Chapter 5
Simple Models of Adsorption

As an illustration of canonical and grand canonical ensembles, we discuss a few variants of a simple model of adsorption. Despite their simplicity, these models provide important insights into diverse phenomena ranging from oxygen binding to hemoglobin to vapor–liquid phase coexistence.

5.1 Exact Solutions

Let us first look at simple exactly solvable model. It forms a basis for introducing approximations that become necessary when we deal with more complex model systems.

5.1.1 Single Site

Consider a single adsorption site exposed to a gas phase. We assume that the site can accommodate at most a single gas particle. The quantity of our primary interest is the average number $\langle N\rangle$ of gas particles adsorbed at the site. Before proceeding, we note that this quantity is actually the probability p_1 that the site is occupied by a particle since

$$\langle N\rangle = 0\times(1-p_1)+1\times p_1 = p_1\ . \tag{5.1}$$

If we define our system as in Fig. 5.1, it is an open system, for which the relevant ensemble is the grand canonical ensemble with the surrounding gas phase setting the temperature T and the chemical potential μ for the system.

We recall from Exercise 4.10 that

$$\langle N\rangle = \left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_{\beta,V}\ . \tag{5.2}$$

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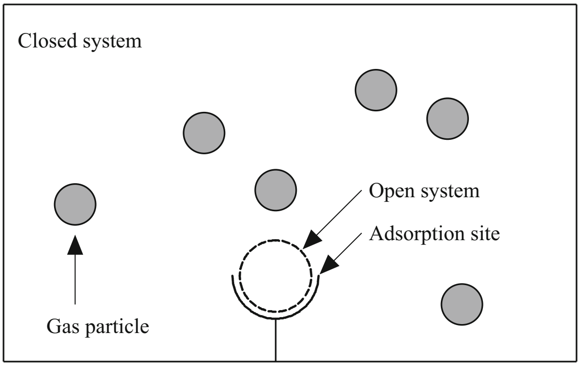


Fig. 5.1 A single adsorption site model.

So, to figure out $\langle N \rangle$, our first task is to compute Ξ, for which we need $\overline{\Omega}(E,N)$.

To simplify our analysis, we suppose that the system can take only two distinct states: the unoccupied state for which $E = 0$ and the occupied state for which $E = -\varepsilon < 0$. We shall refer to ε as the **binding energy** and take a closer look at it in the next subsection. In a meanwhile, the following three cases need to be considered:

a. $N = 0$. In this case, the energy E of the system can only be zero. Thus, there is no state if $E < 0$ or $E > 0$, but there is a single state if $E = 0$, leading to the picture in Fig. 5.2a. Thus,

$$\mathscr{W}(E,0) = \theta(E) \tag{5.3}$$

and hence

$$\overline{\Omega}(E,0) = \frac{\partial \mathscr{W}(E,0)}{\partial E} = \delta(E)\,, \tag{5.4}$$

which is nothing but (4.135).

b. $N = 1$. Now, the energy can only be $-\varepsilon$ and a consideration similar to case a leads to the picture in Fig. 5.2b, from which we obtain

$$\mathscr{W}(E,1) = \theta(E+\varepsilon) \tag{5.5}$$

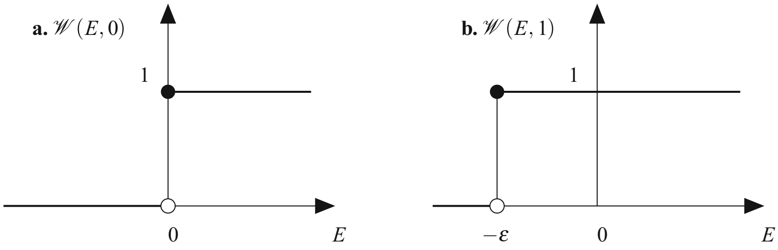


Fig. 5.2 $\mathscr{W}(E,N)$ for $N = 0$ and $N = 1$.

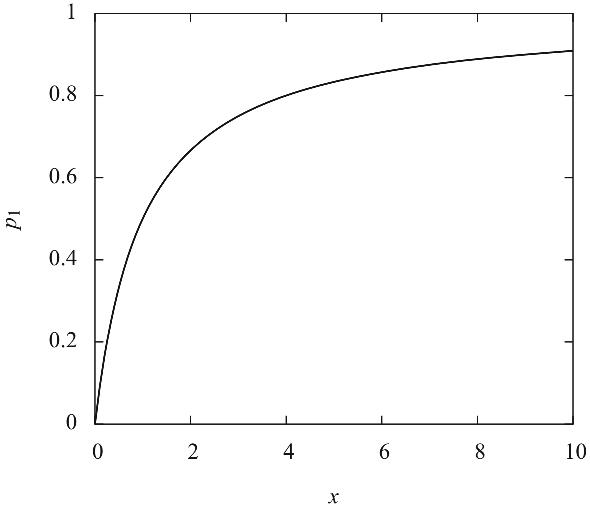


Fig. 5.3 Dependence of p_1 on $x := e^{\beta\mu}e^{\beta\varepsilon}$.

and

$$\overline{\Omega}(E,1) = \frac{\partial \mathscr{W}(E,1)}{\partial E} = \delta(E+\varepsilon)\,. \tag{5.6}$$

c. $N \geq 2$. In this case, $\mathscr{W}(E,N) \equiv 0$ and hence $\overline{\Omega}(E,N) \equiv 0$.

Using these results in (4.128), we find

$$\begin{aligned}\Xi &= e^{\beta\mu 0}\int \delta(E)e^{-\beta E}\mathrm{d}E + e^{\beta\mu 1}\int \delta(E+\varepsilon)e^{-\beta E}\mathrm{d}E + \sum_{N=2}^{\infty} e^{\beta\mu N}\int 0e^{-\beta E}\mathrm{d}E \\ &= 1 + e^{\beta\mu}e^{\beta\varepsilon} = 1 + x\,,\end{aligned} \tag{5.7}$$

where we defined $x := e^{\beta(\mu+\varepsilon)}$. Using (5.2), we arrive at

$$p_1 = \langle N \rangle = \frac{\mathrm{d}\ln\Xi}{\mathrm{d}x}\left(\frac{\partial x}{\partial \beta\mu}\right)_{\beta} = \frac{x}{1+x}\,. \tag{5.8}$$

As shown in Fig. 5.3, $\langle N \rangle$ or the probability p_1 that the site is occupied increases with increasing x and approaches unity as x tends toward infinity. Note that the increase in x can be achieved by either decreasing $T = 1/k_B\beta$ or increasing μ.

5.1.2 †*Binding Energy*

In the previous subsection, we assumed that the adsorption site can be in either of the two states, empty or occupied. To the latter state, we assigned the binding energy ε. In reality, however, an adsorbed particle can still move around through a vibrational motion. Let us see how this aspect can be incorporated into our model.

This time, we take the entire box shown in Fig. 5.1 as our system. The system is closed and held at a given temperature T. So the relevant partition function to compute is Z. Let V_t denote the volume of the system. The volume of the open system will be indicated by v. We suppose that there are N_t noninteracting identical particles in the system and write

$$Z = \frac{1}{h^{3N_t} N_t!} \int e^{-\beta H(\boldsymbol{r}^{N_t}, \boldsymbol{p}^{N_t})} \mathrm{d}\boldsymbol{r}^{N_t} \mathrm{d}\boldsymbol{p}^{N_t} = \frac{1}{\Lambda^{3N_t} N_t!} \int e^{-\beta \psi(\boldsymbol{r}^{N_t})} \mathrm{d}\boldsymbol{r}^{N_t} , \tag{5.9}$$

where we carried out the integration with respect to $\boldsymbol{p}^{N_t}$, and denoted the potential energy due to the interaction between a particle and the adsorption site by ψ.

We consider the particle to be adsorbed to the site if its center is anywhere in v. The site is otherwise empty. We set ψ to zero if no particle occupies v. If the ith particle occupies the site and no other particle is in v at the same time, we write $\psi = \psi(\boldsymbol{r}_i)$ to allow for the dependence of ψ on the exact position of the adsorbed particle. As before, we do not allow for multiple particles to occupy the site simultaneously, so we set ψ to infinity in that case. Thus,

$$e^{-\beta \psi(\boldsymbol{r}^{N_t})} = \begin{cases} 1 & \text{if } v \text{ is empty,} \\ e^{-\beta \psi(\boldsymbol{r}_i)} & \text{if } v \text{ is occupied by the } i\text{th particle,} \\ 0 & \text{if } v \text{ is occupied by more than one particle.} \end{cases} \tag{5.10}$$

With this much preparations, we can rewrite the integral with respect to $\boldsymbol{r}^{N_t}$ as

$$\int e^{-\beta \psi(\boldsymbol{r}^{N_t})} \mathrm{d}\boldsymbol{r}^{N_t} = \int_{\boldsymbol{r}^{N_t} \in V_t - v} \mathrm{d}\boldsymbol{r}^{N_t} + \sum_{i=1}^{N_t} \int_{\boldsymbol{r}_i \in v, \boldsymbol{r}^{N_t - 1} \in V_t - v} e^{-\beta \psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}^{N_t} , \tag{5.11}$$

where the subscripts to $\int$ denote the conditions imposed on the coordinates of particles. The first integral is taken under the condition that all the particles are outside v, resulting in $(V_t - v)^{N_t}$. The integrand in the second term depends only on $\boldsymbol{r}_i$. Thus,

$$\int_{\boldsymbol{r}_i \in v, \boldsymbol{r}^{N_t - 1} \in V_t - v} e^{-\beta \psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}^{N_t} = (V_t - v)^{N_t - 1} \int_{\boldsymbol{r}_i \in v} e^{-\beta \psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}_i = (V_t - v)^{N_t - 1} A_i , \tag{5.12}$$

where we defined

$$A_i := \int_{\boldsymbol{r}_i \in v} e^{-\beta \psi(\boldsymbol{r}_i)} \mathrm{d}\boldsymbol{r}_i . \tag{5.13}$$

However, since $\psi(\boldsymbol{r})$ is common to all particles, A_i is independent of i. Stated differently, $\boldsymbol{r}_i$ is simply an integration variable in (5.13) and can be replaced by any $\boldsymbol{r}_{j \neq i}$ without affecting the value of A_i. Thus, dropping the subscript i, we obtain

$$Z = \frac{1}{\Lambda^{3N_t} N_t!} \left[(V_t - v)^{N_t} + N_t A (V_t - v)^{N_t - 1} \right] = \frac{(V_t - v)^{N_t}}{\Lambda^{3N_t} N_t!} \left(1 + \frac{N_t}{V_t - v} A \right) . \tag{5.14}$$

In this expression, the term proportional to A, that is,

$$Z_1 := \frac{(V_t - v)^{N_t}}{\Lambda^{3N_t} N_t!} \frac{N_t}{V_t - v} A \tag{5.15}$$

comes from microstates with the single occupancy of the site. Therefore, the probability p_1 that the site is occupied is given by

$$p_1 = \frac{Z_1}{Z} = \frac{\frac{N_t}{V_t - v} A}{1 + \frac{N_t}{V_t - v} A} \,. \tag{5.16}$$

Ignoring v in comparison to V_t and using the relation

$$\frac{N_t}{V_t} = \frac{e^{\beta\mu}}{\Lambda^3} \tag{5.17}$$

which follows from (4.139) and (4.140) for an ideal gas, we rewrite the above expression for p_1 as

$$p_1 = \frac{e^{\beta\mu} A/\Lambda^3}{1 + e^{\beta\mu} A/\Lambda^3} \,. \tag{5.18}$$

Comparing this expression with (5.8), we find

$$e^{\beta\varepsilon} = \frac{A}{\Lambda^3} \,. \tag{5.19}$$

Thus,

$$-\varepsilon = -k_B T \ln\left[\frac{1}{\Lambda^3} \int_{\boldsymbol{r} \in v} e^{-\beta\psi(\boldsymbol{r})} \mathrm{d}\boldsymbol{r}\right] \,, \tag{5.20}$$

identifying $-\varepsilon$ as the Helmholtz *free energy* of a particle subject to the external field $\psi(\boldsymbol{r})$ generated by the adsorption site.

By incorporating more realism into our model, we did not materially change the behavior of p_1. Instead, we obtained an explicit expression for the binding energy. In principle, this allows us to *predict* $-\varepsilon$ from a detailed molecular level model of particles and the adsorption site.

Exercise 5.1. Analyze the current model using a grand canonical ensemble applied to the open system v. ///

5.1.3 Multiple Independent Sites

Let us consider a collection of M independent adsorption sites instead of just one. By the sites being independent, we mean that whether a given site is occupied or not has no impact on any other site being occupied or not. In this case, we expect that the probability p_1 that a given site is occupied still is given by $x/(1+x)$. Now that there are M such sites, we should have $\langle N \rangle = Mx/(1+x)$. Let us try to reach this conclusion through an explicit computation. Along the way, we are reminded of the notion of the binomial coefficients, which we use later.

As in Sect. 5.1.1, we take a small volume around each of the adsorption sites. The collection of M such volumes forms an open system, which can be treated using a grand canonical ensemble. Our starting point still is (4.128), in which we have to give an expression for $\overline{\Omega}(E,N)$. We need to consider the following cases:

a. $N = 0$. In this case E can only take a single value, zero, and hence

$$\mathscr{W}(E,0) = \theta(E) \quad \text{and} \quad \overline{\Omega}(E,0) = \delta(E)\,. \tag{5.21}$$

b. $N = 1$. In this case, E can only be $-\varepsilon$. But there are M different choices for the site to occupy. Thus,

$$\mathscr{W}(E,1) = M\theta(E+\varepsilon) \quad \text{and} \quad \overline{\Omega}(E,1) = M\delta(E+\varepsilon)\,. \tag{5.22}$$

c. $N = 2$. Now, E can only be -2ε. The number of different ways of choosing two sites to occupy from the M sites is given by $M(M-1)/2$. To see this, note that there are M different ways of choosing the first site to occupy. For each such choice, there are $M-1$ different choices for the second site to occupy. This gives you $M(M-1)$ options. But, all what matters is which pair of sites is being occupied in the end and not the order in which the two sites were occupied. Reversing the order gives you exactly the same state. So, we need to divide $M(M-1)$ by 2. Therefore,

$$\mathscr{W}(E,2) = \frac{M(M-1)}{2}\theta(E+2\varepsilon) \quad \text{and} \quad \overline{\Omega}(E,1) = \frac{M(M-1)}{2}\delta(E+2\varepsilon)\,. \tag{5.23}$$

d. Generalizing the above considerations to $N(\leq M)$ occupied sites, we find

$$\overline{\Omega}(E,N) = \frac{M!}{N!(M-N)!}\delta(E+N\varepsilon) \quad (N \leq M)\,. \tag{5.24}$$

To check the validity of this formula, set $N = 0, 1$, and 2. (Note that $0! = 1$).

e. Needless to say, $\overline{\Omega}(E,N) \equiv 0$ if $N > M$.

Before we continue, we recall the standard notation for the **binomial coefficient**:

$$\binom{M}{N} := \frac{M!}{N!(M-N)!}\,, \tag{5.25}$$

which gives the number of distinct ways of selecting N objects out of M objects without any regard to the particular order in which the selection was made.

Using (5.24) in (4.128), we find

$$\Xi = \sum_{N=0}^{M} e^{\beta\mu N}\binom{M}{N}\int\delta(E+N\varepsilon)e^{-\beta E}\mathrm{d}E = \sum_{N=0}^{M}\binom{M}{N}e^{\beta(\mu+\varepsilon)N} = \sum_{N=0}^{M}\binom{M}{N}x^N\,, \tag{5.26}$$

where $x := e^{\beta(\mu+\varepsilon)}$ as before.

To compute the summation explicitly, we recall (B.30) for the binomial expansion. Then, from (5.26),

$$\Xi = \sum_{N=0}^{M} \binom{M}{N} x^N 1^{M-N} = (1+x)^M \, . \tag{5.27}$$

Using (5.2), we obtain the average number $\langle N \rangle$ of particles in the entire system as

$$\langle N \rangle = \left(\frac{\partial \ln \Xi}{\partial \beta \mu} \right)_{\beta, V} = \frac{Mx}{1+x} , \tag{5.28}$$

in which $V := Mv$ is the volume of the system, that is, the collection of M adsorption sites each with the volume v. Thus,

$$p_1 := \frac{\langle N \rangle}{M} = \frac{x}{1+x} \, . \tag{5.29}$$

Exercise 5.2. Derive (5.29) using (5.9) as the starting point. Assume that $N_t \gg M$ meaning there are far more particles in the entire closed system than there are the adsorption sites. Note that we tacitly made this approximation in this subsection by using a grand canonical ensemble. Without this approximation, μ of the gas phase would depend on the number of adsorbed particles. ///

5.1.4 Four Sites with Interaction Among Particles

Consider an array of four adsorption sites placed at the four vertices of a regular tetrahedron as shown in Fig. 5.4. We assume that these sites are distinguishable

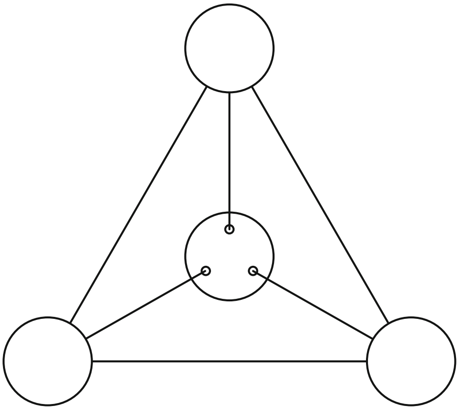


Fig. 5.4 Four adsorption sites on the vertices of a regular tetrahedron.

(That is to say, for example, the state in which only the lower left corner being occupied and the state in which only the middle site being occupied are to be considered as two distinct states.) and that each site can accommodate up to a single particle. The binding energy per site is ε, and the interaction energy between a pair of adjacent particles is $-w$. We immerse this array of adsorption sites in a gas of particles held at constant T and μ. Our goal again is to compute p_1.

We note that there are $2^4 = 16$ states the system can take, which are divided among the following cases:

a. $N = 0$ with energy $E = 0$. As before, we have

$$\overline{\Omega}(E,0) = \delta(E)\,. \tag{5.30}$$

b. $N = 1$, and hence $E = -\varepsilon$. Since there are four distinct states (reflecting the four choices we can make for the occupied site), we have

$$\overline{\Omega}(E,1) = 4\delta(E+\varepsilon)\,. \tag{5.31}$$

c. $N = 2$, in which case, $E = -2\varepsilon - w$ and there are $\binom{4}{2} = 6$ distinct states, leading to

$$\overline{\Omega}(E,2) = 6\delta(E+2\varepsilon+w)\,. \tag{5.32}$$

d. $N = 3$, for which

$$\overline{\Omega}(E,3) = 4\delta(E+3\varepsilon+3w)\,. \tag{5.33}$$

e. $N = 4$, for which

$$\overline{\Omega}(E,4) = \delta(E+4\varepsilon+6w)\,. \tag{5.34}$$

Note that the coefficients of the δ-functions add up to 16 as they should. As before, $\overline{\Omega}(E,N) \equiv 0$ for $N \geq 5$.

The grand canonical partition function follows from the above expressions for $\overline{\Omega}(E,N)$ and (4.128), and is given by

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} \int \overline{\Omega}(E,N) e^{-\beta E} \mathrm{d}E = 1 + 4x + 6x^2y + 4x^3y^3 + x^4y^6\,, \tag{5.35}$$

where $x := e^{\beta(\mu+\varepsilon)}$ and $y := e^{\beta w}$. Then,

$$p_1 = \frac{\langle N \rangle}{4} = \frac{1}{4}\left(\frac{\partial \ln \Xi}{\partial \beta\mu}\right)_{\beta,V} = \frac{x + 3x^2y + 3x^3y^3 + x^4y^6}{1 + 4x + 6x^2y + 4x^3y^3 + x^4y^6}\,. \tag{5.36}$$

When $\beta w = 0$, the sites behave independent of each other. Noting that $y = 1$ in this case, you can verify that this equation reduces to (5.29).

Figure 5.5 illustrates the dependence of p_1 on x for a few values of w. The plot for $\beta w = 0$ is identical to what was shown in Fig. 5.3. For larger values of w, p_1 is seen to change more rapidly over a much smaller range of x compared to the plot for $w = 0$. This is an example of the **cooperative phenomena**. The presence of

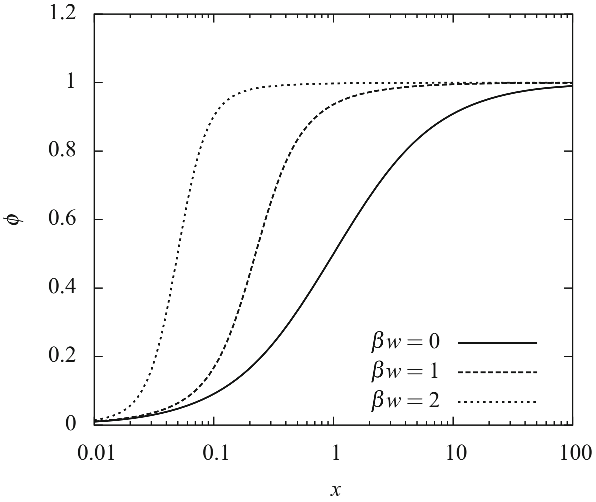


Fig. 5.5 Dependence of p_1 on $x := e^{\beta(\mu+\varepsilon)}$ for a few values of βw.

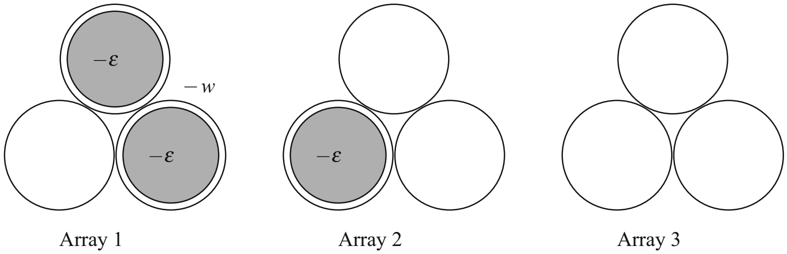


Fig. 5.6 Three triangular arrays of adsorption sites. The *filled circles* represent occupied sites, while the *open circles* are unoccupied. For the configuration shown, we have $E = -3\varepsilon - w$.

adsorbed particles enhance the probability of further adsorption of another, hence the word “cooperative.”

The four-site model we just studied is a classical model for hemoglobin. In this context, the cooperative behavior accounts for the sensitivity of a hemoglobin in regulating the O_2 adsorption/desorption in response to a small change in the partial pressure of O_2.

Exercise 5.3. Consider three triangular arrays, each carrying three adsorption sites as shown in Fig. 5.6. Each site can accommodate up to a single particle. The binding energy per site is ε, while the interaction between a pair of adjacent particles, both in the same array, is $-w$. There is no interaction among particles adsorbed on different arrays.

Now suppose that the arrays are placed in a closed system with only three identical particles and held at a constant temperature. While many distinct states are accessible to the system, we focus only on the following two situations:

a. All three particles are adsorbed to a single array.
b. Each array carries exactly one particle.

For what range of temperature is situation a more likely than situation b? For the sake of this problem, assume that the nine adsorption sites are all distinguishable. ///

5.2 Mean-Field Approximation

So far, we have evaluated the partition functions Ξ, Z, and the probability p_1 that a given site is occupied by carrying out the required computations exactly.

However, it is not hard to see that the computation becomes quickly unmanageable with the increasing number of adsorption sites. There will be too many distinct microstates to enumerate, which may or may not have the same energy. In such cases, we are forced to introduce some approximation. In this section, we will look at one very popular approximation scheme known as the **mean-field approximation**.

Note that the complication in carrying out the exact computation arises from the interaction among adsorbed particles. In fact, M independent site model we saw in Sect. 5.1.3 was no more complicated than a single site model of Sect. 5.1.1. But, if there is no interaction ($w = 0$), there is no cooperative behavior either and the model will not be very interesting to study in the first place.

The basic idea of a mean-field approximation is to treat each site as if it is independent of the others while at the same time trying to capture *some* of the effects of the actual interactions among adsorbed particles.

5.2.1 Four Sites with Interaction Among Particles

We have already obtained the exact expression for p_1 for this model. This forms a basis for evaluating our approximation scheme. We will consider a much larger system in Sect. 5.2.2.

A key observation is that a particle on a given site may be considered as "feeling" the presence of particles on the other sites through an effective field they generate. To illustrate the idea, let us focus on the particle at the central site in Fig. 5.4, which we shall refer to as site 1.

There are three peripheral sites to consider. If only one of them is filled, the interaction energy is $-w$. From the perspective of the particle at site 1, this has the same effect as sitting alone but with the *effective* binding energy $\varepsilon_{\text{eff}} = \varepsilon + w$. When two of the peripheral sites are filled, then ε_{eff} felt by the central particle will be

$\varepsilon + 2w$. Finally, if all three sites are occupied, $\varepsilon_{\text{eff}} = \varepsilon + 3w$. To summarize,

$$\varepsilon_{\text{eff}} = \varepsilon + Nw\,, \tag{5.37}$$

where N is the total number of particles adsorbed at the peripheral sites.

So far, everything is exact. The difficulty of continuing with the exact solution lies in the fact that ε_{eff} at site 1 depends on the value of N, and hence on the state of the peripheral sites, which may change with time. A simple approximation to circumvent this difficulty is to replace the exact N-dependent effective field by its average. Noting that the average number of particles in each of the peripheral sites is p_1, we have

$$\varepsilon_{\text{eff}} \approx \langle \varepsilon_{\text{eff}} \rangle = \varepsilon + \langle N \rangle w = \varepsilon + 3p_1 w\,. \tag{5.38}$$

Being a thermal average, this expression is independent of the instantaneous state of the peripheral sites. According to (5.38), site 1 may be regarded as the binding site in the single site model of Sect. 5.1.1 but with the binding energy $\varepsilon + 3p_1 w$.

Under this approximation, we can immediately take over (5.8) and write down the probability that site 1 is occupied as

$$\frac{e^{\beta(\mu+\varepsilon_{\text{eff}})}}{1+e^{\beta(\mu+\varepsilon_{\text{eff}})}} \approx \frac{e^{\beta(\mu+\varepsilon+3wp_1)}}{1+e^{\beta(\mu+\varepsilon+3wp_1)}} = \frac{xy^{3p_1}}{1+xy^{3p_1}}\,. \tag{5.39}$$

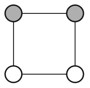
But, this quantity can only be p_1 since all the sites are equivalent and there is nothing in the model that serves to single out site 1. Thus,

$$p_1 = \frac{xy^{3p_1}}{1+xy^{3p_1}}\,. \tag{5.40}$$

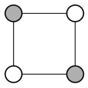
This is, then, the equation for p_1 under the mean-field approximation. The phrase "mean-field" originates from our replacing the actual *fluctuating* field ε_{eff} generated by particles on the peripheral sites by its *average* $\langle \varepsilon_{\text{eff}} \rangle$.

For $w = 0$, we have $y = 1$ and the approximation is, of course, exact. At $\beta w = 1$, the approximation is reasonably good as seen from Fig. 5.7a. With increasing w, however, its prediction starts to deviate from the actual one as indicated by Fig. 5.7b. When $\beta w = 2$, the mean-field approximation incorrectly predicts a sudden jump in p_1, or a phase transition, with increasing x.

Exercise 5.4. Consider an array of four adsorption sites placed at four corners of a square. We assume that these sites are distinguishable and that each site can accommodate up to a single particle. The binding energy per site is ε, and the interaction energy between a pair of particles occupying the nearest neighbor sites is $-w$. There is no interaction across the diagonally separated particles because they are not a nearest neighbor pair. The distance between them is $\sqrt{2}$ times the lattice constant. For example,



$E = -2\varepsilon - w$



$E = -2\varepsilon$

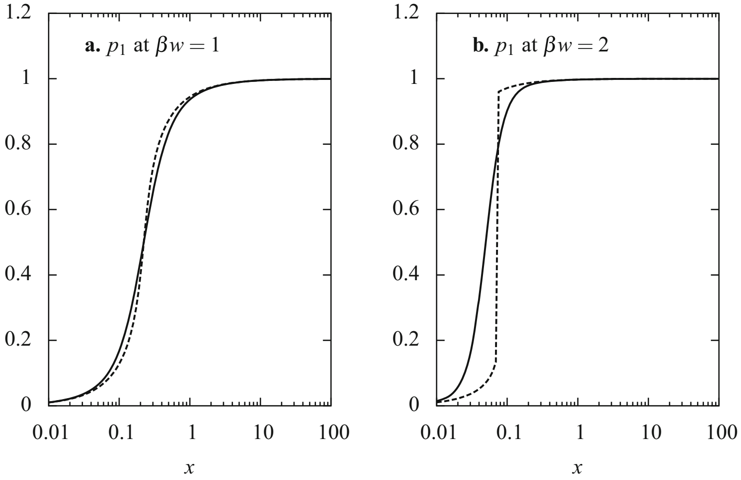


Fig. 5.7 Dependence of p_1 on x in the four interaction site model. Comparison between the exact solution (*solid line*) and the mean-field approximation (*dashed line*).

This array is exposed to a gas phase of particles held at constant T and μ.

a. Let $w = 0$, that is, there is no interaction among adsorbed particles. Find the exact expression for the average number ϕ of adsorbed particles per site.
b. Let $w \neq 0$. Find the exact expression for ϕ.
c. Use the mean-field approximation to derive the equation for ϕ. Rather than computing the partition function, consider the effective field generated by other particles at a given site and then use your answer from part a. ///

5.2.2 Two-Dimensional Lattice

Suppose now that the M adsorption sites are arranged on a two-dimensional square lattice. We continue to assign a binding energy ε per site and the interaction energy of $-w$ between a nearest neighbor pair. The diagrams in Exercise 5.4 illustrate the situation for $M = 4$.

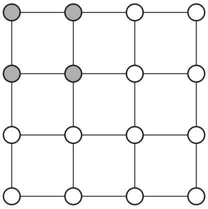
We fix the number of particles $N(\leq M)$ and work with the canonical ensemble. Even before we get started, we see right away that $p_1 = N/M$ in this case. So, what is the point? Why do we even bother with this problem? Well, $p_1 = N/M$ is the probability that a given site is occupied *if the system is, on average, homogeneous throughout*. But, whether the system can remain homogeneous depends on its thermodynamic *stability*. If the phase is unstable or even metastable for a given value of N/M, then the system will eventually separate into two phases, one with p_1 less than N/M and the other with p_1 greater than N/M.

One way to investigate such a possibility is to compute the free energy of the system as a function of p_1 *assuming* that it is homogeneous. The resulting free energy function will tell us about the stability and the eventual fate of any given homogeneous phase.

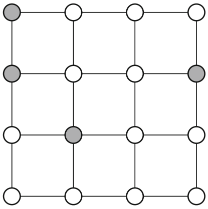
Now, the relevant partition function is given by (4.72). As we saw in Sect. 5.1.3, there are $\binom{M}{N}$ different ways of putting N particles in M sites. For a given configuration, the energy of the system may be written as

$$E = -\varepsilon N - wN_{n.n.} \,, \tag{5.41}$$

where $N_{n.n.}$ is the number of the nearest neighbor pairs in that particular configurations. Note carefully that $N_{n.n.}$ depends on the configuration under consideration. For example, compare the following two configurations, both with $M = 16$, $N = 4$.



$N_{n.n.} = 4$



$N_{n.n.} = 1$

Now, let $\Gamma(N_{n.n.})$ denote the number of configurations containing exactly $N_{n.n.}$ nearest neighbor pairs. Clearly, Γ satisfies

$$\binom{M}{N} = \sum_{N_{n.n.}} \Gamma(N_{n.n.}) \,. \tag{5.42}$$

In terms of Γ, we can write $\overline{\Omega}$ as

$$\overline{\Omega}(E) = \sum_{N_{n.n.}} \Gamma(N_{n.n.}) \delta(E + \varepsilon N + wN_{n.n.}) \,. \tag{5.43}$$

The canonical partition function is now given by

$$\begin{aligned} Z &= \int \sum_{N_{n.n.}} \Gamma(N_{n.n.}) \delta(E + \varepsilon N + wN_{n.n.}) e^{-\beta E} \mathrm{d}E \\ &= \sum_{N_{n.n.}} \Gamma(N_{n.n.}) e^{\beta \varepsilon N} e^{\beta w N_{n.n.}} = e^{\beta \varepsilon N} \binom{M}{N} \sum_{N_{n.n.}} \frac{\Gamma(N_{n.n.})}{\binom{M}{N}} e^{\beta w N_{n.n.}} \,, \end{aligned} \tag{5.44}$$

in which we identify the ratio $\Gamma(N_{n.n.})/\binom{M}{N}$ as the probability of finding $N_{n.n.}$ nearest neighbor pairs in a configuration if it is chosen randomly with an equal probability from $\binom{M}{N}$ configurations. Denoting the average with respect to this probability by $\langle \cdots \rangle_0$, we obtain

$$Z = e^{\beta \varepsilon N} \binom{M}{N} \left\langle e^{\beta w N_{n.n.}} \right\rangle_0 \,. \tag{5.45}$$

Up to this point, everything is exact. But, evaluation of the average in this expression is a difficult task. As a simple approximation, let us replace the average of the exponential by the exponential of the average:

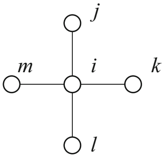
$$Z \approx e^{\beta \varepsilon N} \binom{M}{N} e^{\langle \beta w N_{n.n.} \rangle_0} = e^{\beta \varepsilon N} \binom{M}{N} e^{\beta w \langle N_{n.n.} \rangle_0} \,. \tag{5.46}$$

This step, as carried out at the level of partition function, implements the **mean-field approximation**. We will soon see why this is so.

Exercise 5.5. In this problem, we investigate how the mean-field approximation affects the predicted free energy of the system:

a. Show that $e^x \geq 1 + x$ for any real number x.
b. Noting that $e^x = e^{\langle x \rangle} e^{x - \langle x \rangle}$ and using the result from part a, show that $\langle e^x \rangle \geq e^{\langle x \rangle}$.
c. What is the implication of the inequality in part b on the free energy of the system estimated using the mean-field approximation? ///

To evaluate $\langle N_{n.n.} \rangle_0$, let us focus on a particular site i and its $z = 4$ nearest neighbor sites as shown below:



These sites (i, j, k, l, and m) may or may not be occupied. The probability that i is occupied in a particular configuration we choose from $\binom{M}{N}$ is simply N/M.[27] The same applies to site j. Thus, the probability that both i and j are occupied, that is, the probability that a nearest neighbor pair exists between sites i and j, is $(N/M)^2$. Similarly for other pairs involving site i. Thus, the average number of the nearest neighbor pairs centered around i is given by $(N/M)^2 z$. There is nothing special about site i and the same consideration applies to other sites as well. This suggests that the average number of the nearest neighbor pairs in the system is

$$\left(\frac{N}{M}\right)^2 zM \,, \tag{5.47}$$

But, counting the pairs in this manner, we have counted each pair twice. When counting the number of pairs centered around site i, we counted the i–j pair once. Then, when counting the number of pairs centered around site j, we counted this same pair for the second time. Dividing (5.47) by two to correct for the double counting, we have

$$\langle N_{n.n.} \rangle_0 = \frac{zN^2}{2M} \,. \tag{5.48}$$

So, (5.46) finally becomes

$$Z \approx e^{\beta \varepsilon N} \binom{M}{N} \exp\left(\frac{\beta w z}{2M} N^2\right) . \tag{5.49}$$

Now that we have the partition function, we can compute the Helmholtz free energy of the system:

$$\begin{aligned} \beta F &= -\ln Z = -\beta \varepsilon N - \ln \binom{M}{N} - \frac{\beta z w}{2M} N^2 \\ &\approx N \ln \frac{N}{M} + (M-N) \ln \frac{M-N}{M} - \beta \varepsilon N - \frac{\beta z w}{2M} N^2 , \end{aligned} \tag{5.50}$$

where we used Stirling's formula (3.153). On per site basis, therefore,

$$f := \frac{\beta F}{M} = \phi \ln \phi + (1-\phi) \ln (1-\phi) - \beta \varepsilon \phi - \frac{1}{2} \beta z w \phi^2 , \tag{5.51}$$

where we defined $\phi := N/M$. We already remarked at the beginning of this section that $p_1 = \phi$ holds only in a *homogeneous phase*. The quantity f is the (nondimensional) free energy per site of this homogeneous phase.

Let us assume for a moment that a homogeneous system is stable and find the relationship between ϕ and the chemical potential μ of the particle. The latter follows from the identity:

$$\begin{aligned} \beta \mu &= \left(\frac{\partial \beta F}{\partial N}\right)_{T,M} = \left(\frac{\partial \beta F/M}{\partial N/M}\right)_{T,M} = \left(\frac{\partial f}{\partial \phi}\right)_T \\ &= \ln \phi - \ln (1-\phi) - \beta \varepsilon - \beta z w \phi , \end{aligned} \tag{5.52}$$

where we assumed that the lattice constant is held fixed and treated w as a constant. In this case, holding volume constant is equivalent to fixing M. From (5.52), it follows that

$$\frac{\phi}{1-\phi} = e^{\beta(\mu + \varepsilon + w z \phi)} . \tag{5.53}$$

This result should be compared with (5.8), which may be rewritten as

$$\frac{p_1}{1-p_1} = e^{\beta(\mu+\varepsilon)} . \tag{5.54}$$

Our homogeneous system of interacting N particles is seen to be equivalent to a single-site model provided that ε in the latter is replaced by the effective binding energy, or the mean-field, $\varepsilon + w z \phi$.

Let $x := e^{\beta(\mu+\varepsilon)}$ and $y := e^{\beta w}$ as before, and rewrite (5.53) as

$$\phi = \frac{x y^{z\phi}}{1 + x y^{z\phi}} . \tag{5.55}$$

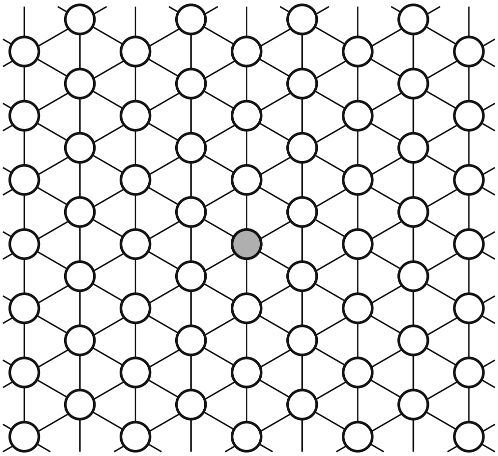


Fig. 5.8 A two-dimensional triangular lattice. A given site *(filled circle)* has six nearest neighbor sites.

This is essentially (5.40) with 3 replaced by z. Thus, under the mean-field approximation, the quantity z, often referred to as the **coordination number** is the only parameter reflecting the lattice structure of the model system. For example, in both two-dimensional triangular lattices (see Fig. 5.8.) and three-dimensional cubic lattices, the mean-field approximation gives (5.55) with $z = 6$. In reality, these two systems behave differently especially near the critical point. For details, see Ref. [1].

Let us now examine the stability of a homogeneous system. The f versus ϕ plot is shown in Fig. 5.9 for a few values of w. For simplicity, we set $\varepsilon = 0$. Note that, as βzw is increased, the graph starts to exhibit two inflection points. Between these points, the graph is concave down and the system is unstable. That is, the free energy of the system can be lowered by splitting into two phases. This mechanism of phase separation is known as the **spinodal decomposition**.

We recall that the inflection points of the curve are determined by

$$\partial^2 f/\partial\phi^2 = 0. \tag{5.56}$$

According to (5.51), this equation has two real solutions in the interval $[0,1]$ if T is sufficiently low. In this case, a homogeneous phase is unstable, metastable, or stable depending on its value of ϕ.

Let us denote the two real solutions of (5.56) by ϕ^a and ϕ^b, where $\phi^a < \phi^b$. Then, a phase with $\phi^a \le \phi \le \phi^b$ is unstable and will separate into two coexisting phases one with p_1^c and the other with p_1^d, where $p_1^c < \phi^a < \phi^b < p_1^d$. If $p_1^c < \phi < \phi^a$ or $\phi^b < \phi < p_1^d$, the phase is metastable and will separate into the two phases (p_1^c and p_1^d) given a sufficient amount of time. Phases with $\phi < p_1^c$ or $\phi > p_1^d$ are stable.

The two solutions ϕ^a and ϕ^b of (5.56) approach each other with increasing T and eventually merge at the **critical temperature** T_c. Above T_c, there is no real solution to (5.56). That is, a homogeneous phase is stable for all values of ϕ and there will be no phase separation.

Exercise 5.6. Show that p_1 values at phase coexistence can be determined by means of the common tangent construction. In this method, one looks for a tangent line to the f versus ϕ plot having two points of contact. If this common tangent exists, then the points of contact give the desired p_1 values. (See Sect. 2.16.2.4 for another example of this graphical method.) ///

Exercise 5.7.

a. For $w > 0$, find the critical temperature below which the system undergoes a phase separation. Note that the result is *independent of* ε.
b. Is there a phase separation if $w < 0$? ///

Can we approach the same problem using a grand canonical ensemble? Combining (4.72) and (4.128), we see that Ξ may be written as

$$\Xi = \sum_{N=0}^{M} e^{\beta\mu N} Z(T,V,N) \,. \tag{5.57}$$

When Z from (5.49) is substituted in this equation, the result is a rather difficult expression to evaluate.

However, based on what we saw in Sect. 4.1, N is expected to be extremely sharply peaked around $\langle N\rangle$ for large enough M. In this case, the summation in (5.57) may be replaced by the maximum term in the summand. Moreover, the value of N

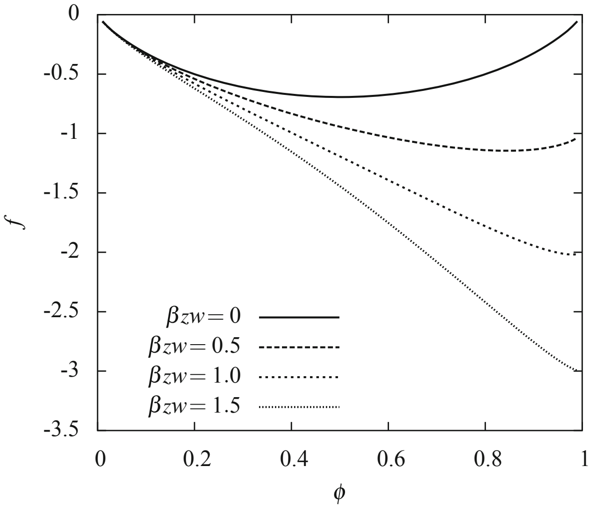


Fig. 5.9 $f := \beta F/M$ versus ϕ when $\varepsilon = 0$.

corresponding to this maximum term may safely be identified with its average $\langle N\rangle$. Thus, we write

$$\Xi \approx e^{\beta\mu N} Z(T,M,N) \tag{5.58}$$

and then maximize Ξ (or minimize $\beta\Omega = -\ln\Xi$) with respect to N. When we identify the optimum value of N with $\langle N\rangle$, the result is (5.52). In fact, from (5.58),

$$\left.\frac{\partial \ln\Xi}{\partial N}\right|_{N=\langle N\rangle} = \beta\mu + \left.\frac{\partial \ln Z}{\partial N}\right|_{N=\langle N\rangle} = 0\,, \tag{5.59}$$

which is just the first equality in (5.52).

Example 5.1. Liquid crystal:[28] Simple liquid crystals are systems consisting of nonspherical, for example, rod-like, molecules. At high temperatures, the orientation of these molecules is random; this is called the isotropic phase. At low temperatures, molecules align parallel to each other; this is called the nematic phase. The simplest lattice model for this transition is a three-state model in which a molecule can take any one of three orthogonal orientations, which we designate as x, y, and z. If two nearest molecules lie parallel to each other, there is an energy gain of $-\varepsilon$, ($\varepsilon > 0$). If they lie perpendicular, the energy gain is zero. Assuming single occupancy on each site and no vacancy, we may define variables $\sigma_x(i)$, $\sigma_y(i)$, and $\sigma_z(i)$, such that $\sigma_x(i) = 1$ if the molecule i lies parallel to the x-axis, $\sigma_x(i) = 0$ otherwise and likewise for other orientations. Of course, $\sigma_x(i) + \sigma_y(i) + \sigma_z(i) = 1$:

a. Construct an energy function for the system.
b. Let

$$\sigma_x := \frac{1}{N}\sum_{i=1}^{N} \sigma_x(i) \tag{5.60}$$

denote the fraction of molecules pointing in the x-direction. What is $\langle \sigma_x\rangle$ in the isotropic phase?
c. Define an order parameter such that it is zero in the isotropic phase, nonzero in the nematic phase and reaches a maximum of 1 at zero temperature.
d. Find the isotropic–nematic transition temperature T_t.

Solution

a. Let

$$\boldsymbol{\sigma}(i) = \sigma_x(i)\boldsymbol{e}_x + \sigma_y(i)\boldsymbol{e}_y + \sigma_z(i)\boldsymbol{e}_z\,. \tag{5.61}$$

If $\boldsymbol{\sigma}(i)$ and $\boldsymbol{\sigma}(j)$ point in the same direction, $\boldsymbol{\sigma}(i)\cdot\boldsymbol{\sigma}(j)=1$. The dot product is zero otherwise. Thus,

$$E=-\frac{1}{2}\varepsilon\sum_{i}\sum_{j\neq i}\boldsymbol{\sigma}(i)\cdot\boldsymbol{\sigma}(j)\;. \tag{5.62}$$

For given i, the summation over j includes only the nearest neighbors of i. The factor $1/2$ corrects for the double counting of each nearest neighbor pair.

b. In an isotropic phase, each direction is equivalent to any other. Thus, we have $\langle\sigma_x\rangle=\langle\sigma_y\rangle=\langle\sigma_z\rangle$. But, because

$$\langle\sigma_x+\sigma_y+\sigma_z\rangle=\langle\sigma_x\rangle+\langle\sigma_y\rangle+\langle\sigma_z\rangle=1\;, \tag{5.63}$$

we see that

$$\langle\sigma_x\rangle=\langle\sigma_y\rangle=\langle\sigma_z\rangle=\frac{1}{3}\;. \tag{5.64}$$

c. From (5.61)

$$\langle\boldsymbol{\sigma}\rangle=\langle\sigma_x\rangle\boldsymbol{e}_x+\langle\sigma_y\rangle\boldsymbol{e}_y+\langle\sigma_z\rangle\boldsymbol{e}_z. \tag{5.65}$$

Because of (5.63), this graphically is a vector pointing from the origin $\mathscr{O}$ to a point, call it X, on the plane defined by the following three points:

$$\mathrm{A}\doteq(1,0,0)\;,\quad \mathrm{B}\doteq(0,1,0)\;,\quad\text{and}\quad \mathrm{C}\doteq(0,0,1)\;. \tag{5.66}$$

Since components $\langle\sigma_x\rangle$, $\langle\sigma_y\rangle$, and $\langle\sigma_z\rangle$ are all nonnegative, the point X is confined to the triangle ABC. The isotropic phase is represented by the point

$$\mathrm{S}\doteq\left(\frac{1}{3},\frac{1}{3},\frac{1}{3}\right)\;. \tag{5.67}$$

One possible choice of an order parameter η is the distance $|\mathrm{SX}|$ between S and X, or more conveniently,

$$\begin{aligned}|\mathrm{SX}|^2&=\left(\langle\sigma_x\rangle-\frac{1}{3}\right)^2+\left(\langle\sigma_y\rangle-\frac{1}{3}\right)^2+\left(\langle\sigma_z\rangle-\frac{1}{3}\right)^2\\&=\langle\sigma_x\rangle^2+\langle\sigma_y\rangle^2+\langle\sigma_z\rangle^2-\frac{1}{3}\;.\end{aligned} \tag{5.68}$$

(We want to avoid the square root, which is a bit awkward to handle.) For an isotropic phase, this quantity is zero. At zero temperature, the system is in a completely ordered state, corresponding to point A, B, or C, for which

$$|\mathrm{SA}|^2=|\mathrm{SB}|^2=|\mathrm{SC}|^2=\frac{2}{3}\;. \tag{5.69}$$

(This is because the minimum energy state completely dominates the summation in Z given below.) Normalizing $|\mathrm{SX}|^2$ so that it is unity for A, B, and C, we arrive at

$$\eta := \frac{3}{2}\left(\langle\sigma_x\rangle^2 + \langle\sigma_y\rangle^2 + \langle\sigma_z\rangle^2\right) - \frac{1}{2} \tag{5.70}$$

d. The canonical partition function is given by

$$Z = \sum e^{-\beta E} , \tag{5.71}$$

where the summation is over all possible orientations of all the molecules in the system. To perform this summation, we organize it according to the number N_α of molecules pointing in the α-direction. We note that for given N_α $(\alpha = x, y, z)$, there are

$$W(N_x, N_y, N_z) := \frac{N!}{N_x!N_y!N_z!} \tag{5.72}$$

distinct configurations. But, not all of them has the same energy, since the latter depends on the number $N_{\alpha\alpha}$ of nearest neighbor pairs of molecules *both* pointing in the α-direction.

Let $\Gamma(N_{xx}, N_{yy}, N_{zz}|N_x, N_y, N_z)$ denote the number of distinct configurations with given values of $N_{\alpha\alpha}$ $(\alpha = x, y, z)$ that are consistent with the given values of N_α. Clearly,

$$W(N_x, N_y, N_z) = \sum_{\{N_{\alpha\alpha}|N_\alpha\}} \Gamma(N_{xx}, N_{yy}, N_{zz}|N_x, N_y, N_z) , \tag{5.73}$$

where the summation is over all possible values of $N_{\alpha\alpha}$ $(\alpha = x, y, z)$ for given values of N_α. We can also express E in terms of $N_{\alpha\alpha}$ as

$$E = -\varepsilon\left(N_{xx} + N_{yy} + N_{zz}\right) . \tag{5.74}$$

Then,

$$Z = \sum_{\{N_\alpha\}} \sum_{\{N_{\alpha\alpha}|N_\alpha\}} \Gamma(N_{xx}, N_{yy}, N_{zz}|N_x, N_y, N_z) e^{\beta\varepsilon\left(N_{xx}+N_{yy}+N_{zz}\right)} \tag{5.75}$$

where the first summation is over all possible values of N_α $(\alpha = x, y, z)$. To introduce the mean-field approximation, we rewrite this expression as

$$Z = \sum_{\{N_\alpha\}} W(N_x, N_y, N_z) \sum_{\{N_{\alpha\alpha}|N_\alpha\}} \frac{\Gamma(N_{xx}, N_{yy}, N_{zz}|N_x, N_y, N_z)}{W(N_x, N_y, N_z)} e^{\beta\varepsilon\left(N_{xx}+N_{yy}+N_{zz}\right)} , \tag{5.76}$$

where the ratio Γ/W is the probability of finding exactly $N_{\alpha\alpha}$ pairs of molecules both pointing in the α-direction if we are to choose randomly with equal probability a single configuration from the total of W configurations. Denoting the average with respect to this probability by $\langle\cdots\rangle_0$, we have

$$\begin{aligned} Z &= \sum_{\{N_\alpha\}} W(N_x, N_y, N_z) \left\langle e^{\beta\varepsilon\left(N_{xx}+N_{yy}+N_{zz}\right)} \right\rangle_0 \\ &\approx \sum_{\{N_\alpha\}} W(N_x, N_y, N_z) e^{\beta\varepsilon\langle N_{xx}+N_{yy}+N_{zz}\rangle_0} \,. \end{aligned} \tag{5.77}$$

We still have to express $\langle N_{\alpha\alpha}\rangle_0$ in terms of N_α. Noting that the desired average is with respect to the probability Γ/W, which does not take the Boltzmann factor into account, we have

$$\langle N_{\alpha\alpha}\rangle_0 = \frac{1}{2} \times \frac{N_\alpha}{N} \times \frac{N_\alpha}{N} z \times N = \frac{z}{2N} {N_\alpha}^2 \,, \tag{5.78}$$

where z is the coordination number. So, we now have

$$Z \approx \sum_{\{N_\alpha\}} W(N_x, N_y, N_z) e^{\frac{\beta\varepsilon z}{2N}\left({N_x}^2+{N_y}^2+{N_z}^2\right)} =: \sum_{\{N_\alpha\}} q(N_x, N_y, N_z) \,. \tag{5.79}$$

To simplify the computation further, we note that the summand q is proportional to the probability of finding exactly N_α molecules pointing in the α-direction. For a macroscopic system, we expect this probability to be extremely sharply peaked around the average. This observation allows us to replace the summation by the maximum term of the summand:

$$Z \approx \max_{\{N_\alpha\}} \{q(N_x, N_y, N_z)\} \,. \tag{5.80}$$

Using Stirling's formula, we have

$$\ln q = -N(\sigma_x \ln \sigma_x + \sigma_y \ln \sigma_y + \sigma_z \ln \sigma_z) + \frac{1}{2}\beta\varepsilon z N \left({\sigma_x}^2 + {\sigma_y}^2 + {\sigma_z}^2\right) \,. \tag{5.81}$$

where $\sigma_\alpha := N_\alpha/N$ by (5.60). We need to maximize $\ln q$ under the constraint that

$$\begin{cases} \sigma_x + \sigma_y + \sigma_z = 1 \,, \\ 0 \le \sigma_x \le 1 \,, \quad 0 \le \sigma_y \le 1 \,, \quad 0 \le \sigma_z \le 1 \,. \end{cases} \tag{5.82}$$

This may also be written as

$$\begin{cases} \sigma_z = 1 - (\sigma_x + \sigma_y)\,, \\ 0 \le \sigma_x \le 1\,, \quad 0 \le \sigma_y \le 1\,, \quad 0 \le \sigma_x + \sigma_y \le 1\,. \end{cases} \tag{5.83}$$

That is, the degrees of freedom here is just 2 not 3. So, in order to find the maximum of $\ln q$, we replace σ_z in (5.81) by $1 - \sigma_x - \sigma_y$ and then compute

$$\frac{\partial \ln q}{\partial \sigma_x} = N \ln \frac{1 - \sigma_x - \sigma_y}{\sigma_x} + \beta \varepsilon z N (2\sigma_x + \sigma_y - 1) \tag{5.84}$$

and

$$\frac{\partial \ln q}{\partial \sigma_y} = N \ln \frac{1 - \sigma_x - \sigma_y}{\sigma_y} + \beta \varepsilon z N (\sigma_x + 2\sigma_y - 1)\ . \tag{5.85}$$

(Just as a check, note that the second equation can be obtained by exchanging x and y in the first. This must be so because the expression for $\ln q$ is symmetric with respect to such an exchange.)

The value of σ_α that maximizes $\ln q$ is just $\langle \sigma_\alpha \rangle$ because q is extremely sharply peaked around the average. Thus,

$$\ln \frac{1 - \langle \sigma_x \rangle - \langle \sigma_y \rangle}{\langle \sigma_x \rangle} + \beta \varepsilon z (2\langle \sigma_x \rangle + \langle \sigma_y \rangle - 1) = 0 \tag{5.86}$$

and

$$\ln \frac{1 - \langle \sigma_x \rangle - \langle \sigma_y \rangle}{\langle \sigma_y \rangle} + \beta \varepsilon z (\langle \sigma_x \rangle + 2\langle \sigma_y \rangle - 1) = 0\,. \tag{5.87}$$

We see that the isotropic phase (at point S)

$$(\langle \sigma_x \rangle \langle \sigma_y \rangle, \langle \sigma_z \rangle) \doteq \left(\frac{1}{3}, \frac{1}{3}, \frac{1}{3} \right) \tag{5.88}$$

is always a solution. But, there might be other solutions. Physically, we expect that, when $T > T_t$, the entropy dominates the free energy and $\ln q$ is the maximum (the corresponding free energy $F \approx -k_B T \ln q$ being minimum) for the isotropic phase. In contrast, if $T < T_t$, we expect that the energy dominates the free energy and we have a nematic phase, that is, the maximum of $\ln q$ should occur elsewhere even though $\ln q$ is still extremum at point S.

This suggests that the extremum at S changes from (local) maximum to local minimum at $T = T_t$. To see this transition, we need to expand $\ln q$ into the Taylor series around S and retain at least up to the second-order terms. The first-order term, as we have just seen, is zero. The second derivatives of $\ln q$ at S are:

$$\left.\frac{\partial^2 \ln q}{\partial {\sigma_x}^2}\right|_S = N\left(-\frac{1}{1-\sigma_x-\sigma_y}-\frac{1}{\sigma_x}\right)+2N\beta\varepsilon z\Big|_S = 2N(\beta\varepsilon z-3)\,,$$

$$\left.\frac{\partial^2 \ln q}{\partial {\sigma_y}^2}\right|_S = 2N(\beta\varepsilon z-3)\,, \quad \text{and} \quad \left.\frac{\partial^2 \ln q}{\partial \sigma_x \partial \sigma_y}\right|_S = N(\beta\varepsilon z-3)\,. \qquad (5.89)$$

Retaining up to the second-order terms and using (B.17),

$$\ln q \approx \ln q_S + N(\beta\varepsilon z-3)\left[(\Delta\sigma_x)^2+\Delta\sigma_x\Delta\sigma_y+(\Delta\sigma_y)^2\right]\,, \qquad (5.90)$$

where q_S is the value of q of the isotropic phase. We also defined

$$\Delta\sigma_x := \sigma_x - \frac{1}{3} \quad \text{and} \quad \Delta\sigma_y := \sigma_y - \frac{1}{3}\,. \qquad (5.91)$$

But,

$$(\Delta\sigma_x)^2+\Delta\sigma_x\Delta\sigma_y+(\Delta\sigma_y)^2 = \left(\Delta\sigma_x+\frac{1}{2}\Delta\sigma_y\right)^2+\frac{3}{4}(\Delta\sigma_y)^2 \qquad (5.92)$$

is zero only for the isotropic phase and positive otherwise. If $\beta < 3/\varepsilon z$, $\ln q$ is a (local) maximum at S and the isotropic phase prevails. On the other hand, if $\beta > 3/\varepsilon z$, $\ln q$ is a local minimum at S. That is, the isotropic phase is unstable and we have a nematic phase. Thus, the transition temperature T_t is $\varepsilon z/3k_B$.

5.3 Frequently Used Symbols

$\langle A \rangle$, ensemble average of a dynamical variable A.

p_1 , probability that an adsorption site is occupied.
$\boldsymbol{p}_i$, linear momentum of the ith particle.
$\boldsymbol{p}^N$, collective notation for $\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N$.
$\boldsymbol{r}_i$, position vector of the ith particle.
$\boldsymbol{r}^N$, collective notation for $\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N$.
w , interaction energy between two nearest neighbor particles.
z , coordination number.

A , a generic dynamical variable.
E , energy of a system.

F , Helmholtz free energy.
T , absolute temperature.
Z , canonical partition function.

$\mathscr{W}(E)$, the number of microstates with $H \leq E$.

β , $1/k_B T$.
ε , binding energy.
$\delta(x)$, Dirac δ-function.
μ , chemical potential.
$\theta(x)$, step function defined by (D.2).

Λ , thermal wavelength $h/\sqrt{2\pi m k_B T}$ of a particle of mass m.
Ξ , grand canonical partition function.
$\overline{\Omega}$, density of states.

Reference

1. N. Goldenfeld (1992), *Lectures on phase transitions and the renormalization group*, Addison-Wesley, Reading Massachusetts