

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 σ_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 β 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

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

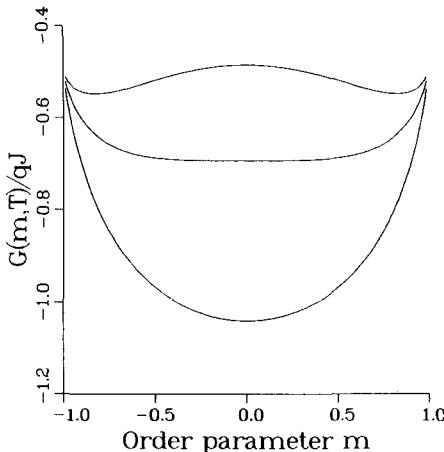


Figure 3.1: Free energy in the Bragg–Williams approximation for the Ising model. The three curves correspond to, respectively, $T = 1.5T_c$, $T = T_c$, and $T = 0.77T_c$.

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.

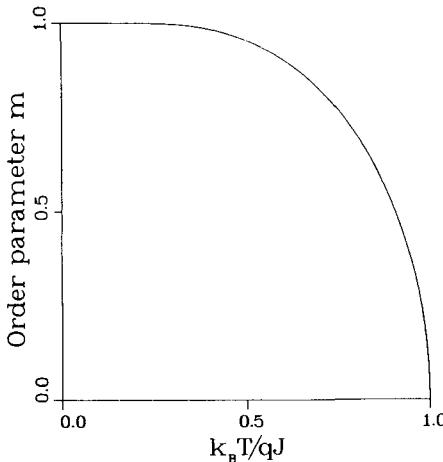


Figure 3.2: Temperature dependence of order parameter below T_c .

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 $\sigma_i = -1$, $i > l$:

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

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

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

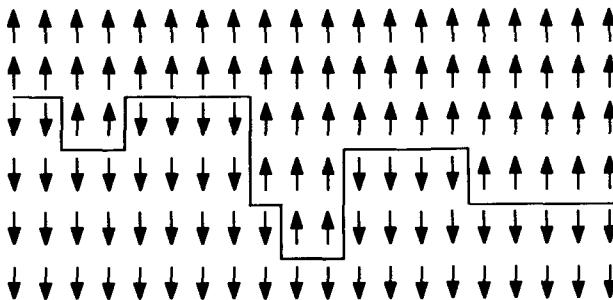


Figure 3.3: Domain wall in a two-dimensional Ising model.

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 Peierls¹ [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 σ_0 with its first neighbor shell by a mean energy.

The partition function of the cluster is given by

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

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

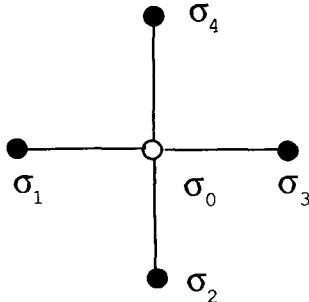


Figure 3.4: Spin cluster used in the Bethe approximation calculation.

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 $j = 1, \dots, q$,

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

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 2β 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

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

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, γ 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:

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

It is clear that χ 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 α 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 σ_{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

$$Z_N = (2 \cosh \beta J)^{N-2} Z_2$$

$$Z_2 = \sum_{\sigma_1=\pm 1} \sum_{\sigma_2=\pm 1} e^{\beta J \sigma_1 \sigma_2} = 4 \cosh \beta J$$

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 2×2 *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 λ_1 and λ_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 λ_1^N , λ_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 λ_1 , associated with the positive root, is always larger than λ_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 $G(T \rightarrow 0) = -N J$ 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 σ_i , σ_{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 $\sigma_i^2 = 1$,

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

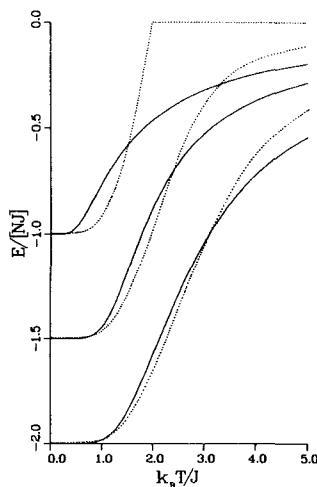


Figure 3.5: Comparison between exact and Bragg–Williams results for the internal energy of the one-dimensional Ising chain. Solid line, exact theory; dotted line, mean field theory. The three sets of curves correspond to $h = 0$, $h = 0.5J$, and $h = J$, respectively.

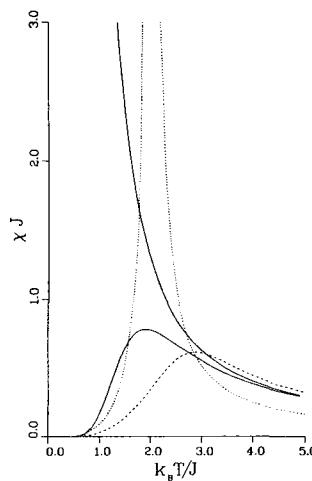


Figure 3.6: Comparison between exact (solid lines) and Bragg–Williams susceptibilities for a one-dimensional Ising chain. The two sets of curves correspond to $h = 0$ and $h = 0.5J$ respectively.

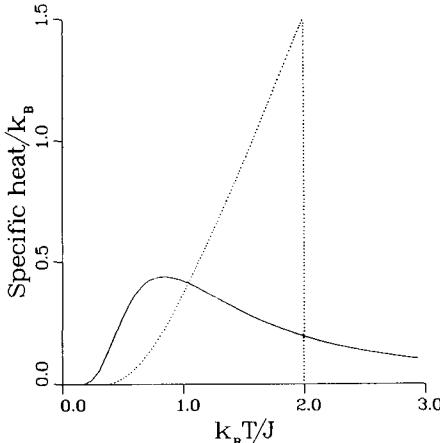


Figure 3.7: Specific heat calculated exactly (solid line) and in the Bragg–Williams approximation (dotted line) for the one-dimensional Ising chain. Only results for $h = 0$ are shown. For $h \neq 0$ the difference between the exact and approximate calculations is similar to that found for the susceptibility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

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

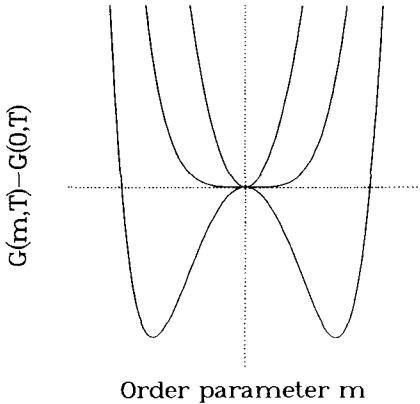


Figure 3.8: Free energy when $c, d \dots > 0$ and $b(T) = b_0(T - T_c)$.

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

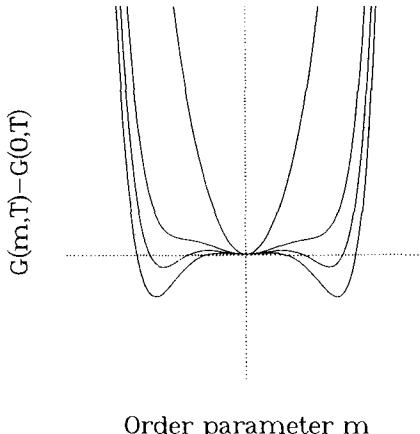


Figure 3.9: Free energy for a sequence of temperatures in the case that $c(T)$ changes sign above the temperature at which $b(T)$ changes sign.

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

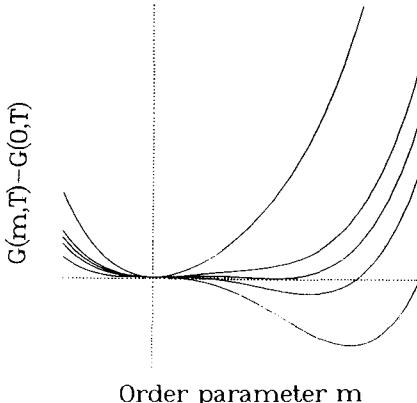


Figure 3.10: Free energy for different temperatures in the case where the Landau expansion contains a cubic term.

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 Δ 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

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

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

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

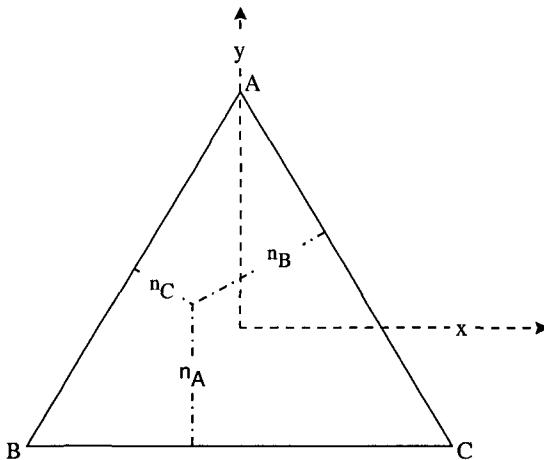


Figure 3.11: The allowed values of x, y are inside the triangle with corners $(0,1)$, $(\sqrt{3}/2, -1/2)$, $(-\sqrt{3}, -1/2)$ corresponding to states of all A , B and C respectively.

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

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

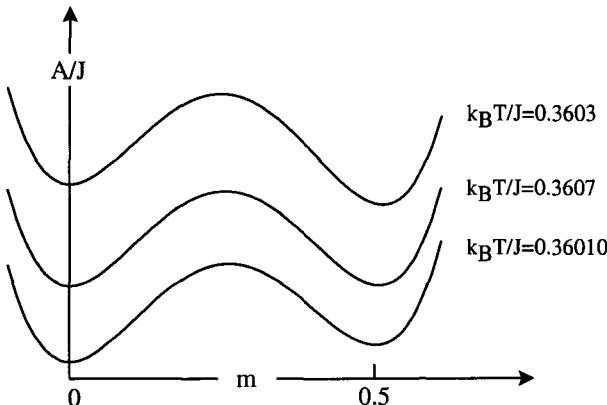


Figure 3.12: Free energy A/J plotted versus order parameter m for $k_B T/J = 0.3603, 0.3607, 0.361$, respectively. The value of y at the transition is seen to be close to $1/2$.

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 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 NH_4Cl , whose orientational transition changes from second to first order as a function of pressure; the ferroelectric 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 Δ . In the case of 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 Δ an applied uniform magnetic field. In the case of the uniaxial-biaxial transition

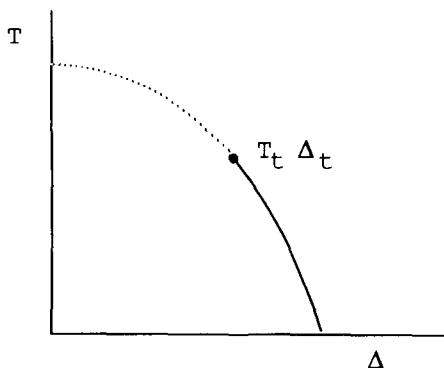


Figure 3.13: Phase behavior near a tricritical point. Solid line, first-order transitions; dotted line, critical points.

in liquid crystals, m and x are the order parameters P and Q of (4.24) and h , Δ 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 (Δ_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 $b = 0$,

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

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

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

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

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

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

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

and

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

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

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

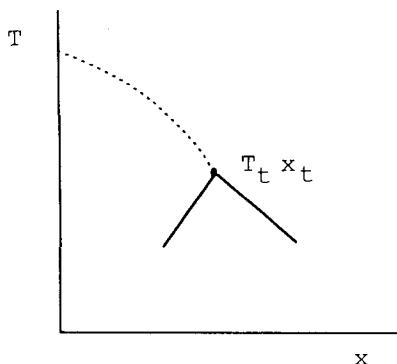


Figure 3.14: Phase diagram in the $T - x$ plane near the tricritical point.

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 β 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 $d \geq 4$.

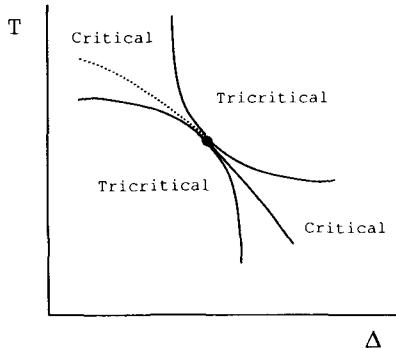


Figure 3.15: Critical and tricritical regions near a tricritical point.

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 energy² 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

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

²We 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 ϕ 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 ν dependent on the model and the dimensionality.

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

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

is included in the Hamiltonian, we have

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

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

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

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 ∇^2 by the analogous d -dimensional operator and the δ -function by the appropriate d -dimensional δ -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 ξ . 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 Br^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 α 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

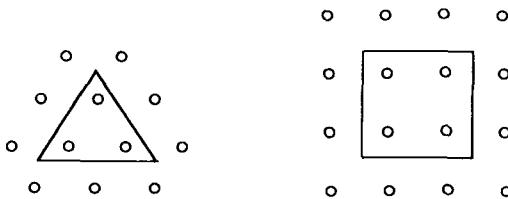


Figure 3.16: Clusters for the two-dimensional Ising model on the square and triangular lattices.

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 (\triangle) lattice and (b) the square (\square) lattice and compare with the exact values

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

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

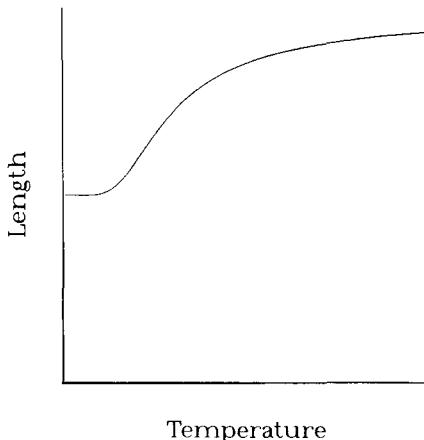


Figure 3.17: Temperature dependence of the average length l of long chain-like polymer molecules.

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

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

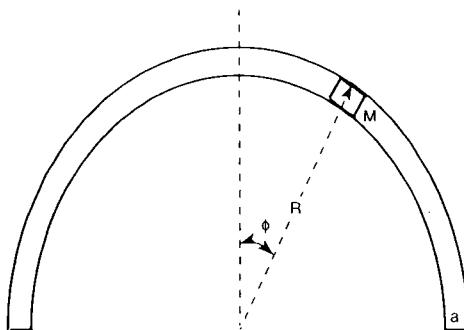


Figure 3.18: Alben model.

- (b) Plot the “order parameter” ϕ 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 ϵ . Nonzero values of ϵ 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 λ be the largest eigenvalue of the transfer matrix \mathbf{PQ} . The partition function for the whole system can then be written as $N \rightarrow \infty$

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

where

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

If $g(\epsilon)$ has an absolute minimum at ϵ_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 β at the transition.
- (c) Show that if $\omega = 0.24$ the system will undergo a first order transition to a dimerized state. Estimate β at the transition (*e.g.* by plotting the free energy as a function of epsilon for a few temperatures).
- (d) Estimate the values of ω and β 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

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

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Chapter 4

Applications of Mean Field Theory

We now continue our discussion of mean field theories. While the previous chapter concentrated on presenting the various techniques available, we now wish to give some typical examples of the very wide range of applications allowed by the method. In Section 4.1 we show that the usefulness of the Ising model is not limited to the magnetic problems for which it was originally intended, and apply it to a problem involving order-disorder transitions in alloys. Further examples are given as problems.

In Section 3.8 we showed that the presence of cubic terms in the Landau expansion led to a prediction of first order (or discontinuous) transitions and illustrated the argument by a discussion of the 3-state Potts model. In Section 4.2 we give an important further example, the Maier Saupe model for the isotropic to nematic transitions in liquid crystals. The discussion of tricritical points of Section 3.9 is applied in Section 4.3 to the problem of phase separation in ^3He - ^4He mixtures at low temperatures.

The van der Waals theory of fluids of Section 4.4 was the first modern mean field theory of phase transitions. It also led to the theory of “corresponding states”, hinting at the idea of universality, which we will discuss further in Chapters 6 and 7. In Section 4.5 we extend mean field theory to a problem of population biology and consider a model of insect infestations that is mathematically very similar to the van der Waals model. We argue that it is possible frame the problem as one of equilibrium phase transitions. We return to the

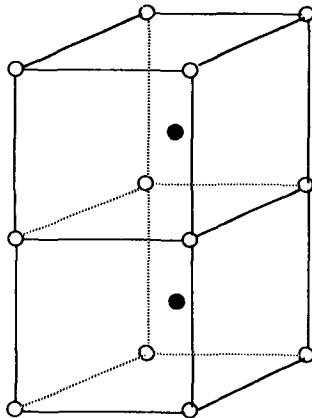


Figure 4.1: Ordered structure for β' brass: open circles, Zn filled circles Cu.

insect infestation problem in Section 8.2 where we calculate the equilibrium fluctuations of the model. Finally in Section 4.6 we consider a more explicitly non-equilibrium model. Again the model exhibits phase transitions similar to those of equilibrium theory.

4.1 Order–Disorder Transition

In the binary alloy of Cu and Zn (brass), at compositions in a narrow range around 50 atomic % Cu, 50 atomic % Zn, the atoms occupy the sites of a body-centered cubic (bcc) lattice forming β -brass. The distribution of atoms on these sites is disordered above a temperature T_c which is close to 740K. Below T_c there is ordering with atoms of each kind preferentially distributed on one of the two simple cubic sublattices of the bcc lattice (β' phase, see Figure 4.1).

The simplest model that can account for the low-temperature structure is one in which the energy of nearest-neighbor pairs depends on what kind of pair it is. We define the quantities N_{AA} , N_{BB} , N_{AB} to be the number of nearest-neighbor pairs of the Cu-Cu, Zn-Zn, and Cu-Zn type, respectively, and take the energy of the configuration to be

$$E = N_{AA}e_{AA} + N_{AB}e_{AB} + N_{BB}e_{BB} \quad (4.1)$$

where e_{AA} , e_{AB} , and e_{BB} are, respectively, the energies of an AA , AB , and BB bond.

Let N be the numbers of lattice sites and N_A , N_B the number of Cu and Zn atoms, respectively. Referring to Figure 4.1, we introduce the occupation numbers for each of the two simple cubic sublattices: N_{A1} and N_{B1} are the number of atoms of each type on sublattice 1, N_{A2} and N_{B2} the number of atoms of each type on sublattice 2. We have

$$\begin{aligned} N_{A1} + N_{A2} &= N_A = c_A N \\ N_{B1} + N_{B2} &= N_B = c_B N \\ N_{A1} + N_{B1} &= \frac{1}{2}N \\ N_{A2} + N_{B2} &= \frac{1}{2}N . \end{aligned} \quad (4.2)$$

For the sake of definiteness we let $N_A \leq N_B$ and define the order parameter

$$m = \frac{N_{A1} - N_{A2}}{N_A} . \quad (4.3)$$

With this definition $-1 \leq m \leq 1$ and

$$\begin{aligned} N_{A1} &= \frac{1}{2}N_A(1+m) & N_{B1} &= \frac{1}{2}(N_B - N_A m) \\ N_{A2} &= \frac{1}{2}N_A(1-m) & N_{B2} &= \frac{1}{2}(N_B + N_A m) . \end{aligned} \quad (4.4)$$

Up to this point our treatment is exact. We now make the crucial approximations

$$\begin{aligned} N_{AA} &= q \frac{N_{A1} N_{A2}}{\frac{1}{2}N} & N_{BB} &= q \frac{N_{B1} N_{B2}}{\frac{1}{2}N} \\ N_{AB} &= q \left(\frac{N_{A1} N_{B2}}{\frac{1}{2}N} + \frac{N_{A2} N_{B1}}{\frac{1}{2}N} \right) \end{aligned} \quad (4.5)$$

where q is the number of nearest neighbors surrounding each atomic site. The mean energy is obtained by substituting (4.5) into (4.1), while the entropy can be evaluated using the method of Section 3.2. The appropriate free energy is

$$A = E - TS \quad (4.6)$$

with

$$E = \frac{1}{2}qN(e_{AA}c_A^2 + 2e_{AB}c_Ac_B + e_{BB}c_B^2) - qNc_A^2\epsilon m^2 \quad (4.7)$$

where

$$\epsilon = \frac{1}{2}(e_{AA} + e_{BB}) - e_{AB} \quad (4.8)$$

and

$$\begin{aligned} S &= -k_B \left(N_{A1} \ln \frac{2N_{A1}}{N} + N_{A2} \ln \frac{2N_{A2}}{N} + N_{B1} \ln \frac{2N_{B1}}{N} + N_{B2} \ln \frac{2N_{B2}}{N} \right) \\ &= -\frac{1}{2} N k_B \left(c_A (1+m) \ln [c_A (1+m)] + c_A (1-m) \ln [c_A (1-m)] \right. \\ &\quad \left. + (c_B - mc_A) \ln [c_B - mc_A] + (c_B + mc_A) \ln [c_B + mc_A] \right). \end{aligned} \quad (4.9)$$

The quantities c_A and c_B are held fixed while m must be adjusted to minimize the free energy. Differentiation of A with respect to m gives

$$0 = -2qc_A\epsilon m + \frac{1}{2} k_B T \ln \frac{(1+m)(c_B + c_A m)}{(1-m)(c_B - c_A m)}. \quad (4.10)$$

For low temperature and $\epsilon > 0$ there are three solutions to (4.10): a trivial solution $m = 0$, and two nonzero solutions symmetric about $m = 0$. At high temperatures only the trivial solution exists. As can easily be verified by differentiating (4.10) with respect to m , the trivial solution yields a minimum of the free energy for

$$T > T_c = \frac{2q\epsilon c_A c_B}{k_B}.$$

This situation is very similar to that of Section 3.2; if we were to plot the free energy (4.6) as a function of the order parameter m , the resulting figure would look similar to Figure 3.1. In the special case $c_A = c_B = \frac{1}{2}$, (4.10) can be written

$$0 = -q\epsilon m + k_B T \ln \frac{1+m}{1-m} \quad (4.11)$$

which is equivalent to (3.15) if in that equation we take $h = 0$ and $J = \epsilon/2$. The nature of the phase transition in the alloy system is thus identical to the phase transition of the Ising ferromagnet. This last conclusion is independent of the mean field approximation, as we now show.

We introduce the variables n_{iA} , n_{iB} , where $n_{iA} = 1$ if an atom of type A occupies site i and $n_{iA} = 0$ otherwise. Similarly, $n_{iB} = 1 - n_{iA}$. These variables can be expressed in terms of Ising spin variables

$$\begin{aligned} n_{iA} &= \frac{1}{2}(1 + \sigma_i) \\ n_{iB} &= \frac{1}{2}(1 - \sigma_i) \end{aligned} \quad (4.12)$$

with $\sigma_i = \pm 1$. With $\epsilon = 2J$, the energy (4.1) becomes

$$H = J \sum_{\langle ij \rangle} \sigma_i \sigma_j + \frac{q}{4} (e_{AA} - e_{BB}) \sum_i \sigma_i + \frac{q}{8} N (e_{AA} + e_{BB} + 2e_{AB}). \quad (4.13)$$

Remembering that we have a system with a fixed total number of particles of each kind, we see that the last two terms are constant and therefore irrelevant. We obtain the equivalent Hamiltonian

$$H = J \sum_{\langle ij \rangle} \sigma_i \sigma_j . \quad (4.14)$$

If $J > 0$, that is, if it is energetically favorable for atoms of opposite kind (spin) to be nearest neighbors, this Hamiltonian represents an antiferromagnet.

We can also show that under certain circumstances the ferromagnetic and antiferromagnetic Ising models are equivalent. Consider a crystal structure that can be divided into two *sublattices*, so that the nearest neighbors to the sites on one of the sublattices belong to the other (*e.g.*, the square, honeycomb, simple cubic, and body-centered cubic lattices, but not the triangular, face-centered cubic, or hexagonal close-packed lattices). We may then make the transformation $\sigma_i = -\tau_i$ for i on one of the sublattices and $\sigma_i = +\tau_i$ for i on the other sublattice and have

$$H = -J \sum \tau_i \tau_j . \quad (4.15)$$

Since $\tau_i = \pm 1$, the partition function for the Hamiltonian (4.15) is the same as that of the Ising ferromagnet with $h = 0$. Thus the two systems have identical thermodynamic properties at all temperatures.

In the derivations given above, we allowed the concentrations of the two components of the alloy to vary freely. In practice, β -brass occurs only in a fairly narrow concentration range¹ around 50% Cu, 50% Zn. At other stoichiometries the face-centered cubic, more complex cubic structures, or the hexagonal closed packed structure may be thermodynamically stable, or the system may be in a mixture of different phases. In general, there is no guarantee that a particular choice of lattice structure, division into sublattices, or selection of order parameter is the correct one. One should therefore be guided by physical intuition in trying out a number of different alternatives, selecting the one with lowest free energy.

The homogeneous phase with the lowest free energy may also be unstable with respect to *phase separation*. The difference in concentration of each species is analogous to the magnetization in the Ising model, and since we are dealing with a system with fixed magnetization (rather than external field), we use the symbol A in preference to G for the free energy. Consider a sample with concentration $c_A = c_0$ and let the minimum single-phase free energy be

¹see *e.g.* [156]

$A(c_0)$. If the sample were to split into two phases, one with a fraction y of the total number of sites, the constraint that the overall concentration of A -atoms is c_0 is expressed through the *lever rule*,

$$yc_1 + (1 - y)c_2 = c_0 \quad (4.16)$$

where c_1 and c_2 are the concentrations of A atoms in the two phases. The homogeneous phase is stable against phase separation if for all c_1 and c_2

$$yA(c_1) + (1 - y)A(c_2) > A(c_0) . \quad (4.17)$$

Geometrically, (4.17) corresponds to requiring that $A(x)$ be a *convex function*. If $A(x)$ can be differentiated twice, (4.17) is equivalent to the condition that

$$\frac{\partial^2 A}{\partial c^2} > 0 \quad \text{for all } c . \quad (4.18)$$

When the convexity requirement is violated, phase separation will occur. The resulting free energy lies on the convex envelope of $A(c)$. The equilibrium concentrations c_1 , and c_2 are given by the lever rule (4.16) and by the condition $\partial A / \partial c|_{c_1} = \partial A / \partial c|_{c_2}$ i.e., that the chemical potential is the same in the two phases. This constitutes the double tangent construction of Figure 4.2. A simple model for phase separation is found in Problem 4.1.

4.2 Maier–Saupe Model

An example of a model that gives rise to a Landau expansion with a cubic term is the Maier–Saupe model for the isotropic to nematic transition in liquid crystals² [186][187]. We consider a system of anisotropic molecules with a symmetry axis. The center of the i 'th molecule is taken to be at \mathbf{r}_i and the unit vector pointing in the direction of the symmetry axis is denoted by $\hat{\mathbf{n}}_i$. We further assume that the directions $\hat{\mathbf{n}}_i$ and $-\hat{\mathbf{n}}_i$ are equivalent. The interaction between the molecules is represented by a pair potential $W(\mathbf{r}_j - \mathbf{r}_i, \hat{\mathbf{n}}_j, \hat{\mathbf{n}}_i)$. We assume that the number of molecules ρ per unit volume is constant and let $f(\hat{\mathbf{n}})$ be the probability density that a molecule is oriented along $\hat{\mathbf{n}}$, and define $\mathbf{r}_{ji} = \mathbf{r}_j - \mathbf{r}_i$. We introduce the pair distribution function $g(\mathbf{r}_{ji}, \hat{\mathbf{n}}_j, \hat{\mathbf{n}}_i)$ as the conditional probability that there is a molecule at \mathbf{r}_i with orientation $\hat{\mathbf{n}}_i$ given that there is a molecule at \mathbf{r}_j with orientation $\hat{\mathbf{n}}_j$. In analogy with

²For an introduction to the properties of liquid crystals, we recommend de Gennes and Prost [71], Priestley et al. [251], Stephens and Straley [288] and Chandrasekhar [59].

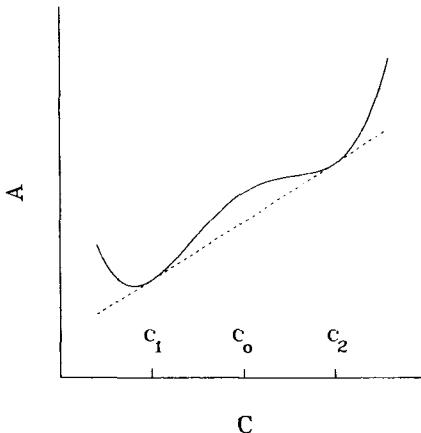


Figure 4.2: Phase separation. Material of initial concentration c_0 splits up into two phases with concentrations c_1 and c_2 . The amount of material in each phase is given by the double tangent construction.

our discussion of the Weiss molecular field in Section 3.1 we write for the *pseudopotential* or the term in the average total energy which depends on the orientation $\hat{\mathbf{n}}_i$:

$$\epsilon(\hat{\mathbf{n}}_i) = \text{const.} + \rho \int d^3 r_{ji} \int d\Omega_j W(\mathbf{r}_{ji}, \hat{\mathbf{n}}_i, \hat{\mathbf{n}}_j) f(\hat{\mathbf{n}}_j) g(\mathbf{r}_{ji}, \hat{\mathbf{n}}_j, \hat{\mathbf{n}}_i)$$

where the integration over Ω_j extends over the solid angle of $\hat{\mathbf{n}}_j$. Apart from the mean field approach, a fundamental approximation of the Maier–Saupe model consists of ignoring the dependence of the pair distribution function on orientation. This allows us to write

$$\epsilon(\hat{\mathbf{n}}_i) = \text{const.} + \rho \int d\Omega_j f(\hat{\mathbf{n}}_j) \int d^3 r_{ji} W(\mathbf{r}_{ji}, \hat{\mathbf{n}}_i, \hat{\mathbf{n}}_j) g(\mathbf{r}_{ji}) . \quad (4.19)$$

We can expand the second integral in (4.19) in a Legendre series in $\hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j$ to obtain

$$\epsilon(\hat{\mathbf{n}}_i) = \text{const.} + \rho \int d\Omega_j f(\hat{\mathbf{n}}_j) (\gamma - 2U P_2(\hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j) + \mathcal{O}[P_4(\hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j)] \dots) \quad (4.20)$$

where γ and U are constants and $U > 0$ corresponds to the situation where it is energetically advantageous for the molecules to parallel align. In (4.20)

$P_2(x) = \frac{1}{2}(3x^2 - 1)$ is the second Legendre polynomial, and P_4 is the fourth polynomial. Note that since we have assumed that the directions $\hat{\mathbf{n}}$ and $-\hat{\mathbf{n}}$ are equivalent, there will be no odd-index Legendre polynomials in the series (4.20). The final approximation in the Maier–Saupe model is to stop at second order in the Legendre expansion. We define

$$\sigma_{i\alpha\beta} = \frac{1}{2}(3n_{i\alpha}n_{i\beta} - \delta_{\alpha\beta})$$

where $\alpha, \beta = x, y, z$ and $n_{i\alpha}$ is a Cartesian component of $\hat{\mathbf{n}}_i$ and $\delta_{\alpha\beta}$ is the Kronecker delta. Using the identity

$$P_2(\hat{\mathbf{n}}_j \cdot \hat{\mathbf{n}}_i) = \frac{2}{3} \sum_{\alpha,\beta=1}^3 \sigma_{i\alpha\beta} \sigma_{j\alpha\beta}$$

and defining

$$Q_{\alpha\beta} = \langle \sigma_{j\alpha\beta} \rangle = \int d\Omega_j \sigma_{j\alpha\beta} f(\hat{\mathbf{n}}_j) \quad (4.21)$$

we can rewrite (4.20) to obtain

$$\epsilon(\hat{\mathbf{n}}_i) = -\frac{4}{3}\rho U \sum_{\alpha\beta} Q_{\alpha\beta} \sigma_{i\beta\alpha}$$

where we have omitted terms that do not depend on particle orientation. Taking into account the double counting that occurs when we sum the pair potential over all molecules, we find for the orientational contribution to the internal energy,

$$E = -\frac{2}{3}\rho U N \sum_{\alpha\beta} Q_{\alpha\beta} Q_{\beta\alpha}. \quad (4.22)$$

The orientational contribution to the entropy is given by

$$S_{or} = -Nk_B \int d\Omega f(\hat{\mathbf{n}}) \ln f(\hat{\mathbf{n}}).$$

It then follows from the argument used in Section 2.5 that the single-particle distribution function

$$f(\hat{\mathbf{n}}) = \frac{\exp\{-\beta\epsilon(\hat{\mathbf{n}})\}}{\int d\Omega \exp\{-\beta\epsilon(\hat{\mathbf{n}})\}}$$

will minimize the free energy $G = E - TS_{or}$, and the order parameter $Q_{\alpha\beta}$ can then be determined from the self-consistency criterion

$$Q_{\alpha\beta} = \int d\Omega \sigma_{\alpha\beta} f(\hat{\mathbf{n}}). \quad (4.23)$$

In analogy with the Weiss molecular field theory there will always be a solution $Q_{\alpha\beta} = 0$ and we identify such solutions with the isotropic high-temperature phase. At low temperatures nonzero solutions of (4.23) will appear. Each such solution corresponds to a preferential orientation of the *director field* \hat{n} and we call this phase *nematic*. The nematic phase does not exhibit long range spatial order, and we distinguish it from the more complicated *smectic* phases, which exhibit varying degrees of translational ordering. The nonzero solutions of (4.23) will not be unique, because of the overall rotational symmetry of the system. However, since $Q_{\alpha\beta}$ is real and symmetric, there will always be a principal-axis coordinate system in which $Q_{\alpha\beta}$ is diagonal. We let θ and ϕ be the polar angles of \hat{n} in such a system

$$\begin{aligned} n_x &= \sin \theta \cos \phi \\ n_y &= \sin \theta \sin \phi \\ n_z &= \cos \theta . \end{aligned}$$

Defining

$$\begin{aligned} p &= \frac{3}{2} \sin^2 \theta \cos 2\phi; & q &= \frac{1}{2}(3 \cos^2 \theta - 1) \\ P &= \langle p \rangle; & Q &= \langle q \rangle \end{aligned} \quad (4.24)$$

we find after some algebra

$$\mathbf{Q} = \begin{bmatrix} -\frac{1}{2}(Q - P) & 0 & 0 \\ 0 & -\frac{1}{2}(Q + P) & 0 \\ 0 & 0 & Q \end{bmatrix}$$

$$\begin{aligned} \epsilon(\hat{n}) &= -2\rho U(Qq + \frac{1}{3}Pp) \\ E &= -N\rho U(Q^2 + \frac{1}{3}P^2) . \end{aligned}$$

If we choose the z -axis to be in the direction of the eigenvector belonging to the largest eigenvalue of \mathbf{Q} , we will, for molecules with a symmetry axis, have $P = 0$, and with $\mu = \cos \theta$

$$g = \frac{G}{N} = -k_B T \ln \left(4\pi \int_0^1 d\mu \exp\{\rho U \beta[(3\mu^2 - 1)Q - Q^2]\} \right) . \quad (4.25)$$

It is now a straightforward matter to obtain a Taylor expansion of (4.25) in powers of Q , and after some algebra we obtain the expansion

$$\begin{aligned} g &= -k_B T \ln(4\pi) + \rho U Q^2 \left(1 - \frac{2}{5}\beta\rho U \right) \\ &\quad - \frac{8}{105}\beta^2 \rho^3 U^3 Q^3 + \frac{4}{175}\beta^3 \rho^4 U^4 Q^4 + \dots . \end{aligned} \quad (4.26)$$

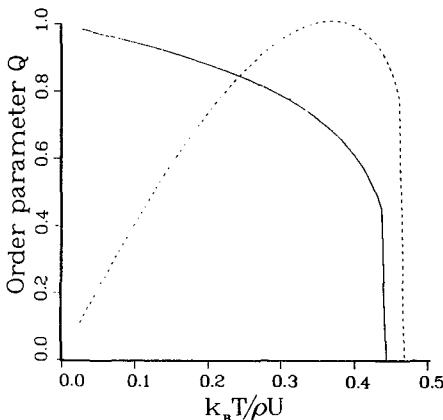


Figure 4.3: Order parameter as a function of temperature. The dashed line was obtained from the Landau expansion (4.26) and the solid line from the self-consistent equation (4.23).

This expansion is indeed of the form (3.43). We leave it as an exercise for the reader (Problem 4.2) to work out further details of the model.

In Figure 4.3 we plot the order parameter obtained by minimizing (4.26) as a function of the temperature. We also plot the order parameter resulting from the self-consistent equation (4.23). In the principal-axis frame with the molecules aligned preferentially along the z axis, this equation takes the form

$$Q = \frac{1}{2} \langle 3\mu^2 - 1 \rangle = \frac{\int_0^1 d\mu \frac{1}{2}(3\mu^2 - 1) \exp\{3\beta\rho U Q \mu^2\}}{\int_0^1 d\mu \exp\{3\beta\rho U Q \mu^2\}} . \quad (4.27)$$

Equation (4.27) is most easily solved by choosing a value for $x = 3\beta\rho U Q$, evaluating Q numerically and then using the calculated value of Q to obtain the temperature.

Figure 4.3 illustrates that while the Landau theory gives a correct qualitative picture, there are difficulties associated with using the Landau expansion for quantitative purposes in the case of a first-order transition. The problem is that the jump in the order parameter is not necessarily small and the expansion (3.43) to low order may not be accurate.

We note that the simple mean field theory (4.27) predicts that the discontinuity in the order parameter Q at the transition should be 0.43. Both smaller and larger values have been observed experimentally. When steric effects are included in the theory, as in the van der Waals theory of Section 4.4, one

tends to get a more strongly first-order transition. On the other hand, when one takes into account the fact that actual molecules do not have cylindrical symmetry (see, *e.g.*, Straley [291]) the discontinuity in the order parameter tends to be smaller than in the Maier-Saupe theory. It is then also possible, in principle, to obtain biaxial phases [59].

It is of interest to extend the Maier-Saupe theory to include the effect of a magnetic (or electric) field. The magnetic susceptibility will in general be anisotropic and we let χ_{\parallel} and χ_{\perp} correspond to orientations of the field parallel and perpendicular to the molecular axis. The energy of a molecule in the field is then

$$-\chi_{\parallel}(\hat{\mathbf{n}} \cdot \mathbf{H})^2 - \chi_{\perp}[H^2 - (\hat{\mathbf{n}} \cdot \mathbf{H})^2] = -\frac{1}{3}H^2\{(\chi_{\parallel} + 2\chi_{\perp}) + (\chi_{\parallel} - \chi_{\perp})[3(\hat{\mathbf{n}} \cdot \hat{\mathbf{H}})^2 - 1]\}. \quad (4.28)$$

We assume for simplicity that $\Delta\chi = (\chi_{\parallel} - \chi_{\perp}) > 0$ (*i.e.*, there is a tendency for the molecules to align parallel to the field). The field direction then becomes the preferred axis. We drop the first term in (4.28), which is independent of the molecular orientation, and write for the molecular pseudopotential in the presence of a field,

$$\epsilon_H(\hat{\mathbf{n}}) = -2\rho U(Q + \gamma)q \quad (4.29)$$

where

$$\gamma = \frac{\Delta\chi H^2}{3\rho U}. \quad (4.30)$$

The self-consistent equation now becomes

$$Q = \frac{\int_0^1 d\mu \frac{1}{2}(3\mu^2 - 1) \exp\{3\rho U\beta(Q + \gamma)\mu^2\}}{\int_0^1 d\mu \exp\{3\rho U\beta(Q + \gamma)\mu^2\}}. \quad (4.31)$$

The order parameter Q can easily be evaluated numerically for a given value of $x = 3\rho U\beta(Q + \gamma)$; once Q is determined, we can solve for the effective temperature. The results are depicted in Figure 4.4.

We see that for γ below a critical value γ_c there is a narrow temperature range for which Q is a triple-valued function of T . Not all these values correspond to a minimum in the free energy. This can be seen by plotting g and T as the parameter x is varied. The resulting curves are plotted in Figure 4.5. The region that is not a minimum of the free energy is the loop in the top curve of Figure 4.5. This region corresponds to the dashed curve in Figure 4.4. A first-order transition occurs at the intersection point. The point T_c , γ_c at which the loop has degenerated into a point is an ordinary critical point where

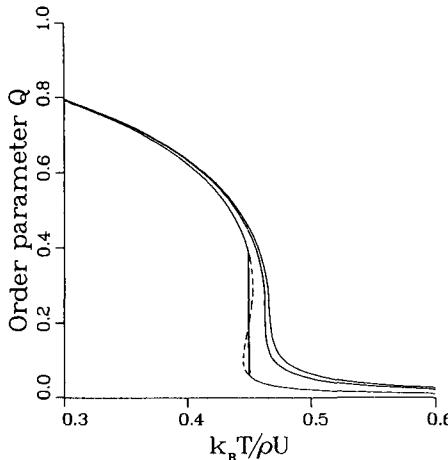


Figure 4.4: The order parameter as a function of temperature for different fields when $\Delta\chi > 0$. Solid curves, $\gamma = 0.005$, $\gamma = 0.011 = \gamma_c$, and $\gamma = 0.013$. The dashed curve for the lowest γ value corresponds to the unphysical region discussed in the text.

the transition is second order. We refer the interested reader to Wojtowicz and Sheng [329] and Palfy-Muhoray and Dunmur [229] for further details (the latter authors also discuss the interesting case $\gamma < 0$, for which there is a tricritical point and a biaxial phase occurs). The full phase diagram is given by Frisken et al. [104].

4.3 Blume–Emery–Griffiths Model

We next consider, as an example of a system exhibiting a tricritical point, (see also Section 3.9) a mixture of ^3He and ^4He in the liquid phase. When the temperature is lowered, pure ^4He undergoes a transition to the superfluid state (see Section 11.2). This transition is continuous, and is known as the λ transition, because of the λ -like shape of the specific heat singularity. If ^3He is added to the system, the transition temperature is lowered and the mixture remains homogeneous for low ^3He concentrations both below and above the critical temperature. At concentrations greater than $x_t = n_3/(n_3 + n_4) \approx 0.670$, the transition is discontinuous and accompanied by phase separation. One of the coexisting phases is a ^4He -rich superfluid, the other a ^3He -rich

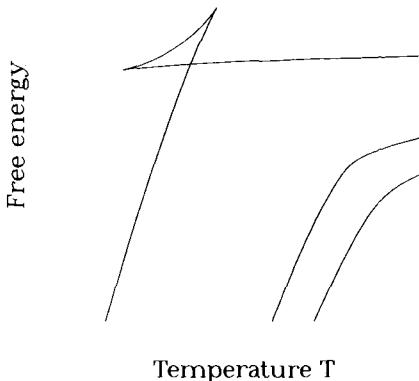


Figure 4.5: $g = G/N$ as a function of T for different values of γ .

normal fluid. The dividing point x_t , T_t , is the tricritical point alluded to above. A simple model exhibiting a tricritical point is found in Problem 3.13. Here we discuss a model for the ${}^3\text{He}$ – ${}^4\text{He}$ system described above. This model, known as the Blume–Emery–Griffiths model [45], is a classical lattice gas model which ignores the quantum-statistical nature of the λ transition (Section 11.2) but does take into account the effect of non-ordering impurities (${}^3\text{He}$) on the transition. The simplest version of the BEG model has the Hamiltonian

$$H = -J \sum_{\langle ij \rangle} S_i S_j + \Delta \sum_i S_i^2 - \Delta N$$

where $S_i = 0$ or ± 1 and the spins occupy a three-dimensional lattice with coordination number q . The connection between this “magnetic” Hamiltonian and the ${}^3\text{He}$ – ${}^4\text{He}$ system is made by identifying $S_i = \pm 1$ with a ${}^4\text{He}$ atom on site i (or in cell i) and $S_i = 0$ with a ${}^3\text{He}$ atom. The parameter Δ controls the number of ${}^3\text{He}$ atoms and represents the difference $\mu_3 - \mu_4$ in chemical potentials. The concentration of ${}^3\text{He}$ atoms is given by

$$x = 1 - \langle S_i^2 \rangle$$

and it is clear that $x \rightarrow 0$ as $\Delta \rightarrow -\infty$ and $x \rightarrow 1$ as $\Delta \rightarrow +\infty$. The normal to superfluid transition is modeled by the transition from a high-temperature paramagnetic phase, $\langle S_i \rangle = 0$, to an ordered ferromagnetic phase, $\langle S_i \rangle = m$, and we now proceed to construct a mean field theory for this transition. The expectation value $m = \langle S_i \rangle$ is the order parameter in this theory. Let $p_i(S_i)$ be the probability that the spin on site i takes on the value S_i and assume, in

the spirit of mean field theory, that

$$\tilde{p}(S_1, S_2, \dots, S_N) = \prod_{i=1}^N p_i(S_i) .$$

By translational invariance the probabilities will be the same on all sites

$$p_i(S_i) = p(S) .$$

We then have

$$\frac{G(T, \Delta)}{N} = -\frac{qJ}{2} \left(\sum_S p(S) S \right)^2 + \Delta \sum_S p(S) S^2 + k_B T \sum_S p(S) \ln p(S) - \Delta . \quad (4.32)$$

Minimizing (4.32) subject to the constraint $\sum_S p(S) = 1$ as in Section 2.5, we obtain

$$p(S) = \frac{\exp\{\beta(qJmS - \Delta S^2)\}}{1 + 2e^{-\beta\Delta} \cosh(\beta qJm)} . \quad (4.33)$$

Substituting (4.33) into (4.32), we obtain the approximate free energy

$$\frac{G(T, \Delta, m)}{N} = -\frac{1}{2} qJm^2 + \Delta \langle S_i^2 \rangle + k_B T \left[\frac{e^{\beta(qJm - \Delta)}}{D} \ln \frac{e^{\beta(qJm - \Delta)}}{D} + \frac{e^{-\beta(qJm + \Delta)}}{D} \ln \frac{e^{-\beta(qJm + \Delta)}}{D} - \frac{1}{D} \ln D \right] - \Delta \quad (4.34)$$

where

$$D = 1 + 2e^{-\beta\Delta} \cosh \beta qJm$$

and

$$\langle S_i^2 \rangle = \frac{2e^{-\beta\Delta} \cosh \beta qJm}{D} .$$

The expression for G may be simplified by decomposing the logarithms and we find

$$\frac{G(T, \Delta, m)}{N} = \frac{1}{2} qJm^2 - k_B T \ln(1 + 2e^{-\beta\Delta} \cosh \beta qJm) - \Delta . \quad (4.35)$$

This function must still be minimized with respect to the parameter m in order to obtain the equilibrium state for each (Δ, T) . We construct the Landau expansion for the free energy

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

By comparing terms, one finds

$$\begin{aligned} a(T, \Delta) &= -k_B T \ln(1 + 2e^{-\beta\Delta}) - \Delta \\ b(T, \Delta) &= qJ \left(1 - \frac{qJ}{\delta k_B T}\right) \\ c(T, \Delta) &= \frac{qJ}{2\delta^2} (\beta qJ)^3 \left(1 - \frac{\delta}{3}\right) \end{aligned}$$

where $\delta = 1 + \frac{1}{2}e^{\beta\Delta}$. In the disordered phase $m = 0$ and

$$x(T, \Delta) = \frac{1}{1 + 2e^{-\beta\Delta}} = \frac{\delta - 1}{\delta} .$$

Combining this with $b(T_c(\Delta)) = 0$ we find

$$\frac{T_c(x)}{T_c(0)} = 1 - x \quad (4.36)$$

and using $c(T_t, \Delta_t) = 0$ we have $x_t = \frac{2}{3}$.

This value of the tricritical concentration is in remarkable agreement with the experimental value $x_t \approx 0.670$. The predicted linear dependence of the transition temperature on concentration is not observed. The actual transition temperature varies as $(1 - x)^{2/3}$ for small x and the discrepancy is a consequence of the use of classical rather than quantum statistics in our model. The tricritical temperature in the BEG model [$T_t/T_c(0) = \frac{1}{3}$] is for this reason somewhat lower than the observed value of 0.4.

The nomenclature “tricritical point” is a consequence of the fact that at this point three lines of critical points meet. In our treatment of the BEG model we have not considered the effect of the field h that couples to the order parameter m and have therefore found only the line of λ transitions. The other two lines emerge in a symmetrical fashion from the tricritical point in the $\pm h$ directions. The interested reader is encouraged to consult the original paper [45] for a more general treatment of the model that makes the full structure of the critical surface apparent.

4.4 Mean Field Theory of Fluids: van der Waals Approach

With the exception of the Maier-Saupe model, our examples of mean field theories to this point have been lattice models. We now turn to the case of

a fluid consisting of particles interacting via a pair potential which contains a hard core, preventing the particles from overlapping, and a weak attractive tail. We wish to obtain an approximate equation of state for such a system in the spirit of mean field theory. Various modifications of the ideal gas law have been put forward to take into account the effect of interparticle interaction. One approach, with considerable physical appeal, was put forward by van der Waals, more than a hundred years ago. The van der Waals equation of state can be derived through many different routes; perhaps the simplest approach is through the following observations:

1. The internal energy of the ideal gas is purely kinetic in origin and independent of the volume. The entropy (2.15) can be written

$$S = Nk_B \ln V + \text{terms independent of volume.}$$

The Helmholtz free energy is thus

$$A = -Nk_B T \ln \frac{V}{N} + \text{terms independent of volume.}$$

This form of the free energy can be used to derive the equation of state for the pressure

$$P = - \left(\frac{\partial A}{\partial V} \right)_T = \frac{Nk_B T}{V}. \quad (4.37)$$

2. In a first approximation, the attraction between the particles reduces the internal energy per particle by an amount proportional to the average number of surrounding particles (*i.e.*, to the density). This allows us to approximate the volume-dependent part of the internal energy

$$E = -a \left(\frac{N}{V} \right) N$$

where a is a constant that depends on molecular properties.

3. Short distance repulsion prevents particles from approaching each other too closely. This has no direct effect on the internal energy, but reduces the free volume available to each particle. Let b be the excluded volume per particle. The total free volume is thus $V_f = V - Nb$. It is in the spirit of the derivation of the expression (2.15) for the entropy to interpret the volume-dependence as being due to the free volume, while the energy in (2.15) is the kinetic energy. With this interpretation we obtain for the free energy

$$A = -a \frac{N^2}{V} - Nk_B T \ln \frac{V - Nb}{N} + \text{terms independent of volume.}$$

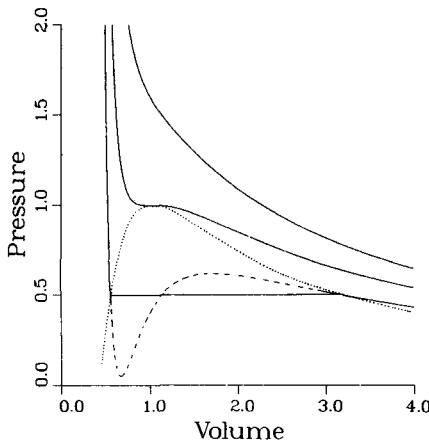


Figure 4.6: Isotherms and coexistence region according to van der Waals theory. Solid line: isotherm; dashed line: unphysical part of isotherm in coexistence region; dotted line: coexistence region. Pressure and volume in units of P_c and V_c .

The van der Waals equation of state follows by differentiation as in (4.37). After rearranging terms, we have

$$\left[P + a \left(\frac{N}{V} \right)^2 \right] (V - Nb) = Nk_B T . \quad (4.38)$$

This equation crudely describes the condensation of a gas into a liquid. For an extremely dilute gas $N/V \rightarrow 0$, $Nb \ll V$ and (4.38) reduces to the ideal gas equation of state. We are concerned here with lower temperatures and higher densities.

In Figure 4.6 we plot the behavior predicted by the van der Waals equation of state in the P – V plane. The critical isotherm is characterized by an infinite compressibility at the critical temperature, that is,

$$\left. \frac{\partial P}{\partial V} \right|_{N,T} = 0$$

at $T = T_c$, $V = V_c$. The isotherms predicted by (4.38) will, below $T = T_c$, have both a maximum and a minimum, that is, for certain values of the pressure below the critical point there will be three real roots when solving for the

volume. As $T \rightarrow T_c$ from below, the maximum and minimum of the isotherm merge and we obtain an inflection point. The critical point is therefore given by

$$\left(\frac{\partial P}{\partial V} \right)_T = \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0. \quad (4.39)$$

These equations yield

$$V_c = 3Nb \quad P_c = \frac{a}{27b^2} \quad k_B T_c = \frac{8a}{27b}. \quad (4.40)$$

Using these values of the critical parameters, it is possible to rewrite the van der Waals equation in a parameter-independent way. Defining the reduced dimensionless variables

$$v = \frac{V}{V_c} \quad p = \frac{P}{P_c} \quad t = \frac{T}{T_c}$$

and substituting the reduced quantities into the van der Waals equations gives the *law of corresponding states*,

$$\left(p + \frac{3}{v^2} \right) \left(v - \frac{1}{3} \right) = \frac{8t}{3}. \quad (4.41)$$

We must now deal with the coexistence region. For $t < 1$, the system undergoes a first-order phase transition from the gas to the liquid phase. The unphysical behavior of the isotherms given by (4.41) in this region (mechanical stability does not allow $\partial p / \partial v > 0$) is a characteristic of mean field theory. There is a simple method known as the equal-area or Maxwell construction for removing the unphysical regions. The coexisting regions must be at the same pressure and on the same isotherm for reasons of mechanical and thermal equilibrium. Consider the chemical potential (or Gibbs free energy per particle)

$$\mu = \frac{G}{N} = \frac{A + PV}{N} \quad (4.42)$$

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP. \quad (4.43)$$

Two coexisting phases must have the same chemical potential and along an isotherm we have

$$\int_1^2 d\mu = \mu(2) - \mu(1) = \frac{1}{N} \int V dP = 0 \quad (4.44)$$

where the coexisting phases have been labeled 2 and 1. In Figure 4.7 we have exchanged the axes of the plot of Figure 4.6 and it is easy to see that (4.44)

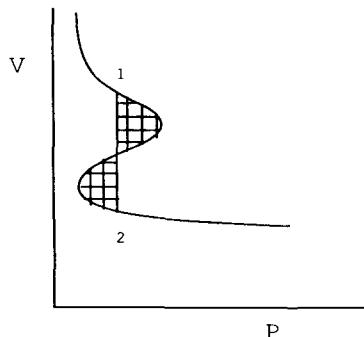


Figure 4.7: Maxwell construction.

implies that the areas of the two shaded regions must be the same—hence the name “equal-area construction”.

We note that for $T < T_c$, the equation $(\partial P/\partial v)_T = 0$ defines a curve known as the spinodal. Van der Waals suggested that the states between the coexistence curve and the spinodal are metastable single-phase states. In the case of phase separation discussed in Section 4.1, the spinodal is given by $(\partial^2 A/\partial c^2)_T = 0$. Spinodals also occur in the Maier–Saupe model of Section 4.2. They are a general feature of first order transitions in mean field theory.

Since (4.41) does not contain any free parameters, the law of corresponding states implies that when expressed in terms of the reduced variables, all fluids should exhibit similar behavior (*i.e.*, the coexistence region in reduced units should look the same for all fluids). Experimental evidence (Figure 4.8) indicates that the law of corresponding states is a valid concept, but that the van der Waals equation of state does not provide a good quantitative approximation to it.

The van der Waals theory outlined above can be generalized in a number of different ways. Different phenomenological equations of state which are parameterized in terms of the van der Waals constants a and b , and which give better agreement with observed corresponding states than the original van der Waals theory have been put forward by a number of authors [123], [300], [179].

The van der Waals approach can also be generalized to more complicated systems. Consider first an isotropic mixture containing N_i molecules of species i . We can obtain a van der Waals theory of mixing by writing, in the spirit of the Bragg–Williams approximation in Section 3.2, for the configurational part

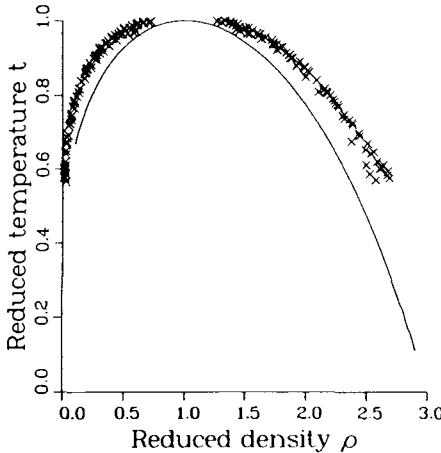


Figure 4.8: Density versus temperature in reduced units. Curve from van der Waals law of corresponding states. Data points are experimental results for several fluids quoted in [124].

of the internal energy per particle

$$E = \frac{1}{2} \sum_{ij} N_i \rho_j e_{ij}$$

where $\rho_j = N_j/V$ is the number density of species j and the e_{ij} 's are constants. If we write for the entropy of mixing

$$S_m = -k_B \sum_i N_i \ln \frac{N_i}{V_f^i}$$

and for the free volume of particles of species i ,

$$V_f^i = V \left(1 - \frac{1}{2} \rho_j v_{ij} \right)$$

we may approximate the Helmholtz free energy by

$$A = E + k_B T \sum_i N_i \ln \frac{N_i}{V_f^i} .$$

It is now straightforward to compute the pressure from $P = -\partial A / \partial V$ to obtain the equation of state. Depending on the values of the parameters, this theory

produces a rich variety of possible phase diagrams. Phase coexistence curves can be obtained by imposing the condition of mechanical and thermodynamic stability (*i.e.*, that the pressure and chemical potential $\mu_i = \partial A / \partial N_i$ of each species be the same in each phase). For a discussion of this type of calculation, we refer the interested reader to Hicks and Young [130].

It is also possible to construct van der Waals theories for anisotropic systems such as nematics in a similar spirit [98], [99], [228]. The van der Waals theory for interfaces is discussed in Section 5.4.

4.5 Spruce Budworm Model

Some time ago Ludwig et al. [181] proposed a simple ecological model intended to describe spruce budworm infestations. The model has three components *trees*, which are parasitized by *budworms*, who in turn are prey to *birds*. Changes in the respective populations take place on different timescales, with the budworm timescale being the fastest. In the simplest version of the model the tree and bird population are taken to be constant external parameters. The time derivative of the number N of insects is governed by the ordinary differential equation

$$\frac{dN}{dt} = r_B N \left(1 - \frac{N}{K_B}\right) - \frac{BN^2}{A^2 + N^2} + \Delta . \quad (4.45)$$

Here r_B is the net population growth rate (birth rate – death rate in the absence of predation). The constant K_B , commonly referred to as “the carrying capacity”, takes into account that even in the absence of predators the insect population will saturate. It is proportional to the number of trees available for infestation. The constant B is proportional to the number of predators (birds) present. If the number of budworms is too low the birds will prefer other insects species, hence the proportionality to N^2 rather than N in the predation term. The denominator is intended to describe a saturation effect — there are only so many budworms that a bird can eat. Because of its simplicity the model serves as an important toy model in population biology [210]. The last term on the right hand side of (4.45) represents *immigration*. This term was not present in the original model, but it is necessary to include such a term in the presence of fluctuations (to be discussed in Section 8.2). The reason for this is that in the absence of immigration the zero population state is an *absorbing state*, meaning that once such a state is reached there is no escape. Since there is also a finite, albeit extremely small probability that

the system will evolve towards the absorbing state the insect population will strictly speaking eventually go extinct if $\Delta = 0$. We note that equation (4.45) is mean-field-like in the following sense: A more complete description of the system would retain as dynamical variable at least the budworm populations on individual trees rather than simply the total number N .

Fick's law for diffusion assumes that the particle current is proportional to the gradient of the chemical potential. It is tempting to generalize this law and assume that the rate of approach of an order parameter to thermal equilibrium is proportional to the deviation of the appropriate free energy from its equilibrium value. In the context of Landau theory for phase transitions this approach is referred to as the time dependent Landau approximation. We then consider N to be the *order parameter* of the system:

$$\frac{dN}{dt} \propto -\frac{\partial G}{\partial N} . \quad (4.46)$$

The stable steady states of (4.46) are then the ones for which the *free energy* G has a local minimum. This assumption cannot hold for an arbitrary system, *e.g.*, if the model is extended to more species that evolve dynamically, (*e.g.*, trees and birds of prey). The problem is that we cannot in general find an exact differential³

$$dG = \sum_i \frac{\partial G}{\partial N_i} dN_i \quad (4.47)$$

yielding transport near the steady state for

$$\dot{N}_i \propto -\frac{\partial G}{\partial N_i} . \quad (4.48)$$

Following the notation of [210], we introduce the reduced variables

$$u = \frac{N}{A}; r = \frac{Ar_B}{B}, q = \frac{K_B}{A}, \delta = \frac{\Delta}{B} \quad (4.49)$$

³This issue has led to a controversy in theoretical economics which dates back to J. Willard Gibbs according to the book *More Heat than Light* by Mirowski [206]. Often attempts are made to exploit an analogy between thermodynamics and economics in which *utility* plays the role of a free energy and with quantities such as price given by derivatives in a manner similar to what we did for the *pressure* and *chemical potential* (for a recent example see *e.g.* [277]). Gibbs's objection, that realistic utilities will not have exact differentials, was according to Mirowski never satisfactorily answered nor even understood, hence the title of Mirowski's book.

in terms of which (4.45) becomes

$$\frac{A}{B} \frac{du}{dt} = ru\left(1 - \frac{u}{q}\right) - \frac{u^2}{1+u^2} + \delta . \quad (4.50)$$

Integrating (4.50) with respect to u we find that for fixed values of the parameters r, q, δ the reduced “free energy” will be proportional to

$$g = -\frac{ru^2}{2} + \frac{ru^3}{3q} + (u - \arctan u) - \delta u . \quad (4.51)$$

Of the parameters describing the mean field theory (4.45) we expect K_B , A , B to be proportional to system size (extensive) while r_B is intensive (independent of system size). Similarly the dependent variable N is extensive, while the reduced variables u, r, q, g, δ are all intensive.

The *steady states* are obtained by putting the right hand side of (4.50) to zero. This gives rise, in the limit $\delta \rightarrow 0$, to a cubic equation somewhat analogous to the law of corresponding states of the van der Waals theory of fluids (Section 4.4)

$$r(1+u^2)\left(1 - \frac{u}{q}\right) - u^2 = 0 . \quad (4.52)$$

In Figure 4.9 we plot a few “isoqs” (analogous to the isotherms of van der Waals theory). The system has a *critical point* $r = r_c$, $q = q_c$ for which $u = u_c$ is a triple root of (4.52). We have in the limit $\delta \rightarrow 0$

$$r_c = \frac{3\sqrt{3}}{8}; \quad q_c = 3\sqrt{3}; \quad u_c = \sqrt{3} . \quad (4.53)$$

For $q < q_c$ (4.52) has only a single real root while for $q > q_c$ there is a region $r_1 < r < r_2$ for which (4.52) has three real roots $u_g < u_i < u_l$. We refer to the two curves $r_1(q)$ and $r_2(q)$ as the *spinodals* (again exploiting the analogy with van der Waals theory). Of the three roots u_l and u_g are locally stable while the intermediate root is always unstable.

In Figure 4.10 we plot the phase diagram of the system. If we allow the interpretation of $g(u)$ as a free energy, the coexistence line will separate the regions where $g(u_l) < g(u_g)$ and $g(u_l) > g(u_g)$. Below this line we expect the low density phase (g) to be globally stable and the high density phase (l) to be *metastable*, while it is the other way around immediately above the coexistence line. This behavior corresponds to a first order (or discontinuous transition). In Section 8.2 we show how one can construct a different coexistence line from a microscopic stochastic version of the model.

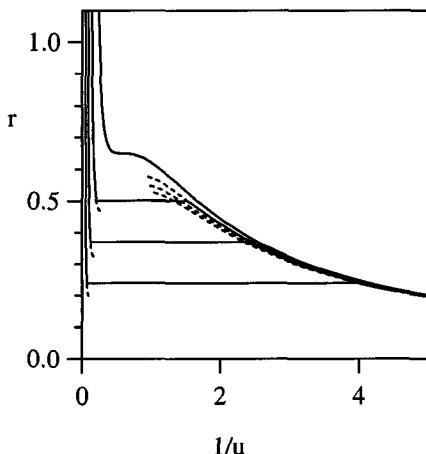


Figure 4.9: “Isoq”-curves. From top to bottom: $q = q_c$, $q = 8$, $q = 12$, $q = 20$. Dotted curves: metastable (local) minimum in free energy. Solid curves global (equilibrium) minimum in free energy.

Figures 4.9 and 4.10 suggest that $1/q$ is a temperature-like variable and that r is analogous to the pressure and u is analogous to the density in van der Waals theory.⁴ We will return to the spruce budworm model in Section 8.2 where we discuss fluctuations.

4.6 A Non-Equilibrium System: Two Species Asymmetric Exclusion Model

We argued in Section 3.3 that a one-dimensional system in equilibrium, with short range (local) interactions, cannot undergo a symmetry breaking phase transition at nonzero temperature. The argument was based on an estimate of

⁴There is a certain arbitrariness in this assignment, but this need not be of concern to us, since even in van der Waals theory the two-phase coexistence line is not parallel to either the pressure or temperature axis. Hence the pressure and temperature are not the scaling fields (see Section 7.2) in van der Waals theory.

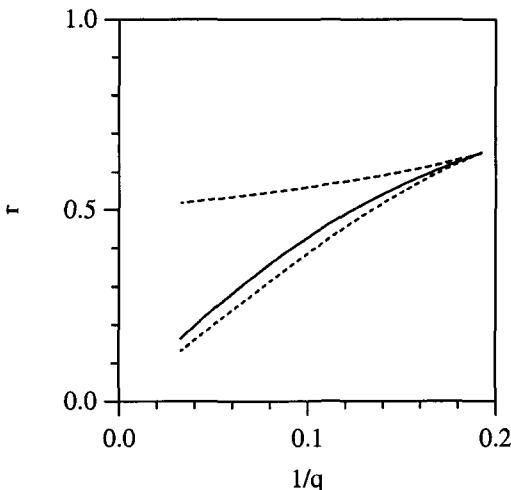


Figure 4.10: Phase diagram of spruce budworm model. Solid curve coexistence line, dotted curve spinodals (see text).

the free energy of a domain wall separating two symmetry-equivalent phases. If a system is kept out of equilibrium, the defect probability may not follow the equilibrium distribution, and the argument need not hold. Maintaining the system out of equilibrium will, however, require a supply of free energy. In a biological system this energy is provided by the metabolism of the organism. In the case of an electric current in a conductor the energy is provided by a battery or a power supply. In these cases the non-equilibrium nature of the system manifests itself by violation of the principle of *detailed balance* to be discussed in Sections 9.2.2 and 12.1.

In this section we wish to show that a symmetry breaking phase transition can take place in a one-dimensional *driven* diffusive system with short range interactions. The model has been studied by Evans et al. [86] and we refer to the original articles for some of the details and will here only summarize the results.

The model consists of a one-dimensional lattice. Each site on this lattice is either empty, or occupied by a positive charge, or by a negative charge. Positive charges can only move from left to right, while negative charges only

move from right to left never in reverse⁵ (this is the non-equilibrium feature of the model).

The model should be regarded as a “toy model” without any direct application, although the exclusion models were originally motivated by *superionic conductors*, materials that conduct electricity at elevated temperatures by ionic hopping under the influence of an applied field between empty sites in a lattice. The one species version has also been applied to the problem of pumping ions through pores in biological membranes and in zeolites [61].

Another possible motivation is *molecular motors*: certain proteins such as myosin, dynein and kinesin move within cells along filaments such as microtubulin and actin. These filament are *polar* in the sense that the different motor proteins only move in one direction along the filaments although different proteins can move in different directions (just like the two charges in our model). These small motors (their size is typically of the order 10nm) perform important biological functions. They transport chemicals across the cells, e.g. neurotransmitters along the axons, they help move chromosomes around during cell division, and they power muscles. Molecular motors are combustion engines; the energy for the unidirectional motion violating detailed balance is provided by the hydrolysis and reaction of adenosine triphosphate (ATP) \rightarrow adenosine diphosphate (ADP) + P.

Returning to our toy model: the time evolution of the model is specified by the following rules:

1. + particles jump to an empty site to the right at unit rate (*i.e.*, the particle will move with probability dt to the right in the time interval dt).
2. – particles jump to an empty site to the left at unit rate.
3. A + particle immediately to the left of a – particle will exchange position with the – particle ($+ - \rightarrow - +$) at rate q .
4. If the left-most site is empty it will become occupied by a + particle in a time interval dt with probability αdt (*i.e.*, the rate is α).
5. An empty right-most site will become occupied by a – particle with probability αdt in a time interval dt .

⁵For this reason the model is called *asymmetric*. Since only one charge can occupy a given site at any time we are dealing with an *exclusion* model. Hence the name *Two species asymmetric exclusion model*.

6. A – particle occupying the left-most site jumps off the chain at the rate β .
7. A + particle occupying the right-most site jumps off the chain at the same rate β .

Note the symmetry between + and – particles. We expect that when the system has been operating under the above rules for some time a *steady state* will establish itself with approximately constant currents j_+ and j_- of the two types of particles. From the symmetry one would expect the two currents to be the same. Somewhat surprisingly this turns out not always to be the case. The mechanism is as follows: If the rate α is large compared to β there is a tendency for the particles to pile up and cause a “traffic jam” as will happen on a highway if too many vehicles enter the road. Suppose now that a fluctuation causes there to be more + than – particles in the system. The +– exchange rule makes it possible for the – particles and some of the + particles to move, but some of the + particles will have + neighbors and be stuck in the traffic. This effect may cause an amplification of the fluctuation and result in symmetry breaking, somewhat in analogy with the Alben model of Problem 3.12.

It is relatively straightforward to set up an approximate mean field theory for the steady state in a chain of length N . In the steady state the current must be constant along the chain. Let p_i be the probability that site i from the left is occupied by a + particle and let m_i be the corresponding probability for – particles, while the probability that site i is empty is given by $1 - p_i - m_i$. This allows us to write for the two currents

$$j_+ = p_i(1 - p_{i+1} - m_{i+1}) + qm_{i+1} \quad (4.54)$$

$$j_- = m_i(1 - p_{i-1} - m_{i-1}) + qp_{i-1} \quad (4.55)$$

where $i \neq 1, N$. The currents will be subject to the boundary conditions

$$j_+ = \alpha(1 - p_1 - m_1) = \beta p_N \quad (4.56)$$

$$j_- = \beta m_1 = \alpha(1 - p_N - m_N) . \quad (4.57)$$

In the special case $q = 1$ the two equations (4.54) and (4.55) decouple and it is possible to obtain analytic results. We here only summarize some of these and refer the interested reader to Evans et al. [86] for the details.

1: Maximum current phase. If

$$\frac{\alpha\beta}{\alpha + \beta} > \frac{1}{2}$$

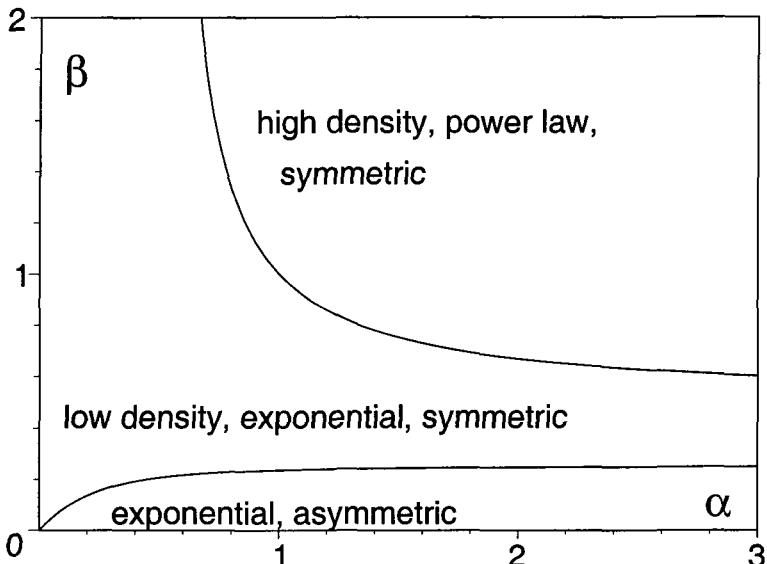


Figure 4.11: Mean field phase diagram for the 2-species asymmetric exclusion model of Evans et al. [86].

the particle densities slowly approach the constant value $\frac{1}{2}$ in the middle of the chain. This approach follows a power law and there is \pm symmetry. The current takes on its maximum value $j\pm = 1/4$.

2: *Low density \pm symmetric phase.* If

$$\frac{1}{2} > \frac{\alpha\beta}{\alpha + \beta} > \frac{1}{2} - \frac{\alpha\beta}{\alpha - \beta}$$

the particle density in the middle of the chain is less than $1/2$. There is a pile-up of particles near the exit end and the approach to the asymptotic density in the middle of the chain is exponential (fast).

3: *Asymmetric phase.* For

$$\frac{\alpha\beta}{\alpha + \beta} < \frac{1}{2} - \frac{\alpha\beta}{\alpha - \beta}$$

the symmetry between $+$ and $-$ particles is broken. For a narrow range of parameter values the density of both types of particles is low, but in most of this region the density is low for one species and high for the other.

The overall phase diagram for $q = 1$ is depicted in Figure 4.11. The phase transitions between the different phases outlined above are believed to be continuous. The qualitative features of the mean field phase diagrams has been confirmed by simulations. If $q \neq 1$, the mean field equations can only be solved numerically. One still finds the same phases as before, but some of the phase transitions are now discontinuous (first order).

4.7 Problems

4.1. Solid–Solid Solutions.

A crystalline solid is composed of constituents A and B . The energies associated with nearest-neighbor pairs of different types are, respectively, e_{AA} , e_{BB} and e_{AB} . Assume that

$$\epsilon = \frac{1}{2}e_{AA} + \frac{1}{2}e_{BB} - e_{AB} < 0$$

and that each site has q nearest neighbors.

- (a) Calculate the Helmholtz free energy in the Bragg–Williams approximation for a homogeneous system in which the concentration of type A atoms is c_A and that of B atoms is $c_B = 1 - c_A$.
 - (b) Show that the system will phase separate when $c_A = c_B = \frac{1}{2}$ below the temperature
- $$k_B T_c = \frac{1}{2}q|\epsilon| .$$
- (c) For $c_A \neq c_B$, show that phase separation will occur at a lower temperature than the T_c of part (b).
 - (d) Find the coexistence curve numerically and plot the result in the $k_B T/q|\epsilon|$, c_A plane.

4.2. Maier–Saupe Model of a Liquid Crystal.

- (a) Using the Maier–Saupe expression (4.25) for the free energy, derive the Landau expansion (4.26).
- (b) Find the transition temperature and the discontinuity in the order parameter at the transition predicted by the expansion found in part (a).

- (c) Evaluate numerically the transition temperature and the discontinuity of the order parameter and entropy at the transition in the Maier–Saupe model. (One of the weaknesses of the Maier–Saupe approximation is that the predicted latent heat is usually too large.)

4.3. Critical Point of Liquid Crystal with Positive Susceptibility Anisotropy

Consider a liquid crystal described by the Maier–Saupe model with a pseudopotential of the form (4.29) and $\gamma > 0$. As the field strength parameter γ is increased from zero the ordering transition will become more weakly first order until a critical point is reached. Find the critical value of the inverse temperature β and γ at the critical point in units where $\rho U = 1$.

4.4. Tricritical Point of Liquid Crystals with Negative Susceptibility Anisotropy

Consider a liquid crystal for which the anisotropy constant γ given by (4.29) is *negative*. It is now energetically favorable for the molecules to orient perpendicular to the magnetic field. If we choose the field to be the z -axis the order parameter Q will then be negative and the biaxial order parameter P will be non-zero in the low temperature phase and we can write for the pseudopotential in the Maier–Saupe model

$$\epsilon(\hat{n}) = 2\rho U[(Q + \gamma)q + \frac{1}{3}Pp] .$$

The model will exhibit a tricritical point for a certain value of β and γ . The problem is to locate this point. It is convenient to work in units of the inverse temperature parameter for which $\rho U = 1$. A possible way to proceed is as follows.

- (i) Find expressions for the coefficients a and b in the Landau expansion

$$G = a(\beta, \gamma) + \frac{1}{2}b(\beta, \gamma) + \frac{1}{4}c(\beta, \gamma) + \dots$$

assuming that Q has been determined selfconsistently from (4.31).

- (ii) For given values of $x = 3\beta(Q + \gamma)$ and γ Q can be determined numerically and from the definition of x the order parameter Q .
- (iii) Adjust β so that $b(\beta, \gamma)$ vanishes and evaluate $c(\beta, \gamma)$.
- (iv) Modify the value of *gamma* and repeat steps ii and iii until b and c vanish simultaneously. The resulting values of β and γ locate the tricritical point!

4.5. Lotka Volterra Model. Big fish sometimes eat little fish. If they don't find little fish they starve, but if they find them the population prospers. The little fish reproduce at a certain rate, but when too many are eaten by the big fish the population declines. Vito Volterra modeled this by the differential equations

$$\begin{aligned}\frac{dN_B}{dt} &= -aN_B + bN_B N_L \\ \frac{dN_L}{dt} &= cN_L - dN_B N_L .\end{aligned}\quad (4.58)$$

- (a) Find the steady state values of N_L and N_B and discuss the stability of the steady state. Describe the nature of the solutions to (4.58) for arbitrary starting states.
- (b) If one or both populations become very small immigration may become important. Modify (4.58) to

$$\begin{aligned}\frac{dN_B}{dt} &= -a(N_B - \lambda) + bN_B N_L \\ \frac{dN_L}{dt} &= c(N_L + \gamma) - dN_B N_L\end{aligned}\quad (4.59)$$

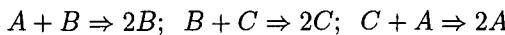
and assume that λ and γ are small compared to the steady state values of the populations found in a. How do the properties of the steady state change?

- (c) If the big fish disappear (4.58) allows the population of little fish to grow without limit. Modify the differential equation so that

$$\begin{aligned}\frac{dN_B}{dt} &= -aN_B + bN_B N_L \\ \frac{dN_L}{dt} &= cN_L(1 - \frac{N_L}{K_L}) - dN_B N_L\end{aligned}\quad (4.60)$$

where K_L is the *prey carrying capacity* of the environment. Assume that K_L is large compared with the steady state value of N_L found in a. Discuss how the steady state properties change and stability of the steady states.

4.6. Paper-Scissor-Stone Model. Consider a set of reactions



described by the differential equations

$$\begin{aligned}\frac{dN_A}{dt} &= \beta N_A(N_C - N_B) \\ \frac{dN_B}{dt} &= \beta N_B(N_A - N_C) \\ \frac{dN_C}{dt} &= \beta N_C(N_B - N_A) .\end{aligned}\quad (4.61)$$

- (a) Show that the system of equations admits the conservation laws

$$N_A + N_B + N_C = N = \text{constant}$$

$$N_A N_B N_C = p = \text{constant} .$$

- (b) Use the conservation laws to describe the family of solutions. Parametrize the concentrations $n_A = N_A/N$, $n_B = N_B/N$; $n_C = N_C/N$ in the same way as we did for the 3-state Potts model in (3.44) and plot a family of curves inside the triangle of Figure 3.11 using different values of the constant p .

4.7. Mean Field Theory for the Transverse Field Ising Model. Consider a system of half integer Ising spins with the Hamiltonian

$$H = -J \sum_{\langle ij \rangle} \sigma_{iz} \sigma_{jz} - \Gamma \sum_i \sigma_{ix}$$

where

$$\sigma_{iz} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_i ; \quad \sigma_{ix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_i .$$

This model was originally proposed by de Gennes [69] and has recently been much studied as a model for “quantum phase transitions” in systems such as LiHoF₄ (see e.g. Rönnnow et al. [257] and references therein).

In the spirit of mean field theory we approximate the magnetization components by

$$\begin{aligned}m_z &\equiv \langle \sigma_{iz} \rangle = \frac{\text{Tr} \sigma_z \exp(K\sigma_z + h\sigma_x)}{\text{Tr} \exp(K\sigma_z + h\sigma_x)} \\ &= \frac{\partial}{\partial K} (\ln \text{Tr} \exp(K\sigma_z + h\sigma_x))\end{aligned}\quad (4.62)$$

$$m_x = \frac{\partial}{\partial h} (\ln \text{Tr} \exp(K\sigma_z + h\sigma_x)) \quad (4.63)$$

where q is the number of neighbors to each spin, $K = \beta q J m_z$ and $h = \beta \Gamma$.

- (a) Evaluate the trace by diagonalizing

$$K\sigma_z + h\sigma_x = \begin{pmatrix} K & h \\ h & -K \end{pmatrix}$$

and show that

$$m_z = \frac{K}{\sqrt{K^2 + h^2}} \tanh(\sqrt{K^2 + h^2})$$

$$m_x = \frac{h}{\sqrt{K^2 + h^2}} \tanh(\sqrt{K^2 + h^2}) .$$

- (b) Show that the result in (a) gives rise to a phase transition between a high temperature paramagnetic phase and a low temperature ferromagnetic phase at a temperature $k_B T_c = 1/\beta_c$ given by

$$\tanh(\beta_c \Gamma) = \frac{\Gamma}{qJ} .$$