Chapter 8

Systems of Interacting

Particles and Magnetism

8.1 INTRODUCTION

Up to this point, we have only treated various forms of ideal systems, that is, systems without interparticle interactions. The analysis of lattice vibrations may seem to be an exception to this statement, in that the particles in the solid interact with harmonic forces, but the system of lattice vibrations was completely equivalent to a collection of noninteracting harmonic oscillators. In any real system, the interactions are essential in determining the physical properties of the substance. It is the interactions between the molecules that cause a gas to condense to a liquid state and that create the varieties of crystal structure in the solid state. Unfortunately, with the exception of certain simple models in one and two dimensions, a complete statistical mechanical calculation cannot be carried through exactly for any interacting system. This is not surprising. In classical and quantum mechanics, even the three-body problem cannot be solved exactly, and in statistical mechanics we are faced with the N_A-body problem. What is remarkable is how much progress has been made in making reliable and accurate approximate calculations of the properties of interacting systems.

In this chapter we will discuss three important methods of dealing with interactions. The first is a method that generates a power series expansion, called the *cluster expansion*, that is particularly useful in deriving the properties of dense gases. It allows a systematic calculation of the equations of state of a gas in terms of the intermolecular interaction potential of the gas molecules. Often it is used in the reverse mode; that is, the equations of state are experimentally determined and that information is then used, via the cluster expansion, to calculate the interaction potential. The second method is called the *mean-field approximation*. It is a method of calculating, approximately, the properties of phase transitions i strongly interacting systems by neglecting the statistical correlations between neighboring particles. The third method is a numerical computational scheme, called the *Monte Carlo method.* It has been vital in obtaining accurate results for many strongly interacting systems, such as liquids and solids. It is basically an efficient method of generating a sampling sequence, in the sense of Chapter 1, for the canonical ensemble probability density.

8.2 THE IDEAL GAS IN THE GRAND CANONICAL ENSEMBLE

In preparation for deriving the cluster expansion, it is useful to calculate the grand partition function and the grand potential of a classical ideal gas. The grand partition function is given in terms of H_N, the

Hamiltonian function of the system with N particles, by

$$\Lambda = 1 + \sum_N \frac{e^{-\alpha N}}{h^{3N} N!} \int e^{-\beta H_N} d^{3N}x d^{3N}p \tag{8.1}$$

We define a function $\zeta(\alpha, \beta)$, called the *activity,* by

$$\zeta(\alpha, \beta) \equiv \frac{e^{-\alpha}}{h^3} \int e^{-\beta p^2/2m} d^3p$$
$$e^{-\alpha}(2\pi m/\beta h^2)^{3/2} \tag{8.2}$$
$$= e^{-\alpha}/\lambda^3$$

where λ is the thermal de Broglie wavelength. For an ideal gas, $H_N = \sum p^2/2m$, and therefore the integral in Eq. (8.1) can be expressed easily in terms of the activity.

$$\frac{e^{-\alpha N}}{h^{3N}} \int e^{-\beta H_N} d^{3N}x d^{3N}p = V^N \zeta^N \tag{8.3}$$

Λ is then given as a well-known power series in the activity.

$$\Lambda = \sum_{N=0}^{\infty} \frac{V^N \zeta^N}{N!} = e^{V\zeta} \tag{8.4}$$

The grand potential is therefore

$$\psi = \log \Lambda = V\zeta \tag{8.5}$$

The thermodynamic relation $N = -\partial\psi/\partial\alpha$ and the fact that $\partial\zeta/\partial\alpha = -\zeta$ yields $N = V\zeta$, which shows that for the ideal gas ζ is equal to the particle density.

$$\zeta = \frac{N}{V} = n \tag{8.6}$$

This suggests that, for gases with interactions (usually called *real gases*), an expansion of ψ as a power series in the activity would be essentially an expansion in terms of the density. But at low density the ideal gas approximation is accurate. Therefore, such an expansion would yield systematic corrections to the ideal gas equations of state due to the interparticle interactions.

8.3   THE CLUSTER EXPANSION FOR A REAL GAS

A gas of N interacting particles has a Hamiltonian function that is a sum of a kinetic energy term and a potential energy term.

$$H_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) \tag{8.7}$$

Using Eqs. (8.1) and (8.2), the grand partition function Λ can be written in terms of the activity and the $3N$-dimensional integrals

$$I_N = \int e^{-\beta U_N} d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \tag{8.8}$$

in the form

$$\Lambda = 1 + I_1\zeta + \frac{1}{2}I_2\zeta^2 + \frac{1}{3!}I_3\zeta^3 + \ldots \tag{8.9}$$

Using the following expansion for the logarithmic function

$$\log(1+x) = x - \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 - \tfrac{1}{4}x^4 + \ldots \tag{8.10}$$

the grand potential, $\psi = \log \Lambda$, can be expressed as a power series in the activity (only terms necessary to carry out the expansion to order ζ^3 are shown explicitly).

$$\psi = (I_1\zeta + \tfrac{1}{2}I_2\zeta^2 + \frac{1}{3!}I_3\zeta^3 + \ldots) - \tfrac{1}{2}(I_1\zeta + \tfrac{1}{2}I_2\zeta^2 + \ldots)^2 + \tfrac{1}{3}(I_1\zeta + \ldots)^3 - \ldots \tag{8.11}$$

Expanding out the brackets, we get, to third order in ζ,

$$\psi = I_1\zeta + \tfrac{1}{2}(I_2 - I_1^2)\zeta^2 + \tfrac{1}{6}(I_3 - 3I_1I_2 + 2I_1^3)\zeta^3 + \ldots \tag{8.12}$$

The coefficient of ζ^N divided by the volume is called the Nth *cluster integral* C_N. It is easy to see that the first cluster integral is equal to one. ($C_1 = I_1/V = 1$). In terms of the cluster integrals,

$$\psi = V(\zeta + C_2\zeta^2 + C_3\zeta^3 + \ldots) \tag{8.13}$$

The thermodynamic identity $\psi = \beta p V$ shows that the grand potential is proportional to the system volume. Since ζ is a function of α and β, and therefore independent of V, Eq. (8.13) implies that for large systems the cluster integrals are functions only of the inverse temperature β. This will be confirmed immediately for C_2 and in the exercises for C_3. Comparing Eqs. (8.12) and (8.13), we see that

$$C_2 = \frac{1}{2V}(I_2 - I_1^2) = \frac{1}{2V}\int (e^{-\beta U_2} - 1)d^3\mathbf{r}_1 d^3\mathbf{r}_2 \tag{8.14}$$

The interaction potential for two particles is a function only of the distance between them. That is, $U_2 = v(|\mathbf{r}_2 - \mathbf{r}_1|)$. In the integral, we can transform to center-of-mass and relative variables, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. Because the interaction potential is negligible beyond a few Ångstroms, the integrand is zero unless $\mathbf{r}_1$ is very close to $\mathbf{r}_2$. Therefore, the relative variable can be extended to infinity and the center-of-mass variable can be integrated over the volume of the system. This gives

$$C_2 = \frac{1}{2}\int (e^{-\beta v(r)} - 1)d^3\mathbf{r} = 2\pi \int_0^\infty (e^{-\beta v(r)} - 1)r^2 dr \tag{8.15}$$

If the interparticle interaction potential is known, then this equation allows one to compute $C_2(\beta)$.

Equation (8.12), when combined with the relations $\beta p = \psi/V$, $n = -\partial(\psi/V)/\partial\alpha$, and $\partial\zeta/\partial\alpha = -\zeta$, gives both the pressure and density as power series expansions in the activity.

$$\frac{p}{kT} = \zeta + C_2\zeta^2 + C_3\zeta^3 + \ldots \tag{8.16}$$

$$n = \zeta + 2C_2\zeta^2 + 3C_3\zeta^3 + \ldots \tag{8.17}$$

8.4   THE POTENTIAL ENERGY OF A REAL GAS

The justification for studying the ideal gas has been the assumption that, under ordinary conditions, the average value of the potential energy of most common gases is only a small fraction of the value of the kinetic energy. When that assumption is true, it is reasonable to ignore the potential energy term in the Hamiltonian function. Now that we have a method for dealing with interparticle interactions (namely, the cluster expansion), it is possible to check on the accuracy of the ideal gas approximation by actually calculating the expectation value of the potential energy for typical real gases.

Equation (8.12) gives an expansion for the grand potential as a power series in the activity.

$$\psi = V[\zeta + C_2(\beta)\zeta^2 + C_3(\beta)\zeta^3 + \ldots] \tag{8.18}$$

The energy of the gas is given by the thermodynamic relation $E = -\partial\psi(\alpha, \beta, V)/\partial\beta$. Remembering that the activity ζ is a function of α and β, we can express E in the form

$$E = -V(1 + 2C_2\zeta + 3C_3\zeta^2 + \ldots)\frac{\partial\zeta}{\partial\beta} - V(C_2'\zeta^2 + C_3'\zeta^3 + \ldots) \tag{8.19}$$

where $C'_n = \partial C_n(\beta)/\partial\beta$. From Eq. (8.2) we see that

$$\frac{\partial\zeta}{\partial\beta} = -\frac{3}{2}\beta^{-1}\zeta \tag{8.20}$$

When this is used in Eq. (i.19), and one recognizes the series for the density $n = N/V$ from Eq. (8.17), the equation becomes

$$E = \frac{3}{2}NkT - V[C'_2(\beta)\zeta^2 + C'_3(\beta)\zeta^3 + \ldots] \tag{8.21}$$

The first term is clearly the kinetic energy which, for a classical monatomic gas is always equal to $\frac{3}{2}NkT$. The expansion that follows that term must therefore give the potential energy in terms of the inverse temperature and the activity.

$$\frac{E_{\text{pot}}}{V} = -C'_2(\beta)\zeta^2 + C'_3(\beta)\zeta^3 - \ldots \tag{8.22}$$
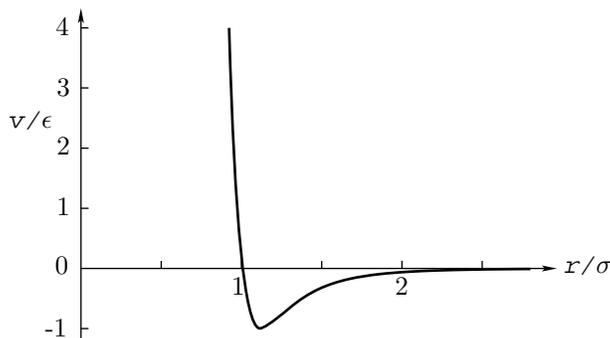
Fig. 8.1   The Lennard-Jones potential: $v(r)/\varepsilon$ is plotted as a function of r/σ. It is clear that the potential $v(r)$ is zero at the point $r = \sigma$ and has a minimum value of $-\varepsilon$.

For a low-density gas we can keep only the first term and also use the first term in Eq. (8.17) to replace ζ by n. When that is done, we obtain the following approximation for the average potential energy per particle.

$$\frac{E_{\text{pot}}}{N} \approx -C'_2(\beta)n \tag{8.23}$$

Using Eq. (8.15), which gives $C_2(\beta)$ as a one-dimensional integral involving the interaction potential, this can be written as

$$\frac{E_{\text{pot}}}{N} \approx 2\pi n \int_0^\infty v(r)e^{-\beta v(r)}r^2 dr \tag{8.24}$$

In order to proceed further, we must know the interaction potential $v(r)$. The interaction potentials of real atoms cannot be expressed exactly in any simple algebraic form. However, a simple function containing two parameters that gives a reasonably good fit to the interaction potentials of many common substances is the *Lennard-Jones potential.*

$$v(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{8.25}$$

The parameters ε and σ, which must be chosen separately for each gas, have simple physical interpretations. ε is the depth of the potential at its lowest point. σ is the distance at which the potential is zero. As can be seen from Fig. 8.1, the distance σ is a reasonable definition of the diameter of the atom. Table 8.1 gives Lennard-Jones parameters and the ratio of the potential energy to the kinetic energy for four noble gases at standard temperature and pressure. One can see that, although the average value of the potential energy is much smaller that the average of the kinetic energy, it is by no means undetectably small.

8.5   THE VIRIAL EXPANSION
In order to compare theory with experiment, one would like to eliminate the affinity (or the activity) and write the pressure as a function of the temperature and the density of the gas. The cluster expansions for p

	$\sigma(\AA)$	$\varepsilon(K)$	$\frac{E(\text{pot})}{E(\text{kin})}I$
Ne	2.8	35	$-.005$
A	3.4	120	$-.023$
Kr	3.6	180	$-.36$
Xe	4.1	225	$-.063$

TABLE 8.1 Lennard-Jones parameters for selected atoms

and n allow us to write the pressure as an expansion in powers of the density. That expansion is called the *virial expansion*, and the coefficients in it are known as the *virial coefficients*. It is of the form

$$\frac{p}{kT} = n + B_2(T)n^2 + B_3(T)n^3 + \dots \tag{8.26}$$

It is fairly easy to use Eqs. (8.16), (8.17), and (8.26) to write the first few virial coefficients in terms of the cluster integrals. Working out higher ones becomes progressively more complicated. In Problem 8.1 the reader is asked to show that

$$B_2 = -C_2 \qquad \text{and} \qquad B_3 = -2C_3 + 4C_2^2 \tag{8.27}$$

Istead of going any further in the formal analysis, we will look at the effects, on the equation of state of a very simple two-particle interaction for which B_2 can be calculated exactly.

8.6   THE HARD-CORE PLUS STEP POTENTIAL

Realistic interactions between noble gas atoms are strongly repulsive at short distances but mildly attractive at larger distances. The interaction potential shown in Fig. 8.1 is typical. The simplest potential function with those characteristics is the combination of a hard-core potential plus an attractive step potential. It is defined here and illustrated in Fig. 8.2.

$$v(r) = \begin{cases} +\infty, & 0 < r < a \\ -V_o, & a < r < b \\ 0, & b < r < \infty \end{cases} \tag{8.28}$$

For this potential the second virial coefficient can be computed exactly.

$$\begin{aligned} B_2(T) &= -2\pi \int_o^\infty (e^{-v(r)/kT} - 1)r^2 dr \\ &= -2\pi \left(-\int_o^a r^2 dr + \int_a^b (e^{V_o/kT} - 1)r^2 dr \right) \\ &= \tfrac{2}{3}\pi a^3 - \tfrac{2}{3}\pi(e^{V_o/kT} - 1)(b^3 - a^3) \end{aligned} \tag{8.29}$$

The behavior of B_2 as a function of T in this very simple model is typical of what is found for more realistic interction potentials. At low temperatures the second term, which is negative, becomes much larer that the first term, which is positive. Therefore, at low T the second virial coefficient is negative. This indicates that the pressure at low temperature is less that it would be for an ideal gas.
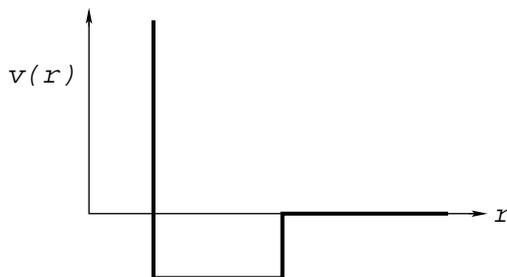
Fig. 8.2   The simple potential used in the calculation of Section 8.6

When the particles are moving more slowly, the weak but long-range attractive force pulls the particles together, reducing the pressure on the container walls. At high temperature, when kT is much larger that V_o, the particles have such large kinetic energies that the weak attractive interaction is negligible, and the only feature of the interparticle interaction that is significant is the hard core. The coefficient approaches a positive constant equal to one-half of the volume of a hard-core particle of radius A. Thus the gas behaves like a gas with a simple hard-core interaction, which has a pressure that is larger than that of an ideal gas at the same temperature and density. Figure 8.3 shows the equation of state for a gas of these model particles. The reader should keep in mind that this thwo-term virial equation of state is only velid when the gas density is much less than the density of a liquid of the same substance.
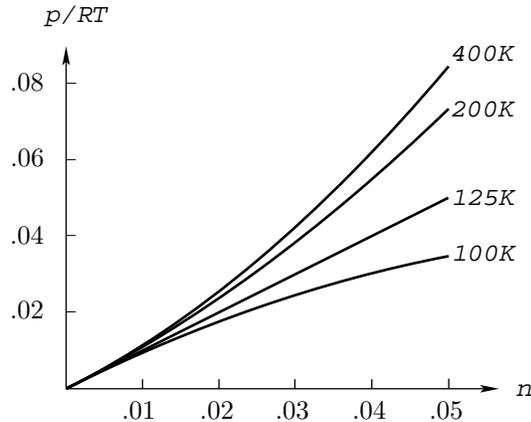
Fig. 8.3   A graph of p/RT (in units of moles/cm^3) as a function of the density for a gas satisfying a two-term virial equation of state with $B_2(T)$ given by Eq. (8.29). The constants a, b, and V_o, have been chosen to approximately match the second virial coefficient of neon. For neon, $B_2(T)$ is negative for $T < 125\,\mathrm{K}$ and positive for $T > 125\,\mathrm{K}$. Since $B_2(T) = 0$ at $T = 125\,\mathrm{K}$, the curve for that temperature is identical with the ideal gas equation, $p = nRT$. For positive B_2, the pressure increases, with increasing density, faster than that of an ideal gas. For negative B_2, it increases more slowly. For negative B_2 the pressure would eventually become negative, but the two-term virial equation of state is not velid in that range of density.

8.7   THE MEAN-FIELD APPROXIMATION

The number and complexity of the terms appearing in the cluster expansion increase very rapidly with the order of the expansion. For that reason, the method is restricted to densities at which the first few terms give an adequate approximation to the entire series, and therefore it cannot be used to analyze phase transitions. In fact, it can be proved that neither the cluster expansion nor the virial expansion is a convergent expansion at any phase transition point. In contrast, the mean-field approximation, to be presented in this section, can be used in the presence of phase transitions. However, it is an inherently approximate method. There are no higher-order "corrections" that can be invoked if the basic approximation is not accurate enough. The cluster expansion and the virial expansion are both precisely defined approximation techniques. Once the interaction potential is known, there can be no ambiguity about what are the coefficients in an expansion of the equations of state, either as a power series in the activity or as a power series in the particle density. In contrast, the "mean-field approximation" is a phrase that describes any method in which, at some crucial step in computing the partition function, statistical correlations among the particles are ignored. For a single system, there may be more than one detailed implementation of the mean-field approximation that make somewhat different predictions.

As mentioned previously, the great advantage of the mean-field approximation is that it provides a way of analyzing phase transitions in systems with strong interactions. For reasons that we will not discuss, the mean-field approximation tends to become more accurate as the dimensionality of the system increases. For one-dimensional systems it is often qualitatively wrong, predicting phase transitions when an exact calculation shows that they do not occur. In two dimensions the method is usually qualitatively correct,

predicting the phase transition at roughly the right place, but it is seldom quantitatively accurate. In three dimensions the quantitative accuracy of mean-field calculations usually improves, and the qualitative predictions are more reliable.

To illustrate the mean-field approximation, we will consider models that exhibit two different types of phase transitions. Each case will be done independently, so that the reader may skip either one without losing continuity.

8.8   NEMATIC LIQUID CRYSTALS

Nematic liquid crystals are solutions of long, rigid or partially rigid molecules that, in certain ranges of density and temperature, develop an *orientational ordering,* in which all the molecules in the large region in space tend to point in the same direction. That is not to say that they are all precisely parallel; they are not. In the *nematic phase,* the statistical distribution of their orientations is peaked in some direction, called the *director.* At lower densities or higher temperatures the same system exists in an *isotropic phase,* in which equal numbers of molecules are oriented in all directions. There are also other, more complicated types of liquid crystal phases, called *smectic* and *cholesteric* liquid crystals, that we will not consider. Figure 8.4 illustrates the two phases we want to study. The mnethod that we are going to use to analyze the phase transition can be applied to realistic models of specific liquid crystals. However, when considering realistic liquid crystals, whaich are always composed of large complex organic molecules, the mathematical details bbecome very complicated and tedious. Therefore, we will consider only an extremely simplified model, which is intended to capture the essential mechanism of the nematic phase transition, but which is obviously not intended to be a picture of any real liquid crystal.

The model is a two-dimensional gas of straight, infinitely thin, rodlike molecules, each of length ℓ. Instead of allowing the molecules to point in every possible direction, the molecules are constrained to point eigher horizontally or vertically. The horizontally and vertically pointing molecules will be treated as two different kinds of particles, called, respectively, x particles and y particles. The particles will not interact, except for the absolute constraint that no two particles can overlap. That is, the particles cannot touch one another. Since the particles are infinitely thin, the probability of two x particles or two y particles touching is zero, so that the constraint would have no effect on a gas composed purely of x particles or purely of y particles. As shown in Fig. 8.5, if a y particle has a given location, then no x particle can be located within an $\ell \times \ell$ square around its center of mass. (The "location" of a particle means the location of its center of mass.)

isotropic   nematic
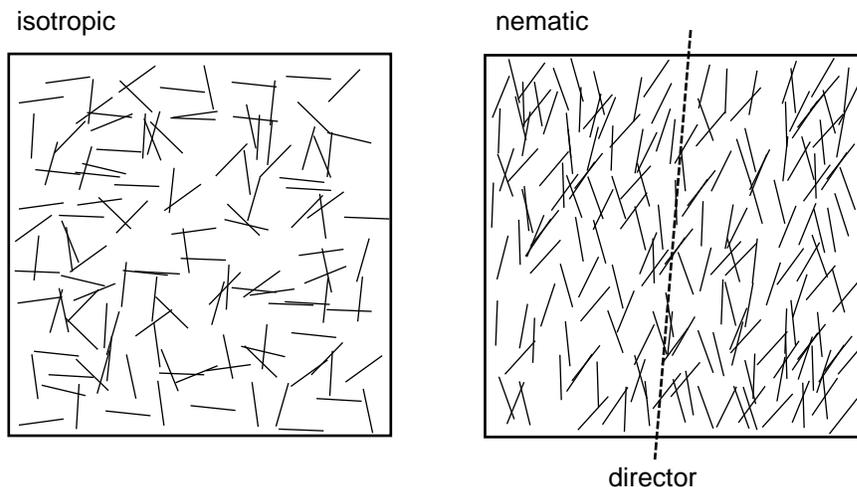
director

Fig. 8.4   The nematic phase transition. Above the phase transition temperaturee, the rodlike molecules are oriented in all directions with equal probabilities. Below the transition themperature, an orientation parallel to the director is favored over one perpendicular to it.

Using a canonical ensemble, we will consider a system composed of N_x x particles and N_y y particles, within a two-dimensional area A, where, of course, $A >> \ell^2$. To avoid cumbersome notation, the collection

of all the coordinates of the x particles will be called C_x and the set of all the coordinates of the y particles will be called C_y.

$$C_x \equiv (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_x}) \qquad \text{and} \qquad C_y \equiv (b r_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_y}) \tag{8.30}$$

The cononical partition function should involve an integral over all allowed configurations of the particles. We can extend the integral to an integral over all possible configurations of the particles, ignoring the no-overlap constraints, if we include a factor in the integrand that is zero whenever the configuration violates any constraint. We define such a constraint function by

$$F(C_x, C_y) = \begin{cases} 0, & \text{if any } x \text{ particle overlaps any } y \text{ particle} \\ 1, & \text{otherwise} \end{cases} \tag{8.31}$$

If λ is the thermal de Broglie wavelength, then

$$Z(N_x, N_y, \beta, A) = \frac{1}{N_x! N_y! \lambda^{2(N_x + N_y)}} \int_A F(C_x, C_y) dC_x dC_y \tag{8.32}$$

where $dC_x \equiv d^2\mathbf{r}_1 d^2\mathbf{r}_2 \ldots d^2\mathbf{r}_{N_x}$, with a similar definition for dC_y.
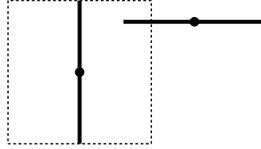
Fig. 8.5   The center of mass of any x particle is constrained to lie outside the square region shown in order to prevent an intersection of the two particles.

The canonical potential is given by

$$\phi(N_x, N_y, \beta, A) = \log Z \tag{8.33}$$

Because there are two kinds of particles, there will be two affinities, which we will call α_x and α_y. The affinity for x particles can be written as (we do not indicate β and A explicitely)

$$\alpha_x = \phi(N_x + 1, N_y) - \phi(N_x, N_y) = \log\left(\frac{Z(N_x + 1, N_y)}{Z(N_x, N_y)}\right) \tag{8.34}$$

We will see that, if we can calculate $\alpha(N_x, N_y)$, then we will be able to predict the exact location of the phase transition and the composition of the two phases. Therefore, we need to analyze carefully the ratio of $Z(N_x + 1, N_y)$ to $Z(N_x, N_y)$. According to Eq. (8.32), this is given by [we will call the position of the $(N_x + 1)$st particle, simply $\mathbf{r}$]

$$\frac{Z(N_x + 1, N_y)}{Z(N_x, N_y)} = \frac{\int F(\mathbf{r}, C_y) F(C_x, C_y) d^2\mathbf{r} dC_x dC_y}{(N_x + 1)\lambda^2 \int F(C_x, C_y) dC_x dC_y} \tag{8.35}$$

The factor $F(\mathbf{r}, C_y)$ is zero whenever the (N_x+1)st x particle overlaps any y particle. For a given configuration of all the y particles (that is, for a given C_y), we define an observable $a(C_y)$ that is equal to the area that would be available to an x particle within the system (Fig. 8.6). This can be expressed as

$$a(C_y) = \int_A F(\mathbf{r}, C_y) d^2\mathbf{r} \tag{8.36}$$
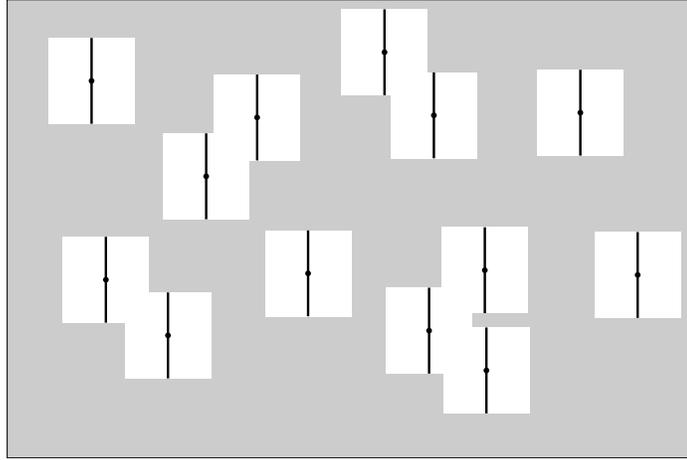
Fig. 8.6   For a given distribution of the y particles, the variable $a(C + y)$ is defined as the area available to an x particle—that is, the area outside all the squares.

Then the ratio of integrals in Eq. (8.35) can be written as

$$\frac{\int F(C_x, C_y)a(C_y)dC_xdC_y}{\int F(C_x, C_y)dC_xdC_y} \tag{8.37}$$

This can be interpreted as the expectation value of the observable $a(C_y)$ in an ensemble composed of all the allowed configurations of the system having N_x x particles and N_y y particles; that is, in an ensemble with a probability density $P(C_x, C_y)$ that is proportional to $F(C_x, C_y)$. We will write the expectation value of any quantity in such an ensemble as $\langle \ldots \rangle_F$. Thus

$$R = \langle a(C_y) \rangle_F \tag{8.38}$$

Up to this point, everything has been exact. Now we will make the crucial appoximation. We replace the value of $\langle a(C_y) \rangle_F$ by the expectation value of $a(C_y)$ in an ensemble where the N_y y particles are distributed at random within the area Z. We will call this $\langle a(C_y) \rangle_{\mathrm{random}}$. For any configuration of the y particles, $a(C_y)/A$ is equal to the probability that, if an x particle is placed at random within A, it well miss all the y particles. We will now calculate that probability for a random distribution of y particles. The probability that an x particle will miss a single y particle is

$$p = 1 - \frac{\ell^2}{A} \tag{8.39}$$

In the random distribution, the y particles are statistically uncorrelated, and therefore the probability that an x particle will miss all of them is just p^{N_y}. Therefore

$$\frac{\langle a(C_y) \rangle_{\mathrm{random}}}{A} = \left(1 - \frac{\ell^2}{A}\right)^{N_y} = \left(1 - \frac{\ell^2 n_y}{N_y}\right)^{N_y} = e^{-\ell^2 n_y} \tag{8.40}$$

where $n_y = N_y/A$ is the density of y particles and we have used the definition of the exponential function $e^x \equiv \lim_{N \to \infty}(1 + x/N)^N$. This gives for the ratio of the partition functions

$$\frac{Z(N_x + 1, N_y)}{Z(N_x, N_y)} = \frac{Ae^{1\ell^2 n_y}}{(N_x + 1)\lambda^2} \tag{8.41}$$

and, for the x particle affinity,

$$\alpha_x = \phi(N_x + 1, N_y) - \phi(N_x, N_y) = -\log n_x - \log \lambda^2 - \ell^2 n_y \tag{8.42}$$

By the obvious symmetry between x partiicles and y particles, we can write an equivalent formula for the y particle affinity.

$$\alpha_y = -\log n_y - \log \lambda^2 - \ell^2 n_x \tag{8.43}$$

The x particles and y particles actually represent two possible orientations of a single type of molecule. Therefore, N_x and N_y should not be considered as separately conserved variables; only the sum, $N_x + N_y$, is fixed. The cange of an x particle to a y particle and vice versa is best treated as a simple chemical reaction. $x \leftrightarrow y$. The condition of equilibrium in the presence of such a chemical reaction is that $\alpha_x = \alpha_y$. Let n be the conserved total density. Then, if we assume that, at equilibrium,

$$n_x = \tfrac{1}{2}n(1+\gamma) \tag{8.44}$$

where γ is some parameter to be determined, then

$$n_y = n - n_x = \tfrac{1}{2}n(1-\gamma) \tag{8.45}$$

The condition that $\alpha_x = \alpha_y$ gives

$$\begin{aligned}
&-\log\left(\frac{n}{2}(1+\gamma)\right) - \log\lambda^2 - \tfrac{1}{2}\ell^2 n(1-\gamma) \\
&= -\log\left(\frac{n}{2}(1-\gamma)\right) - \log\lambda^2 - \tfrac{1}{2}\ell^2 n(1+\gamma)
\end{aligned} \tag{8.46}$$

Cancelling identical terms from both sides, we get

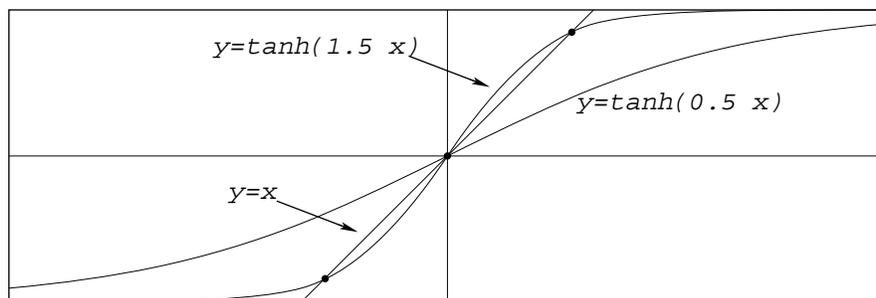$$-\log(1+\gamma) + cf12\ell^2 n\gamma = -\log(1-\gamma) - \tfrac{1}{2}\ell^2 n\gamma \tag{8.47}$$

which can be rearranged as

$$\log(1+\gamma) - \log(1-\gamma) = \ell^2 n\gamma \tag{8.48}$$

Using the identity, $\log(1+\gamma) - \log(1-\gamma) = 2\tanh^{-1}\gamma$, this can be written as

$$\gamma = \tanh(\ell^2 n\gamma/2) \tag{8.49}$$

Fig. 8.7   In order to solve the equation $x = \tanh(ax)$, we plot the curves $y = x$ and $y = \tanh(ax)$. The value of x at their intersection is a solution to the equation. For $a < 1$ the only intersection occurs at $x = 0$. For $a > 1$ there are also two nonzero solutions.

This equation always has the trivial solution $\gamma = 0$, which describes a state with equal densities of x particles and y particles. When $\ell^2 n/2 > 1$ it also has two nontrivial solutions, describing states in which the symmetry between x and y particles is spontaneously broken. In one of these two states, which we will call the x phase, there is an excess of x particles; in the other there is an excess of y particles. In Problem 8.8 the reader is asked to show that, whenever these nontrivial solutions exist, the trivial solution is unstable and therefore does not really represent an equilibrium state.

If the density is gradually increased, the system will remain in the isotropic state, with $n_x = n_y = n/2$, until the density reaches the critical value of $n = 2/\ell^2$. If it is increased beyond that value, the isotropic state becomes unstable and the system will spontaneously transform into one of the two nematic liquid crystal phases, either the x phase, with an excess of x-oriented particles, or the y phase, with an excess of y-oriented particles. Which of these broken symmetry states will appear cannot be calculated within the model. In a real system, it would usually depend on small, neglected terms, such as unsymmetric interactions with the wall of the container. If a real system is kept very carefully symmetric, and the system is repeatedly cycled back and forth through the critical density, it will sometimes go into the x phase and sometimes go into the y phase, in a wholly unpredictable way that depends on the detailed microscopic state of the system at the time of the stransition. As can be seen in Fig. 8.8, the value of n_x varies continuously through the nematic phase transition, but the slope of the function $n_x(n)$ is discontinuous. This indicates that the nematic phase transition is a second-order phase transition.
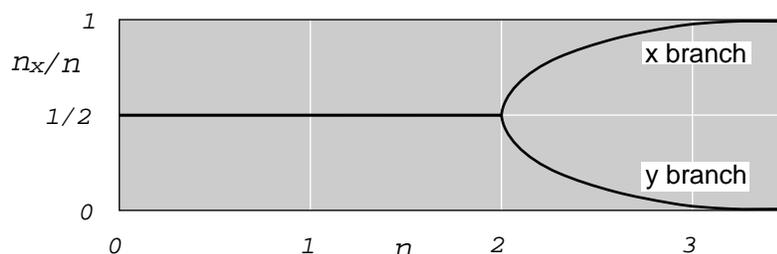
Fig. 8.8   The density of x particles as a function of the total density for the case $\lambda = 1$. If the density is increased beyond the critical density, the macroscopic state of the system shifts, in an unpredictable way, to one of the two *broken symmetry* states.

8.9   ADSORPTION WITH INTERACTIONS The particles in an adsorbed surface layer are generally much closer to one another than those in the gas with which the adsorbed particles are in equilibrium. Because of their proximity, interactions between neighboring adsorbed particles are often significant. We will see that such interactions between neighboring partices can drastically change the adsorption characteristics by causing a phase transition in the adsorbed layer.

The model that will be used is similar to the one considered in Section 7.2. There is an $L \times L$ square lattice of adsorption sites, each of which can accommodate a single particle. For simplicity, it will be assumed that there is only a single adsorption state, of energy ε, at each site. The new element that will be introduced here is the assumption that two particles at neighboring sites interact with a potential energy v. If v is negative, then the interaction describes a short-range attraction between the adsorbed particles, in that it would require an amount of energy $|v|$ to separate a pair of neighboring particles. A positive value of v corresponds to a repulsive force between particles. This system is often referred to as a two-dimensional *lattice gas*. The lattice sites can be described bya two-dimensional vector with components $(x, y) = (Xa, Ya)$, where a is the lattice spacing and X and Y are integers in the range, $1, 2, \ldots, L$. Assuming that L is very large, we will always ignore the special case of particles at the very edge sites that have only 3, rather than 4, neighboring sites. It will be convenient to work in a peculiar system of units in which the lattice spacing a is our unit of length. Then the total area of the surface A is equal to L^2, the number of adsorption sites.

In analyzing a macroscopic system, one is free to use whatever ensemble is most convenient. A change of ensemble cannot lead to a change in the thermodynamic relations for the system, but only to the same thermodynamic relations, expressed in a different representation. Although the adsorption calculation was done in Chapter 7 using the grand canonical ensemble, it is more convenient to do this calculation in the canonical ensemble.

The system consists of N indistinguishable particles, to be distributed among A sites. A configuration is defined by choosing N occupied sites from the A available sites. Thus the total number of configurations is

$$\binom{A}{N} = \frac{A!}{N!(A-N)!} \tag{8.50}$$

The energy of interaction between the particles and the adsorption sites is simply $N\varepsilon$. The energy of

interaction between the particles themselves depends on the detailed configuration of the particles. In the mean-field approximation we calculate the interparticle interaction energy by assuming that the particles are randomly distributed over the sites. That is, instead of taking the proper canonical distribution of configurations, we take a uniform distribution, in which all possible configurations are equally likely, in spite of the fact that they do not all have the same energy.

At this point we could make a false argument that seems to prove that, in the thermodynamic limit, this mean-field approximation is perfectly accurate. It is useful to do so, because the refutation of the argument will point out certain properties of the canonical ensemble that are important in understanding the Monte Carlo method, which is the next topic in this chapter. The argument goes as follows: The interaction potential is a macroscopic observable. Therefore, in the limit of large N and A, almost all the configurations give the same value of the observable. Since the observable has the same value for almost all states, we will make a negligible error in using an equal probability ensemble of configurations rather than a canonical ensemble in calculating the expectation value of the interaction energy. What is wrong with this argument? Recall that it was shown that the equal probability ensemble would give the same value of $\langle A \rangle$ as any other probability function, *provided that the other probability function did not, in the thermodynamic limit, concentrate all the probability on the tiny fraction of exceptional states.* Now let us see that this is exactly what the canonical ensemble does. Suppose we consider the case of particles with attractive interactions. Then the low-energy configurations are those in which the particles are huddled together so that they can interact. The high-energy configurations are those in which the particles are spread out. As N becomes large, the difference in energy between an average energy state and a typical low-energy state, call it ΔE, is proportional to N. But the ratio of probabilities in the canonical ensemble is then

$$\frac{P(\text{low})}{P(\text{ave.})} = e^{\beta \Delta E} \sim e^{N} \tag{8.51}$$

Thus, in the thermodynamic limit, the canonical ensemble probability becomes extremely concentrated on a very small fraction of the possible states of the system. It is this characteristic that invalidates the argument given, based on the law of large numbers.

The expectation value of the interaction energy for a collection of N particles, randomly distributed over A lattice sites, can be calculated as follows. We first concentrate our attention on any one of the particles. That particle has 4 nearest-neighbor sites. The probability that any one of those sites is filled is equal to N/A. Therefore, the average interaction energy of that particle is $4vN/A$. Adding up this number for each of the N particles actually double counts the interaction potential by counting the interaction between any pair of particles twice, once from each end. Therefore, the mean-field approximation for the total energy is

$$E = \varepsilon N + 2vN^2/A \tag{8.52}$$