

## Chapter 3

# Mean Field and Landau Theory

In this chapter we begin our discussion of the statistical mechanics of systems that display a change in phase as a function of an intensive variable such as the temperature or the pressure. In recent years a great deal of progress has been achieved in our understanding of phase transitions, notably through the development of the renormalization group approach of Wilson, Fisher, Kadanoff, and others. We postpone a discussion of this theory until Chapters 6 and 7. In the present chapter we discuss an older approach known as mean field theory, which generally gives us a qualitative description of the phenomena of interest. We limit ourselves to discussing the most common approaches taken, and postpone our discussion of a number of important applications to Chapter 4. A common feature of mean field theories is the identification of an order parameter. One approach is to express an approximate free energy in terms of this parameter and minimize the free energy with respect to the order parameter (we have used this approach in Section 2.6 in connection with our discussion of Schottky defects in a crystal). Another, often equivalent approach is to approximate an interacting system by a noninteracting system in a self-consistent external field expressed in terms of the order parameter.

To understand the phenomena associated with the sudden changes in the material properties which take place during a phase transition, it has proven most useful to work with simplified models that single out the essential aspects of the problem. One important such model, the Ising model, is introduced

in Section 3.1 and discussed in the Weiss molecular field approximation, an example of the self-consistent field approach mentioned earlier. In Section 3.2 we discuss the same model in the Bragg–Williams approximation, which is a free energy minimization approach.

In Section 3.3 we point out that while very useful, mean field theories can give rise to misleading results, particularly in low dimensional problems. In Section 3.4 we discuss an improved version of mean field theory, the Bethe approximation. This method gives better numerical values for the critical temperature and other properties of the system. However, we show in Section 3.5 that the asymptotic critical behavior of mean field theories is always the same.

The most serious fault of mean field theories lies in the neglect of long-range fluctuations of the order parameter. As we shall see, the importance of this omission depends very much on the dimensionality of the problem, and in problems involving one- and two-dimensional systems the results predicted by mean field theory are often qualitatively wrong. In Section 3.6 we illustrate this by discussing properties of the exact solution to the one dimensional Ising model.

Because of its close relation to mean field theory we discuss in Section 3.7 the Landau theory of phase transitions. Symmetry considerations are in general important in determining the order of a transition, and we show in Section 3.8 that the presence of a cubic term in the order parameter will in general predict that phase transitions are first order (discontinuous).

In Section 3.9 we extend the Landau theory to the case where more than one thermodynamic quantity can be varied independently, and discuss the occurrence of tricritical points. In Section 3.10 we discuss the limitations of mean field theory and derive the Ginzburg criterion for the relevance of fluctuations. We conclude our discussion of Landau theory in Section 3.11 by considering multicomponent order parameters which are needed for a discussion of the Heisenberg ferromagnet and other systems.

An important reference for much of the material in this chapter is Landau and Lifshitz [165]. Many examples are discussed in Kubo et al. [161].

### 3.1 Mean Field Theory of the Ising Model

We consider here a simple model, known as the Ising model, for a magnetic material. We assume that  $N$  magnetic atoms are located on a regular lattice, with the magnetic moments interacting with each other through an exchange

interaction of the form

$$H_{Ising} = -J_0 \sum_{\langle ij \rangle} S_{zi} S_{zj} \quad (3.1)$$

where  $J_0$  is a constant and the symbol  $\langle ij \rangle$  denotes that the sum is to be carried out over nearest-neighbor pairs of lattice sites. This exchange interaction has a preferred direction, so that the Ising Hamiltonian is diagonal in the representation in which each spin  $S_{zj}$  is diagonal. The  $z$  component of the spins then takes on the discrete values  $-S, -S + \hbar, \dots, S$ . The eigenstates of (3.1) are labeled by the values of  $S_{zj}$  on each site, and the model has no dynamics. This makes it easier to work with than the Heisenberg model,

$$H = -J_0 \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j \quad (3.2)$$

where the local spin operators  $S_{\alpha j}$  do not commute with  $H$ . We specialize to the case  $S = \frac{1}{2}\hbar$ , and also add a Zeeman term for the energy in a magnetic field directed along the  $z$  direction to obtain the final version of the Ising Hamiltonian (which in accordance with the definitions in Chapter 1 should be considered as an enthalpy, but in conformity with common usage will be referred to as an energy),

$$H = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i \quad (3.3)$$

where  $\sigma_i = \pm 1$  and  $h$  is proportional to the magnetic field, but has the unit of energy. To obtain an intuitive feeling for the behavior of such a system, consider the limits  $T \rightarrow 0$  and  $T \rightarrow \infty$  for the temperature in the case  $J > 0$ . At  $T = 0$  the system will be in its ground state, with all spins pointing in the direction of the applied field. At  $T = \infty$  the entropy dominates and the spins will be randomly oriented. In certain cases the two regimes will be separated by a *phase transition*, that is, there will be a temperature  $T_c$  at which there is a sudden change from an ordered phase to a disordered phase as the temperature is increased. Suppose that at a certain temperature the expectation value of the magnetization is  $m$ , that is,

$$\langle \sigma_i \rangle = m \quad (3.4)$$

for all  $i$ . We refer to  $m$  as the *order parameter* of the system. Consider the terms in (3.3) which contain a particular spin  $\sigma_0$ . These terms are, with  $j$

restricted to nearest neighbor sites of site 0,

$$\begin{aligned} H(\sigma_0) &= -\sigma_0 \left( J \sum_j \sigma_j + h \right) \\ &= -\sigma_0 (qJm + h) - J\sigma_0 \sum_j (\sigma_j - m) \end{aligned} \quad (3.5)$$

where  $q$  is the number of nearest neighbors of site 0. If we disregard the second term on the right hand side in (3.5), we are left with a noninteracting system; that is, each spin is in an effective magnetic field composed of the applied field and an average exchange field due to the neighbors. The magnetization has to be determined self-consistently from the condition

$$m = \langle \sigma_0 \rangle = \langle \sigma_j \rangle . \quad (3.6)$$

This approximation constitutes a form of mean field theory—the fluctuating values of the exchange field are replaced by an effective average field—and is commonly referred to as the Weiss molecular field theory. We obtain the constitutive equation for  $m$

$$\begin{aligned} m &= \langle \sigma_0 \rangle = \frac{\text{Tr } \sigma_0 \exp\{-\beta H(\sigma_0)\}}{\text{Tr } \exp\{-\beta H(\sigma_0)\}} \\ &= \tanh[\beta(qJm + h)] . \end{aligned} \quad (3.7)$$

To find  $m(h, T)$  we must solve (3.7) numerically. However, it is easy to see that  $m(h, T) = -m(-h, T)$  and that for each  $h \neq 0$  there is at least one solution, and sometimes three. For  $h = 0$  there is always the solution  $m = 0$  and if  $\beta qJ > 1$ , two further solutions at  $\pm m_0$ . We will show in Section 3.2 that the equilibrium state for  $T < T_c = qJ/k_B$  is either of the *broken symmetry* states with spontaneous magnetization  $\pm m_0(T)$ . As  $T \rightarrow 0$ ,  $\tanh(\beta qJm) \rightarrow \pm 1$  for  $m \neq 0$ , and  $m_0 \rightarrow \pm 1$ . As  $T \rightarrow T_c$  from below,  $|m_0(T)|$  decreases and we may obtain its asymptotic dependence by making a low-order Taylor expansion of the hyperbolic tangent, that is

$$m_0 = \beta qJm_0 - \frac{1}{3}(\beta qJ)^3 m_0^3 + \dots \quad (3.8)$$

or

$$m_0(T) \approx \pm \sqrt{3} \left( \frac{T}{T_c} \right)^{3/2} \left( \frac{T_c}{T} - 1 \right)^{1/2} . \quad (3.9)$$

Therefore, we see that the order parameter  $m_0$  approaches zero in a singular fashion as  $T$  approaches  $T_c$  from below, vanishing asymptotically as

$$m_0(T) \propto \left( \frac{T_c}{T} - 1 \right)^{1/2}. \quad (3.10)$$

The exponent for the power law behavior of the order parameter is in general given the symbol  $\beta$  and in more sophisticated theories, as well as in real ferromagnets, is not the simple fraction  $\frac{1}{2}$  found here.

## 3.2 Bragg–Williams Approximation

An alternative approach to mean field theory is to construct an approximate expression for the free energy in terms of the order parameter and apply the condition that its equilibrium value minimizes the free energy. The Hamiltonian for the Ising model of the previous section can be written

$$H = -J(N_{++} + N_{--} - N_{+-}) - h(N_+ - N_-) \quad (3.11)$$

where  $N_{++}$ ,  $N_{--}$ ,  $N_{+-}$  are the number of nearest neighbor spins that are both +, both – or opposite, and the number of spins of each kind are

$$N_+ = \frac{N(1+m)}{2}; \quad N_- = \frac{N(1-m)}{2}. \quad (3.12)$$

We now assume that the states of the individual spins are *statistically independent*. This lets us write for the entropy

$$S = -k_B N \left( \frac{N_+}{N} \ln \frac{N_+}{N} + \frac{N_-}{N} \ln \frac{N_-}{N} \right) \quad (3.13)$$

and for the number of pairs

$$N_{++} = q \frac{N_+^2}{2N}; \quad N_{--} = q \frac{N_-^2}{2N}; \quad N_{+-} = q \frac{N_+ N_-}{N}. \quad (3.14)$$

Substituting (3.14) and (3.12) into (3.11) and (3.13) yields

$$G(h, T) = -\frac{qJN}{2} m^2 - Nhm + Nk_B T \left( \frac{1+m}{2} \ln \frac{1+m}{2} + \frac{1-m}{2} \ln \frac{1-m}{2} \right).$$

Minimizing with respect to the variational parameter  $m$ , we obtain

$$0 = -qJm - h + \frac{1}{2} k_B T \ln \frac{1+m}{1-m} \quad (3.15)$$

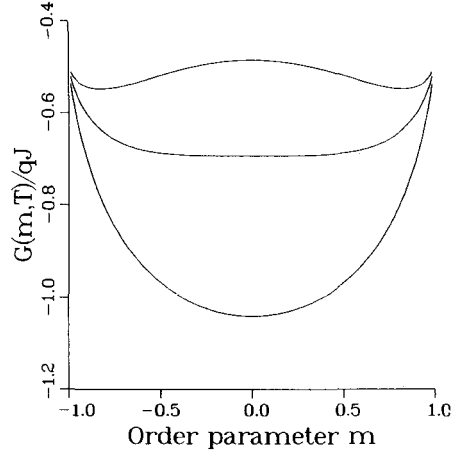


Figure 3.1: Free energy in the Bragg–Williams approximation for the Ising model. The three curves correspond to, respectively,  $T = 1.5T_c$ ,  $T = T_c$ , and  $T = 0.77T_c$ .

or

$$m = \tanh[\beta(qJm + h)] \quad (3.16)$$

as in the previous approach (3.7). In the special case  $h = 0$  the free energy becomes

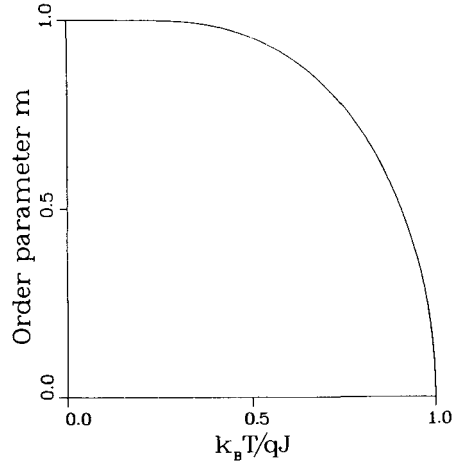
$$G(0, T)/N = -\frac{1}{2}qJm^2 + \frac{1}{2}k_B T [(1+m) \ln(1+m) + (1-m) \ln(1-m) - 2 \ln 2].$$

For small values of  $m$  we may expand in a power series to obtain

$$G(0, T)/N = \frac{m^2}{2}(k_B T - qJ) + \frac{k_B T}{12}m^4 + \dots - k_B T \ln 2 \quad (3.17)$$

with all higher order terms of even power in  $m$  with positive coefficients. The form of  $G(0, T)$  is shown for  $T$  above and below  $T_c = qJ/k_B$  in Figure 3.1. It is clear that the ordered phase is the state of lower free energy when  $T < T_c$ .

The type of transition seen in this system is known as *continuous*, or second order, since the order parameter increases continuously from zero as a function of  $(T_c - T)$  below the transition (Figure 3.2). We shall encounter examples of discontinuous, or first-order, transitions later in this chapter.

Figure 3.2: Temperature dependence of order parameter below  $T_c$ .

### 3.3 A Word of Warning

The theory presented above is remarkably general. Note that neither the type of lattice nor the spatial dimensionality plays a role in the transition—the sole parameter characterizing the system is the number,  $q$ , of nearest neighbors. Therefore, in this approximation, the Ising models on the two-dimensional triangular lattice and the three-dimensional simple cubic lattice have identical properties. This result is quite incorrect and we demonstrate below how one can be misled by mean field arguments.

Consider a one-dimensional chain with free ends. The Hamiltonian in zero field is

$$H = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} \quad (3.18)$$

with ground state energy  $E_0 = -(N-1)J$ . Suppose that the system is at a very low temperature and consider the class of excitations defined by  $\sigma_i = 1$ ,  $i \leq l$  and  $\sigma_i = -1$ ,  $i > l$ :

$$\begin{array}{cccccccc} \uparrow & \uparrow & \cdots & \uparrow & \downarrow & \downarrow & \cdots & \downarrow \\ 1 & 2 & & l & l+1 & & & N \end{array}$$

There are  $N-1$  such states, all with the same energy  $E = E_0 + 2J$ . At temperature  $T$  the free energy change due to these excitations is

$$\Delta G = 2J - k_B T \ln(N-1)$$

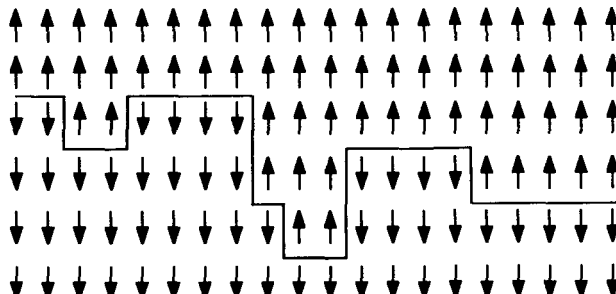


Figure 3.3: Domain wall in a two-dimensional Ising model.

which is less than zero for all  $T > 0$  in the limit  $N \rightarrow \infty$ . These excitations disorder the system; the expectation value of the magnetization is zero. Therefore, there cannot be a phase transition to a ferromagnetic state in the one-dimensional Ising model with nearest-neighbor (or with any finite-range) interactions.

A similar argument can be used to give a crude estimate of the transition temperature for the two-dimensional Ising model. Consider an  $N \times N$  square lattice with free surfaces. We wish to study the set of excitations of the type shown in Figure 3.3, that is, excitations which divide the lattice into two large domains separated by a wall that extends from one side to the other and has no loops. The energy of the domain wall is

$$\Delta E = 2LJ$$

where  $L$  is the number of segments in the wall. If we start the wall from the left there are at least two, sometimes three choices for the direction of the next step if we neglect the possibility of reaching the upper and lower boundaries. The entropy associated with non-looping chains of length  $L$  is then at least  $k_B \ln 2^L$ . There are  $N$  possible starting points for the chain. If we assume two choices per site, one of which takes us to the right, the average length of the chain will be  $2N$  with a standard deviation  $\propto N^{1/2}$ , which is small compared to  $N$  if  $N$  is large enough. The free energy associated with dividing the lattice into two domains is thus approximately

$$\Delta G \approx 4NJ - k_B T \ln(N \times 2^{2N}).$$

The system is therefore stable against domain formation if

$$T < T_c \approx \frac{2J}{k_B \ln 2} = \frac{2.885J \dots}{k_B}.$$

This estimate is surprisingly close to the exact result (see Section 6.1)  $T_c = 2.269185\dots J/k_B$ .

A more sophisticated version of this type of argument was first devised by Peierls<sup>1</sup> [237] to prove that in two dimensions a phase transition indeed occurs. The one-dimensional argument was presented here to raise a warning flag—mean field arguments, although useful, are not invariably correct. We return to this topic in Section 3.6, where we discuss some exact properties of the Ising model in one dimension.

### 3.4 Bethe Approximation

In this section we wish to consider an approximation scheme due to Bethe [35]. An extension of the approach, which provides the same results for the order parameter but also yields an expression for the free energy, is due to Fowler and Guggenheim [101].

Consider again the simple Ising model (3.3) of Section 3.1. In our mean field approximation we ignored all correlations between spins and, even for nearest neighbors, made the approximation  $\langle \sigma_i \sigma_j \rangle = \langle \sigma_i \rangle \langle \sigma_j \rangle = m^2$ . It is possible to improve this approximation in a systematic fashion. We suppose that the lattice has coordination number  $q$  and now retain as variables a central spin and its shell of nearest neighbors. The remainder of the lattice is assumed to act on the nearest-neighbor shell through an effective exchange field which we will calculate self-consistently. The energy of the central cluster can be written as

$$H_c = -J\sigma_0 \sum_{j=1}^q \sigma_j - h\sigma_0 - h' \sum_{j=1}^q \sigma_j .$$

The situation is depicted in Figure 3.4 for the square lattice. The fluctuating field acting on the peripheral spins  $\sigma_1 \dots, \sigma_4$  has been replaced by an effective field  $h'$ , just as we previously replaced the interaction of  $\sigma_0$  with its first neighbor shell by a mean energy.

The partition function of the cluster is given by

$$Z_c = \sum_{\sigma_j = \pm 1} e^{-\beta H_c} = e^{\beta h} (2 \cosh[\beta(J + h')])^q + e^{-\beta h} (2 \cosh[\beta(J - h')])^q .$$

---

<sup>1</sup>A clear exposition of the arguments is also given in Section 15.4 of [318].

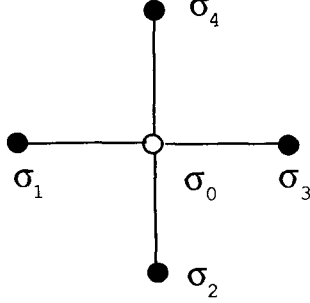


Figure 3.4: Spin cluster used in the Bethe approximation calculation.

The expectation value  $\langle \sigma_0 \rangle$  is given by

$$\langle \sigma_0 \rangle = \frac{1}{Z_c} (e^{\beta h} \{2 \cosh[\beta(J + h')]\}^q - e^{-\beta h} \{2 \cosh[\beta(J - h')]\}^q)$$

while for  $j = 1, \dots, q$ ,

$$\begin{aligned} \langle \sigma_j \rangle = \frac{1}{Z_c} & (2e^{\beta h} \sinh[\beta(J + h')] \{2 \cosh[\beta(J + h')]\}^{q-1} \\ & - 2e^{-\beta h} \sinh[\beta(J - h')] \{2 \cosh[\beta(J - h')]\}^{q-1}) . \end{aligned} \quad (3.19)$$

For simplicity we now set  $h = 0$ . Since the ferromagnet is translationally invariant we must require  $\langle \sigma_j \rangle = \langle \sigma_0 \rangle$ . This yields the equation

$$\begin{aligned} \cosh^q[\beta(J + h')] - \cosh^q[\beta(J - h')] = \\ \sinh[\beta(J + h')] \cosh^{q-1}[\beta(J + h')] - \sinh[\beta(J - h')] \cosh^{q-1}[\beta(J - h')] \end{aligned}$$

or

$$\frac{\cosh^{q-1}[\beta(J + h')]}{\cosh^{q-1}[\beta(J - h')]} = e^{2\beta h'} \quad (3.20)$$

which must be solved for the unknown effective field  $h'$ . It is clear that equation (3.20) always has a solution  $h' = 0$  corresponding to the disordered high-temperature phase. As  $h' \rightarrow \infty$  the left side of (3.20) approaches  $\exp(2\beta J(q-1))$ , *i.e.* a constant, while the right side diverges. Therefore, if the slope of the function on the left at  $h' = 0$  is greater than  $2\beta$  the two functions must intersect again at finite  $h'$ . Since (3.20) is invariant under  $h' \rightarrow -h'$ ,

there will be two further solutions in this case. The critical temperature, below which these solutions exist, is given by

$$\coth \beta_c J = q - 1$$

or

$$\beta_c J = \frac{1}{2} \ln \left( \frac{q}{q-2} \right) . \quad (3.21)$$

On the square lattice this yields  $k_B T_c / J = 2.885 \dots$ , which may be compared with the exact result  $k_B T_c / J = 2.269 \dots$  of Onsager [222] and the prediction  $k_B T_c / J = 4$  of the simple mean field theory of the preceding sections. We see that we have achieved a substantial improvement in the prediction of the critical temperature. It is interesting to note that for the one-dimensional Ising model ( $q = 2$ ) the Bethe approximation does not predict a phase transition. This is in agreement with the exact results of Section 3.6.

It is often important to have expressions for the free energy as well as the order parameter. We write the Hamiltonian (3.3) in the form

$$H = H_0 + \lambda V \quad (3.22)$$

where

$$H_0 = -h \sum_i \sigma_i \quad V = - \sum_{\langle ij \rangle} \sigma_i \sigma_j .$$

The physical system we wish to consider has  $\lambda = J$  but we can also imagine systems with different values of the exchange coupling strength. The free energy associated with (3.22) is

$$G = -k_B T \ln \text{Tr} e^{-\beta H_0 - \beta \lambda V} . \quad (3.23)$$

We define

$$G_0 \equiv -k_B T \ln \text{Tr} e^{-\beta H_0} \quad (3.24)$$

and

$$\langle \mathcal{O} \rangle_\lambda \equiv \frac{\text{Tr} \mathcal{O} e^{-\beta H_0 - \beta \lambda V}}{\text{Tr} e^{-\beta H_0 - \beta \lambda V}} \quad (3.25)$$

and see that

$$\frac{\partial G}{\partial \lambda} = \langle V \rangle_\lambda . \quad (3.26)$$

Finally,

$$G = G_0 + \int_0^J d\lambda \langle V \rangle_\lambda . \quad (3.27)$$

Equation (3.27) is exact if the expectation value  $\langle V \rangle_\lambda$  can be computed exactly. Useful approximations to the free energy can frequently be obtained by substituting approximate expressions into (3.27). As an example, consider the one-dimensional Ising model ( $q = 2$ ) in zero field. Then

$$G_0 = -Nk_B T \ln 2 . \quad (3.28)$$

There is no phase transition in this case and  $h' = 0$ . The Bethe approximation then corresponds to writing

$$\langle \sigma_i \sigma_j \rangle_\lambda = \frac{e^{\beta\lambda} - e^{-\beta\lambda}}{e^{\beta\lambda} + e^{-\beta\lambda}} = \tanh \beta\lambda \quad (3.29)$$

when  $i, j$  are nearest neighbors. We obtain

$$G = -Nk_B T \ln 2 - \frac{1}{2} Nq \int_0^J d\lambda \tanh \beta\lambda = -Nk_B T \ln(2 \cosh \beta J) .$$

As we shall see in Section 3.6, this happens to be exact, whereas in general the Bethe approach produces only approximate free energies.

It should be obvious that still better results can be obtained by considering larger clusters. However, all approximations that depend in an essential way on truncation of correlations beyond a certain distance will break down in the vicinity of a critical point. To show this explicitly, we discuss the critical properties of mean field theories in the next section.

### 3.5 Critical Behavior of Mean Field Theories

In Section 3.1 we showed that as  $T \rightarrow T_c$ , the order parameter (magnetization) of our Ising model has the asymptotic form (3.10)

$$m(T) \propto (T_c - T)^{1/2}$$

as  $T \rightarrow T_c$  from below. We now calculate several other thermodynamic functions in the vicinity of the critical point. Consider first the susceptibility per spin,

$$\chi(h, T) = \left( \frac{\partial m}{\partial h} \right)_T .$$

From (3.7) we obtain

$$\chi(0, T) = \frac{\beta}{\cosh^2(\beta q J m) - \beta q J} = \frac{1}{k_B(T - T_c)} \quad (3.30)$$

as  $T \rightarrow T_c^+$ . For  $T < T_c$  we use the asymptotic expansion for  $m$  to obtain

$$\chi(0, T) \approx \frac{1}{2k_B(T_c - T)} \quad (3.31)$$

and we see that the susceptibility diverges as the critical point is approached from either the low- or high-temperature side. It is conventional to write, for  $T$  near  $T_c$ ,

$$\chi(0, T) \approx A_{\pm} |T - T_c|^{-\gamma}$$

and we conclude that in our mean field theory,  $\gamma = 1$ . The exact solution of the two-dimensional Ising model (6.1) yields  $\gamma = 7/4$ ; for the three-dimensional Ising model,  $\gamma$  is not known exactly, but is approximately 1.25. This failure of mean field theory can be understood in terms of the following exact expression for the susceptibility:

$$\begin{aligned} \chi &= \left( \frac{\partial m}{\partial h} \right)_T = \frac{\partial}{\partial h} \left( \frac{\text{Tr } \sigma_0 e^{-\beta H}}{\text{Tr } e^{-\beta H}} \right)_T \\ &= \beta \sum_j \langle (\sigma_j \sigma_0) - \langle \sigma_j \rangle \langle \sigma_0 \rangle \rangle . \end{aligned} \quad (3.32)$$

It is clear that  $\chi$  can diverge only if the *spin-spin correlation function*

$$\Gamma(|\mathbf{r}_j - \mathbf{r}_0|) = \langle \sigma_j \sigma_0 \rangle - \langle \sigma_j \rangle \langle \sigma_0 \rangle$$

is long-ranged; for example, in three dimensions it must not decay faster than

$$\frac{1}{|\mathbf{r}_j - \mathbf{r}_0|^3}$$

for large separations at  $T = T_c$ . In our simple mean field approximation, and also in the more sophisticated Bethe approximation, we clearly discarded long-range correlations, and it is therefore not surprising that finite cluster approximations will break down as  $T \rightarrow T_c$ .

Let us next examine the specific heat in both the simple mean field and the Bethe approximations. In zero magnetic field the internal energy in the mean field approximation of Sections 3.1 and 3.2 is given by

$$\begin{aligned} E = \langle H \rangle &= -J \sum_{\langle ij \rangle} \langle \sigma_i \rangle \langle \sigma_j \rangle \\ &= -\frac{N}{2} J q m^2 \end{aligned}$$

giving

$$C_h = \left( \frac{\partial E}{\partial T} \right)_{h=0} = \begin{cases} -\frac{N}{2} J q \left( \frac{\partial m^2}{\partial T} \right) \rightarrow \frac{3}{2} N k_B & \text{as } T \rightarrow T_c^- \\ 0 & \text{for } T > T_c \end{cases} \quad (3.33)$$

that is, the mean field theory produces a discontinuity at the transition. This behavior is in contrast to more correct theories and experimental results, which yield a power law of the form

$$C_h \approx B_{\pm} |T - T_c|^{-\alpha}$$

where  $\alpha$  is the conventional notation for the specific heat exponent.

The determination of the specific heat singularity in the Bethe approximation is somewhat more tedious. It is easy to show that the correlation function  $\langle \sigma_0 \sigma_j \rangle$  which determines the internal energy is given by

$$\langle \sigma_0 \sigma_j \rangle = \frac{\sinh \beta(J + h') \cosh^{q-1} \beta(J + h') + \sinh \beta(J - h') \cosh^{q-1} \beta(J - h')}{\cosh^q \beta(J + h') + \cosh^q \beta(J - h')}$$

if  $j$  is a nearest neighbor of site 0. For  $T > T_c$ ,  $h' = 0$  and

$$E = -\frac{N}{2} q J \langle \sigma_0 \sigma_j \rangle = -\frac{N}{2} q J \tanh \beta J .$$

For  $h' \neq 0$  we note that  $\langle \sigma_0 \sigma_j \rangle_{h'} = \langle \sigma_0 \sigma_j \rangle_{-h'}$  and we must therefore have

$$\langle \sigma_0 \sigma_j \rangle_{h'} = \langle \sigma_0 \sigma_j \rangle_{h'=0} + a(T) h'^2 + \dots .$$

The first piece of this expansion joins continuously with the high temperature form of the internal energy. The second term will yield a discontinuity at  $T_c$  if  $\partial h'^2 / \partial T$  approaches a constant as  $T \rightarrow T_c$ . We leave the explicit demonstration of this as an exercise (Problem 3.4). In a similar way it is possible to show that  $m(T) = \langle \sigma_0 \rangle \propto |T - T_c|^{1/2}$  in the Bethe approximation. The critical properties of cluster theories thus seem to be in a sense universal and not dependent on the level of sophistication of the approximation.

Another quantity that shows similar behavior in all mean field theories is the critical isotherm  $m(T_c, h)$ . In the simplest mean field theory we have (3.7)

$$m = \tanh[\beta(qJm + h)] .$$

At  $T = T_c = qJ/k_B$ , we obtain, on expanding the hyperbolic tangent,

$$m \approx m + \beta h - \frac{1}{3}(m + \beta h)^3$$

which gives, near  $h = 0$ ,

$$h \propto |m|^\delta \text{sign}(m)$$

with  $\delta = 3$ . We again leave it as an exercise for the reader to show that  $\delta = 3$  as well in the Bethe approximation. In Section 3.7 we discuss a general theory of phase transitions due to Landau which exhibits the same behavior as mean field and cluster theories near the critical point.

### 3.6 Ising Chain: Exact Solution

The one-dimensional Ising model is one of a small number of models in statistical mechanics for which one can calculate the partition function exactly. Moreover, the result is simple enough that thermodynamic functions can be evaluated without too much difficulty. Let us first consider a chain of length  $N$  with free ends and zero external field:

$$H = -J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} .$$

The partition function is given by

$$Z_N = \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \exp \left\{ \beta J \sum_{i=1}^{N-1} \sigma_i \sigma_{i+1} \right\} .$$

The last spin occurs only once in the sum in the exponential and we have, independently of the value of  $\sigma_{N-1}$ ,

$$\sum_{\sigma_N=\pm 1} e^{\beta J \sigma_{N-1} \sigma_N} = 2 \cosh \beta J$$

giving

$$Z_N = [2 \cosh \beta J] Z_{N-1} .$$

We can repeat this process to obtain

$$\begin{aligned} Z_N &= (2 \cosh \beta J)^{N-2} Z_2 \\ Z_2 &= \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} e^{\beta J \sigma_1 \sigma_2} = 4 \cosh \beta J \end{aligned}$$

so that we finally obtain

$$Z_N = 2(2 \cosh \beta J)^{N-1} . \quad (3.34)$$

The free energy is then

$$G = -k_B T \ln Z_N = -k_B T [\ln 2 + (N-1) \ln(2 \cosh \beta J)] .$$

In the thermodynamic limit only the term proportional to  $N$  is important and

$$G = -N k_B T \ln(2 \cosh \beta J) . \quad (3.35)$$

We can also find the free energy in the presence of a magnetic field. To avoid end effects (which do not matter in the thermodynamic limit) we assume periodic boundary conditions, that is, assume that the  $N$ 'th spin is connected to the first so that the chain forms a ring. Then

$$H = -J \sum_{i=1}^N \sigma_i \sigma_{i+1} - h \sum_{i=1}^N \sigma_i$$

where the spin labels run modulo  $N$  (i.e.,  $N+i=i$ ). The Hamiltonian can be rewritten

$$H = - \sum_{i=1}^N \left[ J \sigma_i \sigma_{i+1} + \frac{h}{2} (\sigma_i + \sigma_{i+1}) \right]$$

giving for the partition function

$$\begin{aligned} Z_N &= \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \exp \left\{ \beta \sum_{i=1}^N \left[ J \sigma_i \sigma_{i+1} + \frac{h}{2} (\sigma_i + \sigma_{i+1}) \right] \right\} \\ &= \sum_{\sigma_i} \prod_{i=1}^N \exp \left\{ \beta \left[ J \sigma_i \sigma_{i+1} + \frac{h}{2} (\sigma_i + \sigma_{i+1}) \right] \right\} . \end{aligned}$$

It is convenient to introduce the  $2 \times 2$  transfer matrix

$$\mathbf{P} = \begin{bmatrix} P_{11} & P_{1-1} \\ P_{-11} & P_{-1-1} \end{bmatrix}$$

where

$$\begin{aligned} P_{11} &= e^{\beta(J+h)} \\ P_{-1-1} &= e^{\beta(J-h)} \\ P_{-11} &= P_{1-1} = e^{-\beta J} . \end{aligned}$$

We may now use this to express the partition function in terms of a product of these matrices:

$$Z_N = \sum_{\{\sigma_i\}} P_{\sigma_1 \sigma_2} P_{\sigma_2 \sigma_3} \cdots P_{\sigma_N \sigma_1} = \text{Tr} \mathbf{P}^N .$$

The matrix  $\mathbf{P}$  can be diagonalized and the eigenvalues  $\lambda_1$  and  $\lambda_2$  are the roots of the secular determinant

$$|\mathbf{P} - \lambda\mathbf{I}| = 0. \quad (3.36)$$

Similarly, the matrix  $\mathbf{P}^N$  has eigenvalues  $\lambda_1^N$ ,  $\lambda_2^N$  and the trace of  $\mathbf{P}^N$  is the sum of the eigenvalues:

$$Z_N = \lambda_1^N + \lambda_2^N.$$

The solution of (3.36) is

$$\lambda_{1,2} = e^{\beta J} \cosh \beta h \pm \sqrt{e^{2\beta J} \sinh^2 \beta h + e^{-2\beta J}}.$$

We note that  $\lambda_1$ , associated with the positive root, is always larger than  $\lambda_2$ . The free energy is

$$\begin{aligned} G &= -k_B T \ln(\lambda_1^N + \lambda_2^N) = -k_B T \left\{ N \ln \lambda_1 + \ln \left[ 1 + \left( \frac{\lambda_2}{\lambda_1} \right)^N \right] \right\} \\ &\rightarrow -N k_B T \ln \lambda_1 \quad \text{as } N \rightarrow \infty. \end{aligned}$$

This gives for the free energy in the thermodynamic limit,

$$G = -N k_B T \ln \left[ e^{\beta J} \cosh \beta h + \sqrt{e^{2\beta J} \sinh^2 \beta h + e^{-2\beta J}} \right]. \quad (3.37)$$

For the special case  $h = 0$  we obtain the previous result (3.35). We may compute the magnetization from

$$m = \langle \sigma_0 \rangle = -\frac{1}{N} \frac{\partial G}{\partial h} = \frac{k_B T}{\lambda_1} \frac{\partial \lambda_1}{\partial h}.$$

After some straightforward manipulations we find

$$m = \frac{\sinh \beta h}{\sqrt{\sinh^2 \beta h + e^{-4\beta J}}}. \quad (3.38)$$

We see that for  $h = 0$  there is no spontaneous magnetization at any nonzero temperature. However, in the limit of low temperatures

$$\sinh^2 \beta h \gg e^{-4\beta J}$$

for any  $h \neq 0$  and only a very small field is needed to produce saturation of the magnetization. The zero-field free energy will, in the limit  $T \rightarrow 0$ , approach the value  $G(T \rightarrow 0) = -NJ$  corresponding to completely aligned spins. We can thus say that we have a phase transition at  $T = 0$ , while for  $T \neq 0$  the free

energy is an analytic function of its variables. This behavior contrasts with that of mean field (Section 3.1) or Bragg–Williams approximations (Section 3.2) in which a coexistence line extending from  $T = 0$  to  $T = T_c$  separates regions of positive and negative order parameter, with a discontinuity of the order parameter across the line. It is interesting to compare in more detail the exact and the mean field solution. For this reason we plot in Figure 3.5 the energy calculated exactly and in the Bragg–Williams approximation for different values of the external field. In Figure 3.6 we plot the susceptibility for different fields, as a function of temperature, in the two approximations, while the specific heat is shown in Figure 3.7. Results from the Bethe approximation are not shown since they agree with the exact ones in this case.

In Sections 3.4 and 3.5 we introduced the pair distribution function

$$g(j) = \langle \sigma_0 \sigma_j \rangle$$

and argued that in mean field theories one neglects long-range correlations between spins. In the simplest mean field theory, one makes the approximation

$$\langle \sigma_0 \sigma_j \rangle = \langle \sigma_0 \rangle \langle \sigma_j \rangle .$$

The error introduced by this approximation can be analyzed by studying the spin-spin correlation function

$$\Gamma(j) = \langle \sigma_i \sigma_{i+j} \rangle - \langle \sigma_i \rangle \langle \sigma_{i+j} \rangle$$

which can be calculated quite straightforwardly for the Ising chain. For simplicity we consider only the zero-field case ( $h = 0$ ). Since there is no spin ordering for  $T \neq 0$  we have  $\langle \sigma_l \rangle = 0$  and  $\Gamma(j) = g(j)$  in this case. We assume an Ising chain with free ends and assume that the spins  $\sigma_i, \sigma_{i+j}$  are far from the ends. We also let the exchange energy between spins  $l$  and  $l + 1$  be a variable  $J_l$  which will be set equal to a constant,  $J$ , at the end of the calculation. We have

$$\langle \sigma_i \sigma_{i+j} \rangle = \frac{1}{Z_N} \sum_{\{\sigma_l\}} \sigma_i \sigma_{i+j} \exp \left\{ \beta \sum_{l=1}^{N-1} J_l \sigma_l \sigma_{l+1} \right\}$$

and from (3.34)

$$Z_N = 2 \prod_{l=1}^{N-1} (2 \cosh \beta J_l) .$$

Since  $\sigma_i^2 = 1$ ,

$$\langle \sigma_i \sigma_{i+j} \rangle = \frac{1}{Z_N} \sum_{\{\sigma_l\}} (\sigma_i \sigma_{i+1}) (\sigma_{i+1} \sigma_{i+2}) \cdots (\sigma_{i+j-1} \sigma_{i+j}) \exp \left\{ \beta \sum_{l=1}^{N-1} J_l \sigma_l \sigma_{l+1} \right\}$$

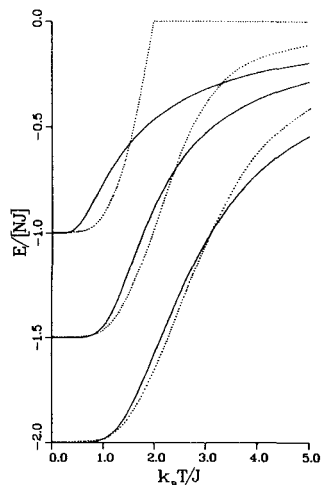


Figure 3.5: Comparison between exact and Bragg–Williams results for the internal energy of the one-dimensional Ising chain. Solid line, exact theory; dotted line, mean field theory. The three sets of curves correspond to  $h = 0$ ,  $h = 0.5J$ , and  $h = J$ , respectively.

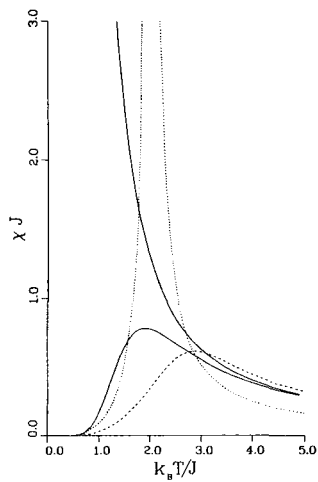


Figure 3.6: Comparison between exact (solid lines) and Bragg–Williams susceptibilities for a one-dimensional Ising chain. The two sets of curves correspond to  $h = 0$  and  $h = 0.5J$  respectively.

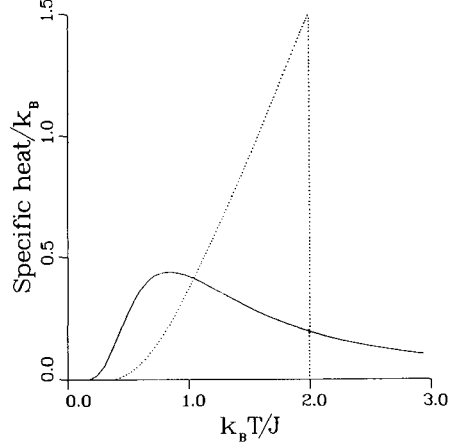


Figure 3.7: Specific heat calculated exactly (solid line) and in the Bragg-Williams approximation (dotted line) for the one-dimensional Ising chain. Only results for  $h = 0$  are shown. For  $h \neq 0$  the difference between the exact and approximate calculations is similar to that found for the susceptibility shown in Figure 3.6.

$$\begin{aligned}
 &= \frac{1}{Z_N \beta^j} \left. \frac{\partial^j Z_N(J_0 \cdots J_N)}{\partial J_i \cdots \partial J_{i+j-1}} \right|_{J_i=J} \\
 &= (\tanh \beta J)^j = e^{-j/\xi}
 \end{aligned} \tag{3.39}$$

where we have defined the *correlation length*  $\xi$  through

$$\xi = -[\ln(\tanh \beta J)]^{-1} .$$

Since  $\tanh \beta J < 1$ , we have  $\xi > 0$ , and the spin-spin correlation function decays exponentially with increasing  $j$  for all nonzero temperatures. The concept of correlation length will prove most useful later. At low temperatures

$$\ln(\tanh \beta J) \approx -e^{-2\beta J}$$

and we see that the correlation length can become quite large. The divergence of the correlation length at the critical point is a universal feature of continuous phase transitions.

### 3.7 Landau Theory of Phase Transitions

In 1936, Landau constructed a general theory of phase transitions. The crucial hypothesis is that in the vicinity of the critical point we may expand the free energy in a power series in the order parameter, which we denote by  $m$ . The equilibrium value of  $m$  is then the value that minimizes the free energy. It is worth pointing out immediately that the basic assumption, that the free energy is an analytic function of  $m$  at  $m = 0$ , is not correct. Nevertheless, Landau theory is of great utility as a qualitative tool and also plays an important role, after suitable generalization, in the modern renormalization theory of Wilson.

We begin by discussing a system in which the Gibbs free energy has the simple symmetry  $G(m, T) = G(-m, T)$ . We have tacitly assumed that the field  $h$ , which is conjugate to the order parameter  $m$ , is zero. With this symmetry the most general expansion of  $G(m, T)$  is

$$G(m, T) = a(T) + \frac{1}{2}b(T)m^2 + \frac{1}{4}c(T)m^4 + \frac{1}{6}d(T)m^6 + \dots, \quad (3.40)$$

where the fractional coefficients have been introduced in view of later manipulations. We have already encountered this type of expansion in the mean field treatment of the Ising model (Section 3.2), but formula (3.40) is more general than a specific instance of mean field theory.

The coefficients  $b(T)$ ,  $c(T)$ ,  $d(T) \dots$  are at this point unspecified, and we will investigate the consequences of different types of behavior of these functions. The first case we wish to consider is when  $c, d, e, \dots > 0$  and  $b(T)$  changes sign at some temperature  $T_c$ . We write

$$b(T) = b_0(T - T_c)$$

in the vicinity of  $T = T_c$ . In this case the function  $G(m, T)$  takes the form shown in Figure 3.8 for various values of  $T$ .

For  $T < T_c$  the point  $m = 0$  corresponds to a local maximum of the free energy, and the equilibrium state is one of the two states of spontaneously broken symmetry for which  $G$  has an absolute minimum. It is easy to work out the temperature dependence of the order parameter

$$\left(\frac{\partial G}{\partial m}\right)_T = 0 = bm + cm^3 + dm^5 + \dots$$

Ignoring the term  $dm^5$ , we find that

$$m \approx \pm \sqrt{\frac{b_0}{c(T_c)}} \sqrt{T_c - T}$$

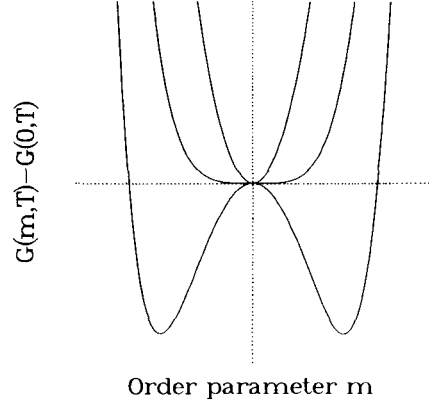


Figure 3.8: Free energy when  $c, d \dots > 0$  and  $b(T) = b_0(T - T_c)$ .

for  $T \rightarrow T_c^-$ . We may also obtain the behavior of the heat capacity

$$C = T \left( \frac{\partial S}{\partial T} \right).$$

We let a prime indicate differentiation with respect to  $T$  and obtain

$$S = -\frac{\partial G}{\partial T} = -a' - \frac{b'}{2}m^2 - \frac{c'}{4}m^4 - \dots - \frac{b}{2}(m^2)' - \frac{c}{4}(m^4)' - \dots.$$

As  $T \rightarrow T_c^-$

$$C \rightarrow -Ta'' - Tb'(m^2)' - \frac{Tc(m^4)''}{4}$$

where

$$\begin{aligned} (m^2)' &\rightarrow -\frac{b_0}{c} \\ b' &\rightarrow b_0 \\ (m^4)'' &\rightarrow \frac{2b_0}{c^2} \end{aligned}$$

giving

$$C \rightarrow \begin{cases} -Ta'' + Tb_0^2/2c & T \rightarrow T_c^- \\ -Ta'' & T \rightarrow T_c^+ \end{cases}.$$

We see that the order parameter and specific heat have the same form that we obtained previously in our mean field treatment of the Ising model.

We now consider a slightly different situation. Assume that  $c$  changes sign at some temperature, while  $d(T) > 0$  and  $b$  is a decreasing function of the

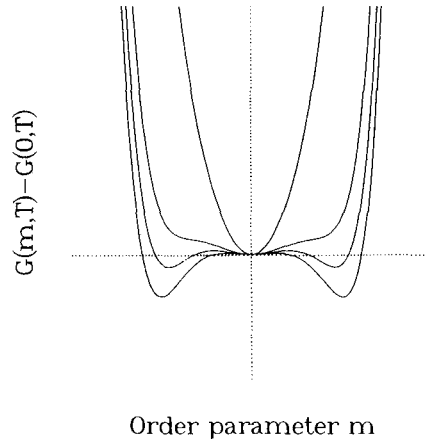


Figure 3.9: Free energy for a sequence of temperatures in the case that  $c(T)$  changes sign above the temperature at which  $b(T)$  changes sign.

temperature, but is still positive in the region of interest. The free energy in this case will be as shown in Figure 3.9. In this situation a discontinuous jump in the order parameter is expected. To see this, let  $m_0 \neq 0$  be the location of a minimum of  $G$ . We must show that when  $G(m_0, T_c) = G(0, T_c)$ ,  $b(T_c) > 0$ ; that is, there is a local, rather than global minimum at the point  $m = 0$ . The equilibrium condition is

$$\left. \frac{\partial G}{\partial m} \right|_{m_0} = 0 = bm_0 + cm_0^3 + dm_0^5 + \dots .$$

The phase transition occurs when

$$G(m_0) - G(0) = 0 = \frac{b}{2}m_0^2 + \frac{c}{4}m_0^4 + \frac{d}{6}m_0^6 .$$

Solving for the nontrivial value of  $m_0$ , we obtain

$$m_0^2 = -\frac{3c(T_c)}{4d} \quad (3.41)$$

and

$$b(T_c) = \frac{3c^2}{16d} > 0 \quad (3.42)$$

which justifies the claim that the first order transition occurs before a continuous transition can take place. The case where  $b$  and  $c$  approach zero at the same temperature seems at this stage rather unlikely. In Section 3.9 we

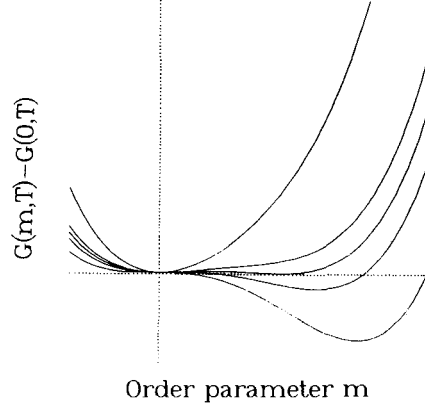


Figure 3.10: Free energy for different temperatures in the case where the Landau expansion contains a cubic term.

shall see that these special points can occur when the coefficients depend on other thermodynamic parameters besides the temperature and when there is competition between different ordered phases.

### 3.8 Symmetry Considerations

In this section we discuss the situation when  $G(m, T) \neq G(-m, T)$ ; that is, there are terms of odd order in  $m$  in the Landau expansion. Below, we shall illustrate this situation by considering the 3-state Potts model. A further example, the Maier Saupe model of nematic liquid crystals, will be considered in Section 4.2, but first consider the general case. Any term in the Landau expansion which is linear in the order parameter can be eliminated by making the transformation  $m \rightarrow m + \Delta$  and choosing  $\Delta$  to make the linear term vanish. We therefore assume that the leading term of odd order in  $m$  is cubic and write

$$G(m, T) = a(T) + \frac{1}{2}b(T)m^2 - \frac{1}{3}c(T)m^3 + \frac{1}{4}d(T)m^4 + \dots \quad (3.43)$$

We assume for stability that  $d(T) > 0$  and that  $c(T) > 0$ ;  $c(T) < 0$  corresponds simply to changing the sign of the order parameter. We also assume as before that  $b(T)$  is a decreasing function of  $T$  which changes sign at some temperature  $T^*$ . With these assumptions the free energy will have the general form shown in Figure 3.10.

As we shall see, a first-order transition will again preempt the second order transition. At the transition point  $T_c$  we have

$$G(m_0, T_c) = G(0, T_c)$$

and

$$\left. \frac{\partial G}{\partial m} \right|_{m_0} = 0 = bm_0 - cm_0^2 + dm_0^3 .$$

Solving, we obtain

$$m_0 = \frac{2c}{3d}$$

and

$$b(T_c) = \frac{2c^2}{9d} > 0 .$$

We see, therefore, that the appearance of a cubic term in the Landau expansion signals a first-order phase transition. This prediction of the theory has been found to hold for three-dimensional systems, but the result turns out to be incorrect in the case of the three-state Potts model in two dimensions (see Sections 3.8.1 and 7.5.2). This is another indication that mean field theory is not reliable for low-dimensional systems.

### 3.8.1 Potts model

An example that gives rise to a Landau expansion with cubic terms, indicating a first order transition, is the Potts model [248]. Consider a system of  $N$  spins, each of which can be in any of  $q$  states. Each spin only interacts with nearest neighbor spins of the same type as itself, and the interaction energy is negative. The Hamiltonian is

$$H = -J \sum_{\langle i,j \rangle} \delta_{S_i, S_j}$$

where  $J > 0$ .

For  $q = 2$  this is just the Ising model. We will restrict our attention to the case  $q = 3$ , and label the states  $A, B, C$ . Let  $n_A = N_A/N$ ,  $n_B = N_B/N$  and  $n_C = N_C/N$ . The free energy in the Bragg-Williams approximation is then

$$A = -\frac{qNJ}{2}[n_A^2 + n_B^2 + n_C^2] + Nk_B T[n_A \ln n_A + n_B \ln n_B + n_C \ln n_C] .$$

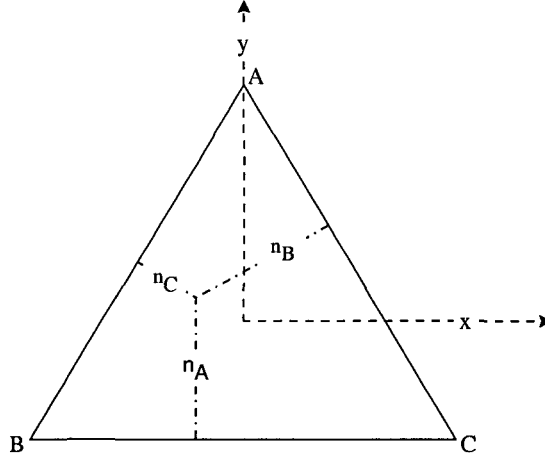


Figure 3.11: The allowed values of  $x, y$  are inside the triangle with corners  $(0,1)$ ,  $(\sqrt{3}/2, -1/2)$ ,  $(-\sqrt{3}/2, -1/2)$  corresponding to states of all  $A, B$  and  $C$  respectively.

In the disordered high temperature phase  $n_A = n_B = n_C = 1/3$ . In the general case the concentrations are subject to the constraint

$$n_A + n_B + n_C = 1 .$$

A possible parametrization is

$$\begin{aligned} n_A &= \frac{1}{3}(1 + 2y) \\ n_B &= \frac{1}{3}(1 + \sqrt{3}x - y) \\ n_C &= \frac{1}{3}(1 - \sqrt{3}x - y) \end{aligned} \quad (3.44)$$

with the allowed values restricted to being inside the equilateral triangle of Figure 3.11.

The possible ordered phases have preferential occupation of either the  $A, B$  or  $C$  state. Because of symmetry the free energy in the three cases will be the same, and to be specific we choose the order parameter to be of the form  $x = 0, y = m$ , with  $-1/2 \leq m \leq 1$ . We find for the free energy

$$A = -\frac{qNJ}{6}[1+2m^2] + Nk_B T \left[ \frac{2}{3}(1-m) \ln(1-m) + \frac{1}{3}(1+2m) \ln(1+2m) - \ln(3) \right] .$$

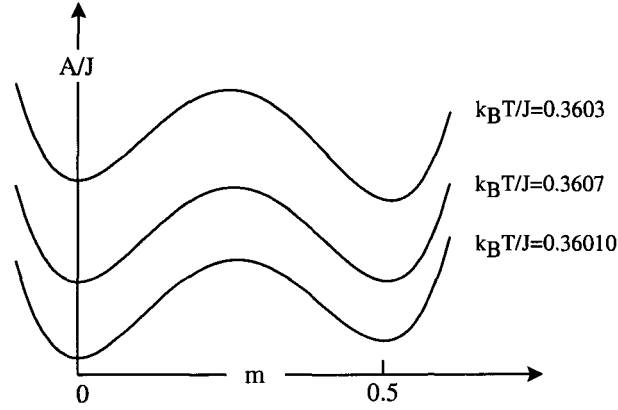


Figure 3.12: Free energy  $A/J$  plotted versus order parameter  $m$  for  $k_B T/J = 0.3603, 0.3607, 0.361$ , respectively. The value of  $y$  at the transition is seen to be close to  $1/2$ .

We next wish to show that the system, when cooled, will undergo a first-order transition at some temperature  $T_c$  as  $N \rightarrow \infty$  to a phase in which one of the three states  $A, B$  or  $C$  is selected in preference to the other two states.

The free energy has the power series expansion

$$\frac{A}{N} = -\frac{qJ}{6} - k_B T \ln(3) - \left(\frac{qJ}{3} - k_B T\right)m^2 - \frac{k_B T}{3}m^3 + \frac{k_B T}{2}m^4 + \dots$$

The presence of a cubic term indicates that the ordering transition will be first order. This result can be confirmed by plotting the free energy vs. the order parameter for some temperatures.

The transition temperature in units of  $J/k_B$  can be found numerically. In Figure 3.12 we show the free energy vs. the order parameter for values of  $T$  near the transition temperature. The order parameter  $y$  was found to be very close to  $1/2$  at the transition. This result turns out to be exact and we find the transition temperature to be

$$T_C = \frac{J}{4k_B \ln 2}.$$

At the transition we therefore have  $n_C = 2/3, n_A = n_B = 1/6$ .

Since the transition is first order it will be accompanied by latent heat. When  $m = 0$  the entropy per spin is  $k_B \ln 3$ . We find that for  $x = 0, y = 1/2$

the entropy per spin is  $\frac{k_B}{3} \ln \frac{27}{2}$ . We find then that the latent heat

$$L = T\Delta S = \frac{J}{12} .$$

We will come back to the 3-state Potts model in Section 7.5.2 where it is employed to model Helium monolayers on graphite at 1/3 coverage. In this case the dimensionality is  $d = 2$  and mean field theory gives misleading results; the actual transition is continuous, not first order. In higher dimension the mean field treatment given here will be qualitatively correct. A comprehensive review of the Potts model is given by Wu [330].

### 3.9 Landau Theory of Tricritical Points

In Section 3.7 we pointed out that it is conceivable that the coefficients  $b$  and  $c$  in the Landau expansion (3.40) may approach zero simultaneously and that this could lead to new types of critical behavior. This situation is likely to occur when there are more control parameters than just the temperature, and there is more than one order parameter. As an example we consider in Problem 3.13 a simple solvable model in which an elastic field is coupled to an Ising chain. In Section 4.3 we consider another system, the Blume–Emery–Griffiths model for  $^3\text{He}$ – $^4\text{He}$  mixtures. Other examples of systems exhibiting tricritical points are the antiferromagnet  $\text{FeCl}_2$ , which undergoes a continuous transition in low applied magnetic fields and a first-order transition to a mixed phase (coexisting antiferromagnetic and ferromagnetic phases) at sufficiently high magnetic fields; the solid  $\text{NH}_4\text{Cl}$ , whose orientational transition changes from second to first order as a function of pressure; the ferroelectric  $\text{KDPO}_4$ ; ternary liquid mixtures; and a number of liquid crystal systems. Below we discuss the general Landau approach. For a review of tricritical phenomena see Lawrie and Sarbach [167].

We denote, as is our practice, the order parameter of the system by  $m$  while  $h$  is the field that couples to  $m$ . The field that couples to the subsidiary order parameter  $x$  is denoted by  $\Delta$ . In the case of  $\text{FeCl}_2$ ,

$$m = M_Q = \sum_{\mathbf{r}} S_{\mathbf{r}} \exp\{i\mathbf{Q} \cdot \mathbf{r}\}$$

is a staggered magnetization, with  $S_{\mathbf{r}}$  the spin at site  $\mathbf{r}$ ,  $h$  a staggered magnetic field which is not realizable in the laboratory,  $x$  a uniform magnetization, and  $\Delta$  an applied uniform magnetic field. In the case of the uniaxial-biaxial transition

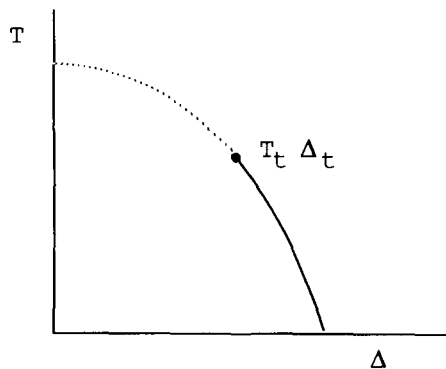


Figure 3.13: Phase behavior near a tricritical point. Solid line, first-order transitions; dotted line, critical points.

in liquid crystals,  $m$  and  $x$  are the order parameters  $P$  and  $Q$  of (4.24) and  $h$ ,  $\Delta$  two associated fields (*e.g.*, one electric and one magnetic) in two orthogonal directions (see Problem 4.4).

We assume the following form for the free energy:

$$\frac{G(m, \Delta, T)}{N} = a(T, \Delta) + \frac{1}{2}b(T, \Delta)m^2 + \frac{1}{4}c(T, \Delta)m^4 + \frac{1}{6}d(T, \Delta)m^6.$$

The line of critical points is given by  $b(T, \Delta) = 0$ , which defines a curve in the  $T-\Delta$  plane (Figure 3.13). The tricritical point is given by  $b(T, \Delta) = c(T, \Delta) = 0$ , which, in general, is a unique point  $(\Delta_t, T_t)$ .

We assume that when the temperature is lowered and  $\Delta > \Delta_t$ , the coefficient  $c$  becomes zero at a higher temperature than does  $b$ . The usual equations for first-order transitions will then apply. For  $\Delta < \Delta_t$ , the transition is continuous. We first show that the line of first-order transitions joins the line of critical points in a smooth fashion. The equation for the first-order line is given by (3.42)

$$b(\Delta, T) - \frac{3c^2(\Delta, T)}{16d(\Delta, T)} = 0. \quad (3.45)$$

The equation  $b(\Delta, T) = 0$  for the line of critical points yields for the slope of this line at  $b = 0$ ,

$$\left. \frac{d\Delta}{dT} \right|_{crit} = - \frac{\left. \frac{\partial b}{\partial T} \right|_{\Delta}}{\left. \frac{\partial b}{\partial \Delta} \right|_T} \equiv - \frac{b_T}{b_{\Delta}}. \quad (3.46)$$

We let the subscript indicate partial differentiation and find from (3.45) for the slope of the first-order line,

$$\left. \frac{d\Delta}{dT} \right|_{\text{first order}} = - \frac{b_T d + d_T b - \frac{3}{8} c c_T}{b_{\Delta} d + d_{\Delta} b - \frac{3}{8} c c_{\Delta}}. \quad (3.47)$$

As  $(T, \Delta) \rightarrow (T_t, \Delta_t)$ ,  $c \rightarrow 0$ ,  $b \rightarrow 0$ , and equations (3.46) and (3.47) become the same.

It is also easy to see that the first-order transition for  $\Delta > \Delta_t$ , implies coexistence of two phases with different values of the density  $x$ . We suppose that the expectation value of  $x$  may be obtained from the free energy through

$$x = - \frac{1}{N} \left. \frac{\partial G}{\partial \Delta} \right|_T \quad (3.48)$$

where the minus sign implies a suitable sign convention for  $\Delta$ . The first-order transition occurs when

$$G(m, T, \Delta) = G(0, T, \Delta) \quad (3.49)$$

and

$$\left. \frac{\partial G}{\partial m} \right|_{T, \Delta} = 0. \quad (3.50)$$

We leave it as an exercise to prove that (3.48)–(3.50) yield an equation for the discontinuity in  $x$ . As the tricritical point is approached along the first-order line, the discontinuity in  $x$  takes the form

$$\delta x = - \frac{3}{8d} (b_{\Delta} c + c_{\Delta} b) + \mathcal{O}(c^2) \quad (3.51)$$

where we have used (3.41). Therefore, in the  $T - x$  plane the phase diagram has the shape shown in Figure 3.14.

It is also of interest to calculate the asymptotic behavior of the order parameter and specific heat as the tricritical point is approached. Solving (3.50) we obtain

$$m^2 = \sqrt{\frac{c^2}{4d^2} - \frac{b}{d} - \frac{c}{2d}}. \quad (3.52)$$

There are two different asymptotic forms of this function, depending on how the tricritical point is approached. Since both  $b$  and  $c$  approach zero linearly, we expect that in most cases

$$\left| \frac{b}{d} \right| \gg \frac{c^2}{4d^2}.$$

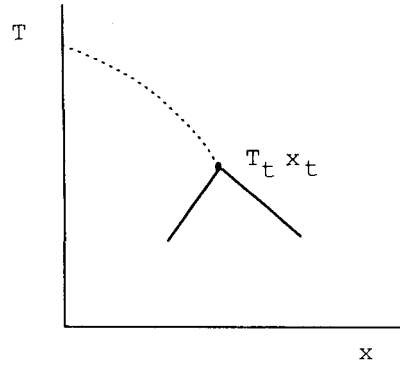


Figure 3.14: Phase diagram in the  $T - x$  plane near the tricritical point.

If  $b(T, \Delta) = b_0(T - T_t)$ , we obtain

$$m(T) \approx \left[ \frac{b_0}{d(T_t)} \right]^{1/4} (T_t - T)^{1/4} .$$

The exponent  $\beta$  at a tricritical point is therefore  $\frac{1}{4}$  rather than the value  $\frac{1}{2}$  found near a critical point. There is, however, a narrow region in the  $T - \Delta$  plane given by

$$\left| \frac{b}{d} \right| < \frac{c^2}{4d^2}$$

in which the asymptotic behavior given above does not hold. In this region all terms in (3.52) are proportional to  $T_t - T$  and

$$m \propto \sqrt{T_t - T} .$$

A rough sketch of the critical and tricritical regions is shown in Figure 3.15.

The exponents for a path of approach that lies in the tricritical region are often subscripted with a  $t$ , those for a path in the critical region with a  $u$ . Thus  $\beta_t = \frac{1}{4}$ ,  $\beta_u = \frac{1}{2}$ . We leave it as an exercise (Problem 3.12) to show that  $\gamma_u = 2$ ,  $\gamma_t = 1$ ,  $\alpha_t = \frac{1}{2}$ ,  $\alpha_u = -1$ . It is a remarkable fact that in three dimensions the predictions regarding the tricritical exponents are exact (to within logarithmic corrections [320]). In Section 3.10 we present self-consistency arguments which indicate the reasons for this result and which also show that the Landau–Ginzburg theory of critical points will be correct for spatial dimensionality  $d \geq 4$ .

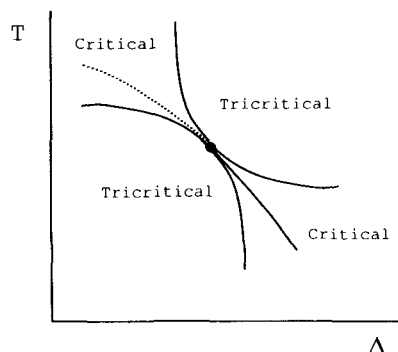


Figure 3.15: Critical and tricritical regions near a tricritical point.

### 3.10 Landau–Ginzburg Theory for Fluctuations

We have pointed out in Section 3.5 that the failure of mean field theories at a critical point is due to the neglect of long-range correlations. It is possible to generalize the Landau theory to incorporate fluctuations at least in an approximate fashion. Instead of the Gibbs free energy<sup>2</sup> which we have used throughout this chapter, we now make a Legendre transformation to a Helmholtz free energy which in the homogeneous case is  $A(M, T) = G + hM$  with  $dA = -SdT + hdM$ . We will allow the independent variable to depend on position

$$M = \int d^3r m(\mathbf{r})$$

and assume that the free energy can be written

$$A(\{m(\mathbf{r})\}, T) = \int d^3r \left\{ a(T) + \frac{b(T)}{2} m^2(\mathbf{r}) + \frac{c(T)}{4} m^4(\mathbf{r}) + \frac{d(T)}{6} m^6(\mathbf{r}) + \dots + \frac{f}{2} [\nabla m(\mathbf{r})]^2 \right\}. \quad (3.53)$$

<sup>2</sup>We could equally well use the Gibbs potential

$$G(\{h(\mathbf{r})\}, T, \{m(\mathbf{r})\}) = A - \int d^3r h(\mathbf{r})m(\mathbf{r})$$

and treat  $m(\mathbf{r})$  as a variational parameter. The resulting expressions (3.54)–(3.59) are identical.

The first three terms are a simple generalization of (3.40); the last term expresses the fact that the free energy is increased when the order parameter is not constant in space. The coefficient  $f$  can thus be assumed to be positive. We have in (3.53) expressed the free energy as a volume integral over the free-energy density. This is valid even for discrete systems, such as spins on a lattice, as long as  $m(\mathbf{r})$  varies significantly only over sufficiently large distances that we may “coarse grain” dynamical variables. Near a critical point this approximation will certainly be valid. However, the fundamental objection to the Landau theory of Section 3.7, namely that the free energy is not necessarily an analytic function of the order parameter, applies equally to the inhomogeneous form (3.53). In the homogeneous case we have

$$h = \left. \frac{\partial A}{\partial M} \right|_T .$$

In the inhomogeneous case the generalization is the functional derivative

$$h(\mathbf{r}) = \frac{\delta A}{\delta m(\mathbf{r})} .$$

We construct the variation of  $A$ ,

$$\delta A = \int d^3r \{ \delta m(\mathbf{r}) [bm(\mathbf{r}) + cm^3(\mathbf{r}) + dm^5(\mathbf{r}) + \dots] + f \nabla \delta m(\mathbf{r}) \cdot \nabla m(\mathbf{r}) \} .$$

The last term can be simplified by carrying out an integration by parts and demanding that  $\delta m(\mathbf{r}) = 0$  at the surface of the sample. We then obtain

$$h(\mathbf{r}) = bm(\mathbf{r}) + cm^3(\mathbf{r}) + dm^5(\mathbf{r}) + \dots - f \nabla^2 m(\mathbf{r}) . \quad (3.54)$$

From this equation we may recover the results of the homogeneous Landau theory by letting  $h(\mathbf{r}) = 0$  and  $\nabla m(\mathbf{r}) = 0$ . Near a second-order transition the (uniform) order parameter then obeys the equation

$$m_0^2 = -\frac{b}{c} \quad T < T_c \quad (3.55)$$

which is familiar from Section 3.7.

Imagine now that a localized perturbation  $h_0 \delta(\mathbf{r})$  is applied to the material. Equation (3.54) allows us to calculate the effect of this perturbation throughout the system. Let  $m(\mathbf{r}) = m_0(T) + \phi(\mathbf{r})$ . Neglecting nonlinear terms in  $\phi$  we write  $m^3(\mathbf{r}) = m_0^3 + 3m_0^2 \phi(\mathbf{r})$ . With these approximations we obtain

$$\nabla^2 \phi(\mathbf{r}) - \frac{b}{f} \phi(\mathbf{r}) - 3m_0^2 \frac{c}{f} \phi(\mathbf{r}) - \frac{b}{f} m_0 - \frac{c}{f} m_0^3 = -\frac{h_0}{f} \delta(\mathbf{r}) . \quad (3.56)$$

With  $m_0 = 0$  for  $T > T_c$ , and given by (3.55) for  $T < T_c$ , we find

$$\begin{aligned} \nabla^2 \phi - \frac{b}{f} \phi &= -\frac{h_0}{f} \delta(\mathbf{r}) & T > T_c \\ \nabla^2 \phi + 2\frac{b}{f} \phi &= -\frac{h_0}{f} \delta(\mathbf{r}) & T < T_c . \end{aligned} \quad (3.57)$$

In three dimensions, these equations are easily solved in spherical coordinates:

$$\phi = \frac{h_0}{4\pi f} \frac{e^{-r/\xi}}{r} \quad (3.58)$$

with

$$\begin{aligned} \xi(T) &= \sqrt{\frac{f}{b(T)}} & T > T_c \\ \xi(T) &= \sqrt{-\frac{f}{2b(T)}} & T < T_c . \end{aligned} \quad (3.59)$$

The function  $\xi(T)$  is the correlation length, and with

$$b(T) = b'(T - T_c)$$

we see that it diverges as  $T \rightarrow T_c$  from both the low- and high-temperature sides. In this theory

$$\xi(T) \propto |T - T_c|^{-1/2} .$$

Experimentally, and in more exact theories,

$$\xi(T) \propto |T - T_c|^{-\nu}$$

with the critical exponent  $\nu$  dependent on the model and the dimensionality.

We may relate the function  $\phi(\mathbf{r})$  to a correlation function. Assuming that a term

$$- \int d^3r m(\mathbf{r}) h(\mathbf{r})$$

is included in the Hamiltonian, we have

$$\langle m(\mathbf{r}) \rangle = \frac{\text{Tr } m(\mathbf{r}) \exp\{-\beta[H_0 - \int d^3r' h(\mathbf{r}') m(\mathbf{r}')] \}}{\text{Tr } \exp\{-\beta[H_0 - \int d^3r' h(\mathbf{r}') m(\mathbf{r}')] \}}$$

where  $H_0$  refers to the part of  $H$  which is independent of  $h(\mathbf{r})$ . We see that

$$\frac{\delta \langle m(\mathbf{r}) \rangle}{\delta h(0)} = \phi(\mathbf{r})/h_0 = \beta (\langle m(\mathbf{r}) m(0) \rangle - \langle m(\mathbf{r}) \rangle \langle m(0) \rangle) = \beta \Gamma(\mathbf{r}) . \quad (3.60)$$

The function  $\phi(\mathbf{r})$  is thus proportional to the order parameter–order parameter correlation function. The susceptibility (a similar expression holds for the compressibility in the case of a fluid) is given by

$$\chi = \beta \int d^3r \Gamma(\mathbf{r})$$

and it is easily seen that the usual mean field result

$$\chi \propto |T - T_c|^{-1}$$

is recovered.

The results obtained above allow us to establish a self-consistency criterion for mean field (or Landau) theories known as the Ginzburg criterion. We first generalize the analysis to systems of spatial dimensionality  $d$ . Equations (3.57) and (3.58) are quite general—one simply replaces the operator  $\nabla^2$  by the analogous  $d$ -dimensional operator and the  $\delta$ -function by the appropriate  $d$ -dimensional  $\delta$ -function. The solutions to (3.57)–(3.58) are generally not of the simple form (3.59). However, one can show that in arbitrary dimension,  $d$ , for  $r \ll \xi$ ,  $\phi \propto r^{-d+2}$ , while for  $r \gg \xi$ ,  $\phi \propto e^{-r/\xi}$ . For the purpose of order of magnitude estimates we can thus write

$$\phi(\mathbf{r}) \approx \frac{e^{-r/\xi}}{r^{d-2}}.$$

In mean field theories we always crudely approximate the correlation functions (3.60) at large distances. Therefore, one might expect that such approximations would be valid if the ratio

$$\frac{\int_{\Omega(\xi)} d^d r [\langle m(\mathbf{r})m(0) \rangle - \langle m(\mathbf{r}) \rangle \langle m(0) \rangle]}{\int_{\Omega(\xi)} d^d r m_0^2} \ll 1 \quad (3.61)$$

where the integral is carried out over a  $d$ -dimensional hypersphere of radius  $\xi$ . It is of interest to estimate the dimensionality  $d$  at which Landau theory correctly describes the critical behavior of the system. To do this we substitute the asymptotic form, as calculated from the Landau model, for the various functions appearing in (3.61). Substitution of

$$m_0^2 \approx |T - T_c|^{2\beta}$$

and

$$\langle m(\mathbf{r})m(0) \rangle - \langle m(\mathbf{r}) \rangle \langle m(0) \rangle \approx \frac{\exp\{-r/\xi\}}{r^{d-2}}$$

and carrying out the integration in spherical coordinates, we obtain the condition

$$\frac{Bd \int_0^\xi dr r^{d-1} e^{-r/\xi} r^{-(d-2)}}{B\xi^d |T - T_c|^{2\beta}} \ll 1 \quad (3.62)$$

where  $B r^d$  is the volume of a  $d$ -dimensional sphere of radius  $r$ . Letting  $r = \xi x$  in the numerator produces

$$\left( d \int_0^1 dx x e^{-x} \right) |T - T_c|^{d\nu - 2\beta - 2\nu} \ll 1 .$$

The first factor is simply a constant of order unity and the inequality will be satisfied as  $T \rightarrow T_c$ , if and only if  $d\nu - 2\beta - 2\nu > 0$ , or

$$d > 2 + \frac{2\beta}{\nu} . \quad (3.63)$$

At critical points the Landau theory yields  $\beta = \frac{1}{2}$ ,  $\nu = \frac{1}{2}$ , and we obtain  $d_c \geq 4$ . At tricritical points we have  $\beta_t = \frac{1}{4}$ ,  $\nu_t = \frac{1}{2}$ , and hence  $d_t \geq 3$ . The borderline values  $d_c = 4$  and  $d_t = 3$  are called *upper critical dimensionalities* and play an important role in the development of the renormalization group approach to critical phenomena. At these marginal dimensionalities there are small corrections to the Landau critical exponents. The Landau theory of tricritical points thus provides an excellent representation of the correct cooperative effect in three dimensions.

Another application of the Ginzburg criterion is that estimates of the correlation length can be used to determine the range of temperatures near  $T_c$  where critical fluctuations play an important role [146]. We return to this question in Section 11.3.4 where we argue that in the case of the BCS theory of superconductivity the temperature range is too small to be significant. On the other hand in the recently discovered high temperature superconductors fluctuations are quite significant in the critical region [147]. A further example of Landau–Ginzburg theory is given in Section 5.4 where we study properties of liquid–vapor interfaces.

### 3.11 Multicomponent Order Parameters: $n$ -Vector Model

In many cases of physical interest the ground state of the system has a degeneracy which is greater than the twofold degeneracy of the zero-field Ising model.

An example of such a system is the Heisenberg model with the Hamiltonian

$$H = - \sum_{i < j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (3.64)$$

in the absence of an applied field. The dynamical variables are the three-dimensional spin operators

$$\mathbf{S}_i = (S_{xi}, S_{yi}, S_{zi})$$

obeying the usual angular momentum commutation relations. The Hamiltonian (3.64) favors the parallel alignment of neighboring spins if  $J_{ij} > 0$ , and it is easily shown that the ground state has all the spins aligned in the same direction, which we label  $z$ ,  $S_{zi} = S$ . The Hamiltonian (3.64) is rotationally invariant in spin space, and the  $z$  direction may be taken to be any direction. The application of a magnetic field breaks this symmetry, but the nature of the correlated fluctuations that determine the critical behavior of the system depend essentially on the existence of rotational symmetry. In this section we only wish to demonstrate the appropriate generalizations of Landau theory to take such symmetries into account. The equilibrium state of the Heisenberg model may be expressed in terms of the three thermal expectation values

$$\begin{aligned} m_x &= \frac{1}{N} \left\langle \sum_i S_{xi} \right\rangle \\ m_y &= \frac{1}{N} \left\langle \sum_i S_{yi} \right\rangle \\ m_z &= \frac{1}{N} \left\langle \sum_i S_{zi} \right\rangle . \end{aligned}$$

The rotational symmetry of (3.64) can then be incorporated into the Landau theory by constructing an expansion that is invariant under arbitrary rotations of the vector  $\mathbf{m}$ , that is,

$$G = a + \frac{1}{2}b(T)(m_x^2 + m_y^2 + m_z^2) + \frac{1}{4}c(T)(m_x^2 + m_y^2 + m_z^2)^2 + \dots$$

The general  $n$ -vector model, in which the three-component order parameter of the Heisenberg model is replaced by an  $n$ -component order parameter, will thus have its Landau expansion in terms of the quantity

$$m^2 = \sum_{\alpha=1}^n m_\alpha^2 .$$

Similarly, in the case of a nematic liquid crystal where the order parameter is the symmetric and traceless tensor  $Q_{\alpha\beta}$  defined by (4.21), the Landau expansion must be expressible in terms of the two invariants which can be formed from such a tensor, namely

$$\sum_{\alpha,\beta} Q_{\alpha\beta} Q_{\beta\alpha} \\ \sum_{\alpha,\beta,\gamma} Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} .$$

It is clear from the foregoing that specific forms of symmetry breaking may easily be incorporated in the Landau free energy. For example, a magnet in a cubic lattice is in general subject to a crystal field of cubic symmetry. For a Heisenberg model on a cubic lattice the appropriate form of the Landau free energy is

$$G(\{m\}, T) = a + \frac{b}{2}(m_x^2 + m_y^2 + m_z^2) + \frac{c}{4}(m_x^2 m_y^2 + m_x^2 m_z^2 + m_y^2 m_z^2) \\ + \frac{d}{4}(m_x^4 + m_y^4 + m_z^4) + \dots \quad (3.65)$$

where in the absence of crystal fields  $c(T) = 2d(T)$ . The equilibrium behavior of the system is obtained for an  $n$ -component order parameter from the equations

$$\frac{\partial G}{\partial m_\alpha} = 0 \quad \alpha = 1, 2, \dots, n .$$

Other examples of systems with a multicomponent order parameter include superfluid  $^4\text{He}$  (two components), superconductors (two components), and the  $q$ -state Potts model ( $q - 1$  components) which describes the critical behavior of a number of two- and three-dimensional materials [see, *e.g.*, Sections 3.8.1 7.5.2].

## 3.12 Problems

**3.1. Ising Model with Long Range Interactions.** Consider a long chain of spins  $\sigma_i = 1$  or  $-1$ . The interaction between the spins is not just between nearest neighbors, but long range

$$H = - \sum_{i=1}^N \sum_{j < i} \frac{J}{|i-j|^\alpha} \sigma_i \sigma_j$$

where  $\alpha$  is a constant between 1 and 2, and  $J > 0$  (ferromagnetic coupling). Assume periodic boundary conditions.

- (a) Make a mean field approximation for the system in the limit  $N \rightarrow \infty$  and estimate the transition temperature for ferromagnetic order, and the order parameter  $m = \langle \sigma \rangle$  below the transition temperature. You will need to approximate the sum over neighboring spins by an integral.
- (b) If the interaction between the spins had been between nearest neighbors only

$$H = - \sum_{i=1}^N \sigma_i \sigma_{i+1}$$

it was argued in the text that the energy associated with creating a “domain wall” separating regions with up and down spins would have been  $2J$  while the entropy associated with creating two domains would have been proportional to  $\ln N$ . Since  $\ln N > 2J$  in the limit  $N \rightarrow \infty$  the system would be unstable against splitting up into domains and ferromagnetic ordering impossible. Show that this argument has to be modified if the interaction is long range and that ordering at a non-zero temperature is possible if  $\alpha < 2$ .

### 3.2. One-Dimensional Ising Model in Bethe Approximation.

Calculate the magnetization for the one-dimensional Ising model in a magnetic field in the Bethe approximation and compare with the exact result (3.38).

### 3.3. Critical Exponents.

- (a) Fill in the missing steps to obtain equations (3.30)–(3.31).
- (b) Show that the specific heat  $C_h$  at  $h = 0$  is discontinuous in the Bethe approximation at  $T = T_c$  for  $q > 2$ .
- (c) Show that in the Bethe approximation to the Ising model  $m(h = 0) \propto |T - T_c|^{1/2}$  near  $T_c$ .
- (d) Show that the exponent for the critical isotherm in the Bethe approximation for the Ising model satisfies  $\delta = 3$ .

### 3.4. Cluster Approximation for the Two-Dimensional Ising Model.

The Bethe approximation can be modified to treat clusters of a more

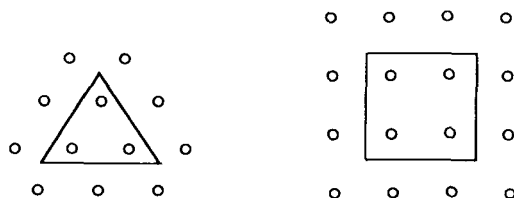


Figure 3.16: Clusters for the two-dimensional Ising model on the square and triangular lattices.

general type. Consider as an example the two-dimensional Ising model on the square and triangular lattices. Divide the lattice into blocks of four and three spins as shown in Figure 3.16. Treat the interactions within a block exactly, while using the molecular field approximation for the interactions between spins in different blocks. Calculate the critical temperature for (a) the triangular ( $\Delta$ ) lattice and (b) the square ( $\square$ ) lattice and compare with the exact values

$$\frac{J}{k_B T_c} = 0.441 \dots (\square) \quad \frac{J}{k_B T_c} = 0.275 \dots (\Delta)$$

and with results from the simplest molecular field theory.

**3.5. Application of the One-Dimensional Ising Model to a Polymer Problem.**

Use the one-dimensional Ising model to describe the following observation: The length  $l$  of molecules in a dilute solution of long chain-like polymer molecules is found to change with the temperature  $T$  as shown in Figure 3.17.

**3.6. One-Dimensional Ising Model with Spin 1.**

Calculate the internal energy of the one-dimensional Ising model defined by the Hamiltonian

$$H = -J \sum_i \sigma_i \sigma_{i+1} \quad \sigma_i = 0, \pm 1, \quad J > 0.$$

The solution of this problem requires differentiation of the root of a cubic equation. You may wish to do this numerically.

**3.7. Generalized Random Walk Problem.**

Use the transfer matrix formalism to solve the following generalized

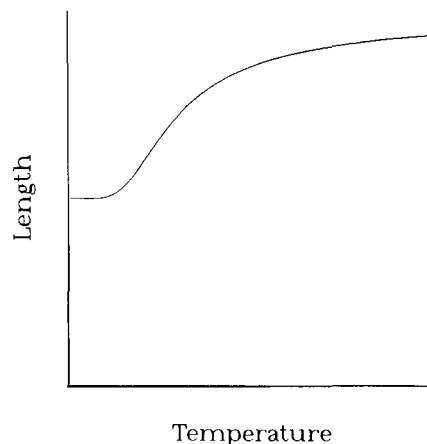


Figure 3.17: Temperature dependence of the average length  $l$  of long chain-like polymer molecules.

random walk problem: By observing drunks, one may notice that the completely random walk is only a crude first approximation in describing the motion. Inertia plays an important role in determining which way to take the next step. For this reason the next step will take place with greater probability in the direction of the previous one. A simple model for the motion can be constructed by assuming that there is a correlation between nearest neighbor steps, namely that the next step will be in the same direction as the previous one with probability  $p$  and in the opposite direction with probability  $(1 - p)$ .

Calculate the mean-square displacement after  $N$  steps. The motion can be assumed to be one-dimensional.

**3.8. Clusters of Spins for the Ising Chain.**

- (a) Consider the one-dimensional Ising model in a magnetic field  $h$  subject to periodic boundary conditions. Suppose that spin  $j$  is in a specific state, either up or down. Using the transfer matrix of Section 3.6, calculate the probability that spins  $j + 1, j + 2, \dots, j + n$  will be in the same state as spin  $j$  and that spin  $j + n + 1$  will be in the opposite state.
- (b) Remove the restriction on spin  $j + n + 1$  and again calculate the probability.

**3.9. Latent Heat of a First-Order Transition.**

Consider the Landau free energy

$$G(m, T) = a(T) + \frac{b}{2}m^2 + \frac{c}{4}m^4 + \frac{d}{6}m^6$$

and assume that  $b > 0, c < 0$ , so that a first-order transition takes place. Derive an expression for the latent heat of transition.

**3.10. Asymptotic Behavior near a Tricritical Point.**

- (a) Derive the result (3.51) for the discontinuity of the order parameter  $x$  across the first-order line near the tricritical point.
- (b) Show that  $\gamma_t = 1, \alpha_t = \frac{1}{2}$  in the tricritical region.
- (c) Show that in the critical region the exponents predicted by Landau theory are  $\gamma_u = 2, \alpha_u = -1$ .

**3.11. Heisenberg Model in a Crystal Field.**

In Section 3.11 the Landau free energy in the presence of a cubic crystal field was given by equation (3.65). Assuming that the coefficients of higher than fourth order in  $m$  are all positive, determine the nature of the ordered phase. You may assume that the system will order in a (100), (111), or (110) preferred spin orientation and minimize the free energy with respect to a simple amplitude. In which situations will the transition be discontinuous?

**3.12. Alben Model.**

The symmetry breaking aspect of second order phase transitions can be nicely illustrated in a simple mechanical model [9]. An airtight piston of mass  $m$  is inside a tube of cross sectional area  $a$ . The tube is bent into a semicircular shape (see Figure 3.18) of radius  $R$ . The system is kept at temperature  $T$ . On each side of the piston there is an ideal gas consisting of  $N$  atoms. The volume to the right of the piston is  $aR(\frac{\pi}{2} - \phi)$ , while the volume to the left is  $aR(\frac{\pi}{2} + \phi)$ . Using the formula derived in problem 2.6 for the Helmholtz free energy of an ideal gas we find for the free energy of the system

$$A = MgR \cos \phi - Nk_B T \left[ \ln \frac{aR(\frac{\pi}{2} + \phi)}{N\lambda^3} + \ln \frac{aR(\frac{\pi}{2} - \phi)}{N\lambda^3} + 2 \right].$$

- (a) Show by minimizing the free energy that the system undergoes a symmetry breaking phase transition ( $\phi \neq 0$ ) at a temperature

$$T_c = \frac{MgR\pi^2}{8Nk_B}.$$

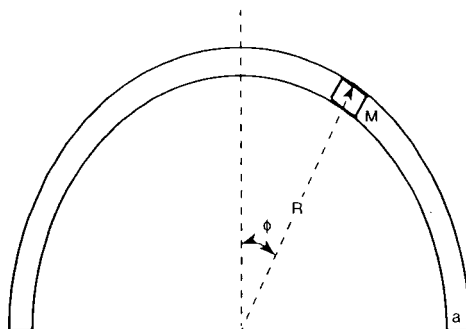


Figure 3.18: Alben model.

- (b) Plot the “order parameter”  $\phi$  vs.  $T/T_c$  for  $T < T_c$ .
- (c) Describe what happens to the phase transition if the number of atoms on the left and right side of the piston is  $N(1-\delta)$  and  $N(1+\delta)$ , respectively.
- (d) At a certain temperature the right chamber (containing  $N(1+\delta)$  molecules) is found to contain a puddle of liquid coexisting with its vapor. Which of the following statements may be true at equilibrium:
- The left chamber will contain a liquid in coexistence with its vapor.
  - The left chamber contains only vapor.
  - The left chamber contains only liquid.

**3.13. Solvable Model with Tricritical Point.**

Consider an Ising chain with  $N$  spins  $\sigma_i = \pm 1$  and periodic boundary conditions. The chain is coupled to an elastic field  $\epsilon$ . Nonzero values of  $\epsilon$  causes a dimerization of the chain, *i.e.* alternating bonds are strengthened (or weakened). The dimensionless Hamiltonian for the system can be written (a similar model which includes a magnetic field has been described by Zaspel [333]).

$$H = - \sum_{i=1}^N [1 - \epsilon(-1)^i] \sigma_i \sigma_{i+1} + N\omega\epsilon^2 .$$

The partition function associated with the summation over spins can be computed by the transfer matrix method as discussed in Section 3.6

$$Z_\sigma = \text{Tr}(\mathbf{PQ})^{\frac{N}{2}}$$

where

$$\mathbf{P} = \begin{pmatrix} e^{\beta(1+\epsilon)} & e^{-\beta(1+\epsilon)} \\ e^{-\beta(1+\epsilon)} & e^{\beta(1+\epsilon)} \end{pmatrix}$$

is associated with even numbered sites and

$$\mathbf{Q} = \begin{pmatrix} e^{\beta(1-\epsilon)} & e^{-\beta(1-\epsilon)} \\ e^{-\beta(1-\epsilon)} & e^{\beta(1-\epsilon)} \end{pmatrix}$$

corresponds to odd numbered sites. Let  $\lambda$  be the largest eigenvalue of the transfer matrix  $\mathbf{PQ}$ . The partition function for the whole system can then be written as  $N \rightarrow \infty$

$$Z_{tot} = \int_{-\infty}^{\infty} d\epsilon e^{-\beta N g(\epsilon)}$$

where

$$g(\epsilon) = -\frac{k_B T}{2} \ln \lambda(\epsilon) + \omega \epsilon^2 .$$

If  $g(\epsilon)$  has an absolute minimum at  $\epsilon_0$  we find that  $\epsilon = \epsilon_0$  at equilibrium, and that the free energy per spin is  $g(\epsilon_0)$ .

(a) Show that the largest eigenvalue of the transfer matrix is

$$\lambda = 2[\cosh(2\beta) + \cosh(2\beta\epsilon)] .$$

(b) There will be no phase transition if  $\omega > 0.25$ . Show that if  $\omega = 0.20$  the system will undergo a second order phase transition to a dimerized state  $\epsilon \neq 0$ . Estimate the value of  $\beta$  at the transition.

(c) Show that if  $\omega = 0.24$  the system will undergo a first order transition to a dimerized state. Estimate  $\beta$  at the transition (*e.g.* by plotting the free energy as a function of epsilon for a few temperatures).

(d) Estimate the values of  $\omega$  and  $\beta$  at the tricritical point.

**3.14.** *The Potts Chain.* Consider a chain of  $N$  spins, each of which can be in any of three spin states. The system is subject to periodic boundary conditions and an external field with different components in the direction

of each state. If two neighboring spins are in the same state, the energy of interaction between them is  $-J$ , otherwise the interaction is zero:

$$H = - \sum_{i=1}^N \left( J \delta_{S_i, S_{i+1}} + \sum_{\alpha=1}^3 H_{\alpha} \delta_{S_i, \alpha} \right)$$

where

$$\delta_{i,j} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases} .$$

- (a) Construct a transfer matrix for the system.
- (b) Calculate the free energy per spin of the system in the thermodynamic limit  $N \rightarrow \infty$  for the special case  $H_1 = H, H_2 = H_3 = 0$ .
- (c) Plot the “magnetization”  $m = \langle S_1 \rangle$  vs.  $H/k_B T$  for  $J/k_B T = 0.1, 1, 4$  respectively.

**3.15.** *Mean Field Theory for  $q$ -state Potts Model.* Use the method of Section 3.8.1 to analyze the general case of the  $q$ -state Potts model, with  $q \geq 3$ .

- (a) Show that there is a first order phase transition when the temperature is

$$k_B T = \frac{J(q-2)}{2(q-1) \ln(q-1)}$$

with order parameter jump to

$$m = \frac{q-2}{q-1} .$$

- (b) Show that the latent heat of the transition is

$$L = \frac{J(q-2)^2}{2q(q-1)} .$$