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EFFECT OF THE NEXT-NEAREST NEIGHBOR INTERACTION ON THE ORDER-DISORDER PHASE TRANSITION

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Abstract

In this work, one and two-dimensional lattices are studied theoretically by a statistical mechanical approach. The nearest and next-nearest neighbor interactions are both taken into account, and the approximate thermodynamic properties of the lattices are calculated. The results of our calculations show that: (1) even though the next-nearest neighbor interaction may have an insignificant effect on the entropy of either the almost purely ordered or disordered phase, it does have a significant effect on the entropy of the lattice when the order-disorder transition is taking place. (2) The next-nearest neighbor interaction broadens the range of temperature on which the transition occurs. (3) The transition takes place more slowly with respect to temperature, when the next-nearest neighbor interaction is considered.(4) The average temperature, at which the transition occurs, shifts to a higher one when there is an increase in the next-nearest neighbor interaction.

Introduction

The first exact solution to the one-dimensional lattice was given by Ising [1] in 1925, by taking only the nearest neighbor interaction into account. A matrix method was then introduced by Kramer [2]. This matrix method was used by Onsager [3] who, after a very long and sophisticated argument, was able to obtain the solution to the two-dimensional square lattice in closed form, but only when the fractions of both species were equal (F=0.5). A new method has recently been introduced, by which an exact solution can be obtained for the macroscopic properties of the one-dimensional Ising model, if three exact constraints, which are given in this paper, are used [4]. However, this method gives an approximate solution to the higher dimensional models, if four constraints, which are given in this work, are used. In this approach, a method called "the extended sequential construction method" (ESCM) is used for the cases in which only the nearest neighbor interaction is considered. The main aim in this work is to use ESCM in such a way that one can take the next-nearest neighbor interaction into account, as well as the nearest neighbor interaction.

Keywords: Order-disorder transition; Next-nearest neighbor interaction

There is no exact solution available either for the one-dimensional or for the two and three-dimensional lattice models, when the nearest and the next-nearest neighbor interactions are both taken into account. However, there are some approximation methods like the quasi-chemical method [5] and Kikuchi's approach [6] by which the nearest and the next-nearest neighbor interactions may be taken into account by using some larger groups of sites than pairs. Here, we shall use the ESCM approach.

The next-nearest neighbor interaction becomes more important when the interaction among atoms have a longer range. For example, if the interaction is Coulombic, the next-nearest neighbor interaction is 50% of the nearest neighbor interaction for one-dimensional lattices, and 71% of the nearest neighbor interaction for two-dimensional square lattices. If we consider the interaction between two molecules to be proportional to $1/r^6$ (where r is the intermolecular distance) then these numbers will

reduce to 1.6 (for one-dimensional lattices) and 12.5 (for two-dimensional square lattices), respectively. In most cases, however, the interaction is within the same range as the above two cases (the interaction energy between two ions is proportional to $1/r$ and the attraction between two spherical neutral molecules with uniform charge distribution is proportional to $1/r^6$).

There are some systems in which the long-range interactions play an important role in their physical properties. For example, the properties of the diluted magnetic semiconductors depend on the long-range interaction between magnetic ions [7]. In these systems, even the interaction with a longer range than the nearest and the next-nearest neighbor interaction should be considered.

Experimental Section

Thermodynamic Properties of the One-Dimensional Lattice

We shall carry out calculations for the one-dimensional model in detail, and then extend the results to the two-dimensional square lattice. The approach is, in principle, the same as that presented in reference 4 and is called the extended sequential construction method, or ESCM. In order to take the next-nearest neighbor interaction into account, however, the sites must be divided into "solid" and "nonsolid" in a different way from that presented in reference 4, even though sites are all identical and such a division is quite artificial. We consider a binary one-dimensional lattice with N sites which are located along a straight line. Unlike the previous case (ESCM) [4], both the nearest and the next-nearest neighbors of each solid site are considered to be nonsolid sites, as shown in Figure 1(a). Therefore, one third of the sites (full circles in Figure 1(a)) are considered to be solid sites and the others (open circles) are considered to be nonsolid sites.

We consider a binary one-dimensional lattice with N sites, where each site is occupied by only one atom (or molecule), A or B. We also assume an interaction energy between two atoms which are located on two nearest neighbor sites. The energy for such interaction will be denoted by ε_{AA}, ε_{AB}, and ε_{BB} if the sites are occupied by two A, one A and one B, and two B atoms, respectively. Similarly, the interaction energy between two atoms

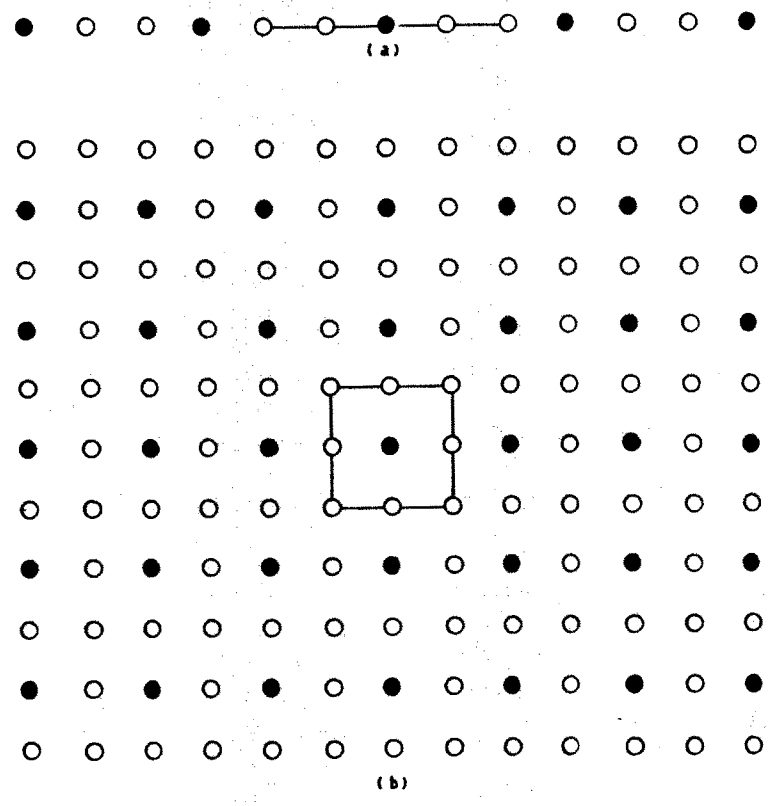

Figure 1. (a) One-dimensional and (b) two-dimensional square lattice. The full circles are solid sites and the open ones are nonsolid sites. The group of sites which are connected by lines are considerd as a "basic unit".

located on two next-nearest neighbor sites will be denoted by ε'_{AA}, ε'_{AB}, and ε'_{BB} if the sites are occupied by an AA, AB, and BB pair, respectively. We shall calculate the combinatorial factor, configurational entropy and energy for this model lattice, when A and B atoms are distributed among the sites. The calculations may be carried out as follows:

(1) Consider the nearest and the next-nearest neighbor sites of a solid site, the number of which is equal to 2+2 in this case (see Figure 1(a)). We shall call this group of sites the "basic unit" and denote it by Z_{ij}, where the subscripts i and j represent the configuration of the basic unit. A basic unit has a total number of $2^4 = 16$ configurations, excluding the configurations of its solid site. Each configuration for the basic unit will be represented by Z_{ij}, where the subscripts i and j are used for the number of A atoms on the nearest and the next-nearest neighbor sites of the solid site, respectively. All configurations for a basic unit are shown in Table I, on the left-hand side. If the configurations of the solid site of a basic unit are included, then there are $2^5 = 32$ configurations for a basic unit, as shown in Table I (on the right-hand side). The number of basic units in the lattice

Basic unit	Configuration	Number	Configuration	Number/(N/3)
Z_{22}	A A ● A A	Q_{22} N/3	A A ● A A	Q_{22} P_{22}
			A A ● A A	$Q_{22}(1-P_{22})$
Z_{21}	B A ● A A	$2Q_{21}$ N/3	B A ● A A	$2Q_{21}$ P_{21}
			B A ● A A	$2Q_{21}(1-P_{21})$
Z_{12}	A B ● A A	$2Q_{12}$ N/3	A B ● A A	$2Q_{12}$ P_{12}
			A B ● A A	$2Q_{12}(1-P_{12})$
Z_{20}	B A ● A B	Q_{20} N/3	B A ● A B	Q_{20} P_{20}
			B A ● A B	$Q_{20}(1-P_{20})$
Z_{02}	A B ● B A	Q_{02} N/3	A B ● B A	Q_{02} P_{02}
			A B ● B A	$Q_{02}(1-P_{02})$
Z_{11}	B B ● A A	$4Q_{11}$ N/3	B B ● A A	$4Q_{11}$ P_{11}
			B B ● A A	$4Q_{11}(1-P_{11})$
Z_{01}	A B ● B B	$2Q_{01}$ N/3	A B ● B B	$2Q_{01}$ P_{01}
			A B ● B B	$2Q_{01}(1-P_{01})$
Z_{10}	B A ● B B	$2Q_{10}$ N/3	B A ● B B	$2Q_{10}$ P_{10}
			B A ● B B	$2Q_{10}(1-P_{10})$
Z_{00}	B B ● B B	Q_{00} N/3	B B ● B B	Q_{00} P_{00}
			B B ● B B	$Q_{00}(1-P_{00})$

Table 1. Basic unit, configurations for a basic unit, and the number of basic units for the one-dimensional lattice.

with different configurations are all given in this Table. Note that on the one hand, each basic unit has one solid site, while on the other hand, one third of sites are solid, thus the total number of basic units in the lattice must be equal to N/3.

(2) First we consider a basic unit with a Z_{22} configuration (four A atoms on its nonsolid sites, see Table I). Suppose there are $Q_{22}N/3$ of such basic units in the lattice, where Q_{22} is the probability of having such a configuration, and N/3 is the total number of basic units in the lattice. If the probability of having A atom on the solid site of such a basic unit is presented by P_{22}, then the probability of having B atom on this solid site is equal to $(1-P_{22})$. Note that the subscripts for the Z's, Q's, and P's are the same for any given configuration of a basic unit, and are given by two numbers, i and j, where i and j represent the number of A atoms on the nearest and the next-nearest neighbor sites of a solid site of a basic unit, respectively. Therefore, there are Q_{22} N/3 solid sites belonging to basic units with Z_{22} configurations, on which $Q_{22}P_{22}$ N/3 A atoms and $Q_{22}(1-P_{22})$ N/3 B atoms must be distributed. Such a distribution can of course be done in g_{22} ways, where

$$g_{22}=\frac{(Q_{22}N/3)!}{(Q_{22}P_{22}N/3)!\,[Q_{22}(1-P_{22})N/3]!}$$

The number of ways for the distribution of atoms among eight other types of solid sites (each of which belongs to a basic unit with a specific configuration) can be calculated in exactly the same way as we calculated g_{22} above. For example, there are $2Q_{21}$ N/3 solid sites belonging to basic units with Z_{21} configurations, which are occupied by A and B atoms with the probabilities of P_{21} and $(1-P_{21})$, respectively. Hence, the number of ways for the distribution of atoms among such solid sites is equal to g_{21}, where

$$g_{21}=\frac{(2Q_{21}N/3)!}{(2Q_{21}P_{21}N/3)!\,[2Q_{21}(1-P_{21})N/3]!}$$

Similarly, the number of ways for the distribution of atoms among the solid sites of basic units with the configurations of $Z_{12}, Z_{20}, Z_{02}, Z_{11}, Z_{01}, Z_{10}$, and Z_{00} is given by $g_{12}, g_{20}, g_{02}, g_{11}, g_{01}, g_{10}$, and g_{00} respectively, where

$$g_{12}=\frac{(2Q_{12}N/3)!}{(2Q_{12}P_{12}N/3)!\,[2Q_{12}(1-P_{12})N/3]!}$$

$$g_{20}=\frac{(Q_{20}N/3)!}{(Q_{20}P_{20}N/3)!\,[Q_{20}(1-P_{20})N/3]!}$$

$$g_{02}=\frac{(Q_{02}N/3)!}{(Q_{02}P_{02}N/3)!\,[Q_{02}(1-P_{02})N/3]!}$$

$$g_{11}=\frac{(4Q_{11}N/3)!}{(4Q_{11}P_{11}N/3)!\,[4Q_{11}(1-P_{11})N/3]!}$$

$$g_{01}=\frac{(2Q_{01}N/3)!}{(2Q_{01}P_{01}N/3)!\,[2Q_{01}(1-P_{01})N/3]!}$$

$$g_{10}=\frac{(2Q_{10}N/3)!}{(2Q_{10}P_{10}N/3)!\,[2Q_{10}(1-P_{10})N/3]!}$$

$$g_{00}=\frac{(Q_{00}N/3)!}{(Q_{00}P_{00}N/3)!\,[Q_{00}(1-P_{00})N/3]!}$$

Therefore, the total number of distribution of atoms among the solid sites is given by $g^{1/3}=(g_{22}g_{21}g_{12}g_{20}g_{02}g_{11}g_{01}g_{10}g_{00})$. Since solid and nonsolid sites are indeed identical, we assume that the number of distribution of atoms among nonsolid sites is equal to the square of that for solid sites, namely $g^{2/3}$. The square is taken due to the fact that the number of nonsolid sites is twice as many as the solid sites. The total combinatorial factor is, therefore, given by

$$g=(g_{22}g_{21}g_{12}g_{20}g_{02}g_{11}g_{01}g_{10}g_{00})^3$$

By using the Boltzmann equation, S=k ln g, the following expression will be obtained for the entropy:

$$\begin{aligned}-\frac{S}{NK}&=Q_{22}\{P_{22}\ln P_{22}+(1-P_{22}\ln(1-P_{22})\}\\&+2Q_{21}\{P_{21}\ln P_{21}+(1-P_{21})\ln(1-P_{21})\}+\\&2Q_{12}\{P_{12}\ln P_{12}+(1-P_{12})\ln(1-P_{12})\}+\\&+Q_{20}\{P_{20}\ln P_{20}+(1-P_{20})\ln(1-P_{20})\}\\&+Q_{02}\{P_{02}\ln P_{02}+(1-P_{02})\ln(1-P_{02})\}+\\&4Q_{11}\{P_{11}\ln P_{11}+(1-P_{11})\ln(1-P_{11})\}\\&+2Q_{01}\{P_{01}\ln P_{01}+(1-P_{01})\ln(1-P_{01})\}+\\&2Q_{10}\{P_{10}\ln P_{10}+(1-P_{10})\ln(1-P_{10})\}+\\&Q_{00}\{P_{00}\ln P_{00}+(1-P_{00})\ln(1-P_{00})\}\end{aligned}\qquad(1)$$

(3) In order to calculate the number of pairs on the nearest and the next-nearest neighbor sites with different configurations, and the configurational energy, we have to consider all basic units with different configurations which are given in Table I. We shall first consider only the interaction of atoms located on solid sites with those atoms located on their nearest and next-nearest neighbor sites. There are $Q_{22}P_{22}N/3$ basic units with Z_{22} configurations, each with one A atom on its solid site. This A atom interacts with two A atoms located on its nearest neighbor sites, and also with two other A atoms located on its next-nearest neighbor sites. Therefore, each of these A atoms makes two nearest and two next-nearest neighbor pairs with AA configurations, and there is a total number of $2(Q_{22}P_{22}N/3)$ nearest and the same number of next-nearest neighbor pairs with AA configurations, in which one A atom is located on the solid site belonging to the Z_{22} configuration. Similarly, each A atom located on a solid site which belongs to a basic

unit with $Z_{21}, Z_{12}, Z_{20}, Z_{02}, Z_{11}, Z_{01}, Z_{10}$, and Z_{00} configurations makes 2,1,2,0,1,0,1, and 0 nearest neighbor pairs, and 1,2,0,2,1,1,0, and 0 next-nearest neighbor pairs with AA configurations, respectively. Therefore, all A atoms located on solid sites make a total number of α_{AA} nearest neighbor and α'_{AA} next-nearest neighbor pairs with AA configurations, respectively, where,

$$\alpha_{AA}=\frac{N}{3}\{2(Q_{22}P_{22})+2(2Q_{21}P_{21})+2Q_{12}P_{12}+2(Q_{20}P_{20})+4Q_{11}P_{11}+2Q_{10}P_{10}\} \quad (2)$$

$$\alpha'_{AA}=\frac{N}{3}\{2(Q_{22}P_{22})+2Q_{21}P_{21}+2(2Q_{12}P_{12})+2(Q_{02}P_{02})+4Q_{11}P_{11}+2Q_{01}P_{01}\} \quad (3)$$

We should emphasize that in the above expressions only those AA pairs which have one A atom located on the solid site and the other on the nonsolid site are counted. Now we can calculate the total number of the nearest and the next-nearest pairs in the lattice with the AA configuration. The fact that solid and nonsolid sites are really identical, and also the number of solid sites is one third of all sites, gives the total number of, $3\alpha_{AA}$, and $3\alpha'_{AA}$ nearest and next-nearest neighbor pairs, respectively, with AA configuration. Since each AA pair is counted twice, then, the actual number is equal to $\frac{1}{2}(3\alpha_{AA})$ and $\frac{1}{2}(3\alpha'_{AA})$ respectively. Therefore, the lattice has a total of N_{AA} nearest neighbor pairs and N'_{AA} next-nearest neighbor pairs with AA configurations, where

$$N_{AA}=N\{Q_{22}P_{22}+2Q_{21}P_{21}+Q_{12}P_{12}+Q_{20}P_{20}+2Q_{11}P_{11}+Q_{10}P_{10}\} \quad (4)$$

$$N'_{AA}=N\{Q_{22}P_{22}+Q_{21}P_{21}+2Q_{12}P_{12}+Q_{02}P_{02}+2Q_{11}P_{11}+Q_{01}P_{01}\} \quad (5)$$

For simplicity, we shall assume that there exists only an interaction energy between two A atoms, either when they are located on the two nearest neighbor sites (with the interaction energy of ε_{AA}), or when are located on the two next-nearest neighbor sites (with the interaction energy of ε'_{AA}). This is a specific case in which we set $\varepsilon_{AB}=\varepsilon'_{AB}=\varepsilon_{BB}=\varepsilon'_{BB}=0$. This specific case is appropriate for a "lattice gas model", and the more general case, $\varepsilon s \neq 0$, for a binary lattice model. These two problems are physically identical, and one can be related to the other [8-9]. We are using the lattice gas model simply to avoid calculating the number of other nearest and next-nearest neighbor pairs.

Now, by having N_{AA} and N'_{AA} in equations 4 and 5, the configurational energy can be readily calculated, it is given by,

$$E=(NUkT)\{(Q_{22}P_{22}+2Q_{21}P_{21}+Q_{12}P_{12}+Q_{20}P_{20}+2Q_{11}P_{11}+Q_{10}P_{10})+K(Q_{22}P_{22}+Q_{21}P_{21}+2Q_{12}P_{12}+Q_{02}P_{02}+2Q_{11}P_{11}+Q_{01}P_{01})\} \quad (6)$$

where U is the reduced interaction energy between two A atoms located on two nearest neighbor sites, being specifically defined as,

$$U=\varepsilon_{AA}/kT \quad (7)$$

(k is the Boltzmann factor) and K is the degree of importance of the next-nearest neighbor interaction, relative to the nearest neighbor interaction, and is defined as,

$$K=\frac{\varepsilon'_{AA}}{\varepsilon_{AA}} \quad (8)$$

In this work, we are mainly interested in studying the effect of different values of **K** on the ordering behavior of the lattice.

(4) The difference which arises between identical sites, due to the fact that they are artificially divided into two groups (solid and nonsolid), must be minimized. In order to fulfil this condition, those distributions are only accepted in which the following constraints are satisfied.

In the acceptable distributions, the probabilities of occupation of solid and nonsolid sites by atoms must be equal. These probabilities are equal to the fraction of A atom in the lattice, F, where

$$F=\frac{N_A}{N}$$

where N_A is the total number of A atoms in the lattice. The number of A atoms on nonsolid sites, $N_A(N)$, can be calculated by referring to the left-hand side of Table I. A basic unit with the configuration of $Z_{22}, Z_{21}, Z_{12}, Z_{20}, Z_{02}, Z_{11}, Z_{01}, Z_{10}$, and Z_{00} has 4,3,3,2,2,2,1,1,0 A atoms on its nonsolid sites, respectively. $N_A(N)$ is, then, given by

$$N_A(N)=\frac{1}{2}\{4(Q_{22}N/3)+3(2Q_{21}N/3+2Q_{12}N/3)+2(Q_{20}N/3+Q_{02}N/3+4Q_{11}N/3)+2Q_{01}N/3+2Q_{10}N/3\}$$

$$=\frac{N}{3}\{2Q_{22}+3(Q_{21}+Q_{12})+Q_{20}+Q_{02}+4Q_{11}+Q_{01}+Q_{10}\}$$

where the factor 1/2 is to prevent overcounting. If $N_A(N)$ is divided by the number of nonsolid sites, $\frac{2N}{3}$, then we obtain the following constraint,

$$\frac{1}{2}\{2Q_{22}+3(Q_{21}+Q_{12})+Q_{20}+Q_{02}+4Q_{11}+Q_{01}+Q_{10}\}=F \quad (9)$$

Similarly, the number of A atoms on solid sites, $N_A(S)$, can be calculated, by referring to the right-hand side of Table I. If $N_A(S)$ is divided by the number of solid sites, N/3, the following constraint will be found,

$$Q_{22}P_{22}+2Q_{21}P_{21}+2Q_{12}P_{12}+Q_{20}P_{20}+Q_{02}P_{02}+4Q_{11}P_{11}+2Q_{01}P_{01}+2Q_{10}P_{10}+Q_{00}P_{00}=F \quad (10)$$

There is one more additional constraint, that is the normalization of configurations on the basic unit, which is given

by

$$Q_{22}+2Q_{21}+2Q_{12}+Q_{20}+Q_{02}+4Q_{11}+2Q_{01}+2Q_{10}+Q_{00}=1 \quad (11)$$

There are no other exact constraints. We shall impose more constraints which are exact only in the global lattice. They are $Q_{ij}=Q_{ji}$ and $Q_{ij}=Q_{mn}$, if i+j = m+n, or specifically,

$$Q_{21}=Q_{12} \quad (12)$$

$$Q_{20}=Q_{02}=Q_{11} \quad (13)$$

$$Q_{01}=Q_{10} \quad (14)$$

(5) Now we are able to find the equilibrium state of the lattice for any given values of F,K, and U. First we set up an expression for the reduced Helmholtz free energy, A/NkT. This function is given by,

$$\frac{A}{NkT}=\frac{E}{NkT}-\frac{S}{Nk} \quad (15)$$

The reduced configurational energy and entropy have already been obtained in equations 6 and 1, respectively. We can substitute the expressions for the reduced energy and enbropy into equation 15, and then minimize A/NkT in such a way that the constraints given by eqs. 9-14 are satisfied. This minimization is done numerically by computer. Some results of such a calculation are given in Table II and the configurational entropy is also plotted versus 4/|U| (or temperature) in Figure 2, for some given values of the next-nearest neighbor interaction energy.

Application to two-Dimensional Lattice

As in the case of the one-dimensional model, we first have to choose solid and nonsolid sites appropriately, in such a way that the nearest neighbor and the next-nearest neighbor interactions are both taken into account. The appropriate way for dividing the sites here into solid and nonsolid groups is shown in Figure 1(b). One fourth of the

K	0	0.1	0.2	0.3	0.4
-U			S/Nk		
10	.040	.026	.017	.011	.007
8	---	.066	.047	.034	.024
6	.191	.154	.123	.097	.077
5	.269	.227	.191	.159	.132
4	.365	.325	.286	.251	.220
3	.475	.442	.408	.376	.345
2	.582	.562	.541	.519	.497
1	.663	.657	.650	.643	.635
2/3	.679	.677	.674	.670	.667
0	.693	.693	.693	.693	.693

Table II. The configurational entropy of the one-dimensional lattice for some given values of the nearest neighbor interaction, U, and some different values of the next-nearest neighbor interaction, K.

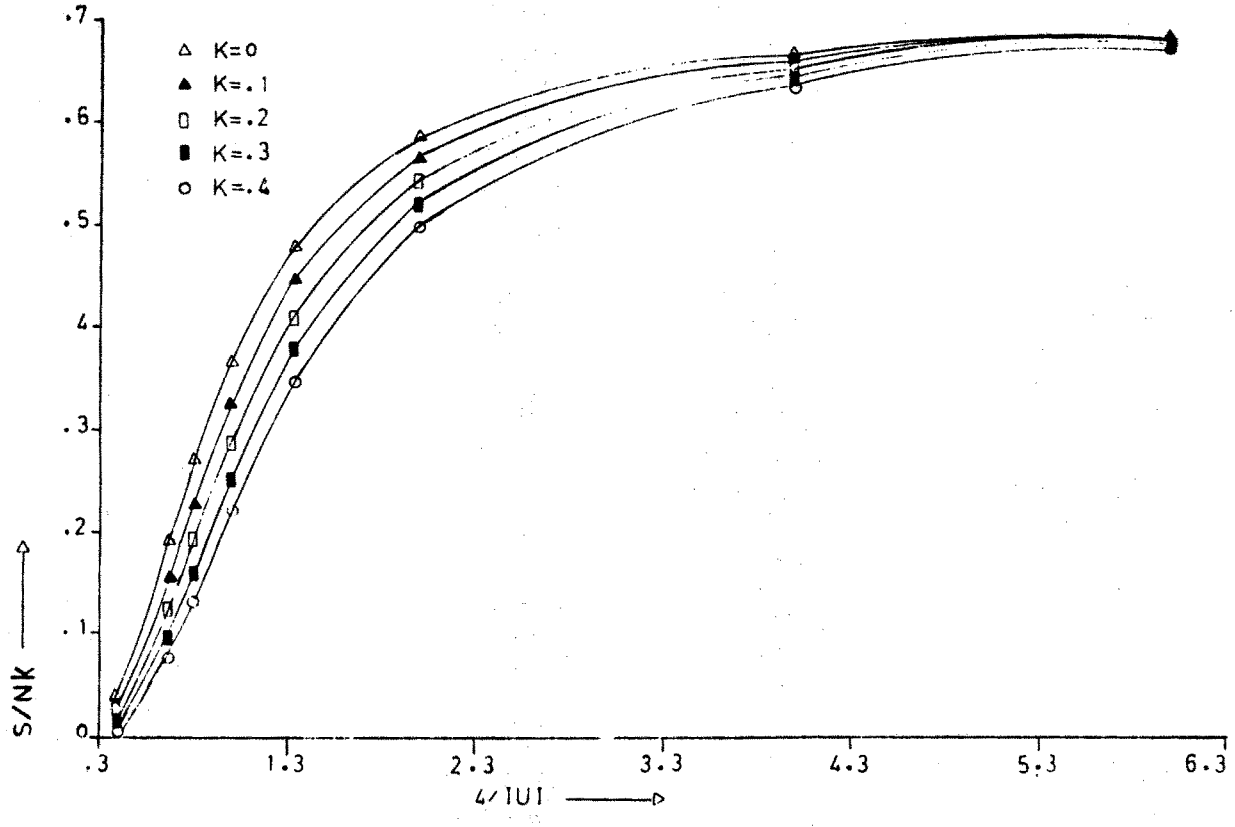

Figure 2. The configurational entropy of a one-dimensional lattice versus 4/|U| (or temperature) for some given values of K and F=.5 .

sites (full circles) are taken as solid sites and those remaining (open circles) are considered to be nonsolid sites. As shown in this figure, the basic unit is a square with eight nonsolid sites located around a solid site, four of which (located at the corners) are the next-nearest neighbors and the others (located on the middle of the sides) are the nearest neighbors of the solid site (located at the center of the square). As in the case of the one-dimensional lattice, we represent each basic unit configuration by Z_{ij}, where the subscripts i and j are again the number of the nearest neighbor and the next-nearest neighbor sites of a given solid site, respectively, which are occupied by A atoms. There is a total number of $2^8=256$ configurations for a basic unit (excluding the configurations of its solid site), many of which are identical and have equal probabilities. We shall consider a multiplicity factor, λ_{ij}, for those basic units with identical configurations of Z_{ij} (the subscripts i and j on λ have the same meaning as those for Z). A basic unit may have 25 different configurations (i=0, 1, ... , 4 and j=0,1, ... , 4). The values of the multiplicity factor for all basic unit configurations are given in Table III, as a two-dimensional matrix. Of course, the sum of the elements of this matrix must be equal to 256.

i	j				
	0	1	2	3	4
0	1	4	6	4	1
1	4	16	24	16	4
2	6	24	36	24	6
3	4	16	24	16	4
4	1	4	6	4	1

Table III. The multiplicity factor of a basic unit with different configurations for the two-dimensional square lattice, λ_{ij}.

The probability for the basic unit with Z_{ij} configuration will be denoted by Q_{ij} (excluding the configurations for its solid site). The probabilities for occupation of those solid sites belonging to the basic units with Z_{ij} configurations, by A and B atoms, will be denoted by P_{ij} and $(1-P_{ij})$ respectively. If we follow steps (1) and (2), exacty as we did in the case of the one-dimensional lattice, the following expression will be obtained for the reduced configurational entropy, S/Nk,

$$\frac{S}{Nk} = -\Sigma_i \Sigma_j \lambda_{ij} Q_{ij} \{P_{ij} \ln P_{ij} + (1-P_{ij}) \ln (1-P_{ij})\} \qquad (16)$$

where the values for λ s are given in Table III.

If we follow step (3) for the two-dimensional square lattice, the number of nearest neighbor pairs with AA configuration, N_{AA}, the number of next-nearest neighbors with the same configuration, M_{AA}, and the reduced configurational energy of the lattice, $E/_{NkT}$ will be obtained as,

$$\frac{N_{AA}}{2N} = Q_{44}P_{44} + 4Q_{43}P_{43} + 3Q_{34}P_{34} + 6Q_{42}P_{42} + 3Q_{24}P_{24} + 12\,Q_{33}P_{33} + 4Q_{41}P_{41} + 18Q_{32}P_{32} + 12Q_{23}P_{23} + Q_{14}P_{14} + Q_{40}P_{40} + 12Q_{31}P_{31} + 18Q_{22}P_{22} + 4Q_{13}P_{13} + 6Q_{12}P_{12} + 12Q_{21}P_{21} + 3Q_{30}P_{30} + 4Q_{11}P_{11} + 3Q_{20}P_{20} + Q_{10}P_{10} \qquad (17)$$

$$\frac{M_{AA}}{2N} = Q_{44}P_{44} + 3Q_{43}P_{43} + 4Q_{34}P_{34} + 3Q_{42}P_{42} + 6Q_{24}P_{24} + 12Q_{33}P_{33} + Q_{41}P_{41} + 12Q_{32}P_{32} + 18Q_{23}P_{23} + 4Q_{14}P_{14} + 4Q_{31}P_{31} + 18Q_{22}P_{22} + 12Q_{13}P_{13} + Q_{04}P_{04} + 3Q_{03}P_{03} + 12Q_{12}P_{12} + 6Q_{21}P_{21} + 3Q_{02}P_{02} + 4Q_{11}P_{11} + Q_{01}P_{01} \qquad (18)$$

$$\frac{E}{NkT} = 2U\left(\frac{N_{AA}}{N} + K\frac{M_{AA}}{N}\right) \qquad (19)$$

where $U=\varepsilon_{AA}/kT$ and ε_{AA} is the interaction energy between two A atoms located on a pair of nearest neighbor sites. As before, K is the degree of importance of interaction between two A atoms located on two next-nearest neighbor sites, relative to ε_{AA}.

For the reason which has already been given for the one-dimensional model, some appropriate constraints must be satisfied. Similar arguments which resulted from equations 12 to 14 (for the one-dimensional lattice) give the following constraints for the two-dimensional lattice:

$$Q_{43} = Q_{34} \qquad (20)$$
$$Q_{42} = Q_{24} = Q_{33} \qquad (21)$$
$$Q_{41} = Q_{32} = Q_{23} = Q_{14} \qquad (22)$$
$$Q_{40} = Q_{31} = Q_{22} = Q_{13} = Q_{04} \qquad (23)$$
$$Q_{03} = Q_{12} = Q_{21} = Q_{30} \qquad (24)$$
$$Q_{02} = Q_{11} = Q_{20} \qquad (25)$$
$$Q_{01} = Q_{10} \qquad (26)$$

The following constraint is obtained by using similar arguments that resulted from equation 9.

$$Q_{44} + \frac{11}{3}Q_{43} + \frac{10}{3}Q_{34} + 5Q_{42} + 4Q_{24} + 12Q_{33} + 3Q_{41} + 16Q_{32} + 14\,Q_{23} + 2Q_{14} + \frac{2}{3}Q_{40} + \frac{28}{3}Q_{31} + 18Q_{22} + \frac{20}{3}Q_{13} + \frac{1}{3}Q_{04} + Q_{03} + 8Q_{12} + 10\,Q_{21} + 2\,Q_{30} + Q_{02} + 4\,Q_{11} + 2Q_{20} + \frac{1}{3}Q_{01} + \frac{2}{3}Q_{10} = F \qquad (27)$$

(For obtaining this equation, one should note that a nonsolid site located at the corner of a basic unit belongs to four basic units in the lattice, but the one located in the middle of the side of a basic unit belongs to two basic units in the lattice). The following constraint can be obtained by similar arguments which resulted from equation 10 for the one-dimensional lattice).

$$Q_{44}P_{44} + 4Q_{43}P_{43} + 4Q_{34}P_{34} + 6Q_{42}P_{42} + 6Q_{24}P_{24} + 16Q_{33}P_{33} + 4Q_{41}P_{41} + 24Q_{32}P_{32} + 24Q_{23}P_{23} + 4Q_{14}P_{14} + Q_{40}P_{40} + 16Q_{31}P_{31} +$$

$$36Q_{22}P_{22}+16Q_{13}P_{13}+Q_{04}P_{04}+4Q_{03}P_{03}+24Q_{12}P_{12}+24Q_{21}P_{21}+4Q_{30}P_{30}+6Q_{02}P_{02}+16Q_{11}P_{11}+6Q_{20}P_{20}+4Q_{01}P_{01}+4Q_{10}P_{10}+Q_{00}P_{00}=F \quad (28)$$

The equation for the normalization of configurations of a basic unit, corresponding to equation 11 for the one-dimensional lattice, is given by:

$$Q_{44}+4Q_{43}+4Q_{34}+6Q_{42}+6Q_{24}+16Q_{33}+4Q_{41}+42Q_{32}+24Q_{23}+4Q_{14}+Q_{40}+16Q_{31}+36Q_{22}+16Q_{13}+Q_{04}+4Q_{03}+24Q_{12}+24Q_{21}+4Q_{30}+6Q_{02}+16Q_{11}+6Q_{20}+4Q_{01}+4Q_{10}+Q_{00}=1 \quad (29)$$

One more constraint is used in the two dimensional model in ESCM, that is the fraction of nonsolid-nonsolid and solid-nonsolid pairs with AA configurations are equal. This constraint, which may be only globally good, is given by,

$$Q_{44}+3Q_{43}+3Q_{34}+3Q_{42}+3Q_{24}+9Q_{33}+Q_{41}+9Q_{32}+9Q_{23}+Q_{14}+3Q_{31}+9Q_{22}+3Q_{13}+3Q_{12}+3Q_{21}+Q_{11}=Q_{44}P_{44}+4Q_{43}P_{43}+3Q_{34}P_{34}+6Q_{42}P_{42}+3Q_{24}P_{24}+12Q_{33}P_{33}+4Q_{41}P_{41}+18Q_{32}P_{32}+12Q_{23}P_{23}+Q_{14}P_{14}+Q_{40}P_{40}+12Q_{31}P_{31}+18Q_{22}P_{22}+4Q_{13}P_{13}+6Q_{12}P_{12}+12Q_{21}P_{21}+3Q_{30}P_{30}+4Q_{11}P_{11}+3Q_{20}P_{20}+Q \quad (30)$$

We are now able to set up an expression for the reduced free energy of the lattice, it is given by:

$$\frac{A}{NkT}=2U(N_{11}+KM_{11})+\sum_{i=0}^{4}\sum_{j=0}^{4}\lambda_{ij}Q_{ij}\{P_{ij}\ln P_{ij}+(1-P_{ij})\ln(1-P \quad (31)$$

where $N_{11}=N_{AA}/N$ and $M_{11}=M_{AA}/N$, which are the fractions (or probabilities) of the nearest neighbor and next-nearest neighbor sites having AA configurations in the lattice, respectively. In order to find the equilibrium state, we should minimize the free energy in such a way that equations 20 through 30 are all satisfied. Such a minimization is done by computer, and one sample of the results is given in Table IV. The thermodynamic properties of the lattice have been calculated in terms of the nearest neighbor interaction energy, for some given values of the next-nearest neighbor interaction (K). Some of the results are given in Table V.

Q_{44}	0	P_{44}	.405	P_{40}	.692	P_{11}	.393
$Q_{43}=Q_{34}$	0	P_{43}	.413	P_{31}	.613	P_{20}	.399
$Q_{42}=Q_{24}=Q_{33}$	.015	P_{34}	.412	P_{22}	.444	P_{01}	.289
$Q_{41}=Q_{32}=Q_{23}=Q_{14}$	0	P_{42}	.814	P_{13}	.284	P_{10}	.324
$Q_{40}=Q_{31}=Q_{22}=Q_{13}=Q_{04}$	.003	P_{24}	.528	P_{04}	.216	P_{00}	.098
$Q_{03}=Q_{12}=Q_{21}=Q_{30}$	0	P_{33}	.681	P_{03}	.398	P_{14}	.399
$Q_{02}=Q_{11}=Q_{20}$	0	P_{41}	.400	P_{12}	.390	P_{02}	.395
$Q_{01}=Q_{10}$	0	P_{32}	.399	P_{21}	.393	N_{11}	.261
Q_{00}	.408	P_{23}	.396	P_{30}	.399	M_{11}	.240

Table IV. The probabilities for a basic unit with different configurations, Q_{ij} the probabilities for occupation of different solid sites (each belongs to a basic unit with a specific configuration) by A atoms, P_{ij} and the fraction of the nearest and the next-nearest neighbor sites with AA configuration, N_{11} and M_{11} respectively, for U=-1, K=0.3, and F=0.4, for the two-dimensional square lattice.

K	0			0.2			0.3			0.4		
-U	-A/NkT	-E/NkT	S/Nk	A/NkT	-E/NkT	S/Nk	-A/NkT	-E/NkT	S/Nk	-A/NkT	E/NkT	S/Nk
0	.673	0	.673	.673	0	.673	.673	0	.673	.673	0	.673
1/3	.783	.114	.669	.805	.137	.668	.816	.147	.669	.827	.161	.666
2/3	.903	.252	.651	.951	.313	.638	.974	.340	.634	.998	.372	.626
1	1.038	.436	.602	1.122	.576	.546	1.165	.665	.500	1.220	.786	.434
2	1.620	1.368	.252	1.926	1.879	.047	2.083	2.060	.023	2.240	2.240	0
3	2.405	2.400	.005	2.879	2.868	.011	3.120	3.119	.001	3.360	3.360	0
4	3.205	3.200	.005	3.835	3.824	.011	4.159	4.159	0	4.480	4.480	0
5	4.000	3.999	.001	4.791	4.780	.011	5.199	5.198	.001	5.600	5.600	0
6	4.800	4.800	0	5.747	5.736	.011	6.238	6.238	0	6.720	6.720	0

Table V. The reduced thermodynamic properties of the two- dimensional square lattice for some given values of the nearest and the next-nearest neighbor interaction energies.

Results and Discussion

The order-disorder transition phenomenon is very difficult to study experimentally because the kinetics of the solid-solid transition is very slow. It is for this reason that solid phase systems are not often found in their stable form, thermodynamically. Therefore, the solid-solid phase transition and the related problems, such as obtaining the phase diagram, should be studied theroretically. Statistical mechanics is a powerful tool for the investigation of this type of problem.

At low temperatures, $T \rightarrow 0$ or $U \rightarrow -\infty$, the lattice becomes completely ordered and $S \rightarrow 0$, and at very high temperatures, $T \rightarrow \infty$ or $U \rightarrow 0$, atoms are distributed randomly and the configurational entropy is given by:

$$S=k \ln \frac{N!}{(NF)! [N(1-F)]!}$$

Where, when F=.5 and F=.4 the reduced entropies of the lattice are equal to .693 and .673 respectively.

These values are in agreement with the results of Table II (for the one-dimensional lattice) and Table V(for the two-dimensional lattice). At these limits, on which the lattice is either completely ordered or completely disordered, the next-nearest neighbor interaction (K) has no effect on the distribution of atoms on the sites. It has a significant effect, however, within the intermidiate temperatures where the order-disorder transition takes place.

Devoting an attraction energy for the next-nearest neighbors, besides the attraction for the nearest neighbors, is the same as relating a longer range attraction force to atoms in the lattice. One then expects the lattice to become more ordered as K becomes larger, for any given temperature and U. Our results are in agreement with this expectation, see Fig.2 (for one-dimensional) and Table V (two-dimensional). Relating a longer attraction force to atoms (the next nearest neighbor interaction) causes the atoms to be held more strongly together in the lattice, and gives them more resistance against molecular agitation. The entropy will then increase more slowly with raising the temperature, and the average temperature, at which the order-disorder transition occurs, shifts to a higher one. These phenomena are quite in agreement with our results as shown in Figure 2 and Table V.

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