The energy required to cut across a group is $\varepsilon = N^{2/3}\,\Delta$, where Δ is roughly the value of the energy required for taking one atom away from the group. Thus, the probability for splitting up the group is $e^{-N^{2/3}\Delta/KT}$. The larger N is, the higher T is required to be for a finite probability of breaking up a large group of atoms. Thus, in the one-dimensional case, a finite energy is required for breaking up a group of atoms, a finite number of groups exist, and the *fraction* of atoms (essentially infinite in number) in the condensed state (that is, in the largest group) is zero. In the three-dimensional case, because of the probability factor $e^{-N^{2/3}\Delta/KT}$, a finite fraction of the total gas can exist in the condensed state at a finite temperature.

For solids the difference is more subtle. In one dimension, as the temperature is raised, let the mean square error in the position of one atom relative to the ones on each side of it be δ^2. Then, over a group of N atoms, the mean square error in positions of the first and last atoms is $N\delta^2$ from the perfect lattice configuration. The error "propagates" (in a sense), and when temperature is increased, the solid expands monotonically. There is only one path along which information can be transmitted. In three dimensions, the position of an atom in one place influences that of a distant atom much more strongly than in one dimension—there are many paths connecting the two along which forces are being transmitted. Thus to melt a solid T must become high enough that the thermal energy can overcome these "multipath" forces.

CHAPTER 5

ORDER-DISORDER THEORY

5.1 INTRODUCTION

We will now consider a new class of statistical-mechanical problems, problems that do not involve motions of atoms but instead involve their positions in a lattice. More precisely, we will consider alloys made up of two types of atoms. For instance, in the cubic lattice shown in Fig. 5.1, there will be some preferred arrangement for the manner in which the lattice sites are occupied by type A and type B atoms. Let us take the case of zero temperature. Essentially, two types of lattice arrangements are possible, one of which is depicted in the figure, and they can be understood from a physical point of view as follows. Let V_{AB} be the interaction potential between unlike atoms and V_{AA}, V_{BB} the potential between the like atoms. If $V_{AB} > (V_{AA} + V_{BB})/2$, then A atoms prefer to be near A atoms and likewise for the B atoms. The solid would tend to exist in two distinct parts—one of A atoms only, and one of B atoms only. If $V_{AB} < (V_{AA} + V_{BB})/2$, the A and B atoms would tend to alternate in position throughout the solid. If the solid is heated, then gradually A and B atoms will exchange positions in a random way until, at the Curie temperature, the order "melts"; at still higher temperatures, disorder sets in. It is of interest to compute the partition function for such a system:

$$e^{-\beta F} = \sum_{\substack{\text{arrangements}\\ \text{of atoms}}} \exp\left(-\sum_{(i,j,\text{bonds})} \beta V_{ij}\right).$$

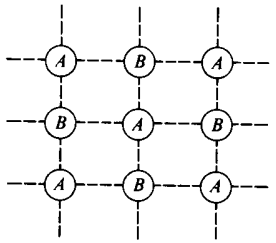


Fig. 5.1 Cubic lattice with two types of atoms, A and B.

Define:

$$\varepsilon_i = +1 \text{ for } A \text{ atom}$$
$$= -1 \text{ for } B \text{ atom}$$

N_A, N_B = number of A, B atoms, respectively.

Thus,

$$\varepsilon_i\varepsilon_j = +1 \text{ if } AA \text{ pair}$$
$$= +1 \text{ if } BB \text{ pair}$$
$$= -1 \text{ if } AB \text{ pair.}$$

Considering nearest-neighbor interactions only and the total $N_A + N_B$ as constant, we will write the interaction energy in the form

$$V_{ij} = a\varepsilon_i\varepsilon_j + b\left(\frac{\varepsilon_i + \varepsilon_j}{2}\right) + c.$$

Then,

$$V_{AA} = a + b + c$$
$$V_{BB} = a - b + c$$
$$V_{AB} = -a + c$$

and

$$2a = \frac{V_{AA} + V_{BB}}{2} - V_{AB}.$$

Thus, the exponential in the partition-function equation above is

$$\exp\left(-\beta a \sum_{i,j} \varepsilon_i\varepsilon_j\right) \exp\left(-\beta b \sum_{i,j} \frac{\varepsilon_i + \varepsilon_j}{2}\right) \exp(-\beta c).$$

The last exponential, $e^{-\beta c}$, is a constant and does not enter into calculations.

In the sum $\sum_{\text{bonds}} (\varepsilon_i + \varepsilon_j)/2$, each atom contributes to the sum a certain number of times. The number of times an atom contributes is equal to the number of bonds it makes, that is, the number of nearest neighbors it has. For example, in the case of a two-dimensional square lattice, each atom has four nearest neighbors; so

$$\sum_{\text{bonds}} \frac{\varepsilon_i + \varepsilon_j}{2} = 2(N_A - N_B).$$

In general, if N_A and N_B are kept constant, we can ignore $\sum (\varepsilon_i + \varepsilon_j)/2$ because it does not depend on the arrangement of the atoms. The problem then is to calculate for the partition function the quantity

$$\sum \exp\left(-\beta a \sum_{i,j} \varepsilon_i\varepsilon_j\right) = \sum \exp\left(-H \sum_{\text{bonds}} \varepsilon_i\varepsilon_j\right).$$

But when we sum quantities over all possible arrangements of the atoms, the restriction that $N_A - N_B$ be constant may cause difficulties. To relax this restriction, we put in the usual "chemical potential." In other words, we change the problem (but not the results of the solution of the problem) by saying that $N_A - N_B$ can vary. Associated with variation of $N_A - N_B$ is a proportionate amount of chemical potential, which has the effect of making a certain ratio N_A/N_B the most probable. In such a case, we cannot ignore

$$\sum_{\text{bonds}} \frac{\varepsilon_i + \varepsilon_j}{2} = \sum_{\text{atoms}} \varepsilon_i.$$

Our problem reduces to the calculation of

$$\sum \exp\left(-H \sum_{\text{bonds}} \varepsilon_i\varepsilon_j - J \sum_{\text{atoms}} \varepsilon_i\right),$$

where, in summing over possible arrangements, we still take $N_A + N_B = N$ fixed but no longer fix N_A and N_B, separately. If $J = 0$, we are obviously solving the problem of $\langle N_A\rangle = \langle N_B\rangle$. For practice, we will evaluate the above sum for the one-dimensional case. Then we will consider an approximate method that works for two and three dimensions, and finally we will find the sum exactly for two dimensions. The exact solution for three dimensions has not yet been found.

It should be noted that the above model can be taken as a model of ferromagnetism. We interpret $\varepsilon_1 = +1$ as spin up and $\varepsilon_1 = -1$ as spin down, where the atoms are taken to have half-integer spin. A better model for ferromagnetism is to take the

$$\text{Hamiltonian} = H \sum_{\text{bonds}} \boldsymbol{S}_i \cdot \boldsymbol{S}_j$$

where $\boldsymbol{S}_i$ is the spin operator for the ith atom. This model is not equivalent to the model with $\varepsilon_i\varepsilon_j$ terms. For example, a two-atom system has

$$\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 = \tfrac{1}{2}[(\boldsymbol{S}_1 + \boldsymbol{S}_2)^2 - \tfrac{3}{2}\hbar^2],$$

which has the value $\frac{1}{4}\hbar^2$ with *a priori* probability three times as large as that for which the value of $\boldsymbol{S}_1 \cdot \boldsymbol{S}_2$ has value $-\frac{3}{4}\hbar^2$. That is, there are three ways in which two atoms of spin $\frac{1}{2}$ can combine to give a system with total spin 1, but only one way in which they can combine to give spin 0. On the other hand, $\varepsilon_i\varepsilon_j$, takes on its two possible values with equal *a priori* probability.

Although the two models are different, the qualitative results might be similar. For the rest of this chapter we will discuss the model in which the energy has terms $\varepsilon_i\varepsilon_j$. This is the Ising model.

5.2 ORDER-DISORDER IN ONE-DIMENSION

For practice, let us evaluate

$$e^{-\beta F} = \sum_{\substack{\varepsilon_1 = \pm 1 \\ \varepsilon_2 = \pm 1 \\ \cdots}} \exp\left(-H \sum \varepsilon_i \varepsilon_{i+1} - J \sum \varepsilon_i\right)$$

in one dimension.

First, suppose $J = 0$. Then an easy way of doing the problem is to define a new variable:

$$\eta_i = \begin{cases} 1 & \text{if } \varepsilon_i = \varepsilon_{i+1} \\ -1 & \text{if } \varepsilon_i = -\varepsilon_{i+1} \end{cases}.$$

Then

$$e^{-\beta F} = \sum_{\substack{\eta_1 = \pm 1 \\ \eta_2 = \pm 1 \\ \cdots}} \exp\left[-H \sum_i \eta_i\right] = \left(\sum_{\eta_1 = \pm 1} e^{-H\eta_1}\right)\left(\sum_{\eta_2 = \pm 1} e^{-H\eta_2}\right) \cdots$$

$$= (2 \cosh H)^N.$$

So $F = -N/\beta \ln (2 \cosh H)$, and we have completed the calculation.

If $J \neq 0$, the above method does not work. We have to use what is, by now, a familiar trick. That is, we make up a new problem that, for large N, is almost the same as the old one, but for which a recursion relation can be found. We will try to evaluate the partition function for a system in which the particle on the end has a fixed ε.

Let

$$X_N(\varepsilon_{N+1}) = \sum_{\varepsilon_1, \varepsilon_2 \cdots \varepsilon_N} \exp\left[-H(\varepsilon_1\varepsilon_2 + \cdots + \varepsilon_N\varepsilon_{N+1}) - J(\varepsilon_1 + \varepsilon_2 + \cdots + \varepsilon_{N+1})\right].$$

Then

$$X_{N+1}(\varepsilon_{N+2}) = \sum_{\varepsilon_{N+1} = \pm 1} X_N(\varepsilon_{N+1}) \exp\left[-H\varepsilon_{N+1}\varepsilon_{N+2} - J\varepsilon_{N+2}\right].$$

The free energy for a large number of atoms should be proportional to the number of atoms; therefore

$$X_{N+1}(\varepsilon_{N+2}) = e^{\beta\mu} X_N(\varepsilon_{N+2}),$$

where μ is independent of N for large N. The free energy is then $F = -\mu N$. The recursion relation then becomes two simultaneous linear equations

$$e^{\beta\mu} X_N(y) = \sum_{\chi = \pm 1} X_N(\chi) e^{-H\chi y - Jy} \qquad \text{where} \qquad y = \pm 1.$$

If we think of $(X_N(1), X_N(-1))$ as an eigenvector and $e^{\beta\mu}$ as an eigenvalue of the above equation, then it is easy to see what to do next. To find $e^{\beta\mu}$ it is necessary to solve

$$0 = \det\begin{pmatrix} e^{-H-J} - e^{\beta\mu} & e^{H+J} \\ e^{H-J} & e^{-H+J} - e^{\beta\mu} \end{pmatrix}.$$

The result is

$$e^{\beta\mu} = e^{-H} \cosh J \pm e^{H}\sqrt{1 + e^{-4H} \sinh^2 J}.$$

There are two solutions here; which one do we want? If we look back at the case of $J = 0$, it is obvious that $e^{\beta\mu}$ becomes $2 \cosh H = e^{-H} + e^{H}$, so the general result is

$$e^{\beta\mu} = e^{-H} \cosh J + e^{H}\sqrt{1 + e^{-4H} \sinh^2 J}.$$

Problem: Try to get the free energy as a function of the ratio between the number of A's and the number of B's.

5.3 APPROXIMATE METHODS FOR TWO DIMENSIONS

You may have noticed that in Section 5.2, none of the equations were considered important enough to number. This is because we were not especially interested in the answers, but instead wanted to examine some possible ways of looking at problems. Perhaps you will be able to improve upon and use some of the methods described here, or maybe you will find these methods useful for solving a completely different problem. In this section we will nibble at the edges of another problem: that of order–disorder for a two-dimensional square lattice. For simplicity, let us take $J = 0$.

One approach is to find a recursion relation. To do this, find the partition function for the case where all the ε's in the last column are fixed. Suppose there are M columns of N particles each, and let $X_M(\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_N)$ be the partition function. As in the one-dimensional case, the free energy is proportional to the number of atoms. It follows that

$$e^{\beta\mu N} X_M(\varepsilon_1, \ldots, \varepsilon_N) = X_{M+1}(\varepsilon_1, \ldots, \varepsilon_N)$$
$$= \sum_{\theta_1, \ldots, \theta N} \exp\left\{-H[\varepsilon_1\theta_1 + \varepsilon_2\theta_2 + \cdots + \varepsilon_N\theta_N]\right\}$$
$$\times \exp\left\{-H[\varepsilon_1\varepsilon_2 + \cdots + \varepsilon_{N-1}\varepsilon_N]\right\} X_M(\theta_1, \ldots, \theta_N). \tag{5.1}$$

The analogous equation in Section 5.2 required for its solution the diagonalization of a two-by-two matrix. The above equation requires the diagonalization of a 2^N-by-2^N matrix.

Given the matrix equation $MA = \lambda A$ with M hermitian, a well-known way for finding the solution with the minimum or maximum λ is to try to find the extremum of $A \cdot MA/A \cdot A$. This method might be applicable to Eq. (5.1). Let

$$X_N(\varepsilon_1, \ldots, \varepsilon_N) = \exp\{-\tfrac{1}{2}H[\varepsilon_1\varepsilon_2 + \cdots + \varepsilon_{N-1}\varepsilon_N]\}Z(\varepsilon_1, \ldots, \varepsilon_N).$$

Then Eq. (5.1) becomes

$$\begin{aligned} e^{\beta\mu N}Z(\varepsilon_1, \ldots, \varepsilon_N) = \sum_{\theta_1, \ldots, \theta_N} & \exp\{-\tfrac{1}{2}H[\varepsilon_1\varepsilon_2 + \cdots + \varepsilon_{N-1}\varepsilon_N]\} \\ & \times \exp\{-\tfrac{1}{2}H[\theta_1\theta_2 + \cdots + \theta_{N-1}\theta_N]\} \\ & \times \exp\{H[\varepsilon_1\theta_1 + \cdots + \varepsilon_N\theta_N]\}Z(\theta_1, \ldots, \theta_N). \end{aligned}$$

We made this substitution in order to get an eigenvalue equation with a symmetric real matrix, that is, a hermitian matrix. Then, to solve this equation, we must find the extremum of I/D, where

$$\begin{aligned} I = \sum_{\theta_i, \varepsilon_i} & Z(\theta_1, \ldots, \theta_N)Z(\varepsilon_1, \ldots, \varepsilon_N) \exp\{-\tfrac{1}{2}H[\varepsilon_1\varepsilon_2 + \cdots + \varepsilon_{N-1}\varepsilon_N]\} \\ & \times \exp\{-\tfrac{1}{2}H[\theta_1\theta_2 + \cdots + \theta_{N-1}\theta_N]\} \exp\{-H[\varepsilon_1\theta_1 + \cdots + \varepsilon_N\theta_N]\}. \end{aligned}$$

$$D = \sum_{\varepsilon_i} |Z(\varepsilon_1, \ldots, \varepsilon_N)|^2.$$

Of course, it is not likely that you will be able to get an exact extremum of I/D. But it should be possible to get an approximate one by cleverly choosing an appropriate function $Z(\varepsilon_1, \ldots, \varepsilon_N)$. To be more systematic, one might choose a class of functions $Z_\alpha(\varepsilon_1, \ldots, \varepsilon_N)$ and maximize I/D with respect to α. $e^{\beta\mu N}$ should be equal to the maximum possible value of I/D.

Problem: Find as large a value of I/D as you can. In evaluating certain sums, try setting $\theta_N = \theta_1$ and $\varepsilon_N = \varepsilon_1$; it might simplify matters if the two-dimensional lattice were wrapped around a cylinder.

We have been considering interactions such that when the temperature is absolute zero, atoms of type A and of type B alternate in the lattice. For the case of two or three dimensions, if the temperature is low enough, the crystal has long-range order. If we know what type of atoms are found at each lattice point in one region of the crystal, we know what type of atoms are likely to be found fairly far off. Note that in one dimension one wrong atom at a lattice point reverses the expected order of atoms on the other side of the defect. Thus, in two or more dimensions, we can speak of α sites and β sites, where α sites are those lattice points at which an A is more likely to be found. In one dimension we cannot do this. For the case of two dimensions, Bethe used the concept of α and β sites to describe order-disorder phenomena approximately.*

* Bethe, H. "Statistical Theory of Superlattices," *Proc. Roy. Soc.*, **150**, 552 (1935).

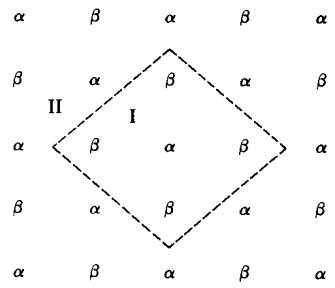


Fig. 5.2 Two-dimensional lattice with α sites and β sites.

Following Bethe, we will work with only a few atoms of the lattice and will try to describe the effect of the rest of the atoms by one parameter. We will look closely at only the atoms pictured within the dotted line (region I) of Fig. 5.2.

The relative probability of a given distribution of atoms in the entire crystal is $\exp(-H\sum_{\text{bonds}}\varepsilon_i\varepsilon_j)$ (we are assuming there are just as many A atoms as B atoms). If we consider only the five atoms in region I we have to allow for the fact that the four outer β sites are affected by region II. We do this approximately by saying that the relative probability of a given distribution of the five atoms is $\varepsilon^n \exp(-H\sum\varepsilon_i\varepsilon_j)$ where n is the number of β sites in region I that have the wrong type of atom (A) on them. The sum is only over the four bonds in region I. ε can be thought of as

$$\varepsilon = \frac{a\ priori \text{ probability that a } \beta \text{ site in region I has an } A \text{ atom}}{a\ priori \text{ probability that a } \beta \text{ site in region I has a } B \text{ atom}}.$$

By "*a priori* probability" I mean the probability that would be assumed before the thermodynamic effects of the interaction are taken into account. That is, even if there were no interactions between the atoms of region I, the interaction of the four external atoms of region I with region II would still tend to cause the β sites to be occupied by B atoms. Notice that n is not the total number of sites of region I that have the wrong atom. If the α site in the center has a B atom, we do not multiply the relative probability by another ε because region II does not interact directly with that atom. Note also that the atoms inside region I can affect each other by way of region II, so ε is only an approximate way of describing the effect of region II.

For a given value of ε we can compute w, the relative probability that the α site in region I is occupied by a B atom. We can also compute w', the relative probability that a given β site of region I is occupied by an A atom. We require that $w = w'$, because the probability of a wrong atom occupying a given site is independent of the site. The equation $w = w'$ will allow us to fix ε.

Some of the results of Bethe's method will be derived below.

$w = \sum_{n=0}^{4}$ (relative probability that the α site in region I is occupied by a B atom and there are n β sites occupied by A atoms).

There are

$$\binom{4}{n} = \frac{4!}{n!\,(4-n)!}$$

ways in which $n\beta$ sites may be occupied by A atoms. It is easy to see that

$$\sum_{\text{bonds}} \varepsilon_i \varepsilon_j = 4 - 2n.$$

Then

$$w = \sum_{n=0}^{4} \binom{4}{n} \varepsilon^n e^{-H(4-2n)} = e^{-4H} \sum_{n=0}^{4} \binom{4}{n} (\varepsilon e^{2H})^n = e^{-4H}(1 + \varepsilon e^{2H})^4$$

$$= (e^{-H} + \varepsilon e^{H})^4. \tag{5.2}$$

w is a relative, not an actual, probability. The actual probability that the α site has a B atom is w multiplied by the appropriate normalization factor.

Let r be the relative probability that the α site has an A atom. The equation for r is the same as that for w, except $H \leftrightarrow -H$.

$$r = (e^{H} + \varepsilon e^{-H})^4. \tag{5.3}$$

The normalization factor is $1/(w + r)$; so the actual probability that the site has a B atom is

$$\frac{(e^{-H} + \varepsilon e^{H})^4}{(e^{-H} + \varepsilon e^{H})^4 + (e^{H} + \varepsilon e^{-H})^4}.$$

$w' \propto \frac{1}{4}$ (expected number of β sites of region I with A atoms)

$w' = \frac{1}{4} \sum_{n=0}^{4} n$[(relative probability that n β sites are occupied by A atoms and the α site has a B atom) + (relative probability that n β sites are occupied by A atoms and the α site has an A atom)]

$$= \tfrac{1}{4} \sum_{n=0}^{4} n \binom{4}{n} \varepsilon^n [e^{-H(4-2n)} + e^{H(4-2n)}]$$

$$= \sum_{n=1}^{4} \binom{3}{n-1} \varepsilon^n [e^{-H(4-2n)} + e^{H(4-2n)}]$$

$$= \varepsilon e^{H}(e^{-H} + \varepsilon e^{H})^3 + \varepsilon e^{-H}(e^{H} + \varepsilon e^{-H})^3. \tag{5.4}$$

Equating w and w' from Eqs. (5.2) and (5.4), we find

$$(e^{-H} + \varepsilon e^{H})^4 = \varepsilon e^{H}(e^{-H} + \varepsilon e^{H})^3 + \varepsilon e^{-H}(e^{H} + e\varepsilon^{-H})^3.$$

So

$$(e^{-H} + \varepsilon e^{H})^3(e^{-H} + \varepsilon e^{H} - \varepsilon e^{H}) = \varepsilon e^{-H}(e^{H} + \varepsilon e^{-H})^3.$$

Simplifying our equation for ε, we get

$$\varepsilon^{1/3} = \frac{e^{-H} + \varepsilon e^{H}}{e^{H} + \varepsilon e^{-H}}. \tag{5.5}$$

Notice that if ε satisfies Eq. (5.5), so does $1/\varepsilon$. This fact holds because nowhere in the mathematics of our derivation did we specify that α sites, rather than β sites, are the locations for which A atoms are more probable.

Solving for e^{2H} in terms of ε, we find two solutions: either

$$e^{2H} = \frac{e^{2/3} - \varepsilon^{-2/3}}{e^{1/3} - \varepsilon^{-1/3}} = \varepsilon^{1/3} + \varepsilon^{-1/3} \tag{5.6}$$

or else $\varepsilon = 1$ and H is arbitrary (the latter solution is most easily seen from Eq. (5.5)).

The minimum value of $\varepsilon^{1/3} + \varepsilon^{-1/3}$ is 2; so if H is too small (high temperature) we must take $\varepsilon = 1$. From the definition of ε, $\varepsilon = 1$ corresponds to complete disorder. We can expect discontinuities in certain thermodynamic quantities or their derivatives at the temperature for which complete disorder sets in.

As an example of a thermodynamic calculation using the above model for order-disorder, let us calculate the energy.

Suppose a bond is an A–B bond with probability p. Then with probability p a given bond contributes energy $-H/\beta$, and with probability $(1 - p)$ the bond contributes $+H/\beta$. The expected value of the energy is

$$E = (\text{number of bonds})\left[p\left(\frac{-H}{\beta}\right) + (1-p)\left(\frac{+H}{\beta}\right)\right] = \frac{2NH}{\beta}(1 - 2p) \tag{5.7}$$

where N is the number of atoms.

$$\frac{1}{w + r}[\varepsilon e^{H}(e^{-H} + \varepsilon e^{H})^3]$$

is the probability that a given β site of region I is occupied by an A atom given that the α site has a B atom. Except for the normalizing factor $1(w + r)$, this is one of the terms in w'.

$$1 - \frac{1}{w + r}[\varepsilon e^{-H}(e^{H} + \varepsilon e^{-H})^3]$$

is the probability that a given β site of region I is occupied by a B atom, given that the α site has an A atom. The probability that a given bond between an α and a β site is an A–B bond is therefore

$$p = \frac{\varepsilon e^{H}(e^{-H} + \varepsilon e^{H})^3}{w + r} + \left(1 - \frac{\varepsilon e^{-H}(e^{H} + \varepsilon e^{-H})^3}{w + r}\right). \tag{5.8}$$

H/β is a constant independent of temperature. Using Eqs. (5.7) and (5.8) we can get $C_V = \partial E/\partial T$. We get the entropy from the equation

$$S(T) = S(T) - S(0) = \int_0^T C_V \frac{dT'}{T'}. \tag{5.9}$$

At $T = \infty$, we can compute the entropy exactly from its definition. Recall that $S = -k \sum_n P_n \ln P_n$, where P_n is the probability of state n. There are 2^N states of our N-atom system, and each has equal probability at infinite temperature. So

$$S = -k(2^N)\left(\frac{1}{2^N} \ln \frac{1}{2^N}\right) = Nk \ln 2. \tag{5.10}$$

Our approximate calculation, using Eq. (5.9) gives $S = Nk(0.697)$ instead of $Nk(0.693)$.

5.4 THE ONSAGER PROBLEM

Consider a two-dimensional square lattice of N atoms. Each atom is designated by $+1$ or -1. That is, the ith atom carries a number ε_i, which is $+1$ or -1. The energy of interaction of nearest neighbors is $+H\varepsilon_i\varepsilon_j$ in units of kT. A state of the system is denoted by giving the ε_i for each atom. The problem is to calculate the free energy of the system.

The partition function

$$Q = \sum_{\text{all states}} e^{-\beta E_K}$$

$$Q = \sum_{\text{all states}} e^{-\Sigma^* H\varepsilon_i\varepsilon_j} = \sum_{\text{all states}} \Pi^* e^{-H\varepsilon_i\varepsilon_j},$$

where Σ^* and Π^* mean the sum and product on pairs of points i and j that are adjacent on the lattice. It is easy to see that if the sign of H is changed, Q remains the same. For convenience we will write

$$Q = \sum_{\text{all states}} \Pi^* e^{H\varepsilon_i\varepsilon_j} \tag{5.11}$$

and take H positive.

Since $\varepsilon_i\varepsilon_j = \pm 1$,

$$\frac{e^{H} + e^{-H}}{2} + \varepsilon_i\varepsilon_j \frac{e^{H} - e^{-H}}{2} = e^{+\varepsilon_i\varepsilon_j H}$$

is obviously true. So

$$e^{H\varepsilon_i\varepsilon_j} = \cosh H + \varepsilon_i\varepsilon_j \sinh H$$
$$= \cosh H(1 + \varepsilon_i\varepsilon_j T), \tag{5.12}$$

where $T = \tanh H$. (Note that T does *not* represent temperature in this section.) From Eqs. (5.11) and (5.12) we find

$$Q = \sum \prod^* [\cosh H(1 + \varepsilon_i\varepsilon_j T)]. \tag{5.13}$$

Remembering that for an N atom lattice there are $2N$ bonds, we have

$$Q = \cosh^{2N} H \sum_{\text{all states}} \Pi^*(1 + \varepsilon_i\varepsilon_j T) \equiv 2^N Q' \cosh^{2N} H. \tag{5.14}$$

We must now find the modified partition function

$$Q' = \frac{1}{2^N} \sum_{\text{all states}} \Pi^*(1 + \varepsilon_i\varepsilon_j T). \tag{5.15}$$

Expanding the product we use the notation $\sum_l^*$ to indicate a sum over all possible sets of l different bonds. Then

$$2^N Q' = \sum_{\varepsilon_1 = \pm 1} \cdots \sum_{\varepsilon_N = \pm 1} \{1 + T\Sigma_1^* \varepsilon_i\varepsilon_j + T^2\Sigma_2^*(\varepsilon_i\varepsilon_j)(\varepsilon_{i'}\varepsilon_{j'}) + \cdots\}. \tag{5.16}$$

Note that in each term, the ε's occur in pairs corresponding to nearest neighbors, and no such pair occurs twice in the same product.

Associate with each pair $\varepsilon_i\varepsilon_j$ a bond connecting the ith and jth atoms (i and j are nearest neighbors). With each term or product of $2l$ ε's, we associate a graph or set of l bonds. Because no pair $\varepsilon_i\varepsilon_j$ appears twice in a given term, no bond appears twice in a given graph. For example, Fig. 5.3 gives the graph associated with the term

$$(\varepsilon_1\varepsilon_2)(\varepsilon_3\varepsilon_4)(\varepsilon_5\varepsilon_6)(\varepsilon_1\varepsilon_5)(\varepsilon_2\varepsilon_6)(\varepsilon_3\varepsilon_7)(\varepsilon_4\varepsilon_8)(\varepsilon_7\varepsilon_8)(\varepsilon_{10}\varepsilon_{11})(\varepsilon_{10}\varepsilon_{14}).$$

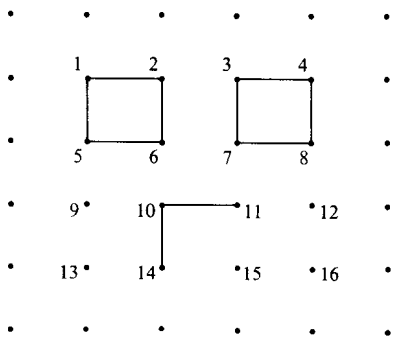


Fig. 5.3 A graph or set of l bonds.

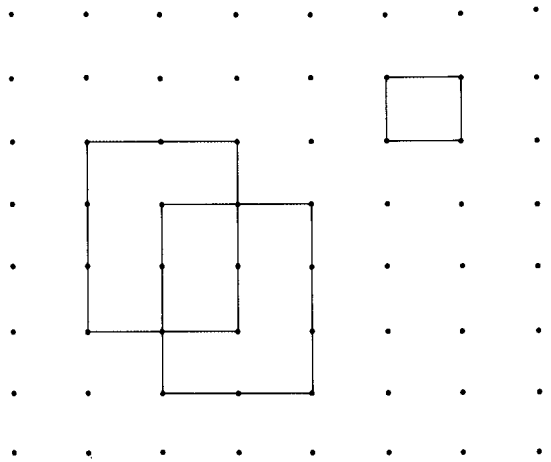


Fig. 5.4 Example of a closed graph

Now,

$$\sum_{\varepsilon=\pm 1} \varepsilon = 0 \quad \text{and} \quad \sum_{\varepsilon=\pm 1} \varepsilon^2 = 2. \tag{5.17}$$

From Eqs. (5.16) and (5.17), it is clear that only those terms where each ε_i appears an even number of times will contribute to Q'. This is equivalent to saying that the only graphs that count (or contribute to Q') are those in which each atom or lattice point has an even number (0, 2, or 4) of bonds emanating from it. In other words, the contributing graphs must be superpositions of simple closed polygons having no common sides. Such graphs may be called "closed graphs."

Figure 5.4 gives an example of a closed graph. Note that the graph of Fig. 5.3 is not closed and does not contribute to Q'. Figure 5.5 is another example of

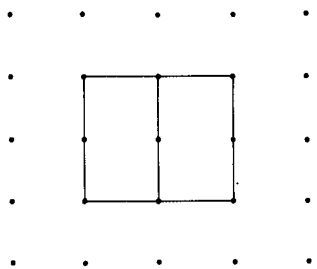


Fig. 5.5 Example of an "Unclosed" Graph.

a nonclosed graph, which contributes zero. Each term in Eq. (5.16) corresponding to a closed graph has each ε_i occuring to an even power (0, 2, or 4), and therefore equals simply T^L, where L is the number of bonds. Summing over all ε_i gives a factor 2^N, which is cancelled by the 2^N on the left side of Eq. (5.16). Each closed graph of length L thus contributes a term T^L to Q'; so

$$Q' = \sum_L g(L)T^L, \tag{5.18}$$

where $g(L)$ is the number of closed graphs of length L that can be drawn on the lattice. Notice that $g(L) = 0$ unless L is even, so the sign of T (and therefore the sign of H) is immaterial, as we expected.

Method of Finding Transition Point

We now digress for a moment to show a method (due to Kramers and Wannier) by which the transition point of the Onsager problem can be found. This method is not powerful enough to yield an analytic expression for the partition function.

Consider a closed graph on the lattice. Label the midpoints of the lattice squares $\mu_i = +1$ if inside the graph and $\mu_i = -1$ if outside. (See Fig. 5.6.)

Consider a bond (---) between midpoints of unlike μ values. Each of these bonds corresponds to a bond of the closed graph (because each -- bond cuts a — bond).

We now have two lattices. The new lattice is formed by putting "atoms" described by μ_i at the midpoint of the old lattice. For the new lattice we can discuss Q at a temperature T' and such that the interaction energy is h in units at kT'. Then

$$Q(h) = \sum_{\text{all states}} \Pi^* e^{h\mu_i\mu_j}.$$

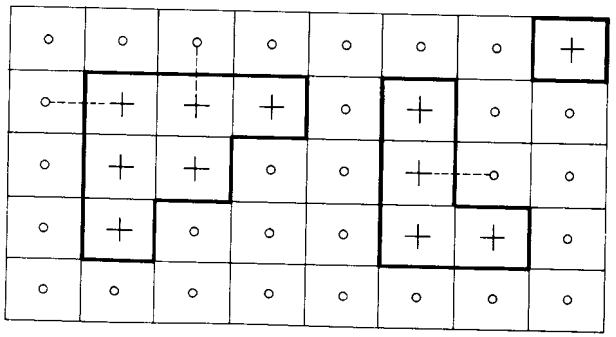


Fig. 5.6 Midpoints of lattice squares labelled + inside the closed graph and – outside it.

If $\mu_i = +\mu_j$, then $\mu_i\mu_j = +1$, and there is a contribution e^{+h}. If $\mu_i = -\mu_j$, then the contribution is e^{-h}.

Now, if in a given state there are L unlike bonds and $2N - L$ like bonds, then its contribution to $Q(h)$ is

$$e^{-Lh}e^{(2N-L)h}$$

so that

$$Q(h) = e^{2Nh}\sum_L m(L)e^{-2Lh}$$

where $m(L)$ is the number of ways by which unlike pairs can be arranged on the lattice.

But from the preceding argument (concerning --- and — bonds), $m(L) = g(L)$, where $g(L)$ is defined by Eq. (5.18).

Thus

$$Q(h) = e^{2Nh}\sum_L g(L)e^{-2Lh},$$

$$Q(H) = 2^N \cosh^{2N} H \sum_L g(L)T^L.$$

Let us now define h by $e^{-2h} = T = tghH$. Then:

$$Q(h) = \tanh^{-N} H \sum_l g(l)T^l$$

and we get the identity

$$Q(H) = 2^N \cosh^{2N} H \tanh^N H\, Q(h).$$

Now, when H is large, h is small; if $Q(H)$ has a singular point, so does $Q(h)$. That is, if there is a transition at H_{cr}, there is also a transition at h_{cr}. If we assume that there is only one transition or Curie point, $H_{cr} = h_{cr}$ and $H_{cr} = -\frac{1}{2}\ln(\tanh H_{cr})$. This can be solved to give

$$H_{cr} = \tfrac{1}{2}\log(1 - \sqrt{2}).$$

You might hope that we could use the identity

$$Q[x] = 2^N \cosh^{2N} x \tanh^N x Q[-\tfrac{1}{2}\ln\tanh x] \qquad (5.19)$$

to find $Q(x)$ for many values of x given $Q(x)$ for one value of x. Just plug in x on the left side of Eq. (5.19) and get Q evaluated at another value,

$$x' = -\tfrac{1}{2}\ln\tanh x.$$

We can then get Q evaluated at

$$x'' = -\tfrac{1}{2}\ln\tanh x'.$$

Unfortunately, $x'' = x$, so this method is not useful.

Continuation of Onsager Problem

Call $h(l)$ the number of ways that, starting from the atom (origin), we can proceed in l steps (l bonds) through the lattice and return to the origin without using the same bond twice. In $h(l)$ we do not count separately the two or more different paths we can use to form the same polygon.

For carrying out the calculation we shall need the sum over all different l polygons of the crystal. Our $h(l)$ polygons for atom A in Fig. 5.7, say, will be counted again in the $h(l)$ polygons of other atoms, say B in Fig. 5.7. Each polygon will occur l times. Therefore, the number of polygons per atom is $h(l)/l$. Let

$$q = \sum_{l=1}^{\infty}\frac{h(l)}{l}T^l. \qquad (5.20)$$

We have

$$Q' = \sum_L g(L)T^L = \sum_{\substack{\text{closed}\\ \text{diagrams}}} T^L,$$

but need an expression for Q' that we can hope to evaluate. We will work up to such an expression by finding an approximation to Q', which we will then correct by means of a trick.

A term from a closed diagram can be thought of as a product of terms made up of graphs formed by polygons. The contribution to Q' from no polygons is simply 1. The contribution from graphs consisting of one polygon is Nq, for the number of graphs consisting of one polygon of length l is $Nh(l)/l$. The contribution from pairs of polygons, one of length l and the other of length l' is $(Nh(l)/l)(Nh(l')/l')T^{l+l'}$ so the contribution from pairs of polygons of any length is about

$$\frac{1}{2}\sum_{l,l'}\left(\frac{Nh(l)}{l}\right)\left(\frac{Nh(l')}{l'}\right)T^{l+l'},$$

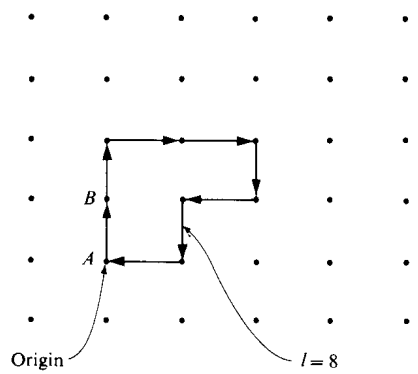
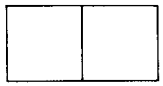
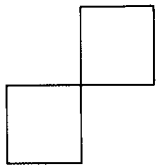


Fig. 5.7 A polygon formed by proceeding through the lattice back to the starting point, without using the same bond twice.

where the factor of 1/2 is to account for the fact that we count each pair twice. So the contribution from pairs is about $\frac{1}{2}N^2q^2$. I say "about" because we have counted such graphs as



even though that pair of squares is not "closed," since one bond appears twice. Furthermore



is a pair of squares and is also a single polygon of length 8, so we have counted it twice. If we continue to ignore such errors, we get

$$Q' \approx 1 + Nq + \tfrac{1}{2}(Nq)^2 + \tfrac{1}{3}!(Nq)^3 + \cdots = e^{Nq}. \qquad (5.21)$$

Our next step logically should be to correct q in order to get Q' right. We can correct q by correcting $h(l)$. Let us write down a few of the correction terms.

Because of the presence of polygon 5.8a

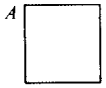
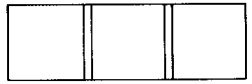


Fig. 5.8a

in the first-order term in Q, we obtained the forbidden graph of 5.8b

Fig. 5.8b

in *second* order (i.e., as a product of *two* polygons). To cancel graph 5.8b, we insert graph 5.8b into $h(8)$ with a negative sign. But then in Q' we seem to get terms such as



in both second and third order. In second order, there are two terms that form a diagram of type 5.8c, and both have a negative sign:

and

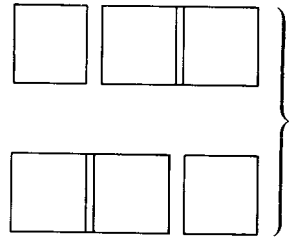


Fig. 5.8c

that is, there are two ways of writing 5.8c as a product of 5.8a and a 5.8b type term. In third order, one of the two second-order terms is canceled by the positive product of three type (a) terms. To cancel the other second order term of type (c), we must insert (c) with a positive sign into $h(12)$.

In Eq. (5.21), we counted polygon 5.8d twice; therefore when we get a rule for what terms belong in our corrected $h(l)$ and what their signs should be, we will have to have an excuse for not counting (d) in the corrected $h(l)$.

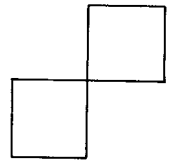


Fig. 5.8d

Now, let us look at where we stand. In evaluating $h(l)$ we expected trouble because of the restriction to certain allowed polygons. In correcting $h(l)$ we found that there must be other polygons with not necessarily positive contribution, and some of the allowed polygons should not be counted. The natural thing to do is assign each polygon an appropriate weight, and not ignore any polygon in the sum. Recall that formerly we did not count separately the two or more different paths we can follow when starting our from an atom and forming a polygon. Now we will count all the different paths, but we will choose the weight of each path so that our corrected "q" will lead to the right value of Q' when we use Eq. (5.21).

A Topological Theorem

Give a weight $\alpha = e^{i\pi/4}$ for a left turn and $\alpha^{-1} = e^{-i\pi/4}$ for a right turn, and keep track of the left and right turns as a closed path (returning to origin) is traversed in the lattice. The topological argument of Kac and Ward is that the

closed graphs (or ones that we want to count) will be counted, and the forbidden graphs (e.g., Fig. 5.5) will cancel out when different ways of traversing them are considered. That this theorem is true for simple cases will now be demonstrated by a few examples. The complete proof was given by Sherman* and is rather involved.

Consider the simple closed polygon in Fig. 5.8a.

Starting at A and returning to A in a clockwise direction we note that 4 right turns were made giving a total weight of

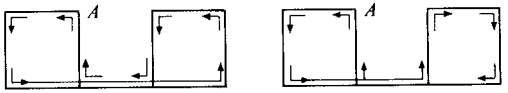
$$\alpha^{-4} = (e^{-i\pi/4})^4 = -1.$$

Proceeding in a counterclockwise way gives a weight of

$$(\alpha)^4 = (e^{i\pi/4})^4 = -1.$$

The total weight is thus -2, and the simple polygon is indeed counted. To get the correct weight of 1, we multiply everything by $-1/2$.

Now, consider the polygons in Fig. 5.8e and e′:



(e) (e′)

Fig. 5.8

In Fig. 5.8(e), the path is traced out in such a way (starting from A) that there are 6 left turns and 2 right turns for a total weight of $\alpha^6(\alpha^{-2}) = (\alpha^4) = -1$. In Fig. 5.8(e′) the path is traced out in such a way that there are 4 left turns and 4 right turns for a total weight of $\alpha^4\alpha^{-4} = 1$. The total weight then of the two clockwise paths is $-1 + 1 = 0$. It is clear that the two counterclockwise paths have weight 0 also.

Similarly you should be able to show that 5.8(b), 5.8(c), and 5.8(d) and all simple polygons give the correct contribution (remember that everything is multiplied by $-1/2$).

Method of Calculating partition Function

Let q denote our corrected value of q. Then

$$q = \sum_{l=1}^{\infty} \frac{\{\text{corrected } h(l)\}}{l} T^l$$

and

$$Q' = e^{Nq} - 2T\frac{dq}{dT} = -2\sum_{l=1}^{\infty} \{\text{corrected } h(l)\}T^l$$

* Sherman, S., *J. Math. Phys.*, **1**, 202 (1960); **4**, 1213 (1963).

which is the sum over all paths leaving and returning to the origin of a complex "amplitude" or weight for each path. This amplitude is the product of amplitudes for each lattice point passed:

T if one continues forward:

$T\alpha$ if one turns counterclockwise: $\alpha = e^{i\pi/4}$;
$T\alpha^{-1}$ if one turns clockwise: $\alpha^{-1} = e^{-i\pi/4}$;
0 if one turns 180°.

In our rule for determining the amplitude for each lattice point passed, we have neglected to say how to deal with the first step, whose amplitude depends on the last step. In what follows, we will calculate the amplitude to start at the origin and arrive back at the origin from below, that is, moving upward. Thus, we will choose as our rule for the amplitude of the first step:

T if one starts upward;
$T\alpha$ if one starts to the left;
$T\alpha^{-1}$ if one starts to the right;
0 if one starts downward.

More generally, we will use the above rule for the first step and work with amplitudes for starting at the origin and arriving at any lattice point (x, y). We shall have to describe the amplitude by giving four components: $U(x, y)$, the amplitude to arrive at x, y moving upward; $D(x, y)$, the amplitude to arrive moving downward; $R(x, y)$, the amplitude to arrive *from* the right; and $L(x, y)$, the amplitude to arrive *from* the left. This, as mentioned before, is because the amplitude to make the next step depends on the arrival direction, and we shall have to keep track of it.

Roughly, what we will do is calculate the amplitudes for arriving at (x, y) from various directions in exactly n steps, and then sum over n. $U_n(x, y)$ is the amplitude to arrive at (x, y) in exactly n steps with the last step upward and similarly for D_n, R_n, and L_n. We assume that in the zeroth step we arrive at the origin moving upward. Thus $U_0(x, y) = \delta_{x,0}\delta_{y,0}$, $D_0 = R_0 = L_0 = 0$.

In other words, the amplitude to arrive in zero steps is one if we arrive upward at the origin and zero for any other point or any other direction of arrival. With these amplitudes for the zeroth step, we can get the amplitudes for any number of steps by recursion. We can write for the amplitude to arrive upward at (x, y) in $n + 1$ steps in terms of amplitudes to arrive from $(x, y - 1)$ in n steps.

$$U_{n+1}(x, y) = TU_n(x, y - 1) + T\alpha L_n(x, y - 1) + T\alpha^{-1}R_n(x, y - 1).$$

If we came to $x, y-1$ going up, we have an additional amplitude factor T. If we came to $x, y-1$ from the left, we need to turn counterclockwise and add a factor $T\alpha$, and so on. We cannot get to x, y going up if we previously entered $x, y-1$ going down, for we do not allow paths that reverse themselves. Similar expressions for $R_n(x, y)$, $L_n(x, y)$, and $D_n(x, y)$ are easily written.

Then we see that our assumption for the amplitude of the zeroth step will give, for the first step, the correct amplitudes (such as T if one starts upwards). When summing over n, we will eventually have to subtract out the $n = 0$ term, because we do not consider a figure with zero side to be a polygon, even though it starts and ends at the origin.

To simplify the summation over n, we define the transform of $U_n(x, y)$

$$U_n(\xi, \eta) = \sum_{x=-\infty}^{\infty} \sum_{y=-\infty}^{\infty} U_n(x, y) e^{-i\xi x} e^{-i\eta y}. \tag{5.22}$$

Then

$$U_n(x, y) = \int_0^{2\pi} \int_0^{2\pi} e^{i\xi x} e^{i\eta y} U_n(\xi, \eta) \frac{d\xi\, d\eta}{(2\pi)^2}.$$

For example, the transform of $U_n(x, y-1)$ is $e^{-i\eta} u_n(\xi, \eta)$, and the transform of $U_0(x, y)$ is 1. The transformed equation then reads

$$\begin{aligned} U_{n+1}(\xi, \eta) = {} & Te^{-i\eta} U_n(\xi, \eta) + 0 \cdot e^{-i\eta} D_n(\xi, \eta) + T\alpha e^{-i\eta} L_n(\xi, \eta) \\ & + T\alpha^{-1} e^{-i\eta} R_n(\xi, \eta). \end{aligned} \tag{5.23}$$

and similarly for $D_{n+1}(\xi, \eta)$, $L_{n+1}(\xi, \eta)$, and $R_{n+1}(\xi, \eta)$.

If we let ψ_n be a four-component symbol (column vector) with components (U_n, D_n, L_n, R_n), we can write the matrix equation

$$\psi_{n+1}(\xi, \eta) = TM(\xi, \eta)\psi_n(\xi, \eta) \tag{5.24}$$

where $M(\xi, \eta)$ is the matrix

$$M(\xi, \eta) = \begin{vmatrix} e^{-i\eta} & 0 & \alpha e^{-i\eta} & \alpha^{-1} e^{-i\eta} \\ 0 & e^{i\eta} & \alpha^{-1} e^{i\eta} & \alpha e^{i\eta} \\ \alpha^{-1} e^{-i\xi} & \alpha e^{-i\xi} & e^{-i\xi} & 0 \\ \alpha e^{i\xi} & \alpha^{-1} e^{i\xi} & 0 & e^{i\xi} \end{vmatrix}. \tag{5.25}$$

$$\begin{aligned} \psi_0(\xi, \eta) &= (1, 0, 0, 0). \\ \psi_1(\xi, \eta) &= TM\psi_0 \\ \psi_2 &= TM\psi_1 = (TM)^2\psi_0 \\ &\vdots \\ \psi_n &= (TM)^n \psi_0. \end{aligned}$$

Then

$$\psi = \sum_{n=0}^{\infty} (TM)^n \psi_0 = \frac{1}{1 - TM} \psi_0$$

is the transform of the amplitude to arrive in any number of steps. The amplitude to arrive at the origin moving upward is

$$\begin{aligned} \sum_{n=1}^{\infty} U_n(0, 0) &= -1 + \sum_{n=0}^{\infty} U_n(0, 0) = -1 + \psi_0 \cdot \int_0^{2\pi} \int_0^{2\pi} e^{i\xi 0} e^{i\eta 0} \\ &\quad \times \frac{1}{1 - TM} \psi_0 \frac{d\xi\, d\eta}{(2\pi)^2} \\ &= \int_0^{2\pi} \int_0^{2\pi} \left(\psi_0 \cdot \frac{1}{1 - TM} \psi_0 - 1 \right) \frac{d\xi\, d\eta}{(2\pi)^2}. \end{aligned}$$

We could have arrived at the origin moving in any direction, so we must sum over all four values of ψ_0, that is $\psi_0 = (1, 0, 0, 0)$, $\psi_0 = (0, 1, 0, 0)$, $\psi_0 = (0, 0, 1, 0)$, $\psi_0 = (0, 0, 0, 1)$. The result is a trace. Thus,

$$-2T \frac{dq}{dT} = \int_0^{2\pi} \int_0^{2\pi} \operatorname{Tr} \left[\frac{1}{1 - TM} - 1 \right] \frac{d\xi\, d\eta}{(2\pi)^2} \tag{5.26}$$

$$\begin{aligned} q &= \int_0^{2\pi} \int_0^{2\pi} \frac{d\xi\, d\eta}{(2\pi)^2} \operatorname{Tr} \left[\int_0^T - \frac{1}{2t(1 - tM)} + \frac{1}{2t} \right] dt \\ &= \int_0^{2\pi} \int_0^{2\pi} \frac{d\xi\, d\eta}{(2\pi)^2} \operatorname{Tr} \left[\int_0^T \frac{-M}{2(1 - tM)} dt \right] \\ &= \frac{1}{2} \int_0^{2\pi} \int_0^{2\pi} \frac{d\xi\, d\eta}{(2\pi)^2} \operatorname{Tr} [\log (1 - TM)] \\ &= \frac{1}{2} \int_0^{2\pi} \int_0^{2\pi} \frac{d\xi\, d\eta}{(2\pi)^2} \log \det (1 - TM), \end{aligned} \tag{5.27}$$

we have used the following theorem:

$$\operatorname{Tr} \log A = \log \det A.$$

To prove this identity, note that

$$\begin{aligned} \det e^B &= \lim_{N \to \infty} (\det e^{B/N})^N = \lim_{N \to \infty} \left[\det \left(1 + \frac{B}{N} \right) \right]^N \\ &= \lim_{N \to \infty} \left(1 + \frac{1}{N} \operatorname{Tr} B \right)^N = e^{\operatorname{Tr} B}. \end{aligned}$$

Therefore, $\log\det e^B = \operatorname{Tr} B$. Let $B = \log A$. Then $\operatorname{Tr}\log A = \log\det A$.

M is given by Eq. (5.25), and one obtains

$$\det[1 - TM] = (T^2 + 1)^2 - 2T(1 - T^2)(\cos\xi + \cos\eta). \quad (5.28)$$

Summarizing, we see that

$$BF/N = -\ln Q/N,$$
$$Q = 2^N(\cosh^{2N} H)Q',$$
$$Q' = e^{Nq}$$
$$q = \frac{1}{2}\int_0^{2\pi}\int_0^{2\pi}\frac{d\xi\, d\eta}{(2\pi)^2}\log\det(1 - TM),$$
$$\det(1 - TM) = (T^2 + 1)^2 - 2T(1 - T^2)(\cos\xi + \cos\eta)$$
$$T = \tanh H.$$

Putting all this together we obtain*

$$\frac{BF}{N} = -\ln 2 - \frac{1}{2}\int_0^{2\pi}\int_0^{2\pi}\frac{d\xi\, d\eta}{(2\pi)^2}\ln[\cosh^2 2H - \sinh 2H(\cos\xi + \cos\eta)]. \quad (5.29)$$

5.5 MISCELLANEOUS COMMENTS

In the above we sometimes assumed that the lattice was finite (with N points) and we sometimes assumed it was infinite (when we neglected the boundary for example). Because N was assumed to be very large, it is plausible to suppose that our inconsistency made little difference. However, let us modify the above work to make it consistent.

Assume the lattice has the topology of a torus. If we pass through L points in one direction (or L' points in the perpendicular direction) we finish back where we started. Formerly, to compute the amplitude to arrive back at the origin moving upward, we took the sum

$$\sum_{n=1}^{\infty} U_n(0, 0).$$

Now, we must take the sum

$$\sum_{p=-\infty}^{\infty}\sum_{q=-\infty}^{\infty}\sum_{n=1}^{\infty} U_n(pL, qL').$$

* A slightly different treatment for the Onsager problem was given by N.V.Vdovichenko, *Soviet Phys. JETP* **20**, 2, 477 (1965); also see *Soviet Phys. JETP* **21**, 2, 350 (1965).

Continuing as before, we get in place of Eq. (5.29),

$$\frac{\beta F}{N} = -\ln 2 - \frac{1}{2}\int_0^{2\pi}\int_0^{2\pi}\frac{d\xi\, d\eta}{(2\pi)^2}\sum_{p,q} e^{ipL\xi}e^{iqL'\eta} \times \ln[\cosh^2 2H - \sinh 2H(\cos\xi + \cos\eta)].$$

But

$$\sum_{p=-\infty}^{\infty} e^{ipL\xi} = \frac{2\pi}{L}\sum_{n=-\infty}^{\infty}\delta\left(\xi - \frac{2\pi n}{L}\right).$$

So

$$\frac{\beta F}{N} = -\ln 2 - \frac{1}{2}\sum_{m=0}^{L}\sum_{n=0}^{L'}\left(\frac{2\pi}{L}\right)\left(\frac{2\pi}{L'}\right)\frac{1}{(2\pi)^2} \times \ln\left[\cosh^2 2H - \sinh 2H\left(\cos\frac{2\pi m}{L} + \cos\frac{2\pi n}{L'}\right)\right]. \quad (5.30)$$

As L and L' tend to infinity, Eq. (5.30) approaches Eq. (5.29).

A few comments about the form of Eq. (5.29) are in order. If we use the expression

$$\beta F = -\log\sum_{\text{states}} e^{-\beta E}$$

we can verify that Eq. (5.29) is correct for high temperatures ($H \to 0$) and low temperatures ($H \to \infty$). Another check of Eq. (5.29) is by way of Eq. (5.19). If we consider Q as a function of $y = \sinh 2H$ instead of as a function of H, Eq. (5.19) can be written in an especially simple form. Because $\sinh 2H = 2\cosh H \sinh H = 2\cosh^2 H \tanh H$,

$$Q(y) = 2^N\cosh^{2N} H\tanh^N HQ\left(\frac{1}{y}\right) = \sinh^N 2HQ\left(\frac{1}{y}\right) = y^NQ\left(\frac{1}{y}\right). \quad (5.19a)$$

Equation (5.29) can be written

$$\frac{\beta F}{N} = -\ln 2 - \tfrac{1}{2}\ln y - \frac{1}{2}\int_0^{2\pi}\int_0^{2\pi}\frac{d\xi\, d\eta}{(2\pi)^2}\ln\left[y + \frac{1}{y} - (\cos\xi + \cos\eta)\right]. \quad (5.29a)$$

from which it can be seen that Eq. (5.19a) holds.

Kac made the conjecture that the solution for the three-dimensional Onsager problem (cubic lattice), is of the same form as Eq. (5.29) except that $\cos\xi + \cos\eta$ is replaced by $\cos\xi + \cos\eta + \cos\zeta$ and $d\xi\, d\eta/(2\pi)^2$ by $d\xi\, d\eta\, d\zeta/(2\pi)^3$. However, this conjecture is false.

Instead let us conjecture that the specific linkage of the Ising lattice will not greatly affect the character of the transition point in the specific heat curve. Also, an approximation starting from the transition point should prove very

valuable. If a magnetic field is added to the Onsager problem, the problem of evaluating the partition function can again be converted to a path problem, which has not been solved. The problem here is to keep track of the area encircled as well as the length of the path.

We have done a lot of work just to evaluate the expression

$$Q = \sum_{\varepsilon_i = \pm 1} \exp\left(-H \sum_{\text{bonds}} \varepsilon_i \varepsilon_j\right).$$

One reason for going to all this trouble is that maybe you will be able to generalize the methods used, or apply them somewhere else. For example, we considered a statistical-mechanical problem for which we eventually had to evaluate a sum over all paths leaving and returning to the origin, with an amplitude depending on the preceding step. This is essentially a Markovian walk, with each step depending only on the one previous step. A Markovian-walk problem, however, can be handled when each step depends on a specific finite number of preceding steps. In a way analogous to the method used above, Q_n can be found for the case where the amplitude of a step depends on the n steps preceding it. The question is: Can one find an interesting problem whose partition function is Q_n?

CHAPTER 6

CREATION AND ANNIHILATION OPERATORS

6.1 A SIMPLE MATHEMATICAL PROBLEM

In this chapter we shall describe an operator formalism that has widespread applications in quantum mechanics, notably in dealing with harmonic oscillators and in describing many-particle systems.

We begin by formulating and solving the following simple problem: Suppose an operator a satisfies

$$[a, a^+] = 1. \tag{6.1}$$

The problem is to find the eigenvalues of the Hermitian operator a^+a, and to relate the eigenvectors. (Note: a^+ denotes the Hermitian conjugate of a, and $[A, B]$ is, of course, the commutator $AB - BA$.)

We first note that, if $|\alpha\rangle$ is a normalized eigenvector with

$$a^+a|\alpha\rangle = \alpha|\alpha\rangle, \tag{6.2}$$

then

$$\alpha = \langle\alpha|a^+a|\alpha\rangle = \|a|\alpha\rangle\|^2 \geq 0. \tag{6.3}$$

That is, the eigenvalues are all real and nonnegative. Using the identity $[AB, C] = A[B, C] + [A, C]B$, we observe that

$$[a^+a, a] = [a^+, a]a = -a, \tag{6.4}$$

$$[a^+a, a^+] + a^+[a, a^+] = a^+; \tag{6.5}$$

or, equivalently,

$$(a^+a)a = a(a^+a - 1), \tag{6.4'}$$

$$(a^+a)a^+ = a^+(a^+a + 1). \tag{6.5'}$$

From Eq. (6.4') we have, for an eigenvector $|\alpha\rangle$,

$$(a^+a)a|\alpha\rangle = a(a^+a - 1)|\alpha\rangle = a(\alpha - 1)|\alpha\rangle = (\alpha - 1)a|\alpha\rangle. \tag{6.6}$$

Therefore $a|\alpha\rangle$ is an eigenvector with eigenvalue $\alpha - 1$, unless $a|\alpha\rangle = 0$. Similarly $a^+|\alpha\rangle$ is an eigenvector with eigenvalue $\alpha + 1$, unless $a^+|\alpha\rangle = 0$. The norm of $a|\alpha\rangle$ is found from

$$\|a|\alpha\rangle\|^2 = \langle\alpha|a^+a|\alpha\rangle = \alpha\langle\alpha|\alpha\rangle = \alpha,$$