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On Disorder Entropy of Ice*

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Abstract

According to the Bernal-Fowler-Pauling model, ice should have additional entropy due to randomness of its proton arrangements. The entropy, S , of a finite ice crystal, consisting of n molecules and having f surface bonds, is given by

$$S/k = n(\ln(3/2) + \ln q_\infty) + (f/2)(\ln 2 - \delta),$$

where k is Boltzmann's constant, $\ln q_\infty$ is a non-negative number depending on the structure of the oxygen lattice, and δ is a positive number being less than $\ln 2$ and depending on the shape and size of the crystal. For the square oxygen lattice, the value of $\ln q_\infty$ is shown 0.0261 ± 0.0006 or about 6.5% of $\ln(3/2)$, which may probably be several times larger than that for real ice.

I. Introduction**

In order to explain the residual entropy of ice found experimentally by Giauque *et al.* (1933, 1936), Pauling (1935) considered that due to randomness of proton arrangements ice should have additional entropy, which was defined by him quite mathematically and which we shall call the disorder entropy to distinguish it from a physical concept, the residual entropy. He estimated the disorder entropy of an infinitely large ice crystal as $k \ln(3/2)$ per molecule, where k is Boltzmann's constant. As has been pointed out, for instance, by DiMarzio and Stillinger, Jr. (1964), the estimated value is not exact.

We have shown that the entropy, S , of a finite ice crystal, consisting of n water molecules and having f surface bonds, is given by

$$S/k = n(\ln(3/2) + \ln q_\infty) + (f/2)(\ln 2 - \delta), \quad (1)$$

where $\ln q_\infty$ is a non-negative number depending only on the structure of the oxygen lattice and δ is a positive number being less than $\ln 2$ and depending on the shape and size of the crystal (Suzuki, 1966 c. Hereafter referred as paper I).

In paper I, concrete definitions of q_∞ for the wurtzite-like oxygen lattice (real ice) and for the two dimensional square oxygen lattice and methods of computing the q_∞ 's were given. Especially, for the square lattice, a series $q(b, \infty, \infty)$, converging to q_∞ with increasing b , was defined and values of $q(b, \infty, \infty)$ for b up to seven were given.

In the present paper, the content of paper I is summarized with several revisions in sections II through VII. In section VIII, the value of δ for a rectangular lattice bounded by {01} boundaries is shown to be less than $\ln(4/3)$. Values of $q(b, \infty, \infty)$ for b up to

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** A note was added in proof. See p. 41.

nine, calculated by a revised method, are given in section IX. They reveal an important character of the convergence, enabling us to compute $\ln q_\infty$ in a fairly good accuracy, as is seen also in section IX.

II. Definition of the Disorder Entropy of a Finite Ice Crystal

An infinite lattice in which each lattice point has four nearest neighbors is said an oxygen lattice. Examples are the square, the Kagomé, the wurtzite-like and the diamond-like lattices. An oxygen lattice is said an infinite ice lattice, if and only if two sites (for a proton) are set on each bond of the lattice.

A finite ice lattice is a connected part of an infinite ice lattice surrounded by surface or surfaces which cut bonds in such a manner as to leave one and only one sites on each cut bond to the part (Fig. 1). Here, a connected part means that between any pair of lattice points in the part one can trace along bonds through lattice points in the part.*

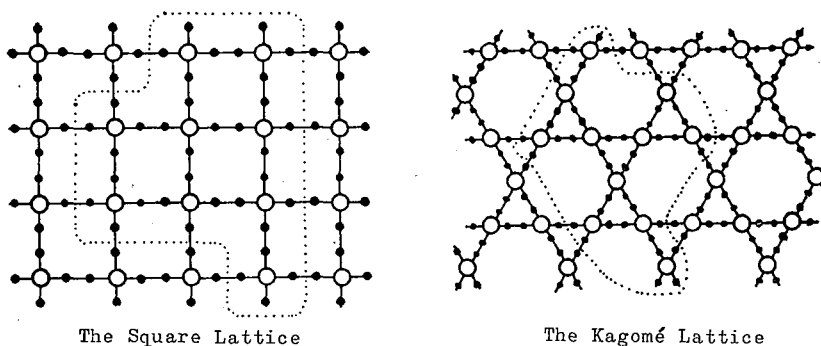


Fig. 1. Examples of two-dimensional ice lattices

O : Lattice point —●— : Bond with two sites
 : Example of surface

Among three numbers specifying a finite ice lattice, that is, the number of lattice points, n , that of inner (*i. e.* non-cut) bonds, h , and that of surface (*i. e.* cut) bonds, f , the following relation holds, which can be easily verified by counting sites:

$$4n = 2h + f. \quad (2)$$

An arrangement (of protons) on an ice lattice is a way of assigning to every site of the lattice a value, either unity or zero, which is said the state value of the site. If the state value of a site is unity, the site is said occupied (by a proton) and, if it is zero, vacant.

An arrangement is said possible if it satisfies the following two conditions for every inner bond and for every lattice point

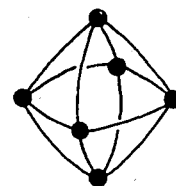


Fig. 2. An imaginary ice, $H_{12}O_6$

* Most of discussions in sections up to the fifth do not make use of lattice properties and can be applied to a more general type of ice crystal, which is defined as follows: A finite ice network is such a network containing a finite number of vertices that each vertex is linked to four vertices and that on each linkage (bond) are set two sites for a proton. Such a network may have no surface bonds. An example is shown in Fig. 2.

in the lattice, respectively: 1) One and only one of two sites on a bond is occupied and 2) two and only two of four sites around a lattice point are occupied.

The two conditions are due to Bernal and Fowler (1935). The first is said the (hydrogen) bond condition and the second the (water) molecule condition.

Note that they are invariable by changing the word "occupied" to "vacant", or in terms of the state value, by interchanging zero and unity of all state values concerned. This invariancy, which shall be called the *c*-invariancy ("*c*" after "complementary"), plays an important role in section IV.

Following Pauling (1953), we define the disorder entropy, S , of a finite ice crystal, consisting of n molecules, by

$$S/k = \ln w, \quad (3)$$

where w is the number of all possible arrangements on a finite ice lattice, corresponding to the crystal.

III. Reduction of the Expression for the Entropy to a Manageable Form

Let W_0 be a set of all arrangements on a finite ice lattice, each satisfying the bond condition for every inner bond of the lattice. The size of W_0 is denoted by w_0 (A set shall be denoted by a roman capital with, if necessary, some specifications. The corresponding small italic with the same specifications shall be always understood to denote the size of the set). Evidently,

$$w_0 = 2^{h+f} = 2^{2n+(f/2)}, \quad (4)$$

since in order an arrangement to be in W_0 either of two sites on each of h inner bonds can and must be occupied and f sites on surface bonds can be either occupied or vacant.

Let all lattice points be numbered arbitrarily from the first to the n -th. Let W_i be a subset of W_0 consisting of all arrangements in W_0 each satisfying the molecule condition for every lattice point up to the $i-1$ -th (inclusive).

The number, w , which is the same as w_n , can be written as

$$w = w_0 \prod_{i=1}^n (w_i/w_{i-1}) = (3/2)^n 2^{f/2} \prod_{i=1}^n q_i, \quad (5)$$

where q_i is defined by

$$q_i = (8/3) (w_i/w_{i-1}). \quad (6)$$

From eqs. (3) and (5), we have

$$S/k = n \ln (3/2) + (f/2) \ln 2 + \sum_{i=1}^n \ln q_i. \quad (7)$$

The disorder entropy per molecule of an infinitely large ice crystal, s_∞ , is reasonably defined by

$$s_\infty = \lim_{n/f \rightarrow \infty} (S/n) = k \ln (3/2) + \lim_{n/f \rightarrow \infty} \left(\sum_{i=1}^n \ln q_i/n \right). \quad (8)$$

Let $W_{i-1}(s_1, \dots, s_k; \beta_1, \dots, \beta_k)$ be a subset of W_{i-1} specified by state values of k given sites s_j , or in other words, a set, composed of all arrangements in W_{i-1} having state

values β_j on the given sites $s_j (j=1, \dots, k)$. In particular, if the sites are four sites around the i -th lattice point, a simplified notation, $W_{i-1}(\beta_1, \beta_2, \beta_3, \beta_4)$, is used instead.

From the definitions,

$$w_{i-1} = \sum w_{i-1}(\beta_1, \beta_2, \beta_3, \beta_4) \quad (\text{sum over sixteen terms}), \quad (9)$$

$$w_i = \sum' w_{i-1}(\beta_1, \beta_2, \beta_3, \beta_4) \quad (\text{sum over six terms with } \sum_k \beta_k = 2). \quad (10)$$

Using eqs. (5), (9) and (10), we can express q_i in terms of relative sizes of the sixteen subsets of W_{i-1} .

The procedure given in this section is a logical reconstruction of Pauling's reasoning, where, however, the factor $2^{f/2}$ in eq. (3) and the term $(f/2) \ln 2$ in eq. (9) were absent since he did not care about crystal surface.

Pauling considered that with increasing i the probability (defined by W_{i-1}) for a site around the i -th lattice point to be occupied might tend to one-half independently of states of the other sites around the lattice point. Then, the sixteen subsets could be considered all equal in size and, hence, q_i equal to unity, for almost all i 's of a sufficiently large crystal, so that s_∞ would be $k \ln(3/2)$.

IV. Correlation between the States of Two Sites

A site is said to be correlated by W_{i-1} to the second site, if and only if one can trace along bonds from the first to the second without passing through no lattice points other than those up to the $i-1$ -th. Such a trace is said a path, if no bond is retraced. The number of lattice points on a path is said the length of the path and that of sites the parity number of the path.

A set of sites, consisting of a site and all sites correlated by W_{i-1} to it, is said a family on W_{i-1} . As an example, two sites on a bond, terminating at no lattice points up to the $i-1$ -th, make a family by themselves. A grain, a concept used in paper I, is the largest of ice lattices, whose sites are all contained in a family.

A part of an arrangement, concerned with all sites in a family and only with them, is said a component of the arrangement on the family. A component on a family is said possible, if and only if it satisfies the bond condition for each pair of sites both being in the family and on a bond and the molecule condition for each quartet of sites all being in the family and around a lattice point up to the $i-1$ -th.

Let $W_{i-1,k}$ be a set of all possible components on the k -th family and let $U_k(s_1, \dots, s_h: \beta_1, \dots, \beta_h)$ be a subset of $W_{i-1,k}$, specified by state values β_j on h given sites s_j in the family. Owing to the c -invariancy of the bond and the molecule conditions, an operation, interchanging zero and unity of the state value of every site in the k -th family, transforms $W_{i-1,k}$ onto itself, giving the following equalities among sizes of the subsets:

$$u_k(s_1, \dots, s_h: \beta_1, \dots, \beta_h) = u_k(s_1, \dots, s_h: 1-\beta_1, \dots, 1-\beta_h). \quad (11)$$

Evidently, a site belongs to one and only one family on W_{i-1} and a family contains either none or all of four sites around any lattice point and of two sites on any bond. Using these two facts, we can show that W_{i-1} is a direct product of $W_{i-1,k}$'s over all values of k and that a subset of W_{i-1} , specified by state values of given sites, is that of appropriate U_k 's over some values of k and $W_{i-1,k}$'s over other values of k . For

instance, if the sites s_1 to s_j are in the first family and s_{j+1} to s_n in the second family, we have, in terms of sizes,

$$w_{\varepsilon-1}(s_1, \dots, s_n : \beta_1, \dots, \beta_n) = u_1(s_1, \dots, s_j : \beta_1, \dots, \beta_j) u_2(s_{j+1}, \dots, s_n : \beta_{j+1}, \dots, \beta_n) \prod_{k \geq 3} w_{\varepsilon-1, k}. \quad (12)$$

Equations (11) and (12) give equalities among the 2^k sizes of the subsets of $W_{\varepsilon-1}$.

We easily see that if there are m families containing some of the sites s_1 to s_n , the 2^k sizes are classified by size into 2^{k-m} classes each composed of 2^m elements, and that in any case

$$w_{\varepsilon-1}(s_1, \dots, s_n : \beta_1, \dots, \beta_n) = w_{\varepsilon-1}(s_1, \dots, s_n : 1-\beta_1, \dots, 1-\beta_n). \quad (13)$$

Before using these considerations for reducing the expression of q_ε , we digress for a while and introduce two quantities, $x(s_1, s_2)$ and $\varepsilon(s_1, s_2)$, by

$$x(s_1, s_2) = \frac{1 + \varepsilon(s_1, s_2)}{1 - \varepsilon(s_1, s_2)} = \frac{w_{\varepsilon-1}(s_1, s_2 : 1, 0) + w_{\varepsilon-1}(s_1, s_2 : 0, 1)}{w_{\varepsilon-1}(s_1, s_2 : 0, 0) + w_{\varepsilon-1}(s_1, s_2 : 1, 1)} = \frac{w_{\varepsilon-1}(s_1, s_2 : 1, 0)}{w_{\varepsilon-1}(s_1, s_2 : 0, 0)}. \quad (14)$$

Since $x(s_1, s_2)$ is the ratio of the probability defined by $W_{\varepsilon-1}$ that the states of s_1 and s_2 are different to that that they are identical, we call $\varepsilon(s_1, s_2)$ the correlativity between s_1 and s_2 and expect it to be a quantitative measure of the correlation defined at the beginning of this section.

In fact, we easily see that $\varepsilon(s_1, s_2) = 0$, if s_1 and s_2 are not correlated to each other, and that $\varepsilon(s_1, s_2) = 1$, if s_1 and s_2 are on a bond. (We have not yet succeeded to prove the converses of these statements, but this does not matter.)

We can also show that when there is only one path between s_1 and s_2

$$\varepsilon(s_1, s_2) = (-1)^k 3^{-j}, \quad (15)$$

where j and k are the length and the parity number of the path, respectively. Several indications suggests that when there are many paths they contribute to the correlativity approximately additively (paper I. Appendix A):

$$\varepsilon(s_1, s_2) \cong \sum_{\text{path}} (-1)^k 3^{-j}. \quad (16)$$

V. Further Reduction

Five and only five types of family relation can be conceivable among four sites: 1) No pair in the same family, 2) one pair in the same family, 3) three sites in the same family, 4) all in the same family and 5) one pair in one and the other in the other family.

The type of family relation on $W_{\varepsilon-1}$ among the four sites around the i -th lattice point is said the type of the point, which evidently depends on a way of the numbering. A numbering is said basic, if by it the type of every lattice point is either the first or the second. We can prove that the number $n^{(1)}$ of lattice points of the first type appearing by a basic numbering is given by

$$n^{(1)} = (f/2) - 1 \quad (\text{for any basic numbering}). \quad (17)$$

Hence, in order that every lattice points are of the first type by some numbering, n must be equal to $(f/2) - 1$. Such lattices are one-dimensional trees, which are not interesting from physical point of view.

We can actually give several basic numberings for the wurtzite-like and for the two-dimensional lattices. In paper I, we used only them, but in the present paper we shall also use a numbering by which the third type appears together with the first and the second. Hence, we shall investigate these three types.

Assume that the i -th lattice point is of the third type. Designating the correlated three sites as the first, the second and the third, we have from eqs. (11) and (12)

$$\begin{aligned} w_{i-1}(0, 0, 0, 1) &= w_{i-1}(0, 0, 0, 0) = w_{i-1}(1, 1, 1, 0) = w_{i-1}(1, 1, 1, 1) = y_0, \\ w_{i-1}(1, 0, 0, 0) &= w_{i-1}(1, 0, 0, 1) = w_{i-1}(0, 1, 1, 0) = w_{i-1}(0, 1, 1, 1) = y_1, \\ w_{i-1}(0, 1, 0, 0) &= w_{i-1}(0, 1, 0, 1) = w_{i-1}(1, 0, 1, 0) = w_{i-1}(1, 0, 1, 1) = y_2, \\ w_{i-1}(0, 0, 1, 0) &= w_{i-1}(0, 0, 1, 1) = w_{i-1}(1, 1, 0, 0) = w_{i-1}(1, 1, 0, 1) = y_3. \end{aligned} \quad (18)$$

From eqs. (6), (9), (10) and (18), we have

$$q_i = (4/3)(y_1 + y_2 + y_3)/(y_0 + y_1 + y_2 + y_3) \leq 4/3, \quad (19)$$

where the inequality is due to a fact that y_k 's cannot be negative.

The q_i can be expressed in terms of three correlativities as

$$q_i = 1 + (\varepsilon(s_1, s_2) + \varepsilon(s_2, s_3) + \varepsilon(s_3, s_1))/3 \quad (\text{for the third type}), \quad (20)$$

where the correlativities are evidently given by

$$\begin{aligned} (1 + \varepsilon(s_1, s_2))/(1 - \varepsilon(s_1, s_2)) &= (y_1 + y_2)/(y_3 + y_0), \\ (1 + \varepsilon(s_2, s_3))/(1 - \varepsilon(s_2, s_3)) &= (y_2 + y_3)/(y_1 + y_0), \\ (1 + \varepsilon(s_3, s_1))/(1 - \varepsilon(s_3, s_1)) &= (y_3 + y_1)/(y_2 + y_0). \end{aligned} \quad (21)$$

The second type is a special case of the third type where $\varepsilon(s_2, s_3) = \varepsilon(s_3, s_1) = 0$, and the first type that of the second type where $\varepsilon(s_1, s_2) = 0$. Hence,

$$q_i = 1 + \varepsilon(s_1, s_2)/3 \quad (\text{for the second type}), \quad (22)$$

$$q_i = 1 \quad (\text{for the first type}). \quad (23)$$

For the second, third and fourth types, q_i evidently depends only on a family containing mutually correlated sites around the i -th lattice point, which is said the family of the i -th lattice point.

VI. Body Disorder Entropy and Surface Disorder Entropy

Equation (7) can be rewritten as

$$S/k = n(\ln(3/2) + \ln \bar{q}) + (f/2) \ln 2 \quad (24)$$

or

$$S/k = n(\ln(3/2) + \ln q^*) + (f/2)(\ln 2 - \ln q^*), \quad (25)$$

where \bar{q} and q^* are defined by

$$(\bar{q})^n = (q^*)^{(n-f/2)} = \prod_{i=1}^n q_i = Q. \quad (26)$$

Namely, \bar{q} is a geometric mean of all q_i 's. The meaning of q^* becomes clear if we use a basic numbering. Then, because of eqs. (18) and (23), Q is the product of $n - (f/2) + 1$ q_i 's for the second type by a basic numbering. Hence, q^* is practically equal to a geometric mean of q_i 's for the second type by a basic numbering.

We might call the coefficients of n and f in eq. (24) or (25) the body disorder entropy per molecule and the surface disorder entropy per surface bond, respectively. But such definitions are ambiguous.

Physically, surface entropy is defined of a sufficiently broad surface parallel to a definite crystal plane, by the increase in entropy of the system gained by cutting a large crystal in such a way that the surface appears.

We now rewrite eq. (7) as

$$S/k = n(\ln(3/2) + \ln q_\infty) + (f/2)(\ln 2 - \delta), \quad (27)$$

where

$$\ln q_\infty = \lim_{n/f \rightarrow \infty} \ln \bar{q} = \lim_{n/f \rightarrow \infty} \ln q^* = \lim_{n/f \rightarrow \infty} \left(\sum_{i=1}^n \ln q_i/n \right) \quad (28)$$

and

$$\delta = (2/f) \sum_{i=1}^n \ln(q_\infty/q_i), \quad (29)$$

and call the coefficients of n and f the body disorder entropy per molecule of ice and the surface disorder entropy per surface bond of the ice crystal, respectively.

The former is the quantity denoted by s_∞ in section III. We expect that for crystals bounded by one kind of crystal planes the latter may converge with increase in n/f , so that the name may be consistent with the physical definition of surface entropy. That this is actually the case shall be demonstrated in section VIII for {01} planes in the two dimensional square lattice.

For a basic numbering, we can generally find such semi-infinite families F_i each with a step that q_∞ can be expressed in terms of correlativities $\epsilon(F_i)$ between two sites at their steps as

$$\ln q = \sum f_i (\ln(1 + (\epsilon(F_i)/3))) / \sum f_i, \quad (30)$$

where f_i 's are definite positive integers. Examples of the families, which shall be called the characteristic families, are shown in Fig. 3.

An intuitive but not strict proof of eq. (30) for these examples is obtained by considering that a semi-infinite part, corresponding to one of F_i 's, of an infinite ice lattice has been already numbered. Then, by continuing the numbering, lattice points whose families are F_i will appear by frequency f_i .

Approximate values of q_∞ can be obtained by computing $\epsilon(F_i)$ with the aid of eq. (16). Taking account of contributions from the shortest paths in each oxygen lattice, we easily see from Fig. 3 that

$$\begin{aligned} \epsilon(F) &\cong 3^{-3} && \text{for the square lattice,} \\ \epsilon(F_1) &\cong \epsilon(F_2) \cong 3^{-2}; \epsilon(F_3) \cong 3^{-5} \cong 0 && \text{for the Kagomé lattice, and} \\ \epsilon(F_1) &\cong \epsilon(F_2) \cong 2 \times 3^{-5} && \text{for the wurtzite-like lattice,} \end{aligned} \quad (31)$$

and hence from eq. (30) we have

$$\begin{aligned} \ln q_\infty &\cong \ln(1 + 3^{-4}) \cong 1/81 \cong 3.04\% \text{ of } \ln(3/2) && \text{for the square lattice,} \\ \ln q_\infty &\cong (2/3) \ln(1 + 3^{-3}) \cong 2/81 \cong 6.1\% \text{ of } \ln(3/2) && \text{for the Kagomé lattice, and} \\ \ln q_\infty &\cong \ln(1 + 2 \times 3^{-6}) \cong 2/729 \cong 0.68\% \text{ of } \ln(3/2) && \text{for the wurtzite-like lattice.} \end{aligned} \quad (32)$$

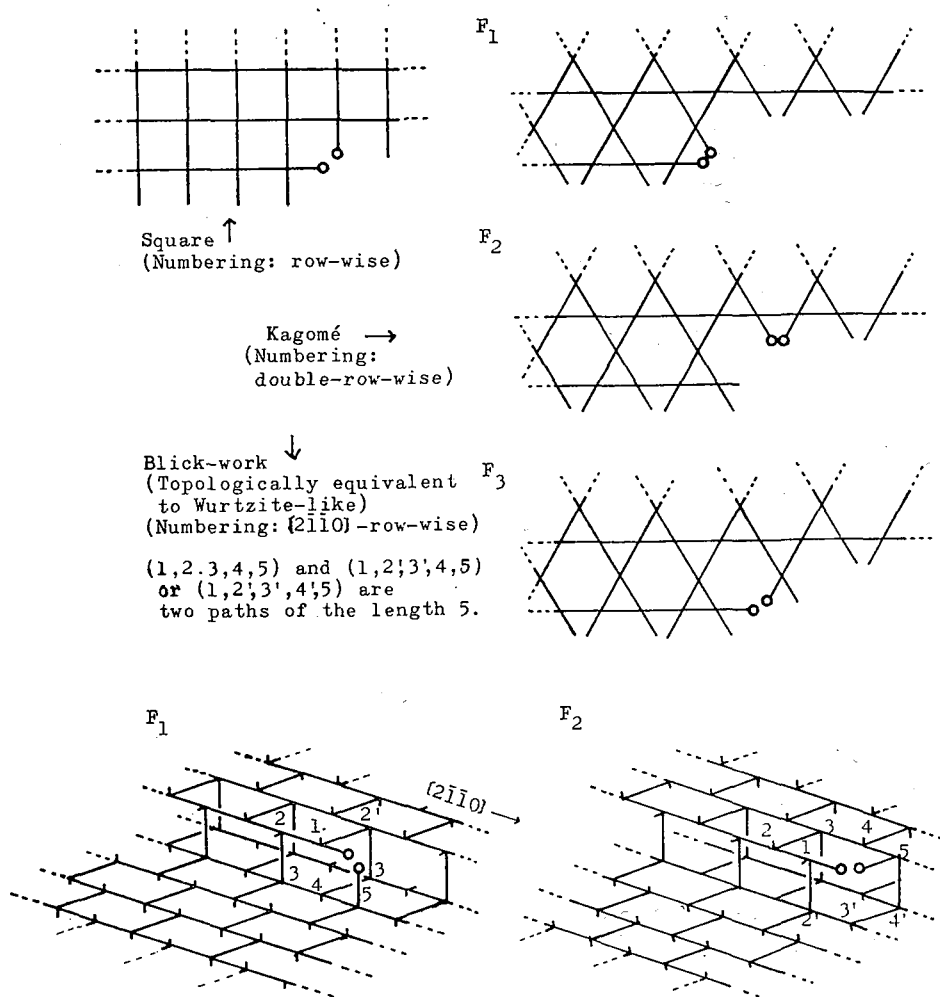


Fig. 3. Characteristic families (shown by bonds on which their sites lie)

The first approximate values for the square lattice and for the wurtzite-like lattice are identical with those obtained by DiMarzio and Stillinger, Jr. (1964) by another method.

VII. Infinitely Long Rectangular Crystals

Consider a rectangular lattice $L(B, M)$ of length M and width B , bounded by $\{01\}$ surfaces in the square oxygen lattice (Fig. 4). The numbering is done row-wise (rightward on each row and row after row downward). Evidently, the lattice points on the first row or on the first column are of the first type and others are of the second type. Hence, the numbering is basic.

Let the number of all possible arrangements on $L(B, M)$ be denoted by $w(B, M)$, a lattice point at the cross of the m -th column and the b -th row by (b, m) (shown by a black dot in Fig. 4), its family by $F(b, m)$ (whose sites are on thick bonds in Fig. 4) and the q -value of (b, m) by $q(b, m)$.

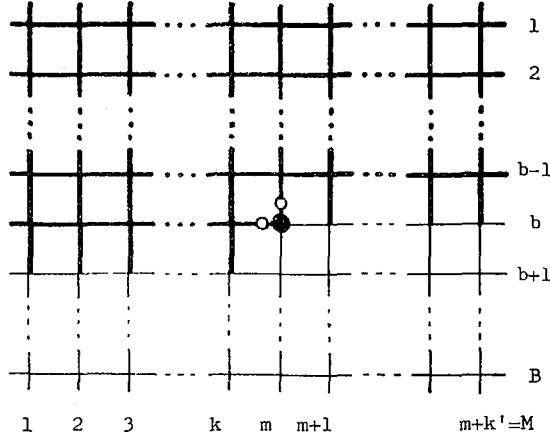


Fig. 4. $L(B, M)$, a rectangular lattice of width B and length M

Then, from eq. (5),

$$\ln w(B, M) = M \times B \ln(3/2) + (M+B) \ln 2 + \sum_{b=1}^B \sum_{m=1}^M \ln q(b, m). \quad (33)$$

Evidently, $q(b, m)$ depends only on b , m and M . For convenience's sake, we introduce k and k' by

$$k = m-1 \text{ and } k' = M-m, \quad (34)$$

and a function $q(b, k, k')$ by

$$q(b, m) = q(b, k, k') = q(b, m-1, M-m). \quad (35)$$

Now, since $F(b, m)$ can be constructed by linear repetition of elemental units (columns in one view and rows in another view), the number of all possible components having state values β_1 and β_2 on sites s_1 and s_2 at the step (shown by open circles in Fig. 4), $u(s_1, s_2; \beta_1, \beta_2)$, can be expressed by a standard procedure used in lattice combinatorics as

$$\begin{aligned} u(s_1, s_2; \beta_1, \beta_2) &= (\mathbf{u}_{b-1}, (\mathbf{B}_{b-1})^{k'} \mathbf{Q}_{b-1, b}(\beta_1, \beta_2) (\mathbf{B}_b)^k \mathbf{u}_b) \quad (\text{in the former view}), \\ &= (\mathbf{u}_m, \mathbf{Q}_{m, M}(\beta_1, \beta_2) (\mathbf{B}_M)^{b-1} \mathbf{u}_M) \quad (\text{in the latter view}), \end{aligned} \quad (36)$$

where \mathbf{B}_p is a $2^{p-1} \times 2^{p-1}$ symmetric matrix, $\mathbf{Q}_{p, r}$ a $2^{p-1} \times 2^{r-1}$ matrix and \mathbf{u}_p a vector consisting of 2^{p-1} components all being equal to unity. From eqs. (36), we can prove that $x(s_1, s_2)$ and hence $q(b, k, k')$ converge with increase in b and/or k and/or k' . In particular

$$\lim_{k, k' \rightarrow \infty} q(b, k, k') = q(b, \infty, \infty), \quad (37)$$

$$\lim_{b \rightarrow \infty} q(b, \infty, \infty) = q(\infty, \infty, \infty). \quad (38)$$

(See Appendix B of paper I for complete deductions, which may be guessed from considerations given in Appendix of the present paper.)

From eqs. (37) and (38), we easily have

$$\lim_{M \rightarrow \infty} \left(\left(\sum_{m=1}^M \ln q(b, m) \right) / M \right) = \ln q(b, \infty, \infty), \quad (39)$$

$$\lim_{B \rightarrow \infty} \left(\left(\sum_{b=1}^B \ln q(b, \infty, \infty) \right) / B \right) = \ln q(\infty, \infty, \infty). \quad (40)$$

Using eqs. (33), (39) and (40), we have

$$\begin{aligned} \lim_{M \rightarrow \infty} (\ln (w(B, M))/M) &= B \ln (3/2) + \lim_{M \rightarrow \infty} (1 + (B/M)) \ln 2 + \sum_{b=1}^B \lim_{M \rightarrow \infty} \left(\sum_{m=1}^M \ln q(b, m)/M \right) \\ &= B \ln (3/2) + \ln 2 + \sum_{b=1}^B \ln q(b, \infty, \infty) \end{aligned} \quad (41)$$

and

$$\lim_{B \rightarrow \infty} (\lim_{M \rightarrow \infty} (\ln (w(B, M))/M)/B) = \ln (3/2) + \ln q(\infty, \infty, \infty).$$

Hence, $\ln q_\infty$ for the square oxygen lattice is $\ln q(\infty, \infty, \infty)$, which is obviously $\ln(1 + \varepsilon(F)/3)$. Thus, eq. (30) in the last section has been proven for the square oxygen lattice.

Equation (41) expresses the disorder entropy (divided by k) per column of an infinitely long rectangular crystal. By rewriting the right-hand side as

$$B(\ln (3/2) + \ln q(\infty, \infty, \infty)) + \ln 2 - \sum_{b=1}^B \ln (q(\infty, \infty, \infty)/q(b, \infty, \infty)) \quad (43)$$

and taking account of a fact that each column has B molecules and two surface bonds, we can regard the quantity

$$\mathcal{A}_1(B) = \sum_{b=1}^B \ln (q(\infty, \infty, \infty)/q(b, \infty, \infty)) \quad (44)$$

as δ in eq. (27) in this case. Its convergence with increasing B shall be proven in the next section.

Reasonings given in the present section can be extended, in principle, for arbitrary oxygen lattices and for arbitrary crystal planes so as to prove eq. (30) and to get the expression of δ for the crystal planes.

VIII. A Lowerbound of Surface Disorder Entropy

In paper I, we have proven that δ cannot be larger than $\ln 2$. In this section, we will prove that it is less than $\ln(4/3)$.

Consider a rectangular lattice of length M and width $2B+1$ and use the following numbering: Row-wise from $(1, 1)$ to (B, M) , skip the $B+1$ -th row, again row-wise from $(B+2, 1)$ to $(2B+1, M)$, and lastly from $(B+1, 1)$ to $(B+1, M)$. The lattice points on the $B+1$ -th row are of the third type except $(B+1, 1)$ which is of the first type. Evidently,

$$q(b, m) = q(b+B+1, m) \text{ for } 1 \leq b \leq B. \quad (45)$$

Therefore,

$$\begin{aligned} \ln w(2B+1, M) &= M(2B+1) \ln (3/2) + (M+2B+1) \ln 2 + \sum_{b=1}^{2B+1} \sum_{m=1}^M \ln q(b, m) \\ &= M \ln (3/2) + \ln 2 - M \ln 2 + \sum_{m=1}^M \ln q(B+1, m) \\ &\quad + 2(M \times B \ln (3/2) + (M+B) \ln 2) + \sum_{b=1}^B \sum_{m=1}^M \ln q(b, m) \\ &= M \ln (3/2) + \ln 2 - M \ln 2 + \sum_{m=1}^M \ln q(B+1, m) + 2 \ln w(B, M). \end{aligned} \quad (46)$$

Hence,

$$\begin{aligned} & \lim_{M \rightarrow \infty} (\ln (\omega(2B+1, M))/M) \\ &= \ln (3/2) - \ln 2 + \lim_{M \rightarrow \infty} \left(\sum_{m=1}^M (\ln q(B+1, m))/M \right) + 2 \lim_{M \rightarrow \infty} (\ln (\omega(M, B))/M). \end{aligned} \quad (47)$$

From eqs. (41) and (47),

$$\begin{aligned} & (2B+1) (\ln (3/2) + \ln q(\infty, \infty, \infty)) + \ln 2 - \mathcal{A}_1(2B+1) = \ln (3/2) - \ln 2 \\ & + \lim_{M \rightarrow \infty} \left(\sum_{m=1}^M (\ln q(B+1, m))/M \right) + 2(B (\ln (3/2) + \ln q(\infty, \infty, \infty)) + \ln 2 - \mathcal{A}_1(B)) \end{aligned}$$

or

$$\ln q(\infty, \infty, \infty) - \mathcal{A}_1(2B+1) + 2\mathcal{A}_1(B) = \lim_{B \rightarrow \infty} \left(\sum_{m=1}^M (\ln q(B+1, m))/M \right) \leq \ln (4/3). \quad (48)$$

Inequality is due to relation (19). Now, eq. (40) can be rewritten as

$$\lim_{B \rightarrow \infty} (\mathcal{A}_1(B)/B) = 0. \quad (49)$$

From relations (48) and (49), we can prove

$$\ln q(\infty, \infty, \infty) + \lim_{B \rightarrow \infty} \mathcal{A}_1(B) = \lim_{B \rightarrow \infty} \left(\lim_{M \rightarrow \infty} \left(\sum_{m=1}^M (\ln q(B+1, m))/M \right) \right) \leq \ln (4/3). \quad (50)$$

Since, as will be seen later, $\ln q(\infty, \infty, \infty)$ is positive, relation (50) shows that $\lim_{B \rightarrow \infty} \mathcal{A}_1(B)$ is less than $\ln (4/3)$.

Note that relation (48) alone is not sufficient for relation (50).

Reasonings in this section can also be extended to surface disorder entropies defined of arbitrary crystal planes, so that convergences of them expected in section VI might be proven.

IX. Numerical Values

If we know four matrices B_{b-1} , B_b , $Q_{b-1,b}(0, 1)$ and $Q_{b-1,b}(0, 0)$, we can calculate $q(b, k, k')$ through eqs. (14), (22) and (36). Formerly this procedure was adopted and values of $q(b, k, k')$ for $k, k'=1, 2, 4, 8, 16$ and 32 and for $b \leq 7$ were calculated with the aid of electronic computers. Values of $\ln q(b, \infty, \infty)$ were obtained from them in relative accuracy of 10^{-5} or better. Rounded in four effective figures, they are given in paper I.

Now, from eq. (41), we have

$$\ln q(b, \infty, \infty) = \lim_{M \rightarrow \infty} (\ln (\omega(b, M))/M) - \lim_{M \rightarrow \infty} (\ln (\omega(b-1, M))/M) - \ln (3/2). \quad (51)$$

As was proven in Appendix B of paper I (see also Appendix of this paper),

$$\lim_{M \rightarrow \infty} (\ln (\omega(b, M))/M) = \ln \lambda_b, \quad (52)$$

where λ_b is the maximum eigenvalue of B_b . Hence, we can obtain $\ln q(b, \infty, \infty)$ from the knowledge of B_b and B_{b-1} . Furthermore, by maximal use of symmetric characters in shape of a rectangle, the dimension of the matrix B_b can be reduced considerably, for instance, from $2^7 \times 2^7$ to 72×72 for $b=8$ and from $2^8 \times 2^8$ to 136×136 for $b=9$ (See Appendix). Owing to these two simplifications, we now need much less memories of an electronic computer for calculating $\ln q(b, \infty, \infty)$ than before and we have calculated

Table 1. Values of $\ln q(b, \infty, \infty)$ and related quantities

b	2	3	4	5	6	7	8	9
$\ln q(b, \infty, \infty) \times 10^5$	1359	1877	2128	2269	2355	2412	2452	2481
$\ln q(b, \infty, \infty) / \ln(3/2)$ (%)	3.352	4.629	5.249	5.595	5.809	5.950	6.047	6.118
$A(b) \times 10^5$	1359	2395	3149	3711	4145	4487	4764	4993
$A(b) / \ln 2$ (%)	1.960	3.455	4.543	5.354	5.979	6.473	6.873	7.203

values of $\ln q(b, \infty, \infty)$ for b up to nine. Rounded in four effective figures, they are given in Table 1 together with related quantities, of which $A(B)$ is defined by

$$A(B) = \sum_{b=1}^B \ln(q(B, \infty, \infty) / q(b, \infty, \infty)). \quad (53)$$

It evidently satisfies the relation

$$\lim_{B \rightarrow \infty} A(B) = \lim_{B \rightarrow \infty} A_1(B) \quad (54)$$

and is used for computing $\lim_{B \rightarrow \infty} A_1(B)$.

At a glance, $\ln q(b, \infty, \infty)$ seems to be very closely approximated by a function $f(b) = 0.028(1 - b^{-1})$, whose values are given in the third column of Table 2. Comparing them with the values of $\ln q(b, \infty, \infty)$, which are retabulated in the second column of the table, we see that the maximal relative difference is only about 3% at $b=2$.

Table 2. Values of functions for approximating $\ln q(b, \infty, \infty)$

b	$\ln q \times 10^5$	$f(b) \times 10^5$	$G(b, b') \times 10^5$						
			b' 2	3	4	5	6	7	8
2	1359	1400	1359*	1390	1422	1451	1475	1496	1515
3	1877	1867	1877*	1877*	1892	1912	1930	1947	1962
4	2128	2100	2158	2128*	2128*	2137	2147	2159	2169
5	2269	2240	2338	2281	2269*	2269*	2274	2280	2287
6	2355	2333	2463	2387	2362	2355*	2355*	2358	2362
7	2412	2400	2556	2463	2429	2415	2412*	2412*	2414
8	2452	2450	2629	2520	2470	2462	2455	2452*	2452*
9	2481	2489	2687	2565	2518	2496	2487	2482	2481*
	$B(b')$		0.765	0.913	1.009	1.080	1.132	1.175	1.211
	$A(b') \times 10^5$		3302	2964	2826	2753	2712	2685	2667
	$(A(b') + \ln q(b', \infty, \infty)) \times 10^5$		4661	4841	4954	5022	5081	5097	5119

However, $f(b)$ cannot describe the overall nature of $\ln q(b, \infty, \infty)$, since $\sum (f(\infty) - f(b))$ diverges while $\sum (\ln q(\infty, \infty, \infty) - \ln q(b, \infty, \infty))$ should converge.

Now, we introduce a function $G(b, b')$ by

$$G(b, b') = A(b')(1 - b^{-B(b')}), \quad (55)$$

where $A(b')$ and $B(b')$ are given by

$$\begin{aligned}\ln q(b', \infty, \infty) &= A(b')(1 - b'^{-B(b')}), \\ \ln q(b'+1, \infty, \infty) &= A(b'+1)(1 - (b'+1)^{-B(b')}).\end{aligned}\quad (56)$$

Values of $G(b, b')$, $A(b')$ and $B(b')$ are given in Table 2. We see that both $A(b')$ and $B(b')$ are monotonic at least for $b' \leq 8$. It is very probable that they may be monotonic for $b' < \infty$. Then, we may have

$$\ln q(\infty, \infty, \infty) = \lim_{b \rightarrow \infty} A(b) < A(b) \quad (57)$$

and

$$\ln(q(\infty, \infty, \infty)/q(b, \infty, \infty)) = A(b)b^{-B(b)} < A(b')b^{-B(b')} \text{ for } b > b'. \quad (58)$$

The last row of Table 2 shows values of a function $A(b') + \ln q(b', \infty, \infty)$, which is also monotonic for $b' \leq 8$. Assuming that it is monotonic for $b' < \infty$, we have

$$\ln q(\infty, \infty, \infty) = (A(\infty) + \ln q(\infty, \infty, \infty))/2 < (A(b') + \ln q(b', \infty, \infty))/2. \quad (59)$$

From relations (57) and (59), we have

$$A(8) \doteq 0.02667 > \ln q(\infty, \infty, \infty) > (A(8) + \ln q(8, \infty, \infty))/2 \doteq 0.02559. \quad (60)$$

An upperbound of $A_1(\infty)$ can be obtained as follows:

$$\begin{aligned}A_1(\infty) &= \sum_{b=1}^{\infty} \ln(q(\infty, \infty, \infty)/q(b, \infty, \infty)) = \sum_{b=1}^9 \ln(q(9, \infty, \infty)/q(b, \infty, \infty)) \\ &\quad + 9 \times \ln(q(\infty, \infty, \infty)/q(9, \infty, \infty)) + \sum_{b=10}^{\infty} \ln(q(\infty, \infty, \infty)/q(b, \infty, \infty)) \\ &< A(9) + 9 \times (0.02667 - 0.02481) + A(8) \int_9^{\infty} b^{-B(8)} db \doteq 0.04993 + 0.01674 \\ &\quad + 0.02667 \int_9^{\infty} b^{-1.211} db \doteq 0.14615.\end{aligned}\quad (61)$$

This upperbound is about 21% of $\ln 2$ or 50% of $\ln(4/3)$.

X. Concluding Remarks

The disorder entropy of ice, that is, the additional entropy due to randomness of proton arrangements in the Bernal-Fowler-Pauling model of ice, has been unambiguously separated into two parts, the body disorder entropy and the surface disorder entropy, by eqs. (27), (28) and (29) in section VI. The methods for computing them have been developed in sections VII and VIII for crystals bounded by {01} surfaces in the square oxygen lattice and numerical values have been given in section IX by relations (60) and (61), of which the former is of sufficient accuracy while the latter may require some refinement.

As stated in sections VII and VIII, the methods can be extended for any oxygen lattices and any crystal planes, at least in principle. But actual numerical computation of the disorder entropy for the three dimensional oxygen lattice is almost prohibitive because of the enormous number of memories required for an electronic computer to carry out it. The results given in relations (32), which have been obtained on the basis of a very plausible approximate equation, eq. (16), shows that the value of $\ln q_{\infty}$ for the wurtzite-like oxygen lattice (real ice) may be of the order of a few tenths of that for the square oxygen lattice. If we assume that the value of $\ln q_{\infty}$ for the wurtzite-like lattice be 1.5 ($\cong 6.5 \times 0.68/3.04$) % of $\ln(3/2)$, we have 0.82 cal/deg·mol as the body disorder entropy

instead of 0.806 cal/deg·mol of Pauling's value. This may be an important result because then the residual entropy, 0.82 ± 0.05 cal/deg·mol, obtained by Giauque *et al.* (1933, 1936) can be possibly explained by the disorder entropy alone, while if the disorder entropy would be less than the residual entropy we should consider some other reasons to explain the residual entropy completely.

Another interesting result is that $\ln q(b, \infty, \infty)$ is very closely approximated by $f(b) = 0.028(1 - b^{-1})$ for small values of b . This means that the effect of the surface decreases in a sense as b^{-1} and practically disappears at the depth of ten or twenty layers below the surface. The question, if this is also true for other surfaces than {01} planes and for surfaces in the Kagomé lattice, can and shall be answered in near future.

Acknowledgments

Numerical values of $\ln q(b, \infty, \infty)$ were calculated with the aid of electronic computers, NEAC 2203 G of Hokkaido University (for $b \leq 5$) and HITAC 5020 of the University of Tokyo (for $b \leq 9$).

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Appendix. Calculation of $\lim_{m \rightarrow \infty} ((\ln w(b, m))/m)$

A I. SIMPLIFIED ELEMENTAL MATRICES

Let $L(b, m)$ be a rectangular lattice of length m and width b (Fig. 5). Let S_b be a set of b sites on its lower edge (shown by open circles) and S_b' be that of those on its upper edge (shown by black dots). We regard b state values of b ordered sites as a binary expression of an integer j , which is said the state number of the set of the b sites. An integer, obtained by interchanging zero and unity of all binary digits of j , is denoted by \bar{j} :

$$\bar{j} + j = 2^b - 1. \quad (\text{A } 1)$$

Let $w(b, m; i, j)$ be the number of all possible arrangements on $L(b, m)$ having the

state numbers i on S_b and \bar{j} (not j) on S'_b . Since S_b and S'_b exchange their roles by a rotation of $L(b, m)$ by π around its horizontal axis,

$$w(b, m : i, j) = w(b, m : \bar{j}, \bar{i}). \quad (\text{A } 2)$$

On the other hand, because of eq. (13) in the text,

$$w(b, m : i, j) = w(b, m : \bar{i}, \bar{j}). \quad (\text{A } 3)$$

Since $L(b, m)$ can be considered as a combination of $L(b, m-1)$ and $L(b, 1)$ in such a manner that the bonds with S_b of the former are linked to the bonds with S'_b of the latter, we easily have

$$w(b, m : i, j) = \sum_{k=0}^{2^b-1} w(b, 1 : i, k) w(b, m-1 : k, j) \quad (\text{A } 4)$$

and

$$w(b, m : i) = \sum_k w(b, 1 : i, k) w(b, m-1 : k), \quad (\text{A } 5)$$

where

$$w(b, m : i) = \sum_k w(b, m : i, k) \quad (\text{A } 6)$$

is the number of all possible arrangements on $L(b, m)$ having the state number i on S_b . Evidently

$$w(b, m : i) = w(b, m : \bar{i}). \quad (\text{A } 7)$$

The number of all possible arrangements on $L(b, m)$ is given by

$$w(b, m) = \sum_{i=0}^{2^b-1} w(b, m : i). \quad (\text{A } 8)$$

From eqs. (A 5) to (A 8), we have

$$w(b, m : i) = \sum_{k=0}^{2^{b-1}-1} (w(b, 1 : i, k) + w(b, 1 : i, \bar{k})) w(b, m-1 : k), \quad (\text{A } 9)$$

$$w(b, 1 : i) = \sum_k (w(b, 1 : i, k) + w(b, 1 : i, \bar{k})), \quad (\text{A } 10)$$

$$w(b, m) = 2 \sum_k w(b, m : k). \quad (\text{A } 11)$$

It is convenient to consider $w(b, m : k)$ as the k -th component of a 2^{b-1} dimensional vector \mathbf{u}_b^m and $(w(b, 1 : i, k) + w(b, 1 : i, \bar{k}))$ as the (i, k) -component of a $2^{b-1} \times 2^{b-1}$ matrix B_b :

$$B_b(i, k) = w(b, 1 : i, k) + w(b, 1 : i, \bar{k}) \quad (i, k = 0, 1, \dots, 2^{b-1}-1). \quad (\text{A } 12)$$

Introducing a 2^{b-1} dimensional vector \mathbf{u}_b whose components are all unity and using eq. (A 9) iteratively, we have, in notations of matrix and vector calculus,

$$w(b, m) = 2(\mathbf{u}_b, (B_b)^m \mathbf{u}_b). \quad (\text{A } 13)$$

Thus, $w(b, m)$ can be calculated by knowing the matrix B_b , which was called in paper I the simplified elemental matrix for a rectangle of width b . The name, the elemental matrix, was given to a matrix whose (i, k) -component is $w(b, 1 : i, k)$.

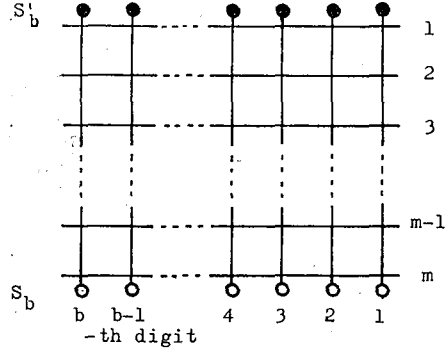


Fig. 5. $L(b, m)$, a rectangular lattice of length m and width b

A II. CONVERGENCE OF $\lim_{m \rightarrow \infty} ((\ln w(b, m))/m)$

Because of eqs. (A 2) and (A 3), B_b is symmetric. Hence, its eigenvalues are all real and it can be transformed into a diagonal form by an orthogonal matrix:

$$B_b = T B_D \tilde{T}, \quad (\text{A 14})$$

$$\tilde{T} T = 1, \quad (\text{A 15})$$

$$B_D(i, j) = \lambda_j \delta(i, j), \quad (\text{A 16})$$

where λ_j is the j -th eigenvalue of B_b , \tilde{T} the transpose of T and $\delta(i, j)$ the Kronecker's delta.

From eqs. (A 13), (A 14), (A 15) and (A 16), we have

$$w(b, m) = 2(\mathbf{u}_0, T (B_D)^m \tilde{T} \mathbf{u}_0) = 2 \sum_j \sum_i \sum_k T(i, j) T(k, j) (\lambda_j)^m = (\lambda_{\max})^m C(m), \quad (\text{A 17})$$

where

$$C(m) = \sum_j c_j (\lambda_j / \lambda_{\max})^m, \quad (\text{A 18})$$

$$c_j = 2 \sum_k \sum_i T(i, j) T(k, j)$$

and λ_{\max} is the largest absolute value of the eigenvalues.

Evidently,

$$\lim_{m \rightarrow \infty} C(m) = C_1 + (-1)^m C_2, \quad (\text{A 19})$$

where

$$C_1 = \sum' c_j \quad (\text{sum over those } j \text{ such that } \lambda_j = \lambda_{\max}), \quad (\text{A 20})$$

$$C_2 = \sum'' c_j \quad (\text{sum over those } j \text{ such that } \lambda_j = -\lambda_{\max}).$$

Since $w(b, 2m+1)$ is larger than $w(b, 2m)$ and since $w(b, m)$ is always positive

$$C_1 - C_2 > (C_1 + C_2) / \lambda_{\max} > 0. \quad (\text{A 21})$$

(Actually, C_2 does not exist and C_1 consists of only one term.)

From relation (A 19), we have

$$\lim_{m \rightarrow \infty} (\ln(C(m))/m) = 0. \quad (\text{A 22})$$

From eqs. (A 17) and (A 22),

$$\lim_{m \rightarrow \infty} (\ln(w(b, m))/m) = \ln \lambda_{\max}. \quad (\text{A 23})$$

A III. REDUCED ELEMENTAL MATRICES

A number, whose binary expression is a mirror of that of j with respect to the center of b digits, is denoted by j^* . Because of the mirror symmetry of a rectangle with respect to its vertical axis, we have

$$w(b, m : j) = w(b, m : j^*). \quad (\text{A 24})$$

Define an integer function $h(j)$ for $j=0, 1, \dots, 2^{b-1}-1$ by

$$\begin{aligned} h(j) &= j^* & \text{if } j^* < 2^{b-1}, \\ h(j) &= \bar{j}^* & \text{if } j^* \geq 2^{b-1}. \end{aligned} \quad (\text{A 25})$$

Table A 1. Relations among state numbers for $b=4$

j	binary	0000	0001	0010	0011	0100	0101	0110	0111
	decimal	0	1	2	3	4	5	6	7
\bar{j}	binary	1111	1110	1101	1100	1011	1010	1001	1000
	decimal	15	14	13	12	11	10	9	8
j^*	binary	0000	1000	0100	1100	0010	1010	0110	1110
	decimal	0	8	4	12	2	10	6	14
\bar{j}^*	binary	1111	0111	1011	0011	1101	0101	1001	0001
	decimal	15	7	11	3	13	5	9	1
$h(j)$	decimal	0	7	4	3	2	5	6	1

Evidently, the function defines a permutation of $(0, 1, \dots, 2^{b-1})$ and also

$$h(h(j)) = j. \quad (\text{A } 26)$$

As an example, relations among state numbers are shown above for $b=4$.

Because of eqs. (A 7), (A 24) and (A 25),

$$w(b, m : j) = w(b, m : h(j)). \quad (\text{A } 27)$$

Using eqs. (A 12), (A 26) and (A 27), we now rewrite eqs. (A 9), (A 10) and (A 11) as follows:

$$\begin{aligned} w(b, m : i) &= \sum_{k=0}^{2^{b-1}-1} B_b(i, k) w(b, m-1 : k) = \sum_{k \leq h(k)} B_b(i, k) w(b, m-1 : k) \\ &+ \sum_{k > h(k)} B_b(i, k) w(b, m-1 : k) = \sum_{k \leq h(k)} B_b(i, k) w(b, m-1 : k) \\ &+ \sum_{h(k) > h(h(k))} B_b(i, h(k)) w(b, m-1 : h(k)) = \sum_{k \leq h(k)} B_b(i, k) w(b, m-1 : k) \\ &+ \sum_{h(k) > k} B_b(i, h(k)) w(b, m-1 : k) = \sum_{k \leq h(k)} (B_b(i, k) + B_b(i, h(k)) (1 - \delta(k, h(k)))) w(b, m-1 : k), \end{aligned} \quad (\text{A } 28)$$

$$\begin{aligned} w(b, 1 : i) &= \sum_{k \leq h(k)} B_b(i, k) + \sum_{k > h(k)} B_b(i, k) = \sum_{k \leq h(k)} B_b(i, k) + \sum_{h(k) > h(h(k))} B_b(i, h(k)) \\ &= \sum_{k \leq h(k)} (B_b(i, k) + B_b(i, h(k)) (1 - \delta(k, h(k)))) \end{aligned} \quad (\text{A } 29)$$

$$\begin{aligned} w(b, m) &= \sum_{k \leq h(k)} w(b, m : k) + \sum_{k > h(k)} w(b, m : k) = \sum_{k \leq h(k)} w(b, m : k) \\ &+ \sum_{h(k) > h(h(k))} w(b, m : h(k)) = \sum_{k \leq h(k)} (2 - \delta(k, h(k))) w(b, m : k). \end{aligned} \quad (\text{A } 30)$$

Let i_1, i_2, \dots, i_N be the set of integers i such that $i \leq h(i)$. N is the number of independent components of the vector \mathbf{u}_b^m . Integers in the set satisfy

$$i_s \leq h(i_s) < 2^{b-1} \leq \bar{h}(i_s) \leq \bar{i}_s. \quad (\text{A } 31)$$

Defining a $N \times N$ matrix $R_b(r, s)$ by

$$\begin{aligned} R_b(r, s) &= B_b(i_r, i_s) + B_b(i_r, h(i_s)) (1 - \delta(i_s, h(i_s))) = w(b, 1 : i_r, i_s) + w(b, 1 : i_r, \bar{i}_s) \\ &+ (w(b, 1 : i_r, h(i_s)) + w(b, 1 : i_r, \bar{h}(i_s))) (1 - \delta(i_s, h(i_s))) \end{aligned} \quad (\text{A } 32)$$

and two N -dimensional vectors \mathbf{v}_b and \mathbf{v}'_b by

$$\mathbf{v}_b(r) = 1; \quad \mathbf{v}'_b(r) = 2 - \delta(i_r, h(i_r)), \quad (\text{A } 33)$$

we have from eqs. (A 28) to (A 30)

Table A 2. b , 2^{b-1} and N

b	1	2	3	4	5	6	7	8	9	10
2^{b-1}	1	2	4	8	16	32	64	128	256	512
N	1	2	3	6	10	20	36	72	136	272

$$w(b, m) = (v'_b, (R_b)^m v_b). \quad (\text{A } 34)$$

We shall call the matrix R_b the reduced elemental matrix for a rectangle of width b . It has considerably less number of components than B_b as seen from Table A 2.

A IV. CONSTRUCTION OF MATRICES

In order to get numerical values of $w(b, 1: i, j)$, we consider a procedure of composing a new row by adding lattice points one after one under the mother lattice having the state number j on its S_b (Fig. 6). An intermediate stage where k new lattice points has been added shall be called the k -th stage and a set of $b+1$ sites on the lower edge at that stage (shown by open circles) shall be denoted by $S_{b+1}(k)$. We investigate what state numbers $j^{(k)}$ can be conceivable for $S_{b+1}(k)$ when the state number j on S_b has been given.

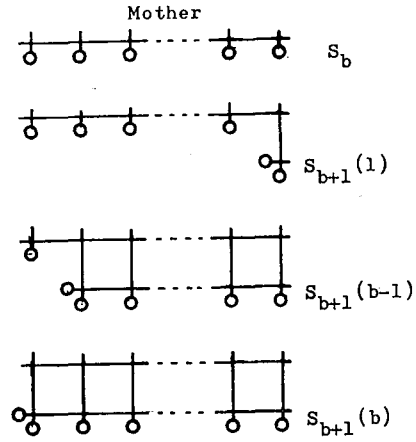


Fig. 6. Construction of a new row

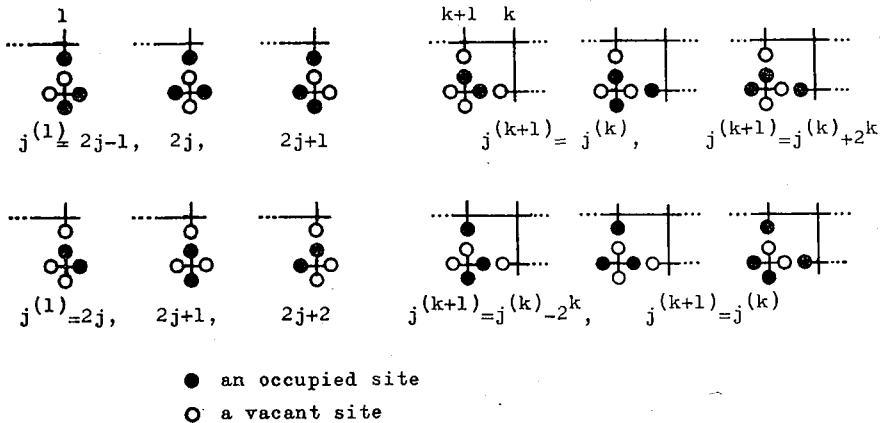


Fig. 7. a) Transfer to the first stage

b) Transfer from the k -th to the $k+1$ -th stage

The transfer to the first stage is shown in Fig. 7 a, from which we see that three numbers are possible for $j^{(1)}$:

$$\begin{aligned} j_1^{(1)} = 2j-1, \quad j_2^{(1)} = 2j \text{ and } j_3^{(1)} = 2j+1 \quad (\text{if } j \text{ is odd}), \\ j_1^{(1)} = 2j, \quad j_2^{(1)} = 2j+1 \text{ and } j_3^{(1)} = 2j+2 \quad (\text{if } j \text{ is even}). \end{aligned} \quad (\text{A } 35)$$

The transfer from the k -th to the $k+1$ -th stage is shown in Fig. 7 b, from which we see that when the $k+1$ -th and the $k+2$ -th digits of $j^{(k)}$ are identical $j^{(k)}$ yields one $j^{(k+1)}$ which is the same as $j^{(k)}$ and when otherwise $j^{(k)}$ yields one more $j^{(k+1)}$ which is obtained by interchanging the $k+1$ -th and the $k+2$ -th digits of $j^{(k)}$.

From the definition, we easily have

$$w(b, 1; i, j) = \text{The number of } j^{(b)} \text{ satisfying } j^{(b)} = i \pmod{2^b}. \quad (\text{A } 36)$$

For a manual practice of the procedure of obtaining $j^{(b)}$, it is convenient to write $j^{(k)}$ in binary forms and put a semi-colon between the $k+1$ -th and the k -th digits as done below for two values of j and for b up to three. But the work is most suitable for an electronic computer. See next section.

Table A 3. Examples of the procedure of obtaining $j^{(b)}$

j	$j^{(1)}$	$j^{(2)}$	$j^{(3)}$	j	$j^{(1)}$	$j^{(2)}$	$j^{(3)}$
010	010; 0	01; 00	0; 100 1; 000	011	010; 1	01; 01	0; 101 1; 001
		00; 10	0; 010			00; 11	0; 011
	010; 1	01; 01	0; 101 1; 001		011; 0	01; 10	0; 110 1; 010
		00; 11	0; 011		011; 1	01; 11	0; 111 1; 011
	011; 0	01; 10	0; 110 1; 010				

A V. A PROGRAM FOR CALCULATING $\ln \lambda_{\max}$

A program actually used for $b=9$ is shown below in Fortran IV language. In order to spare calculating time, we omit all parts concerning printing of intermediate results such as the matrix components of R_b from the program for $b \leq 8$. The program required about 39K memories and 1600 seconds by the electronic computer, HITAC 5020 (a little slower computer than IBM 7090).

PROGRAM	COMMENTS
DIMENSION MA (136), MB (136), MC (200), LE (9), D (136, 136), E (136, 136), P (136), B (136), Q (136)	
N=9	N for b
NA=N-1	
NB=2**NA	NB for 2^{b-1}
NC=NB+NB-1	
M=1	
DO 107 J=1, NB	
L=J-1	L for j
KS=0	
DO 100 K=1, NA	Construction of j^*
I=L/2	
KA=L-I-I	KA is the value of the K-th digit of j .

```

      KS=KS+KA*2**(N-K)
100 L=I
      IF(KS-NB) 16, 17, 17
      17 KS=NC-KS
      16 IF(J-1-KS) 105, 106, 107
105 B(M)=2.
      GO TO 108
106 B(M)=1.
108 MA(M)=J-1
      MB(M)=KS
      M=M+1
107 CONTINUE
      M=M-1
      DO 30 I=1, M
      IF(MA(I)-(MA(I)/2)*2) 35, 36, 35
35 MC(1)=MA(I)+MA(I)-1
      GO TO 37
36 MC(1)=MA(I)+MA(I)
37 MC(2)=MC(1)+1
      MC(3)=MC(2)+1
      MC(4)=-2
      LE(1)=4
      L=5
      DO 38 K=1, NA
      J=1
45 ME=MC(J)/2**K
      MD=ME-(ME/4)*4
      IF(MD) 40, 41, 42
42 IF(MD-2) 43, 44, 41
41 J=J+1
      GO TO 45
44 MC(L)=MC(J)-2**K
      GO TO 46
43 MC(L)=MC(J)+2**K
46 L=L+1
      GO TO 41
40 MC(L)=-2**(K+1)
      LE(K+1)=L
38 L=L+1
      L=LE(N)-1
      L1=LE(N-1)+1
      DO 39 J=L1, L
39 MC(J)=MC(J)-(MC(J)/(NC+1))*(NC+1)
      DO 31 J=1, M
      S=0.
      DO 51 K=1, L
      IF(MC(K)-MA(J)) 51, 52, 53
53 IF(MC(K)-MB(J)) 51, 52, 54
54 IF(MC(K)+MB(J)-NC) 51, 52, 55

```

KS is j^* .

KS is now $h(j)$.

$B(M)$ is $v'_b(m)$ (eq. (A 33)).

$MA(M)$ is i_m .

Now M is N in Table A 2.

$MC(1)$ is $j_1^{(1)}$ for odd j .

$MC(1)$ is $j_1^{(1)}$ for even j .

Endmark for $j^{(1)}$'s

$LE(1)-1$ is the number of $j^{(1)}$'s.

MD is a number composed of the $(k+2)$ -th and $(k+1)$ -th digits of $MC(J)$.

Endmark for $j^{(k+1)}$'s.

$LE(K+1)-K-1$ is the number of $j^{(k+1)}$'s.

Erasing the $b+1$ -th digit.

Construction of R_b .

Use is made of eq. (A 31) for the order of these four statements.

```

55 IF (MC(K)+MA(J)-NC) 51, 52, 51
52 S=S+1.                               S is  $R_b(I, J)$ .
51 CONTINUE
31 D(J, I)=S                             D(J, I) is  $R_b(I, J)$ .
30 CONTINUE
   DO 80 I=1, M
80 Q(I)=D(I, I)
   DO 60 K=1, 5
   DO 61 J=1, M
   DO 64 L=1, M
   S=0.
   DO 63 I=1, M
63 S=S+D(J, I)*D(I, L)
64 E(J, L)=S/16.                         16 for preventing overflow.
   S=0.
   DO 62 I=1, M
62 S=S+E(J, I)*B(I)
61 P(J)=S                                For K=1, 2, 3, 4 and 5, P(J)'s
   DO 65 J=1, M                          are proportional to compo-
   DO 65 I=1, M                          nents of vectors,  $R_b^2 v'_b$ ,  $R_b^{4+2} v'_b$ ,
65 D(J, I)=E(J, I)                        $R_b^{8+6} v'_b$ ,  $R_b^{16+14} v'_b$ , and  $R_b^{32+30} v'_b$ ,
   S=0.                                    respectively.
   DO 67 I=1, M
   B(I)=P(I)
67 S=S+Q(I)*P(I)
   S=S/P(1)
   R=ALOG(S)
60 WRITE(6, 68) S, R
68 FORMAT(2F 16.7)
   STOP
   END

```

Note Added in Proof

J. F. Nagle computed q_∞ for the square, wurtzite-like and diamond lattices by different methods from ours. His results are:

$$\begin{aligned}
 1.5387 < (3/2)q_\infty < 1.5410 & \quad (\text{square}), \\
 1.50681 < (3/2)q_\infty < 1.50686 & \quad (\text{diamond}), \\
 1.50683 < (3/2)q_\infty < 1.50687 & \quad (\text{wurtzite-like}).
 \end{aligned}$$

He said he had also calculated λ_b for b up to seven.

We are obliged to Dr. J. W. Glen for notifying us the work of J. F. Nagle.

Reference Added

NAGLE, J. F. 1966 Lattice statistics of hydrogen bonded crystals. I. The residual entropy of ice. *J. math. Phys.*, **7**, 1484-1491.