



Title	Disorder Entropy of Ice
Author(s)	SUZUKI, Yosio
Citation	Contributions from the Institute of Low Temperature Science, A21, 1-44
Issue Date	1966-09-14
Doc URL	http://hdl.handle.net/2115/20233
Type	bulletin (article)
File Information	A21_p1-44.pdf



[Instructions for use](#)

Disorder Entropy of Ice*

By

Yosio SUZUKI

鈴木 義 男

Physics Section, The Institute of Low Temperature Science.

Received March 1966

Abstract

On the basis of the Bernal-Fowler-Pauling model, additional entropy of ice due to random arrangements of hydrogen atoms is strictly defined for a finite ice crystal, consisting of n water molecules and having f surface free bonds. The entropy, S , thus defined, is called the disorder entropy of the crystal and is shown to be given by

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

where k is BOLTZMANN's constant, q_∞ is a definite quantity, depending on the structure of the oxygen lattice, and δ is a positive quantity, depending on the detailed form of the crystal.

For the wurtzite-like oxygen lattice and for the two-dimensional square oxygen lattice, q_∞ 's are concretely defined and a method for enumeration of approximate values of them is given. In particular, for the two-dimensional square lattice, two series of quantities, $q(b, \infty, \infty)$ and $s(\infty, b)$, converging to q_∞ with b from the underside and from the upperside respectively and each term of them being exactly enumerable, are defined so as to enable one to obtain the value of q_∞ to the desired accuracy. The values of $q(b, \infty, \infty)$ are given for b being up to seven.

For a sufficiently large rectangular crystal in the two-dimensional square lattice, the quantity, δ , is concretely defined by a quantity denoted by Δ_∞ . A series of quantities $\Delta(B)$, converging to Δ_∞ with B , is defined and the values of them for B being up to seven are calculated.

Contents

Introduction	2
1. Definitions and Preliminary Deductions	5

* Contribution No. 775 from the Institute of Low Temperature Science. This paper is based on a thesis presented to Nagoya University in partial fulfillment of the degree of Doctor of Science.

I. 1.	Definition of the Disorder Entropy of a Finite Ice Crystal	5
I. 2.	The Set of All Arrangements Satisfying the Bond Condition, Its Subsets, and Quantities, q_i	7
I. 3.	Complements of an Arrangement	8
I. 4.	Five Cases for Relations among the Subsets, W_{i-1}^{ϕ}	9
I. 5.	Special Numberings of the Lattice Points	12
I. 6.	Expressions of q for the First and the Second Cases.	14
I. 7.	Correlativities and a Rule for Approximate Evaluations of Them	15
II.	Answers to the Three Questions Raised in the Introduction	16
II. 1.	Approximate Expressions for the Disorder Entropy	16
II. 2.	Series of Duplicated Crystals	19
II. 3.	Surface Disorder Entropy	22
II. 4.	Concluding Remarks	26
	Acknowledgements	26
	References	27
	Appendix A. Several Properties of Correlativities	28
A. 1.	Correlativities between Two Bonds	28
A. 2.	Correlativities Re-Interpreted in Terms of Possible Arrangements	28
A. 3.	Two Lattices Coupled by One Bond. I	29
A. 4.	Two Lattices Coupled by One Bond. II	30
A. 5.	Two Lattices Coupled by Two Bonds	30
A. 6.	One Lattice Point and a Lattice Coupled by Two Bonds	32
	Appendix B. A Method for Calculating the Number of Possible Arrange- ments on Lattices of Simple Forms	33
B. 1.	State Values of a Set of Ordered Sites	33
B. 2.	Elemental Matrices	33
B. 3.	Simplified Elemental Matrices	35
B. 4.	Calculation of $s(\infty, b)$	36
B. 5.	Calculation of $q(b, k, k')$	37
B. 6.	Construction of Matrices	38
	A Program for Constructing Matrices	42
	Tables of Matrices and $q(b, k, k')$	43

Introduction

It is well known that in ordinary ice the oxygen atoms lie at the zinc and sulfur sites of the wurtzite lattice. This was confirmed many years ago by x-ray diffraction, which, however, could give little knowledge about the location of the hydrogen atoms because of their weak x-ray scattering power.

BERNAL and FOWLER (1933) considered that each oxygen atom should be linked to its four nearest neighbors by hydrogen bonds, on each of which there should be two possible hydrogen atom sites, one closer to the first and the other to the second oxygen atom. They proposed that hydrogen atoms

should occupy (i) one and only one of two sites on each bond and (ii) two and only two of four sites around each oxygen atom. (The first part of this proposition shall be called the "bond condition" and the second part the "molecule condition".) If these conditions are the only restrictions which the arrangement of hydrogen atoms must obey, a large number of possible arrangements result, which may give additional entropy to ice.

PAULING (1935) suggested that this would be the case even at the absolute zero of the temperature and called the additional entropy the residual entropy of ice. Assuming equal probability of occurrence for every arrangement which satisfies the two conditions of BERNAL and FOWLER, he estimated the entropy of a sufficiently large ice crystal as $k \ln(3/2)$ per molecule, where k is BOLTZMANN's constant.

The close agreement between the value, 0.806 cal/deg-mol, estimated by PAULING, and the value, 0.82 ± 0.05 cal/deg-mol, found experimentally by GIAUQUE *et al.* (1933, 1936) has been generally accepted as a strong support for the suggestion of PAULING. But the agreement might be accidental, because the assumption of equal probability of occurrence would be unbelievable at very low temperatures.

For instance, on the basis of a rough estimate, BJERRUM (1951) stated that energy differences among arrangements satisfying the two conditions mentioned above might be so large that the equal probability of occurrence for them would hardly be acceptable even at the melting point of ice.

The more elaborated calculation by PITZER and POLISSAR (1956), however, gave such values for the energy differences that the assumption of PAULING would be acceptable above 60°K. Moreover, recent results of x-ray and neutron diffraction experiments at higher temperatures also support the assumption (OWSTON 1958).

Therefore, the estimation, based on the assumption of PAULING, of the additional entropy, which shall be called hereafter the disorder entropy instead of the residual entropy because of the improbability of its existence at the absolute zero of temperature, is considered to be significant for the studies of thermodynamic properties of a real ice crystal.

Furthermore, since the disorder entropy of ice is a typical combinatoric quantity, any attempt of calculating it may be useful for studies of general order-disorder phenomena, which are combinatoric in nature.

It has been pointed out by several authors (BJERRUM 1951, also see Footnote 6 of ANDERSON 1956) that the reasoning of PAULING in calculating the disorder entropy lacked in logical rigor, and a recent paper by DIMARZIO and STILLINGER (1964) seems to give a right answer to the problem of estimating

the disorder entropy per molecule of an infinitely large crystal. In the present paper, however, we will discuss the problem of the disorder entropy from a point of view other than that of those authors.

None of them, including PAULING himself, seems to have taken account of the surface effect, which may be negligible compared with the total disorder entropy for a sufficiently large crystal. We consider, however, the effect must be taken into account because of the following three reasons :

First, one used to talk about the disorder entropy per molecule of a sufficiently large ice crystal, and yet one cannot give a concrete figure of sufficient size unless he takes account of the surface effect. Secondly, the effect may not be negligible for a minute crystal, such as a crystal nucleus, a crystalline at the very beginning stage of growth. Thirdly, even if negligible, the surface effect may play an important role in the discussion of surface properties, just as the surface energy does in spite of its negligible contribution to total energy.

Corresponding to these reasons, the following questions may arise :

Question 1 : In what manner does the disorder entropy per molecule converge to a definite non-zero value with the increase of crystal size ?

Question 2 : How is the disorder entropy for a minute crystal expressed ?

Question 3 : How should the surface disorder entropy be defined ?

These three questions can be combined into a single problem, the problem of the disorder entropy for a finite ice crystal, which will be discussed in the present paper.

Since the surface effect is small compared with the total entropy, more strict reasoning may be required for studies of the former than for studies of the latter. Hence, a large part of the paper is devoted to preliminary deductions, of which the first chapter consists.

In section 1.1, the disorder entropy of a finite ice crystal is exactly defined. After several deductions in sections 1.2 through 1.6 the problem of the estimation of the disorder entropy of a finite ice crystal is shown to narrow down to the problem of the estimation of quantities, which are given the name of correlativites in section 1.7, where a rule for approximate estimation of correlativities is also given.

In section 11.1, the disorder entropy is expressed as the sum of two terms, one proportional to the number of molecules and the other that of free bonds. The coefficients of them are approximately estimated, giving the first approximate equation of disorder entropy, which may serve as a complete reply to the second question and also as a partial reply to the first question stated above. Then, the disorder entropy per molecule of an infinitely large crystal, denoted by s_{∞} , is concretely defined and approximated from the underside. In section

11.2, s_∞ is approximated from the upperside and is shown to be underbounded by $\ln(3/2)$. In section 11.3, the surface disorder entropy per free bond of a crystal is unambiguously defined by using s_∞ and is estimated for a sufficiently large rectangular crystal.

In Appendix A, several properties of correlativities, from which the rule stated in section 1.7 is induced, are discussed. In Appendix B, an exact method of calculating the number of possible arrangements on lattices of simple form in the square lattice is given.

Basic ideas in the present paper were already given in two papers published in Japanese (SUZUKI 1966 a, b). But, several new concepts such as correlativities, duplicated crystals, semi-infinite grains, etc. are introduced in the present paper, so that the ideas are more clearly developed in the present paper than in the former is papers.

1. Definitions and Preliminary Deductions

1.1. Definition of the disorder entropy of a finite ice crystal

We will first define an ice lattice, on which hydrogen atoms are arranged. Since the disorder entropy of ice has been known mainly dependent on the number of nearest neighbors of the oxygen atoms, we will generalize the model of ice a little and will define as follows :

Definition: An infinite lattice of the first coordination number four is said an infinite ice lattice when two hydrogen sites are set on each bond of the lattice.

Thus, either the diamond lattice or the two-dimensional Kagomé lattice can be adopted as the basis of an infinite ice lattice as well as either the wurtzite lattice or the two-dimensional square lattice, though in the present paper the latter two lattices shall be treated in detail.

A finite ice lattice shall be defined as follows :

Definition: A finite ice lattice is a connected part of an infinite ice lattice surrounded by a surface or surfaces which cut bonds in such a manner as to leave one and only one hydrogen site on each cut bond to the part. Here, a connected part means that, for any pair of lattice

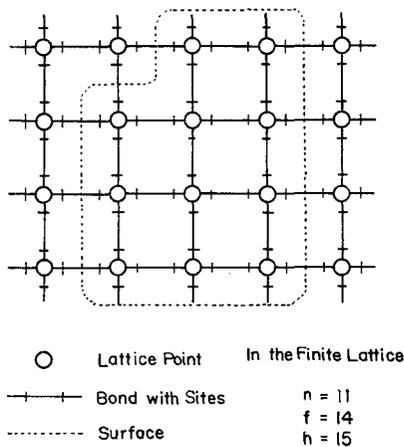


Fig. 1. Square lattice

points in the part, there is a chain of nearest neighbors terminating at the pair and being entirely in the part. A bond is said a free bond or an inner bond, according as the bond has been cut or not. (Fig. 1.)

Among three numbers characterizing a finite ice lattice, that is, the number of lattice points (oxygen atoms), n , that of inner bonds, h , and that of free bonds, f , there is a relation,

$$4n = 2h + f, \quad (1.1.1)$$

which can be easily verified by the enumeration of the sites in the lattice.

Because of eq. (1.1.1), we can specify a finite ice lattice by two of these three numbers. Although the disorder entropy of a finite ice crystal defined below is not uniquely determined by these numbers together with the specification of an infinite ice lattice, we need no further specifications at present.

An arrangement of hydrogen atoms on a finite ice lattice shall be defined in a somewhat abstract manner as follows:

Definition: An arrangement on an ice lattice is a way of an assignment of the value, either one or zero, to every site on the ice lattice. The assigned value is said the state value of the site. A hydrogen site is said occupied or vacant according as its state value is one or zero.

Using the concept of the state value, we can describe the two conditions of BERNAL and FOWLER as follows:

The bond condition: Let β be the state value of one site and β' be that of the other site on a bond. Then the following relation should hold:

$$\beta + \beta' = 1. \quad (1.1.2)$$

The molecule condition: Let β_k be the state value of the k -th site around a lattice point. Then the following relation should hold:

$$\beta_1 + \beta_2 + \beta_3 + \beta_4 = 2. \quad (1.1.3)$$

We will now define a possible arrangement.

Definition: A possible arrangement on a finite ice lattice is such an arrangement on the lattice as satisfies the bond condition for each inner bond and the molecule condition for each lattice point.

It must be noted that the sum of all state values in an arrangement on a finite ice lattice, that is, the number of hydrogen atoms in the arrangement, ranges from zero to $4n$, while that in a possible arrangement is $2n$.

Finally, we will define the disorder entropy after PAULING:

Definition: The disorder entropy, S , of a finite ice crystal is a quantity given by

$$S = k \ln w, \quad (1.1.4)$$

where w is the number of all possible arrangements on the corresponding ice lattice and k BOLTZMANN'S constant.

1.2. *The set of all arrangements satisfying the bond condition, its subsets, and quantities, q_i*

We first consider a set of all arrangements each of which satisfies the bond condition for all inner bonds. We denote the set by W_0 and its size, that is, the number of arrangements contained in the set, by w_0 . (A set shall be denoted by a roman capital with, if necessary, specifications such as superscripts, subscripts and so on. The corresponding expression in which the small italic is substituted for the roman capital should be always understood to denote the size of the set.)

It is evident that

$$w_0 = 2^h \cdot 2^f = 2^{(2n+1/2)}, \quad (1.2.1)$$

because either of two sites on each of h inner bonds can be occupied and because site on each of f free bonds can be either occupied or vacant.

Now, we number all lattice points. Let W_i be a set of all arrangements each of which satisfies the bond condition for all inner bonds and the molecule condition for all lattice points up to the i -th (inclusive). The set, W_i , is evidently a subset of W_{i-1} . Let p_i be the ratio of w_i to w_{i-1} . Then, w , which is the same as w_n , can be written as

$$w = w_0 \prod_{i=1}^n p_i. \quad (1.2.2)$$

Introducing q_i by

$$q_i = 8p_i/3 = 8w_i/3w_{i-1}, \quad (1.2.3)$$

we get from eqs. (1.2.1) and (1.2.2)

$$w = (3/2)^n 2^{f/2} \prod_{i=1}^n q_i. \quad (1.2.4)$$

In order to investigate q_i , we classify W_{i-1} into sixteen subsets $W_{i-1}^{(k)}$ ($\beta_1, \beta_2, \beta_3, \beta_4$), where $W_{i-1}^{(k)}$ ($\beta_1, \beta_2, \beta_3, \beta_4$) is a set of all arrangements in W_{i-1} with the state value of the k -th site around the i -th lattice point being β_k ($k=1, 2, 3, 4$). Naturally,

$$w_{i-1} = \sum_{\beta_k} w_{i-1}^{(k)}(\beta_1, \beta_2, \beta_3, \beta_4), \quad (1.2.5)$$

and since W_i is such a subset of W_{i-1} that each arrangements in W_i satisfies the molecule condition for the i -th lattice point,

$$w_i = \sum_{\beta_1+\beta_2+\beta_3+\beta_4=2} w_i^{(k)}(\beta_1, \beta_2, \beta_3, \beta_4). \quad (1.2.6)$$

From eqs. (1.2.3), (1.2.5), and (1.2.6), we have

$$q_i = \frac{8 \sum_{\beta_1 + \beta_2 + \beta_3 + \beta_4 = 2} \tau w_{i-1}^{(\phi)}(\beta_1, \beta_2, \beta_3, \beta_4)}{3 \sum \tau w_{i-1}^{(\phi)}(\beta_1, \beta_2, \beta_3, \beta_4)}. \quad (1.2.7)$$

PAULING considered that the sixteen subsets, $W_{i-1}^{(\phi)}$, are all equal in size and hence he put q_i equal to one. Things are not so simple as he considered, but still, owing to the nature of the two conditions of BERNAL and FOWLER, among the sizes of these subsets are found several equalities, which considerably simplify the expression of q_i .

1.3. Complements of an arrangement

We will introduce two useful concepts, which play an important role in the search for the equalities among the sizes of the subsets of W_{i-1} .

Definition: Let B be a set of bonds. A complement of an arrangement with respect to B is an arrangement in which the state value of each site is different from or identical with the state value of that site in the original arrangement, according as that site is on a bond in B or not.

In other words, if the state value of a site in an arrangement is denoted by β and that of the same site in its complement with respect to B by $\bar{\beta}$, then

$$\begin{aligned} \bar{\beta} &= 1 - \beta & \text{for each site on a bond in B} \\ \bar{\beta} &= \beta & \text{for each site on a bond not in B.} \end{aligned} \quad (1.3.1)$$

Definition: An operation which transforms every arrangement into its complement with respect to B is said the complementary operation with respect to B.

Following lemmas are evident:

Lemma 1: A complementary operation cannot transform two different arrangements into one and the same arrangement.

Lemma 2: The bond condition (1.1.2) is conserved by any complementary operation.

Lemma 3: The molecule condition (1.1.3) for a lattice point is conserved by a complementary operation with respect to B, if and only if B contains all or none of the four bonds around the lattice point.

Though we are looking for the relations among such subset of W_{i-1} as defined in the last section, we will consider more general subsets of W_{i-1} , since we will use them later.

Let a set of m sites be S. Let a subset of W_{i-1} consisting of all arrangements in W_{i-1} each with the state value of the k -th site in S being β_k ($k=1, \dots, m$) be denoted by $W_{i-1}^S([\beta_k])$. Here, $[\beta_k]$ stands for a set of the m state

values each either one or zero. The number of different W_{i-1}^S is evidently 2^m .

The following theorem gives relations among the sizes of them :

Theorem 1: If B is such that a complementary operation with respect to B transforms any arrangement in W_{i-1} into an arrangement in W_{i-1} , then

$$\omega_{i-1}^S([\beta_k]) = \omega_{i-1}^S([\bar{\beta}_k]) \quad (1.3.2)$$

where $\bar{\beta}_k$ is given by

$$\begin{aligned} \bar{\beta}_k &= 1 - \beta_k && \text{for each site on a bond in B} \\ \bar{\beta}_k &= \beta_k && \text{for each site on a bond not in B.} \end{aligned} \quad (1.3.3)$$

By the choice of a set of the four sites around the i -th lattice point for S, relation (1.3.2) leads to

$$\omega_{i-1}^{(S)}(\beta_1, \beta_2, \beta_3, \beta_4) = \omega_{i-1}^{(S)}(\bar{\beta}_1, \bar{\beta}_2, \bar{\beta}_3, \bar{\beta}_4). \quad (1.3.4)$$

Proof of the Theorem: Let α be an arrangement in $W_{i-1}^S([\beta_k])$ and α' be its complement with respect to B. By the assumption, α' is in W_{i-1} . The state value of the k -th site in α' is $\bar{\beta}_k$ by the definition of a complement. Hence, α' must be in $W_{i-1}^S([\bar{\beta}_k])$. Because of lemma 1, $\omega_{i-1}^S([\bar{\beta}_k])$ cannot be less than $\omega_{i-1}^S([\beta_k])$. Conversely, an arrangement in $W_{i-1}^S([\bar{\beta}_k])$ is transformed into an arrangement in $W_{i-1}^S([\beta_k])$ by the operation. Hence, $\omega_{i-1}^S([\beta_k])$ cannot be less than $\omega_{i-1}^S([\bar{\beta}_k])$. Therefore, they must be equal. Q. E. D.

It is obvious from lemmas 2 and 3 that a complementary operation with respect to a set of all bonds of the lattice transforms any arrangement in W_{i-1} into an arrangement in W_{i-1} (for $i=1, \dots, n+1$). Hence, by the theorem

$$\omega_{i-1}^S([\beta_k]) = \omega_{i-1}^S([1 - \beta_k]) \quad (1.3.5)$$

for arbitrary S and for every i , and in particular,

$$\omega_{i-1}^{(S)}(\beta_1, \beta_2, \beta_3, \beta_4) = \omega_{i-1}^{(S)}(1 - \beta_1, 1 - \beta_2, 1 - \beta_3, 1 - \beta_4). \quad (1.3.6)$$

1.4. Five cases for relations among the subsets, $W_{i-1}^{(S)}$

In order to search further relations than eqs. (1.3.6) among the subsets, $W_{i-1}^{(S)}$, it is convenient to introduce several terminologies since in the definition of W_{i-1} the lattice points up to the $i-1$ -th play a different role from others.

Definition: The lattice points up to the $i-1$ -th (inclusive) are said regular. Others are said irregular. A bond which links two irregular lattice points is said irregular.

Definition: Two regular lattice points are said to be regularly connected to each other if and only if between them there is at least one chain of nearest neighbors each being regular.

Definition: A set, consisting of one regular lattice point and all lattice

points regularly connected to it, is said a grain.

Definition: A bond which links a lattice point in a grain to an irregular point is said a marginal bond of the grain. A bond which links two lattice points in a grain is said a regular bond of the grain.

The words, regular, irregular, marginal, regularly connected, and a grain, should be understood to be modified by a phrase, for the i -th lattice point, which has been and shall be hereafter dropped for the sake of simplicity. It must be noted that all concepts defined above depend on a way of the numbering of the lattice points up to the i -th.

Now, from lemmas 2 and 3 in the last section, it is evident that:

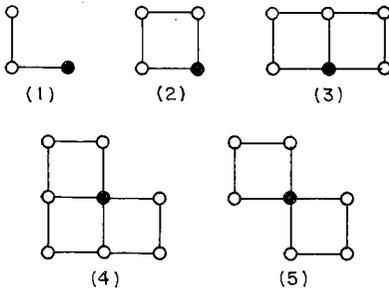
Theorem 2: A complementary operation with respect to B transforms any arrangement in W_{i-1} into a arrangement in W_{i-1} , if and only if B is such that, when it contains a bond of a grain, it contains all bonds of the grain.

Because of theorem 2, if the first bond, that is, the bond on which the first site around the i -th point lies, is irregular, a set consisting only of the bond can be chosen for B in theorem 1 in the last section. By this choice, from eqs. (1.3.3) and (1.3.4) we have

$$w_{i-1}^{(i)}(\beta_1, \beta_2, \beta_3, \beta_4) = w_{i-1}^{(i)}(1 - \beta_1, \beta_2, \beta_3, \beta_4). \quad (1.4.1)$$

If the first bond is a marginal bond of a grain, a set of all bonds of the grain can be chosen for B in theorem 1. In this case, if none of the other sites around the i -th lattice point than the first lies on a bond of the grain, we have again eqs. (1.4.1). But, if the second bond belongs to the grain, while the third and the fourth do not, we have

$$w_{i-1}^{(i)}(\beta_1, \beta_2, \beta_3, \beta_4) = w_{i-1}^{(i)}(1 - \beta_1, 1 - \beta_2, \beta_3, \beta_4), \quad (1.4.2)$$



● the i -th Lattice Point ○ Regular Point

Fig. 2. Five cases for relative location of the i -th point to its grain or grains

and if the first, the second, and the third belong to one grain, while the fourth does not, we have

$$\begin{aligned} w_{i-1}^{(i)}(\beta_1, \beta_2, \beta_3, \beta_4) \\ = w_{i-1}^{(i)}(1 - \beta_1, 1 - \beta_2, 1 - \beta_3, \beta_4), \end{aligned} \quad (1.4.3)$$

instead of eqs. (1.4.1). When all of the four bonds belong to one grain, the choice of the set of all bonds of the grain for B leads to eqs. (1.3.6).

Examining the other bonds successively, we can easily see that there are five

essentially different (that is, trivial differences due to different numberings of the four sites being neglected) groups of equalities among $\omega_{i-1}^{(g)}$'s corresponding five cases of relative location of the i -th lattice point to a grain or grains for it. (See Fig. 2.) The cases and the equalities are listed below where $(\beta_1\beta_2\beta_3\beta_4)$ stands for $\omega_{i-1}^{(g)}(\beta_1, \beta_2, \beta_3, \beta_4)$:

Case 1: No pair of the four bonds around the i -th lattice point belong to one and the same grain:

$$\begin{aligned} (0000) &= (0001) = (0010) = (0011) = (0100) = (0101) = (0110) = (0111) \\ &= (1111) = (1110) = (1101) = (1100) = (1011) = (1010) = (1001) = (1000). \end{aligned} \quad (1.4.4)$$

Case 2: Two of the four bonds (chosen as the first and the second) belong to one and the same grain:

$$\begin{aligned} (0000) &= (0001) = (0010) = (0011) = (1100) = (1101) = (1110) = (1111); \\ (1000) &= (1001) = (1010) = (1011) = (0100) = (0101) = (0110) = (0111). \end{aligned} \quad (1.4.5)$$

Case 3: Three of the four bonds (chosen as the first, the second, and the third) belong to one and the same grain:

$$\begin{aligned} (0000) &= (0001) = (1110) = (1111); & (0010) &= (0011) = (1100) = (1101); \\ (0100) &= (0101) = (1010) = (1011); & (0110) &= (0111) = (1000) = (1001). \end{aligned} \quad (1.4.6)$$

Case 4: All belong to one grain:

$$\begin{aligned} (0000) &= (1111); & (0001) &= (1110); & (0010) &= (1101); & (0011) &= (1100); \\ (0100) &= (1011); & (0101) &= (1010); & (0110) &= (1001); & (0111) &= (1000). \end{aligned} \quad (1.4.7)$$

Case 5: Two (chosen as the first and the second) belong to the first and the other two to the second grain:

$$\begin{aligned} (0000) &= (1100) = (0011) = (1111); & (0100) &= (1000) = (0111) = (1011); \\ (0001) &= (1101) = (0010) = (1110); & (0101) &= (1001) = (0110) = (1010). \end{aligned} \quad (1.4.8)$$

Thus, the equality of sizes of all $W_{i-1}^{(g)}$ considered by PAULING holds only for the first case.

After the numbering of the lattice points has been fixed, the case is determined for each of all lattice points. Then, we shall say as follows:

Definition: A lattice point is of the m -th kind, if the m -th case occurs

for it.

1.5. Special numberings of the lattice points

We can simplify the expression of q_i , eq. (1.2.8), by relations obtained in the last section. But, before doing so, we will show that, for the wurtzite lattice and for the two-dimensional square lattice, there are special numberings in which every lattice point is of either the first or the second kind:

a) *The square lattice.* We choose the row-wise numbering. That is, starting from the leftest lattice point on the uppermost [01] row, we proceed rightward along the row and after finishing the numbering in this row, we go to the leftest point in the second row just below the first. It is easily seen from Fig. 3 that in this numbering every lattice point is either of the first or of the second kind, which is designated by a double or a single circle in the figure, respectively.

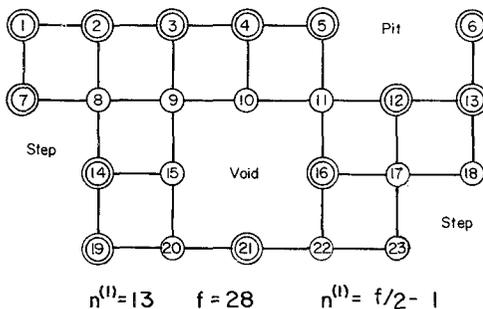


Fig. 3. Numbering in square lattice

b) *The wurtzite lattice.* The lattice points form a two-dimensional hexagonal lattice on an uneven basal (0001) layer as shown in Fig. 4, where a lattice point designated by a triangle has the upward fourth bond and is a little over the plane of the paper, while a lattice point designated by a reversed triangle has the downward fourth bond and is a little under the plane of the paper. It must be noted that there are two kinds of basal layers: Three a -axes being chosen as shown in Fig. 4, a lattice point with the $[0\bar{1}10]$ -ward bond has an upward bond or a downward bond according as the point lies on a layer of one kind or on the other. We will provisionally call the former an even layer and the latter an odd layer. The numbering will be done layer by layer upward from the base and on each layer along each $[2\bar{1}\bar{1}0]$ zig-zag row of lattice points. In order to avoid the appearance of the lattice points of the third kind, we must carefully choose the order of the rows.

We must proceed $[01\bar{1}0]$ -ward on an even layer, while reversely on an odd layer. In each row we may start from either ends. (See Fig. 4).

An important theorem holds for these numberings:

Theorem 3: If all lattice points are either of the first or of the second kind, the number of the points of the first kind, $n^{(1)}$, in a finite lattice is given by

$$n^{(1)} = f/2 - 1, \quad (1.5.1)$$

where f is the number of free bonds of the lattice.

For the proof, it is convenient to state the theorem more generally:

Theorem 3': If all lattice points are either of the first or of the second kind, the number of the lattice points of the first kind, $n^{(1)}$, is given by

$$n^{(1)} = f/2 - N, \quad (1.5.2)$$

where N is the number of lattices and f is the total number of free bonds.

Proof: Let us consider to construct the system of the lattice by adding lattice points one after one according to the order of the numbering. Assume that relation (1.5.2) would hold for the system thus constructed of m lattice points. Now, we add the $m+1$ -th lattice point to the system. Let the added point be linked to k points of the system. Naturally, k must be zero, one, two, three, or four. By the addition, f changes by $4-2k$, because a linking annihilates two free bonds. $n^{(1)}$ increases by one or remains unchanged according as the added point is of the first kind or of the second kind. Now, we investigate case by case how N changes. Case $k=0$. N increases by one since the added point form a lattice by itself. Case $k=1$. Evidently, N remains unchanged. Case $k=2$. a) The added point is of the first kind; The two lattice points to which the added point is linked cannot be in the same lattice, because, if they were, the added point would be of the second kind. Hence, the added point must combine two lattices into one, decreasing N by one. b) The added point is of the second kind: Evidently, N remains

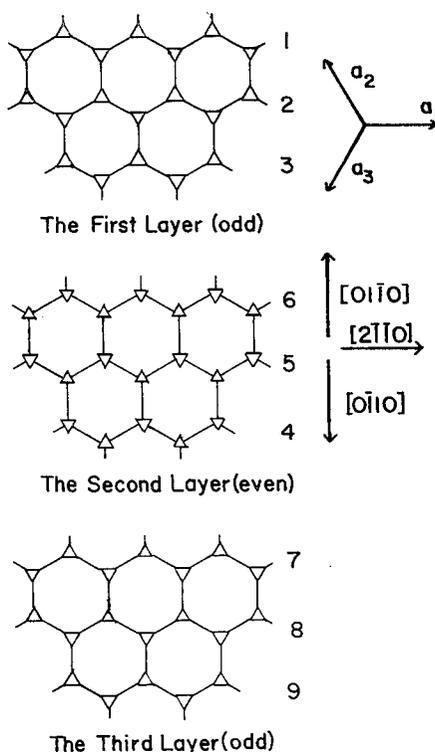


Fig. 4. Numbering in wurtzite lattice

unchanged. Investigating cases $k=3$ and $k=4$ similarly, we have the following results :

k	0	1	2	2	3	3	4	4
$\Delta n^{(1)}$	1	1	1	0	1	0	1	0
$-\Delta(f/2)$	-2	-1	0	0	1	1	2	2
ΔN	1	0	-1	0	-2	-1	-3	-2
$\Delta(n^{(1)}-(f/2)+N)$	0	0	0	0	0	0	0	0

Thus in any case relation (1.5.2) is conserved. The relation holds for the lattice consisting of one lattice point, since $n^{(1)}=1$, $f=4$, and $N=1$. Q. E. D.

1.6. Expressions of q_i for the first and the second cases

Since we will hereafter use only the numberings given in the last section, it is sufficient to investigate only the first and the second cases, of which the first case is trivial because from eqs. (1.2.7) and (1.4.4) we have

$$q_i^{(1)} = 1, \quad (1.6.1)$$

where the superscript (1) stands for the first case.

We will now define $w_{i-1}^{12}(\beta_1, \beta_2)$ by

$$w_{i-1}^{12}(\beta_1, \beta_2) = \sum_{\beta_3, \beta_4} w_{i-1}^{(4)}(\beta_1, \beta_2, \beta_3, \beta_4). \quad (1.6.2)$$

Evidently, $w_{i-1}^{12}(\beta_1, \beta_2)$ is the number of such arrangements in W_{i-1} that the state values of the first and of the second site around the i -th lattice point are β_1 and β_2 respectively.

From eqs. (1.4.5) (which are naturally included in eqs. (1.4.4)), we have

$$w_{i-1}^{(4)}(\beta_1, \beta_2, \beta_3, \beta_4) = w_{i-1}^{12}(\beta_1, \beta_2)/4 \quad (\text{for cases 1 and 2}), \quad (1.6.3)$$

and

$$w_{i-1}^{12}(1, 0) = w_{i-1}^{12}(0, 1); \quad w_{i-1}^{12}(0, 0) = w_{i-1}^{12}(1, 1). \quad (1.6.4)$$

Eqs. (1.6.4) are in fact generally valid because of eqs. (1.3.5).

From eqs. (1.6.3), (1.6.4), and (1.2.7) we have

$$q_i^{(2)} = 2(w_{i-1}^{12}(0, 0) + 2w_{i-1}^{12}(1, 0))/3(w_{i-1}^{12}(0, 0) + w_{i-1}^{12}(1, 0)), \quad (1.3.5)$$

where the superscript (2) stands for the second case.

Introducing quantities, x_i^{12} and ε_i^{12} , by

$$x_i^{12} = (1 + \varepsilon_i^{12})/(1 - \varepsilon_i^{12}) = \frac{w_{i-1}^{12}(1, 0)}{w_{i-1}^{12}(0, 0)} = \frac{w_{i-1}^{12}(1, 0) + w_{i-1}^{12}(0, 1)}{w_{i-1}^{12}(0, 0) + w_{i-1}^{12}(1, 1)}, \quad (1.6.6)$$

we can rewrite eq. (1.6.5) as

$$q_i^{(2)} = 2(1 + 2x_i^{12})/3(1 + x_i^{12}) = 1 + (1/3)\varepsilon_i^{12}. \quad (1.6.7)$$

The problem of estimating disorder entropy thus narrows down to the estimation of x_i^{12} or ε_i^{12} for the second case. An exact method of evaluating x_i^{12} for grains of special form shall be given in Appendix B, while a rule for approximate estimation of ε_i^{12} for grains of general form shall be given in the next section.

It must be noted here that BJERRUM (1951) already introduced the quantity x_i^{12} , denoted by B/A in his paper, for estimating disorder entropy. He, however, incorrectly deduced it to be one for a large grain.

1.7. Correlativities and a rule for approximate estimation of them

We may regard x_i^{12} as the ratio of the probability in W_{i-1} , that the first and the second sites around the i -th lattice point are in different states, to that, that the both sites are in the same state. Hence, we will call ε_i^{12} the correlativity between the two sites around the i -th lattice point.

We can generalize the concept of the correlativity and define the correlativity between two sites (not necessarily around the i -th lattice point), ε , by

$$(1 + \varepsilon)/(1 - \varepsilon) = w_{i-1}(1, 0)/w_{i-1}(0, 0) \quad (1.7.1)$$

where $w_{i-1}(\beta_1, \beta_2)$ is the number of such arrangements in W_{i-1} that the state value of one site is β_1 and that of the other site is β_2 .

In Appendix A, several properties of ε shall be discussed which suggest a rule for approximate estimation of ε when the two sites are on marginal bonds of a grain of general form. The rule itself shall be given below instead in Appendix for the sake of convenience.

A concept, a path between two marginal bonds, plays a basic role in the rule:

Definition: A sequence of regular (or inner) bonds between two marginal (or free) bonds is said a path between the two bonds, if and only if the sequence can be traversed continuously from one bond to the other without retracing any bond. (Words in parentheses are for a lattice. See Appendix A.)

Evidently, a path can be unambiguously designated by the list of successive points along the path, because in an ice lattice no two points are linked together by two or more bonds. In listing up paths between two definite bonds in above manner, it is convenient and practical to start always from one bond and never from the other.

A path may cross over itself, that is, there may be a lattice point, all four bonds around which are members of the path.

Definition: A path is said simple, if it does not cross over itself.

Now, we will define the length of a path.

Definition: The length of a path is the number of different lattice points along the path.

Note that the length of a path is not the number of bonds in it.

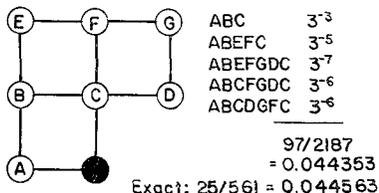


Fig. 5. Paths between two bonds. (The exact value of correlativity, $\varepsilon(3, 1, 1)$ is calculated by the method in Appendix B. cf. Table of $q(b, k, k')$ at the end)

An example may serve for easy understanding of the concepts. In the grain shown in Fig. 5, between the two bonds of the black point, there are five and only five paths listed below with each length in parentheses:

AEC(3); ABEFC(5); ABEFGDC(7);
ABCFGDC(6); ABCDGFC(6).

The last two paths are not simple. A sequence designated by ABCFEBC cannot be a path because the bond linking B and C is retraced.

Now, the rule says as follows:

Rule: Make the list of all paths between the two marginal bonds. Assign the proper correlativity given by

$$\varepsilon(j) = 3^{-j} \quad (1.7.2)$$

to each path of length j . The correlativity, ε , between two sites on the two marginal bonds is approximately given by

$$\pm\varepsilon = \sum_{\text{path}} \varepsilon(j) \quad (1.7.3)$$

where the plus sign is chosen in the case when both sites are near to or far from regular points and the minus sign in the other case.

II. Answers to the Three Questions Raised in the Introduction

II. 1. Approximate expressions for the disorder entropy

A finite ice lattice consisting of n lattice points and having f free bonds shall be treated in this section. Let us consider that all lattice points have been numbered in the manners mentioned in section 1.5. Then, a definite value has been assigned for q_i to the i -th lattice point. The value is said a q -value of the lattice point.

From eqs. (1.2.4) and (1.5.1), we get

$$\omega = (3/2)^n 2^{f/2} \prod_{m=1}^{n-f/2+1} q_m^{(2)}. \quad (II. 1. 1)$$

In trivial case of a one-dimensional tree, where there is no point of the second kind, τw can be exactly given by

$$\tau w = (3/2)^n 2^{f/2}. \quad (\text{II. 1. 2})$$

In general case, we have

$$\ln \tau w = n (\ln(3/2) + \ln \bar{q}) + (f/2) (\ln 2 - \ln \bar{q}) + \ln \bar{q}, \quad (\text{II. 1. 3})$$

where \bar{q} is a geometrical mean of all $q^{(2)}$ and hence

$$q_{\max} \geq \bar{q} \geq q_{\min} \quad (\text{II. 1. 4})$$

where q_{\max} denotes the maximum of $q^{(2)}$'s and q_{\min} the minimum.

We will now assume that the lattice has no hollow spaces or voids. Then, for any lattice point of the second kind there is a path of the length 3 in the square lattice or of the length 5 in the wurtzite lattice. From the rule for approximate estimation of correlativities stated in the last section, we may put q_{\min} equal to $q(1)$, given by

$$q_s(1) = 1 + 3^{-4} \quad (\text{for the square lattice}) \quad (\text{II. 1. 5})$$

$$q_w(1) = 1 + 3^{-6} \quad (\text{for the wurtzite lattice}). \quad (\text{II. 1. 6})$$

The notation $q(1)$ stands for the first approximation of q_∞ which shall be defined later.

Since the contribution to ε from a long path is small, q_{\max} may be so close to $q(1)$ that \bar{q} is closely approximated by $q(1)$. Then, from eq. (II.1.3), we have

$$\ln \tau w \simeq n (\ln(3/2) + \ln q(1)) + (f/2) (\ln 2 - \ln q(1)). \quad (\text{II. 1. 7})$$

(The last term in eq. (II.1.3) should naturally be neglected in this approximation.)

It is awkward to get higher approximate equations than eq. (II.1.7) by successively taking account of contributions to ε from paths other than the shortest, because then we must classify the lattice points of the second kind into those with only the shortest path, those with so-and-so paths and so on.

Even if \bar{q} is close to $q(1)$, the term proportional to f in eq. (II.1.7) may become meaningless when n is so large compared with f that the approximation error surpasses the term. Hence, we should use eq. (II.1.7) only for small crystals. In the case where n/f is sufficiently large, a meaningful first approximate equation may be

$$(\ln \tau w)/n \simeq \ln(3/2) + \ln \bar{q} \simeq \ln(3/2) + \ln q(1), \quad (\text{II. 1. 8})$$

or

$$\begin{aligned} \lim_{n, f \rightarrow \infty} ((\ln \tau w)/n) &= \ln(3/2) + \lim_{n/f \rightarrow \infty} (\ln \bar{q}) \\ &= \ln(3/2) + \ln q_\infty \simeq \ln(3/2) + \ln q(1). \end{aligned} \quad (\text{II. 1. 9})$$

The quantity, $\ln(3/2) + \ln q_\infty$, denoted hereafter by s_∞ , is the disorder entropy per molecule of the infinite crystal divided by BOLTZMANN'S constant. Since $\ln(3/2)$ is the value estimated by PAULING for s_∞ , we shall call $\ln q_\infty$ the correction to the PAULING value.

Now, consider a semi-infinite grain, G^S , bounded by a stepped [01] row in the square lattice (Fig. 6 a) and two semi-infinite grains, G^{W_1} and G^{W_2} , each bounded by a basal (0001) plane with a step running $[2\bar{1}10]$ ward and having a kink (Fig. 6 b and c). Let the q -values of a lattice point (shown by solid circle in each figure) be denoted by q^S , q^{W_1} , and q^{W_2} . From the way of the numbering of lattice points, it is easily seen that q_∞ , the limiting value of \bar{q} , is given by q^S in the square lattice or by a geometrical mean of q^{W_1} and q^{W_2} in the wurtzite lattice.

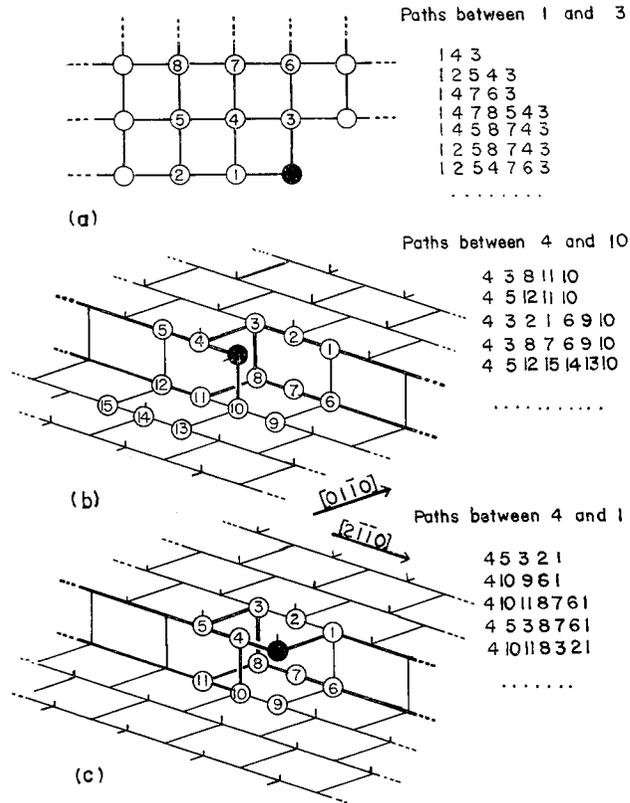


Fig. 6. Semi-infinite grains for defining q_∞ .

a) G^S , b) G^{W_1} , and c) G^{W_2} . (For the sake of simplicity, the latter two are illustrated in the blick-work lattice, a topological equivalent of the wurtzite-lattice.)

Equation (II.1.9) shows that $q(1)$ may be considered as the first approximate value of q_∞ . The higher approximate values of q_∞ are easily obtained. Namely, let $q^s(\text{app.})$, $q^{w_1}(\text{app.})$, or $q^{w_2}(\text{app.})$ be a q -value of the point due to contributions from a part of the semi-infinite grain, G^s , G^{w_1} , or G^{w_2} , and let $q(\text{app.})$ be $q^s(\text{app.})$ or a geometrical mean of $q^{w_1}(\text{app.})$ and $q^{w_2}(\text{app.})$. Since $q^s(\text{app.})$ etc. seem to increase with enlargement of the part, we may have more and more closely approximate value of q_∞ by $q(\text{app.})$, by taking larger and larger part in each of the semi-infinite grains.

If $\varepsilon(\text{app.})$, that is, the ε -value corresponding to $q(\text{app.})$, is very small compared with unity, we can write

$$\ln q_\infty \simeq \ln q(\text{app.}) \simeq (1/3) \varepsilon(\text{app.}). \quad (\text{II. 1. 10})$$

At the end of the section, we will give numerical values of $\ln q(\text{app.})$ by relation (II.1.10) and the rule for approximate estimation of ε , so as to show the close relation between this method and that of DiMARZIO and STILLINGER, JR. (1964).

In the square lattice, a part of the semi-infinite grain, denoted in Fig. 5 by numbers one to eight, contains one path of the length 3, two paths of the length 5, two paths of the length 6 and four paths of the length 7. These paths contribute to $\ln q_\infty$ by

$$3^{-4} + 2 \cdot 3^{-6} + 2 \cdot 3^{-7} + 4 \cdot 3^{-7} \quad (\text{II. 1. 11})$$

of which the first two terms are exactly corresponding to the contributions from the first figure and from the second group of figures in eq. (16) in the paper by DiMARZIO and STILLINGER, JR.

In the wurtzite lattice, in each of the semi-infinite grains, there are two paths of the length 5, three paths of the length 7, and so on, which contribute to $\ln q_\infty$ by

$$2 \cdot 3^{-6} + 3 \cdot 3^{-8} + \dots \quad (\text{II. 1. 12})$$

The first term is just the correction given by DiMARZIO and STILLINGER, JR.

II. 2. Series of duplicated crystals

In this section, we will show the existence of series of crystals such that in each series size of crystal increases infinitely while the disorder entropy per molecule decreases, converging to a value not less than $\ln(3/2)$.

Consider a linear lattice, L_1 , consisting of b lattice points in a [01] row. The number of all possible arrangement on L_1 , now denoted by $w(1, b)$ instead by w , is evidently given by

$$w(1, b) = (3/2)^b 2^{b+1} \quad (\text{II. 2. 1})$$

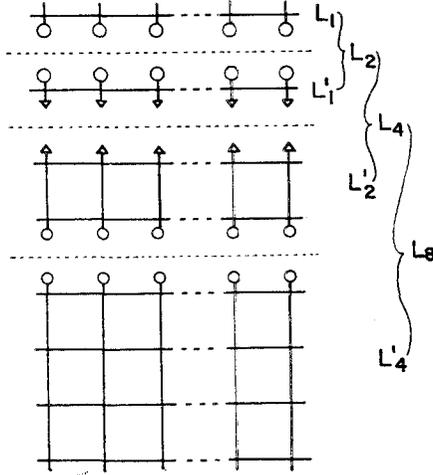


Fig. 7. Duplication of rectangular lattices

since every point is of the first kind.

We will now classify all possible arrangements into 2^b subsets according to the states of b sites shown by circles on L_1 in Fig. 7. Each of the states can evidently be specified by a b bits binary number j , corresponding to the b ordered state values. Hence, we designate each subsets as $W(1, b; j)$ and its size as $w(1, b; j)$. Naturally,

$$w(1, b) = \sum_{j=0}^{2^b-1} w(1, b; j). \quad (11.2.2)$$

Since a complement of a possible

arrangement with respect to a set of all sites is a possible arrangement, we easily have (see eq. (1.3.5))

$$w(1, b; j) = w(1, b; \bar{j}), \quad (11.2.3)$$

where

$$\bar{j} = 2^b - 1 - j. \quad (11.2.4)$$

Consider L_1' to be a rotational image of L_1 by π around the dotted line in Fig. 7. An image of $W(1, b; j)$, denoted by $W'(1, b; j)$, is evidently a set of all such possible arrangement on L_1' that in each the state of the b sites (shown by circles on L_1') is specified by j .

Now, imagine L_1 and L_1' to be combined into a lattice, L_2 , by linking corresponding bonds on both sides of the dotted line.

Since an arrangement of $W(1, b; j)$ can combine with an arrangement of $W'(1, b; \bar{j})$ to make a possible arrangement on L_2 and, conversely, a possible arrangement on L_2 can be divided into two parts, one belonging to some $W(1, b; j)$ and the other to the corresponding $W'(1, b; \bar{j})$, we have

$$w(2, b) = \sum_{j=0}^{2^b-1} w(1, b; j) w(1, b; \bar{j}), \quad (11.2.5)$$

where $w(2, b)$ is the number of all possible arrangements on L_2 . Because of eq. (11.2.3), eq. (11.2.5) can be rewritten as

$$w(2, b) = \sum_{j=0}^{2^b-1} w(1, b; j) w(1, b; j). \quad (11.2.6)$$

From eqs. (11.2.2) and (11.2.6), we have

$$w(2, b) < w(1, b)^2, \quad (11.2.7)$$

because $w(1, b; j)$'s are all non-negative and at least two of them are positive, and

$$2^b w(2, b) - w(1, b)^2 = \sum_{j>k} (w(1, b; j) - w(1, b; k))^2 \quad (11.2.8)$$

From relations (11.2.7) and (11.2.8), we have

$$0 < 2 \ln w(1, b) - \ln w(2, b) \leq b \ln 2. \quad (11.2.9)$$

Similarly duplicating L_2 into L_4 , L_4 into L_8 , and so on, we get similar relations as relation (11.2.9):

$$\begin{aligned} 0 < 2 \ln w(2, b) - \ln w(4, b) &\leq b \ln 2 \\ 0 < 2 \ln w(4, b) - \ln w(8, b) &\leq b \ln 2 \\ \dots\dots\dots, \end{aligned} \quad (11.2.10)$$

where $w(m, b)$ denotes the number of all possible arrangement on L_m . Defining the disorder entropy per molecule (divided by BOLTZMANN'S constant) of L_m by

$$s(m, b) = \ln w(m, b) / (mb), \quad (11.2.11)$$

we have from relations (11.2.10)

$$\begin{aligned} 0 < s(1, b) - s(2, b) &\leq (\ln 2) / 2 \\ 0 < s(2, b) - s(4, b) &\leq (\ln 2) / 2^2 \\ \dots\dots\dots \\ 0 < s(2^{r-1}, b) - s(2^r, b) &\leq (\ln 2) / 2^r \\ \dots\dots\dots, \end{aligned} \quad (11.2.12)$$

which by addition lead to

$$0 < s(1, b) - s(2^r, b) \leq (\ln 2) (1 - 2^{-r}). \quad (11.2.13)$$

From eqs. (11.2.1) and (11.2.11), we have

$$s(1, b) = \ln(3/2) + \ln 2 + (\ln 2) / b. \quad (11.2.14)$$

Hence, we have

$$s(1, b) > s(2, b) > s(4, b) > \dots > s(2^r, b) > \dots > s(\infty, b) > \ln(3/2) + (\ln 2) / b. \quad (11.2.15)$$

Since b can be chosen arbitrarily, we put b infinitely large and have

$$s(1, \infty) > s(2, \infty) > \dots > s(\infty, \infty) > \ln(3/2). \quad (11.2.16)$$

The quantity, $s(\infty, \infty)$, is evidently the same as s_∞ in the last section. Therefore, eq. (11.2.16) strictly proves a statement that q_∞ is larger than unity. (The statement is naturally deduced from the rule of approximate estimation

of ε , but the rule has not been proven strictly.)

Similar procedure can be carried out in the wurtzite lattice. We first duplicate $[2\bar{1}\bar{1}0]$ row on (0001) layer, and then duplicate (0001) layer using mirror images instead of rotational images. Since in duplication on (0001) layer the number of bonds to be linked is different from that in the square lattice, we get a different relation from relation (II.2.15) or (II.2.16) for the two-dimensional infinite crystal on (0001) layer of the wurtzite lattice. But for the three-dimensional infinite crystal we reach to the similar relation to relation (II.2.16).

The method of calculating $s(\infty, b)$ shall be given in Appendix B.

II. 3. Surface disorder entropy

After the disorder entropy per molecule of the infinite crystal having been given in section 2.1 by a definite value, $k \cdot s_\infty$, the surface disorder entropy of a finite crystal, denoted by S_{surface} , can be defined unambiguously and most reasonably by the remainder of $k \cdot s_\infty$ times the number of molecules from the total disorder entropy :

$$S_{\text{surface}} = S - k \cdot n \cdot s_\infty . \quad (\text{II. 3. 1})$$

From eqs. (I.2.4) and (I.1.4), we have

$$S_{\text{surface}}/k = (f/2) \ln 2 - \sum_{i=1}^n (\ln q_\infty - \ln q_i) = (f/2) (\ln 2 - \delta) . \quad (\text{II. 3. 2})$$

We may call the quantity, $(\ln 2 - \delta)/2$, the surface disorder entropy per free bond. The newly introduced quantity, δ , may be expected to be positive since it is very probable that q_∞ is larger than any q_i . (The fact can naturally be deduced from the rule of approximate estimation of ε . The rule is, however, not strict.)

In this section, we will calculate the surface disorder entropy per free bond of a sufficiently large rectangular crystals in the square lattice. Columnar crystals in the wurtzite lattice can be treated analogously.

Consider a rectangular lattice of length L and width B . The numbering of the lattice points has been done row (along length)-wise. The q -value for the lattice point at the cross of the b -th row and the m -th column is denoted by q_{bm} (Fig. 8). Then, from eq. (I.2.4), we have

$$\omega = (3/2)^n 2^{f/2} \prod_{b=1}^B \prod_{m=1}^L q_{bm} , \quad (\text{II. 3. 3})$$

where

$$n = B \cdot L ; \quad f = 2(B + L) . \quad (\text{II. 3. 4})$$

It is evident that q is dependent only on b , m , and L . For the sake of

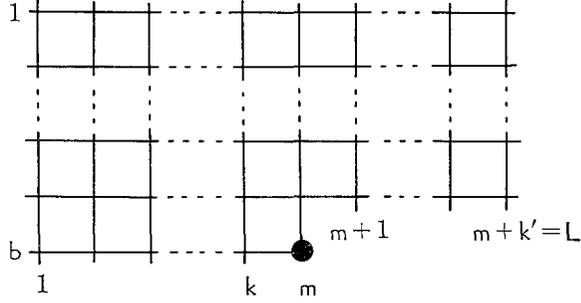


Fig. 8. Stepped rectangular lattice

convenience, we introduce k and k' instead of m and L by

$$k = m - 1, \quad k' = L - m \quad (\text{II. 3. 5})$$

and consider q_{bm} as a function of b , k , and k' :

$$q_{bm} = q(b, m - 1, L - m) = q(b, k, k'). \quad (\text{II. 3. 6})$$

In Appendix B, the convergence of $q(b, k, k')$ with increase in b and/or k and/or k' shall be proven: Thus, in particular:

$$\lim_{\substack{k \rightarrow \infty \\ k' \rightarrow \infty}} q(b, k, k') = q(b, \infty, \infty) \quad (\text{II. 3. 7})$$

$$\lim_{b \rightarrow \infty} q(b, \infty, \infty) = q(\infty, \infty, \infty). \quad (\text{II. 3. 8})$$

It is evident that $q(\infty, \infty, \infty)$ is the same as q_∞ in section 2.1.

From eqs. (II.3.3) and (II.3.4), we have

$$\ln w = (BL) \ln(3/2) + (B+L) \ln 2 + \sum_{b=1}^B \sum_{m=1}^L \ln q_{bm}. \quad (\text{II. 3. 9})$$

Using the limiting values of eqs. (II.3.7) and (II.3.8), we rewrite eq. (II.3.9) as

$$\ln w = B \cdot L \cdot s_\infty + (B+L) \ln 2 - L \cdot A_1(B) - B \cdot A_2(B, L), \quad (\text{II. 3. 10})$$

where

$$A_1(B) = \sum_{b=1}^B (\ln q(\infty, \infty, \infty) - \ln q(b, \infty, \infty)), \quad (\text{II. 3. 11})$$

$$A_2(B, L) = \left(\sum_{b=1}^B \sum_{m=1}^L (\ln q(b, \infty, \infty) - \ln q_{bm}) \right) / B, \quad (\text{II. 3. 12})$$

and

$$s_\infty = \ln(3/2) + \ln q(\infty, \infty, \infty). \quad (\text{II. 3. 13})$$

From eqs. (II.3.7) and (II.3.8), we easily have

$$\lim_{B \rightarrow \infty} \mathcal{A}_1(B)/B = 0, \quad (\text{II. 3. 14})$$

and

$$\lim_{L \rightarrow \infty} \mathcal{A}_2(B, L)/L = 0. \quad (\text{II. 3. 15})$$

Let $\delta(L, B)$ denote δ for our rectangular crystal. From eqs. (II.3.1), (II.3.2), (II.3.4), and (II.3.10), we have

$$\delta(L, B) = \left(L/(B+L) \right) \mathcal{A}_1(B) + \left(B/(B+L) \right) \mathcal{A}_2(B, L). \quad (\text{II. 3. 16})$$

Considering eq. (II.3.15), we have

$$\lim_{L \rightarrow \infty} \delta(L, B) = \delta(\infty, B) = \mathcal{A}_1(B). \quad (\text{II. 3. 17})$$

Thus, $\mathcal{A}_1(B)$ is just the quantity δ for the infinitely long crystal of width B .

Dividing $\ln w$ by $B \cdot L$ and increasing B or L infinitely, we clearly obtain the disorder entropy per molecule of an infinitely long rectangular crystal, the quantity already introduced in the last section. Using a notation consistent with that in the last section, we get from eqs. (II.3.10), (II.3.14), and (II.3.15)

$$s(\infty, B) \equiv \lim_{L \rightarrow \infty} \left(\ln w / (B \cdot L) \right) = s_\infty + (\ln 2)/B - \mathcal{A}_1(B)/B \quad (\text{II. 3. 18})$$

and

$$s(\infty, L) \equiv \lim_{B \rightarrow \infty} \left(\ln w / (B \cdot L) \right) = s_\infty + (\ln 2)/L - \lim_{B \rightarrow \infty} \mathcal{A}_2(B, L)/L. \quad (\text{II. 3. 19})$$

Substituting L for B in eq. (II.3.18) and comparing it with eq. (II.3.19), we have

$$\lim_{B \rightarrow \infty} \mathcal{A}_2(B, L) = \mathcal{A}_1(L). \quad (\text{II. 3. 20})$$

Hence, from eq. (II.3.10), for sufficiently large B and L we have

$$\ln w \cong B \cdot L \cdot s_\infty + (B+L) (\ln 2 - \mathcal{A}_\infty), \quad (\text{II. 3. 21})$$

where \mathcal{A}_∞ is defined by

$$\lim_{B \rightarrow \infty} \mathcal{A}_1(B) = \mathcal{A}_\infty. \quad (\text{II. 3. 22})$$

Naturally, from eqs. (II.3.17) and (II.3.22), we have

$$\lim_{\substack{L \rightarrow \infty \\ B \rightarrow \infty}} \delta(L, B) = \mathcal{A}_\infty, \quad (\text{II. 3. 23})$$

which is consistent with eq. (II.3.21).

Now, we will prove that

$$0 < \ln 2 - \mathcal{A}_\infty \leq \ln 2. \quad (\text{II. 3. 24})$$

Let $w(L, B)$ denote the number of all possible arrangements on a rec-

tangular lattice of length L and width B . Then, we have

$$\ln w(L, B) = B \cdot L \cdot s_\infty + (B+L) (\ln 2 - \delta(L, B)). \quad (\text{II. 3. 25})$$

By a duplicating procedure similar to that in the last section, we have

$$0 < 2 \ln w(L, B) - \ln w(2L, B) \leq B \ln 2, \quad (\text{II. 3. 26})$$

which, owing to eq. (II.3.25), leads to

$$0 < (\ln 2 - \delta(L, B)) + (2(L/B) + 1) (\delta(2L, B) - \delta(L, B)) \leq \ln 2. \quad (\text{II. 3. 27})$$

Putting L equal to B in eq. (II.3.27) and increasing B infinitely, we obtain eq. (II.3.4).

For approximate estimation of A_∞ , it is convenient to introduce $A(B)$, which converges to A_∞ with increase in B , by

$$A(B) = \sum_{b=1}^B (\ln q(B, \infty, \infty) - \ln q(b, \infty, \infty)). \quad (\text{II. 3. 28})$$

Table 1. Corrections to disorder entropy per molecule and to surface disorder entropy per free bond

b	$q(b, \infty, \infty)$	$\ln q(b, \infty, \infty)$	$\ln q/\ln(3/2)$	$A(b)$	$A(b)/\ln 2$
2	1.013678	0.01359	0.03351	0.01359	0.01960
3	1.018946	0.01877	0.04629	0.02395	0.03455
4	1.021509	0.02128	0.05249	0.03149	0.04543
5	1.022947	0.02269	0.05595	0.03711	0.05354
6	1.023833	0.02355	0.05809	0.04145	0.05980
7	1.024418	0.02412	0.05950	0.04487	0.06473
8*		0.02452	0.06047	0.04763	0.06872
9*		0.02481	0.06112	0.04993	0.07203

* Note added in proof: From eq. (II.3.29) we easily have

$$B \cdot s(\infty, B) - (B-1) s(\infty, B-1) = \ln(3/2) + \ln q(B, \infty, \infty).$$

As shown in section B.4, $B \cdot s(\infty, B)$ is the logarithm of the largest eigenvalue, $\lambda_0(B)$, of the elemental matrix, W_B , or the simplified elemental matrix, B_B . The calculation of $\ln q$ by this equation through λ_0 is much less tedious than the direct calculation of q based on eqs. (B.5.8) and (B.5.9). Furthermore, one can show that $\lambda_0(B)$ is the largest eigenvalue of an asymmetric matrix, R_B , which is smaller in size than B_B (Cf. the end of section B.4). For example, R_8 has 72×72 and R_9 136×136 elements while B_8 has 128×128 and B_9 256×256 elements. Thus, the use of R instead of B considerably spares time and the number of memories of a computer required for calculating λ_0 . We have calculated the quantities for B up to nine. Some results are added in table 1. The details of the method shall be presented at the International Conference on Low Temperature Science held in August 1966 in Sapporo.

It must be noted that $\Delta(B)$ gives a convenient relation between $s(\infty, B)$ and $q(B, \infty, \infty)$. From eqs. (II.3.11), (II.3.18) and (II.3.28), we easily have

$$s(\infty, B) = \ln(3/2) + \ln q(B, \infty, \infty) + (\ln 2 - \Delta(B)) / B. \quad (\text{II. 3. 29})$$

Values of $q(b, \infty, \infty)$'s have been calculated up to b equal to seven by the method given in Appendix B. They are shown in Table 1 with values of related quantities.

II. 4. *Concluding remarks*

As stated in section 2.3, the disorder entropy, S , of any ice crystal can be expressed as

$$S/k = n (\ln(3/2) + \ln q_\infty) + f(\ln 2 - \delta), \quad (\text{II. 4. 1})$$

where q_∞ is the quantity defined concretely in section 2.1.

The problem of the estimation of q_∞ may be said to be solved because we give the concrete definition of it and also the method of its estimation. Moreover, the numerical results shown in Table 1 indicate that $q(7, \infty, \infty)$ may be a rather good approximation of q_∞ . In wurtzite lattice we have not yet evaluated such high approximations as in the square lattice, but the fact that the leading term of q_∞ given in section 2.1 in the wurtzite lattice is in the order of a tenth of that in the square lattice may indicate the unimportance of high approximations in the wurtzite lattice.

The estimation of δ is a main aim of the present paper. For sufficiently large rectangular crystals, δ is given by a limiting value Δ_∞ of a series of quantities $\Delta(B)$. The convergence of $\Delta(B)$ is much slower than that of $q(b, \infty, \infty)$, showing that surface effect penetrates rather deeply. It is hoped that the problem shall be investigated by calculating values of $q(b, \infty, \infty)$ for b larger than seven.

Acknowledgements

The author is indebted to Professor Z. YOSIDA of the Institute for suggesting this problem. His encouragement and that of Professor D. KUROIWA of the Institute are deeply appreciated.

The author wishes to express his gratitude to Professors K. HUSIMI, T. USUI and H. NAKANO of Nagoya University and Professor I. SYOZI of Osaka University for many useful suggestions. Special thanks are due Professor M. SIMIZU of Nagoya University for his critical reading and correcting of the manuscript.

For the preparation of the manuscript, the author owes much to Miss

Y. KAIMAI. But for her help, the paper would not have been completed.

The numerical values given in the tables and in the appendix were calculated by the aid of electronic computers, NEAC 2203 G of Hokkaido University, and HITAC 5020 of University of Tokyo.

References

- ANDERSON, P. W. 1956 Ordering and antiferromagnetism in Ferrites. *Phys. Rev.*, **102**, 1008-1013.
- BERNAL, J. D. and FOWLER, R. H. 1933 Theory of water and ionic solution with particular reference to H⁺ and OH⁻ ions. *J. Chem. Phys.*, **1**, 515-548.
- BJERRUM, N. 1951 Structure and properties of ice. *K Danske Vidensk. Selsk. mat-fys. Medd.*, **27**, No. 1, 56 pp.
- DIMARZIO, E. A. and STILLINGER JR., F. H. 1964 Residual entropy of ice. *J. Chem. Phys.*, **40**, 1577-1581.
- GIAUQUE, W. F. and ASHLEY, M. F. 1933 Molecular rotation in ice at 10 K free energy of formation and entropy of water. *Phys. Rev.* **43**, 81-82.
- GIAUQUE, W. F. and STOUT, J. W. 1936 Entropy of water and third law of thermodynamics. Heat capacity of ice from 15 to 273 K. *J. Am. Chem. Soc.*, **58**, 1144-1150.
- OWSTON, P. G. 1958 Structure of ice-I, as determined by x-ray and neutron diffraction analysis. *Advances in Phys.*, **7**, 171-188.
- PAULING, L. 1935 Structure and entropy of ice and of other crystals with randomness of atomic arrangements. *J. Am. Chem. Soc.*, **57**, 206-2684.
- PITZER, K. S. and POLISSAR, J. 1956 The order-disorder problem for ice. *J. Phys. Chem.*, **60**, 1140-1142.
- SUZUKI, Y. 1966 a PAULING entropy of a finite ice crystal. *Low Temp. Sci.* **A 24**, 19-39 (in Japanese with English summary).
- SUZUKI, Y. 1966 b A method of evaluating PAULING entropy of two-dimensional ice. *Low Temp. Sci.* **A 24**, 41-56 (in Japanese with English summary).

Appendix A. Several Properties of Correlativities

A.1. *Correativity between two bonds*

In section 1.7, the correlativity is defined between two sites. It is often convenient to consider the correlativity between two bonds.

Let two sites on a bond b_1 be s_1 and s'_1 and those on another bond b_2 be s_2 and s'_2 . The correlativity between s_1 and s_2 , denoted by $\varepsilon(s_1, s_2)$, is, for instance, given by

$$(1 + \varepsilon(s_1, s_2)) / (1 - \varepsilon(s_1, s_2)) = \omega_{i-1}(s_1 \neq s_2) / \omega_{i-1}(s_1 = s_2), \quad (\text{A. 1. 1})$$

where $\omega_{i-1}(s_1 \neq s_2)$ is the number of such arrangements in W_{i-1} that the state values of s_1 and s_2 are different from each other and $\omega_{i-1}(s_1 = s_2)$ is that they are equal to each other.

Considering the bond condition, we easily see that

$$\varepsilon(s_1, s_2) = \varepsilon(s'_1, s'_2) = -\varepsilon(s_1, s'_2) = -\varepsilon(s'_1, s_2). \quad (\text{A. 1. 2})$$

Thus, the correlativity between b_1 and b_2 can be defined by $\varepsilon(s_1, s_2)$ with an ambiguity in sign. When the two bonds are marginal, we will fix the sign by choosing both sites near to regular points. By this choice, ε_i^{12} in section 1.6 is said the correlativity between the first and the second bond around the i -th lattice point (including sign).

A.2. *Correlativities re-interpreted in terms of possible arrangements*

When two bonds do not belong to one grain, the correlativity between them is easily seen to be zero. Now, let the two bonds b_1 and b_2 belong to a grain G . The site s_k used for defining the correlativity between b_1 and b_2 is chosen near a regular point if b_k is marginal.

Any arrangement in W_{i-1} , α , consists of two parts α_1 and α_2 , the former concerning sites on G and the latter concerning sites not on G . Since α_1 is independent of α_2 , W_{i-1} is a direct product of the set of all α_1 's and that of all α_2 's. Let $u(s_1 \neq s_2)$ be the number of such α_1 's that the state values of s_1 and s_2 are different from each other and $u(s_1 = s_2)$ be that that they are equal to each other, and let v be the number of all α_2 's. Then, naturally,

$$v \cdot u(s_1 \neq s_2) = \omega_{i-1}(s_1 \neq s_2); \quad v \cdot u(s_1 = s_2) = \omega_{i-1}(s_1 = s_2), \quad (\text{A. 2. 1})$$

and hence,

$$(1 + \varepsilon(s_1, s_2)) / (1 - \varepsilon(s_1, s_2)) = u(s_1 \neq s_2) / u(s_1 = s_2). \quad (\text{A. 2. 2})$$

Now, consider a finite ice lattice, L_G , obtained by cutting all marginal bonds of G . The sites s_1 and s_2 are on L_G . The set of all α_1 's evidently

corresponds one to one to U , a set of all possible arrangements on L_G , and $u(s_1 \neq s_2)$ and $u(s_1 = s_2)$ are evidently the number of such possible arrangements on L_G as with the state values of the two sites being different from each other and that as with the state values of the two sites being equal to each other, respectively. Hence, the correlativity, which is originally defined in W_{i-1} and expresses the correlation in W_{i-1} , can be defined in U and considered to express the correlation in U .

Hereafter, we shall consider the correlativity always on a lattice.

A. 3. Two lattices coupled by one bond. I (Fig. A 1)

In the following sections, we shall give several bases for the rule of approximate estimation of correlativities stated in section 1.7. In this section, we shall show that lattice points not on a path between two bonds do not affect on the correlativity between the two bonds.

Let s_1 and s_2 be two sites on a lattice L_1 and s_3 be a site on a free bond b_3 of L_1 . Let s_4 be a site on a free bond b_4 of another lattice L_2 . Let $u(\beta_1, \beta_2, \beta_3)$ be the number of such possible arrangements on L_1 as the state value of s_k being β_k , and $v(\beta_4)$ be the number of such possible arrangements on L_2 as with the state value of s_4 being β_4 .

Combine L_1 and L_2 into a lattice L by linking b_3 with b_4 . Let $\tau w(\beta_1, \beta_2)$ be the number of such possible arrangements on L as with the state value of s_k being β_k .

The correlativity defined on L_1 between s_1 and s_2 , denoted by $\varepsilon(L_1 : s_1, s_2)$, is given by

$$(1 + \varepsilon(L_1 : s_1, s_2)) / (1 - \varepsilon(L_1 : s_1, s_2)) = \frac{(u(1, 0, \beta_3) + u(0, 1, \beta_3))}{(u(0, 0, \beta_3) + u(1, 1, \beta_3))}, \quad (\text{A. 3. 1})$$

while that defined on L , denoted by $\varepsilon(L : s_1, s_2)$, is given by

$$(1 + \varepsilon(L : s_1, s_2)) / (1 - \varepsilon(L : s_1, s_2)) = \frac{\tau w(1, 0) + \tau w(0, 1)}{\tau w(0, 0) + \tau w(1, 1)}. \quad (\text{A. 3. 2})$$

It is easily seen that

$$\tau w(\beta_1, \beta_2) = u(\beta_1, \beta_2, 0) \cdot v(1) + u(\beta_1, \beta_2, 1) \cdot v(0) \quad (\text{A. 3. 3})$$

and

$$v(1) = v(0). \quad (\text{A. 3. 4})$$

From these four equations, we have

$$\varepsilon(L : s_1, s_2) = \varepsilon(L_1 : s_1, s_2), \quad (\text{A. 3. 5})$$

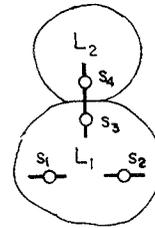


Fig. A 1.
Two lattices
coupled by
one Bond. I

from which the fact stated at the beginning can be easily deduced.

A. 4. *Two lattices coupled by one bond. II* (Fig. A 2)

In this section, we shall show a basis for the value of proper correlativity.

Let s_1 and s_2 be on free bonds b_1 and b_2 of a lattice L_1 and s_3 and s_4 on free bonds b_3 and b_4 of another lattice L_2 . Let

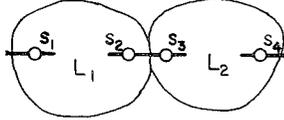


Fig. A 2. Two lattices coupled by one bond. II

$u(\beta_1, \beta_2)$ be the number of such possible arrangements on L_1 that the state value of s_k is β_k and $v(\beta_3, \beta_4)$ be the number of such possible arrangements on L_2 that the state value of s_k is β_k . Let ε^{12} be the correlativity defined on L_1 between s_1 and s_2 and ε^{34} that defined on L_2 between s_3 and s_4 :

$$(1 + \varepsilon^{12})/(1 - \varepsilon^{12}) = u(1, 0)/u(0, 0), \quad (\text{A. 4. 1})$$

$$(1 + \varepsilon^{34})/(1 - \varepsilon^{34}) = v(1, 0)/v(0, 0). \quad (\text{A. 4. 2})$$

Consider L_1 and L_2 be coupled into L by linking b_2 with b_3 . Let $w(\beta_1, \beta_4)$ be the number of such possible arrangements on L that the state value of s_k is β_k . It is easily seen that

$$w(1, 0) = u(1, 0)v(1, 0) + u(1, 1)v(0, 0) = u(1, 0)v(1, 0) + u(0, 0)v(0, 0),$$

$$w(0, 0) = u(0, 0)v(1, 0) + u(0, 1)v(0, 0) = u(0, 0)v(1, 0) + u(1, 0)v(0, 0).$$

$$(\text{A. 4. 3})$$

The correlativity defined on L between s_1 and s_4 , denoted by ε^{14} , is given by

$$(1 + \varepsilon^{14})/(1 - \varepsilon^{14}) = w(1, 0)/w(0, 0) \quad (\text{A. 4. 4})$$

From eqs. (A.4.1) through (A.4.4), we have

$$\frac{1 + \varepsilon^{14}}{1 - \varepsilon^{14}} = \frac{(1 + \varepsilon^{12})(1 + \varepsilon^{34}) + (1 - \varepsilon^{12})(1 - \varepsilon^{34})}{(1 - \varepsilon^{12})(1 + \varepsilon^{34}) + (1 + \varepsilon^{12})(1 - \varepsilon^{34})} = \frac{1 + \varepsilon^{12}\varepsilon^{34}}{1 - \varepsilon^{12}\varepsilon^{34}}$$

and hence

$$\varepsilon^{14} = \varepsilon^{12}\varepsilon^{34}. \quad (\text{A. 4. 5})$$

When L_1 consists of only one lattice point, $u(1, 0)$ is two and $u(0, 0)$ is one, and hence

$$\varepsilon^{12}(\text{single point}) = 1/3. \quad (\text{A. 4. 6})$$

We have induced the concept of the proper correlativity from eqs. (A.4.5) and (A.4.6).

A. 5. *Two lattices coupled by two bonds* (Fig. A 3)

Let $s_1, s_2,$ and s_3 be sites on free bonds $b_1, b_2,$ and

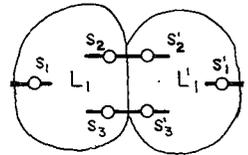


Fig. A 3. Two lattices coupled by two bonds

b_3 of a lattice L_1 . Let $u(\beta_1, \beta_2, \beta_3)$ denote the number of possible arrangements on L_1 with the state value of s_k being β_k . Let ε^{ik} be the correlativity defined on L_1 between s_i and s_k :

$$\begin{aligned} (1 + \varepsilon^{12})/(1 - \varepsilon^{12}) &= \left(u(1, 0, 0) + u(1, 0, 1) \right) / \left(u(0, 0, 1) + u(0, 0, 0) \right), \\ (1 + \varepsilon^{23})/(1 - \varepsilon^{23}) &= \left(u(1, 1, 0) + u(0, 1, 0) \right) / \left(u(1, 0, 0) + u(0, 0, 0) \right), \quad (\text{A. 5. 1}) \\ (1 + \varepsilon^{31})/(1 - \varepsilon^{31}) &= \left(u(1, 1, 0) + u(1, 0, 0) \right) / \left(u(0, 1, 0) + u(0, 0, 0) \right). \end{aligned}$$

Introducing y_k and y by

$$\begin{aligned} y_0 &= u(0, 0, 0) = u(1, 1, 1), & y_1 &= u(0, 0, 1) = u(1, 1, 0), \\ y_2 &= u(0, 1, 0) = u(1, 0, 1), & y_3 &= u(0, 1, 1) = u(1, 0, 0); \quad (\text{A. 5. 2}) \\ y &= y_0 + y_1 + y_2 + y_3, \end{aligned}$$

we have from eqs. (A.5.1)

$$\begin{aligned} y \cdot \varepsilon^{12} &= y_3 + y_2 - y_1 - y_0, & y \cdot \varepsilon^{23} &= y_1 + y_2 - y_3 - y_0, \\ y \cdot \varepsilon^{31} &= y_1 + y_3 - y_2 - y_0, \end{aligned} \quad (\text{A. 5. 3})$$

which in turn result

$$\begin{aligned} y_0 &= y(1 - \varepsilon^{12} - \varepsilon^{23} - \varepsilon^{31})/4, & y_1 &= y(1 - \varepsilon^{12} + \varepsilon^{23} + \varepsilon^{31})/4, \\ y_2 &= y(1 + \varepsilon^{12} + \varepsilon^{23} - \varepsilon^{31})/4, & y_3 &= y(1 + \varepsilon^{12} - \varepsilon^{23} + \varepsilon^{31})/4. \end{aligned} \quad (\text{A. 5. 4})$$

Now, consider another lattice L'_1 , on three free bonds $b'_1, b'_2,$ and b'_3 of which lies three sites $s'_1, s'_2,$ and s'_3 . Let quantities, $u'(\beta_1, \beta_2, \beta_3), y'_k, y'$, and ε'^{ik} be introduced analogously as done on L_1 .

Combine L_1 and L'_1 into L by linking b_2 with b'_2 and b_3 with b'_3 . Let $\varepsilon^{11'}$ denote the correlativity defined on L between s_1 and s'_1 . Then we easily see that

$$\begin{aligned} (1 + \varepsilon^{11'})/(1 - \varepsilon^{11'}) &= \left(\sum_{\rho, \sigma} u(1, \rho, \sigma) u'(0, 1 - \rho, 1 - \sigma) \right) / \left(\sum_{\rho, \sigma} u(0, \rho, \sigma) u'(0, 1 - \rho, 1 - \sigma) \right). \end{aligned} \quad (\text{A. 5. 5})$$

From eq. (A.5.5), using eq. (A.5.4) and corresponding equations on L'_1 , we have

$$(1 + \varepsilon^{11'})/(1 - \varepsilon^{11'}) = \frac{1 + \varepsilon^{12} \varepsilon'^{12} + \varepsilon^{23} \varepsilon'^{23} + \varepsilon^{31} \varepsilon'^{31}}{1 - \varepsilon^{12} \varepsilon'^{12} + \varepsilon^{23} \varepsilon'^{23} - \varepsilon^{31} \varepsilon'^{31}}$$

or

$$\varepsilon^{11'} = (\varepsilon^{12} \varepsilon'^{12} + \varepsilon^{31} \varepsilon'^{31}) / (1 + \varepsilon^{23} \varepsilon'^{23}) = \varepsilon^{12} \varepsilon'^{12} + \varepsilon^{31} \varepsilon'^{31} + \dots \quad (\text{A. 5. 6})$$

Now, any path between s_1 and s'_1 must pass one and only one of s_2 and

s_3 . Equation (A.5.6) shows the approximate additivity of contributions from all paths via s_2 and those from all paths via s_3 .

A.6. *One lattice point and a lattice coupled by two bonds* (Fig. A 4)

Let s'_1, s'_2, s'_3 , and s'_4 be sites around a lattice point P . Let $v(\beta_1, \beta_2, \beta_3, \beta_4)$ denote the number of possible arrangements on a lattice consisting only of P with the state value of s'_k being β_k . Evidently,

$$\begin{aligned} v(0, 0, 1, 1) &= v(0, 1, 0, 1) = v(1, 0, 0, 1) = v(1, 0, 1, 0) \\ &= v(1, 1, 0, 0) = v(0, 1, 1, 0) = 1, \\ \text{others} &= 0. \end{aligned} \quad (\text{A. 6. 1})$$

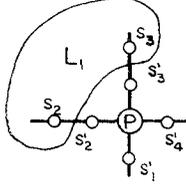


Fig. A 4.

One lattice point and a lattice coupled by two bonds

Now, combine P and L_1 of the last section into a lattice L by linking the bond of P , on which s'_2 lies, with the bond b_2 and that, on which s'_3 lies, with the bond b_3 , and consider the correlativity defined on L between s'_1 and s'_4 , which is denoted by ε'^{14} and is given by

$$\begin{aligned} &(1 + \varepsilon'^{14}) / (1 - \varepsilon'^{14}) \\ &= \left(\sum_{\rho, \sigma, \tau} v(1, \rho, \sigma, 0) u(\tau, 1 - \rho, 1 - \sigma) \right) / \left(\sum_{\rho, \sigma, \tau} v(0, \rho, \sigma, 0) u(\tau, 1 - \rho, 1 - \sigma) \right). \end{aligned} \quad (\text{A. 6. 2})$$

Using eqs. (A.6.1) and (A.5.2), from eq. (A.6.2), we have

$$(1 + \varepsilon'^{14}) / (1 - \varepsilon'^{14}) = 2(y_1 + y_2) / (y_0 + y_3) = 2(1 + \varepsilon^{23}) / (1 - \varepsilon^{23}),$$

or

$$\varepsilon'^{14} = (1 + 3\varepsilon^{23}) / (3 + \varepsilon^{23}) = (1/3) + (8/9)\varepsilon^{23} + \dots \quad (\text{A. 6. 3})$$

Now, a path on L_1 between s_2 and s_3 corresponds to two pathes on L between s'_1 and s'_4 , each of which crosses over itself at P and has a length longer than that of the corresponding path on L_1 by one. There is only one more path between s'_1 and s'_4 , that is, a direct path of the length one. Thus, from the rule in section 1.7, we may expect that

$$\varepsilon'^{14} \simeq (1/3) + (2/3)\varepsilon^{23}$$

which is a fairly good approximation of ε'^{14} . This fact may show the adequacy of our definition of the length of a cross-over path.

Let a set of b free sites on its lower edge (shown by open circles in Fig. B 2) be denoted by S_b and that of those on its upper edge (shown by black dots) by S'_b . In each set, natural order is chosen as the order for defining the state value.

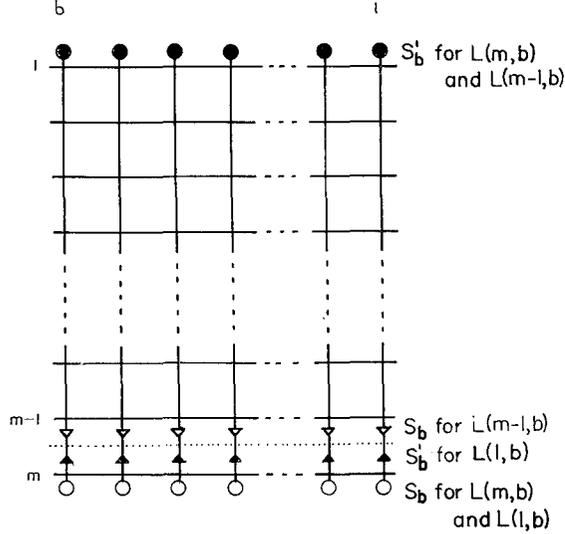


Fig. B 2. Rectangular lattice and sites used for classifying possible arrangements on L

Let $w_{m,b}(i, j)$ be the number of such possible arrangements on $L(m, b)$ as having the state value 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 $L(m, b)$ by π around its horizontal axis, $w_{m,b}(i, \bar{j})$ can be regarded as the number of such possible arrangements as having the state values i on S'_b and \bar{j} on S_b . Hence,

$$w_{m,b}(i, j) = w_{m,b}(\bar{j}, \bar{i}). \quad (\text{B. 2. 1})$$

On the other hand from the fact that the complement with respect to all bonds of $L(m, b)$ of a possible arrangement on $L(m, b)$ is again a possible arrangement, we easily deduce the following relation (eq. (1.3.5)):

$$w_{m,b}(i, j) = w_{m,b}(\bar{i}, \bar{j}). \quad (\text{B. 2. 2})$$

We will define $w_{m,b}(i)$ and $\bar{w}_{m,b}(j)$ by

$$w_{m,b}(i) = \sum_{j=0}^{2^b-1} w_{m,b}(i, j), \quad \text{and} \quad \bar{w}_{m,b}(j) = \sum_{i=0}^{2^b-1} w_{m,b}(i, j). \quad (\text{B. 2. 3})$$

It is evident that $w_{m,b}(i)$ is the number of such possible arrangements as having the state value i on S_b and $\bar{w}_{m,b}(j)$ that of those having the state

value \bar{j} on S'_b .

Using eqs. (B.3.1), (B.2.2), and (B.2.3), we have

$$\omega_{m,b}(\bar{i}) = \omega_{m,b}(\bar{i}) = \bar{\omega}_{m,b}(\bar{i}) = \bar{\omega}_{m,b}(\bar{i}). \quad (\text{B.2.4})$$

The number of all possible arrangements on $L(m, b)$, denoted by $\omega(m, b)$ in section 2.2 of the text, is naturally given by

$$\omega(m, b) = \sum_{i=0}^{2^b-1} \omega_{m,b}(i). \quad (\text{B.2.5})$$

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

$$\omega_{m,b}(i, j) = \sum_{k=0}^{2^b-1} \omega_{1,b}(i, k) \omega_{m-1,b}(k, j) \quad (\text{B.2.6})$$

and

$$\omega_{m,b}(i) = \sum_{k=0}^{2^b-1} \omega_{1,b}(i, k) \omega_{m-1,b}(k). \quad (\text{B.2.7})$$

It is convenient to regard $\omega_{m,b}(i, j)$ as the (i, j) -component of a $2^b \times 2^b$ matrix \mathbb{W}_b^m and $\omega_{m,b}(i)$ as the i -th component of a 2^b -dimensional vector $\boldsymbol{\omega}_{m,b}$ and further to introduce a 2^b -dimensional vector $\boldsymbol{\omega}_{0,b}$ with all components being one.

Then, using notations in matrix and vector calculus, we can rewrite eq. (B.2.5) as

$$\omega(m, b) = (\boldsymbol{\omega}_{0,b}, \boldsymbol{\omega}_{m,b}) \quad (\text{B.2.8})$$

and eq. (B.2.6) as

$$\mathbb{W}_b^m = \mathbb{W}_b^1 \mathbb{W}_b^{m-1}. \quad (\text{B.2.9})$$

Using eq. (B.2.9) iteratively, we have

$$\mathbb{W}_b^m = (\mathbb{W}_b^1)^m, \quad (\text{B.2.10})$$

which enables one to regard the superscript m of \mathbb{W}_b^m as an index. Hence, we rewrite \mathbb{W}_b^1 as \mathbb{W}_b . The equation (B.2.7) is now rewritten as

$$\boldsymbol{\omega}_{m,b} = \mathbb{W}_b \boldsymbol{\omega}_{m-1,b}. \quad (\text{B.2.11})$$

We will call the matrix \mathbb{W}_b the elemental matrix for a row of width b . Because of eqs. (B.2.1) and (B.2.2), it is a symmetric matrix.

B.3. Simplified elemental matrices

Owing to eq. (B.2.4), we can rewrite eq. (B.2.5) and eq. (B.2.7) as

$$\omega(m, b) = 2 \sum_{i=0}^{2^{b-1}-1} \omega_{m,b}(i) \quad (\text{B.3.1})$$

and

$$\omega_{m,b}(i) = \sum_{k=0}^{2^{b-1}-1} (\omega_{m,b}(i, k) + \omega_{m,b}(i, \bar{k})) \omega_{m-1,b}(k). \quad (\text{B. 3. 2})$$

Introducing a $2^{b-1} \times 2^{b-1}$ matrix B_b , whose (i, j) -component is given by

$$B_b(i, j) = \omega_{m,b}(i, k) + \omega_{m,b}(i, \bar{k}) \quad (i, k=0, \dots, 2^{b-1}-1) \quad (\text{B. 3. 3})$$

and a 2^{b-1} -dimensional vector $\boldsymbol{u}_{m,b}$, which consists of the first half of $\boldsymbol{u}_{m,b}$, from eq. (B.3.1) and eq. (B.3.2), we have

$$\omega(m, b) = 2(\boldsymbol{u}_{0,b}, \boldsymbol{u}_{m,b}) \quad (\text{B. 3. 4})$$

and

$$\boldsymbol{u}_{m,b} = B_b \boldsymbol{u}_{m-1,b} \quad (m=1, \dots). \quad (\text{B. 3. 5})$$

From eqs. (B.3.3), (B.2.1), and (B.2.2), we easily see that B_b is also symmetric. We call B_b the simplified elemental matrix for a row of width b .

The number of independent components of $\boldsymbol{u}_{m,b}$ is less than 2^{b-1} . For instance, in the case $b=3$, we easily see that $\omega_{m,3}(1) = \omega_{m,3}(4) = \omega_{m,3}(3) = \omega_{m,3}(3)$. Hence, we can further reduce the dimension of the matrix, needed for calculating $\boldsymbol{u}_{m,b}$. The reduction, however, yields a non-symmetric matrix.

B. 4. Calculation of $s(\infty, b)$

Since B_b is symmetric, its eigenvalues are all real and it can be transformed into a diagonal matrix B_D by an orthogonal transformation :

$$B_D(i, j) = \lambda_j \delta_{i,j}, \quad (\text{B. 4. 1})$$

and

$$B_b = T B_D \tilde{T}; \quad T \tilde{T} = 1, \quad (\text{B. 4. 2})$$

where λ_j is the j -th eigenvalue of B_b and \tilde{T} stands for the transpose of T . We choose T as such that λ_0 has the largest absolute value of λ 's :

$$|\lambda_0| \geq |\lambda_j|. \quad (\text{B. 4. 3})$$

(Such a choice is always possible as is well known.)

From eqs. (B.3.4), (B.4.1), and (B.4.2), we have

$$\omega(m, b) = 2(\boldsymbol{u}_{0,b}, T(B_D)^m \tilde{T} \boldsymbol{u}_{0,b}) = 2 \sum_{i,j,k=0}^{2^{b-1}-1} T(i, j) T(k, j) (\lambda_j)^m = 2(\lambda_0)^m C, \quad (\text{B. 4. 4})$$

where

$$C \equiv C_0 + \sum_{j=1}^{2^{b-1}-1} C_j (\lambda_j / \lambda_0)^m \quad (\text{B. 4. 5})$$

$$C_j \equiv \sum_{i,k=0}^{2^{b-1}-1} T(i, j) T(k, j). \quad (j=0, \dots, 2^{b-1}-1) \quad (\text{B. 4. 6})$$

Evidently,

$$\lim_{m \rightarrow \infty} C = C_0 + \left(\sum_{\substack{\lambda_0 = \lambda_j \\ j > 0}} C_j \right) + (-1)^m \left(\sum_{\lambda_0 = -\lambda_j} C_j \right). \quad (\text{B. 4. 7})$$

Since $w(m, b)$ must increase monotonously with m , we expect that λ_0 and C may be positive and the second summation term may disappear. (According to a theorem due to FROBENIUS, $\lambda_0 > 0$ and $|\lambda_0| > |\lambda_j|$ for $j \neq 0$. Hence, terms in parentheses in eq. (B.4.7) disappear.)

Owing to eq. (B.4.7), we have

$$s(\infty, b) = \lim_{m \rightarrow \infty} (\ln w(m, b)/mb) = (\ln \lambda_0)/b + \lim_{m \rightarrow \infty} ((\ln 2C)/mb) = (\ln \lambda_0)/b. \quad (\text{B. 4. 8})$$

Completely analogous deductions can be carried out on basis of eqs. (B.2.8) and (B.2.11) instead of eqs. (B.3.4) and (B.3.5), showing that λ_0 is also the eigenvalue of W_b of the largest absolute value.

B. 5. Calculation of $q(b, k, k')$

Consider a stepped lattice L (Fig. B 3 a). Let the number of possible arrangements on it having state values β_1 and β_2 on the two sites s_1 and s_2 at the step be denoted by $w(\beta_1, \beta_2)$. We can calculate $q(b, k, k')$ from $w(0, 0)$ and $w(0, 1)$.

Let $w_{b-1}(\beta_2: x, y)$ be the number of possible arrangement on $L(1, b-1)$, having the state values, β_2 on s_2 , x on S_{b-1} , and \bar{y} on S'_{b-1} (See Fig. B 3 b). Here, x and y are $(b-1)$ -bits binary integers and the bar over them stands for $(b-1)$ -complement :

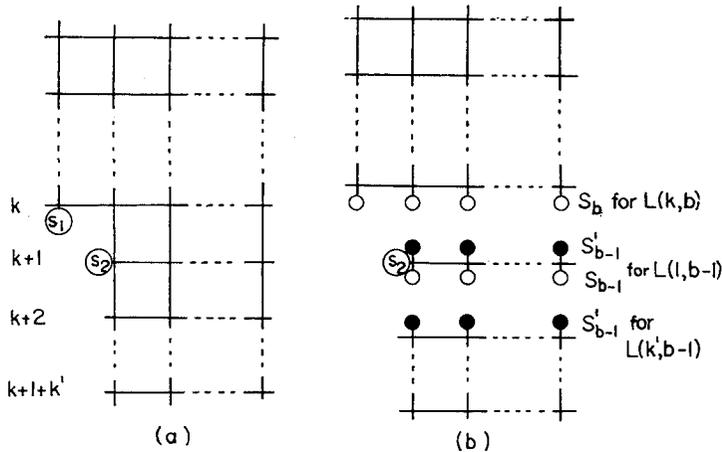


Fig. B 3. a) Stepped rectangular lattice
b) decomposition of it

$$\bar{y} = 2^{b-1} - 1 - y. \quad (\text{B. 5. 1})$$

It is evident that

$$w_{b-1}(0 : x, y) = w_{b-1}(1 : \bar{x}, \bar{y}) \quad (\text{B. 5. 2})$$

and

$$w_{b-1}(0 : x, y) + w_{b-1}(1 : x, y) = w_{1,b-1}(x, y). \quad (\text{B. 5. 3})$$

Since L can be decomposed into three parts $L(k, b)$, $L(1, b-1)$, and $L(k', b-1)$ as shown in Fig. B 3 b, we easily deduce that

$$w(0, \beta) = \sum_{x=0}^{2^{b-1}-1} \sum_{y=0}^{2^{b-1}-1} \bar{w}_{k',b-1}(x) w_{b-1}(\beta : x, y) w_{k,b}(y). \quad (\text{B. 5. 4})$$

Introducing two $2^{b-1} \times 2^{b-1}$ matrices P_{b-1}^β by

$$P_{b-1}^\beta(x, y) = w_{b-1}(\beta : x, y) \quad (\beta=0, 1) \quad (\text{B. 5. 5})$$

and using eq. (B.2.4), we can rewrite eq. (B.5.4) in a concise form as

$$w_{b-1}(0, \beta) = (\mathbf{u}_{k',b-1}, P_{b-1}^\beta \mathbf{u}_{k,b}), \quad (\text{B. 5. 6})$$

or defining two $2^{b-1} \times 2^{b-2}$ rectangular matrices Q_{b-1}^β by

$$Q_{b-1}^\beta(x, y) = P_{b-1}^\beta(x, y) + P_{b-1}^\beta(\bar{x}, y) = w_{b-1}(\beta : x, y) + w_{b-1}(\beta : \bar{x}, y) \\ (x=0, \dots, 2^{b-2}-1; y=0, \dots, 2^{b-1}-1), \quad (\text{B. 5. 7})$$

as

$$w_{b-1}(0, \beta) = (\mathbf{u}_{k',b-1}, Q_{b-1}^\beta \mathbf{u}_{k,b}). \quad (\text{B. 5. 8})$$

We will call the matrices P^β the semi-simplified parity matrices and Q^β the simplified parity matrices.

Now, $q(b, k, k')$ is defined in terms of the ratio of $w_{b-1}(0, 1)$ to $w_{b-1}(0, 0)$, which shall be denoted by $x(b, k, k')$:

$$q(b, k, k') = 2 \left(1 + 2x(b, k, k') \right) / 3 \left(1 + x(b, k, k') \right), \quad (\text{B. 5. 9})$$

$$x(b, k, k') = (\mathbf{u}_{k',b-1}, Q_{b-1}^1 \mathbf{u}_{k,b}) / (\mathbf{u}_{k',b-1}, Q_{b-1}^0 \mathbf{u}_{k,b}) \\ = (\mathbf{u}_{0,b-1}, (B_{b-1})^{k'} Q_{b-1}^1 (B_b)^k \mathbf{u}_{0,b}) / (\mathbf{u}_{0,b-1}, (B_{b-1})^{k'} Q_{b-1}^0 (B_b)^k \mathbf{u}_{0,b}). \quad (\text{B. 5. 10})$$

The convergence of $x(b, k, k')$ and hence of $q(b, k, k')$ with the increase in k and/or k' can be deduced analogously to deductions in the last section. Further, considering L as a rectangle of width $k+k'+1$, we can express $x(b, k, k')$ in terms of Q_k^β and $B_{k+k'+1}$ and can deduce its convergence with increase in b .

B. 6. Construction of matrices

In order to find the components of the matrices, W_b , B_b , P_b^β , and Q_b^β , we

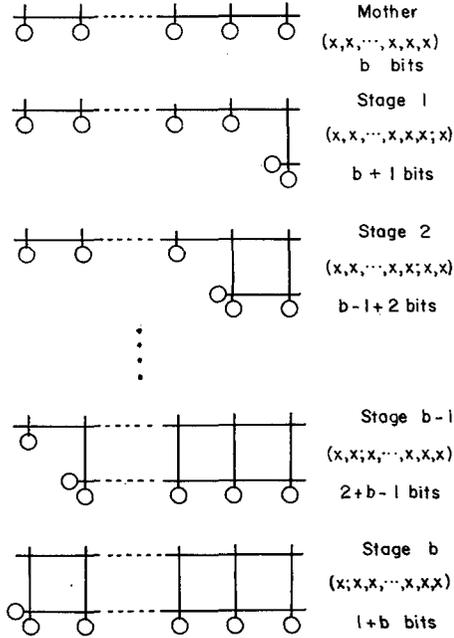


Fig. B 4. Construction of a new row

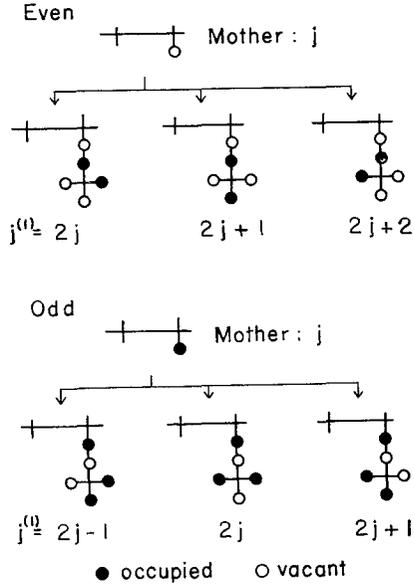


Fig. B 5. Transfer to the first stage

consider a procedure of composing a new row by adding lattice points one after one under the mother lattice having the state value j on its S_b (See Fig. B 4). An intermediate stage where k new lattice points has been added shall be called the k -th stage and a set of $b + 1$ free sites on the lower edge at that stage (denoted by open circles) shall be denoted by $S_{b+1}^{(k)}$. We investigate what state values $j^{(k)}$ are conceivable for $S_{b+1}^{(k)}$ when the state value of j on S_b of the mother lattice has been given.

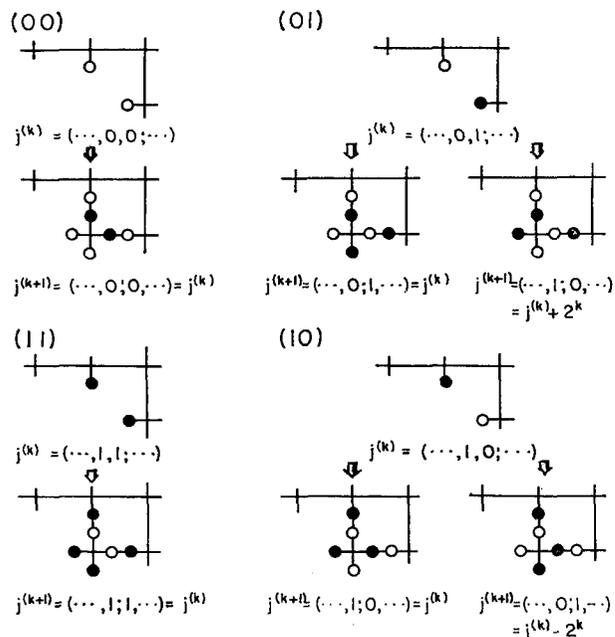
The transfer to the first stage is shown in Fig. B 5, from which one can easily see that three numbers are possible for $j^{(1)}$. They are given by

$$j_1^{(1)} = 2j - 1, \quad j_2^{(1)} = 2j, \quad \text{and} \quad j_3^{(1)} = 2j + 1 \quad (\text{when } j \text{ is odd}) \quad (\text{B. 6. 1})$$

or

$$j_1^{(1)} = 2j, \quad j_2^{(1)} = 2j + 1, \quad \text{and} \quad j_3^{(1)} = 2j + 2 \quad (\text{when } j \text{ is even}). \quad (\text{B. 6. 2})$$

The transfer from the k -th to the $(k + 1)$ -th stage is shown in Fig. B 6. It is easily seen from the figure that $j^{(k+1)}$ must be the same as $j^{(k)}$ when the $(k + 1)$ -th and the $(k + 2)$ -th bits of $j^{(k)}$ has same state values, while if otherwise, $j^{(k+1)}$ must be equal to either $j^{(k)}$ or the number obtained from $j^{(k)}$ by exchanging the $(k + 1)$ -th bit and the $(k + 2)$ -th bit in it.

Fig. B 6. Transfer from the k -th to the $k+1$ -th stage

From the definition of the matrices, it is evident that

$$W_b(i, j) = \text{Number of } j^{(b)} \text{ satisfying } j^{(b)} = i \pmod{2^b},$$

$$P_b^0(i, j) = \text{''} \quad \quad \quad j^{(b)} = i, \quad (\text{B. 6. 3})$$

and $P_b^1(i, j) = \text{''} \quad \quad \quad j^{(b)} = 2^b + i.$

The components of the simplified matrices are obtained from them.

For manual practice of the procedure of obtaining $j^{(b)}$, it is convenient to write $j^{(k)}$ in binary form and put semi-colon between the $(k+1)$ -th and the k -th digit as done in Fig. B 7 for two values of j in case of $b=3$. But the work is most suitable for an electronic computer. An example of a program for obtaining B_b and Q_b^0 is shown below, where N , $B(I, J)$, $D(I, J)$ and $E(I, J)$ stand for b , $B_b(i-1, j-1)$, $Q_b^1(i-1, j-1) \equiv Q_b^0(i-1, 2^b-j)$ and $Q_b^1(i-1, 2^b-j) \equiv Q_b^0(i-1, j-1)$, respectively.

Values of $q(b, k, k')$ for $3 \leq b \leq 7$ and for several values of k and k' have been actually calculated on basis of eqs. (B.5.8) and (B.5.9) and of the construction of the matrices given in this section. They are shown in the table at the end of paper. From the table one can concretely see the convergence of $q(b, k, k')$ with increase in k and/or k' and also see that $q(b, 32, 32)$ is equal

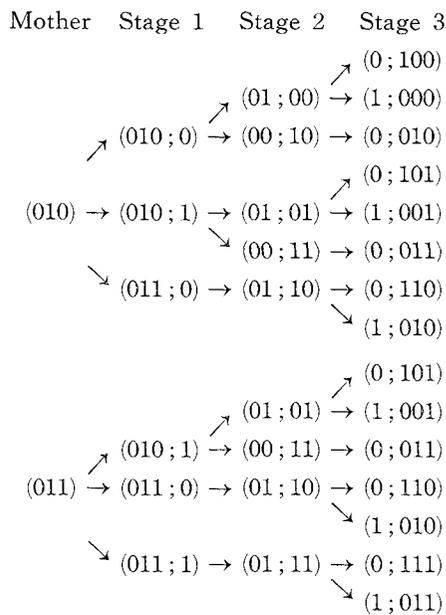


Fig. B 7. Examples of construction of $j^{(3)}$

to $q(b, \infty, \infty)$ at least in seven effective decimal digits even for $b=7$. The value of $q(2, \infty, \infty)$ in table 1 of section 2.3 was calculated by diagonalizing B_2 in eq. (B.5.9).

Program for Constructing Matrices B_b and P_b^s

```

N2=N-1
N1=2**N2
N3=N1*2
DO 4 I=1, N1
MC=I-1
IF(MC-(MC/2)**2) 15, 16, 15
15 MA(1)=2*MC-1
MA(2)=2*MC
MA(3)=2*MC+1
GO TO 17
16 MA(1)=2*MC
MA(2)=2*MC+1
MA(3)=2*MC+2
17 MA(4)=-2
LE(1)=4
L=5
DO 18 K=1, N2
J=1
25 MC=MA(J)/2**K
-(MA(J)/2**(K+2))*4
IF(MC) 20, 21, 22
22 IF(MC-2) 23, 24, 21
21 J=J+1
GO TO 25
24 MA(L)=MA(J)-2**K
GO TO 26
23 MA(L)=MA(J)+2**K
26 L=L+1
GO TO 21
20 MA(L)=-2**(K+1)
LE(K+1)=L
18 L=L+1
L=LE(N)-1
DO 30 J=1, N1
S=0.
S1=0.
DO 41 K=1, L
MC=MA(K)-(MA(K)/N3)*N3
IF(MC) 41, 42, 42
42 IF(MC-J+1) 44, 45, 44
44 IF(MC+J-N3) 41, 45, 41
45 MC=MA(K)-N3
IF(MC) 46, 43, 43
43 S=S+1.
GO TO 41
46 S1=S1+1
41 CONTINUE
D(J,I)=S
E(J,I)=S1
30 B(J,I)=S+S1
4 CONTINUE

```

Table of Matrices B_b and Q_b^f

$B_1:$ 3	$B_3:$ 2 1 1 1 1 2 2 2 1 2 3 2 1 2 2 2	$B_5:$ 2 1 1 0 1 0 0 0 1 0 0 0 0 0 0 1 1 2 1 1 1 1 0 0 1 1 0 0 0 0 1 1 1 1 2 1 1 1 1 0 1 1 1 0 0 1 1 1 0 1 1 2 0 1 1 1 0 1 1 1 1 1 1 1 0 1 1 1 0 2 1 1 0 1 1 1 1 1 1 1 1 1 0 1 1 1 1 2 1 1 0 1 2 2 2 2 1 0 0 0 1 1 1 1 2 1 0 1 2 2 2 2 1 0 0 0 0 1 0 1 1 2 1 1 1 1 1 1 1 1 1 1 1 1 0 1 0 0 1 2 1 1 1 1 1 1 1 1 0 1 1 1 1 1 1 1 1 2 2 2 2 2 1 0 0 0 1 1 1 2 2 1 1 2 3 2 2 2 1 0 0 0 0 1 1 2 2 1 1 2 2 2 1 1 1 1 0 0 0 1 1 2 2 1 1 2 2 1 2 1 1 0 0 0 1 1 1 2 2 1 1 2 2 1 1 2 1 1 0 1 1 1 1 1 1 1 1 1 1 1 1 1 1 2 1 1 1 1 0 1 0 0 1 1 0 0 1 0 1 1 1 2
$B_2:$ 2 2 2 3	$Q_3^f:$ 1 1 1 1 0 1 2 2	
$Q_1^f:$ 1 2		
$Q_1^f:$ 2 1	$Q_2^f:$ 1 1 1 1 2 2 1 0	
$B_4:$ 2 1 1 0 1 0 0 1 1 2 1 1 1 1 1 1 1 1 2 1 1 2 2 1 0 1 1 2 1 2 2 1 1 1 1 1 2 2 2 1 0 1 2 2 2 3 2 1 0 1 2 2 2 2 2 1 1 1 1 1 1 1 1 2		$Q_4^f:$ 1 1 1 0 1 0 0 0 1 0 0 0 0 0 0 1 0 1 1 1 1 1 0 0 1 1 0 0 0 0 1 1 0 0 1 1 1 1 0 1 1 1 0 0 1 1 1 0 0 0 1 0 1 1 1 0 1 1 1 1 1 1 1 0 0 0 0 0 1 1 1 0 1 1 1 1 1 1 1 1 0 0 0 0 0 1 1 1 0 1 2 2 2 2 1 0 0 0 0 0 0 0 1 1 0 1 2 2 2 2 1 0 0 0 0 0 0 0 0 1 1 1 1 1 1 1 1 1 1 0 0 0 0 0 0 0 1 1 1 1 1 1 1 1 1 1
$Q_3^f:$ 1 1 1 0 1 0 0 1 0 1 1 1 1 1 1 1 0 0 1 1 1 2 2 1 0 0 0 1 1 2 2 1		$Q_4^f:$ 1 0 0 0 0 0 0 1 0 0 0 1 0 1 1 1 1 1 0 0 0 0 1 1 0 0 1 1 1 1 1 0 1 1 1 0 0 1 1 1 0 1 1 1 1 1 0 0 0 1 1 1 1 1 1 0 1 1 1 0 1 0 0 0 1 1 1 1 1 1 1 1 0 1 1 1 0 0 0 0 0 1 2 2 2 2 1 0 1 1 1 0 0 0 0 0 0 1 2 2 2 2 1 0 1 1 0 0 0 0 0 0 1 1 1 1 1 1 1 1 1 0 0 0 0 0 0 0
$Q_3^f:$ 1 0 0 1 0 1 1 1 1 1 1 1 1 1 1 0 1 2 2 1 1 1 0 0 1 2 2 1 1 0 0 0		

Table of $q(b, k, k')$

$\begin{matrix} b=3 \\ k' \setminus k \end{matrix}$	1	2	4	8	16	32
1	1.01485443	1.01796715	1.01873728	1.01877078	1.01877084	1.01877084
2	1.01497981	1.01811839	1.01889490	1.01892868	1.01892874	1.01892874
4	1.01499302	1.01813432	1.01891141	1.01894532	1.01894537	1.01894537
8	1.01499314	1.01813447	1.01891166	1.01894547	1.01894553	1.01894553
16	1.01499314	1.01813447	1.01891166	1.01894547	1.01894553	1.01894553
$\begin{matrix} b=4 \\ k' \setminus k \end{matrix}$	1	2	4	8	16	32
1	1.01536098	1.01926276	1.02072096	1.02085611	1.02085710	1.02085710
2	1.01570860	1.01973070	1.02123555	1.02137505	1.02137607	1.02137607
4	1.01579421	1.01984590	1.02136223	1.02150280	1.02150383	1.02150383
8	1.01579793	1.01985091	1.02136773	1.02150836	1.02150938	1.02150938
16	1.01579793	1.01985092	1.02136774	1.02136774	1.02150939	1.02150939
32	1.01579793	1.01985092	1.02136774	1.02136774	1.02150939	1.02150939
$\begin{matrix} b=5 \\ k' \setminus k \end{matrix}$	1	2	4	8	16	32
1	1.01546373	1.01963965	1.02153493	1.02181294	1.02181785	1.02181785
2	1.01591892	1.02030937	1.02231864	1.02261400	1.02261922	1.02261922
4	1.01608842	1.02055968	1.02261199	1.02291390	1.02291923	1.02291924
8	1.01610410	1.02058284	1.02263913	1.02294166	1.02294700	1.02294700
16	1.01610422	1.02058301	1.02263913	1.02294189	1.02294720	1.02294720
32	1.01610422	1.02058301	1.02263933	1.02294189	1.02294720	1.02294721
$\begin{matrix} b=6 \\ k' \setminus k \end{matrix}$	1	2	4	8	16	32
1	1.015485	1.019749	1.021875	1.022291	1.022305	1.022305
2	1.015980	1.020518	1.022824	1.023380	1.023295	1.023295
4	1.016206	1.020877	1.023272	1.023747	1.023763	1.023763
8	1.061240	1.020930	1.023339	1.023817	1.023832	1.023832
16	1.061240	1.020931	1.023340	1.023818	1.023833	1.023833
32	1.061240	1.020931	1.023340	1.023818	1.023833	1.023833
$\begin{matrix} b=7 \\ k' \setminus k \end{matrix}$	1	2	4	8	16	32
1	1.015489	1.019781	1.022017	1.022545	1.022571	1.022571
2	1.015998	1.020594	1.023061	1.023653	1.023683	1.023683
4	1.016255	1.021023	1.023627	1.024259	1.024290	1.024291
8	1.016306	1.021109	1.023742	1.024381	1.024414	1.024414
16	1.016308	1.021112	1.023745	1.024385	1.024418	1.024418
32	1.016308	1.021112	1.023745	1.024385	1.024418	1.024418