(d) What is the asymptotic expression of the curve of coexistence of phases in the immediate vicinity of the critical point?

(e) Use your results to obtain the critical exponents β, γ, δ, and α.

5. Consider the Curie–Weiss equation for ferromagnetism,

$$m = \tanh\left(\beta H + \beta\lambda m\right).$$

Obtain an asymptotic expression for the isothermal susceptibility, $\chi(T,H)$, at $T = T_c$ for $H \to 0$. Obtain asymptotic expressions for the spontaneous magnetization for $T << T_c$ (that is, for $T \to 0$) and $T \approx T_c$ (that is, for $t \to 0-$).

13 The Ising Model

Most of the experiments in the neighborhood of critical points indicate that critical exponents assume the same universal values, far from the predictions of the "classical theories" (as represented by Landau's phenomenology, for example). We now recognize that the universal values of the critical exponents depend on a just few ingredients:

(i) The dimension of physical systems. Usual three-dimensional systems are associated with a certain class of critical exponents. There are experimental realizations of two-dimensional systems, whose critical behavior is characterized by another class of distinct and well-defined critical exponents.

(ii) The dimension of the order parameter. For simple fluids and uniaxial ferromagnets, the order parameter is a scalar number. For an isotropic ferromagnet, the critical parameter is a three-dimensional vector.

(iii) The range of the microscopic interactions. For most systems of physical interest, the microscopic interactions are of short range. We will see that statistical systems with long-range microscopic interactions lead to the set of classical critical exponents.

Owing to the universal behavior of critical exponents, it is enough to analyze very simple (but nontrivial) models in order to construct a microscopic theory of the critical behavior. The Ising model, including short-range interactions between spin variables on the sites of a d-dimensional lattice, plays the role of a prototypical system. The Ising spin Hamiltonian is given by

$$\mathcal{H} = -J\sum_{(ij)}\sigma_i\sigma_j - H\sum_{i=1}^{N}\sigma_i, \tag{13.1}$$

where σ_i is a random variable assuming the values ±1 on the sites $i = 1, 2, ..., N$ of a d-dimensional hypercubic lattice. The first term, where the sum is over pairs of nearest-neighbor sites, represents the interaction energies introduced to bring about an ordered ferromagnetic state (if $J > 0$). The second term, involving the interaction between the applied field H and the spin system, is of a purely paramagnetic character (as we have already seen in previous chapters of this book). Since it was proposed by Lenz and solved in one dimension by Ernst Ising in 1925, the Ising model has gone through a long history [see, for example, the paper by S. G. Brush, in Rev. Mod. Phys. **39**, 883 (1967)].

The Ising model can represent the main features of distinct physical systems. In the usual magnetic interpretation, the Ising spin variables are taken as spin components (that may be pointing either up or down, along the direction of the applied field) of crystalline magnetic ions. We may also consider a binary alloy of type AB. In this case, the spin variables indicate whether a certain site on the crystalline lattice is occupied by an atom of either type A or type B (neighbors of the same type contribute with an energy $-J$; neighbors of different types, contribute with $+J$). As another example, take the ±1 spin variables to indicate either the presence $(+1)$ or the absence (-1) of a molecule in a certain cell of a "lattice gas" (which is a useful model for the critical behavior of a fluid system). This multiplicity of interpretations is compatible with the ability of the Ising model to represent the main features of the critical behavior of many different physical systems.

From the point of view of magnetism, the Ising Hamiltonian may be regarded as a kind of approximation for the Heisenberg Hamiltonian, associated with a highly anisotropic spin-1/2 magnetic insulator. The energy J is interpreted as the quantum exchange parameter of electrostatic origin. In this chapter, we take advantage of the more intuitive language of this magnetic analogy to derive some properties of the Ising model.

In order to solve the Ising problem, we have to obtain the canonical partition function

$$Z_N = Z(T, H, N) = \sum_{\{\sigma_i\}} \exp(-\beta\mathcal{H}), \tag{13.2}$$

where the sum is over all configurations of spin variables, and the Hamiltonian is given by equation (13.1). From this partition function, we have the magnetic free energy per site,

$$g = g(T, H) = \lim_{N\to\infty}\left[-\frac{1}{\beta N}\ln Z_N\right]. \tag{13.3}$$

In one dimension, it is relatively easy to obtain an expression for this free energy. We will use the technique of the transfer matrices, which can also be written in higher dimensions, to obtain a solution for the Ising chain. However, as shown by Ising in 1925, this one-dimensional solution is quite deceptive, since the free energy is an analytic function of T and H (except at the trivial point $T = H = 0$), which precludes the existence of a spontaneous magnetization (and of any phase transition).

Several approximate techniques have been developed to solve the Ising model in two and three dimensions. Some of them are quite simple and useful, and may lead to reasonable qualitative results for the phase diagrams (besides providing useful tools to investigate more complex model systems). However, as pointed out before, phase transitions are associated with a nonanalytic behavior of the free energy in the thermodynamic limit. As a consequence, we should be warned against any truncations or perturbative expansions around the critical point. Indeed, most of the approximate schemes can be written as a Landau expansion, leading to classical critical exponents.

In a mathematical "tour de force," Lars Onsager, in 1944, obtained an analytical solution for the Ising model on a square lattice, with nearest-neighbor interactions, in the absence of an external field. For $T \to T_c$, the specific heat diverges according to a logarithmic asymptotic form,

$$c_{H=0} \sim \ln|T - T_c|, \tag{13.4}$$

with a well-defined critical temperature, $k_B T_c/J = 2/\ln\left(1+\sqrt{2}\right)$. Therefore, the free energy is not analytic at T_c, and cannot be written as a Landau expansion. The Onsager solution has been reproduced and confirmed by different techniques on many planar lattices (with first-neighbor interactions). It represents a true milestone in the development of the modern theories of critical phenomena. By the first time, it was shown that a microscopic model leads to nonanalytic behavior within the framework of equilibrium statistical mechanics. The origins of this nonanalyticity were later explained, under much more general grounds, by the Yang and Lee theory of phase transitions (see Chapter 7), including the remarkable "circle theorem" about the zeros of the partition function in the thermodynamic limit. In the 1950s, C. N. Yang checked a result of Onsager for the spontaneous magnetization of the Ising ferromagnet on the square lattice to obtain the exponent $\beta = 1/8$, in sharp contrast with the classical value. Nowadays, although there are no exact solutions in a field, we may be sure that $\gamma = 7/4$ in two dimensions. All planar lattices, with short-range interactions, lead to the same set of critical exponents ($\alpha = 0$, $\beta = 1/8$, $\gamma = 7/4$), which are far from the experimental values for three-dimensional systems, and far as well from the classical Landau results.

The solution of the Ising model in three dimensions remains an open (and probably impossible) problem. However, we can use an argument due to

Peierls to prove the existence of spontaneous magnetization at sufficiently low temperatures. Also, since the 1960s there have been many efforts to obtain quite long series expansions (at high as well as low temperatures) for several thermodynamic quantities associated with the three-dimensional Ising model. From refined asymptotic analyses of these series, we obtain a range of values for the critical exponents in agreement with experimental measurements ($\beta \approx 5/16$, $\gamma \approx 5/4$, $\alpha \approx 1/8$). Also, more recent, and much more sophisticated, renormalization-group techniques lead to similar results. In the table below, we give the values of some usual thermodynamic critical exponents.

	Landau	Ising ($d = 2$)	Ising ($d = 3$)	Experiments
β	1/2	1/8	$\approx 5/16$	0.3 – 0.35
γ	1	7/4	$\approx 5/4$	1.2 – 1.4
δ	3	15	≈ 5	4.2 – 4.8
α	0	0 (log)	$\approx 1/8$	≈ 0

13.1 Exact solution in one dimension

In one dimension ($d = 1$), the Ising Hamiltonian is written as

$$\mathcal{H} = -J \sum_{i=1}^{N} \sigma_i \sigma_{i+1} - H \sum_{i=1}^{N} \sigma_i. \tag{13.5}$$

The canonical partition function is given by

$$Z_N = \sum_{\{\sigma_i\}} \exp \left[K \sum_{i=1}^{N} \sigma_i \sigma_{i+1} + \frac{L}{2} \sum_{i=1}^{N} (\sigma_i + \sigma_{i+1}) \right], \tag{13.6}$$

where $K = \beta J$, $L = \beta H$, and the second term has been rearranged to take advantage of a more symmetric form. As a matter of convenience, we adopt periodic boundary conditions, $\sigma_{N+1} = \sigma_1$. Now it is interesting to write the partition function as

$$Z_N = \sum_{\sigma_1, \sigma_2, \cdots, \sigma_N} \prod_{i=1}^{N} T(\sigma_i, \sigma_{i+1}), \tag{13.7}$$

where

$$T(\sigma_i, \sigma_{i+1}) = \exp \left[K \sigma_i \sigma_{i+1} + \frac{L}{2} (\sigma_i + \sigma_{i+1}) \right]. \tag{13.8}$$

This last expression can also be written as a standard 2×2 matrix, whose indices are the spin variables, $\sigma_i = \pm 1$ and $\sigma_{i+1} = \pm 1$. We then define a **transfer matrix**,

$$\mathbf{T} = \begin{pmatrix} T(+,+) & T(+,-) \\ T(-,+) & T(-,-) \end{pmatrix} = \begin{pmatrix} \exp(K+L) & \exp(-K) \\ \exp(-K) & \exp(K-L) \end{pmatrix}, \tag{13.9}$$

and use the matrix formalism to see that equation (13.7) for the canonical partition function is a trace of a product of N identical transfer matrices,

$$Z_N = \mathrm{Tr}\,(\mathbf{T})^N. \tag{13.10}$$

Furthermore, the transfer matrix (13.9) is symmetric, and can thus be diagonalized by a unitary transformation,

$$\mathbf{U}\mathbf{T}\mathbf{U}^{-1} = \mathbf{D}, \quad \text{with} \quad \mathbf{U}^{-1} = \mathbf{U}^{\dagger}, \tag{13.11}$$

where $\mathbf{D}$ is a diagonal matrix. Therefore, the canonical partition function can be written in terms of the eigenvalues of the transfer matrix,

$$Z_N = \mathrm{Tr}\,(\mathbf{U}^{-1}\mathbf{D}\mathbf{U})^N = \mathrm{Tr}\,(\mathbf{D})^N = \lambda_1^N + \lambda_2^N, \tag{13.12}$$

where

$$\lambda_{1,2} = e^K \cosh L \pm \left[e^{2K} \cosh^2 L - 2 \sinh(2K) \right]^{1/2}, \tag{13.13}$$

are given by the roots of the secular equation, $\det(\mathbf{T} - \lambda \mathbf{I}) = 0$. It is easy to see that these eigenvalues are always positive, and that $\lambda_1 > \lambda_2$ (except at the trivial point $T = H = 0$). In zero field, we have,

$$\lambda_1 = 2 \cosh K \geq \lambda_2 = 2 \sinh K, \tag{13.14}$$

with a degeneracy ($\lambda_1 = \lambda_2$) in the limit $K \to \infty$ (that is, for $T \to 0$).

To obtain the free energy in the thermodynamic limit, it is convenient to write

$$Z_N = \lambda_1^N \left[1 + \left(\frac{\lambda_2}{\lambda_1} \right)^N \right]. \tag{13.15}$$

Since $\lambda_2 < \lambda_1$, we have the limit

$$g(T, H) = \lim_{N \to \infty} \left[-\frac{1}{\beta N} \ln Z_N \right] = -\frac{1}{\beta} \ln \lambda_1, \tag{13.16}$$

that is,

$$g(T, H) = -\frac{1}{\beta} \ln \left\{ e^{\beta J} \cosh(\beta H) + \left[e^{2\beta J} \cosh^2(\beta H) - 2 \sinh(2\beta J) \right]^{1/2} \right\}, \tag{13.17}$$

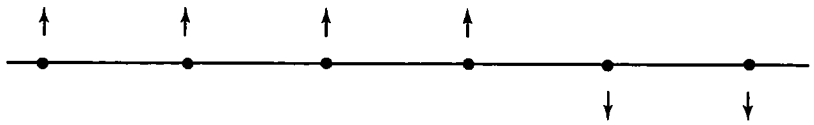

FIGURE 13.1. Ising chain with six sites and two different domains (at left and at right of a point wall).

which is an analytic function of T and H, from which we derive all the thermodynamic properties of the one-dimensional system.

The magnetization per spin is given by

$$m(T,H) = -\left(\frac{\partial g}{\partial H}\right)_T = \frac{\sinh(\beta H)}{\left[\sinh^2(\beta H) + \exp(-4\beta J)\right]^{1/2}}. \tag{13.18}$$

We then see that, as $m(T, H=0) = 0$, this model is unable to explain ferromagnetism. From the entropy per spin, $s = s(T,H) = -(\partial g/\partial T)_H$, we can calculate the specific heat at constant field. In zero field, we have

$$c_{H=0} = \frac{J^2}{k_B T^2}\left[\operatorname{sech}\left(\frac{J}{k_B T}\right)\right]^2, \tag{13.19}$$

which is a well-behaved function, displaying just a broad maximum as a function of temperature.

According to an argument attributed to Landau, we can show that there is no ordered state (therefore, no phase transition) in a one-dimensional system with short-range interactions. Consider the ground state of the Ising chain, in the absence of an external field, with all spins pointing up. To create two distinct domains, it is enough to reverse the sign of just a single spin (see figure 13.1).This costs an amount of energy $\Delta U = 2J > 0$. However, there is an enormous increase of entropy, $\Delta S = k_B \ln N$, since there are N distinct positions to locate the separating wall between domains (for a chain with $N+1$ sites). At finite temperatures, the free energy of this one-dimensional model undergoes a change

$$\Delta G = 2J - k_B T \ln N,$$

which becomes negative for sufficiently large values of N. Therefore, as the free energy decreases, there is a tendency to create more and more domains, which precludes the stability of any ordered phase. It is not difficult to check that similar arguments do not work in two dimensions, since the domain walls are not so simple, and both ΔU and ΔS are much more complicated.

Using the technique of the transfer matrices, we can calculate the spin–spin correlations,

$$\langle \sigma_k \sigma_l \rangle_N = \frac{1}{Z}\sum_{\{\sigma_i\}} \sigma_k \sigma_l \exp(-\beta\mathcal{H}). \tag{13.20}$$

For $l > k$, and a fair amount of algebra, it is possible to show that

$$\langle \sigma_k \sigma_l \rangle_N = \frac{\lambda_1^{N-(l-k)}\lambda_2^{(l-k)} + \lambda_1^{(l-k)}\lambda_2^{N-(l-k)}}{\lambda_1^N + \lambda_2^N}. \tag{13.21}$$

Thus, in the thermodynamic limit, we have

$$\langle \sigma_k \sigma_l \rangle = \lim_{N\to\infty} \langle \sigma_k \sigma_l \rangle_N = \left(\frac{\lambda_2}{\lambda_1}\right)^{(l-k)}, \tag{13.22}$$

which still works for $l < k$, if we replace the difference $(l-k)$ by its absolute value, $|l-k|$. In zero field, we write the pair correlation,

$$\langle \sigma_k \sigma_l \rangle_{H=0} = (\tanh K)^r, \tag{13.23}$$

where $r = |l-k|$ is the distance between sites k and l. This expression can also be written as

$$\langle \sigma_k \sigma_l \rangle_{H=0} = \exp\{r \ln(\tanh K)\} = \exp\left(-\frac{r}{\xi}\right), \tag{13.24}$$

from which we define the **correlation length**,

$$\xi = \frac{1}{|\ln(\tanh K)|}. \tag{13.25}$$

Now, we see that ξ diverges for $K \to \infty$ (that is, at the trivial critical point, $T = 0$). For $T \neq 0$, correlations decay exponentially, with the characteristic length ξ. For the Ising model in two dimensions, at $T \neq T_c$, and for large enough distances, it can be exactly shown that correlations decay exponentially, with a correlation length of the form $\xi \sim |t|^{-\nu}$, where $\nu = 1$ and $t = (T - T_c)/T_c \to 0$. At the critical point ($T_c = H = 0$), spin–spin correlations decay asymptotically as a power law,

$$\langle \sigma_k \sigma_l \rangle_{cr} \sim \frac{1}{r^{d-2+\eta}},$$

where $\eta = 1/4$, for $d = 2$ and $r \to \infty$. From the classical Ornstein and Zernike theory for the decay of the critical correlations, we obtain the (classical) critical exponents $\nu = 1/2$ and $\eta = 0$.

13.2 Mean-field approximation for the Ising model

The standard mean-field approximation, also known as the Bragg–Williams method, can be obtained in the canonical formalism if we suppose that, besides the constraints of fixed temperature and external magnetic field, there is an additional internal constraint that fixes the magnetization per spin.

For a spin-1/2 model, we write

$$N_+ + N_- = N \tag{13.26}$$

and

$$N_+ - N_- = Nm, \tag{13.27}$$

where N_+ (N_-) is the number of spins up (down), N is the total number of spins, and m is the dimensionless magnetization per spin. Given N_+ and N_- (that is, N and m), we can write the total entropy,

$$S = k_B \ln \frac{N!}{N_+!N_-!} = k_B \ln \frac{N!}{\left(\frac{N+Nm}{2}\right)!\left(\frac{N-Nm}{2}\right)!}. \tag{13.28}$$

Now, if we take into account the translational symmetry of the Hamiltonian, the internal energy of a nearest-neighbor Ising model on a d-dimensional hypercubic lattice is given by

$$U = \langle \mathcal{H} \rangle = -JdN \langle \sigma_i \sigma_j \rangle - HNm. \tag{13.29}$$

Therefore, with the additional constraint of fixed magnetization, the magnetic free energy per spin is given by

$$\begin{aligned} g(T,H;m) &= \frac{1}{N}(U - TS) = -Jd\langle \sigma_i \sigma_j \rangle - Hm \\ &\quad - \frac{k_B T}{N} \ln \frac{N!}{\left(\frac{N+Nm}{2}\right)!\left(\frac{N-Nm}{2}\right)!}. \end{aligned} \tag{13.30}$$

Up to this point there are no approximations. The difficult problem is the calculation of the pair correlations in terms of T, H, and m.

The Bragg–Williams approximation consists in neglecting fluctuations in the correlation functions. We then assume the approximation

$$\langle \sigma_i \sigma_j \rangle \approx \langle \sigma_i \rangle \langle \sigma_j \rangle = m^2. \tag{13.31}$$

Introducing a Stirling expansion to take care of the factorials, using the approximate form of the spin–spin correlations, and taking the thermodynamic limit, we can write the following Bragg–Williams free energy per spin,

$$\begin{aligned} g_{BW}(T,H;m) &= -Jdm^2 - Hm - \frac{1}{\beta}\ln 2 \\ &\quad + \frac{1}{2\beta}\left[(1+m)\ln(1+m) + (1-m)\ln(1-m)\right]. \end{aligned} \tag{13.32}$$

To remove the internal constraint of fixed magnetization, we minimize g_{BW} with respect to m. Hence, we obtain

$$\frac{\partial g_{BW}}{\partial m} = -2Jdm - H + \frac{1}{2\beta}\ln\frac{1+m}{1-m} = 0, \tag{13.33}$$

from which the Curie–Weiss equation follows,

$$m = \tanh(\beta 2Jdm + \beta H), \tag{13.34}$$

where the phenomenological parameter λ is identified as the product $2dJ$. In this approximation, the critical temperature is given by $k_B T_c = 2dJ$, and there is a transition even in one dimension. Although this result is completely wrong, especially at low dimensions, we anticipate that mean-field approximations become much better as the dimension increases.

The Bragg–Williams free energy, given by equation (13.32), can also be written as

$$g_{BW}(T,H;m) = -Jdm^2 - Hm - \frac{1}{\beta}\ln 2 + \frac{1}{\beta}\int \left(\tanh^{-1} m\right) dm, \tag{13.35}$$

which leads to an identification with the function $g(T,H;m)$, as obtained in the last chapter from the phenomenological equation of Curie–Weiss. We thus recover all of the classical results for the critical behavior.

The mean-field approximation can also be obtained from an elegant variational formalism based on the Peierls–Bogoliubov inequality, coming from convexity arguments, already known by Gibbs himself [see, for example, H. Falk, Am. J. Phys. **38**, 858 (1970)]. For all classical systems (in fact, also for quantum systems), we can write the inequality

$$G(\mathcal{H}) \le G_o(\mathcal{H}_o) + \langle \mathcal{H} - \mathcal{H}_o \rangle_o = \Phi, \tag{13.36}$$

where $G(\mathcal{H})$ and $G_o(\mathcal{H}_o)$ are free energies associated with two different systems given by the Hamiltonians $\mathcal{H}$ and $\mathcal{H}_o$, respectively, and the thermal average is taken with respect to a canonical distribution associated with $\mathcal{H}_o$. If we choose a noninteracting (trial) Hamiltonian,

$$\mathcal{H}_o = -\eta \sum_{i=1}^{N} \sigma_i, \tag{13.37}$$

where η is a parameter, we have

$$Z_o = \sum_{\{\sigma_i\}} \exp(-\beta \mathcal{H}_o) = (2\cosh \beta\eta)^N. \tag{13.38}$$

Thus

$$G_o = -\frac{N}{\beta}\ln[2\cosh \beta\eta] \tag{13.39}$$

and

$$\langle \mathcal{H} - \mathcal{H}_o \rangle_o = -JdN \langle \sigma_i \sigma_j \rangle_o - HN \langle \sigma_i \rangle_o + \eta N \langle \sigma_i \rangle_o , \tag{13.40}$$

with

$$\langle \sigma_i \sigma_j \rangle_o = \langle \sigma_i \rangle_o^2 = (\tanh \beta\eta)^2 \text{ and } \langle \sigma_i \rangle_o = \tanh \beta\eta. \tag{13.41}$$

Hence, we have

$$\begin{aligned} \frac{1}{N}\Phi &= \frac{1}{N}\Phi (T, H, N; \eta) = -\frac{1}{\beta}\ln 2 - \frac{1}{\beta}\ln(\cosh \beta\eta) \\ &\quad -Jd(\tanh \beta\eta)^2 - H\tanh \beta\eta + \eta \tanh \beta\eta. \end{aligned} \tag{13.42}$$

This expression is just an upper bound for the free energy of the Ising system under consideration. In the (mean-field) approximation, the free energy per spin will be given by the minimum of $\Phi(T, H, N; \eta)$ with respect to the field parameter η,

$$g_{MF} = \frac{1}{N}\min_{\eta} \Phi (T, H, N; \eta), \tag{13.43}$$

which corresponds to the smaller upper bound that comes from Bogoliubov's inequality with a free trial Hamiltonian. It should be noted that η depends on m through the relation $m = \tanh \beta\eta$, from which we recover the previous results of the Bragg–Williams approximation.

13.3 The Curie–Weiss model

Instead of working with an approximate solution on a Bravais lattice, it may be interesting to introduce a (simplifying) modification in the very definition of the statistical model. With a suitable modification, some physical features are not lost, and the new problem can be exactly solved. According to this strategy, a deformation of the interaction term of the nearest-neighbor Ising Hamiltonian leads to the **Curie–Weiss model**,

$$\mathcal{H}_{CW} = -\frac{J}{2N}\sum_{i=1}^{N}\sum_{j=1}^{N}\sigma_i\sigma_j - H\sum_{i=1}^{N}\sigma_i, \tag{13.44}$$

in which each spin interacts with all neighbors. The interactions are long ranged (indeed, of infinite range), but very weak, of the order $1/N$, to preserve the existence of the thermodynamic limit. In zero field, the ground-state energy per spin of this Curie–Weiss model is given by $U_{CW}/N = -J/2$, which should be compared with the corresponding result for a nearest-neighbor Ising ferromagnet on a hypercubic d-dimensional lattice, $U/N = -Jd$.

The canonical partition function associated with the Curie–Weiss model is given by

$$Z = \sum_{\{\sigma i\}} \exp\left[\frac{\beta J}{2N}\left(\sum_{i=1}^{N}\sigma_i\right)^2 + \beta H\sum_{i=1}^{N}\sigma_i\right]. \tag{13.45}$$

Now we use the Gaussian identity,

$$\int_{-\infty}^{+\infty} \exp\left(-x^2 + 2ax\right) dx = \sqrt{\pi}\exp\left(a^2\right), \tag{13.46}$$

to calculate the sum over the spin variables in equation (13.45),

$$\begin{aligned} Z &= \sum_{\{\sigma i\}} \frac{1}{\sqrt{\pi}}\int_{-\infty}^{+\infty} dx \exp\left[-x^2 + 2\left(\frac{\beta J}{2N}\right)^{1/2} x\sum_{i=1}^{N}\sigma_i + \beta H\sum_{i=1}^{N}\sigma_i\right] \\ &= \frac{1}{\sqrt{\pi}}\int_{-\infty}^{+\infty} dx \exp\left(-x^2\right)\left\{2\cosh\left[2\left(\frac{\beta J}{2N}\right)^{1/2} x + \beta H\right]\right\}^N. \end{aligned} \tag{13.47}$$

Introducing the change of variables

$$2\left(\frac{\beta J}{2N}\right)^{1/2} x = \beta J m, \tag{13.48}$$

we have

$$Z = \left(\frac{N}{2\pi\beta J}\right)^{1/2}\int_{-\infty}^{+\infty} dm \exp\left[-N\beta g(T, H; m)\right], \tag{13.49}$$

where

$$g(T, H; m) = \frac{1}{2}Jm^2 - \frac{1}{\beta}\ln\left[2\cosh\left(\beta J m + \beta H\right)\right]. \tag{13.50}$$

In order to obtain the free energy per spin in the thermodynamic limit, we use Laplace's method to calculate the asymptotic form, as $N \to \infty$, of the integral (13.49). We thus have

$$g(T, H) = \lim_{N\to\infty}\left\{-\frac{1}{\beta N}\ln Z\right\} = \min_{m}\left\{g(T, H; m)\right\}. \tag{13.51}$$

Hence,

$$\frac{\partial g(T, H; m)}{\partial m} = Jm - J\tanh\left(\beta J m + \beta H\right) = 0, \tag{13.52}$$

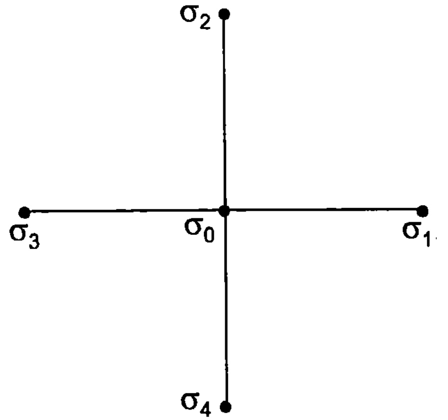

FIGURE 13.2. Spin cluster with a central site and four surrounding sites.

from which we have the (Curie–Weiss) equation of state,

$$m = \tanh\left(\beta J m + \beta H\right), \tag{13.53}$$

which is the trademark of the mean-field approximation for the Ising model. It is easy to check that this model with infinite-range interactions leads to the same classical results of the Bragg-Williams approximation for the Ising model on a Bravais lattice. As in the phenomenological treatment of Landau, the expansion of the "functional" $g(T, H; m)$ in powers of m gives rise to a (rigorous) analysis of the transition in the Curie-Weiss model. Although the coefficients of the various powers of m are different from the corresponding terms in the expansion of the Bragg–Williams "functional," all the critical parameters are exactly the same [see, for example, C. E. I. Carneiro, V. B. Henriques, and S. R. Salinas, Physica A**162**, 88 (1989)].

13.4 The Bethe–Peierls approximation

There are some self-consistent approximations for the Ising model on a Bravais lattice, usually correct in one dimension, which do take into account some short-range fluctuations, and are thus capable of displaying some features of the phase diagrams that are not shown by the standard mean-field approximations (although critical exponents keep their classical values). The Bethe–Peierls approximation is very representative of these self-consistent calculations.

Consider a cluster of a central spin σ_o, in an external field H, and q surrounding spins, in an effective field H_e, which is supposed to mimic the effects of the remaining crystalline lattice (see figure 13.2). The spin

Hamiltonian of this cluster is given by

$$\mathcal{H}_c = -J\sigma_o\left(\sigma_1 + \ldots + \sigma_q\right) - H\sigma_o - H_e\left(\sigma_1 + \ldots + \sigma_q\right). \tag{13.54}$$

Thus, we write the canonical partition function of the cluster,

$$Z_c = \sum_{\{\sigma i\}} \exp\left(-\beta\mathcal{H}_c\right) = \sum_{\sigma_o} \exp\left(\beta H\sigma_o\right)\left[2\cosh\left(\beta J\sigma_o + \beta H_e\right)\right]^q. \tag{13.55}$$

From this expression, we calculate the spin magnetization of the central site,

$$m_o = \frac{1}{\beta}\frac{\partial}{\partial H}\ln Z_c, \tag{13.56}$$

and the spin magnetization of one of the surrounding sites,

$$m_p = \frac{1}{\beta q}\frac{\partial}{\partial H_e}\ln Z_c. \tag{13.57}$$

After some algebraic manipulations, equation (13.56) may be written as

$$m_o = \tanh\left[\beta H + q\tanh^{-1}\left(\tanh\beta J\tanh\beta H_e\right)\right]. \tag{13.58}$$

Also, it is not difficult to write equation (13.57) in the more convenient form

$$\begin{aligned} m_p &= \frac{\left(1-\tanh^2\beta J\right)\tanh\beta H_e + m_o\left(1-\tanh^2\beta H_e\right)\tanh\beta J}{1-\left(\tanh\beta J\tanh\beta H_e\right)^2} \\ &= \frac{\tanh\left(\beta H_e + \beta J\right) + \tanh\left(\beta H_e - \beta J\right)\exp\left(-2\tanh^{-1}m_o\right)}{1+\exp\left(-2\tanh^{-1}m_o\right)}. \end{aligned} \tag{13.59}$$

The self-consistent condition, from which we eliminate the effective field, is given by

$$m_o = m_p = m, \tag{13.60}$$

which leads to the **equation of state** of the Bethe–Peierls approximation, $m = m(T, H)$.

In zero field ($H = 0$), and in the neighborhood of the critical temperature, m and H_e are very small. Therefore, we can write expansions for equations (13.58) and (13.59),

$$m = q\left(\tanh\beta J\right)\tanh\beta H_e + \ldots, \tag{13.61}$$

$$m = \frac{1}{\cosh^2\beta J}\beta H_e + m\tanh\beta J + \ldots. \tag{13.62}$$

From these expansions, it is easy to check that the critical temperature, in this Bethe–Peierls approximation, will be given by

$$\frac{k_B T_c}{J} = 2\left[\ln \frac{q}{q-2}\right]^{-1}. \tag{13.63}$$

In one dimension (that is, for $q = 2$), there is no phase transition ($T_c = 0$). For $q = 4$ (which corresponds to a square lattice), $k_B T_c/J = 2/\ln 2 = 2.885...$, smaller than the critical temperature from the Bragg–Williams approximation, $k_B T_c/J = 4$, but still larger than the exact Onsager value, $k_B T_c/J = 2/\ln\left(1+\sqrt{2}\right) = 2.269....$

Approximations of the Bethe–Peierls type, based on self-consistent calculations for a small cluster of spins, give an equation of state, but do not lead to an expression for the free energy of the system (in general, it is inconsistent to write the free energy from the canonical partition function Z_c of the cluster). In order to obtain a consistent free energy from the equation of state, we write

$$g = -\int m(T,H)\, dH + g_o(T), \tag{13.64}$$

where $g_o(T)$ is a well-behaved function of temperature (which may be found, for example, from a comparison with the high-temperature limit of the exact free energy). For the Ising ferromagnet, we can go through some algebraic manipulations to calculate this integral. Initially, note that equation (13.58) may be written as

$$m = \frac{\exp(2\beta H) - x^q}{\exp(2\beta H) + x^q}, \tag{13.65}$$

where

$$x = \frac{1 - \tanh\beta J \tanh\beta H_e}{1 + \tanh\beta J \tanh\beta H_e}. \tag{13.66}$$

We can now use equation (13.59) to write

$$\exp(2\beta H) = x^{q-1}\frac{\exp(2\beta J) - x}{x\exp(2\beta J) - 1}. \tag{13.67}$$

Therefore, the magnetization m and the field H can be expressed in terms of the new variable x. Hence, from equation (13.64), we have

$$g = -\int m\frac{\partial H}{\partial x}dx + g_o(T), \tag{13.68}$$

where

$$m = \frac{-zx^2 + z}{zx^2 - 2x + z} \tag{13.69}$$

and

$$2\beta\frac{\partial H}{\partial x} = \frac{q-1}{x} - \frac{1}{z-x} - \frac{z}{zx-1}, \tag{13.70}$$

with $z = \exp(2\beta J)$. Now, we perform some additional algebraic manipulations to show that

$$g = -\frac{q-1}{2\beta}\ln x + \frac{1}{2\beta}\ln(z-x) + \frac{1}{2\beta}\ln(zx-1)$$

$$+\frac{q-2}{2\beta}\ln\left(zx^2 - 2x + z\right) + g_o(T), \tag{13.71}$$

which is the free energy associated with the Bethe–Peierls approximation.

Finally, it is interesting to remark that the results of the Bethe–Peierls approximation can be recovered from an exact solution of the Ising model on a Cayley tree. This graph is a peculiar layered structure, in which the spins belonging to a certain generation interact with q other spins belonging to the next generation, such that there are no closed cycles. Indeed, the correspondence between the approximate and exact solutions works in the central part of the limit of a large Cayley tree (which is then called a Bethe lattice). The interested reader may check the works of C. J. Thompson, J. Stat. Phys. **27**, 441 (1982), and of M. J. Oliveira and S. R. Salinas, Rev. Bras. Fis. **15**, 189 (1985).

13.5 Exact results on the square lattice

The discussion of the Onsager solution (and of its several alternatives) is certainly beyond the scope of this book. The interested reader, with plenty of spare time, should check the work of T. D. Schultz, D. C. Mattis, and E. H. Lieb, Rev. Mod. Phys. **36**, 856 (1964), where the technique of the transfer matrix is used to reduce the calculation of the eigenvalues to the problem of diagonalizing the Hamiltonian of a system of free fermions. The transfer matrix is written in terms of Pauli spin operators, which are then changed into fermions through the ingenious Jordan–Wigner transformation. We shall limit our considerations to a mere listing of some of the Onsager results.

In the **thermodynamic limit**, the free energy of the Ising model (on a square lattice, with nearest-neighbor interactions, in zero field) may be written as a double integral,

$$-\beta g(T) = \ln 2 + \frac{1}{2\pi^2}\int_0^\pi\int_0^\pi \ln\left[\cosh^2 2K - \sinh 2K\left(\cos\theta_1 + \cos\theta_2\right)\right] d\theta_1 d\theta_2, \tag{13.72}$$

where $K = \beta J$ (in the original solution, Onsager already considered different interactions along the two directions of the square lattice). Therefore, we have the internal energy

$$u = -\frac{J}{\tanh K}\left[1 + \frac{\sinh^2 2K - 1}{\pi^2} \times \int_0^\pi\int_0^\pi \frac{d\theta_1 d\theta_2}{\cosh^2 2K - \sinh 2K\left(\cos\theta_1 + \cos\theta_2\right)}\right]. \tag{13.73}$$

The integral in this expression logarithmically diverges for

$$\cosh^2 2K = 2\sinh 2K, \tag{13.74}$$

that is,

$$\sinh 2K = 1, \tag{13.75}$$

which gives the Onsager critical temperature,

$$K_c^{-1} = \frac{k_B T_c}{J} = \frac{2}{\ln\left(1+\sqrt{2}\right)} = 2.269.... \tag{13.76}$$

In the neighborhood of the critical temperature, it is convenient to introduce a (small) parameter,

$$\delta = \left(\sinh 2K - 1\right)^2. \tag{13.77}$$

For $\delta \to 0$, we write

$$\int_0^\pi\int_0^\pi \frac{d\theta_1 d\theta_2}{\cosh^2 2K - \sinh 2K\left(\cos\theta_1 + \cos\theta_2\right)} \sim \int_0\int_0 \frac{d\theta_1 d\theta_2}{\delta + \frac{1}{2}\sinh 2K\left(\theta_1^2 + \theta_2^2\right)}$$

$$= 2\pi \int_0 \frac{r dr}{\delta + \frac{1}{2}r^2 \sinh 2K} \sim -2\pi \ln\delta, \tag{13.78}$$

where we have kept the leading term only (and used polar coordinates to simplify the integral in the intermediate step). From this asymptotic form, we have the internal energy in the neighborhood of the critical temperature,

$$u \sim -\frac{J}{\tanh K_c}\left[1 + A\left(K - K_c\right)\ln\left|K - K_c\right|\right], \tag{13.79}$$

where A is a constant. Taking the derivative with respect to temperature, we have the famous asymptotic formula for the zero-field specific heat,

$$c_{H=0} \sim B \ln\left|K - K_c\right|, \tag{13.80}$$

where B is a constant and $K \to K_c$.

From equation (13.73), we can write an analytic expression for the internal energy in terms of an elliptic integral of the first kind,

$$u = -\frac{J}{\tanh K}\left[1 + \left(2\tanh^2 2K - 1\right)\frac{2}{\pi}K\left(k_1\right)\right], \tag{13.81}$$

where

$$k_1 = \frac{2\sinh\left(2K\right)}{\cosh^2 2K}, \tag{13.82}$$

and $K\left(k_1\right)$ is a complete elliptic integral of the first kind,

$$K\left(k_1\right) = \int_0^{\pi/2}\left[1 - k_1^2\sin^2\theta\right]^{-1/2} d\theta. \tag{13.83}$$

The specific heat can also be written in terms of complete elliptic integrals (of first and second kind). Unfortunately, however, we do not have generalizations of these results for either three dimensions or in the presence of an external field!

Exercises

1. Consider a one-dimensional spin-1 model, given by the Hamiltonian

$$\mathcal{H} = -J\sum_{i=1}^N S_i S_{i+1} + D\sum_{i=1}^N S_i^2,$$

where $J > 0$, $D > 0$, and $S_i = -1, 0, +1$, for all lattice sites.

   (a) Assuming periodic boundary conditions, calculate the eigenvalues of the transfer matrix.
   (b) Obtain expressions for the internal energy and the entropy per spin.
   (c) What is the ground state of this model ($T = 0$) as a function of the parameter $d = D/J$? Obtain the asymptotic form of the eigenvalues of the transfer matrix, for $T \to 0$, in the characteristic regimes of the parameter d.

2. The one-dimensional Ising ferromagnet is given by the Hamiltonian

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

with $J > 0$ and $\sigma_i = \pm 1$ for all lattice sites.

(a) In zero field ($H = 0$), show that

$$\langle \sigma_k \sigma_l \rangle = (\tanh \beta J)^{|k-l|} .$$

(b) Consider the fluctuations of the magnetization in the canonical ensemble to show that

$$\chi(T,H) \equiv \left(\frac{\partial m}{\partial H}\right)_\beta = \frac{\beta}{N}\left\langle \sum_{i,j=1}^{N} \sigma_i \sigma_j \right\rangle_N - \frac{\beta}{N}\left\langle \sum_{i=1}^{N} \sigma_i \right\rangle_N \left\langle \sum_{j=1}^{N} \sigma_j \right\rangle_N .$$

(c) Use the previous results to obtain an expression for the magnetic susceptibility in zero field, $\chi_0 = \chi(T, h \to 0)$. Sketch a graph of χ_o versus temperature.

(d) Obtain an expression, in zero field, for the four-spin correlation function, $\langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle$, with $1 \leq i \leq j \leq k \leq l \leq N$.

(e) Show that the specific heat in zero field may be written as a sum over four-spin correlation functions.

3. For a well-behaved convex function $\phi(x)$ of a random variable x, show that

$$\phi(x) \geq \phi(\langle x \rangle) + (x - \langle x \rangle)\phi'(x) .$$

Taking the average with respect to a positive measure, show that

$$\langle \phi(x) \rangle \geq \phi(\langle x \rangle) ,$$

which is known, for $\phi(x) = \exp(x)$, as Jensen's inequality. Show that we obtain the classical version of the Peierls–Bogoliubov inequality if we assume that

$$\langle \cdots \rangle = \frac{1}{Z_o} \mathrm{Tr}[\exp(-\beta \mathcal{H})(\cdots)]$$

and that

$$\phi(x) = \exp[\beta(\mathcal{H}_o - \mathcal{H})] .$$

4. The Blume–Capel model on a lattice of coordination q is given by the spin Hamiltonian

$$\mathcal{H} = -J \sum_{(ij)} S_i S_j + D \sum_{i=1}^{N} S_i^2 - H \sum_{i=1}^{N} S_i,$$

where the first sum is over nearest-neighbor sites, all parameters are positive, and $S_i = -1, 0, +1$ for $i = 1, 2, ..., N$. Use the Bogoliubov–Peierls variational principle, with a trial Hamiltonian of the form

$$\mathcal{H}_o = +D \sum_{i=1}^{N} S_i^2 - \eta \sum_{i=1}^{N} S_i,$$

where η is a variational parameter, to obtain an approximate solution for the free energy of this system,

$$g_{approx}(T,H) = \min_{\eta} \{g(T,H;m)\} ,$$

where m is a function of η that corresponds to the magnetization per spin. In zero field ($H = 0$), obtain the coefficients of the expansion

$$g(T, H = 0; m) = A + Bm^2 + Cm^4 + Dm^6 + \ldots .$$

Now consider the phase diagram in zero field (in the $d = D/J$ versus $t = k_B T/J$ plane, for $H = 0$). Obtain an expression for the line of second-order transitions (λ line), given by $B = 0$ with $C > 0$, and locate the tricritical point ($B = C = 0$, with $D > 0$). What happens in the region of the phase diagram where $C < 0$? What happens at $T = 0$?

5. Sketch a graph of the specific heat in zero field as a function of temperature for the Ising ferromagnet in the Curie–Weiss version. Obtain an expression for the magnetic susceptibility $\chi(T,H)$. Sketch the qualitative form of χ versus the magnetic field H for three typical values of temperature ($T_1 < T_c$, $T_2 = T_c$, and $T_3 > T_c$).

6. The Curie–Weiss version of the Blume–Capel model, with a ferromagnetic ground state, is given by the spin Hamiltonian

$$\mathcal{H} = -\frac{J}{2N}\left(\sum_{i=1}^{N} S_i\right)^2 + D \sum_{i=1}^{N} S_i^2 - H \sum_{i=1}^{N} S_i,$$

where the parameters are positive, and $S_i = +1, 0, -1$ for all sites.

(a) Show that the free energy per spin may be written as

$$g(t,d,h) = \min_{y} \{g(t,d,h;y)\} ,$$

where $t = k_B T/J$, $d = D/J$, and $h = H/J$. Obtain an expression for $g(t,d,h;y)$.

(b) From an expansion of $g(t,d,h;y)$ in powers of y, obtain expressions for the critical line and the tricritical point (compare with the results of problem 3).

(c) Sketch the phase diagram in the $d - t$ plane (for $h = 0$).

(d) Sketch graphs of the spontaneous magnetization versus d for some characteristic values of t.

7. Use the Bethe–Peierls approximation for the ferromagnetic Ising model in the absence of an external field to obtain an expression for the expected value $\langle \sigma_o \sigma_1 \rangle$, where σ_o is the central spin of the cluster and σ_1 is the spin on a surrounding site. Sketch a qualitative graph of $\langle \sigma_o \sigma_1 \rangle$ versus temperature. Sketch a graph of the specific heat in zero field versus temperature (compare with the result for the Curie–Weiss version of the Ising model).

14
Scaling Theories and the Renormalization Group

It is too strong to assume that the free energy of a model system in the critical region can be expanded as a power series of the order parameter. The divergent specific heat of the Onsager exact solution for the two-dimensional Ising model precludes an expansion whose coefficients are analytic functions of temperature. In the 1960s, there appeared a number of (weaker) scaling hypotheses, based on some general assumptions about the form of the thermodynamic potentials. Although these scaling hypotheses do not lead to a microscopic treatment of critical phenomena, they do provide a way of going beyond the phenomenological equations of van der Waals and Curie–Weiss. The microscopic justification of these ideas, as well as a real possibility of calculating values for the critical exponents to compare with experimental data and theoretical predictions, were provided by the advent of the modern renormalization-group techniques.

14.1 Scaling theory of the thermodynamic potentials

In the neighborhood of a critical point, we assume that the free energy per spin $g(T, H)$ of a simple uniaxial ferromagnet can be written as the sum of a regular, and less interesting part, $g_o(T, H)$, and a singular part, $g_s(T, H)$, which contains all of the anomalies of the critical behavior. It is convenient to write the singular part of this thermodynamic potential in terms of the reduced variables $t = (T - T_c)/T_c$ and H, which vanish at the