Residual Entropy of Ice

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We examine the problem of evaluation of residual hydrogen-bond entropy in ice, first noting by way of introduction the results of applying certain well-known approximate lattice theory combinatorial techniques (mean field, Bethe, Kikuchi approximations). Subsequently, a general matrix method is introduced for evaluation of the residual entropy in the square planar lattice analog of ice, in terms of a series of contributions, each of which corresponds to a connected cluster diagram. The leading term in this latter method is the Pauling estimate, and two successive orders of terms are evaluated explicitly to indicate rate of convergence. In the real three-dimensional case the generalization of the matrix method indicates that the Pauling estimate is roughly 1% low.

I. INTRODUCTION

THE residual entropy of ice arises from the fact that each hydrogen atom situated between a pair of oxygen atoms in the wurtzitelike ice lattice can lie in either of two energy minima. Were there no other restrictions on the hydrogen atoms one would immediately have as the total number of different configurations 2^{2N}, where N is the number of oxygen atoms in the lattice. However, many of these are ruled out by the conditions that each oxygen atom must have two and only two attached hydrogen atoms. Consider a particular oxygen atom and the four surrounding hydrogen nuclei. Of the 16 possible arrangements of the four hydrogens only six are acceptable (i.e., only six have two and only two hydrogens close to the oxygen. The number of configurations W for the entire lattice is then roughly

$$W_N \cong 2^{2N}(\tfrac{6}{16})^N = (\tfrac{3}{2})^N. \quad (1)$$

The above estimate is due to Pauling.[1] One wonders whether a little more labor might result in a more accurate value for W_N.

Because each of our allowed configurations are assumed to have about equal energy the statistics are considerably simplified. This allows us to carry through very easily several different approximations. We develop the random mixing (mean field) method for several kinds of figures. We also apply the Kikuchi[2] combinatorial results. These latter usually give a substantial improvement over the Bethe[3] lattice method which in this case, because of the lack of energetics, is equivalent to the random mixing result. Lastly, as the major object of this article, we develop a systematic expansion whose leading term is the Pauling result and whose first two terms taken together are equivalent to the Kikuchi result. Although this expansion is explicitly developed for the square lattice, we actually also evaluate these two terms for the ice lattice.

For the square planar analog of the ice lattice, we have evaluated three terms, giving a rough idea of rapidity of convergence to the exact result. This simplified two-dimensional problem is of interest in its own right, not only because of exceptional ease of visualization of hydrogen bond configurations, but because it apparently exhibits relatively larger deviations from the Pauling approximation on account of its low dimensionality. Furthermore, it may be susceptible in the foreseeable future of exact combinatorial analysis by methods related to those meeting with success for the two-dimensional Ising[4] and dimer configuration[5] problems.

II. METHOD OF HIGHER FIGURES

In Fig. 1 we have depicted a regular square analog of the ice lattice in two dimensions. The oxygen atoms are located at the lattice points and the two arrows represent attached hydrogens. Each line connecting a pair of neighboring oxygen atoms must contain one and only one arrow. These "doubly arrowed" oxygen atoms can each be placed down on a lattice site in six possible ways. However, since two of the four bonds connecting the site to the four neighbors are occupied by other arrows, the probability that a particular line already has an arrow on it is one-half. The probability that two selected lines are both free of arrows is one-fourth, and the expected number of ways to place the water molecule is

$$W_1 = 6 \times \tfrac{1}{4} = \tfrac{3}{2}. \quad (2)$$

In general the expected number of ways to place M molecules on M preselected sites is equal to the total number of ways times $(\frac{1}{2})^K$ where K is the number of arrows of the M molecules which lie on lines connecting these molecules with other molecules in the crystal. K

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[1] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), p. 467.

[2] R. Kikuchi, Phys. Rev. **81**, 988 (1951).

[3] H. A. Bethe, Proc. Roy. Soc. (London) **A150**, 552 (1935).

[4] L. Onsager, Phys. Rev. **65**, 117 (1944).

[5] P. W. Kasteleyn, Physica **27**, 1209 (1961); M. E. Fisher, Phys. Rev. **124**, 1664 (1961); H. N. V. Temperley and M. E. Fisher, Phil. Mag. **6**, 1061 (1961).

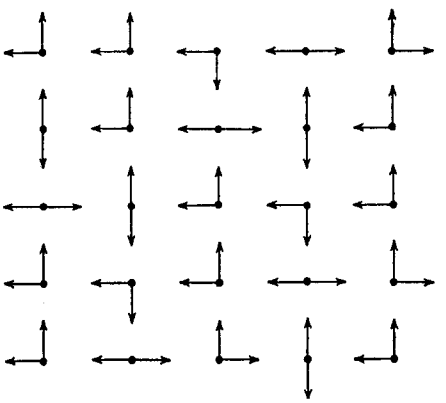


FIG. 1. Two-dimensional regular square lattice analog of real ice. The two protons bound to each oxygen atom (lattice site) are denoted by arrows. All configurations, regardless of bond angles, are regarded as equally probable.

is a number which depends on the connectedness of the chosen set of M sites. The $(\frac{1}{2})$ occurs because there are $2K$ lines connecting the M molecules with the remaining molecules of the lattice, and K of them (which are assumed to be randomly distributed) are already occupied by arrows of the surrounding molecules.[6]

For a pair of adjacent sites there are eighteen separate ways to place two water molecules, and three of the arrows always stick out into the rest of the crystal. Hence

$$W_2=18\times(1/2^3)=(\tfrac{3}{2})^2. \tag{3}$$

Consideration of a pair of sites hence gives the same result on a per-site basis as a central site and its neighbors.[7] Similarly, as one can verify by direct counting, for a given site and its four neighbors we get

$$W_5=(\tfrac{3}{2})^5. \tag{4}$$

As we soon see consideration of any number of sites which are connected as a tree (Cayley tree[8]) always gives the Pauling estimate.

In order to gain a significant improvement over the approximation obtained from these simple Cayley trees one must choose a figure which is closed[9] with respect to them. Accordingly, we choose as the basic figure a square of sites for the two-dimensional lattice (hexagon for the real ice lattice). Matrix methods are directly applicable. Consider the matrix displayed in Fig. 2. The figure in the left-hand column represent the six possible states of a chosen site and the figures on the top represent states on the adjacent site (moving in the clockwise direction around the polygon). In the column the lower right-hand position for an arrow lies on the line of the basic figure connecting the two sites. In the row the lower left-hand position lies on this same line. The two upper positions for both row and column represent lines pointing into the rest of the lattice. The numbers in the matrix are obtained as follows:

(1) The value zero is assigned if either two or no arrows lie on the connecting line between the two sites in question; otherwise,

(2) The value $(\frac{1}{2})^K$ is assigned if the figure of the column has K arrows pointing into the rest of the crystal.

The expected number of ways to arrange N figures on the closed N-gon is related to the resulting matrix $\mathbf{A}$,[10]

$$W_N=\sum_{i,j,k,\cdots,l} A_{ij}A_{jk},\cdots,A_{li}=\mathrm{Tr}\mathbf{A}^N=\sum_{i=1}^{6}\lambda_i^N. \tag{5}$$

The eigenvalues λ_i of the matrix are $\frac{3}{2}$, $\frac{1}{2}$, 0, 0, 0, 0. This gives for W_N, the expected number of ways to place N oxygen atoms on a ring of N sites;

$$W_N=(\tfrac{3}{2})^N[1+(1/3^N)]. \tag{6}$$

Since the smallest closed figure in the ice lattice is a hexagon we have for the entropy correction $\Delta S_1/k$ $[S_1=k\ln W_N/N$ and $\Delta S_1=S_1-k\ln(\frac{3}{2})]$ a value $0.000228\cdots$ which is to be added to $\ln\frac{3}{2}=0.40547$.

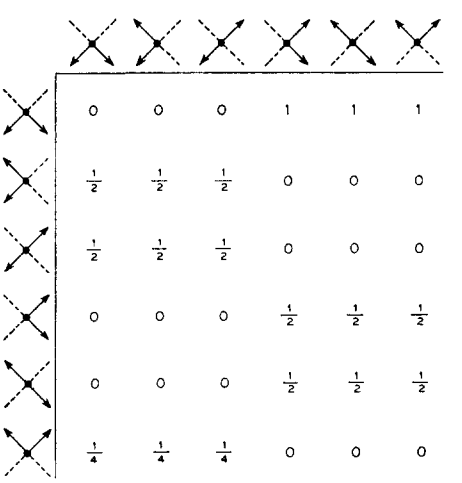


FIG. 2. Six-by-six matrix used in evaluating the expected number of configurations for a closed polygon of sites, within the context of the mean field theory.

[6] The total number of bonds which have at least one end connected to one of the M molecules is $4M-(2M-K)=2M+K$, where $(2M-K)$ is by definition the number of bonds which have both ends connected to the chosen molecules (the number of internal arrows equals the number of internal bonds). We therefore have $(2M+K)-(2M-K)=2K$ bonds connecting the M molecules with the rest of the crystal.

[7] E. A. Guggenheim, *Mixtures* (Oxford University Press, London, 1952), Sec. 4.17.

[8] G. E. Uhlenbeck and G. W. Ford, *Studies in Statistical Mechanics*, edited by J. deBoer and G. E. Uhlenbeck (Interscience Publishers, Inc., New York, 1962), Vol. 1, Part B.

[9] M. Kurata, R. Kikuchi, and T. Watari, J. Chem. Phys. **21**, 434 (1953).

[10] H. A. Kramers and G. H. Wannier, Phys. Rev. **60**, 252, 263 (1941).

III. KIKUCHI METHOD

The Kikuchi method[2] is easy to apply to the square lattice of Fig. 1 because there are no energy differences involved. As a consequence each possible figure has equal probability of occurring. Thus x_i which is defined as the fraction of sites with state i is $\frac{1}{6}$ since there are six possible, y_i which is defined as the fraction of a particular kind of bond is $\frac{1}{18}$ since 18 different kinds of bonds (plus end points) are possible. Likewise, there are 82 different possible states of a square of sites and the probability, z_i, of the occurrence of one such square is $\frac{1}{82}$. One can immediately use Eq. (C1.6) of Kikuchi's paper[2] to get

$$S_1 = S_N/kN = 2\sum y_i \ln y_i - \sum x_i \ln x_i - \sum z_i \ln z_i$$
$$= \log[\tfrac{3}{2}(1+\tfrac{1}{81})] = 0.41774 \qquad (7)$$

which is less than 3% larger than the Pauling estimate.

IV. EXPANSION METHOD

All expansion methods, though formally exact, can as a practical measure be used only to obtain a finite sequence of correction terms. We find that the leading term of the expansion method developed here gives the Pauling result for all lattices with coordination number four. This leading term contains the contributions from all those diagrams (which are associated with terms in the following systematic expansion) which contain at least one bond not in a closed ring. The first correction term comes from the smallest closed figure that can exist on the lattice in question. For our planar lattice of Fig. 1 this is a square, and for the ice lattice it is a hexagon. When the first two terms are evaluated for the square lattice we obtain the same result as the Kikuchi method.

For simplicity we formulate the method in the context of the two-dimensional problem (Fig. 1); the generalization to three-dimensional structures can be accomplished in principle, but involves additional labor by virtue of the larger numbers of equivalent bonds and sites. Let $\xi_{x,y}$ be a state variable for the site at (x, y). The numbers of configurations W may be counted by (see Fig. 3)

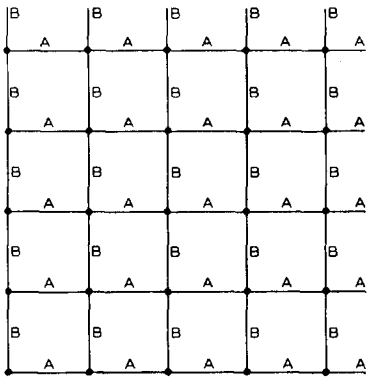
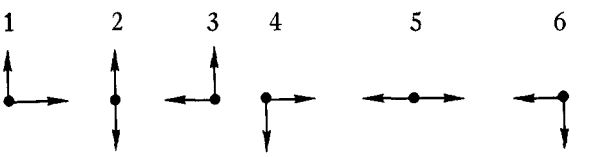


FIG. 3. Matrix assignment pattern for the exact two-dimensional configuration counting expression, Eq. (8). If the site configuration parameters for a pair of neighboring sites imply either zero or two protons along the connecting bond, the corresponding matrix element of A or B vanishes; otherwise the matrix element is unity.

$$W_N = \sum_{\{\xi\}} \prod_{(x,y)} A(\xi_{x,y}; \xi_{x+1,y}) B(\xi_{x,y}; \xi_{x,y+1}). \qquad (8)$$

The matrix elements of A and B are 0 or 1 according to whether the pair of sites involved violate or satisfy the original conditions. Assume for concreteness that the values of $\xi_{x,y}$ correspond to the following:

$\xi_{x,y}=$



One has:

$$1/N \log W = 1/N \log\{\sum_{\{\xi\}} \prod_{(x,y)} A[\xi(x, y), \xi(x+1, y)] B[\xi(x, y), \xi(x, y+1)]\}$$
$$= 1/N \log\{\sum_{\{\xi\}} \prod_{(x,y)} [C + A(\xi(x, y), \xi(x+1, y)) - C][C + B(\xi(x, y), \xi(x, y+1)) - C]\}$$
$$= \log 6C^2 + 1/N \log\{\sum_{\{\xi\}} \prod_{(x,y)} \tfrac{1}{6}[1 + a(\xi(x, y), \xi(x+1, y))] \times [1 + b(\xi(x, y), \xi(x+1, y))]\}; \qquad (9)$$

$$a(\xi_1, \xi_2) = (1/C)[A(\xi_1, \xi_2) - C] \qquad b(\xi_1, \xi_2) = (1/C)[B(\xi_1, \xi_2) - C]. \qquad (10)$$

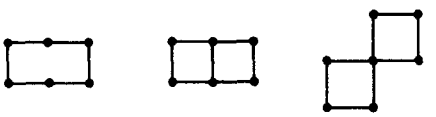
Now we can make an expansion of the product in (9). Every resulting product of a's and b's may be assigned a graph as usual. If either $A(\xi_1, \xi_2)$ or $B(\xi_1, \xi_2)$ is summed over either variable, the result is always 3. Therefore, if we choose $C = \frac{1}{2}$, the contribution from any graph that has free ends vanishes. In particular, Eq. (9) becomes

$$(1/N) \log W_N = \log(\tfrac{3}{2})$$
$$+ (1/N) \log\{6^{-N} \sum_{\{\xi\}} \prod_{(x,y)} [1 + a(\xi_{x,y}; \xi_{x+1,y})]$$
$$\times [1 + b(\xi_{x,y}; \xi_{x,y+1})]\} \qquad (11)$$

and the elements 0, 1 of A and B are -1, $+1$ in a and b. Since no closed-loop graph can occur on infinite Cayley trees, the leading term in (11), the Pauling estimate, is exact for them. The simplest nonvanishing type of term in the two-dimensional lattice remainder is

$$6^{-4}\,\mathrm{Tr}(\mathbf{aba}^{\dagger}\mathbf{b}^{\dagger}), \tag{12}$$

corresponding to the smallest square circuit on the lattice. All graphs which are simple closed polygons may be evaluated as traces. If we order the graphs according to the number of squares they enclose, the next order has as connected graphs:



(plus the rotated figures), as well as the disconnected pair of squares. After taking logarithms, only connected graphs need to be considered, giving in (11) a result independent of N (disregarding graphs which "loop the torus," etc.). But one additionally generates thereby "excluded volume" graphs, also connected. The matrices **a** and **b** are

a

	1	2	3	4	5	6
1	1	1	−1	1	−1	−1
2	−1	−1	1	−1	1	1
3	−1	−1	1	−1	1	1
4	1	1	−1	1	−1	−1
5	1	1	−1	1	−1	−1
6	−1	−1	1	−1	1	1

b

	1	2	3	4	5	6
1	1	−1	1	−1	1	−1
2	1	−1	1	−1	1	−1
3	1	−1	1	−1	1	−1
4	−1	1	−1	1	−1	1
5	−1	1	−1	1	−1	1
6	−1	1	−1	1	−1	1

One easily computes that contribution (12) is

$$6^{-4}\times 16=\frac{1}{81}=0.0123456\cdots.$$

which is to be added to

$$\log(\tfrac{3}{2})=0.40547\cdots.$$

We have the identities

$$(\mathbf{a})^n=2^n\mathbf{a}, \qquad (\mathbf{a}^{\dagger})^n=2^n\mathbf{a}^{\dagger}, \tag{13}$$

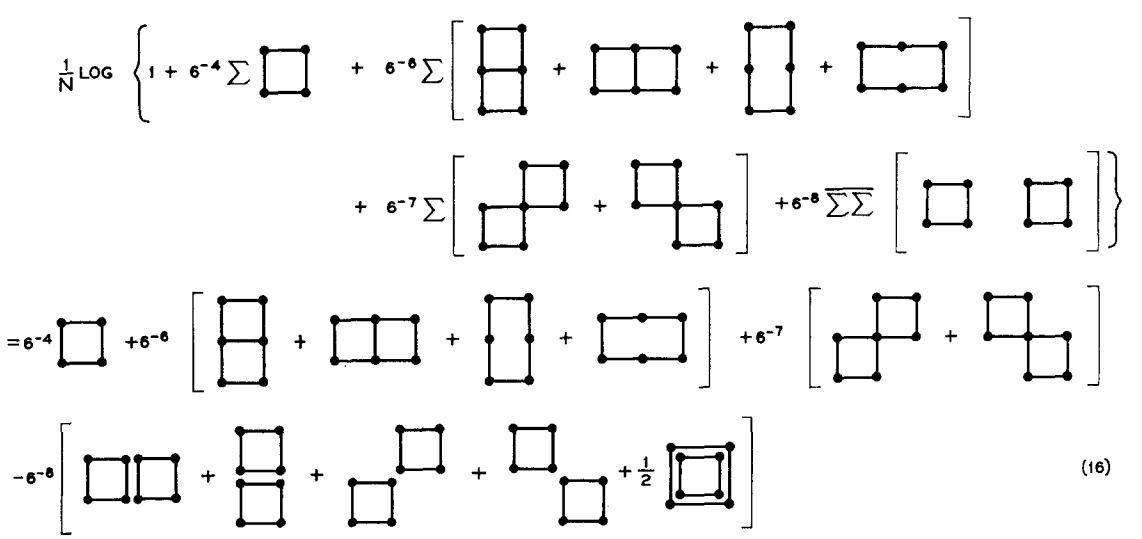
$$(\mathbf{b})^n=2^n\mathbf{b}, \qquad (\mathbf{b}^{\dagger})^n=2^n\mathbf{b}^{\dagger}. \tag{14}$$

In general

$$\mathbf{c}\cdots\mathbf{d}=2^n\mathbf{cd}, \tag{15}$$

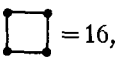
where **c** (and **d**) is either **a** or **b** or $\mathbf{a}^{\dagger}$ or $\mathbf{b}^{\dagger}$ and the dots represent any arbitrary combination of n matrices chosen from these four kinds.

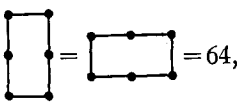
We next carry the calculation to the following order. The second term on the right-hand side of Eq. (11) may be symbolically written (including no more than just graphs encircling a maximum of eight vertices):

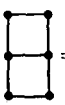


(16)

In this last equation, $\sum\sum$ denotes summation over all ways of placing a pair of nonoverlapping squares on the lattice. The last bracketted terms are the excluded volume terms generated by this nonoverlap restriction; they are to be understood as having the closely drawn vertices in the different squares as actually overlapping on the lattice. We find


$=16,$


$=64,$


$=\sum_{\xi_0,\xi_1} b(\xi_0,\xi_1)(\mathbf{aba}^\dagger)_{\xi_0,\xi_1}(\mathbf{a}^\dagger\mathbf{ba})_{\xi_0,\xi_1}=0, \quad (17)$

and each excluded volume graph is $[\mathrm{Tr}(\mathbf{aba}^\dagger\mathbf{b}^\dagger)]^2$. The same vanishing result as the third of (17) must be obtained from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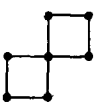
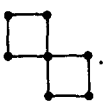

$=\sum_{\xi}(\mathbf{aba}^\dagger\mathbf{b})_{\xi,\xi}(\mathbf{a}^\dagger\mathbf{b}^\dagger\mathbf{ab})_{\xi,\xi}=384$


$. \quad (18)$

Adding these new terms yields a "third-order" entropy:

$$\log(\tfrac{3}{2})+\frac{1}{81}+\frac{7}{1458}=0.42258\cdots. \quad (19)$$

The ratio of the last two terms is $\frac{7}{18}=0.388888\cdots$, indicating only a modest rate of convergence.

Because of the simple nature of the matrices involved one can begin to apply the expansion method to the real three-dimensional ice lattice. The leading term is again $\ln(\frac{3}{2})$ and the first correction term for hexagons has the form

$$2\times 6^{-6}\,\mathrm{Tr}(\mathbf{abcdef}).$$

The factor 2 appears because the lattice has twice as many hexagons as sites. There are four nonequivalent sites on the ice lattice to which we must assign states ξ. However, this can be done so that there are only three basically different kinds of matrices. The trace is easily evaluated and is 2^6 for each hexagon. This gives for the correction term $\Delta S_1/k=0.00274\cdots$, which adds less than 1% to the Pauling estimate.

V. CONCLUSIONS

Whenever approximate methods are necessitated, by virtue of the fact that the exact result is unknown, one relinquishes all hope of knowing for certain how much of an improvement has been made. Nevertheless the fact that the first correction terms in our systematic expansion method gives results equivalent to the Kikuchi method is encouraging. Whenever the exact result is known (for Ising model transition temperatures, say), it is found that the difference between the results of the Bethe and the Kikuchi methods is larger in magnitude than the difference between the result of the Kikuchi method[11] and the exact result.[12] Thus we can expect that the exact residual ice entropy is about 1% larger than the Pauling estimate in three-dimensional, real ice.

ACKNOWLEDGMENT

The authors are indebted to Professor F. P. Buff for the suggestion that the Pauling entropy estimate for a given lattice might represent the leading term in a systematic expansion.

[11] Since the Kramers–Wannier variational method[10] and the Kikuchi method[2] give identical results our estimate is also a lower bound.

[12] C. Domb, Advan. Phys. **9**, 149 (1960).