

Supplement to Chapter 8

REVIEW QUESTIONS

- 8.1** Derive the grand potential ψ for a monatomic ideal gas.
- 8.2** Derive the cluster expansion, up to order ζ^3 , for the grand potential of a real gas.
- 8.3** In terms of the cluster expansion of ψ , write an expression for the potential energy.
- 8.4** What is the form of the Lenard–Jones potential?
- 8.5** From the cluster expansion for ψ , derive the virial expansion for p/kT up to terms of order n^2 .
- 8.6** Describe the phase transition that occurs in a nematic liquid crystal.
- 8.7** Describe our simple two-dimensional model of a nematic liquid crystal.
- 8.8** In the following formula for the partition function of the model, what is the function $F(C_x, C_y)$?

$$Z(N_x, N_y, \beta, A) = \frac{1}{N_x! N_y! \lambda^{2(N_x + N_y)}} \int_A F(C_x, C_y) dC_x dC_y$$

- 8.9** How was the affinity for x -particles expressed as a ratio of partition functions?
- 8.10** What was the crucial approximation made in solving the model by the mean-field method?
- 8.11** Describe, qualitatively, the predictions of the mean-field solution.
- 8.12** For a system of adsorbed particles, with nearest-neighbor interactions, how was the canonical partition function calculated, using the mean-field approximation?
- 8.13** Using the mean-field approximation, calculate the partition function for a system of adsorbed particles with nearest-neighbor interactions.
- 8.14** For a system of interacting adsorbed particles, describe what is wrong with the expression obtained for $\alpha(n)$ by the mean-field method. (n is the particle density.)
- 8.15** What are the two conditions for equilibrium of the high-density and the low-density phases of the adsorbed particle system?
- 8.16** Describe the logic behind the Maxwell construction for the phase transition line in the α - n plane.
- 8.17** For a system with discrete configurations and a transition probability $T(C \rightarrow C')$, derive the master equation.
- 8.18** What is the “condition of detailed balance” in the Monte Carlo method?
- 8.19** What does the Monte Carlo method actually supply; that is, what is its fundamental output?
- 8.20** For a system of a single particle on a one-dimensional lattice with an energy function $E(n)$, describe a computer algorithm that implements the Monte Carlo method.
- 8.21** For a two-dimensional Ising lattice, describe a computer algorithm that implements the Monte Carlo method.

- 8.22** Describe how one can accurately calculate the specific heat and magnetic susceptibility of an Ising system, using the Monte Carlo method.
- 8.23** Qualitatively describe diamagnetism and paramagnetism.
- 8.24** For an atom with a z component of magnetic moment $m_z = \alpha M$, where $-J < M < J$, in a magnetic field B , calculate the magnetic partition function.
- 8.25** From the magnetic partition function, obtain a formula for the magnetic energy per atom.
- 8.26** What is Curie's law?
- 8.27** Describe the process of cooling by adiabatic demagnetization.
- 8.28** What is the source of the interaction between neighboring atoms that leads to ferromagnetism?
- 8.29** What is hysteresis?
- 8.30** Why are magnetic domains formed?
- 8.31** Describe the mean-field solution for the 3D Ising model.
- 8.32** Describe the phase diagram for the 3D Ising model.
- 8.33** Solve the equation $\tanh(T_c \bar{\sigma}/T) = \bar{\sigma}$ for the case where T is slightly below T_c .
- 8.34** Obtain a formula for the specific heat of a 3D Ising model in terms of the spontaneous magnetization $\bar{\sigma}$ according to the mean-field approximation.
- 8.35** How does the mean-field prediction of the specific heat $C(T)$ for the 3D Ising model compare with an accurate numerical solution for the same quantity?

EXERCISES

Exercise 8.1 In order to convert from the expansions for n and βp as power series in the activity to the virial equation of state that gives βp as a power series in n , one is faced with the following mathematical problem. Given two expansions

$$x = t + a_2 t^2 + a_3 t^3 + \dots \quad (\text{S8.1})$$

and

$$y = t + b_2 t^2 + b_3 t^3 + \dots \quad (\text{S8.2})$$

we wish to determine the coefficients A_2, A_3, \dots in the expansion

$$y = x + A_2 x^2 + A_3 x^3 + \dots \quad (\text{S8.3})$$

Illustrate the method of calculating any A_n in terms of the known coefficients a_n and b_n , by calculating A_2, A_3 , and A_4 .

Solution In Eq. (S8.3), we substitute the power series expansions for x and y given by Eqs. (S8.1) and

(S8.2). (We keep only terms up to order t^4 .)

$$\begin{aligned}
 t + b_2t^2 + b_3t^3 + b_4t^4 &= t + a_2t^2 + a_3t^3 + a_4t^4 + \dots \\
 &\quad + A_2(t + a_2t^2 + a_3t^3 + \dots)^2 \\
 &\quad + A_3(t + a_2t^2 + \dots)^3 \\
 &\quad + A_4(t + \dots)^4 + \dots
 \end{aligned}
 \tag{S8.4}$$

Collecting terms of each order in t gives

$$\begin{aligned}
 (b_2 - a_2 - A_2)t^2 + (b_3 - a_3 - 2a_2A_2 - A_3)t^3 \\
 + (b_4 - a_4 - a_2A_2 - 2a_3A_2 - 3a_2A_3 - A_4)t^4 + \dots = 0
 \end{aligned}
 \tag{S8.5}$$

For this to be an identity in t , the coefficient of each power of t must vanish separately. Thus

$$A_2 = b_2 - a_2 \tag{S8.6}$$

$$A_3 = b_3 - a_3 - 2a_2A_2 = b_3 - a_3 - 2a_2b_2 + 2a_2^2 \tag{S8.7}$$

and

$$\begin{aligned}
 A_4 &= b_4 - a_4 - a_2^2A_2 - 2a_3A_2 - 3a_2A_3 \\
 &= b_4 - a_4 - (a_2^2 + 2a_3)(b_2 - a_2) - 3a_2(b_3 - a_3 - 2a_2b_2 + 2a_2^2)
 \end{aligned}
 \tag{S8.8}$$

It is clear that one could calculate any desired A_n in this way, but it is also clear that the terms are becoming rapidly more complicated.

Exercise 8.2 Show that, for a system of particles with short-range forces, the cluster integral C_3 defined in Section 8.3 is independent of V for large V .

Solution $6VC_3$ is defined as the combination of integrals

$$\begin{aligned}
 I_3 - 3I_1I_2 + 2I_1^3 &= \int d^3r_1 d^3r_2 d^3r_3 e^{-\beta(v_{12}+v_{13}+v_{23})} \\
 &\quad - 3 \int d^3r_1 d^3r_2 d^3r_3 e^{-\beta v_{23}} + 2 \int d^3r_1 d^3r_2 d^3r_3
 \end{aligned}
 \tag{S8.9}$$

The second term is unsymmetrical under permutation of the variables \mathbf{r}_1 , \mathbf{r}_2 , and \mathbf{r}_3 . This lack of symmetry can be eliminated by dropping the factor of 3 and writing 3 equivalent terms by renaming the variables. One then gets

$$\begin{aligned}
 6VC_3 &= \int d^3r_1 d^3r_2 d^3r_3 \left(e^{-\beta(v_{12}+v_{13}+v_{23})} - e^{-\beta v_{12}} \right. \\
 &\quad \left. - e^{-\beta v_{13}} - e^{-\beta v_{23}} + 2 \right)
 \end{aligned}
 \tag{S8.10}$$

$v(r)$ is the interaction potential for two atoms separated by a distance r . Certainly $v(r) \approx 0$ unless r is less than some small distance R of the order of 10 \AA . Therefore $e^{-\beta v(r)} \approx 1$ when $r \gg R$. We define a function, called the *Mayer f function* (after the physicist Joseph Mayer), by the formula

$$f(r) = e^{-\beta v(r)} - 1 \tag{S8.11}$$

Then $f(r) \approx 0$ for $r > R$. Writing Eq. (S8.10) in terms of the function f gives

$$6VC_3 = \int d^3r_1 d^3r_2 d^3r_3 (f_{12}f_{13}f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23}) \tag{S8.12}$$

We can do the integral of the first term by introducing variables \mathbf{r}_1 , $\mathbf{x} = \mathbf{r}_2 - \mathbf{r}_1$, and $\mathbf{y} = \mathbf{r}_3 - \mathbf{r}_1$ and noting that $r_{23} = |\mathbf{x} - \mathbf{y}|$.

$$\int d^3r_1 d^3r_2 d^3r_3 f_{12}f_{13}f_{23} = \int d^3r_1 \int d^3x d^3y f(x)f(y)f(|\mathbf{x} - \mathbf{y}|) \quad (\text{S8.13})$$

The integrand on the right vanishes if $x \gg R$ or $y \gg R$, and the integral may therefore be extended over all values of \mathbf{x} and \mathbf{y} . \mathbf{r}_1 is integrated over the volume V . Therefore

$$\int d^3r_1 d^3r_2 d^3r_3 f_{12}f_{13}f_{23} = V \int d^3x d^3y f(x)f(y)f(|\mathbf{x} - \mathbf{y}|) \quad (\text{S8.14})$$

In a similar way, the second term in Eq. (S8.12) gives

$$\int d^3r_1 d^3r_2 d^3r_3 f_{12}f_{13} = V \int d^3x d^3y f(x)f(y) = V \left(4\pi \int_0^\infty f(x)x^2 dx \right)^2 \quad (\text{S8.15})$$

The integrals of the third and fourth terms in Eq. (S8.12) are obviously equal to that of the second term. Thus

$$6C_3 = \int d^3x d^3y f(x)f(y)f(|\mathbf{x} - \mathbf{y}|) + 3 \left(4\pi \int_0^\infty f(x)x^2 dx \right)^2 \quad (\text{S8.16})$$

which is independent of V .

Exercise 8.3 For particles of radius a with hard-core interactions, the interaction potential is

$$v_{ij} = \begin{cases} \infty, & \text{if } r_{ij} < 2a \\ 0, & \text{otherwise} \end{cases} \quad (\text{S8.17})$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. For such particles, the Mayer f function, defined in Exercise 8.2, can be written in terms of the step function $\theta(x)$.

$$f_{ij} = -\theta(2a - r_{ij}) \quad (\text{S8.18})$$

Evaluate the cluster integrals, C_2 and C_3 , for hard-core particles in two dimensions.

Solution The two-dimensional form of Eq. (8.15) is

$$\begin{aligned} C_2 &= \frac{1}{2} \int f(|\mathbf{r}|) d^2r \\ &= -\pi \int_0^\infty \theta(2a - r)r dr \\ &= -2\pi a^2 \end{aligned} \quad (\text{S8.19})$$

Notice that the integral of $f(r)$ is equal to minus one times the area of a circle of radius $2a$, not one of radius a . This is a reflection of the fact that two hard-core particles must maintain a separation of at least twice their radius. The integral for C_3 is more difficult. According to Eq. (S8.16),

$$6C_3 = \int d^2x d^2y [f(x)f(y)f(|\mathbf{x} - \mathbf{y}|) + 3f(x)f(y)] \quad (\text{S8.20})$$

The second term in the square brackets gives $12C_2^2$. [Compare with Eq. (S8.19).]

$$3 \int f(x) d^2x \int f(y) d^2y = 48\pi^2 a^4 \quad (\text{S8.21})$$

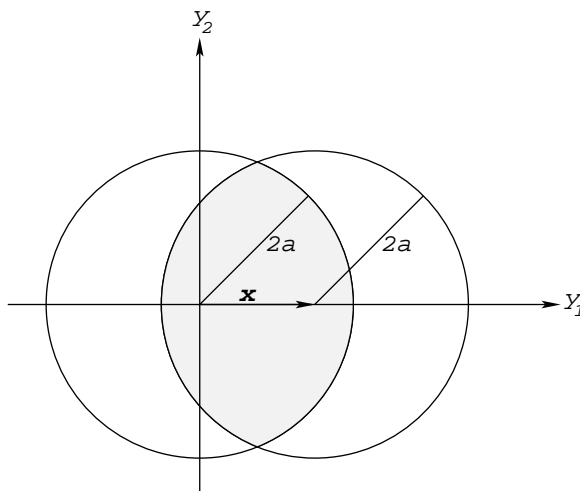


Fig. S8.1 The variable y must remain within the shaded intersection of the two circles.

As an aid in evaluating the integral of the first term in the brackets we have drawn the diagram in Fig. S8.1. We first draw a circle of radius $2a$ about the origin. Because of the factor $f(x)$, the variable \mathbf{x} must remain within this circle, and we draw a second circle of radius $2a$, centered at \mathbf{x} . The variable \mathbf{y} must remain within the shaded intersection of the two circles. Within that restricted region the value of the integrand is just the constant -1 . The area of the shaded region depends only on the magnitude of \mathbf{x} . Let us call it $A(x)$. It is easy to see that

$$\begin{aligned}
 A(x) &= 2 \int_{x/2}^{2a} dy \sqrt{4a^2 - y^2} \\
 &= 2 \left[ay \sqrt{1 - y^2/4a^2} + 2a^2 \sin^{-1}(y/2a) \right]_{x/2}^{2a} \\
 &= 2\pi a^2 - \frac{1}{4}x \sqrt{16a^2 - x^2} - 2a^2 \sin^{-1}(x/4a)
 \end{aligned}
 \tag{S8.22}$$

The needed integral is therefore

$$\begin{aligned}
 \int f(x)f(y)f(|\mathbf{x} - \mathbf{y}|) d^2x d^2y &= -2\pi \int_0^{2a} A(x)x dx \\
 &= -2\pi^2 a^4 + \frac{\pi}{2} \int_0^{2a} x^2 \sqrt{16a^2 - x^2} dx \\
 &\quad + 4\pi a^2 \int_0^{2a} \sin^{-1}(x/4a)x dx \\
 &= 2\pi \left(\sqrt{3} - \frac{\pi}{3} \right) a^4
 \end{aligned}
 \tag{S8.23}$$

Thus

$$C_3 = 8\pi^2 a^4 + \frac{\pi}{3} \left(\sqrt{3} - \frac{\pi}{3} \right) a^4
 \tag{S8.24}$$

Exercise 8.4 Repeat the previous exercise for three-dimensional hard-core particles.

Solution It is only necessary to indicate the changes in the equations for the two-dimensional case.

Equation (S8.19) becomes

$$\begin{aligned}
 C_2 &= \frac{1}{2} \int f(r) d^3r \\
 &= -2\pi \int_0^\infty \theta(2a-r)r^2 dr \\
 &= -\frac{2\pi}{3}(2a)^3
 \end{aligned} \tag{S8.25}$$

From this we see that

$$3 \int f(x) d^3x \int f(y) d^3y = 12C_2^2 = \frac{16}{3}\pi^2(2a)^6 \tag{S8.26}$$

In place of $A(x)$, we must calculate the volume of the intersection of two spheres of radius $2a$, separated by a distance $x < 2a$.

$$\begin{aligned}
 V(x) &= 2 \int_{x/2}^{2a} dy \pi(4a^2 - y^2) \\
 &= \frac{32\pi}{3}a^3 - 4\pi a^2 x + \frac{\pi}{12}x^3
 \end{aligned} \tag{S8.27}$$

Finally

$$\begin{aligned}
 \int f(x)f(y)f(|\mathbf{x} - \mathbf{y}|) d^3x d^3y &= -4\pi \int_0^{2a} V(x)x^2 dx \\
 &= -\frac{5}{6}\pi^2(2a)^6
 \end{aligned} \tag{S8.28}$$

and

$$C_3 = \frac{3}{4}\pi^2(2a)^6 \tag{S8.29}$$

Exercise 8.5 Calculate the virial coefficients, B_2 and B_3 , for a gas that satisfies van der Waals' equation of state (see Problem 5.10).

Solution Van der Waals' equation of state is

$$\frac{p}{RT} = \frac{1}{v - v_0} - \frac{a}{RTv^2} \tag{S8.30}$$

where v is the molar volume and a and v_0 are empirical constants, different for different gases. The density, in moles/m³, is given by $n = 1/v$. We can expand p/RT as a power series in n as follows.

$$\begin{aligned}
 \frac{p}{RT} &= \frac{n}{1 - v_0 n} - \frac{a}{RT}n^2 \\
 &= n + \left(v_0 - \frac{a}{RT}\right)n^2 + v_0^2 n^3 + \dots
 \end{aligned} \tag{S8.31}$$

Comparing this with the virial equation of state [Eq. (8.26)] and using the fact that n (in particles/m³) = $N_A n$ (in moles/m³), we see that

$$N_A B_2 = v_0 - \frac{a}{RT} \tag{S8.32}$$

and

$$N_A^2 B_3 = v_0^2 \tag{S8.33}$$

One sees that the van der Waals second virial coefficient, B_2 , has very reasonable temperature dependence. It approaches a positive constant at large T and becomes negative at small T .

Exercise 8.6 (a) For neon,

$$N_A B_2(T) \rightarrow 1.3 \times 10^{-5} \text{ m}^3/\text{mole}$$

as T becomes large and $B_2(125\text{ K}) = 0$. Use these facts to determine approximate van der Waals parameters, a and v_0 , for neon. (b) Considering Fig. S5.9, one can see that, at the critical temperature and pressure, $(\partial p/\partial v)_T = 0$ and $(\partial^2 p/\partial v^2) = 0$. Use the van der Waals equation to estimate the critical temperature and pressure for neon. Do not expect to get an accurate result—neither the van der Waals equation nor the virial expansion is accurate near the critical point.

Solution (a) According to Exercise 8.5,

$$N_A B_2 = v_0 - \frac{a}{RT} \quad (\text{S8.34})$$

Therefore $v_0 = 1.3 \times 10^{-5} \text{ m}^3/\text{mole}$. Also

$$a = (125\text{ K})Rv_0 = 1.35 \times 10^{-2} \text{ J m}^3/\text{mole}^2 \quad (\text{S8.35})$$

(b) Writing the molar volume and the temperature at the critical point as v_c and T_c , the conditions $\partial p/\partial v = 0$ and $\partial^2 p/\partial v^2$ give the two equations

$$\frac{1}{RT_c} \left(\frac{\partial p}{\partial v} \right) = -\frac{1}{(v_c - v_0)^2} + \frac{2a}{RT_c v_c^3} = 0 \quad (\text{S8.36})$$

and

$$\frac{1}{RT_c} \left(\frac{\partial^2 p}{\partial v^2} \right) = \frac{2}{(v_c - v_0)^3} - \frac{6a}{RT_c v_c^4} = 0 \quad (\text{S8.37})$$

Rewriting these equations as

$$\frac{1}{(v_c - v_0)^2} = \frac{2a}{RT_c v_c^3} \quad (\text{S8.38})$$

and

$$\frac{1}{(v_c - v_0)^3} = \frac{3a}{RT_c v_c^4} \quad (\text{S8.39})$$

and dividing the first equation by the second gives

$$v_c - v_0 = \frac{2}{3}v_c \quad (\text{S8.40})$$

or

$$v_c = 3v_0 = 3.9 \times 10^{-5} \text{ m}^3 \quad (\text{S8.41})$$

Using this in Eq. (S8.38), one finds that

$$T_c = \frac{8a}{27Rv_0} = 37\text{ K} \quad (\text{S8.42})$$

and finally, using these values in the van der Waals equation gives the critical pressure.

$$p_c = 2.9 \times 10^6 \text{ N/m}^2 = 29 \text{ atm} \quad (\text{S8.43})$$

The experimental values of T_c and p_c for neon are 44.5 K and 26.9 atm, not too far from the values estimated using the second virial coefficient.

Exercise 8.7 Develop a cluster expansion for the grand potential ψ for a two-dimensional lattice gas with attractive nearest-neighbor interactions but only one particle allowed at each lattice site.

Solution We choose the lattice constant as our unit of length. Then, in the lattice gas, the position of the n th particle, \mathbf{x}_n , is equal to one of the lattice points

$$\mathbf{x}_n = (k, l) \quad (\text{S8.44})$$

where k and l range over the set of integers $1, 2, \dots, L$. The interaction potential is

$$v_{ij} \equiv v(\mathbf{x}_i - \mathbf{x}_j) = \begin{cases} +\infty, & \text{if } \mathbf{x}_i = \mathbf{x}_j \\ -V, & \text{if } |\mathbf{x}_i - \mathbf{x}_j| = 1 \\ 0, & \text{otherwise} \end{cases} \quad (\text{S8.45})$$

The infinite repulsive interaction at zero distance simply prevents double occupancy of a lattice site. The N -particle canonical partition function is

$$Z_N = \frac{1}{N!} \sum_{\mathbf{x}_1} \cdots \sum_{\mathbf{x}_N} \exp\left(-\beta \sum_{i < j} v_{ij}\right) \equiv \frac{S_N}{N!} \quad (\text{S8.46})$$

where the $N!$ is necessary because we are now using numbered particles so that there are $N!$ of our present configurations for each physically distinct configuration. The grand partition function is

$$\Lambda = 1 + \sum_{N=1}^{\infty} \frac{e^{-\alpha N}}{N!} S_N \equiv 1 + \sum_{N=1}^{\infty} \frac{\zeta^N}{N!} S_N \quad (\text{S8.47})$$

where the activity $\zeta = e^{-\alpha}$. Then, using the expansion of $\log(1+x)$ given in Eq. (8.10), we get

$$\begin{aligned} \psi &= \left(S_1 \zeta + \frac{S_2}{2!} \zeta^2 + \frac{S_3}{3!} \zeta^3 + \cdots\right) - \frac{1}{2} \left(S_1 \zeta + \frac{S_2}{2!} \zeta^2 + \cdots\right)^2 + \frac{1}{3} (S_1 \zeta + \cdots)^3 - \cdots \\ &= S_1 \zeta + \frac{1}{2} (S_2 - S_1^2) \zeta^2 + \frac{1}{6} (S_3 - 3S_1 S_2 + 2S_1^3) \zeta^3 + \cdots \end{aligned} \quad (\text{S8.48})$$

Clearly, we are getting exactly the same expression as one gets for an ordinary gas, with continuous coordinates except for two things. (1) The definition of the activity is simply $e^{-\alpha}$, rather than $e^{-\alpha}/\lambda^3$. (2) The cluster integrals are replaced by cluster sums, taken over a discrete lattice.

According to Eq. (S8.48), $S_1 = L^2$. If we define cluster sums, C_2, C_3, \dots as in the continuous case, that is,

$$L^2 C_2 = \frac{1}{2} (S_2 - S_1^2) \quad (\text{S8.49})$$

$$L^2 C_3 = \frac{1}{6} (S_3 - 3S_1 S_2 + 2S_1^3) \quad (\text{S8.50})$$

and so forth, then

$$\psi = L^2 (\zeta + C_2 \zeta^2 + C_3 \zeta^3 + \cdots) \quad (\text{S8.51})$$

Exercise 8.8 For the lattice gas considered in the previous exercise, calculate the cluster sum C_2 and the virial coefficient B_2 .

Solution

$$\begin{aligned} L^2 C_2 &= \frac{1}{2} (S_2 - S_1^2) \\ &= \frac{1}{2} \sum_{\mathbf{x}_1} \sum_{\mathbf{x}_2} (e^{-\beta v_{12}} - 1) \end{aligned} \quad (\text{S8.52})$$

The quantity in the parentheses is the Mayer f function,

$$f(\mathbf{x}_{12}) = e^{-\beta v_{12}} - 1 = \begin{cases} -1, & \text{if } \mathbf{x}_{12} = 0 \\ e^{\beta V} - 1, & \text{if } |\mathbf{x}_{12}| = 1 \\ 0 & \text{otherwise} \end{cases} \quad (\text{S8.53})$$

Introducing the relative variable $\mathbf{y} = \mathbf{x}_2 - \mathbf{x}_1$, and assuming that L is very large, we can write $L^2 C_2$ as

$$\begin{aligned} L^2 C_2 &= \frac{1}{2} \sum_{\mathbf{x}_1} \sum_{\mathbf{y}} f(\mathbf{y}) \\ &= \frac{1}{2} L^2 (4e^{\beta V} - 5) \end{aligned} \quad (\text{S8.54})$$

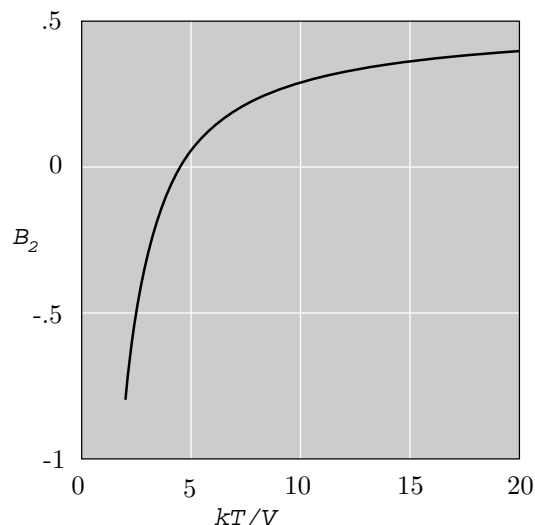


Fig. S8.2 The second virial coefficient B_2 as a function of the dimensionless temperature variable kT/V for a lattice gas with nearest-neighbor interactions.

or

$$C_2 = \frac{1}{2}(4e^{\beta V} - 5) \quad (\text{S8.55})$$

B_2 is related to C_2 by Eq. (8.27).

$$B_2 = -C_2 = \frac{5}{2} - 2e^{\beta V} \quad (\text{S8.56})$$

B_2 is plotted in Fig. S8.2 as a function of kT/V . We see that it has the behavior that is expected of a second virial coefficient; it becomes large and negative at low temperatures and approaches a constant at high T .

Exercise 8.9 Consider a 3D gas of point particles with interparticle interactions given by a potential $v(r_{ij})$. We focus our attention on a particular particle (call it the zero particle) located at \mathbf{r}_o . We want to calculate the density of the other particles around the zero particle. If we take into account the interaction between the zero particle and every other particle in the system, but temporarily ignore the interactions among the other particles, then we would expect the other particles to be distributed in space with a density

$$n(\mathbf{r}) = n_o e^{-\beta v(\mathbf{r}-\mathbf{r}_o)} \quad (\text{S8.57})$$

Therefore, within this approximation, the average of the interaction between the zero particle and all the other particles is

$$\langle v_o \rangle = n_o \int e^{-\beta v(\mathbf{r}-\mathbf{r}_o)} v(\mathbf{r}-\mathbf{r}_o) d^3\mathbf{r} = 4\pi n_o \int_0^\infty e^{-\beta v(R)} v(R) R^2 dR \quad (\text{S8.58})$$

Multiplying this by N will double count the two-particle interaction terms. Thus our approximation for the total potential energy is

$$\left\langle \sum_{i<j} v_{ij} \right\rangle = 2\pi \frac{N^2}{V} \int_0^\infty e^{-\beta v(R)} v(R) R^2 dR \quad (\text{S8.59})$$

Use this approximation to derive the pressure and energy equations of state and compare the result with the virial expansion.

Solution For a classical gas the kinetic energy is always $\frac{3}{2}NkT$. Therefore, the total energy is

$$E(N, \beta, V) = \frac{3}{2} \frac{N}{\beta} + 2\pi \frac{N^2}{V} \int_0^\infty e^{-\beta v(R)} v(R) R^2 dR \quad (\text{S8.60})$$

Integrating the identity $E = -\partial\phi(N, \beta, V)/\partial\beta$ with respect to β yields the following relation for the canonical potential

$$\phi = -\frac{3}{2}N \log \beta + 2\pi \frac{N^2}{V} \int_0^\infty (e^{-\beta v(R)} - 1) R^2 dR + g(N, V) \quad (\text{S8.61})$$

where g is an arbitrary function and we have used the fact that

$$e^{-\beta v} v = -\frac{\partial(e^{-\beta v} - 1)}{\partial\beta} \quad (\text{S8.62})$$

(The constant -1 must be added in order to prevent a divergence in the resulting integral.) When $v(r) = 0$, $\phi(N, \beta, V)$ should reduce to the canonical potential of an ideal gas. This determines the arbitrary function g and gives

$$\phi = \phi_{\text{ideal}} + 2\pi \frac{N^2}{V} \int_0^\infty (e^{-\beta v(R)} - 1) R^2 dR \quad (\text{S8.63})$$

The pressure equation of state is then given by $\beta p = \partial\phi/\partial V$.

$$\beta p = n - 2\pi n^2 \int_0^\infty (e^{-\beta v(R)} - 1) R^2 dR \quad (\text{S8.64})$$

Equations (S8.60) and (S8.64) are identical with the corresponding equations derived from the two-term virial expansion.

The following few exercises concern the one-dimensional Ising model, with and without an external field. While the two-dimensional and three-dimensional Ising models are reasonable approximations to important physical systems, the one-dimensional version is not. However, it can be solved, both exactly and approximately, by a number of different techniques, and therefore is an excellent pedagogical exercise for learning calculational methods that may then be applied to more complex, realistic systems.

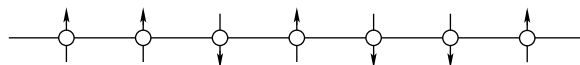


Fig. S8.3 The one-dimensional Ising model is a system of two-valued spins, equally spaced, on a line.

Exercise 8.10 Shown in Fig. S8.3 is a one-dimensional Ising model. It is a system of N quantized spins, located at the points of a one-dimensional lattice. The n th spin can have two possible states that we indicate with a variable $\sigma_n = \pm 1$. A pair of neighboring spins has an interaction energy equal to $-V$ if they are parallel and $+V$ if they are antiparallel. Therefore the total energy of any configuration, defined by specifying the values of $\sigma_1, \sigma_2, \dots, \sigma_N$, is

$$E = -V(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \dots + \sigma_{N-1}\sigma_N) \quad (\text{S8.65})$$

By transforming to new variables, $\zeta_1 = \sigma_1$, $\zeta_2 = \sigma_2\sigma_1$, $\zeta_3 = \sigma_3\sigma_2, \dots, \zeta_N = \sigma_N\sigma_{N-1}$, calculate the energy and specific heat of the system as functions of $x = \tau/V$.

Solution In terms of the new variables

$$E = -V(\zeta_2 + \zeta_3 + \dots + \zeta_N) \quad (\text{S8.66})$$

It is not difficult to show that there is a one-to-one relationship between the set of variables $(\sigma_1, \sigma_2, \dots, \sigma_N)$ and the set of variables $(\zeta_1, \zeta_2, \dots, \zeta_N)$. The definition of the ζ variables gives a definite set of ζ s for a given set of σ s. We need only look at the inverse transformation. For a given set of ζ s it is easy to see that

$$\begin{aligned} \zeta_1 &= \sigma_1 \\ \zeta_1\zeta_2 &= \sigma_1^2\sigma_2 = \sigma_2 \\ \zeta_1\zeta_2\zeta_3 &= \sigma_1^2\sigma_2^2\sigma_3 = \sigma_3 \\ &\dots \\ \zeta_1 \dots \zeta_N &= \sigma_1^2 \dots \sigma_{N-1}^2 \sigma_N = \sigma_N \end{aligned} \quad (\text{S8.67})$$

Thus any set of σ s gives a unique set of ζ s and vice versa. By its definition, the possible values of ζ_n are ± 1 . Thus the canonical partition function is

$$\begin{aligned} Z &= \sum_{\zeta_1} \dots \sum_{\zeta_N} \exp[-\beta V(\zeta_2 + \dots + \zeta_N)] \\ &= 2 \left(\sum_{\zeta} e^{-\beta V \zeta} \right)^{N-1} \\ &= 2^N (\cosh \beta V)^{N-1} \end{aligned}$$

and

$$\phi(\beta) = N [\log(\cosh \beta V) + \log 2] \tag{S8.68}$$

where we have ignored the difference between $N-1$ and N . The average thermal energy is

$$E = -\frac{\partial \phi}{\partial \beta} = -NV \tanh(\beta V) \tag{S8.69}$$

and the specific heat is

$$C = \frac{\partial E}{\partial \tau} = N \frac{V^2}{\tau^2} \operatorname{sech}^2(V/\tau) \tag{S8.70}$$

The fact that E and C , as functions of temperature, are completely smooth shows that no phase transition occurs in this system at any temperature.

Exercise 8.11 In the Ising model considered in the previous exercise, the only source of energy was the interactions between neighboring spins. If the spins are associated with a magnetic moment μ and an external magnetic field is present, then, for each spin, there is another term in the energy, namely $\pm \mu B$, due to the interaction of the magnetic moment with the external field. Denoting the combination μB by the letter H , we can then write the energy for any configuration of a one-dimensional Ising model with an external field as

$$E = -H(\sigma_1 + \sigma_2 + \dots + \sigma_N) - V(\sigma_1 \sigma_2 + \dots + \sigma_{N-1} \sigma_N) \tag{S8.71}$$

The reader can easily verify that the trick that was used in the last exercise to solve the problem when $H = 0$ will no longer work. However, the partition function and canonical potential of this model can also be calculated exactly, but the analysis is somewhat more complicated. It is best first to bend the lattice around to form a circle of length N . Then the N th spin will interact with the first spin so that the expression for E will become

$$E = -H(\sigma_1 + \dots + \sigma_N) - V(\sigma_1 \sigma_2 + \dots + \sigma_{N-1} \sigma_N + \sigma_N \sigma_1) \tag{S8.72}$$

This is referred to as using *periodic boundary conditions*.

Before attempting to calculate the partition function of this model, we will give a short preamble, reviewing some elementary linear algebra. A function of two integer variables $M(k, l)$, where k and l range from 1 to K , defines a K by K matrix in which the number in the i th row and the j th column is $M(i, j)$. In a similar way, a function of two spin variables $M(\sigma_1, \sigma_2)$ can be arranged as a 2×2 matrix, as shown.

$$M = \begin{bmatrix} M(+1, +1) & M(+1, -1) \\ M(-1, +1) & M(-1, -1) \end{bmatrix} \tag{S8.73}$$

$M(\sigma_1, \sigma_2)$ is *symmetric* if $M(+1, -1) = M(-1, +1)$. In the following, we will assume that M is symmetric.

The *trace* of M , written $\operatorname{Tr}(M)$, is the sum of its two diagonal elements. $\operatorname{Tr}(M)$ is also equal to the sum of the two eigenvalues of M .

$$\operatorname{Tr}(M) = \sum_{\sigma} M(\sigma, \sigma) = \lambda_+ + \lambda_- \tag{S8.74}$$

where we define λ_+ as the larger and λ_- as the smaller of the eigenvalues (which are always real for a symmetric matrix).

The determinant of M is equal to the product of its two eigenvalues.

$$\det(M) = M(+1, +1)M(-1, -1) - M(+1, -1)M(-1, +1) = \lambda_+ \lambda_- \quad (\text{S8.75})$$

The matrix M^2 is defined by the usual rule for matrix multiplication.

$$M^2(\sigma_1, \sigma_3) = \sum_{\sigma_2} M(\sigma_1, \sigma_2)M(\sigma_2, \sigma_3) \quad (\text{S8.76})$$

In this way any power of the matrix M can be calculated. For example,

$$M^3(\sigma_1, \sigma_4) = \sum_{\sigma_2} \sum_{\sigma_3} M(\sigma_1, \sigma_2)M(\sigma_2, \sigma_3)M(\sigma_3, \sigma_4) \quad (\text{S8.77})$$

The eigenvalues of the matrix M^n are the n th power of the eigenvalues of M , that is, λ_+^n and λ_-^n .

We are now ready to describe the exercise. (a) Define a symmetric matrix $M(\sigma_1, \sigma_2)$ so that the partition function

$$Z = \sum_{\sigma_1} \dots \sum_{\sigma_N} e^{-\beta E} = \text{Tr}(M^N) \quad (\text{S8.78})$$

(When such a matrix exists, it is called a *transfer matrix*.) (b) Assuming that $N \gg 1$, calculate the canonical potential for the one-dimensional Ising model with an external field. (c) For the special case $H = V$, plot the specific heat per spin as a function of the dimensionless temperature variable $t = \tau/V$ in the range $0 < t < 10$.

Solution (a) If we define parameters A and B by

$$A = \frac{1}{2}\beta H \quad \text{and} \quad B = \beta V \quad (\text{S8.79})$$

then

$$-\beta E = 2A(\sigma_1 + \dots + \sigma_N) + B(\sigma_1\sigma_2 + \dots + \sigma_N\sigma_1) \quad (\text{S8.80})$$

and

$$e^{-\beta E} = (e^{A\sigma_1 + B\sigma_1\sigma_2 + A\sigma_2})(e^{A\sigma_2 + B\sigma_2\sigma_3 + A\sigma_3}) \dots (e^{A\sigma_N + B\sigma_N\sigma_1 + A\sigma_1}) \quad (\text{S8.81})$$

If we define $M(\sigma_1, \sigma_2)$ by

$$M(\sigma_1, \sigma_2) = e^{A\sigma_1 + B\sigma_1\sigma_2 + A\sigma_2} \quad (\text{S8.82})$$

then

$$\begin{aligned} Z &= \sum_{\sigma_1} \dots \sum_{\sigma_N} M(\sigma_1, \sigma_2)M(\sigma_2, \sigma_3) \dots M(\sigma_N, \sigma_1) \\ &= \sum_{\sigma_1} M^N(\sigma_1, \sigma_1) \\ &= \text{Tr}(M^N) \end{aligned} \quad (\text{S8.83})$$

(b) We must now determine the eigenvalues of M . Written out as a 2×2 matrix [see Eq. (S8.73)],

$$M = \begin{bmatrix} e^{B+2A} & e^{-B} \\ e^{-B} & e^{B-2A} \end{bmatrix} \quad (\text{S8.84})$$

From the matrix rules reviewed before, we know that

$$\lambda_+ + \lambda_- = \text{Tr}(M) = e^B(e^{2A} + e^{-2A}) = 2e^B \cosh(2A) \quad (\text{S8.85})$$

and

$$\lambda_+ \lambda_- = \det(M) = e^{2B} - e^{-2B} = 2 \sinh(2B) \quad (\text{S8.86})$$

Using the first equation to eliminate λ_- in the second one obtains a quadratic equation for λ_+ whose solution is

$$\begin{aligned} \lambda_+ &= e^B \left[\cosh(2A) + \sqrt{\sinh^2(2A) + e^{-4B}} \right] \\ &= e^{\beta V} \left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta V}} \right] \end{aligned} \quad (\text{S8.87})$$

λ_- is given by the same formula with the plus sign replaced by a minus sign. The trace of M^N is given by

$$\begin{aligned} \text{Tr}(M^N) &= \lambda_+^N + \lambda_-^N \\ &= \lambda_+^N [1 + (\lambda_-/\lambda_+)^N] \\ &\approx \lambda_+^N \end{aligned} \quad (\text{S8.88})$$

since the N th power of a number less than one is extremely small for large N . Thus

$$\begin{aligned} \phi(\beta) &= \log Z \\ &= N \log(\lambda_+) \\ &= N \left\{ \beta V + \log \left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta V}} \right] \right\} \end{aligned} \quad (\text{S8.89})$$

(c) Having obtained the canonical potential, one can calculate the energy per spin and the specific heat by the usual formulas.

$$(E/N) = -\frac{\partial(\phi/N)}{\partial\beta} \quad (\text{S8.90})$$

and

$$C = \frac{\partial(E/N)}{\partial\tau} \quad (\text{S8.91})$$

However, because the second equation leads to an absolute morass of algebra, the use of a computerized algebra program is strongly recommended. For the case $H = V$, plots of (E/N) and C as functions of $t = \tau/V$ that were obtained using *Mathematica* are shown in Fig. S8.4.

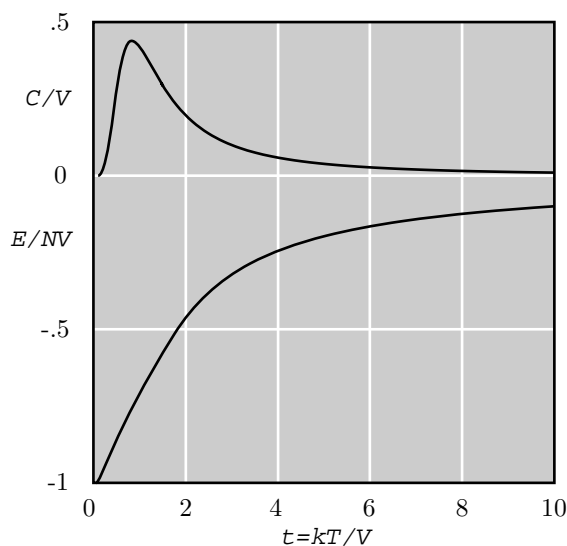


Fig. S8.4 The energy and specific heat of the one-dimensional Ising model as a function of the dimensionless temperature $t = kT/V$ for the case $H=V$.

Exercise 8.12 Show that no spontaneous magnetization takes place in the one-dimensional Ising model at any temperature.

Solution For the 1D Ising model with an external field H , the canonical partition function is given by

$$Z = \sum_{\{\sigma\}} \exp\left(-\beta H \sum \sigma_i - \beta V \sum \sigma_i \sigma_{i+1}\right) \tag{S8.92}$$

From this relation, and the fact that $\phi = \log Z$, it is easy to see that

$$\frac{\partial \phi}{\partial H} = \frac{\partial Z / \partial H}{Z} = -\beta \langle \sum \sigma_i \rangle = -\beta N \bar{\sigma} \tag{S8.93}$$

From Eq. (S8.89), we see that

$$\frac{1}{\beta} \frac{\partial \phi}{\partial H} = N \sinh(\beta H) \left[1 + \cosh(\beta H) / \sqrt{\sinh^2(\beta H) + e^{-4\beta V}} \right] / (\phi - N\beta V) \tag{S8.94}$$

But, because of the factor of $\sinh(\beta H)$, this function approaches zero as $H \rightarrow 0$. Regardless of the temperature, the system is never left with a finite magnetization when the external field is turned off.

For the one-dimensional Ising model, the coordination number c defined in Section 8.22 is two. Therefore, the mean-field approximation predicts that the system undergoes a ferromagnetic phase transition at a Curie temperature of $T_c = 2V/k$. This is an entirely erroneous prediction—the exact solution shows that the system has no phase transition at any temperature.

Hans Bethe and Rudolf Peierls, many years ago, developed an improved version of mean-field theory that avoids that false prediction for the 1D Ising model and makes significantly improved (but still not very accurate) predictions for the 2D and 3D models. Applied to the 1D Ising model, the Bethe–Peierls approximation proceeds as follows.

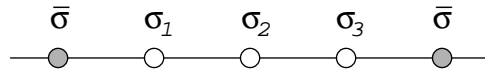


Fig. S8.5 Replacing their neighbor spins by fixed variables of value $\bar{\sigma}$ isolates the triplet from the other spins in the lattice.

1. Consider any triplet of spins, σ_1 , σ_2 , and σ_3 . Replace the spins neighboring the triplet by some as yet unknown average value $\bar{\sigma}$. This effectively replaces the very large lattice by a system composed of only three spins. (See Fig. S8.5.)
2. As functions of $\bar{\sigma}$, calculate the average values $\langle \sigma_1 \rangle = \langle \sigma_3 \rangle$ and $\langle \sigma_2 \rangle$.
3. Determine the value of $\bar{\sigma}$ by demanding that $\langle \sigma_1 \rangle = \langle \sigma_2 \rangle$. (Note that this will not usually guarantee that $\bar{\sigma} = \langle \sigma_1 \rangle$. It is impossible to get an approximate solution to satisfy all possible symmetry relations.)
4. With the value of $\bar{\sigma}$ given by 3, calculate $\langle \sigma_1 \sigma_2 \rangle$ and compute the thermal energy by using the formula

$$E = -NH \langle \sigma_1 \rangle - NV \langle \sigma_1 \sigma_2 \rangle \tag{S8.95}$$

Exercise 8.13 Show that the Bethe–Peierls approximation does not predict a phase transition for the 1D Ising model with no external field. (As a matter of fact, the Bethe–Peierls approximation gives the exact result for the energy of the 1D Ising model, with or without an external field.)

Solution Although we are interested only in the case $H=0$, it will be very convenient first to include an external field term H for spins 1 and 3 and a different external field term H' for the central spin 2. At the

end, we will set H and H' equal to zero. With the definitions $h=\beta H$, $h'=\beta H'$, and $v=\beta V$, the value of βE for the three-spin system is

$$\beta E = -h(\sigma_1 + \sigma_3) - h'\sigma_2 - v(\bar{\sigma}\sigma_1 + \sigma_1\sigma_2 + \sigma_2\sigma_3 + \bar{\sigma}\sigma_3) \quad (\text{S8.96})$$

The partition function of the system is easily evaluated.

$$\begin{aligned} Z &= \sum_{\sigma_1} \sum_{\sigma_2} \sum_{\sigma_3} \exp[h(\sigma_1 + \sigma_3) + h'\sigma_2 + v(\bar{\sigma}\sigma_1 + \sigma_1\sigma_2 + \sigma_2\sigma_3 + \bar{\sigma}\sigma_3)] \\ &= \sum_{\sigma_2} \exp(h'\sigma_2) \sum_{\sigma_1} \exp[(h + v\bar{\sigma} + v\sigma_2)\sigma_1] \sum_{\sigma_3} \exp[(h + v\bar{\sigma} + v\sigma_2)\sigma_3] \\ &= 4 \sum_{\sigma_2} \exp(h'\sigma_2) \cosh^2(h + v\bar{\sigma} + v\sigma_2) \\ &= 4[e^{h'} \cosh^2(h + v\bar{\sigma} + v) + e^{-h'} \cosh^2(h + v\bar{\sigma} - v)] \end{aligned} \quad (\text{S8.97})$$

Using the first line of Eq. (S9.97), it is easy to confirm that

$$\langle \sigma_1 + \sigma_3 \rangle = \frac{\partial Z / \partial h}{Z} \quad \text{and} \quad \langle \sigma_2 \rangle = \frac{\partial Z / \partial h'}{Z} \quad (\text{S8.98})$$

Thus

$$\begin{aligned} \langle \sigma_1 + \sigma_3 \rangle &= 8[e^{h'} \cosh(h + v\bar{\sigma} + v) \sinh(h + v\bar{\sigma} + v) \\ &\quad + e^{-h'} \cosh(h + v\bar{\sigma} - v) \sinh(h + v\bar{\sigma} - v)] / Z \end{aligned} \quad (\text{S8.99})$$

and

$$\langle \sigma_2 \rangle = 4[e^{h'} \cosh^2(h + v\bar{\sigma} + v) - e^{-h'} \cosh^2(h + v\bar{\sigma} - v)] / Z \quad (\text{S8.100})$$

Setting $h = h' = 0$, and demanding that $\langle \sigma_1 + \sigma_3 \rangle = 2\langle \sigma_2 \rangle$, gives the following equation for $\bar{\sigma}$.

$$\begin{aligned} &\cosh(v\bar{\sigma} + v) \sinh(v\bar{\sigma} + v) + \cosh(v\bar{\sigma} - v) \sinh(v\bar{\sigma} - v) \\ &= \cosh^2(v\bar{\sigma} + v) - \cosh^2(v\bar{\sigma} - v) \end{aligned} \quad (\text{S8.101})$$

This equation can be converted to a solvable polynomial equation by the substitutions

$$x = e^{v\bar{\sigma}} \quad \text{and} \quad y = e^v \quad (\text{S8.102})$$

Expressing the hyperbolic functions in terms of exponentials, with a little algebra, one obtains the equation

$$(x^2 - x^{-2})y^{-2} = 0 \quad (\text{S8.103})$$

Since y cannot be zero, this requires that $x=1$, which implies that $\bar{\sigma}=0$. Thus the Bethe–Peierls approximation does not predict spontaneous magnetization for any value of $v = V/kT$.

Exercise 8.14 Apply the Bethe–Peierls approximation to an Ising model, with no external field, on a 2D hexagonal lattice.

Solution A portion of a hexagonal lattice is shown in Fig. S8.6. A central spin σ_1 and its three neighboring spins σ_2 , σ_3 , and σ_4 , are isolated from the rest of the lattice by replacing all the shaded spins by some yet to be determined average value $\bar{\sigma}$. Again, as in Exercise 8.13, it is best to include an external field term that has the value H for spins 2, 3, and 4, and a different value H' for spin 1. The value of βE for the four-spin system is then

$$\beta E = -h'\sigma_1 - h(\sigma_2 + \sigma_3 + \sigma_4) - v(2\bar{\sigma} + \sigma_1)(\sigma_2 + \sigma_3 + \sigma_4) \quad (\text{S8.104})$$

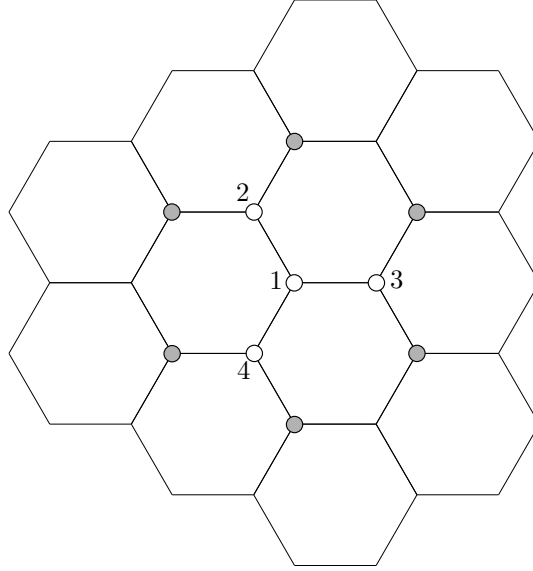


Fig. S8.6 A section of a hexagonal lattice.

where, as before, $h = \beta H$, $h' = \beta H'$, and $v = \beta V$. The partition function is given by summing $e^{-\beta E}$ over all possible values of the four spin variables.

$$\begin{aligned}
 Z &= \sum_{\sigma_1} \sum_{\sigma_2} \sum_{\sigma_3} \sum_{\sigma_4} \exp[h'\sigma_1 + (h + 2v\bar{\sigma} + v\sigma_1)(\sigma_2 + \sigma_3 + \sigma_4)] \\
 &= \sum_{\sigma_1} \exp(h'\sigma_1) \left(\sum_{\sigma} \exp[(h + 2v\bar{\sigma} + v\sigma_1)\sigma] \right)^3 \\
 &= 8 \sum_{\sigma_1} \exp(h'\sigma_1) \cosh^3(h + 2v\bar{\sigma} + v\sigma_1) \\
 &= 8[e^{h'} \cosh^3(h + 2v\bar{\sigma} + v) + e^{-h'} \cosh^3(h + 2v\bar{\sigma} - v)]
 \end{aligned} \tag{S8.105}$$

Using the identities

$$\langle \sigma_1 \rangle = \frac{\partial Z / \partial h'}{Z} \quad \text{and} \quad \langle \sigma_2 + \sigma_3 + \sigma_4 \rangle = \frac{\partial Z / \partial h}{Z} \tag{S8.106}$$

one obtains, after taking the partial derivatives and setting $h = h' = 0$,

$$\langle \sigma_1 \rangle = 8[\cosh^3(2v\bar{\sigma} + v) - \cosh^3(2v\bar{\sigma} - v)]/Z \tag{S8.107}$$

and

$$\begin{aligned}
 \langle \sigma_2 + \sigma_3 + \sigma_4 \rangle &= 24[\cosh^2(2v\bar{\sigma} + v) \sinh(2v\bar{\sigma} + v) \\
 &\quad + \cosh^2(2v\bar{\sigma} - v) \sinh(2v\bar{\sigma} - v)]/Z
 \end{aligned} \tag{S8.108}$$

Setting $\langle \sigma_2 + \sigma_3 + \sigma_4 \rangle = 3\langle \sigma_1 \rangle$ and making the substitutions,

$$x = e^{2v\bar{\sigma}} \quad \text{and} \quad y = e^v \tag{S8.109}$$

one obtains the formidable-looking polynomial equation,

$$\begin{aligned}
 (xy + x^{-1}y^{-1})^2(xy - x^{-1}y^{-1}) + (xy^{-1} + x^{-1}y)^2(xy^{-1} - x^{-1}y) \\
 = (xy + x^{-1}y^{-1})^3 - (xy^{-1} + x^{-1}y)^3
 \end{aligned} \tag{S8.110}$$

Multiplying the equation through by x^3y^3 and collecting terms gives the equation

$$x^6 - (y^4 - 2y^2)x^4 + (y^4 - 2y^2)x^2 - 1 = 0 \quad (\text{S8.111})$$

Letting $u = x^2$ and $A = y^4 - 2y^2$, we see that this is a cubic equation for u .

$$u^3 - Au^2 + Au - 1 = 0 \quad (\text{S8.112})$$

Mean-field theories always have the trivial solution $\bar{\sigma} = 0$. This is reflected in the fact that $u = 1$ is a solution to the cubic equation. When we divide the equation by the factor $(u-1)$, we obtain the simple quadratic equation

$$u^2 - (A-1)u + 1 = 0 \quad (\text{S8.113})$$

Taking into account the fact that u must be positive, the only acceptable solution to this equation is

$$u = \frac{1}{2}(A-1) + \frac{1}{2}\sqrt{(A-1)^2 - 4} \quad (\text{S8.114})$$

This solution is real if and only if $A \geq 3$, which implies that $y \geq \sqrt{3}$. Thus the Bethe–Peierls approximation predicts a ferromagnetic phase transition at a Curie temperature given by setting $e^v = \sqrt{3}$. That is, $\tau_c = 2V/\log 3 \approx 1.82V$. The exact relation, known from the Onsager solution, is $\tau_c/V = 1.518649\dots$ Since the coordination number of the hexagonal lattice is three, simple mean-field theory would predict that the phase transition occurs as $\tau=3V$. We see that the Bethe–Peierls method is a substantial improvement on the results of simple mean-field theory.

Exercise 8.15 A number of exercises in this chapter require that one numerically compute any solution, within the range $0 < \sigma < 1$, of an equation of the form

$$\sigma = f(\sigma) \quad (\text{S8.115})$$

where $f(\sigma)$ is some relatively complicated function with the properties that $f(0) \geq 0$ and $f(1) < 1$. (a) Describe an algorithm for carrying out such a calculation. The algorithm should guarantee a certain fixed precision. (b) Write a Fortran program to implement the algorithm for the function $f(\sigma) = \tanh(A\sigma)$.

Solution (a) The problem posed is equivalent to the problem of finding a solution of the equation $g(\sigma) = 0$ within the range $0 < \sigma < 1$, where $g(\sigma) = \sigma - f(\sigma)$. The conditions on $f(\sigma)$ guarantee that $g(0) \leq 0$ and $g(1) > 0$. The algorithm consists in finding two numbers x_{LO} and x_{HI} such that $g(x_{\text{LO}}) \leq 0$ and $g(x_{\text{HI}}) > 0$ but $x_{\text{HI}} - x_{\text{LO}} \rightarrow 1/2^N$, where N is an integer that determines the precision of the answer. We start with $x_{\text{LO}} = 0$ and $x_{\text{HI}} = 1$, and iterate the following steps N times.

1. Let $x = (x_{\text{LO}} + x_{\text{HI}})/2$.
2. If $g(x) > 0$, then $x_{\text{HI}} = x$, else $x_{\text{LO}} = x$. Go to 1.

Since $x_{\text{HI}} - x_{\text{LO}}$ is reduced by a factor of 2 by each iteration and the two numbers always bound the solution of $g(x) = 0$, we are guaranteed to obtain a root with an accuracy of $1/2^N$. In the case $g(0) = 0$ and $g(\sigma) > 0$ for $0 < \sigma \leq 1$, no positive root exists. In that case x_{LO} will stay at 0 and x_{HI} will end up at $1/2^N$, which means that we have obtained the zero root.

(b) The program, called `Root.for`, can be found in the Program Listings, and is included in the Program Disk.

Exercise 8.16 Two different systems have been considered that “live” on a two-dimensional square lattice. One is a lattice gas, with or without nearest-neighbor interactions. This was considered as a model for surface adsorption. The other is the Ising model, which is a model of a ferromagnetic two-dimensional solid. They are very similar in that in both models the configuration of the system is defined by specifying a variable at each lattice site that can have two possible values. For the lattice gas, the values are 0 and 1, while for the Ising model they are ± 1 .

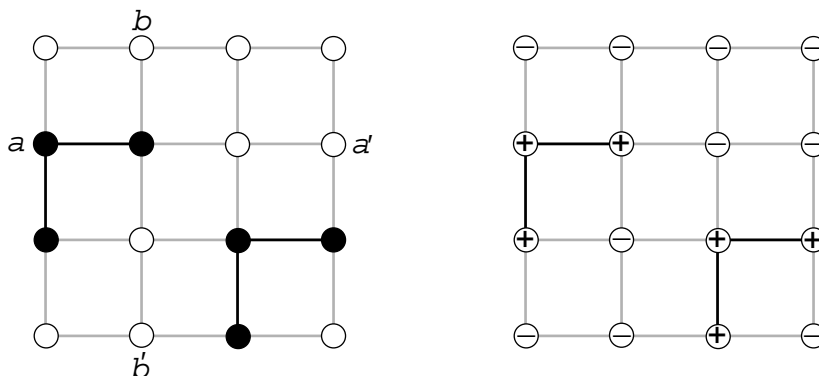


Fig. S8.7 A configuration of a lattice gas and the “corresponding” configuration of an Ising model.

Show that the two systems are not only similar, but are completely equivalent, so that any way of calculating the thermodynamic functions for one system will immediately give the thermodynamic functions of the other.

Solution Shown in Fig. S8.7 are lattice gas and Ising model configurations on 4×4 lattice. We are using periodic using boundary conditions, which means that the pair of points a and a' are neighbors, as are the pair of points b and b' . That is, the lattice “wraps around” in both the x and the y directions. In the lattice gas the occupied sites are black and, for each pair of neighboring particles, the bond between them has been darkened. In the Ising model the up spins are shown as $+$ and the down spins as $-$ and the bond has been darkened for each pair of neighboring up spins.

The grand potential of the lattice gas is the sum, over all configurations, of $\exp(-\alpha N - \beta E)$. We will assume that the binding energy of a particle to a site is zero. (A nonzero value, $-\varepsilon$, could be eliminated simply by redefining the parameter α to be $\alpha - \beta\varepsilon$.) If N_B is the number of darkened bonds in any configuration, and $-v$ is the bond energy, then

$$\Lambda = \sum \exp(-\alpha N + \beta v N_B) \quad (\text{S8.116})$$

where the sum is over all possible configurations.

In any configuration of the Ising model, let N_+ be the number of spin-up sites, N_- the number of spin-down sites, N_{++} the number of bonds with up spins at both ends, N_{--} the number of bonds with down spins at both ends, and N_{+-} the number of bonds with different spins at the two ends. Then the energy of a configuration is

$$E = -H(N_+ - N_-) - V(N_{++} + N_{--} - N_{+-}) \quad (\text{S8.117})$$

The canonical partition function for the Ising lattice is therefore

$$Z = \sum \exp[\beta H(N_+ - N_-) + \beta V(N_{++} + N_{--} - N_{+-})] \quad (\text{S8.118})$$

where again the sum is over all configurations. As they stand, the expressions for Λ and Z look quite different, particularly since the expression for Z contains five parameters, while that for Λ contains only two. But we will see that the parameters in Z are not independent. They satisfy three linear relations, which can be used to eliminate three of them. The resulting expression will be equivalent to the expression for Λ .

The first linear relation is the trivial one that, for an $L \times L$ lattice,

$$N_+ + N_- = L^2 \quad (\text{S8.119})$$

Now imagine that we place coins at both ends of each $++$ bond and at the $+$ end of each $+-$ bond. The number of coins used will be $2N_{++} + N_{+-}$. But then each $+$ vertex will be covered by four coins. Thus

$$2N_{++} + N_{+-} = 4N_+ \quad (\text{S8.120})$$

By the obvious symmetry between + and −, we can get the third linear relation.

$$2N_{--} + N_{+-} = 4N_- \tag{S8.121}$$

It is not difficult to solve these equations for N_- , N_{--} , and N_{+-} in terms of the variables N_+ and N_{++} .

$$N_- = L^2 - N_+, \quad N_{--} = 2L^2 + N_{++} - 4N_+, \quad \text{and} \quad N_{+-} = 4N_+ - 23N_{++} \tag{S8.122}$$

When these are substituted into the expression $H(N_+ - N_-) + V(N_{++} + N_{--} - N_{+-})$, one obtains

$$\begin{aligned} & H(N_+ - N_-) + V(N_{++} + N_{--} - N_{+-}) \\ &= (2V - H)L^2 + (2H - 8V)N_+ + 4VN_{++} \end{aligned} \tag{S8.123}$$

and therefore

$$\begin{aligned} Z &= e^{\beta(2V-H)L^2} \sum \exp\left[\beta(2H - 8V)N_+ + 4\beta VN_{++}\right] \\ &= e^{\beta(2V-H)L^2} \Lambda(\alpha', v') \end{aligned} \tag{S8.124}$$

where $\alpha' = \beta(8V - 2H)$ and $v' = 4V$. Thus a calculation of the grand partition function of the lattice gas is equivalent to a calculation of the canonical partition function of the Ising lattice.

Exercise 8.17 A square two-dimensional lattice has total of K sites. Located on the lattice are particles of two different types. There are N_A A particles and N_B B particles. Two A particles or two B particles at neighboring sites interact with an energy V , but an A particle and a B particle at neighboring sites interact with an energy $-V$. (a) Following the method of Section 8.9, use mean-field theory to calculate the canonical potential $\phi(N_A, N_B, \beta)$. (b) Assume that there is a chemical reaction $A \leftrightarrow B$. This would be true, for example, if A and B were really two different spin states of a single spin- $\frac{1}{2}$ particle. As a function of $n = (N_A + N_B)/K$ and β , calculate the equilibrium value of $(N_A - N_B)/(N_A + N_B)$.

Solution (a) For N_A A particles and N_B B particles, to be distributed among K sites, there are

$$M = \frac{K!}{N_A!N_B!(K - N_A - N_B)!} \tag{S8.125}$$

possible configurations.

Consider any A particle. The mean-field approximations to the average number of A particles and B particles in each of its four nearest-neighbor sites are N_A/K and N_B/K . Thus the average interaction energy of the A particle is

$$4VN_A/K - 4VN_B/K$$

For a B particle, the equivalent expression is

$$4VN_B/K - 4VN_A/K$$

Taking into account the double counting problem, the average energy of a random distribution of N_A A particles and N_B B particles is

$$\begin{aligned} E &= 2VN_A \frac{N_A - N_B}{K} + 2VN_B \frac{N_B - N_A}{K} \\ &= 2V(N_A - N_B)^2/K \end{aligned} \tag{S8.126}$$

Using this approximate energy for every configuration yields the partition function

$$Z = \frac{K! \exp\left[-2\beta V(N_A - N_B)^2/K\right]}{N_A!N_B!(K - N_A - N_B)!} \tag{S8.127}$$

and the canonical potential

$$\begin{aligned}\phi = & K \log K - N_A \log N_A - N_B \log N_B \\ & - (K - N_A - N_B) \log(K - N_A - N_B) - 2\beta V \frac{(N_A - N_B)^2}{K}\end{aligned}\quad (\text{S8.128})$$

With a little algebra, this can be written in terms of the densities $n_A = N_A/K$ and $n_B = N_B/K$, as

$$\begin{aligned}\phi = & -K [n_A \log n_A + n_B \log n_B \\ & + (1 - n_A - n_B) \log(1 - n_A - n_B) + 2\beta V (n_A - n_B)^2]\end{aligned}\quad (\text{S8.129})$$

(b) If we define new variables n and ν by $n = n_A + n_B$ and $\nu = n_A - n_B$, then $n_A = (n + \nu)/2$ and $n_B = (n - \nu)/2$. The canonical potential, expressed in terms of these variables, is

$$\begin{aligned}\phi = & -K \left[\frac{1}{2}(n + \nu) \log\left(\frac{n + \nu}{2}\right) + \frac{1}{2}(n - \nu) \log\left(\frac{n - \nu}{2}\right) \right. \\ & \left. + (1 - n) \log(1 - n) + 2\beta V \nu^2 \right]\end{aligned}\quad (\text{S8.130})$$

In the presence of the chemical reaction, $A \leftrightarrow B$, n is a conserved quantity, but ν can adjust itself so as to maximize the value of ϕ . (Recall from Section 5.21 that the equilibrium condition for a system kept at fixed temperature is that ϕ , rather than S , is a maximum with respect to all nonconserved variables.) Setting $\partial\phi/\partial\nu = 0$ gives the equilibrium equation

$$\frac{1}{2} \log\left(\frac{n + \nu}{2}\right) - \frac{1}{2} \log\left(\frac{n - \nu}{2}\right) + 4\beta V \nu = 0 \quad (\text{S8.131})$$

Letting $\gamma = (N_A - N_B)/(N_A + N_B) = \nu/n$, this equation can be written as

$$\log(1 + \gamma) - \log(1 - \gamma) = -8\beta V n \gamma \quad (\text{S8.132})$$

But this is essentially identical to Eq. (8.48), developed for a model of nematic liquid crystals. Using the identity mentioned after that equation gives

$$\gamma = -\tanh(4\beta V n \gamma) \quad (\text{S8.133})$$

This always has the solution $\gamma = 0$. But if V is negative and $4\beta|V|n > 1$, then it also has two solutions for nonzero values of γ that are equal in magnitude but opposite in sign. When these solutions exist, the solution $\gamma = 0$ does not represent the equilibrium state (see Problem 8.8). In Fig. S8.8, γ is plotted as a function of $\beta|V|n$ for negative V .

In the description of the computer programs at the end of this supplement, this model is called the AB model, and a Monte Carlo program for solving it is given. By investigating the model, using the display program, the reader will discover that there is an antiferromagnetic phase that has been completely missed by this mean-field calculation.

Exercise 8.18 In Exercises 8.12 and 8.13, the Bethe–Peierls approximation, which is an improvement on simple mean-field theory, was presented. In this exercise we will illustrate another of the many possible “improvements” on the simple mean-field approximation. We consider a two-dimensional Ising model on a triangular lattice (see Fig. S8.9). The simple mean-field approximation would consist of looking at a single-spin variable and replacing all of its nearest-neighbor spins by their average values. In this new improved version of the method, we focus our attention on any triangle of three spins and replace all of the nearest neighbors of the triangle by fixed noninteger values $\bar{\sigma}$, to be determined later. This fudge effectively replaces the large lattice of spins by a system of only three spins, which has a total of $2^3 = 8$ possible configurations. Finally, the value of $\bar{\sigma}$ will be calculated by demanding that $\langle\sigma_1 + \sigma_2 + \sigma_3\rangle = 3\bar{\sigma}$. (a) Assuming that there is

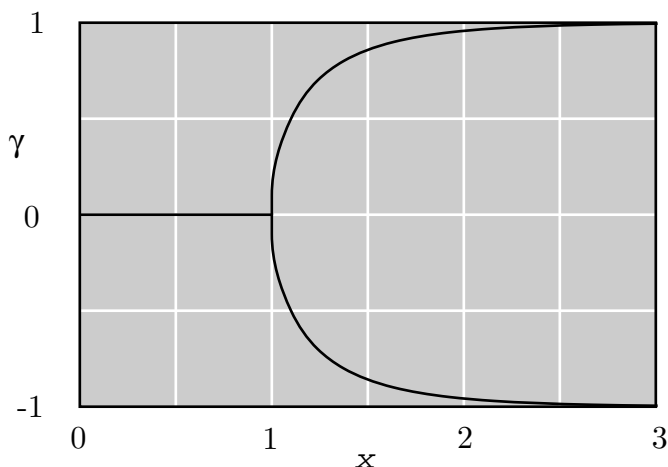


Fig. S8.8 $\gamma = (N_A - N_B)/(N_A + N_B)$ as a function of $x = 4\beta|V|n$. When $x > 1$ (that is, when $kT < 4|V|n$), there are two possible nonzero equilibrium values of γ .

an external field H and a nearest-neighbor interaction V , calculate $\bar{\sigma}$ as a function of H and β . (b) Assuming that the interaction energy within the triangle is typical of the interaction energy throughout the lattice, calculate the energy per spin as a function of β for the special case $H = 0$.

Solution (a) For any configuration $(\sigma_1, \sigma_2, \sigma_3)$ of the three-spin system, its energy is

$$E = -(H - 4\bar{\sigma}V)(\sigma_1 + \sigma_2 + \sigma_3) - V(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_2\sigma_3) \tag{S8.134}$$

The probability of any configuration is

$$P(\sigma_1, \sigma_2, \sigma_3) = \frac{e^{-\beta E}}{Z} = Z^{-1} \exp[h(\sigma_1 + \sigma_2 + \sigma_3) + v(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_2\sigma_3)] \tag{S8.135}$$

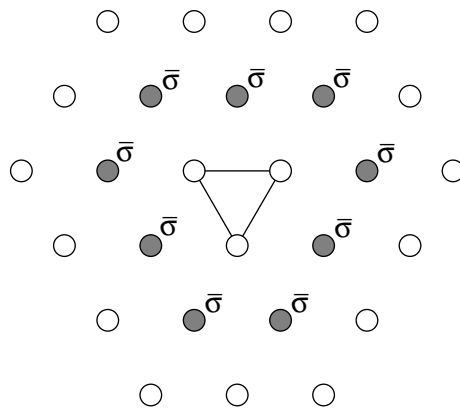


Fig. S8.9 The fixed $\bar{\sigma}$ spins effectively isolate the triangle of Ising spins.

where $h = \beta(H + 4\bar{\sigma}V)$ and $v = \beta V$. The partition function can be calculated by explicitly summing over the 8 possible states.

$$\begin{aligned} Z &= \sum_{\sigma_1\sigma_2\sigma_3} \exp[h(\sigma_1 + \sigma_2 + \sigma_3) + v(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_2\sigma_3)] \\ &= e^{3h+3v} + e^{-3h+3v} + 3e^{h-v} + 3e^{-h-v} \\ &= 2e^{3v} \cosh(3h) + 6e^{-v} \cosh(h) \end{aligned} \tag{S8.136}$$

The average value of $\sigma_1 + \sigma_2 + \sigma_3$ is given by

$$\langle \sigma_1 + \sigma_2 + \sigma_3 \rangle = \sum_{\sigma_1} \sum_{\sigma_2} \sum_{\sigma_3} (\sigma_1 + \sigma_2 + \sigma_3) P(\sigma_1, \sigma_2, \sigma_3) \quad (\text{S8.137})$$

Looking at Eq. (S8.135), we see that

$$\langle \sigma_1 + \sigma_2 + \sigma_3 \rangle = \frac{\partial Z / \partial h}{Z} = 3 \frac{e^{3v} \sinh(3h) + e^{-v} \sinh(h)}{e^{3v} \cosh(3h) + 3e^{-v} \cosh(h)} \quad (\text{S8.138})$$

Demanding that $\bar{\sigma} = \langle \sigma_1 + \sigma_2 + \sigma_3 \rangle / 3$ gives the self-consistency condition

$$\frac{\sinh[3\beta(H + 4V\bar{\sigma})] + e^{-4v} \sinh[\beta(H + 4V\bar{\sigma})]}{\cosh[3\beta(H + 4V\bar{\sigma})] + 3e^{-4v} \cosh[\beta(H + 4V\bar{\sigma})]} = \bar{\sigma} \quad (\text{S8.139})$$

This equation for $\bar{\sigma}$ can be solved numerically. $\bar{\sigma}$ is shown as a function of the dimensionless temperature variable $t = kT/V$ for $H = 0$ in Fig. S8.10.

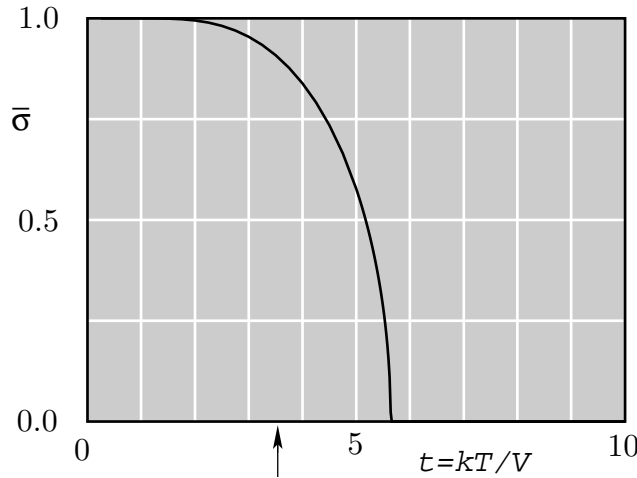


Fig. S8.10 The spontaneous magnetization $\bar{\sigma}$ as a function of the dimensionless temperature $t = kT/V$. In this approximation, the transition occurs at about $t = 5.65$. The exact transition temperature for a triangular lattice, indicated in the figure by an arrow, is $t \approx 3.64$. The simple mean-field approximation, which uses only a single spin, predicts a transition at $t = 6$. Thus this calculation does not give a large improvement on the simpler one.

(b) If $H = 0$ then the energy in the real many-spin system is

$$E = -V \left\langle \sum_{NN} \sigma(\mathbf{x}) \sigma(\mathbf{x}') \right\rangle \quad (\text{S8.140})$$

In the mean-field calculation we will approximate this sum over all bonds by one-half the number of triangles times the same sum over the three bonds in the chosen triangle. The one-half avoids double counting, since each bond lies between two triangles. Looking at Eq. (S8.135), one can see that

$$\langle \sigma_1 \sigma_2 + \sigma_1 \sigma_3 + \sigma_2 \sigma_3 \rangle = \frac{\partial Z / \partial v}{Z} = 3 \frac{\cosh(3h) - e^{-4v} \cosh(h)}{\cosh(3h) + 3e^{-4v} \cosh(h)} \quad (\text{S8.141})$$

In a triangular lattice of N spins, neglecting edge corrections, there are $2N$ triangles. Summing over all the triangles would count each bond twice, since it lies between two triangles. Therefore,

$$E = -3NV \langle \sigma_1 \sigma_2 + \sigma_1 \sigma_3 + \sigma_2 \sigma_3 \rangle \quad (\text{S8.142})$$

and

$$\frac{E}{N} = -V \frac{\cosh(3h) - e^{-4v} \cosh(h)}{\cosh(3h) + 3e^{-4v} \cosh(h)} \quad (\text{S8.143})$$

where $h = 4\beta V \bar{\sigma}$ and $v = \beta V$.

Exercise 8.19 In this exercise, the basic mechanisms of ferrimagnetism and antiferromagnetism will be explored. The two phenomena are closely related, and may be conveniently treated simultaneously. We will restrict ourselves to a two-dimensional model, but the mean-field analysis would be basically unchanged in treating the three-dimensional case.

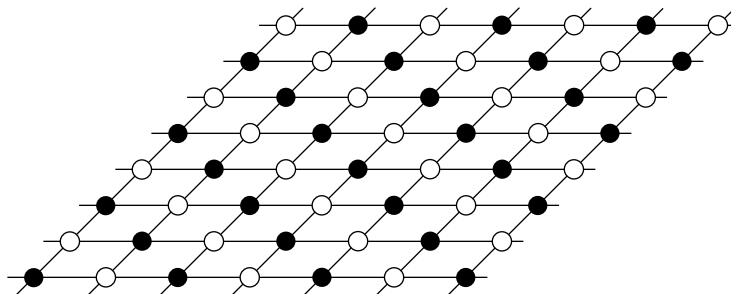


Fig. S8.11 The checkerboard pattern of a ferrimagnetic crystal.

Shown in Fig. S8.11 is a model of a two-dimensional ferrimagnetic substance. Two different types of atoms, which will be called A and B , are arranged in a checkerboard pattern. The magnetization direction is perpendicular to the plane of the lattice. A and B atoms have magnetic moments m_A and m_B , respectively, with $m_A > m_B$. There is an antiferromagnetic interaction between nearest neighbors (which are always A – B pairs). The magnetic moments also interact with a constant external magnetic field of strength B . Using the mean-field approximation, derive equations for the average magnetization of the substance as a function of the temperature and the external field strength.

Solution We introduce spin variables $\sigma_A(\mathbf{x})$ and $\sigma_B(\mathbf{y})$, with the values ± 1 , for the A and B atoms, respectively. The vector \mathbf{x} ranges over the A lattice, while \mathbf{y} ranges over the B lattice (that is, the location of the B atoms). The energy of a configuration in an external field B is

$$E = -B \left(m_A \sum_A \sigma_A(\mathbf{x}) + m_B \sum_B \sigma_B(\mathbf{y}) \right) + V \sum_{\text{NN}} \sigma_A(\mathbf{x}) \sigma_B(\mathbf{y}) \quad (\text{S8.144})$$

where $V > 0$ for an antiferromagnetic interaction. The average spin of an A atom can, in the mean-field approximation, be calculated by replacing its four nearest neighbors by their as yet unknown average values.

$$\bar{\sigma}_A = \frac{\sum_{\sigma_A} \left(\sigma_A e^{\beta(Bm_A - 4V\bar{\sigma}_B)\sigma_A} \right)}{\sum_{\sigma_A} e^{\beta(Bm_A - 4V\bar{\sigma}_B)\sigma_A}} \quad (\text{S8.145})$$

Evaluating the sums, one obtains

$$\bar{\sigma}_A = \tanh[\beta(Bm_A - 4V\bar{\sigma}_B)] \quad (\text{S8.146})$$

A similar calculation for $\bar{\sigma}_B$ gives

$$\bar{\sigma}_B = \tanh[\beta(Bm_B - 4V\bar{\sigma}_A)] \quad (\text{S8.147})$$

Once these two simultaneous equations have been solved for $\bar{\sigma}_A$ and $\bar{\sigma}_B$, the magnetic moment per atom is given by

$$\bar{m} = (m_A \bar{\sigma}_A + m_B \bar{\sigma}_B) / 2 \quad (\text{S8.148})$$

Exercise 8.20 The model that was introduced in the last exercise can describe both ferrimagnetism and antiferromagnetism. It exhibits antiferromagnetic behavior when $m_A = m_B$. This occurs when the crystal is, in fact, composed of only one type of magnetic atom with a nearest-neighbor interaction that favors antiparallel spin alignment. An important example is the set of copper oxide materials involved in high-temperature superconductivity. In these materials, the oxygen atoms play a role in creating an antiferromagnetic interaction between neighboring copper atoms but play no direct part in the magnetic properties of the crystal. For the antiferromagnetic case, $m_A = m_B = m$, take $B = 0$, and determine $\bar{\sigma}_A$ and $\bar{\sigma}_B$ as functions of $\tau = 1/\beta$.

Solution We introduce a parameter $\tau_c = 4V$, which will, of course, turn out to be the critical temperature for the antiferromagnetic transition. With $B = 0$, Eqs. (S8.146) and (S8.147) can be written as

$$\bar{\sigma}_A = -\tanh\left(\frac{\tau_c}{\tau}\bar{\sigma}_B\right) \quad (\text{S8.149})$$

and

$$\bar{\sigma}_B = -\tanh\left(\frac{\tau_c}{\tau}\bar{\sigma}_A\right) \quad (\text{S8.150})$$

It is clear that, if $\bar{\sigma}_A > 0$, then $\bar{\sigma}_B < 0$ and vice versa. In fact, the solutions of these equations for $\bar{\sigma}_A$ and $\bar{\sigma}_B$ all have the symmetry $\bar{\sigma}_A = -\bar{\sigma}_B$. Assuming that symmetry, one can write a single equation for $\bar{\sigma}_A$.

$$\bar{\sigma}_A = \tanh\left(\frac{\tau_c}{\tau}\bar{\sigma}_A\right) \quad (\text{S8.151})$$

This equation is identical to Eq. (8.110), showing that, below the critical temperature τ_c , the A lattice is spontaneously magnetized to exactly the same degree as shown by a ferromagnetic model with the same value for the interaction strength V , but the opposite sign. However, because of the fact that the B lattice magnetization is exactly opposite to that of the A lattice, the total magnetization of the substance remains zero below the transition temperature. Although the antiferromagnetic phase transition does not exhibit spontaneous macroscopic magnetization, it can be clearly detected by monitoring the specific heat. In fact, the specific heat has precisely the same singularity as a two-dimensional ferromagnetic Ising model.

Exercise 8.21 Within the mean-field approximation, calculate the magnetic susceptibility in zero external field of a ferrimagnet for $\tau > \tau_c$.

Solution Above the critical temperature, if we assume that the external field B is very small, then $\bar{\sigma}_A$ and $\bar{\sigma}_B$ are also very small, and the right-hand sides of Eqs. (S8.146) and (S8.147) can be expanded to first order in B , $\bar{\sigma}_A$, and $\bar{\sigma}_B$, giving the linear equations

$$\bar{\sigma}_A = \frac{Bm_A - \tau_c\bar{\sigma}_B}{\tau} \quad (\text{S8.152})$$

and

$$\bar{\sigma}_B = \frac{Bm_B - \tau_c\bar{\sigma}_A}{\tau} \quad (\text{S8.153})$$

which can be rearranged as

$$\tau\bar{\sigma}_A + \tau_c\bar{\sigma}_B = Bm_A \quad \text{and} \quad \tau_c\bar{\sigma}_A + \tau\bar{\sigma}_B = Bm_B \quad (\text{S8.154})$$

These simultaneous linear equations have the solution

$$\bar{\sigma}_A = \frac{\tau m_A - \tau_c m_B}{\tau^2 - \tau_c^2} B \quad \text{and} \quad \bar{\sigma}_B = \frac{\tau m_B - \tau_c m_A}{\tau^2 - \tau_c^2} B \quad (\text{S8.155})$$

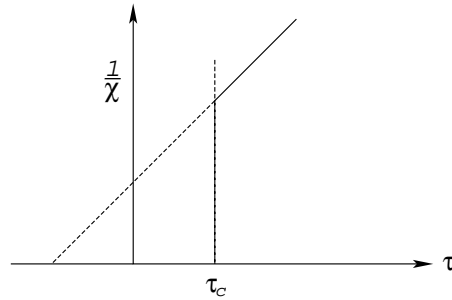


Fig. S8.12 One distinguishing feature of an antiferromagnet is that, above the transition temperature, the inverse of the magnetic susceptibility is a linear function of temperature with a negative intercept.

The susceptibility is given by

$$\chi = \frac{m_A \bar{\sigma}_A + m_B \bar{\sigma}_B}{B} = \frac{(m_A^2 + m_B^2)\tau - 2m_A m_B \tau_c}{\tau^2 - \tau_c^2} \quad (\text{S8.156})$$

In the antiferromagnetic case, $m_A = m_B = m$, and

$$\chi = \frac{2m^2}{\tau + \tau_c} \quad (\text{S8.157})$$

This relation implies that, above τ_c , the inverse of the susceptibility for an antiferromagnet is a linear function of τ with a negative intercept (Fig. S8.12). This is a prediction that is well satisfied by real antiferromagnetic materials (although the detailed formula for the value of the intercept is not reliable).

For a ferrimagnet, the susceptibility has a singularity at $\tau = \tau_c$. The mean-field calculation predicts that the singularity in χ has the form of a simple pole [that is, $\chi \approx C/(\tau - \tau_c)$], a prediction that does not agree with experiment.

The Programs

The remainder of this Supplement will be a description of the computer programs on the Program Disk that accompanies the text. Some of the programs come in two versions: a display version, which is a compiled program to be run on a Macintosh computer or an IBM PC with a graphics board, and a Fortran version, ready to be compiled and run on any computer with a Fortran compiler.

All of the programs described here are applications of the Monte Carlo method to various model systems. The display version of each program gives a visual representation of the sequence of physical states constructed by the Monte Carlo algorithm. It is intended to help the reader in developing physical intuition by actually seeing the sequence of states that the system passes through in approaching equilibrium. Also, by seeing the program in operation, the reader can more easily understand what the corresponding Fortran program, which operates without any display, is doing. The Fortran versions of the programs are necessary for two reasons. The first is that the graphics oriented programs run quite slowly because they use a large part of their time in constructing screen displays. The second is that it would be unreasonable to expect the reader to be familiar with graphics programming and thus capable of modifying and augmenting the programs. But many of the problems associated with the Monte Carlo method do require that ability. Those problems will be done using the Fortran programs, which have been written with that consideration in mind.

Hot Spring 1 (Display)

This program is a Monte Carlo analysis of a particle on a one-dimensional lattice, under the influence of a harmonic oscillator potential. It follows the simple example presented in Section 8.12, with one minor revision. In order to keep the particle on the screen, it limits ℓ to the range $-L \leq \ell \leq L$, where the value of L is determined by the size of the computer screen on the machine that is used to run the program. This is equivalent to setting $E(\ell) = \infty$ for $|\ell| > L$. Each time the particle, shown at the bottom of the screen,

jumps to location ℓ , a white bar above that location grows by a fixed amount. When any white bar reaches the top of the screen, the program halts and waits for the mouse button to be pressed. The white bars therefore give a histogram of the time spent at each location. Theoretically, it should be a Gaussian curve, $f(\ell) = C \exp(-\varepsilon \ell^2 / kT)$, but in any particular run one will see statistical fluctuations about the ideal curve, since the sample is finite.

Hot Spring 2 (Display)

This program adds one additional feature to the previous program. Instead of always considering a move of one lattice unit, either left or right, it chooses a possible move from a uniform distribution over the possibilities $\Delta\ell = \pm 1, \pm 2, \dots, \pm MaxJump$, where the positive integer *MaxJump* is set by the user. Once a possible move has been chosen, it is definitely made if it would lower the energy and it is made with a probability $P = \exp(-\Delta E / kT)$, if it would increase the energy. Although the value of *MaxJump* has no effect on the equilibrium distribution, it can strongly affect the magnitude of the statistical error in a finite sample.

Hot Spring (Fortran)

This has three different Fortran versions. *HotSpring_1.for* is a Fortran version of the display program Hot Spring 1. The output of the program, in the file *HotSpring.out*, is the function $P(\ell)$, which gives the fraction of time that the particle spent at the lattice point ℓ . As the run time is made longer and longer, the function more and more closely approximates a Gaussian function. The parameter $s = \sqrt{kT/\varepsilon}$ is chosen by the user.

The second program, *HotSpring_2.for*, is a Fortran version of the display program Hot Spring 2. The user chooses values of the parameter $s = \sqrt{kT/\varepsilon}$, the maximum jump size, and the number of Monte Carlo moves. The output in the file *HotSpring.out* gives the value of $P(\ell)$, the fraction of time spent at location ℓ .

The third Fortran version, *HotSpring_3.for*, does not impose any artificial discreteness on the position variable x . It illustrates how one treats a system with continuous coordinates by means of the Monte Carlo method. This is a topic that was not covered in Chapter 8. The modifications to the discrete case are fairly minimal. One chooses a suggested jump Δx from a uniform distribution over the interval $-D < \Delta x < D$. If the jump $x \rightarrow x + \Delta x$ would lower the energy, then it is made. If it would increase the energy by an amount ΔE , then it is made with probability $P = \exp(-\beta \Delta E)$. The user chooses the two parameters, $s = \sqrt{kT/\varepsilon}$ and D , and the number of Monte Carlo moves. The output of the calculation is the set of three numbers $\langle x^2 \rangle$, $\langle x^4 \rangle$, and $\langle x^6 \rangle$, which can be compared with theoretical calculations of the same quantities using the canonical probability density.

Hot Ball (Display)

This is essentially the same as Hot Spring 2, but the coordinate is a vertical coordinate and the potential function is that for a uniform gravitational field; that is, $U(z) = mgz$. The parameter that defines the equilibrium distribution is the scale height, $s = kT/mg$. The coordinate z is restricted to positive values by setting $U(z) = \infty$ for negative z , and it is converted to an integer variable. The expected probability distribution is the exponential $P(z) = C \exp(-z/s)$.

Hot Ball (Fortran)

This is a Fortran version of the same program. The output of the program is the distribution $P(z)$, which is the fraction of time the particle spends at the height z and the theoretically exact probability, $P_o(z) = C \exp(-z/s)$, for comparison. The user must choose the values of the scale height s , the maximum jump size, and the number of Monte Carlo moves.

Ising 1 (Display)

This is an implementation of the algorithm described in Section 8.13. It is a Monte Carlo calculation on an L_x by L_y square lattice of two-valued spins. (The lattice structure is square but, if $L_x \neq L_y$, the whole sample is rectangular.) There is an external magnetic field variable H , whose value is chosen by the user. If H is positive, then up spins have lower energy than down spins. There is a nearest-neighbor interaction energy variable V , also chosen by the user. A positive value of V means that any pair of neighboring spins will have a lower energy if they are parallel than if they are antiparallel. If V is negative, antiparallel neighbors have lower energy than parallel ones. Thus positive V favors ferromagnetic ordering while negative V favors antiferromagnetic (checkerboard) ordering. An "up" spin is represented on the screen by a small

white square. A “down” spin is drawn as a gray square. The program starts with a random configuration in which any spin is equally likely to be up or down. The lattice has periodic boundary conditions, which means that the rightmost spins are neighbors of the leftmost spins and the top spins are neighbors of the bottom spins.

The following step is repeated for a number of times N_{moves} that is chosen by the user. A random lattice point is chosen, and the program considers the possibility of changing the spin at that lattice point. If it would lower the energy, the change is made. If it would increase the energy by an amount ΔE , then the change is made with a probability $\exp(-\beta \Delta E)$.

Ising 1 (Fortran)

This is a Fortran version of the above program, written for an $L \times L$ lattice. The periodic boundary conditions are implemented by defining a function called $np1(n, L)$ that has the value

$$np1(n, L) = \begin{cases} n + 1, & \text{for } n = 1, \dots, L - 1 \\ 1, & \text{for } n = L \end{cases} \quad (\text{S8.158})$$

With this definition the nearest neighbor of spin $\sigma(x, y)$ in the $+x$ direction is always $\sigma(np1(x, L_x), y)$. The function

$$nm1(n, L) = \begin{cases} n - 1, & \text{for } n = 2, \dots, L \\ L, & \text{for } n = 1 \end{cases} \quad (\text{S8.159})$$

gives the nearest neighbors in the $-x$ and $-y$ directions.

For given values of H and V , the program carries out calculations at a number of equally spaced temperatures in an interval $\tau_{\min} \leq \tau \leq \tau_{\max}$. At each temperature, the values of \bar{M} , \bar{E} , $(\Delta M)^2$, and $(\Delta E)^2$ are calculated, where $M = |\sum \sigma(x, y)|$. From the values of $(\Delta M)^2$ and $(\Delta E)^2$ one can determine the magnetic susceptibility and the specific heat by using Eqs. (8.82) and (8.83). M is defined as $|\sum \sigma|$, rather than as $\sum \sigma$, in order to avoid a problem that occurs when making calculations using a relatively small number of spins. For a real system of 10^{20} or more spins, below the ferromagnetic transition temperature the system will be found with its polarization in either the up or the down direction. It will never realistically make a spontaneous transition from one polarization state to the other. Therefore, the fluctuation in the polarization is negligibly small at temperatures below the transition temperature. However, for a system of only a few spins, occasional transitions between the two favored polarization states do occur. This causes the fluctuation in the polarization to have a large value. But the large fluctuation is only an uninteresting effect of small system size. It can be eliminated by looking at the observable $|\sum \sigma|$, rather than $\sum \sigma$.

Ising 2

This is identical to Ising 1, except for the following change. Instead of choosing the lattice point at which to consider a spin flip at random, the program methodically sweeps through the lattice in a raster pattern, going from top to bottom through one complete column and then moving to the next column. At each lattice point it uses the usual Monte Carlo algorithm to decide whether to flip the spin or leave it unchanged. It is left as a problem for the reader to show that this procedure is legitimate, in the sense that it produces a sampling sequence with the canonical distribution. Because this procedure requires the generation of much fewer random numbers, it is more efficient than the one used in Ising 1. There are both display and Fortran versions of this program.

Ising 3 (Fortran)

This program, which exists only in the Fortran version, is designed to study the effects of boundary conditions and to study correlation effects in the Ising system. In this program H is set to zero and V is set to one. The user specifies the inverse temperature β . Periodic boundary conditions are used in the y direction, but the first and last columns of spins (that is, those spins with $x = 0$ and $L_x + 1$) are set by the user. Each of the two fixed boundary columns can be set all up, all down, or zero. Setting the final column of spins, at $x = L_x + 1$, to zero has the same effect as having a “free boundary” at $x = L_x$. The user specifies how many sweeps through the lattice should be made. The output, given in the file `Ising_3.out`, consists of the average polarization of the spins in each column as a function of x , the column number. By looking at this output, the reader can see how far into the lattice the effects of the fixed boundaries extend. At high

temperatures the effects are noticeable for only a few lattice distances away from the boundary, but below the ferromagnetic transition it is clear that the effects extend throughout the lattice. This is an example of the fact that, in the presence of spontaneous symmetry breakdown, ordinarily negligible aspects of the system, such as surface interactions, determine the observed equilibrium state.

Ising 4 (Fortran)

This Fortran program introduces random vacancies into a two-dimensional Ising model (with no external field). The user chooses a value for the vacancy rate, which must be less than one. The program first sweeps through the lattice, randomly setting spins equal to zero, with a probability equal to the chosen vacancy rate. A zero spin represents a vacancy in the lattice. During the subsequent Monte Carlo runs, the zero-spin values are never changed. The reader is encouraged to investigate, by means of this program, the effects of random impurities on phase transitions in crystalline materials.

Ising 3D (Fortran)

This is a three-dimensional version of Ising 2.

LatGas (Fortran)

This program makes a Monte Carlo calculation for the lattice gas model, analyzed with the mean-field approximation in Section 8.9. The user sets the lattice size, the range and number of values of the affinity, the value of βV , and the number of sweeps through the lattice in each run. The program gives, as output, the value of $\langle N \rangle$ in the file LatGas.out.

AB Model

This is the lattice gas model that was analyzed, with the mean-field approximation, in Exercise 8.17. Two types of particles, called A and B , can reside at the points of a square lattice. A particles are shown as white squares, B particles as gray squares, and empty lattice sites as black squares. Two A particles or two B particles interact with an energy V , but an A particle and a B particle that are nearest neighbors interact with an interaction energy $-V$. There is no energy binding the particles to the lattice sites. The number of particles is not fixed, but α_A is set equal to α_B . In the grand canonical ensemble, the probability of any configuration of the system is

$$P(C) = \Lambda^{-1} \exp[-\alpha(N_A + N_B) + \beta V(N_{AA} + N_{BB} - N_{AB})] \quad (\text{S8.160})$$

where N_A is the number of A particles, N_B is the number of B particles, and N_{AA} , N_{BB} , and N_{AB} are the number of nearest-neighbor AA , BB , and AB pairs, respectively.

The program comes in both display and Fortran versions. The user chooses the size of the lattice, the values of V/kT , the number of sweeps through the lattice, and the value (in the display program) or the range (in the Fortran program) of α . The configuration of the system is represented by a function $N(x, y)$ that has the value 0 for an empty site, +1 for an A particle, and -1 for a B particle. The program sweeps, raster style, through the points of the lattice. At each point, the program reads the value of $N(x, y)$ and then attempts a change of $N(x, y)$ to either of the other two possible values with equal probabilities. In “attempting a change” from, for instance, $N = +1$ to -1 , the program evaluates ΔF , the change in the function

$$F(C) = \alpha(N_A + N_B) + \beta V(N_{AA} + N_{BB} - N_{AB}) \quad (\text{S8.161})$$

that would result. If ΔF is negative, then the change is made. If ΔF is positive, then the change is made with probability $\exp(-\Delta F)$.

The Fortran program, for each value of α , stores the values of $\langle N \rangle$, $\langle Q \rangle$, $(\Delta N)^2$, and $(\Delta Q)^2$ in the file AB.out, where $N = N_A + N_B$ and $Q = N_A - N_B$.