

This constrained free energy is often called the Landau free energy (or *clamped* free energy). In a “normal” system one would expect the Landau free energy to possess a simple minimum at the equilibrium point, as shown in Fig. 4.24.

4.5.2 Landau free energy for the ferromagnet

In order to visualise what underlies the Landau theory of phase transitions we shall review the Weiss model of the ferromagnetic transition from the

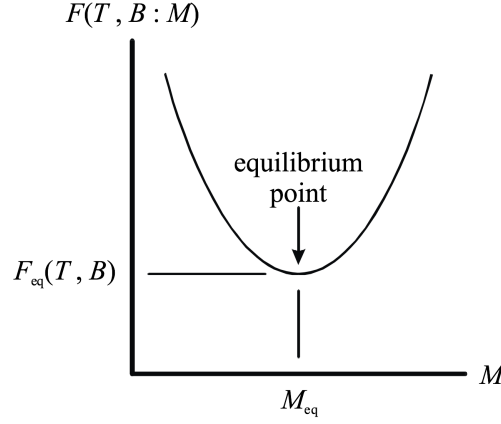


Figure 4.24: Variation of Landau free energy with magnetization.

point of view of constrained free energy. Thus we shall consider the Landau free energy of this system.

The Helmholtz free energy is defined as

$$F = E - TS. \quad (4.5.5)$$

We will evaluate the internal energy and the entropy separately. Since we require the *constrained* free energy we must be sure to keep M as an explicit variable. The internal energy is given by

$$E = - \int B \, dM \quad (4.5.6)$$

(assuming the vectors \mathbf{B} and \mathbf{M} in the same direction). The magnetic field, in the Weiss model, is the sum of the applied field B_0 and the local (mean) field b :

$$B = B_0 + b. \quad (4.5.7)$$

We shall write the local field in terms of the critical temperature:

$$b = \frac{Nk}{M_0^2} T_c M. \quad (4.5.8)$$

Integrating up the internal energy we obtain

$$E = -B_0 M - \frac{NkT_c}{2} \left(\frac{M}{M_0} \right)^2. \quad (4.5.9)$$

For the present we will consider the case where there is no external applied field. Then $B_0 = 0$, and in terms of the reduced magnetization $m = M/M_0$

(the order parameter) the internal energy is

$$E = -\frac{NkT_c}{2}m^2. \quad (4.5.10)$$

Now we turn to the entropy. This is most easily obtained from the expression⁴

$$S = -Nk \sum_j p_j \ln p_j \quad (4.5.11)$$

where p_j are the probabilities of the single-particle states. It is simplest to treat spin one half, which is appropriate for electrons. Then there are two states to sum over:

$$S = -Nk [p_\uparrow \ln p_\uparrow + p_\downarrow \ln p_\downarrow]. \quad (4.5.12)$$

Now these probabilities are simply expressed in terms of m , the fractional magnetization

$$p_\uparrow = \frac{1+m}{2} \quad \text{and} \quad p_\downarrow = \frac{1-m}{2} \quad (4.5.13)$$

so that the entropy becomes

$$S = \frac{Nk}{2} [2 \ln 2 - (1+m) \ln(1+m) - (1-m) \ln(1-m)]. \quad (4.5.14)$$

We now assemble the free energy $F = E - TS$, to obtain

$$F = -\frac{Nk}{2} \left\{ T_c m^2 + T [2 \ln 2 - (1+m) \ln(1+m) - (1-m) \ln(1-m)] \right\}. \quad (4.5.15)$$

This is plotted, in Fig. 4.25, for temperatures less than, equal to and greater than the critical temperature.

The occurrence of the ferromagnetic phase transition can be seen quite clearly from this figure. For temperatures above T_c we see there is a single minimum in the Landau free energy at $m = 0$, while for temperatures below T_c there are two minima either side of the origin. The symmetry changes precisely at T_c . There the free energy has flattened, meaning that m may make excursions around $m = 0$ with negligible cost of free energy—hence the large fluctuations at the critical point.

Strictly speaking, Fig. 4.25 applies to the Ising case where the order parameter is a scalar; the order parameter must choose between the values $\pm m$. The XY model is represented by Fig. 4.31 where, below the transition, the magnetization can point anywhere in the x-y plane in the minimum of the “wine bottle” potential. Similarly for the Heisenberg model Fig. 4.31

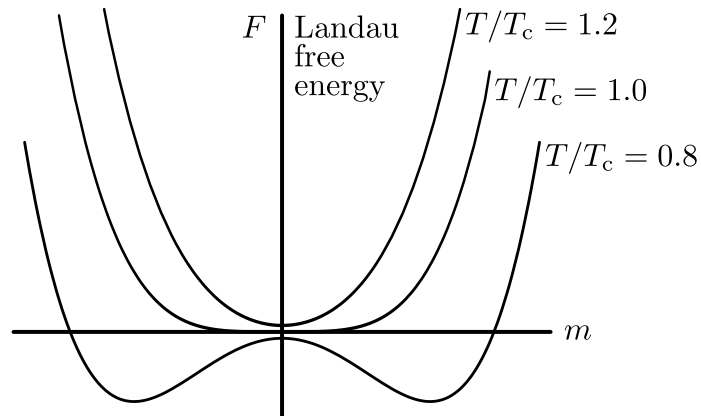


Figure 4.25: Landau free energy

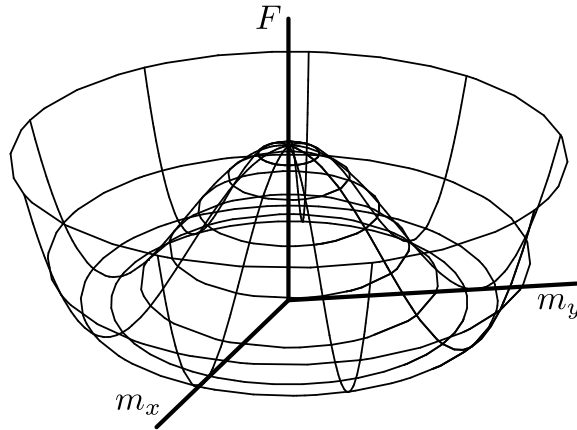


Figure 4.26: Landau free energy for XY model

would apply where the m_x and m_y axes really refer to the three axes of the order parameter m_x , m_y and m_z .

***** Discrete vs continuous symmetry ***** but probably not here (field-hysteresis)

The behaviour in the vicinity of the critical point is even clearer if we expand the free energy in powers of the order parameter. Straightforward evaluation gives, neglecting the constant term,

$$F = \frac{Nk}{2} \left\{ (T - T_c) m^2 + \frac{T_c}{6} m^4 + \dots \right\}. \quad (4.5.16)$$

We see that the essential information is contained in the *quartic* form for the free energy in the vicinity of the critical point. This will have either

⁴This is the *Gibbs* entropy evaluated in a *Boltzmann* ensemble.

one or two minima, depending on the values of the coefficients; the critical point occurs where the coefficient of m^2 changes sign. This abstraction of the *essence* of critical phenomena in terms of the general behaviour of the free energy was formalised by Landau. We have replaced the variable T in the second term by the constant T_c since we are restricting discussion to the vicinity of the critical point.

4.5.3 Landau theory – second order transitions

Landau's theory concerns itself with what is happening in the *vicinity* of the phase transition. In this region the magnitude of the order parameter will be small and the temperature will be close to the transition temperature. When the problem is stated in this way the approach is clear: The Landau free energy should be expanded as a power series in these small parameters. The fundamental assumption of the Landau theory of phase transitions is that in the vicinity of the critical point the free energy is an *analytic* function of the order parameter so that it may indeed be thus expanded. In fact this assumption is, in general, invalid. The Landau theory is equivalent to mean field theory (in the vicinity of the transition) and, as with mean field theory, it is the fluctuations in the order parameter at the transition point which are neglected in this approach. Nevertheless, Landau theory provides a good insight to the general features of phase transitions, describing many of the qualitative features of systems even if the values of the critical exponents are not quite correct.

The free energy is written as a power series in the order parameter φ

$$F = F_0 + F_1\varphi + F_2\varphi^2 + F_3\varphi^3 + F_4\varphi^4 + \dots \quad (4.5.17)$$

First we note that F_0 can be ignored here since the origin of the energy is entirely arbitrary. Considerations of symmetry and the fact that F is a scalar may determine that other terms should be discarded. For instance if the order parameter is a vector (magnetization) then odd terms must be discarded since only $\mathbf{M} \cdot \mathbf{M}$ will give a scalar. In this case the free energy is symmetric in φ , so that

$$F = F_2\varphi^2 + F_4\varphi^4 + \dots \quad (4.5.18)$$

There is a minimum in F when $dF/d\varphi = 0$. Thus the equilibrium state may be found from

$$\frac{dF}{d\varphi} = 2F_2\varphi + 4F_4\varphi^3 = 0. \quad (4.5.19)$$

This has solutions

$$\varphi = 0 \quad \text{and} \quad \varphi = \pm \sqrt{\frac{-F_2}{2F_4}}. \quad (4.5.20)$$

We must have F_4 positive so that F increases far away from the minima to ensure stability: φ must be bounded. Then if $F_2 < 0$ there are three stationary points while if $F_2 > 0$ there is only one. Thus the nature of the solution depends crucially on the sign of F_2 as can be seen in Fig. 4.27.

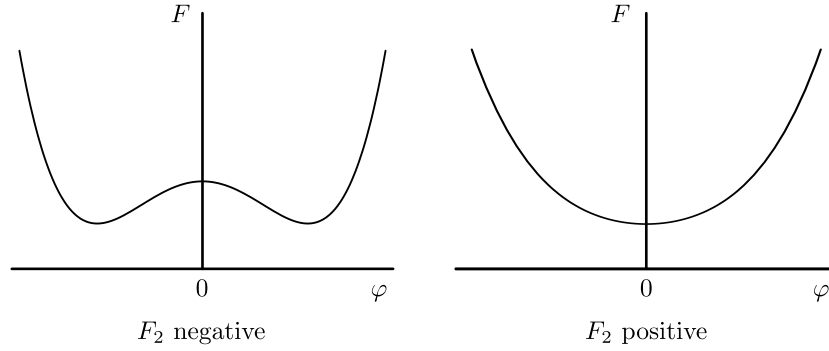


Figure 4.27: Minima in free energy for positive and negative F_2 .

It is clear from the figures that the critical point corresponds to the point where F_2 changes sign. Thus expanding F_2 and F_4 in powers of $T - T_c$ we require, to leading order

$$F_2 = a(T - T_c) \quad \text{and} \quad F_4 = b \quad (4.5.21)$$

so that

$$\begin{aligned} \varphi &= 0 & T > T_c \\ \varphi &= \pm \sqrt{\frac{a(T_c - T)}{2b}} & T < T_c \end{aligned} \quad (4.5.22)$$

This behaviour reproduces the critical behaviour of the order parameter, as we have previously calculated for the Weiss model.

We see that when cooling through the critical point the equilibrium magnetization starts to grow. But precisely at the transition point the magnetization must decide in which way it is going to point. This is a *bifurcation point*. It is referred to as a pitchfork bifurcation because of its shape. **But distinguish Ising/discrete versus continuous.**

This model gives the critical exponent for the order parameter, β , to be $1/2$. This is expected, since in the vicinity of the critical point the description is equivalent to the Weiss model.

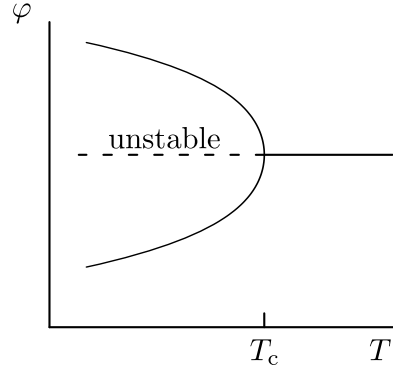


Figure 4.28: Pitchfork bifurcation

When φ is small (close to the transition) it follows that the leading terms in the expansion are the dominant ones and we can ignore the higher-order terms. We have seen in this section that only terms up to fourth order in φ were necessary to give a Landau free energy leading to a second order transition: a free energy that can vary between having a single and a double minimum depending on the values of the coefficients. Landau's key insight here was to appreciate that it is not that the higher order terms *may* be discarded, it is that they *must* be discarded in order to distil the *generic* properties of the transition. When terms above φ^4 are discarded this is known as the φ^4 model.

4.5.4 Thermal capacity in the Landau model

We have already seen that the Weiss model leads to a discontinuity in the heat capacity (critical exponent $\alpha = 0$). We can now examine this from the perspective of the Landau theory. The free energy is given by

$$F = F_0 + a(T - T_c)\varphi^2 + b\varphi^4. \quad (4.5.23)$$

We have included the F_0 term here and we shall permit it to have some smooth temperature variation, which is nothing to do with the transition.

The entropy is found by differentiating the free energy

$$S = -\frac{\partial F}{\partial T} = S_0 - a\varphi^2. \quad (4.5.24)$$

(Note we do not need to consider the temperature dependence of φ here since $\partial F/\partial \varphi = 0$). This shows the way the entropy drops as the ordered phase is

entered. We see that the entropy is continuous at the transition

$$\begin{aligned} T > T_c, \quad \varphi = 0 & \quad S = S_0(T) \\ T < T_c, \quad \varphi = \pm \sqrt{\frac{a(T_c - T)}{2b}} & \quad S = S_0(T) + \frac{a^2}{2b}(T - T_c) . \end{aligned} \quad (4.5.25)$$

The thermal capacity is given by

$$C = \frac{\partial Q}{\partial T} = T \frac{\partial S}{\partial T}. \quad (4.5.26)$$

Thus we find

$$\begin{aligned} T > T_c, \quad C &= C_0 \\ T < T_c, \quad C &= C_0 + \frac{a^2 T}{2b} \end{aligned} \quad (4.5.27)$$

At the transition there is a discontinuity in the thermal capacity given by

$$\Delta C = \frac{a^2 T_c}{2b}. \quad (4.5.28)$$

This is in accord with the discussion of the Weiss model; here we find the magnitude of the discontinuity in terms of the Landau parameters.

4.5.5 Ferromagnet in a magnetic field (really the Ising magnet)

In the presence of a magnetic field a ferromagnet exhibits certain features characteristic of a first order transition. There is no latent heat involved, but the transition can exhibit hysteresis. The literature is divided as to whether this is truly a first or second order transition. In the case of a first order transition the free energy may no longer be symmetric in the order parameter; odd powers of φ might appear in F . And the energy of a ferromagnet in the presence of a magnetic field has an additional term $(-\mathbf{M} \cdot \mathbf{B})$ linear in the magnetization.

For temperatures above T_c the effect of a free energy term linear in φ is to shift the position of the minimum to the left or right. Thus there is an equilibrium magnetization proportional to the applied magnetic field.

Let us consider the Ising magnet in the presence of a magnetic field. For temperatures below T_c the effect of the linear term is to raise one minimum and to lower the other. We plot the form of F as a function of the order parameter for a number of different applied fields.

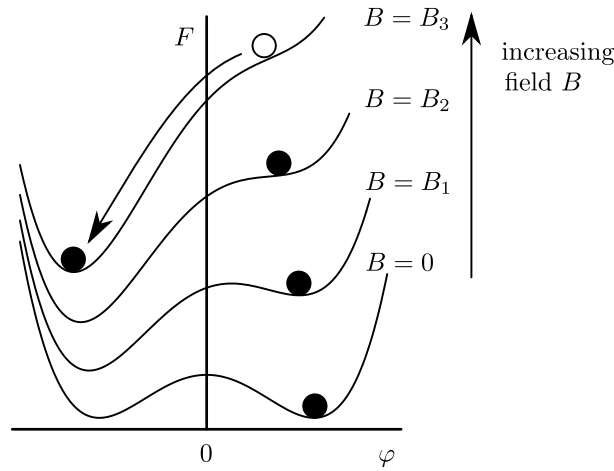


Figure 4.29: Variation in free energy for different magnetic fields – Ising case.

We see that in zero external field, since then F is symmetric in φ , there are two possible values for the order parameter either side of the origin. Once a field is applied the symmetry is broken. Then one of the states is the absolute minimum. But the system will remain in the metastable equilibrium. As the field is increased the left hand side of the right hand minimum gets shallower and shallower. When it flattens it is then possible for the system to move to the absolute minimum on the other side.

These considerations indicate that the behaviour of the magnetization discussed in Section 4.3.1 is not quite correct for the Ising magnet. There we stated that the magnetization inverts as B goes through zero. But in reality there will be *hysteresis*, a specific characteristic of first order transitions. That discussion gave the equilibrium behaviour whereas hysteresis is a quasi-equilibrium phenomenon.

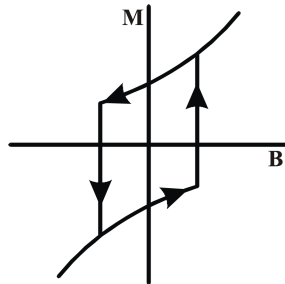


Figure 4.30: Hysteretic variation of magnetization below T_c .

This hysteretic behaviour we have discussed only applies to the Ising magnet, not the XY magnet nor the Heisenberg magnet which both have

broken *continuous* symmetries. Then the magnetization can always shift in the distorted ‘wine bottle’ potential to move to the lowest free energy.

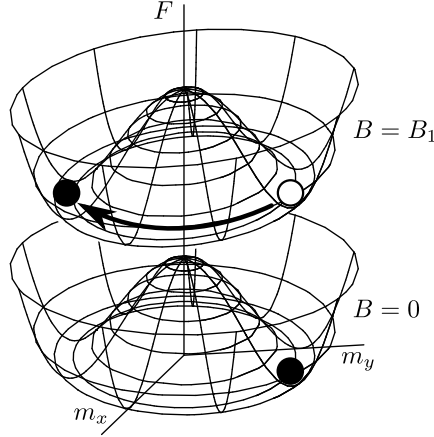


Figure 4.31: Variation in free energy for different magnetic fields – XY case.

Real (Heisenberg) magnets do, however, exhibit hysteresis. This happens through the formation of *domains*: regions where the magnetization points in different directions. Domain formation provides extra entropy from the domain walls at some energy cost. This can lower the free energy at finite temperatures. When one encounters un-magnetized iron at room temperatures, which is way below its critical temperature of 1044 K, this is because of the cancellation of the magnetization of the domains.

4.6 Ferroelectricity

4.6.1 Description of the phenomenon

In certain ionic solids a spontaneous electric polarization can appear below a particular temperature. A typical example of this is barium titanate, which has a transition temperature of about 140 °C. There is a good description of ferroelectricity in Kittel’s *Introduction to Solid State Physics* [21].

The essential feature of the ferromagnetic transition is that the ‘centre of mass’ of the positive charge becomes displaced from that of the negative charge. In this way a macroscopic polarization appears. The polarized state is called a *ferroelectric*. The transition is associated with a structural change in the solid.

In describing this transition we see that the order parameter is the electric polarization \mathbf{P} . However the polarization is restricted in the directions it may

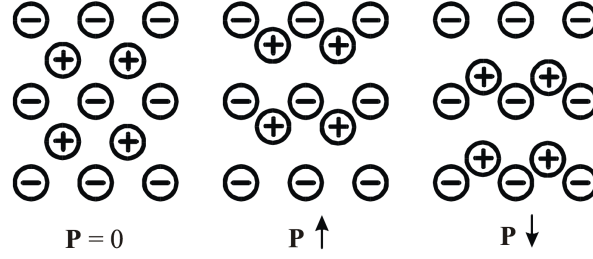


Figure 4.32: Unpolarized state and ferroelectric state showing two polarizations.

point. In the figure it may point either up or down. Thus it is a discrete symmetry that is broken; in reality the effective order parameter is a scalar. We note that this system has a non-conserved order parameter.

At the phenomenological level the transition has many things in common with the Ising model of the magnetic transition of the ferromagnet although the description is very different at the microscopic level. One special feature of the ferroelectric case is that the transition may be first or second order. We will use the Landau approach to phase transitions to examine this system and we shall be particularly interested in what determines the order of the transition.

Our previous example of a first order transition, the liquid–gas system was one with a conserved order parameter. Similarly, phase separation in a binary alloy, to be treated in Section 4.7 is a first order system with a conserved order parameter. Here, however, we will encounter a first order transition where the order parameter is not conserved.

4.6.2 Landau free energy

The order parameter is the electric polarization, but in keeping with our general approach we shall denote it by φ in the following. In the spirit of Landau we shall expand the (appropriate) free energy in powers of φ :

$$F = F_0 + F_1\varphi + F_2\varphi^2 + F_3\varphi^3 + F_4\varphi^4 + F_5\varphi^5 + F_6\varphi^6 + \dots \quad (4.6.1)$$

On the assumption that the crystal lattice has a centre of symmetry the odd terms of the expansion will vanish. Furthermore in the absence of an applied electric field there will be no $F_1\varphi$ term. We can ignore the constant term F_0 and so the free energy simplifies to

$$F = F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6 + \dots \quad (4.6.2)$$

Here we have allowed for the possibility that terms higher than the fourth power may be required (unlike the ferromagnetic case).

When we considered the ferromagnet we truncated the series at the fourth power. A necessary condition to do this was that the final coefficient, F_4 , was positive so that the order parameter remained bounded. If we were to have a system where F_4 were negative then we would have to include higher order terms until a positive (even) one were found. The simplest example is where F_6 is positive and we would truncate there. We will see that in this case the *order* of the transition is determined by the *sign* of the F_4 term.

If F_4 is positive then in the spirit of the Taylor expansion we can ignore the F_6 term and the general behaviour, in the vicinity of the transition, is just as the (Ising) ferromagnet considered previously. As the temperature

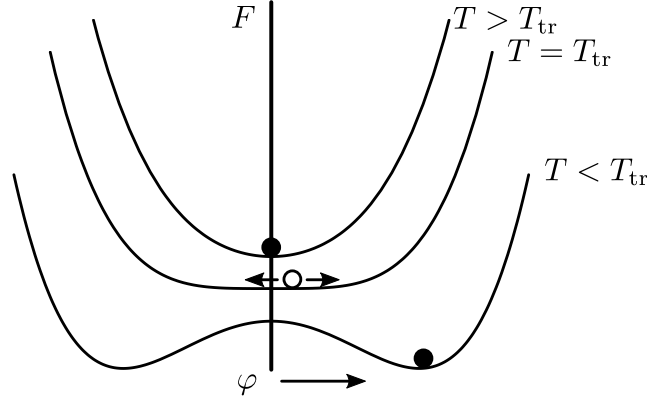


Figure 4.33: Conventional second order transition.

is cooled below the transition point the order parameter grows continuously from its zero value.

If F_4 is negative then in the simplest case we need a positive F_6 term to terminate the series. The general form of the free energy curve then has three minima, one at $\varphi = 0$ and one equally spaced at either side.

At high temperatures the minimum at $\varphi = 0$ is lower while at low temperatures the minima either side will be lower. The transition point corresponds to the case where all three minima occur at the same value of F , since then φ can jump from one minimum to another (at no energy cost).

Here we see that the transition is characterized by a jump in the order parameter and there is the possibility of hysteresis in the transition since the barrier to the lower minimum must be surmounted. These are the characteristics of a first order transition.

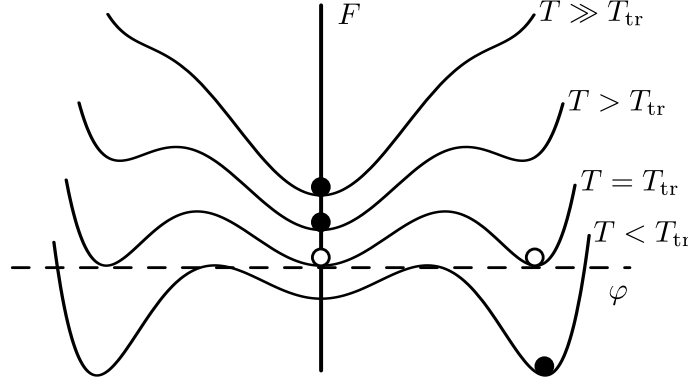


Figure 4.34: Inclusion of sixth order terms.

4.6.3 Second order case

The analysis follows that previously carried out for the ferromagnet case. Here F_4 is positive and the free energy is

$$F = F_2\varphi^2 + F_4\varphi^4 \quad (4.6.3)$$

when we ignore the sixth and higher order terms. There is a minimum in F when $dF/d\varphi = 0$. Thus the equilibrium state may be found from

$$\frac{dF}{d\varphi} = 2F_2\varphi + 4F_4\varphi^3 = 0. \quad (4.6.4)$$

This has solutions

$$\varphi = 0 \quad \text{and} \quad \varphi = \pm\sqrt{-F_2/F_4}. \quad (4.6.5)$$

We recall that the nature of the solution depends crucially on the sign of F_2 .

If we include the sixth order term in the free energy expansion then the nonzero solution for the order parameter is

$$\varphi^2 = -\frac{F_4}{3F_6} \left\{ 1 - \sqrt{1 - \frac{3F_2F_6}{F_4^2}} \right\}. \quad (4.6.6)$$

This reduces to the previously obtained expression when F_6 is neglected, as can be seen from the expansion of φ in terms of F_6 :

$$\varphi = \pm\sqrt{\frac{-F_2}{2F_4}} \left\{ 1 + \frac{3}{8} \frac{F_2F_6}{F_4^2} + \frac{63}{128} \left(\frac{F_2F_6}{F_4^2} \right)^2 + \dots \right\}. \quad (4.6.7)$$

We know that F_4 must be positive and that the critical point corresponds to the point where F_2 changes sign. Thus expanding F_2 and F_4 in powers of $T - T_c$ we require, to leading order

$$F_2 = a(T - T_c) \quad \text{and} \quad F_4 = b \quad (4.6.8)$$

so that

$$\begin{aligned} \varphi &= 0 & T > T_c \\ \varphi &= \sqrt{\frac{a(T_c - T)}{2b}} & T < T_c. \end{aligned} \quad (4.6.9)$$

This is the conventional Landau result for a second order transition.

4.6.4 First order case

In a first order transition we *must* include the sixth order term in the free energy expansion. In this case we have

$$F = F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6. \quad (4.6.10)$$

where we note that now $F_4 < 0$ and $F_6 > 0$.

Order parameter jump at the transition

At the transition point there are three minima of the free energy curve and they have the same value of F , namely zero (since, conveniently, we have taken F_0 to be zero). Thus the transition point is characterized by the

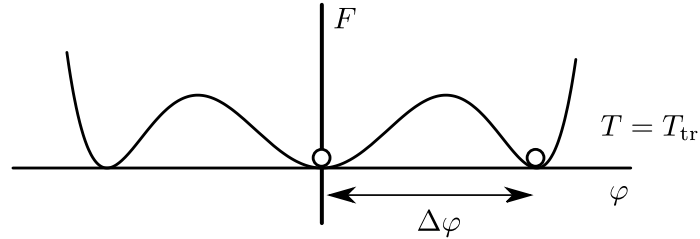


Figure 4.35: Jump in the order parameter at the transition.

conditions

$$F(\varphi) = 0 \quad \text{and} \quad \frac{dF}{d\varphi} = 0 \quad (4.6.11)$$

or

$$\begin{aligned} F_2\varphi^2 + F_4\varphi^4 + F_6\varphi^6 &= 0 \\ 2F_2\varphi + 4F_4\varphi^3 + 6F_6\varphi^5 &= 0. \end{aligned} \quad (4.6.12)$$

We know we have the $\varphi = 0$ root; this can be factored out. The others are found from solving the simultaneous equations

$$\begin{aligned} F_2 + F_4\varphi^2 + F_6\varphi^4 &= 0 \\ F_2 + 2F_4\varphi^2 + 3F_6\varphi^4 &= 0. \end{aligned} \quad (4.6.13)$$

The solution to these is

$$\varphi^2 = -\frac{F_4}{2F_6} \quad (4.6.14)$$

or

$$\varphi = \pm \sqrt{\frac{-F_4}{2F_6}} \quad (4.6.15)$$

as we know that F_4 is negative.

This gives the discontinuity in the order parameter at the transition since φ will jump between zero and this value at the transition. Thus we can write

$$\Delta\varphi = \sqrt{\frac{-F_4}{2F_6}}. \quad (4.6.16)$$

This vanishes as F_4 goes to zero; in other words the transition becomes second order. Thus we have shown that when F_4 changes sign the transition becomes second order. The point of changeover from first to second order is referred to as the *tricritical point*.

Transition temperature

At the transition point the value of F_2 may be found as the second solution to the simultaneous equation pair, Eq. (4.6.13). The result is

$$F_2 = \frac{F_4^2}{4F_6}. \quad (4.6.17)$$

This gives the relation which must hold between F_2 , F_4 and F_6 at the transition. In the second order case we saw that the transition point corresponded to the vanishing of F_2 . We see from Eq. (4.6.17) that this cannot be so in the first order case. Nevertheless we continue to call the point at which F_0 vanishes, the critical point. In other words, for first order, the transition point is different from the critical point.

We make the assumption that F_2 varies with temperature as it does in the second order case

$$F_2 = a(T - T_c) \quad (4.6.18)$$

since, at the microscopic level, the system doesn't know if it is first order or second order. Moreover we assume the coefficients F_4 and F_6 are constant or they vary but slowly in the vicinity of the transition. The “serious”

temperature variation is in F_2 and we take F_4 and F_6 to be temperature independent.

Denote T_{tr} the temperature at the transition; there F_2 takes the value

$$F_2 = a(T_{\text{tr}} - T_c). \quad (4.6.19)$$

Combining this with Eq. (4.6.17) gives

$$a(T_{\text{tr}} - T_c) = \frac{F_4^2}{4F_6} \quad (4.6.20)$$

or

$$T_{\text{tr}} = T_c + \frac{1}{4a} \frac{F_4^2}{F_6}. \quad (4.6.21)$$

The value of F_4 may vary with some external parameter such as strain, (as in Problem 4.5). Then if F_4 increases from a negative value to zero, then T_{tr} reduces to T_c . As F_4 increases through zero the first order transition becomes second order and the transition temperature remains equal to T_c .

$$\begin{aligned} F_4 > 0, \quad T_{\text{tr}} &= T_c, & 2^{\text{nd}} \text{ order} \\ F_4 < 0, \quad T_{\text{tr}} &= T_c + \frac{1}{4a} \frac{F_4^2}{F_6}, & 1^{\text{st}} \text{ order} . \end{aligned} \quad (4.6.22)$$

This is plotted in Fig. 4.36.

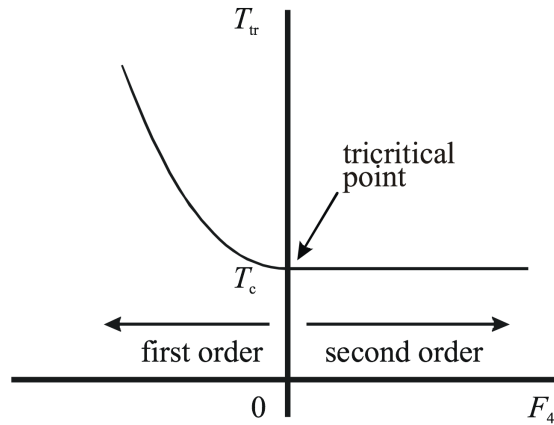


Figure 4.36: Variation of transition temperature with F_4 .

Temperature dependence of the order parameter

In the ordered phase the value of the order parameter is that corresponding to the lowest minimum of the free energy. We thus require

$$\frac{dF}{d\varphi} = 0, \quad \frac{d^2F}{d\varphi^2} > 0 \quad (4.6.23)$$

where the second condition ensures the stationary point is a minimum. Using the sixth order expansion for the free energy, differentiating it and discarding the $\varphi = 0$ solution gives

$$\varphi^2 = \frac{|F_4|}{3F_6} \left\{ 1 \pm \sqrt{1 - \frac{3F_2F_6}{F_4^2}} \right\}. \quad (4.6.24)$$

Remember that F_4 is negative here. We have to choose the positive root to obtain the *minima*; the negative root gives the maxima. Using the conventional temperature variation for F_2 together with the expression for the transition temperature T_{tr} in terms of the critical temperature T_c gives the temperature variation of the order parameter for the first order transition:

$$\varphi^2 = \frac{|F_4|}{3F_6} \left\{ 1 + \sqrt{\frac{4T_{tr} - 3T_c - T}{4(T_{tr} - 3T_c)}} \right\}. \quad (4.6.25)$$

Fig. 4.37 below shows the temperature variation of the order parameter for the case where $T_{tr}/T_c = 1.025$. This shows clearly the discontinuity in the

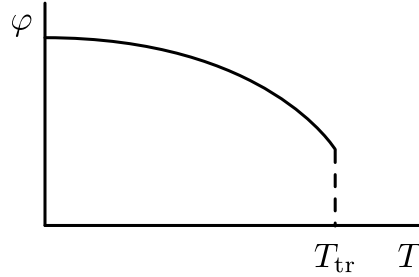


Figure 4.37: Order parameter in a first order transition.

order parameter at T_{tr} , characteristic of a first order transition.

Caveat

There is a contradiction in the use of the Landau expansion for treating first order transitions. The justification for expanding the free energy in powers

of the order parameter and the truncation of this expansion is based on the assumption that the order parameter is very small. Another way of expressing this is to say that the Landau expansion is applicable to the vicinity of the critical point. This is fine in the case of second order transitions where, when the ordered phase is entered, the order parameter grows continuously from zero. However the characteristic of a first order transition is the discontinuity in the order parameter. In this case the assumption of a vanishingly small order parameter is invalid. When the ordered phase is entered the order parameter jumps to a finite value. There is then no justification for a small- φ expansion of the free energy. There are two ways of accommodating this difficulty.

Notwithstanding the invalidity of terminating the free energy expansion, the *qualitative* discussion of Section 4.6.2 still holds. In particular it should be apparent that the general features of a first order transition can be accounted for by a free energy which is a sixth order polynomial in the order parameter. From this perspective we may regard the Landau expansion as putting the simplest of mathematical flesh on the bones of a qualitative model.

It is clear, however, that the free energy expansion becomes more respectable when the discontinuity in the order parameter becomes smaller, particularly as it goes to zero. Thus the theory is expected to describe well the changeover between first order and second order at the tricritical point. Transitions where the discontinuity in the order parameter is small are referred to as being *weakly first order*. We conclude that the Landau expansion should be appropriate for weakly first order transitions.

4.6.5 Entropy and latent heat at the transition

The temperature dependence of the free energy in the vicinity of the transition is given by

$$F = F_0(T) + a(T - T_c)\varphi^2 + F_4\varphi^4 + F_6\varphi^6. \quad (4.6.26)$$

Here $F_0(T)$ gives the temperature dependence in the disordered, high temperature phase, and the coefficient of φ^2 gives the dominant part of the temperature dependence in the vicinity of the transition. The temperature dependence of the free energy here is similar to that of the second order case, treated in the context of the ferromagnet.

The entropy is given by the temperature derivative of F according to the standard thermodynamic prescription

$$S = -\frac{\partial F}{\partial T}, \quad (4.6.27)$$

in this case

$$S = -\frac{\partial F_0}{\partial T} - a\varphi^2. \quad (4.6.28)$$

The second term indicates the reduction in entropy that follows as the order grows in the ordered phase. (As in the previous section, we do not need to consider the temperature dependence of φ since $\partial F/\partial\varphi = 0$). We see that if there is a discontinuity in the order parameter then there will be a corresponding discontinuity in the entropy of the system.

In the first order transition there is a discontinuity in the order parameter at $T = T_{\text{tr}}$. The latent heat is then given by

$$\begin{aligned} L &= -T_{\text{tr}}\Delta S \\ &= aT_{\text{tr}}\Delta\varphi^2. \end{aligned} \quad (4.6.29)$$

This shows how the latent heat is directly related to the discontinuity in the order parameter—both characteristics of a first order transition. The discontinuity in φ is given by

$$\Delta\varphi = \sqrt{\frac{-F_4}{2F_6}} \quad (4.6.30)$$

so we can write the latent heat as

$$L = aT_{\text{tr}}\frac{|F_4|}{2F_6}. \quad (4.6.31)$$

Now F_4 is negative for a first order transition. This expression shows how the latent heat vanishes as F_4 vanishes when the transition becomes second order.

4.6.6 Soft modes

In the ferroelectric the excitations of the order parameter are optical phonons: the positive and negative charges oscillate in opposite directions. In other words the polarization oscillates. These are not Goldstone bosons since it is not a continuous symmetry that is broken; indeed the excitations have a finite energy (frequency) in the $p \rightarrow 0$ ($k \rightarrow 0$) limit. This is a characteristic of optical phonons.

The frequency of the optical phonons depends on the restoring force of the interatomic interaction and the mass of the positive and negative ions. Now let us consider the destruction of the polarization as a ferroelectric is warmed through its critical temperature. We are interested here in the case of a second order transition. At the critical point the Landau free energy

exhibits anomalous broadening; the restoring force vanishes and the crystal becomes unstable. And this means that the frequency of the optical phonon modes will go to zero: they become “soft”.

For further details of soft modes see the books by Burns [22] and by Kittel [21].

4.7 Binary mixtures

We have already seen the gas–liquid transition of a fluid as an example of a system exhibiting a first order transition with conserved order parameter. And in the previous section the ferroelectric had a first order transition with non-conserved order parameter. In this section we shall examine phase separation in a binary mixture. This is a first order transition with a conserved order parameter. By comparing and contrasting these different systems we should be able to identify their similarities and differences. We should also note that the binary alloy model treated in this section is equivalent to the Ising model (with a conserved order parameter). And the procedures described in Sections 4.7.2 and beyond correspond to the mean field treatment of this Ising model

4.7.1 Basic ideas

Consider a mixture of two atomic species A and B, with relative proportions x and $1 - x$. For clarity we shall consider a solid system, but many of the arguments will also apply to liquid mixtures. We thus imagine an alloy whose composition is specified by A_xB_{1-x} . We assume that the energy of the system is determined by the nearest neighbour interactions and we will denote

$$\begin{aligned}\varepsilon_{aa} & \text{ energy of a single A–A bond} \\ \varepsilon_{bb} & \text{ energy of a single B–B bond} \\ \varepsilon_{ab} & \text{ energy of a single A–B bond.}\end{aligned}$$

A microstate of this system is specified by indicating the occupancy of each lattice site as an A or a B atom. Each microstate will have a given energy, found from a consideration of what neighbours each site has, by summing over the bond energies. And from these energies the partition function could be found. This would then give all the thermodynamic properties of the system. Unfortunately such a procedure would be prohibitively complicated. Instead we shall use an approximation method.

4.7.2 Model calculation

We make the assumption that the A and B atoms are distributed randomly: the occupancy of a given site is independent of the occupancy of its neighbours. Thus we are considering a homogeneous mixture. We take the system to be at a specified temperature and volume so we calculate the Landau *Helmholtz* free energy for this system. So we need to know the energy and the entropy.

The key point is to start by considering a given *bond* joining two neighbouring atoms. We label one atom as the *left* atom and the other as the *right*.

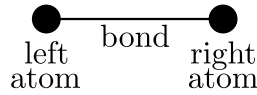


Figure 4.38: Bond joining two atoms.

Each of the atoms may be an A atom or a B atom. Thus there are four different configurations for the bond: A–A, A–B, B–A, B–B.

left atom \ right atom	A	B
A	ε_{aa}	ε_{ab}
B	ε_{ab}	ε_{bb}

Configuration energies

The concentration of the A atoms is taken to be x ; then the concentration of the B atoms is $1 - x$. In the general case we could allow the concentration to vary with position. Then the probability the left atom is A is x_l ; the probability it is B is $1 - x_l$; the probability the right atom is A is x_r ; the probability it is B is $1 - x_r$. The four bond configurations A–A, A–B, B–A, B–B, then have the probabilities: $x_l x_r$, $x_l (1 - x_r)$, $(1 - x_l) x_r$, $(1 - x_l) (1 - x_r)$.

left atom \ right atom	A	B
A	$x_l x_r$	$x_l (1 - x_r)$
B	$(1 - x_l) x_r$	$(1 - x_l) (1 - x_r)$

Configuration probabilities

4.7.3 System energy

We have defined the energies $\{\varepsilon_{aa}, \varepsilon_{bb}, \varepsilon_{ab}\}$ of the three types of bonds above (of course $\varepsilon_{ab} = \varepsilon_{ba}$) and we now know the probability of occurrence of each

configuration. The mean energy for the bonds will be the sum of the energy of each state multiplied by its probability

$$\bar{e}_{lr} = \varepsilon_{aa}x_lx_r + \varepsilon_{ab}x_l(1-x_r) + \varepsilon_{ab}(1-x_l)x_r + \varepsilon_{bb}(1-x_l)(1-x_r). \quad (4.7.1)$$

Now we assume that the composition of the system is homogeneous so that the concentration is independent of position; $x_l = x_r = \text{constant} = x$. In this case the mean energy per bond reduces to

$$\bar{e} = x^2\varepsilon_{aa} + (1-x)^2\varepsilon_{bb} + 2x(1-x)\varepsilon_{ab}. \quad (4.7.2)$$

which may be rearranged as

$$\bar{e} = x\varepsilon_{aa} + (1-x)\varepsilon_{bb} + x(1-x)\{2\varepsilon_{ab} - (\varepsilon_{aa} + \varepsilon_{bb})\}. \quad (4.7.3)$$

The expression for the internal energy is found by considering a system containing N atomic sites in a lattice where each atom has s neighbours. Then the number of neighbour bonds will be $Ns/2$; the divisor of 2 removes double counting. The internal energy of the system is then $E = Ns\bar{e}/2$ or

$$E = \frac{Ns}{2} [x^2\varepsilon_{aa} + (1-x)^2\varepsilon_{bb} + 2x(1-x)\varepsilon_{ab}]. \quad (4.7.4)$$

This may be written in a more suggestive form as

$$E = \frac{Ns}{2} \left\{ x\varepsilon_{aa} + (1-x)\varepsilon_{bb} + 2x(1-x) \left[\varepsilon_{ab} - \frac{1}{2}(\varepsilon_{aa} + \varepsilon_{bb}) \right] \right\}. \quad (4.7.5)$$

Here the first two terms represent the energy of the separate pure phases, which we denote by E_0

$$E_0 = \frac{Ns}{2} [x\varepsilon_{aa} + (1-x)\varepsilon_{bb}]. \quad (4.7.6)$$

The third term gives the extra energy upon mixing the species, E_m :

$$E_m = Nsx(1-x) \left[\varepsilon_{ab} - \frac{1}{2}(\varepsilon_{aa} + \varepsilon_{bb}) \right]. \quad (4.7.7)$$

It is then convenient to define the energy parameter

$$\varepsilon = \varepsilon_{ab} - \frac{1}{2}(\varepsilon_{aa} + \varepsilon_{bb}), \quad (4.7.8)$$

the difference between the “unlike” neighbour energy and the mean of the two “like” neighbour energies. This will turn out to be the characteristic energy of the system. Then the energy of mixing takes the simple form

$$E_m = Nsx(1-x)\varepsilon. \quad (4.7.9)$$

Observe that the energy of mixing is invariant under the transformation $x \rightarrow 1 - x$. This is saying that E_m is symmetric about the line $x = 1/2$. Any system whose energy satisfies this condition (regardless of the precise expression for its energy of mixing) is referred to as a *strictly regular solution*.

An *ideal solution* is one for which $\varepsilon = 0$. In this case the energy of mixing is zero; the energy is independent of the microscopic structure. An ideal solution cannot lower its energy by changing its structure.

By contrast when $\varepsilon \neq 0$ then the solution can lower its energy by rearranging itself in an ordered structure. When $\varepsilon < 0$ then A–B bonds are preferred and the ordered state will be a superlattice. (Clearly this would only happen in a solid.) And when $\varepsilon > 0$ then A–A and B–B bonds are preferred; the ordered state will comprise separate regions of phase-separated atoms. (This would happen in both solids and liquids).

4.7.4 Entropy

Each site can be occupied by an A atom or a B atom; it has two states. The probability that it is an A atom is x and the probability that it is a B atom is $1 - x$. The entropy of a given site is then $-k[x \ln x + (1 - x) \ln(1 - x)]$, so that for a solid of N atomic sites the entropy will be

$$S = -Nk[x \ln x + (1 - x) \ln(1 - x)]. \quad (4.7.10)$$

You should recognise that this expression for the entropy is similar to that for the spin $1/2$ magnet; there each site also had two states.

4.7.5 Free energy

As the system has its temperature and volume fixed the Helmholtz free energy is the appropriate thermodynamic potential to use. Since

$$F = E - TS \quad (4.7.11)$$

we then have

$$F = \frac{Ns}{2} [x\varepsilon_{aa} + (1 - x)\varepsilon_{bb} + 2x(1 - x)\varepsilon] + NkT[x \ln x + (1 - x) \ln(1 - x)]. \quad (4.7.12)$$

This is plotted in Fig. 4.39. We see that at high temperatures the free energy curve is a convex function; it has a single minimum. However at lower temperatures a concave region develops and the curve has a double minimum.

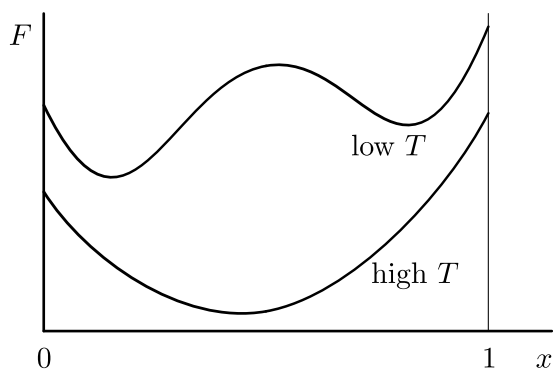


Figure 4.39: Free energy of binary alloy at high and low temperatures

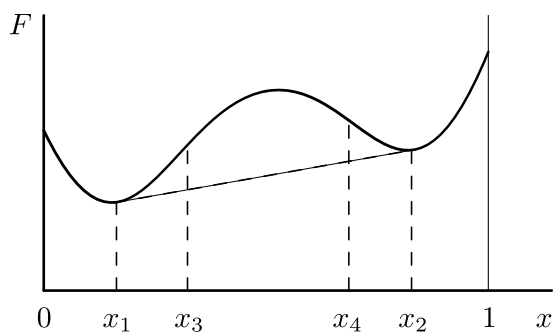


Figure 4.40: Free energy leading to phase separation.

We shall see that the low temperature free energy leads to phase separation.

Between $x = x_1$ and $x = x_2$ it is possible to lower the free energy by phase separation by dropping down from the curve to the double tangent line, with a mixture of phases at densities x_1 and x_2 . This is analogous to the situation with the liquid-gas system treated in the van der Waals approach in Section 4.2.1. And as with the fluid case, in the phase separation region some parts are metastable while some parts are unstable.

Instability occurs whenever $\partial F/\partial x$ is a *decreasing* function of x , that is, when $\partial^2 F/\partial x^2 < 0$. Then the system is unstable with respect to infinitesimal density fluctuations. This happens in the region x_3 to x_4 . This is known as the *spinodal* region. If the temperature is quenched into this region then one has spontaneous phase separation, referred to as *spinodal decomposition*.

By contrast the regions x_1 to x_3 and x_4 to x_2 are *metastable*. Here it is possible to remain in the homogeneous phase unless a density fluctuation of sufficient magnitude occurs. The system is unstable with respect to *finite* density fluctuations. Clearly if one waits long enough a fluctuation of

sufficient magnitude will occur (but it might be a very long wait indeed).

In the phase diagram (the $x - T$ plane) the homogeneous phase and the metastable phase are separated by the phase separation or *binodal* line. The metastable phase and the unstable phase are separated by the spinodal line. We shall see that for the model considered here the locus of these two lines may be calculated.

4.7.6 Phase separation – the lever rule

The phase separation curve is found by the double tangent construction, introduced in Section 4.2.1; this determines the region where the free energy may be reduced from its “homogeneous phase” value by separating into two phases.

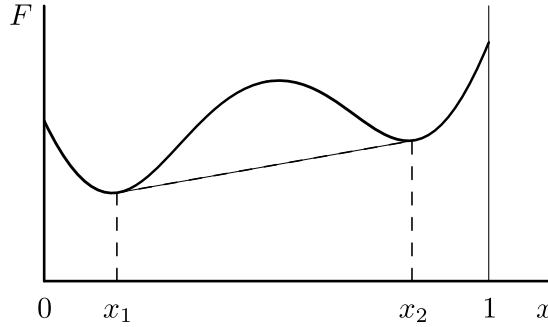


Figure 4.41: Double tangent construction.

The system will separate into regions of concentration x_1 and regions of concentration x_2 . The *fractions* of the substance in the two phases is determined by the *lever rule*. Let us denote the fraction of the substance in the phase of concentration x_1 by α ; then the fraction in the other phase, of concentration x_2 will be $1 - \alpha$. The number of A atoms in the x_1 phase will be $N\alpha x_1$, while the number of A atoms in the x_2 phase will be $N(1 - \alpha)x_2$. The sum of these will give the total number of A atoms in the system, Nx_0 , where x_0 is the concentration of A atoms in the homogeneous phase. Thus we have the equality

$$Nx_0 = N\alpha x_1 + N(1 - \alpha)x_2. \quad (4.7.13)$$

This may be solved for the fractions α and $1 - \alpha$ to give

$$\begin{aligned} \alpha &= \frac{x_2 - x_0}{x_2 - x_1} \\ 1 - \alpha &= \frac{x_0 - x_1}{x_2 - x_1}. \end{aligned} \quad (4.7.14)$$

This has a simple interpretation in terms of distances on the phase diagram. This is called the *lever rule*.

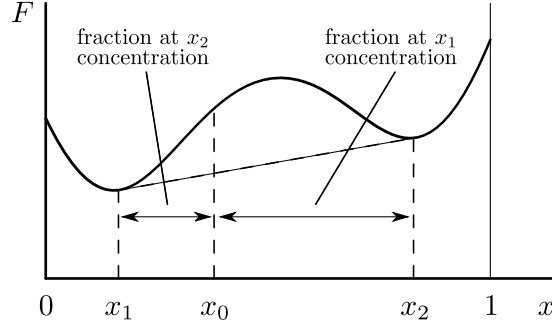


Figure 4.42: The lever rule.

4.7.7 Phase separation curve—the binodal

The concentrations x_1 and x_2 of the two separated phases are determined from the double tangent construction. So essentially we must solve the simultaneous equations

$$\begin{aligned} \frac{dF(x)}{dx} \Big|_{x_1} &= \frac{dF(x)}{dx} \Big|_{x_2} \\ F(x_2) &= F(x_1) + (x_2 - x_1) \frac{dF(x)}{dx} \Big|_{x_1, x_2} \end{aligned} \quad (4.7.15)$$

for x_1 and x_2 .

In general this could be a difficult problem. But there is an important simplification that helps in the case of a strictly regular solution. We can perform the double tangent construction on the free energy of mixing F_m :

$$F_m = E_m - TS. \quad (4.7.16)$$

This is possible because the energy E_0 which we have neglected

$$E_0 = \frac{Ns}{2} [x\varepsilon_{aa} + (1-x)\varepsilon_{bb}]$$

is a linear function of x . This means that removing E_0 from the free energy is equivalent to a vertical shear of the free energy graph. The double tangent construction is unchanged; the straight line still touches the free energy curve tangentially at the two points $x = x_1$ and $x = x_2$.

For a strictly regular solution the free energy of mixing is symmetrical about $x = 1/2$. Thus the two minima will be equally spaced either side of $x = 1/2$, and the symmetry now implies that the minima will be at the same height. In other words, on the free energy of mixing curve the double tangent construction is a *horizontal* line joining the *minima* of the free energy.

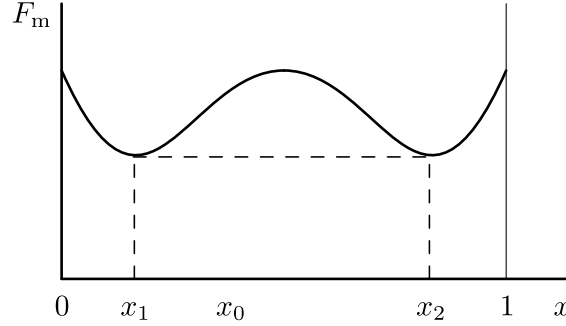


Figure 4.43: Double tangent construction for free energy of mixing.

The concentrations x_1 and x_2 of the two separated phases are determined from the condition

$$\frac{dF_m(x)}{dx} = 0 \quad (4.7.17)$$

where

$$F_m(x) = Nsx(1-x)\varepsilon + NkT[x \ln x + (1-x) \ln(1-x)]. \quad (4.7.18)$$

The derivative of this is

$$\frac{dF_m}{dx} = Ns\varepsilon(1-2x) - NkT \ln\left(\frac{1-x}{x}\right). \quad (4.7.19)$$

We should set this expression equal to zero and then solve the equation for x , giving the two solutions x_1 and x_2 as a function of temperature. Unfortunately an explicit expression cannot be obtained. However it is possible to express T as a function of x , which gives the locus of the phase separation line:

$$T_{\text{ps}} = \frac{s\varepsilon(1-2x)}{k \ln[(1-x)/x]}. \quad (4.7.20)$$

The transformation $x \rightarrow 1-x$ leaves the expression for T_{ps} unchanged, so there are two solutions for x corresponding to a given temperature.

The *critical temperature* T_c corresponds to the maximum T_{ps} , occurring at $x = 1/2$ by symmetry. One must be careful in taking the limit correctly. Since

$$\lim_{x \rightarrow 1/2} \frac{1-2x}{\ln[(1-x)/x]} = \frac{1}{2} \quad (4.7.21)$$

it follows that the critical temperature is given by

$$T_c = \frac{s\varepsilon}{2k}. \quad (4.7.22)$$

From this we can write the phase separation temperature as

$$T_{\text{ps}} = \frac{2(1-2x)}{\ln[(1-x)/x]} T_c. \quad (4.7.23)$$

And from this we plot the phase separation curve as shown in Fig. 4.44.

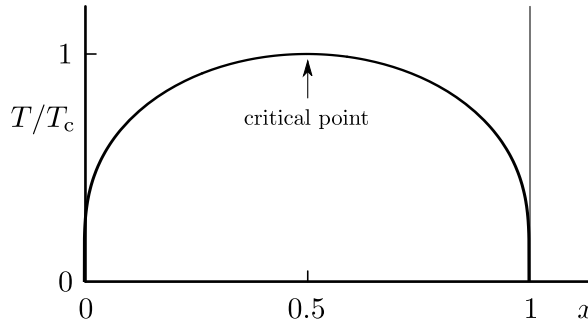


Figure 4.44: Phase separation of a binary alloy.

4.7.8 The spinodal curve

The spinodal curve traces out the region of instability in the $T - x$ plane. This is characterized by the vanishing of the second derivative of F (or the free energy of mixing), points x_3 and x_4 of Fig. 4.40. Thus we require

$$\frac{d^2 F}{dx^2} = 0. \quad (4.7.24)$$

We found the first derivative in the previous section, Eq. (4.7.19):

$$\frac{dF_m}{dx} = Ns\varepsilon(1-2x) - NkT \ln\left(\frac{1-x}{x}\right)$$

and differentiating once more gives

$$\frac{d^2 F_m}{dx^2} = -2Ns\varepsilon + NkT \left(\frac{1}{1-x} + \frac{1}{x} \right). \quad (4.7.25)$$

Setting this equal to zero gives the spinodal temperature as a function of x

$$T_{\text{sp}} = \frac{2s\varepsilon}{k} x(1-x) \quad (4.7.26)$$

or, in terms of the critical temperature

$$T_{\text{sp}} = 4x(1-x)T_c. \quad (4.7.27)$$

The spinodal line is below the phase separation line. They meet at the critical point where $x = 1/2$ (for a strictly regular solution).

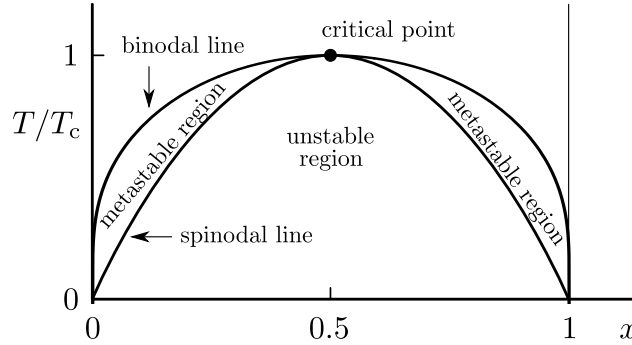


Figure 4.45: Phase separation and spinodal line.

4.7.9 Entropy in the ordered phase

The entropy of a homogeneous mixture, where the concentration of A atoms is x , is given by Eq. (4.7.10)

$$S = -Nk[x \ln x + (1-x) \ln(1-x)].$$

So if x_0 is the concentration of A atoms in the high temperature homogeneous phase, then the entropy of this phase is

$$S_0 = -Nk[x_0 \ln x_0 + (1-x_0) \ln(1-x_0)]. \quad (4.7.28)$$

This is a constant, determined by the chosen concentration x_0 . Thus in the homogeneous phase S is independent of T so that the thermal capacity is zero:

$$C = 0 \text{ in the homogeneous phase.}$$

In the ordered low temperature phase there will be regions of low concentration x_1 and regions of high concentration x_2 . Accordingly the entropy of these regions will be

$$\begin{aligned} S_1 &= -N_1 k[x_1 \ln x_1 + (1-x_1) \ln(1-x_1)] \\ S_2 &= -N_2 k[x_2 \ln x_2 + (1-x_2) \ln(1-x_2)]. \end{aligned} \quad (4.7.29)$$

Now for a *strictly regular solution*, as is our model, the phase diagram is symmetrical about about $x = 1/2$ and we have

$$x_2 = 1 - x_1. \quad (4.7.30)$$

This has the important consequence that

$$S_1/N_1 = S_2/N_2; \quad (4.7.31)$$

the entropy per particle in the dilute phase and in the concentrated phase is the same. In other words each particle (regardless of the phase it is in) “carries the same entropy”.

So the total entropy in the ordered low temperature phase is

$$S = -Nk[x_1 \ln x_1 + (1 - x_1) \ln(1 - x_1)]. \quad (4.7.32)$$

The entropy is independent of the initial concentration x_0 and it depends only on the concentration of the separated states; we can use x_1 or x_2 . This entropy depends on temperature because x_1 (or x_2) depends on temperature

$$S(T) = -Nk[x_1(T) \ln x_1(T) + (1 - x_1(T)) \ln(1 - x_1(T))], \quad (4.7.33)$$

where $x(T)$ is given by the solution to Eq. (4.7.23)

$$T = \frac{2(1 - 2x)}{\ln[(1 - x)/x]} T_c. \quad (4.7.34)$$

Although an explicit expression for S in terms of T cannot be found, we can make a parametric plot by varying x_1 . This is shown in Fig. 4.46.

In the phase separated region the entropy (and therefore the thermal capacity) will be independent of the initial concentration. The temperature at which phase separation occurs will depend on x_0 but once the separated region is entered the entropy (and therefore the thermal capacity) will join a *universal curve*. This happens for a strictly regular solution.

4.7.10 Thermal capacity in the ordered phase

In the heat capacity is found from the entropy

$$C = \frac{dQ}{dT} = T \frac{dS}{dT}. \quad (4.7.35)$$

The differentiation is performed on a function of a function since entropy depends on x_1 , and x_1 depends on T . Thus we use

$$\frac{dS}{dT} = \frac{dS}{dx_1} \bigg/ \frac{dT}{dx_1}. \quad (4.7.36)$$

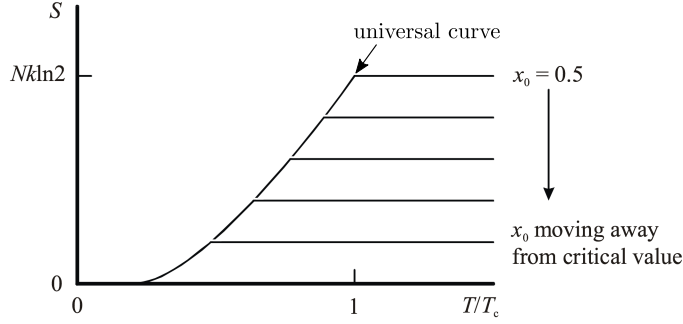


Figure 4.46: Entropy of phase separated binary mixture.

The derivatives are evaluated as

$$\begin{aligned} \frac{dS}{dx_1} &= Nk \ln[(1-x_1)/x_1] \\ \frac{dT}{dx_1} &= \frac{2T_c}{\ln[(1-x_1)/x_1]} \left\{ \frac{1-2x_1}{x_1(1-x_1) \ln[(1-x_1)/x_1]} - 2 \right\}. \end{aligned} \quad (4.7.37)$$

Again we cannot assemble these into an *explicit* function of C in terms of T but we can make use of a parametric plot since

$$T = \frac{2(1-2x_1)}{\ln[(1-x_1)/x_1]} T_c.$$

The thermal capacity is $C = TdS/dT$, so that in this case

$$\begin{aligned} C &= \frac{2(1-2x_1)}{\ln[(1-x_1)/x_1]} T_c \frac{Nk \ln[(1-x_1)/x_1]}{\frac{2T_c}{\ln[(1-x_1)/x_1]} \left\{ \frac{1-2x_1}{x_1(1-x_1) \ln[(1-x_1)/x_1]} - 2 \right\}} \\ &= Nk \frac{(1-2x_1) \ln[(1-x_1)/x_1]}{\left\{ \frac{1-2x_1}{x_1(1-x_1) \ln[(1-x_1)/x_1]} - 2 \right\}} \end{aligned} \quad (4.7.38)$$

Thus we have the implicit pair

$$\left. \begin{aligned} C &= Nk \frac{x_1(1-x_1)(1-2x_1) \ln^2[(1-x_1)/x_1]}{1-2x_1-2x_1(1-x_1) \ln[(1-x_1)/x_1]} \\ T &= \frac{2(1-2x_1)}{\ln[(1-x_1)/x_1]} T_c. \end{aligned} \right\} \quad (4.7.39)$$

We plot this in the Fig. 4.47.

If we eliminate $\ln[(1-x_1)/x_1]$ from these equations then one obtains the expression commonly quoted in the literature (e.g. Slater [23]):

$$\frac{C}{Nk} = \frac{2(1-2x_1)^2}{\frac{T}{T_c} \left(\frac{T/T_c}{2x_1(1-x_1)} - 2 \right)}, \quad (4.7.40)$$

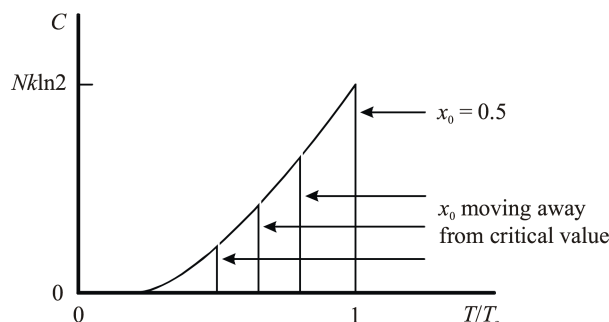


Figure 4.47: Heat capacity of binary mixture.

but this is only one of an implicit pair.

The entropy is continuous at the transition and there is a simple discontinuity in the heat capacity. This means that there is *no latent heat* even though the transition is first order.

The absence of latent heat is due simply to the constraints under which we are studying the transition. The gas – liquid transition (and indeed the liquid – solid transition) are studied conventionally under the condition of constant pressure, often atmospheric pressure. If the transition were studied at constant volume, as in the above analysis, then there would be no latent heat. The fixed concentration x_0 of the binary mixture is analogous to the fluid system at constant density. To investigate the latent heat of the transition in a binary mixture requires the introduction of the *osmotic pressure* of the components and consideration of the transition under the (hypothetical) condition of constant osmotic pressure.

4.7.11 Order of the transition and the critical point

Below the transition there are two coexisting phases. This is a general feature of any system with a conserved order parameter. Below the transition the mean value of the concentration x is fixed x_0 and the proportions of the two phases, of concentrations x_1 and x_2 are determined by the requirement that the mean density be equal to x_0 ; this is the content of the lever rule.

So the order parameter density for a system with conserved order parameter has two distinct values below the transition. Of course this ignores the variation at the boundary between the two phases. For the binary mixture these two values would be x_1 and x_2 .

Above the transition the order parameter density is a constant x_0 . If $x_0 > 1/2$ then on passing through the transition x_2 is continuous, but x_1

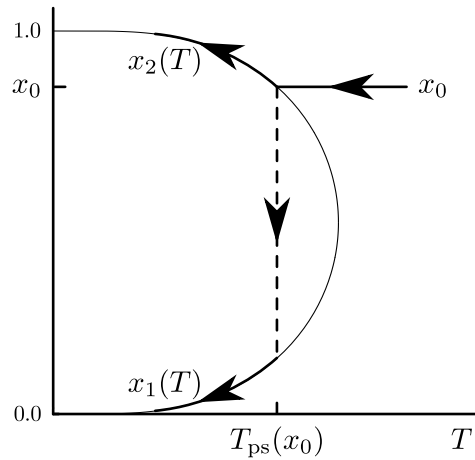


Figure 4.48: Order parameter values of the transition.

is discontinuous. It is the discontinuity that characterizes the transition as being first order. But we reiterate that since x_0 is constant the entropy is continuous, the thermal capacity is not infinite, and there is no latent heat.

Things are different, however, at $x_0 = 1/2$. Here the order parameter density values are both continuous at the transition so this qualifies as a *second order* transition. We also observe that the phase separation point and the spinodal point coincide so that there is no metastable region, and so no hysteresis. And finally since both the first and the second derivatives of the Helmholtz free energy (of mixing) vanish the minimum is anomalously broad so that there can be large fluctuations in the order parameter (with negligible free energy cost). We recall these all as characteristics of a second order transition. The point at $x = 1/2$, where the transition becomes second order is thus called the *critical point*.

We have the general rule that a first order transition becomes second order at a critical point. It was the assumption of a strictly regular solution that placed the critical point at $x = 1/2$. In the general case the critical point occurs at the concentration for which the transition temperature is a maximum (stationary).

4.7.12 The critical exponent β

The critical exponents refer to the critical point so we shall examine the binary mixture specifically in the $x_0 = 1/2$ case. It is convenient to utilise an order parameter that grows from zero at the critical point so we shall define

$$\varphi = 2x - 1. \quad (4.7.41)$$

Then the phase separation curve

$$T = \frac{2(1-2x)}{\ln[(1-x)/x]} T_c \quad (4.7.42)$$

may be expressed in terms of φ as

$$\frac{T}{T_c} = \frac{2\varphi}{\ln[(1+\varphi)/(1-\varphi)]}. \quad (4.7.43)$$

Observe this is identical to the corresponding equation for the Weiss ferromagnet, Eq. (4.3.18).

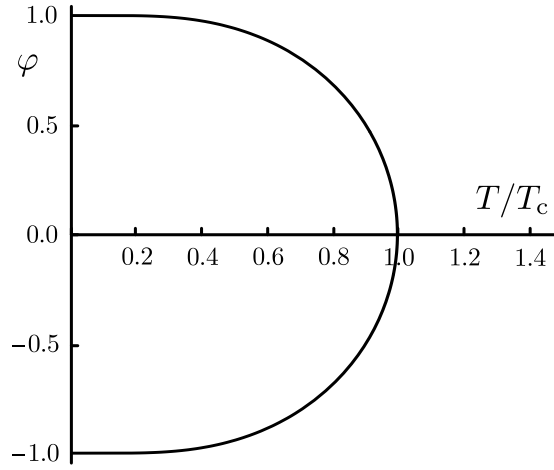


Figure 4.49: Critical behaviour.

We would like to expand φ in powers of $1 - T/T_c$ to investigate the behaviour of the order parameter in the vicinity of the critical point, and to obtain the order parameter critical exponent β . This is most conveniently done by expanding $1 - T/T_c$ in powers of φ and then inverting the series. We find, from Eq. (4.7.43):

$$1 - \frac{T}{T_c} = \frac{1}{3}\varphi^2 + \frac{4}{45}\varphi^4 + \frac{44}{945}\varphi^6 + \dots \quad (4.7.44)$$

which may be inverted to yield

$$\varphi = \sqrt{3} \left(1 - \frac{T}{T_c}\right)^{1/2} - \frac{2\sqrt{3}}{5} \left(1 - \frac{T}{T_c}\right)^{3/2} + \dots \quad (4.7.45)$$

In other words we have found that

$$\varphi \sim \left(1 - \frac{T}{T_c}\right)^{1/2} \quad (4.7.46)$$

at the critical point, the usual mean field value of $\beta = 1/2$.

Finally we must mention an important distinction between systems with conserved and non-conserved order parameters at the critical point. The diagram above, showing the critical point may be similar in both cases, but the *interpretation* is different. For a non-conserved order parameter when the critical point is approached there is a *bifurcation* and the system breaks symmetry by choosing one particular branch. By contrast, for a conserved order parameter *both* possible branches are chosen; we have coexisting fractions determined by the lever rule.

4.8 Quantum Phase Transitions

4.8.1 Introduction

In a conventional second order phase transition there is an ordered phase existing at low temperatures. As the temperature is raised this order is destroyed by thermal fluctuations. And at the critical point the order disappears completely. The temperature of the critical point is determined by the competing requirements of energy minimisation, favouring order, and entropy maximisation, favouring disorder. Our consideration is restricted to second order phase transitions where the ‘anomalous broadening’ of the free energy minimum allows large excursions of the order parameter at negligible cost. These diverging fluctuations in the order parameter result in a collapse of the order and we can thus say that the transition is *driven* by the fluctuations.

Temperature is the control parameter in a conventional phase transition; as the temperature is varied the critical point is traversed. By contrast a *quantum phase transition* occurs at zero temperature. Here the control parameter is some other variable such as pressure, magnetic field, alloy composition, and the transition occurs at $T = 0$ as the control parameter is varied. At $T = 0$ there are no thermal fluctuations present and the transition from the ordered phase to the disordered is driven purely by quantum-mechanical fluctuations. Such fluctuations are a consequence of the Uncertainty Principle.

The study of quantum phase transition thus concerns the different kinds of ground state a system can have for different values of the control parameter. There will be critical exponents associated with the quantum critical point and these display the same sorts of universality as do the conventional critical exponents.

As the temperature is increased from $T = 0$ the thermal fluctuations will make an increasing contribution to the critical behaviour. In the temperature–

control parameter plane there will thus be a region of ordered phase and a region of disordered phase separated by a phase boundary line. While at $T = 0$ the critical point is purely quantum, at the higher temperatures where the transition occurs the critical point will be classical. And the classical critical exponents are related rather simply to the quantum critical exponents – as we shall see.

The figure shows an example of such a transition [24]. The material is LiHoF_4 , where the electrons in Ho are coupled by an Ising-type interaction. The control parameter is a magnetic field applied transverse to the Ising spin direction. The dotted curve shows the result of calculation based on a mean field approximation of the Ising interaction. The solid line incorporates the effects of the nuclear hyperfine interaction as well.

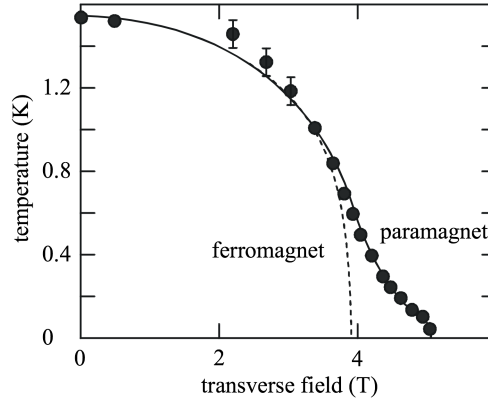


Figure 4.50: Phase boundary in a transverse Ising system.

4.8.2 The transverse Ising model

The transverse Ising model is a simple system exhibiting a quantum critical point. In this model the Ising interaction is supplemented by a magnetic field transverse to the Ising direction. Thus we write the Hamiltonian as

$$\mathcal{H} = -2\hbar J \sum_{i>j \text{ nn}} S_z^i S_z^j - \gamma \hbar B_x \sum_i S_x^i. \quad (4.8.1)$$

The first term is the Ising interaction and the second term represents the interaction with an applied magnetic field in the x direction, B_x .

In the absence of the external field we have the conventional Ising model. The interaction favours parallel spins and the ground state then corresponds to aligned spins either in the $+z$ or the $-z$ direction. When the transverse

field is applied its effect is to induce transitions between the up and down spin states. This is because the hamiltonian no longer commutes with the spin z component

$$[\mathcal{H}, S_z^i] \neq 0, \quad (4.8.2)$$

and using the Heisenberg equation of motion.

Thus the effect of the transverse magnetic field is to cause fluctuations in the z component of the spins. And these fluctuations will act to destroy the order of the Ising ground state. For high enough values of the transverse field the order will be fully destroyed and then the ground state will be qualitatively different. Thus the ground state is altered by the control parameter.

4.8.3 Recap of mean field Ising model

For clarity let us recap the mean field treatment of the conventional Ising model, described now in a form suitable for the addition of a transverse field. In the absence of interactions the magnetization of an assembly of N spin $\frac{1}{2}$ magnetic moments μ is given by

$$M = N\mu \tanh\left(\frac{\mu B}{kT}\right) \quad (4.8.3)$$

where T is the temperature. Clearly the magnetization will point in the direction of the applied magnetic field. The saturation magnetization M_0 is given by

$$M_0 = N\mu \quad (4.8.4)$$

so we may write the magnetization as

$$M = M_0 \tanh\left(\frac{M_0}{N} \frac{B}{kT}\right). \quad (4.8.5)$$

In the mean field approach to the Ising hamiltonian the $S_z^i S_z^j$ interaction is approximated by the average $n S_z^i \langle S_z \rangle$ where n is the number of neighbours surrounding each particle. In terms of the magnetization this may be written as a magnetic field b :

$$b = \lambda M_z \hat{z}. \quad (4.8.6)$$

(Since the magnetization is defined as the total magnetic moment, the dimensions of λ are m_0 over volume.) Spontaneous magnetization then occurs, in the absence of B , as the solution to

$$M_z = M_0 \tanh\left(\frac{M_0}{N} \frac{\lambda M_z}{kT}\right) \quad (4.8.7)$$

or

$$\frac{M_z}{M_0} = \tanh \left(\frac{M_z T_c}{M_0 T_0} \right) \quad (4.8.8)$$

where T_c , the critical temperature is given by

$$T_c = \frac{\lambda M_0^2}{Nk}. \quad (4.8.9)$$

The tanh equation is solved by writing it as

$$\begin{aligned} \frac{M_z T_c}{M_0 T} &= \tanh^{-1} \left(\frac{M_z}{M_0} \right) \\ &= \frac{1}{2} \ln \left(\frac{1 + M_z/M_0}{1 - M_z/M_0} \right), \end{aligned} \quad (4.8.10)$$

and then

$$\frac{T}{T_c} = \frac{2M_z/M_0}{\ln \left(\frac{1+M_z/M_0}{1-M_z/M_0} \right)}. \quad (4.8.11)$$

When plotted, this gives the usual form for the variation of spontaneous magnetization with temperature.

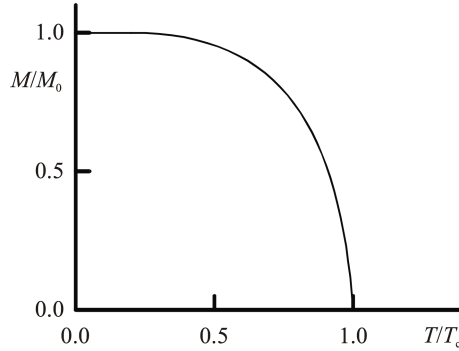


Figure 4.51: Spontaneous magnetization of the Ising ferromagnet.

The critical behaviour may be found from a power series expansion, since M_z is vanishingly small. The expansion is

$$\frac{T}{T_c} = 1 - \frac{1}{3} \left(\frac{M_z}{M_0} \right)^2 + \frac{4}{45} \left(\frac{M_z}{M_0} \right)^4 - \frac{44}{945} \left(\frac{M_z}{M_0} \right)^6 + \dots \quad (4.8.12)$$

and this series may be inverted to yield

$$\frac{M_z}{M_0} = \sqrt{3} \left(1 - \frac{T}{T_c} \right)^{1/2} + \frac{2}{5} \sqrt{3} \left(1 - \frac{T}{T_c} \right)^{3/2} + \frac{12}{175} \sqrt{3} \left(1 - \frac{T}{T_c} \right)^{5/2} + \dots \quad (4.8.13)$$

Thus we see that the magnetization is continuous as $T \rightarrow T_c$; the transition is second order; the critical exponent β has the mean field value of $\frac{1}{2}$ and its critical amplitude is $\sqrt{3}$.

4.8.4 Application of a transverse field

We now have the applied magnetic field

$$\mathbf{B} = B_x \hat{\mathbf{x}} \quad (4.8.14)$$

to which must be added the Ising mean field

$$\mathbf{b} = \lambda M_z \hat{\mathbf{z}}. \quad (4.8.15)$$

Thus the total magnetic field has magnitude

$$B_{\text{tot}} = \sqrt{B_x^2 + \lambda^2 M_z^2} \quad (4.8.16)$$

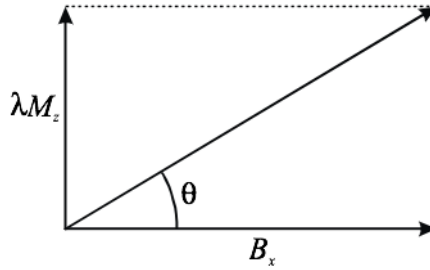


Figure 4.52: Resultant magnetic field.

and it points in a direction q from the x axis, where

$$\sin \theta = \frac{\lambda M_z}{\sqrt{B_x^2 + \lambda^2 M_z^2}}. \quad (4.8.17)$$

Now the mean field recipe says that the magnetization is given by

$$M = M_0 \tanh \left(\frac{M_0}{N} \frac{B_{\text{tot}}}{kT} \right) \quad (4.8.18)$$

and it points in the direction parallel to the field. Thus

$$M = M_0 \tanh \left(\frac{M_0}{N} \frac{\sqrt{B_x^2 + \lambda^2 M_z^2}}{kT} \right). \quad (4.8.19)$$

However what we are interested in is the magnetization in the z direction. We know the direction of \mathbf{M} : parallel to \mathbf{B}_{tot} . So to find the component in the z direction we require

$$M_z = M \sin \theta, \quad (4.8.20)$$

or

$$M_z = \frac{\lambda M_z}{\sqrt{B_x^2 + \lambda^2 M_z^2}} M_0 \tanh \left(\frac{M_0 \sqrt{B_x^2 + \lambda^2 M_z^2}}{N kT} \right). \quad (4.8.21)$$

This may be tidied up a little, but it is helpful first, to re-express in terms of reduced variables. Since M_0 is the saturation magnetization it follows that λM_0 is the “saturation” internal field. Let’s measure the transverse field in multiples of this. That is, we define

$$b_x = B_x / \lambda M_0. \quad (4.8.22)$$

We also define the reduced variables

$$m_z = M_z / M_0 \quad \text{and} \quad t = T / T_c \quad (4.8.23)$$

Then m_z satisfies the implicit equation

$$\sqrt{b_x^2 + m_z^2} = \tanh \frac{\sqrt{b_x^2 + m_z^2}}{t} \quad (4.8.24)$$

4.8.5 Transition temperature

The transition from the ordered phase to disordered phase corresponds to the vanishing of M_z . In general the temperature at which the transition occurs will be a function of the transverse field. Setting $m_z = 0$ in the above equation then gives the (b_x – dependent) critical temperature in the equation

$$b_x = \tanh \frac{b_x}{t_c(b_x)}. \quad (4.8.25)$$

This may be inverted to give

$$\begin{aligned} \frac{b_x}{t_c(b_x)} &= \tanh^{-1} b_x \\ &= \frac{1}{2} \ln \left(\frac{1 + b_x}{1 - b_x} \right) \end{aligned} \quad (4.8.26)$$

so that

$$t_c(b_x) = \frac{2b_x}{\ln \left(\frac{1+b_x}{1-b_x} \right)}. \quad (4.8.27)$$

In terms of the full variables this is

$$\frac{T_c(B_x)}{T_c(B_x=0)} = \frac{2B_x/\lambda M_0}{\ln\left(\frac{\lambda M_0 + B_x}{\lambda M_0 - B_x}\right)} \quad (4.8.28)$$

and this is plotted in Fig. 4.53 below.

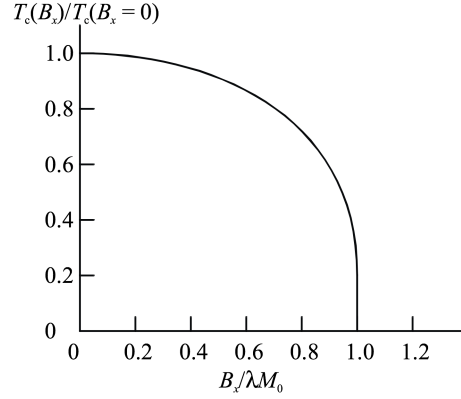


Figure 4.53: Variation of critical temperature with transverse field.

This curve corresponds to the dotted line plotted with the experimental data in Fig. 4.50 in the introduction.

4.8.6 Quantum critical behaviour

In terms of reduced variables, the equation of state for the system may be written as

$$t = \frac{2\sqrt{m_z^2 + b_x^2}}{\ln\left(\frac{1+\sqrt{m_z^2 + b_x^2}}{1-\sqrt{m_z^2 + b_x^2}}\right)}. \quad (4.8.29)$$

The quantum critical behaviour occurs at zero temperature. The control parameter is b_x ; this is the analogue of temperature in the classical case. So to study the zero-temperature phase diagram we need the dependence of m_x on b_z .

Since we are assuming that both m_x and b_z are finite then in the limit of $t \rightarrow 0$ the logarithm must become infinite. And for this to be the case is denominator will go to zero. In other words

$$1 - \sqrt{m_z^2 + b_x^2} = 0 \quad (4.8.30)$$

or

$$m_z^2 = 1 - b_x^2. \quad (4.8.31)$$

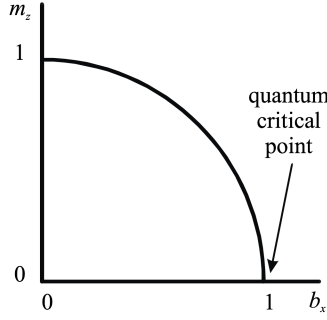


Figure 4.54: Zero temperature phase diagram.

This is plotted in the Fig. 4.54.

To investigate the critical behaviour we want to know what is happening in the vicinity of the quantum critical point, at $b_x = 1$. We write m_z as

$$m_z = (1 - b_x^2)^{1/2} \quad (4.8.32)$$

and a series expansion then gives

$$m_z = \sqrt{2} (1 - b_x)^{1/2} - \frac{1}{2\sqrt{2}} (1 - b_x)^{3/2} - \frac{1}{16\sqrt{2}} (1 - b_x)^{5/2} + \dots \quad (4.8.33)$$

We see that the order parameter goes continuously to zero at the critical point so the transition is second order. And the above expansion gives β , the order parameter critical exponent to be $1/2$. The classical and the quantum critical behaviour can be compared. We have

$$\text{classical case } m_z = \sqrt{3}(1 - t)^{1/2}$$

$$\text{quantum case } m_z = \sqrt{2}(1 - b_x)^{1/2}.$$

We see that the critical *exponents* are the same in the quantum and the classical case but the critical *amplitudes* are different.

4.8.7 Dimensionality and critical exponents

There is a general rule relating classical and quantum critical exponents and the dimensionality of the system. The scaling theory arguments outlined in Section 4.1.8 and in particular the Josephson critical exponent law demonstrate the importance of the system's dimensionality to the critical exponents.

Let us write the Boltzmann factor appearing in the system's partition function as $e^{-E\beta}$ where $\beta = 1/kT$. This has a certain similarity to the quantum generator of time evolution $e^{iEt/\hbar}$. We can thus regard the Boltzmann

factor as a generator of an (imaginary) spatial displacement. And as the temperature goes to zero the spatial displacement goes to infinity – what one understands as the thermodynamic limit. The sum or integral over Boltzmann factors in the partition covers the spatial extent of the system. And in the limit of zero temperature the Boltzmann factors involve an additional dimension to be traversed.

Since it is understood that the partition function contains all thermodynamic information about a system the above argument implies that a zero-temperature critical point in a system of n dimensions will have the same behaviour as a conventional critical point in a system of $n + 1$ dimensions. And since the mean field approximation is independent of the system's dimensionality we conclude that the mean field approximation will give the same critical exponents for the classical and the corresponding quantum critical point.

We know that mean field approaches give behaviour that, while qualitatively true, are often not in quantitative agreement with observed critical behaviour. For each system (hamiltonian) there is a marginal spatial dimensionality d^* such that when the number of dimensions is greater than d^* the results of mean field theory are exact [25]. When the number of dimensions is less than d^* then mean field theory is quantitatively wrong; then fluctuations are significant. When the number of dimensions is equal to d^* there are only logarithmic corrections to the results of mean field theory. Thus the designation *marginal* dimensionality.

The marginal dimensionality for a dipole-coupled Ising system, such as LiHoF_4 described above, is 3. Thus we expect mean field theory to give, to first order, the correct critical behaviour for the classical critical behaviour. And it will then certainly be correct for the quantum critical behaviour. In other words, for *this* system the quantum and the classical critical behaviour should be the same: the mean field behaviour. We saw above that the mean field calculation gave the same value for the exponent β : one half.

We found that the susceptibility critical exponent γ had the value 1 for the mean field Ising ferromagnet. So we conclude that for LiHoF_4 both the classical and the quantum value of the exponent γ should have the value 1. Fig. 4.55 below [24] shows susceptibility measurements in the vicinity of both the classical and the quantum critical points. The lines through the data both have a slope of -1 indicating $\gamma = 1$ in both cases.

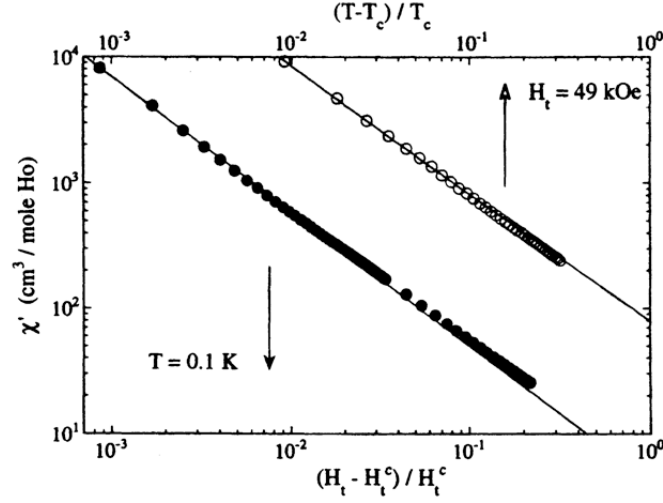


Figure 4.55: Quantum (below) and classical (above) critical behaviour of LiHoF_4 . (After xxxxxxxxxxxxxx).

4.9 Retrospective

We have now completed our survey of different types of phase transitions. You will have observed similarities between systems and you will have observed differences. In this final section we shall look back over the various examples considered and we shall make some general observations and comments.

4.9.1 The existence of order

Ising discovered that his model exhibited no phase transition in one dimension. In other words, in the one-dimensional Ising model displays long-range order only at $T = 0$. Onsager discovered that the Ising model did have a phase transition in two dimensions. In other words the Ising model has a transition to an ordered state at finite temperatures in two (and higher) dimensions.

Somewhat surprisingly, Mermin and Wagner [26] argued that the Heisenberg model would not exhibit long-range order in two, but it would in three and higher dimensions. Thus the Ising model has a transition in two dimensions but the Heisenberg model does not. Why should this be? The key difference is the dimensionality of the order parameter D . For the Ising model $D = 1$ while for the Heisenberg model $D = 3$. We also note that for the spherical model ($D = \infty$), Kac reached the same conclusions as for the

Heisenberg model.

The Mermin-Wagner theorem, sometimes attributed Berezinskii, Hohenberg or Peirls, states that there can be no long range order resulting from a broken continuous symmetry ($D = 2$ or above) in two or lower spatial dimension. But there can be long range order resulting from a broken discrete symmetry ($D = 1$) in a system of two spatial dimensions – the Ising model is an example of this. However in one spatial dimension there can be no long range order at all. This may be established by an energy–entropy argument similar to that in Section 4.4.3 above for the 1d Ising model. We may summarise as follows:

1. For $d \geq 3$ you can always have an ordered phase – a broken discrete or continuous symmetry
2. For $d = 2$ you cannot break a continuous symmetry, only a discrete symmetry. So only the Ising model has a phase transition in 2d; there is no ordered phase for the Heisenberg model or the spherical model.
3. For $d = 1$ you can't break any symmetry; no ordered phase possible in 1d above $T = 0$.

The borderline case corresponds to $d = 2$ and $D = 2$. In this case it is possible to have *orientational* order; this is the Kosterlitz-Thouless [27] transition. Unfortunately this is outside the scope of this book. Fig. 4.56 indicates the various possibilities.

order parameter dimension		spatial dimension		
		$d = 1$	$d = 2$	$d = 3$
Ising model	$n = 1$	no order	long range order	no order
X-Y model	$n = 2$		orientational order	
Heisenberg	$n = 2$			
Spherical	$n = \infty$			

Figure 4.56: Dimensionality and order.

Finally we mention the question (using the magnetic description) of the magnitude of the spin vector. For a spin $S = 1/2$ each moment has one of

two projections along a given axis. For higher spin there will be a larger number of projections. The spin magnitude is another “dimension” which characterizes systems. Of particular importance, when $S \rightarrow \infty$ the moments are classical and there are no quantum effects.

4.9.2 Validity of mean field theory

In Section 4.8.7 we learned that for each system (hamiltonian) there is a marginal spatial dimensionality d^* such that when the number of dimensions is greater than d^* the results of mean field theory are exact. We have also seen that the spatial dimension is crucial in determining whether a system will undergo a phase transition. It is therefore surprising that the spatial dimension enters nowhere in the mean field modelling of phase transitions. In fact we saw that for a spatial dimension of four or greater the mean field description becomes exact.

It is usually the case that for short-range interactions the marginal dimensionality d^* is 4. However when the interactions have longer range, such as dipole or Coulomb interactions, then the marginal dimensionality can be less; an example is the dipole-coupled Ising system treated in Section 4.8.

There is, however, a practical question when considering the validity of mean field theory. How close to the transition must one be to observe the (possible) breakdown of mean field theory? There are some systems, such as superconductors, where one needs to be impossibly close to the transition to observe the breakdown. For such systems, experimentally, they *appear* to follow mean field behaviour even though $d^* = 4$. The Ginzburg criterion specifies how close one must be; an extensive discussion of all these issues is given in the paper by Als-Nielsen and Birgenau [25].

4.9.3 Features of Different Phase Transition Models

The main classification criterion we have used in discussing phase transitions has been the order of the transition: first order or second order. Recall that this is essentially a generalisation/abuse of Ehrenfest’s original classification; in reality we distinguish discontinuous and continuous transitions. The second classification related to whether the order parameter was conserved or non-conserved. During this chapter we have seen examples of all four possible combinations of these possibilities.

The liquid-gas transition is an example of a first order transition in a system with a conserved order parameter. This transition has a critical point, thus one observes a second order transition when travelling along the critical isochore. The solid-fluid transition is another example of a first order

Table 4.3: Some models and their critical exponents (Mattis [Statistical Mechanics made simple] Table 8.2) – But at the moment this table is repeated elsewhere – where should it be????

a	d	n	α	β	γ	δ	ν	η
2d Ising	2	1	0	1/8	7/4	15	1	1/4
3d Ising	3	1	0.1	0.33	5/4	4.8	0.63	0.04
3d XY	3	2	0.01	0.34	1.3	4.8	0.71	0.04
3d Heisenberg	3	3	-0.12	0.36	1.39	4.8	0.71	0.04
3d spherical	3	∞	-1	1/2	2	5	1	0
Mean field	any	any	0	1/2	1	3	1/2	0

transition in a system with a conserved order parameter. However in this case, because there is a change in symmetry between the phases, there is no critical point and the transition never becomes second order.

The ferromagnet and the ferroelectric are both examples of transitions with non-conserved order parameters. The ferroelectric transition can be either first order or second order, depending on the conditions. And the changeover is at the tricritical point. The ferromagnetic transition is second order. However there is no reason why such a transition may not become first order under the right circumstances. The table below summarises these and some other examples.

	First-order		Second-order	Symmetry broken
conserved order parameter	liquid–gas (but \exists critical point)	\rightarrow	liquid–gas along critical isochore	none
	binary alloy (but \exists critical point)	\rightarrow	binary alloy at critical concentration	none
	solid–fluid (no critical point)	\rightarrow	-----	translational invariance
non-conserved order parameter	-----		ferromagnet	rotational invariance
	ferroelectric at high pressure	tricritical \leftarrow point \rightarrow	ferroelectric at low pressure	inversion symmetry

mmmmmmmm

from Mattis: Statistical mechanics made simple and (spherical) nnnn

Table 4.4: 2d Potts model (Mattis Table 8.3)

Type	α	β	γ	δ	ν	η	kT_c/J	a
$q = 2$	0	1/8	7/4	15	1	1/4	2.27	a
$q = 2$	1/3	1/9	13/9	14	5/6	4/15	1.99	a
$q = 2$	2/3	1/12	7/6	15	2/3	1/4	1.82	a

$dE = dW + dQ$ bbb $dW = -pdV$ and $dQ = TdS$
 2d Potts model (Mattis)

Problems for Chapter 4

- 4.1 Obtain an expression for the Helmholtz free energy for the Weiss model in zero external magnetic field, in terms of the magnetization. Plot $F(M)$ for $T > T_c$, $T = T_c$ and $T < T_c$.
- 4.2 Show that $F = \frac{1}{2}Nk \left\{ (T - T_c)m^2 + \frac{1}{6}T_cm^4 + \dots \right\}$ for the Weiss model ferromagnet in the limit of small m . Explain the appearance of T_c in the m^4 term.
- 4.3 Show that $d^2F/d\varphi^2 > 0$ below T_c at the two roots $\varphi = \pm\sqrt{-F_2/2F_4}$ in the Landau model. Show that $d^2F/d\varphi^2 < 0$ below T_c and $d^2F/d\varphi^2 > 0$ above T_c at the single root $\varphi = 0$. What is the physical meaning of this?
- 4.4 In the Landau theory of second order transitions calculate the behaviour of the order parameter below the critical point, $\varphi(T)$, when the *sixth* order term in the free energy expansion is not discarded. What influence does this term have on the critical exponent β ? Comment on this.
- 4.5 A ferroelectric has a free energy of the form

$$F = \alpha(T - T_c)P^2 + bP^4 + cP^6 + DxP^2 + Ex^2$$

where P is the electric polarization and x represents the strain. Minimise the system with respect to x . Under what circumstances is there a first order phase transition for this system?

- 4.6 Consider a one-dimensional binary alloy where the concentration of A atoms varies slowly in space: $x = x(z)$. Show that the spatial variation of x results in an additional term in the free energy per bond proportional

to $a^2\varepsilon(dx/dz)^2$, where a is the spacing between atoms and ε is the energy parameter defined in Section 4.7.3. Determine the numerical coefficient.

- 4.7 Show that in the vicinity of the critical point the free energy of mixing of the binary alloy may be written as

$$F_m = F_0 + Nk \left\{ \frac{1}{2} (T - T_c) \varphi^2 + \frac{1}{12} T_c \varphi^4 + \frac{1}{30} T_c \varphi^6 + \dots \right\}$$

where $\varphi = 2x - 1$.

Discuss the Landau truncation of this expression; in particular, explain at which term the series may/should be terminated.

- 4.8 Plot some isotherms of the Clausius equation of state: $p(V - Nb) = NkT$. How do they differ from those of an ideal gas? Does this equation of state exhibit a critical point? Explain your reasoning.

- 4.9 The scaling expression for the reduced (magnetic) free energy is given in Section 4.1.9 by

$$f(T, B) = A |t|^{2-\alpha} Y \left(D \frac{B}{|t|^\Delta} \right).$$

Show that the heat capacity is given by

$$C \sim \frac{d^2 f(t, B)}{dt^2}$$

and hence identify α as the heat capacity critical exponent.

- 4.10 Using the scaling expression for the reduced free energy in the previous section, show that the magnetization is given by

$$M \sim \frac{df(t, B)}{dB}$$

and hence show that the order parameter exponent β is given by

$$\beta = 2 - \alpha - \Delta. \quad (4.9.1)$$

Show that the magnetic susceptibility is given by

$$\chi \sim \frac{d^2 f(t, B)}{dB^2} \quad (4.9.2)$$

and hence show that the susceptibility exponent γ is given by

$$\gamma = 2 - \alpha - 2\Delta. \quad (4.9.3)$$

- 4.11 Show that the Landau free energy has the scaling form of Problem 4.9 above, with $\alpha = 0$.
- 4.12 The discussion around Fig. 4.18 argued that the transition temperature of a ferromagnet could be estimated from measurements at high temperatures by plotting $1/\chi$ against temperature and extrapolating the line to the axis. While this is reliable for the mean field $\gamma = 1$ case, show that for the realistic case where $\gamma > 1$, the actual transition temperature will be lower than the mean field estimate. You should draw the Curie-Weiss line, as in Fig. 4.18, and note that it has slope of $\gamma = 1$. You should then show how low temperature deviations above and below $\gamma = 1$ alter the extrapolation to $1/\chi \rightarrow 0$.
- 4.13 Show that for a van der Waals fluid the critical parameters are given by $V_c = 3Nb$, $p_c = a/27b^2$, $kT_c = 8a/27b$. Express these critical quantities in terms of the microscopic interaction (Lennard-Jones) parameters ε and σ . ($V_c = 2\pi N\sigma^3$, $p_c = 4\varepsilon/27\pi\sigma^3$, $kT_c = 64\varepsilon/81$.)
- 4.14 Show that, for a van der Waals fluid the critical compressibility factor $z_c = p_c V_c / NkT_c$ has the value $3/8 = 0.375$.
- 4.15 Show that for the Dieterici fluid the critical parameters are given by $V_c = 2Nb$, $p_c = a/4b^2e^2$, $kT_c = a/4b$, and the critical compressibility factor has the value $z_c = 2/e^2 = 0.271$.
- 4.16 Show that for the Berthelot fluid the critical parameters are given by $V_c = 3Nb$, $p_c = \sqrt{a/b^3}/6\sqrt{6}$, $kT_c = (2/3)^{3/2}\sqrt{a/b}$, and the critical compressibility factor has the value $z_c = 3/8 = 0.375$.
- 4.17 Show that for the Redlich-Kwong fluid the critical parameters are given by $V_c = 3.847Nb$, $p_c = 0.0299a^{2/3}/b^{5/3}$, $kT_c = 0.345(a/b)^{2/3}$, and the critical compressibility factor has the value $z_c = 1/3 = 0.333$.

	van der Waals	Dieterici	Berthelot	Redlich-Kwong
equation	$(p + \frac{aN^2}{V^2})(V - Nb) = NkT$	$p(V - Nb) = NkTe^{-\frac{Na}{kTV}}$	$(p + \frac{aN^2}{kTV^2})(V - Nb) = NkT$	$p = \frac{NkT}{V - Nb} - \frac{aN^2}{\sqrt{kT}V(V + Nb)}$
p_c	$a/27b^2$	$a/4b^2e^2$	$\sqrt{a/b^3}/6\sqrt{6}$	$0.0299a^{2/3}/b^{5/3}$
kT_c	$8a/27b$	$a/4b$	$(2/3)^{3/2}\sqrt{a/b}$	$0.345(a/b)^{2/3}$
V_c	$3Nb$	$2Nb$	$3Nb$	$3.847Nb$
reduced equation	$(\pi + \frac{3}{v^2})(v - \frac{1}{3}) = \frac{8}{3}t$	$\pi(v - \frac{1}{2}) = \frac{1}{2}te^2e^{-2/tv}$	$(\pi + \frac{3}{tv^2})(v - \frac{1}{3}) = \frac{8}{3}t$	aaaaaaaa
z_c	$3/8 = 0.375$	$2/e^2 = 0.271$	$3/8 = 0.375$	$1/3 = 0.333$
kT_B	a/b	a/b	$\sqrt{a/b}$	$(a/b)^{2/3}$
kT_i	$2a/b$	$2a/b$	$\sqrt{3a/b}$	$(5a/2b)^{2/3}$
T_c/T_B	$8/27 = 0.296$	$1/4 = 0.250$	$(2/3)^{3/2} = 0.544$	0.345
T_i/T_B	2	2	$\sqrt{3} = 1.73$	$(5/2)^{2/3} = 1.84$

Extras

Infinite range spin interaction

$$\mathcal{H} = \sum_{i \neq j=1}^N \mathbf{S}_i \cdot \mathbf{S}_j \quad (4.9.4)$$

nnn

$$\begin{aligned} \mathcal{H} &= \sum_{i,j=1}^N \mathbf{S}_i \cdot \mathbf{S}_j - \sum_{i=1}^N \mathbf{S}_i^2 \\ &= \left(\sum_{i=1}^N \mathbf{S}_i \right) \cdot \left(\sum_{i=1}^N \mathbf{S}_i \right) - \left(\sum_{i=1}^N \mathbf{S}_i^2 \right) \end{aligned} \quad (4.9.5)$$

mm

$$\mathcal{H} = \mathbf{S}^2 - \sum_{i=1}^N \mathbf{S}_i^2 \quad (4.9.6)$$

Now

$$\mathbf{S}^2 = S(S+1)\hbar^2 \quad (4.9.7)$$

(Not sure if our convention requires the \hbar 's) Write $S = Ns$, then

$$\mathbf{S}^2 = Ns(Ns+1)\hbar^2 \quad (4.9.8)$$

and

$$\sum \mathbf{S}_i^2 = Ns(s+1)\hbar^2 \quad (4.9.9)$$

so

$$\mathcal{H} = \mathbf{S}^2 - \sum_{i=1}^N \mathbf{S}_i^2 = N(N-1)s^2\hbar^2 \quad (4.9.10)$$

And then, for $s = 1/2$

$$\mathcal{H} = N(N-1)\langle s^2 \rangle \hbar^2 \quad (4.9.11)$$

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