Residual Entropy of Square Ice

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At low temperatures, ice has a residual entropy, presumably caused by an indeterminacy in the positions of the hydrogen atoms. While the oxygen atoms are in a regular lattice, each O–H–O bond permits two possible positions for the hydrogen atom, subject to certain constraints called the "ice condition." The statement of the problem in two dimensions is to find the number of ways of drawing arrows on the bonds of a square planar net so that precisely two arrows point into each vertex. If N is the number of molecules and (for large N) W^N is the number of arrangements, then $S=Nk\ln W$. Our exact result is $W=(\frac{4}{3})^{3/2}$.

I. INTRODUCTION

MANY simple substances are observed to have a *residual entropy*, which is to say that at temperatures well below the freezing point there is a *constant* entropy much larger than that caused by any conceivable lattice vibrations. "For example, the observed entropy of crystalline hydrogen shows that even at very low temperature the molecules of orthohydrogen in the crystal are rotating about as freely as in the gas."[1] Most substances with this property are, like water, hydrogen-bonded, although there are notable exceptions such as carbon monoxide and nitrous oxide.

Thirty-four years ago, it was realized that ice also falls in this category when Giauque and Ashley[2] calculated the entropy of gaseous water from its band spectrum and compared the result with $\int C_p d\ln T$ from previous specific-heat data. Three years later, Giauque and Stout[3] accurately remeasured the specific heat of water from 15 to 273°K, being very careful to cool the water slowly to ensure thermal equilibrium. They obtained an entropy of 44.28±0.05 cal/deg mole for gaseous water at 1 atm and 298.1°K, which was less than the spectroscopic value by 0.82±0.05 cal/deg mole. (In arriving at this result, the specific heat between 10 and 15°K was extrapolated from their data and agreed closely with previous measurements of Simon[3] between 9 and 13°K; the entropy at 10°K was calculated from a Debye model and amounted to only 0.022 cal/deg mole, which is a small fraction of the total discrepancy.) They also mention that "MacDougall and Giauque[4] investigated ice from 0.2 to 4°K and found no appreciable heat capacity in this range."

The structure of ice, as determined from x-ray data, is one in which the oxygen atoms are regularly arranged in a crystal lattice. Technically, it is a hexagonal wurtzite structure,[5] but it is simpler to think of it as a distorted tetrahedral diamond structure—for the important point is that each oxygen atom has four nearest neighbors. The hydrogen atoms, however, do not appear to have any regular arrangement discernible by x-rays.

Amplifying earlier ideas of Bernal and Fowler,[6] Pauling[1] made the following hypotheses:

(a) Ice is hydrogen-bonded with one hydrogen atom between every pair of nearest-neighbor oxygen atoms. Since the observed O-O distance is 2.76 Å and since the O-H bond is well known to be only 0.95 Å in the gas, there are two possible positions for each hydrogen atom, these being approximately 0.95 Å from each end of the O-O line. These states are energetically equivalent except for

(b) *The ice condition:* "The concentration of $(OH)^-$ and $(H_3O)^+$ ions in water is very small and we expect the situation to be essentially unchanged in ice."[1] Consequently, each oxygen atom must be surrounded by two hydrogen atoms near to it (0.95 Å) and two on the far side (1.81 Å).

This ice condition can be pictured geometrically by constructing a lattice of coordination number four and by drawing arrows on and parallel to each bond in such a manner that there are precisely two arrows pointing into each vertex. The entropy is then

$$S=Nk\ln W, \tag{1.1}$$

where N is the number of oxygens (vertices), k is Boltzmann's constant, and $Z\equiv W^N$ and is equal to the number of ways of arranging the arrows (for N large). If we ignore the ice condition, then $Z\equiv W^N=2^{2N}$ (because there are $2N$ bonds) and $W=4$. This leads to an entropy that is much too large.

Pauling[1] made a rough estimate of W in the following way: Suppose that the bonds and the vertex configurations are independent (they are not). Then

$$Z\cong 2^{2N}(6/16)^N \quad \text{or} \quad W\cong 1.5, \tag{1.2}$$

where the factor 6/16 comes from the fact that we permit only six out of a total of 16 *a priori* vertex

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[1] L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1935); L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed.; L. K. Runnels, Sci. Am. **215**, 118 (1966).
[2] W. F. Giauque and M. F. Ashley, Phys. Rev. **43**, 81 (1933).
[3] W. F. Giauque and E. L. Stout, J. Am. Chem. Soc. **58**, 1144 (1936).
[4] E. L. MacDougall and W. F. Giauque, J. Am. Chem. Soc. **58**, 1032 (1936).
[5] J. F. Nagle, J. Math. Phys. **7**, 1484 (1966).
[6] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).

configurations. This estimate leads to an entropy of 0.805 cal/deg mole, which is in excellent agreement with the observed value and which must be counted as one of the most successful applications of elementary statistical mechanics to real substances.

Plainly, it is important to improve the calculation of W because W is a sensitive indicator of the soundness of the hypothesized structure of ice. The best numerical estimate of W is due to Nagle,[5,7] who found

$$W_{\text{real ice}}=1.50685\pm0.00015\,, \tag{1.3}$$

or $S=0.8145\pm0.0002$ cal/deg mole. It is truly remarkable that the accurate value (1.3) is so close to the crude estimate (1.2).

It is also possible to consider "square ice," which is the subject matter of this paper. Square ice is the two-dimensional version of real ice and is defined by the same ice condition applied to a square planar lattice (as in the usual Ising model). Nagle gives

$$W_{\text{square ice}}=1.540\pm0.001\,. \tag{1.4}$$

It seemed worthwhile to try to find the value of $W_{\text{square ice}}$ exactly for the following reasons: (a) It will serve as a check on the accuracy of Nagle's calculations. (b) It is an interesting graph theoretic problem. (c) It is the first step toward the solution of much more interesting models having phase transitions—the Rys antiferromagnetic F model and the Slater KDP model of a ferroelectric.[8] (It is believed that hydrogen-bonded ferro and antiferroelectrics have the same "rules" as ice except that the six vertex configurations have different energies according to the total polarization at each vertex. See the Appendix.)

Here we calculate $W_{\text{square ice}}$ exactly by the method of the transfer matrix and our result[9] is

$$W_{\text{sq. ice}}=(\tfrac{4}{3})^{3/2}=1.5396007\cdots. \tag{1.5}$$

II. THE TRANSFER MATRIX

Let the square lattice consist of NM vertices (N horizontally and M vertically). The number of bonds is thus $2NM$, half of which are vertical and half horizontal; these bonds will be called V bonds and H bonds, respectively. Beginning at the bottom, we have a row of NV bonds followed by a row of H bonds and so on alternately. There are M bond rows of each type.

Let φ denote a possible configuration of a row of V bonds, i.e., a definite assignment of up or down arrows on each of the NV bonds. There are obviously 2^N choices for φ. Alternatively, φ may be thought of as a state of a linear chain of N spin-$\frac{1}{2}$ particles (in the S^z representation). If φ and φ' are the configurations of two successive rows of V bonds, let $A(\varphi,\varphi')$ be the number of ways of assigning arrows on the intervening row of H bonds so that the ice condition is satisfied at each of the N vertices lying on the intervening row. Thus $A(\varphi,\varphi')$ is a non-negative integer. If Z is the total number of ways of correctly placing arrows on the lattice, we have

$$Z=\sum_{\varphi_1}\cdots\sum_{\varphi_M}A(\varphi_1,\varphi_2)A(\varphi_2,\varphi_3)\cdots A(\varphi_{M-1},\varphi_M)A(\varphi_M,\varphi_1)$$
$$=[\mathrm{Tr}A]^M. \tag{2.1}$$

In (2.1), $\sum_{\varphi_j}$ means a sum on the 2^N states of the jth row of V bonds. Implicit in (2.1) is the fact that the Mth row is connected by V bonds to the first row. As usual (for large M),

$$Z=\Lambda^M\,, \tag{2.2}$$

where Λ is the largest eigenvalue of the 2^N-square matrix A. The quantity W is thus given by

$$\ln W=\lim_{N\to\infty}N^{-1}\ln\Lambda\,. \tag{2.3}$$

Next, we must elucidate the elements of A. If $\varphi=\varphi'$, there are two possible assignments of horizontal arrows, all running to the left or all running to the right. Thus,

$$A(\varphi,\varphi)=2. \tag{2.4}$$

To simplify the subsequent discussion let us also assume that the lattice is wrapped on a torus instead of merely on a cylinder, i.e., that the Nth column is connected by H bonds to the first column. If $\varphi\neq\varphi'$, then certain up arrows in φ are replaced by down arrows in φ' (a $+-$ exchange) and vice versa (a $-+$ exchange). In order to satisfy the ice condition, the intervening horizontal arrows must point outwards on both sides of a $+-$ vertex and inwards at a $-+$ vertex. If there is no change at a vertex, the two horizontal arrows can be either both to the right or both to the left. Thus,

$$A(\varphi,\varphi')=1 \tag{2.5}$$

if and only if there is a $-+$ exchange between every pair of $+-$ exchanges and vice versa, and if there is an equal number of both kinds of exchange. Otherwise

$$A(\varphi,\varphi')=0. \tag{2.6}$$

To interpret the above rule in spin language, A is

[7] Earlier estimates were made by E. A. DiMarzio and F. H. Stillinger, J. Chem. Phys. **40**, 1577 (1964); H. Takahasi, Proc. Phys. Math. Soc. (Japan) **23**, 1069 (1941).

[8] F. Rys, Helv. Phys. Acta **36**, 537 (1963); J. C. Slater, J. Chem. Phys. **9**, 16 (1941); see also J. F. Nagle [J. Math. Phys. **7**, 1492 (1966)] for useful pictures and a bibliography of earlier work. The solution to the F model is reported in E. H. Lieb, Phys. Rev. Letters **18**, 1046 (1967) and the KDP model **19**, 108 (1967).

[9] A summary of this work was given in E. H. Lieb, Phys. Rev. Letters **18**, 692 (1967).

obviously the same as

$$\mathfrak{A}=2+\sum_{i<j}S_i^-S_j^+ + \sum_{i<j<k<l} S_i^-S_j^+S_k^-S_l^+ + \cdots + (S_1^-S_2^+\cdots S_N^+) + \sum_{i<j}S_i^+S_j^- + \sum_{i<j<k<l} S_i^+S_j^-S_k^+S_l^- + \cdots + (S_1^+S_2^-\cdots S_N^-), \quad (2.7)$$

where we have assumed that N is even in the last term.

From (2.7) we see that $S^z=\sum_1^N S_i^z$ is a constant of the motion, i.e., if n is the number of down arrows in a state φ, then $A(\varphi,\varphi')=0$ unless $n=n'$. $S^z=\frac{1}{2}N-n$. Since A is thus a diagonal block matrix we must decide in which n subspace the maximum eigenvalue lies. Intuition dictates that it is the subspace $n=\frac{1}{2}N$ or $\frac{1}{2}(N-1)$ (i.e., $S^z=0$ or $\frac{1}{2}$) if N is even or odd, respectively. While we can not prove this statement for finite N, we can prove a statement that is sufficient for our purposes, namely, that as $N\to\infty$,

$$N^{-1}\ln\Lambda_{\max}(\text{all } n)=N^{-1}\ln\Lambda_{\max}(n=\tfrac{1}{2}N).$$

This weaker assertion is proved in a general way in the Appendix. It will also be proved in a specific way in Sec. IV when we actually display the largest eigenvalue as a function of n/N in the limit $N\to\infty$.

Since A is non-negative, and since any φ can be connected to every other φ' in the same n subspace by applying A a sufficient number of times, it follows, by the Perron-Fröbenius theorem, that the largest eigenvector in each subspace is nondegenerate and has strictly positive components. This observation will prove to be extremely useful because it will enable us to identify the largest eigenvectors.

It is very fortunate that the largest eigenvalue can be sought in the $n=\frac{1}{2}N$ subspace, for only in this subspace can the calculation be carried to completion. In all other subspaces, the largest eigenvalue must be left as the solution to a linear, but unsolvable, integral equation [cf. (4.8′)].

To proceed, we must find a more tractable form for A than (2.7). Denote by $\varphi(x_1,\ldots,x_n)$ the state (in a given n space) with down arrows (spins) at the sites $1\le x_1<x_2<\cdots<x_n\le N$. Any eigenvector Ψ, of A, may be written as

$$\Psi=\sum_{x_1,\cdots,x_n} f(x_1,\ldots,x_n)\,\varphi(x_1,\ldots,x_n) \quad (2.8)$$

and the equation $A\Psi=\Lambda\Psi$ implies some corresponding equation for the set of $\binom{N}{n}$ coefficients f. We shall write it down and justify it afterwards:

$$\Lambda f(x_1,\ldots x_n)=\sum_{y_1=1}^{x_1}\sum_{y_2=x_1}^{x_2}\cdots\sum_{y_n=x_{n-1}}^{x_n} f(y_1,\ldots,y_n) + \sum_{y_1=x_1}^{x_2}\sum_{y_2=x_2}^{x_3}\cdots\sum_{y_n=x_n}^{N} f(y_1,\ldots,y_n). \quad (2.9)$$

Equation (2.9) is true only in the region R,

$$R:\ 1\le x_1<x_2<\cdots<x_n\le N, \quad (2.10)$$

which is the region in which f is defined. On the right side of (2.9), therefore, f must be taken to be zero if any $y_j=y_{j+1}$ (e.g., $y_1=y_2=x_1$).

To verify (2.9) we ask what states $\varphi(x_1,\ldots,x_n)$ are generated when A acts on a state $\varphi(y_1,\ldots,y_n)$ according to the rules stated above. If $y_j=x_j$ (all j) then $A=2$, and this is in accord with (2.9). [We get one from the upper limits of the first sum and one from the lower limits of the second sum in (2.9).] If $\mathbf{Y}\neq\mathbf{X}$ there are two possibilities: (a) the first exchange reading from the left to the right (i.e., from 1 to N) is a $-+$ exchange, the second is a $+-$ exchange, and so on; (b) the reverse of (a). In order to produce a given state $\varphi(x_1,\ldots,x_n)$ by possibility (a), it is clearly necessary and sufficient that the y_i satisfy

$$x_1\le y_1\le x_2,\ x_2\le y_2\le x_3,\ldots,\ x_n\le y_n\le N, \quad (2.11)$$

but not $y_i=x_i$ (*all* i). If (2.11) is satisfied, then application of A to $\varphi(\mathbf{Y})$ produces $\varphi(\mathbf{X})$ with coefficient unity, (2.5). All these matrix elements are contained the correct number of times in the second sum of (2.9). *Mutatis mutandis*, possibility (b) is contained in the first sum of (2.9).

III. DIAGONALIZATION OF THE TRANSFER MATRIX

We now make an ansatz for f and will verify that it leads to the maximum eigenvalue. Let

$$f(y_1,\ldots,y_n)=\sum_P !\,a(P)\exp\Big[i\sum_{j=1}^n k_{P(j)}y_j\Big]. \quad (3.1)$$

In (3.1) $\{k\}=k_1,k_2,\ldots,k_n$ is a set of N wave numbers and the sum is on $n!$ permutations with certain coefficients $a(P)$. The goal is to choose $a(P)$ and $\{k\}$ so that (2.9) is satisfied. We will also assume that $k_i\neq 0$ (all i) and it will turn out that this assumption is justified if n is even. [We shall not consider the case of n odd. For that case the assumption (3.1) is probably also correct (we have verified it for $n=3$) but the subsequent analysis has to be somewhat modified.]

When (3.1) is inserted into the right side of (2.9) we must remember to sum only over configurations $\mathbf{Y}=(y_1,\ldots,y_n)$ that are in R, (2.10). To do this we will sum (3.1) over all $\mathbf{Y}$ and then explicitly subtract those terms in (2.9) for which one or more $y_i=y_{i+1}$. We shall call these subtracted terms diagonal terms. To clarify this point, suppose $n=2$ and suppose, for simplicity, that $f(y_1,y_2)=\exp(iky_1+iqy_2)$, i.e., a single plane wave. Then, the first sum in (2.9) would give

$$\sum_{y_1=1}^{x_1}\sum_{y_2=x_1}^{x_2} f(y_1,y_2)-f(x_1,x_1) = \alpha(k)\alpha(q)\{e^{ik}-e^{ik(x_1+1)}\}\{e^{iqx_1}-e^{iq(x_2+1)}\}-e^{i(k+q)x_1},$$

where

$$\alpha(k)=[1-e^{ik}]^{-1}. \tag{3.2}$$

Likewise, the second sum in (2.9) would give

$$\alpha(k)\alpha(q)\{e^{ikx_1}-e^{ik(x_2+1)}\}\{e^{iqx_2}-e^{iq(N+1)}\}-e^{i(k+q)x_2}.$$

Thus, for general n (even), performing the first sum or some single plane wave, $\exp i(k_1y_1+\cdots+k_ny_n)$, gives

$$\prod_{j=1}^{n}\alpha(k_j)\{e^{ik_1}-e^{ik_1(x_1+1)}\}\{e^{ik_2x_1}-e^{ik_2(x_2+1)}\}\cdots$$

$$\{e^{ik_nx_{n-1}}-e^{ik_n(x_n+1)}\}-(\text{diagonal terms}), \tag{3.3}$$

while the second sum gives

$$\prod_{j=1}^{n}\alpha(k_j)\{e^{ik_1x_1}-e^{ik_1(x_2+1)}\}\{e^{ik_2x_2}-e^{ik_2(x_3+1)}\}\cdots$$

$$\{e^{ik_nx_n}-e^{ik_n(N+1)}\}-(\text{diagonal terms}). \tag{3.4}$$

If we study (3.3) we see that it contains precisely one term that is proportional to one of the plane waves in (3.1) and that plane wave is, in fact, the very one we started with, namely, the term

$$\left\{\prod_{j=1}^{n}\alpha(k_j)\right\}\exp\left[i\sum_{1}^{n}k_j\right]\exp\left[i\sum_{1}^{n}k_jx_j\right]. \tag{3.5}$$

(Remember that n is even so that there are an even number of minus signs.) All the other terms—the diagonal terms as well as those coming from the curly brackets—have the property that one or more of the x_i's fail to appear. These other terms are unwanted and must be made to cancel.

Likewise, the second sum, (3.4), gives a single wanted term

$$\left\{\prod_{j=1}^{n}\alpha(k_j)\right\}\exp\left[i\sum_{1}^{n}k_jx_j\right], \tag{3.6}$$

the remaining terms being unwanted.

In both (3.5) and (3.6) the coefficient of the wanted term is invariant with respect to any permutation of the set $\{k\}$. Therefore, assuming that we can choose the coefficients $a(P)$ and the set $\{k\}$ so as to eliminate the unwanted terms, (2.9) will be satisfied with an eigenvalue

$$\Lambda=\left\{\prod_{j=1}^{n}\alpha(k_j)\right\}\left\{1+\exp\left[i\sum_{1}^{n}k_j\right]\right\}. \tag{3.7}$$

It is indeed possible to eliminate the unwanted terms. We shall state the requirements and then verify by induction that they suffice:

(1) Condition on $a(P)$: Let P and Q be two permutations of $\{k\}$ that are identical except for the jth and $(j+1)$th position, i.e., $P\{k\}=(\cdots p,q\cdots)$ and $Q\{k\}=(\cdots q,p\cdots)$. Then,

$$a(P)=a(Q)B(p,q), \tag{3.8}$$

with

$$B(p,q)=-\frac{1+e^{i(p+q)}-e^{ip}}{1+e^{i(p+q)}-e^{iq}},$$

$$=-\exp[-i\Theta(p,q)], \tag{3.9}$$

where

$$\tan\tfrac{1}{2}\Theta(p,q)=\frac{\sin\tfrac{1}{2}(p-q)}{2\cos\tfrac{1}{2}(p+q)-\cos\tfrac{1}{2}(p-q)}. \tag{3.10}$$

We assume p and q are real and Θ is continuous with $\Theta(0,0)=0$. The solution to (3.8) is unique, except for a normalization constant, and is

$$a(P)=(-)^P\exp\left[-\frac{i}{2}\sum_{i<j}\Theta(k_{P(i)}\,k_{P(j)})\right]. \tag{3.11}$$

(2) Condition on $\{k\}$: For each $j=1,\cdots,n$

$$\exp(ik_j\cdot N)=-\prod_{i\neq j}B(k_j,k_i). \tag{3.12}$$

An alternative, equivalent statement of (3.12), using (3.8), is this: For every pair of cyclically related permutations,

$$P=[P(1),P(2),\cdots,P(n)]$$

and

$$Q=[P(2),P(3),\cdots,P(n),P(1)],$$

we have

$$a(P)=[\exp ik_{P(1)}N]a(Q). \tag{3.13}$$

We now give an inductive proof that (3.8) and (3.13) guarantee that the ansatz (3.1) satisfies (2.9) with eigenvalue (3.7). A simple artifice to insure that we sum only over R is to introduce the factor

$$w^n(y_1,\ldots,y_n)=\prod_{j=1}^{n-1}[1-\delta(y_{j+1}-y_j)] \tag{3.14}$$

into the sums in (2.9). Here, δ is the Kroenecker delta [$\delta(x)=1$ if $x=0$; $\delta(x)=0$, otherwise]. However, since $x_{j+1}>x_j$ (all j), we can make the following replacement in the first sum, S_1:

$$S_1\colon\ \delta(y_{j+1}-y_j)=\delta(y_{j+1}-x_j)\delta(y_j-x_j). \tag{3.15a}$$

Likewise, in the second sum, S_2:

$$S_2\colon\ \delta(y_{j+1}-y_j)=\delta(y_{j+1}-x_{j+1})\delta(y_j-x_{j+1}). \tag{3.15b}$$

Now, multiply (3.1) by $w^n(y_1,\ldots,y_n)$, insert the product into the first sum in (2.9), and perform the

indicated sums on $y_n, y_{n-1}, \cdots, y_{n-t+1}$ *only*. The partial sum thus obtained is clearly of the form

$$S_1{}^t = w^{n-t}(y_1,\cdots,y_{n-t}) \sum_P{}' \left\{ a(P) \exp\left[i \sum_{j=1}^{n-t} k_{P(j)} y_j \right] \times G_P{}^t(x_{n-t}, x_{n-t+1}, \cdots, x_n;\, y_{n-t}) \right\} . \quad (3.16)$$

Our inductive premise for $G_P{}^t$ is the following (for $1 \le t \le n-1$):

$$G_P{}^t(x_{n-t},\cdots,x_n;\, y_{n-t}) = \prod_{j=n-t+1}^{n} \{-\alpha(k_{P(j)}) \exp[ik_{P(j)}(x_j+1)]\} + [\exp(ik_{P(n-t+1)}x_{n-t})\{\alpha(k_{P(n-t+1)}) - \delta(y_{n-t}-x_{n-t})\} \times g_P{}^t(x_{n-t+1},\cdots,x_n)], \quad (3.17)$$

where $g_P{}^t$ *does not depend upon* $P(1)$, $P(2)$, $\cdots$, $P(n-t+1)$.

To prove (3.17) for $t=1$, we must do the sum on y_n. Suppressing irrelevant factors, this means that for each P we must do the sum

$$\sum_{y_n = x_{n-1}}^{x_n} [1-\delta(y_n - x_{n-1})\delta(y_{n-1}-x_{n-1})] \exp[ik_{P(n)}y_n] = \alpha(k_{P(n)})\{\exp[ik_{P(n)}x_{n-1}] - \exp[ik_{P(n)}(x_n+1)]\} - \delta(y_{n-1}-x_{n-1}) \exp[ik_{P(n)}x_{n-1}]. \quad (3.18)$$

Clearly, (3.18) is of the form (3.16) and (3.17), with

$$g_P{}^1(x_n) = 1. \quad (3.19)$$

To carry through the induction, we must sum (3.16) on y_{n-t}. Again, suppressing irrelevant factors, we must do the sum

$$\sum_{y_{n-t}=x_{n-t-1}}^{x_{n-t}} [1-\delta(y_{n-t}-x_{n-t-1})\delta(y_{n-t-1}-x_{n-t-1})] \times \exp[ik_{P(n-t)}y_{n-t}] G_P{}^t(x_{n-t},\cdots,x_n;\, y_{n-t}). \quad (3.20)$$

The first term on the right side of (3.17), when inserted into (3.20), gives

$$\prod_{j=n-t}^{n} \{-\alpha(k_{P(j)}) \exp[ik_{P(j)}(x_j+1)]\} + \left\{ \prod_{j=n-t+1}^{n} [-\alpha(k_{P(j)}) \exp[ik_{P(j)}(x_j+1)]] \right\} \times \exp[ik_{P(n-t)}x_{n-t-1}] \times \{\alpha(k_{P(n-t)}) - \delta(y_{n-t-1}-x_{n-t-1})\}. \quad (3.21)$$

The second term of (3.17) gives

$$g_P{}^t(x_{n-t+1},\cdots,x_n) \exp[ik_{P(n-t+1)}x_{n-t}] \times \{\alpha(k_{P(n-t+1)})[\alpha(k_{P(n-t)}) \times \{\exp[ik_{P(n-t)}x_{n-t-1}] - \exp[ik_{P(n-t)}(x_{n-t}+1)]\} - \delta(y_{n-t-1}-x_{n-t-1}) \exp[ik_{P(n-t)}x_{n-t-1}]] - \exp[ik_{P(n-t)}x_{n-t}]\}. \quad (3.22)$$

[It is important to recall that $\delta(y_{n-t}-x_{n-t}) \times \delta(y_{n-t}-x_{n-t-1}) = 0$.]

When we multiply out the exponential factors in (3.22) we observe that there are some terms in which x_{n-t} occurs twice, namely,

$$-\{\alpha(k_{P(n-t+1)})\alpha(k_{P(n-t)}) \times \exp[ik_{P(n-t)}] + 1\} g_P{}^t(x_{n-t+1},\cdots,x_n) \times \exp[i(k_{P(n-t)}+k_{P(n-t+1)})x_{n-t}]. \quad (3.23)$$

We would like to make (3.23) vanish. That it does so is a consequence of (3.8), for observe that (a) $g_P{}^t$ is independent of $P(n-t+1)$ and $P(n-t)$; (b) for each permutation $P = \cdots P(n-t), P(n-t+1), \cdots$ in (3.16) that gives rise to a term (3.23) there is a permutation $Q = \cdots P(n-t+1), P(n-t) \cdots$ that gives rise to a term with the same exponential dependence on x_{n-t}, but with a different coefficient. Each such pair of terms will vanish if

$$a(P)\{\alpha(k_{P(n-t+1)})\alpha(k_{P(n-t)}) \exp[ik_{P(n-t)}] + 1\} + a(Q)\{\alpha(k_{P(n-t)})\alpha(k_{P(n-t+1)}) \times \exp[ik_{P(n-t+1)}] + 1\} = 0. \quad (3.24)$$

Using (3.2), condition (3.24) is seen to be identical to (3.8). Consequently, (3.23) can be omitted from (3.22).

Combining the remainder of (3.22) with (3.21), we verify (3.17) for $t+1$ with

$$g_P{}^{t+1}(x_{n-t},\cdots,x_n) = \prod_{j=n-t+1}^{n} \{-\alpha(k_{P(j)}) \exp[ik_{P(j)}(x_j+1)]\} + g_P{}^t(x_{n-t+1},\cdots,x_n)\alpha(k_{P(n-t+1)}) \times \exp[ik_{P(n-t+1)}x_{n-t}]. \quad (3.25)$$

Equation (3.25) also verifies that $g_P{}^{t+1}$ is independent of $P(n-t)$.

The induction proceeds up to and including $t=n-1$. The final summation on y_1 is slightly different, because there is neither a y_0 nor an x_0, but the same reasoning as above gives

$$G_P{}^n(x_1,\cdots,x_n) = \prod_{j=1}^{n} \{-\alpha(k_{P(j)}) \exp[ik_{P(j)}(x_j+1)]\} + \exp[ik_{P(1)}]\alpha(k_{P(1)})g_P{}^n(x_1,\cdots,x_n), \quad (3.26)$$

with $g_P{}^n$ being given correctly by (3.25) with $t=n-1$.

The obvious significance of $G_P{}^n$ is that

$$S_1=\sum_P !\, a(P) G_P{}^n(x_1,\cdots,x_n). \tag{3.27}$$

We turn now to the second sum S_2, of (3.29). This we will do in reverse order, namely, $y_1,y_2,\cdots,y_t$. The partial sum will be denoted $S_2{}^t$. The procedure is exactly the same, *mutatis mutandis*, as for S_1, and it suffices merely to quote the final result, i.e., the analogs of (3.16), (3.17), (3.19), (3.25), (3.26), and (3.27). The analogs of G and g will be denoted by H and h, respectively.

$$S_2=w^{n-t}(y_{t+1},\cdots,y_n) \times\sum_P !\left\{a(P)\exp\left[i\sum_{j=t+1}^{n} k_{P(j)}y_j\right] \times H_P{}^t(x_1,\cdots,x_{t+1};\, y_{t+1})\right\}. \tag{3.28}$$

$$H_P{}^t(x_1,\cdots,x_{t+1};\, y_{t+1})=\prod_{j=1}^{t}\{\alpha(k_{P(j)})\exp[ik_{P(j)}x_j]\} +(-1)^t[\exp[ik_{P(t)}(x_{t+1})] \times\{\alpha(k_{P(t)})\exp[ik_{P(t)}] +\delta(y_{t+1}-x_{t+1})\} \times h_P{}^t(x_1,\cdots,x_t)]. \tag{3.29}$$

$$h_P{}^1(x_1)=1. \tag{3.30}$$

$$h_P{}^{t+1}(x_1,\cdots,x_{t+1})=\prod_{j=1}^{t}\{-\alpha(k_{P(j)})\exp[ik_{P(j)}x_j]\} +h_P{}^t(x_1,\cdots,x_t)\alpha(k_{P(t)}) \times\exp[ik_{P(t)}(x_{t+1}+1)]. \tag{3.31}$$

$$H_P{}^n(x_1,\cdots,x_n)=\prod_{j=1}^{n}\{\alpha(k_{P(j)})\exp[ik_{P(j)}x_j]\} +\exp[ik_{P(n)}(N+1)]\alpha(k_{P(n)}) \times h_P{}^n(x_1,\cdots,x_n), \tag{3.32}$$

with $h_P{}^n$ being given by (3.31) with $t=n-1$. Again,

$$S_2=\sum_P !\, a(P) H_P{}^n(x_1,\cdots,x_n). \tag{3.33}$$

When we compute S_1 and S_2 with (3.27) and (3.33) we note that the first terms in (3.26) and (3.32) give us exactly what we want, namely, $\Lambda f(x_1,\cdots,x_n)$. The second terms in (3.27) and (3.33) must be made to cancel, and to do this we must investigate $g_P{}^n$ and $h_P{}^n$ more closely.

From the initial statement (3.19) and the recursion relation (3.25), it is easy to deduce that $g_P{}^t$ consists of t terms which, for $t>1$, are given by

$$g_P{}^t(x_{n-t+1},\cdots,x_n)=\left\{\prod_{j=n-t+2}^{n}[\alpha(k_{P(j)})]\right\}\sum_{s=1}^{t}(-1)^{s+t} \times\exp\left[i\sum_{j=n-t+2}^{n}k_{P(j)}M_j{}^s\right], \tag{3.34}$$

where, for $1<s<t$,

$$\begin{aligned} M_j{}^s&=x_{j-1}, \quad \text{for} \quad n-t+2\le j\le n-t+s \\ &=x_j+1, \quad \text{for} \quad n-t+s+1\le j\le n, \end{aligned} \tag{3.35}$$

while for $s=1$,

$$M_j{}^1=x_j+1, \tag{3.36}$$

and for $s=t$,

$$M_j{}^t=x_{j-1}. \tag{3.37}$$

Conversely, using the recursion relation (3.31) and the initial relation (3.30) for $h_p{}^t$ we find, for $t>1$,

$$h_P{}^t(x_1,\cdots,x_t)=\left\{\prod_{j=1}^{t-1}[\alpha(k_{P(j)})]\right\}\sum_{s=1}^{t}(-1)^{s+t} \times\exp\left[i\sum_{j=1}^{t-1}k_{P(j)}N_j{}^s\right], \tag{3.38}$$

where, for $1<s<t$,

$$\begin{aligned} N_j{}^s&=x_j, \quad \text{for} \quad 1\le j\le t-s \\ &=x_{j+1}+1, \quad \text{for} \quad t-s+1\le j\le t-1, \end{aligned} \tag{3.39}$$

while for $s=1$,

$$N_j{}^1=x_j \tag{3.40}$$

and for $s=t$,

$$N_j{}^t=x_{j+1}+1. \tag{3.41}$$

When $t=n$, comparison of (3.38) and (3.34) shows that $g_P{}^n$ and $h_P{}^n$ are very similar. The relationship is simply this: Let P and Q be two cyclically related permutations, i.e., $P=[P(1), P(2), \cdots, P(n)]$ and $Q=[P(2), P(3), \cdots, P(n), P(1)]$. Then

$$-h_Q{}^n(x_1,\cdots,x_n)=g_P{}^n(x_1,\cdots,x_n). \tag{3.42}$$

Consider now the unwanted terms in S_1+S_2, i.e., the second terms on the right-hand sides of (3.32) and (3.26). These are

$$\sum_P !\, a(P)\{\exp[ik_{P(n)}(N+1)]\alpha(k_{P(n)})h_P{}^n(x_1,\cdots,x_n) +\exp[ik_{P(1)}]\alpha(k_{P(1)})g_P{}^n(x_1,\cdots,x_n)\}. \tag{3.43}$$

Since the sum in (3.43) is over all permutations we see, using (3.42), that (3.43) vanishes identically if

$$a(P)=a(Q)\exp[ik_{P(1)}N] \tag{3.44}$$

for every pair of cyclically related permutations as above. But (3.44) is the same as our second condition, (3.13).

To summarize the results of this section, for every set of numbers $\{k\}$ satisfying (3.13) and such that no $k_j=0$, we have a solution to the eigenvalue problem with an eigenvalue given by (3.7). The existence and determination of such a solution and the proof that it is, in fact, the largest eigenvalue is the subject of Sec. IV.

IV. DETERMINATION OF THE LARGEST EIGENVALUE

We are indeed very fortunate that Eqs. (3.13) and (3.8) have appeared previously in the literature in another context and have been discussed extensively. Consider the linear chain anisotropic Heisenberg ferromagnet with the Hamiltonian

$$H'=-2\sum_{j=1}^{N} S_j^x S_{j+1}^x+S_j^y S_{j+1}^y+\Delta S_j^z S_{j+1}^z, \quad (4.1)$$

with $S_{N+1}=S_1$. To find the eigenvectors of (4.1), in a given S^z (or n) subspace one makes exactly the same ansatz (3.1) as we have done (known as the Bethe hypothesis). In the particular case $\Delta=\frac{1}{2}$, the resulting equations are exactly the same as our (3.8)–(3.13). Yet, while the eigenvectors of (4.1) and (3.7) are the same, the eigenvalues are quite different. For H' the eigenvalue is

$$E=-(\Delta/2)N+2\sum_{j=1}^{n}(\Delta-\cos k_j). \quad (4.2)$$

The fact that the eigenvalues (4.2) and (3.7) are different is immaterial to the discussion of the existence and value of the set $\{k\}$.

The most recent and complete discussion of (4.1) is due to Yang and Yang.[10] In their first paper, YY prove that the ansatz (3.1) in fact gives the ground state of (4.1) in all n subspaces with $n\leq N/2 (S^z\geq 0)$. The set $\{k\}$ which gives this ground state [and thereby satisfies (3.13)] is real and has the property (YY I.9)

$$-(\pi-\mu)<k_j<\pi-\mu, \quad (\text{all } j) \quad (4.3)$$

with (YY I.10)

$$\cos\mu=-\Delta. \quad (4.4)$$

In our case $\Delta=\frac{1}{2}$, so that

$$\mu=\tfrac{2}{3}\pi. \quad (4.5)$$

We also note that the ground-state eigenfunction of (4.1), when written in the S_z representation (2.8), has the property that the f coefficients are strictly positive (for the same reason that they are positive in our problem). In both cases, these positive eigenfunctions are unique in the sense that there can be only one eigenfunction with this positivity property for each problem.

Another property of $\{k\}$ (YY I.35 and theorem 1) is this:

$$k_i\neq k_j \quad (\text{for } i\neq j) \quad (4.6)$$

and the k's may be ordered so that

$$k_j=-k_{n-j+1}. \quad (4.7)$$

Hence, for n even, $k_j\neq 0$ (all j) and our previous analysis in Sec. III is justified.

These observations together with the YY proof mentioned above establish that there is a solution $\{k\}$ to our Eqs. (3.8) and (3.13) and that this solution leads to an eigenfunction which is simultaneously the ground state of (4.1) and the maximum eigenvector of our transfer matrix.

In their second paper, YY evaluate the set $\{k\}$ as $N\to\infty$. One assumes that as n, $N\to\infty$ with n/N = fixed const., the k's fill some interval $-Q\leq k\leq Q$ (with $Q\leq\pi-\mu$) and that the k's fill this interval without any gaps with a density function $\rho(k)$. That is, the number of k's between k and $k+dk$ approaches $N\rho(k)dk$. While all previous workers have made this assumption, it has to be admitted that a rigorous proof is lacking. YY promise a rigorous proof in a later paper, however (YY II.2 *et seq.*).

Given the assumption of a density function, (3.12) leads to the following integral equation (YY II.6a):

$$1=2\pi\rho(k)-\int_{-Q}^{Q}\frac{\partial\theta(k,q)}{\partial k}\rho(q)dq, \quad (4.8)$$

while the equation that determines Q is (YY II.6b)

$$\frac{n}{N}=\int_{-Q}^{Q}\rho(q)dq. \quad (4.9)$$

YY II prove that (4.8) and (4.9) have a unique solution which is positive (as it should be) and that Q is a differentiable, increasing function of n/N with $Q=\pi-\mu$ for $n/N=\frac{1}{2}$.

To solve (4.8) it is convenient to make a change of variables (YY I.21g and 21h) from k to α:

$$e^{ik}=(e^{i\mu}-e^{\alpha})(e^{i\mu+\alpha}-1)^{-1}. \quad (4.10)$$

If we define a density R for α, so that $R(\alpha)d\alpha=2\pi\rho(k)dk$, then (4.8) and (4.9) become (YY II.7a, 7b and Table II)

$$R(\alpha)=\xi(\alpha)-(2\pi)^{-1}\int_{-b}^{b}K(\alpha-\beta)R(\beta)d\beta, \quad (4.8')$$

[10] C. N. Yang and C. P. Yang, Phys. Rev. **150**, 321 (1966); **150**, 327 (1966). References to equations in these two papers will be denoted (YYI.21) and (YYII.21), respectively. The reader is also referred to these papers for a bibliography of previous work. See also J. des Cloizeaux and M. Gaudin, J. Math. Phys. **7**, 1384 (1966).

$$2\pi\frac{n}{N}=\int_{-b}^{b}R(\alpha)d\alpha, \tag{4.9'}$$

where

$$\xi(\alpha)=\sin\mu[\cosh\alpha-\cos\mu]^{-1}, \tag{4.11}$$

$$2\pi K(\alpha)=\sin 2\mu[\cosh\alpha-\cos 2\mu]^{-1}. \tag{4.12}$$

The obvious advantage of the transformation (4.10) is that the kernel of the integral equation becomes a difference kernel. Thus (4.8') can be solved by Fourier transforms *provided that* $b=\infty$. But $b=\infty$ corresponds to $Q=\pi-\mu$, which occurs for $n/N=\frac{1}{2}$. Fortunately, this is the case we are interested in; for any other value of n/N, (4.8') can not be solved analytically.

Returning to our largest eigenvalue in any given n subspace, with n/N fixed, we have, using (3.7), (3.2), and (4.7),

$$\begin{aligned}
&2\lim_{N\to\infty}N^{-1}\ln\Lambda(n/N)\\
&\quad=-\lim_{N\to\infty}N^{-1}\sum_{j=1}^{n}\ln(2-2\cos k_j)\\
&\quad=-\int_{-Q}^{Q}\ln(2-2\cos q)\rho(q)dq\\
&\quad=-\frac{1}{2\pi}\int_{-b}^{b}\ln[1-3(1+2\cosh\alpha)^{-1}]R(\alpha)d\alpha,
\end{aligned} \tag{4.13}$$

the last expression being the result of the transformation (4.10) (with $\cos\mu=-\frac{1}{2}$). Obviously, in (4.13) we have passed from a sum to an integral in the normal way. Strictly speaking, a proof of this step is required, however, because the function $\ln(2-2\cos k)$ has a mild divergence at $k=0$. We are unable to supply the proof at this time, but we hope that the promised paper of YY on the distribution of the k's will enable us to find a proof.

We have purposely left the quantity n/N arbitrary in (4.13) so that we can now give the proof, promised in Sec. II, that Λ is largest for $n/N=\frac{1}{2}$. As n/N decreases from $\frac{1}{2}$, two things happen: (a) The range of integration b decreases monotonically; (b) for any fixed α, the function $R(\alpha)$ decreases monotonically (YY II.13, *et seq.*). Since the integrand in (4.13) is strictly positive we conclude that $\Lambda(n/N)$ is a strictly increasing function for $0\leq n/N\leq\frac{1}{2}$.

For $n/N=\frac{1}{2}$, $b=\infty$ and

$$R(\alpha)=\pi[2\mu\cosh(\pi\alpha/2\mu)]^{-1}, \tag{4.14}$$

(YY II.14a). Thus, from (2.3)

$$\begin{aligned}
2\ln W&=-\frac{3}{8\pi}\int_{-\infty}^{\infty}\frac{d\alpha}{\cosh(3\alpha/4)}\ln\left[1-\frac{3}{1+2\cosh\alpha}\right]\\
&=-\frac{3}{2\pi}\int_{-\infty}^{\infty}\frac{x^2dx}{x^6+1}\ln\left[\frac{(x^2-1)^2(x^2+1)^2}{1+x^4+x^8}\right].
\end{aligned} \tag{4.15}$$

The latter form is obtained by the substitution $e^{\alpha}=x^4$ and then integrating from $-\infty$ to ∞ because the integrand is symmetric.

The function $(x^6+1)^{-1}$ has three poles in the upper half-plane, three in the lower half-plane, and none on the real axis. Thus, if z is a number with $\mathrm{Im}(z)\neq 0$, it is elementary to do the integral

$$\int_{-\infty}^{\infty}x^2dx(x^6+1)^{-1}\ln(x-z)$$

by closing the contour in the half-plane that does not contain z and evaluating the residues at the three poles. Hence, since x^8+x^4+1 and x^2+1 have no zeros on the real axis, it is tedious, but elementary, to deduce

$$\begin{aligned}
&\int_{-\infty}^{\infty}x^2dx(x^6+1)^{-1}\ln(1+x^4+x^8)=\tfrac{2}{3}\pi\ln 8/3.\\
&\int_{-\infty}^{\infty}x^2dx(x^6+1)^{-1}\ln(1+x^2)=\tfrac{2}{3}\pi\ln\tfrac{3}{2}.
\end{aligned} \tag{4.16}$$

The integral involving $\ln(x^2-1)^2$ is trickier, since x^2-1 has zeros on the real axis. We can, however, write

$$\ln(x^2-1)^2=2\,\mathrm{Re}[\ln(x-1)+\ln(x+1)], \tag{4.17}$$

with the logarithmic branches taken to lie on the real axis. Let C be a contour lying above the real axis, but below the poles of $(x^6+1)^{-1}$. If we integrate along C and close the contour in the upper half-plane, we again pick up the residues of $(x^6+1)^{-1}$. Thus,

$$\begin{aligned}
&\int_{-\infty}^{\infty}x^2dx(x^6+1)^{-1}\ln(x^2-1)^2\\
&\quad=2\,\mathrm{Re}\int_{C}x^2dx(x^6+1)^{-1}[\ln(x+1)+\ln(x-1)]\\
&\quad=\tfrac{2}{3}\pi\ln\tfrac{1}{2}.
\end{aligned} \tag{4.18}$$

Inserting (4.16) and (4.18) into (4.15), we obtain the final result

$$W=(\tfrac{4}{3})^{3/2}. \tag{4.19}$$

Note added in proof. Professor Andrew Lenard has informed me (private communication) that the solution to the ice problem is also the solution to the three color problem on a square "map." The problem posed is this: given a finite planar surface composed of squares (the same lattice we have been discussing), in how many ways can the squares be colored with three colors A, B, and C so that adjacent squares never have the same color. Aside from a factor of 3, the two problems are isomorphic. Lenard's solution is to pick one square and color it A (or B or C). Then, for each ice configuration there is a unique coloring and conversely. First arrange

the colors cyclically (i.e., B follows A, C follows B, and A follows C). Consider one of the four vertices surrounding the given A color. This vertex will have two arrows in and two out. The four squares surrounding this vertex are colored uniquely by proceeding clockwise and using the rule that an outward arrow on a bond separating two squares means that the color of the later square follows that of the previous square in the cyclic order given above. Conversely for an inward arrow. After these four squares (one of which is the original A square) have been colored, one proceeds to the next vertex and so on.

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I should like to thank Professor S. Sherman and Dr. J. Nagle, who, in separate conversations, brought this problem to my attention.

APPENDIX: DEPENDENCE OF THE LARGEST EIVENVALUE ON n

While we are mainly interested in proving that the largest eigenvalue lies essentially in the $n=\frac{1}{2}N$ subspace, we will prove here a much broader theorem relating to more general lattices because it will be useful in subsequent work on the solution of Rys's antiferroelectric F model.[8] We want not only to sum over all allowed configurations, but to do so with a weight that is a product of single vertex weights.

Of the 16 *a priori* vertex configurations, the ice condition permits 6. These are shown in Fig. 1. With these we associate energies $e_1,\ldots,e_6$, respectively, and Boltzmann factors $b_j=\exp(-\beta e_j)$. For the ice problem, $b_j=1$ (all j). The partition function is

$$Z=\sum_{\text{allowed configurations}}\prod_{j=1}^{6} b_j^{m_j}, \tag{A1}$$

where m_j is the number of vertices of type j in a configuration.

Again, we can define a transfer matrix $A(\varphi,\varphi')$, but the elements will be different from before. However, (2.6) will still be true, i.e., $A(\varphi,\varphi')=0$ unless the statement preceding (2.6) is satisfied; in particular A still conserves the value of n. We would also like to retain the "up/down" symmetry of the original problem: If ψ is obtained from φ by reversing all spins (V bonds) and if ψ' is likewise related to φ', then $A(\psi,\psi')=A(\varphi,\varphi')$. To obtain this symmetry, it is necessary to reverse all the arrows on the intervening H bonds. Therefore, to retain this symmetry we require

$$b_1=b_2$$

and

$$b_3=b_4$$

and

$$b_5=b_6 \quad \text{for up/down symmetry.} \tag{A2}$$

The ice problem also has a "left/right" symmetry: If ψ is obtained from φ by reading backwards (i.e., S_j is replaced by S_{n-j+1}) and if ψ' is likewise related to φ' then $A(\psi,\psi')=A(\varphi,\varphi')$. To retain this symmetry we require

$$b_3=b_6$$

and

$$b_4=b_5 \quad \text{for left/right symmetry.} \tag{A3}$$

For the Rys antiferroelectric F model, the assignments are[8]

$$\begin{aligned} &b_1=b_2=1,\\ &0<b_3=b_4=b_5=b_6<1, \end{aligned} \tag{A4}$$

while for the Slater ferroelectric KDP model the assignments are[8]

$$\begin{aligned} &0<b_1=b_2=b_5=b_6<1,\\ &b_3=b_4=1. \end{aligned} \tag{A5}$$

Thus, both models have up/down symmetry but only the F model has left/right symmetry.

While it appears to be possible to prove the following theorems under the assumption of up/down symmetry alone, we shall, in the present discussion, retain both symmetries. The reason we do so is that left/right symmetry adds a useful simplification, namely, that the transfer matrix A is then real and symmetric: $A(\psi,\psi')=A(\psi',\psi)$. (This is proved by reversing all intervening H bonds.) A virtue of the Hermiticity of A is that the largest eigenvalue can be defined by a variational principle. Without this principle, the proofs below become rather involved and the added complication seems unwarranted at this time.

While we exclude the KDP model, we are prepared to distinguish between ferro- and antiferroelectrics according to the criterion

$$\begin{aligned} &b_3=b_4=b_5=b_6>b_1=b_2 \quad \text{ferroelectric,}\\ &b_3=b_4=b_5=b_6<b_1=b_2 \quad \text{antiferroelectric.} \end{aligned} \tag{A6}$$

In analogy with (2.2), we define $f(n,N)$ by

$$e^{Nf(n,N)}=\Lambda(n,N), \tag{A7}$$

where $\Lambda(n,N)$ is the maximum eigenvalue of Λ in a given n subspace with N columns in the lattice (we retain the original "torus" lattice). By up/down symmetry:

$$f(n,N)=f(N-n,N). \tag{A8}$$

We will prove

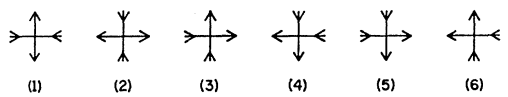

FIG. 1. The six vertex configurations allowed by the "ice condition." The vertex represents an oxygen atom and the arrows indicate on which side of an O-O bond the hydrogen atom lies.

Theorem I: Let $n(N)\leq N$ be any sequence of integers such that the limit

$$\rho=\lim_{N\to\infty} n(N)/N \tag{A9}$$

exists. Then: (a) the limit $f(n(N),N)$ exists, is a function only of ρ, and is continuous, i.e.,

$$F(\rho)=\lim_{N\to\infty} f(n(N),N); \tag{A10}$$

(b) $F(\rho)$ is concave, i.e., for $0\leq\rho_1,\rho_2\leq 1$,

$$F(\tfrac{1}{2}(\rho_1+\rho_2))>\tfrac{1}{2}[F(\rho_1)+F(\rho_2)]. \tag{A11}$$

Corollary 1. By (A8)

$$F(\rho)=F(1-\rho). \tag{A12}$$

Corollary 2.

$$\max_{\rho} F(\rho)=F(\tfrac{1}{2}). \tag{A13}$$

Corollary 3. Let $n(N)$ be a maximal sequence, i.e., for each N

$$g(N)\equiv f(n(N),N)\geq f(n,N), \quad (\text{all } 0\leq n\leq N). \tag{A14}$$

Then g has a limit and

$$\lim_{N\to\infty} g(N)=F(\tfrac{1}{2}). \tag{A15}$$

Proof: Since $n(N)$ is maximal, we have by (A10) and (A13) that $\lim_{N\to\infty}\inf g(N)\geq F(\frac{1}{2})$. Suppose $\lim_{N\to\infty}\sup g(N)>F(\frac{1}{2})$. Then we can find an infinite subsequence, $(N_{\alpha 1},N_{\alpha 2},\ldots)$ such that for some $\epsilon>0$ $g(N_{\alpha j})>F(\frac{1}{2})+\epsilon$(all j). Define $\rho_{\alpha j}\equiv n(N_{\alpha j})/N_{\alpha j}$. There must be at least one point of accumulation, call it ρ. Then we can find an infinite subsequence $(N_{\beta 1},N_{\beta 2},\ldots)$ of the first subsequence such that

$$\lim_{j\to\infty}\rho_{\beta j}=\rho.$$

By (A13),

$$\lim_{j\to\infty} g(N_{\beta j})\leq F(\tfrac{1}{2}),$$

which is a contradiction. Hence

$$F(\tfrac{1}{2})=\lim_{N\to\infty}\sup g\geq\lim_{N\to\infty}\inf g\geq F(\tfrac{1}{2}). \quad \text{Q.E.D.}$$

Obviously, Corollary 3 is what we needed for our ice calculation.

Proof of Theorem I. (a) As before, when $\varphi=\varphi'$ there are two choices for the intervening H bonds, whereas when $\varphi\neq\varphi'$ there is at most one choice. The diagonal part A_D depends only on n and N:

$$\begin{aligned}A_D=A(\varphi,\varphi)&=(b_5)^n(b_3)^{N-n}+(b_4)^n(b_6)^{N-n}\\&=(b_5)^n(b_3)^{N-n}+(b_3)^n(b_5)^{N-n}.\end{aligned} \tag{A16}$$

As $N\to\infty$, A_D has a limit as in the theorem, i.e., (for $b_3\geq b_5$),

$$\begin{aligned}\lim_{N\to\infty} N^{-1}\ln A_D&=F_D(\rho)\\&=\tfrac{1}{2}\ln(b_3b_5)+|\tfrac{1}{2}-\rho|\ln(b_3/b_5),\end{aligned} \tag{A17}$$

but this is a *convex* function. [Note: in (A17) we used only up/down symmetry.] (b) Write

$$A(\varphi,\varphi')=A_D\delta(\varphi,\varphi')+A_L(\varphi,\varphi')+A_R(\varphi,\varphi'),$$

where A_L is the off-diagonal part that produces exchanges $-+$, $+-$, etc., when reading from left to right; A_R is the opposite. Henceforth, assume $n\leq\frac{1}{2}N$. An antiferroelectric upper bound for A_L+A_R is obtained by noticing that there can be at most $2n$ vertices of type (1) or (2). Hence $A_L+A_R\leq(b_1)^{2n}(b_3)^{N-2n}$. A ferroelectric upper bound is $(b_3)^N$. Since there are $\binom{N}{n}$ states in the subspace we have the upper bound

$$\Lambda(n,N)\leq A_D+(b_1)^{2n}(b_3)^{N-2n}\binom{N}{n}, \quad \text{antiferroelectric,} \tag{A18a}$$

$$\leq A_D+(b_3)^N\binom{N}{n}, \quad \text{ferroelectric.} \tag{A18b}$$

A lower bound for Λ can be obtained by the variational function (here we use left/right symmetry in order that A be Hermitian)

$\psi=2^{-1/2}(\varphi_1+\varphi_2)$. For antiferroelectrics:

$$\varphi_1=(\overset{\longleftarrow 2n\longrightarrow}{+-\cdots+-}\ \overset{\longleftarrow N-2n\longrightarrow}{++++\cdots+})$$

and

$$\varphi_2=(\overset{\longleftarrow 2n\longrightarrow}{-+\cdots-+}\ \overset{\longleftarrow N-2n\longrightarrow}{++++\cdots+}).$$

Thus,

$$\Lambda(n,N)\geq\tfrac{1}{2}(b_1)^{2n}(b_3)^{N-2n} \quad \text{(antiferroelectric).} \tag{A19a}$$

For ferroelectrics:

$$\varphi_1=(\overset{\longleftarrow N-n\longrightarrow}{-++\cdots++}\ \overset{\longleftarrow n-1\longrightarrow}{---\cdots-})$$

and

$$\varphi_2=(\overset{\longleftarrow N-n\longrightarrow}{+++\cdots+}\ \overset{\longleftarrow n\longrightarrow}{---\cdots-}).$$

Thus,

$$\Lambda(n,N)\geq\tfrac{1}{2}b_1{}^2b_3{}^{N-2} \quad \text{(ferroelectric).} \tag{A19b}$$

Note that in both cases the lower bound was obtained from A_L+A_R without A_D.

(c) If $\rho=0$, then as $N\to\infty$, (A17) and (A19) agree and we have proved the theorem with

$$F(0)=F_D(0)=\ln b_3. \tag{A20}$$

If $\rho>0$, we see that the lower bound (A19) (which came from A_L+A_R) approaches a limit that is greater than or equal to $F_D(\rho)$. Hence, we shall drop A_D and consider only $A'=A_L+A_R$.

(d) For $\rho>0$, we need consider only $\Lambda'(n,N)=$ largest eigenvalue of A_L+A_R. A useful characterization of Λ' is the following: Define

$$\Lambda_L(n,N)\equiv\max_\Psi(\Psi,A_L\Psi)/(\Psi,\Psi)\,, \qquad \text{(A21a)}$$

where Ψ is restricted to the n subspace and is real. Since the Euler-Lagrange equation for Λ_L is $\frac{1}{2}(A_L+A_L^\dagger)\Psi=\Lambda_L\Psi$, and since $A_L^\dagger=A_R$ (here we use left/right symmetry), it is a trivial conclusion that

$$\Lambda_L(n,N)=\tfrac{1}{2}\Lambda'(n,N)\,. \qquad \text{(A21b)}$$

Define $f_L(n,N)$ in analogy with (A7) using Λ_L. Since the factor $\frac{1}{2}$ in (A21b) is irrelevant as $N\to\infty$, we have

$$F(\rho)=F_L(\rho)\,, \qquad \text{(A22)}$$

assuming that we can prove that f_L satisfies theorem I.

(e) To prove Theorem I for f_L, we shall utilize a method that is by now almost classic.[11] Let $\Psi(n,N)$ be the function that maximizes $\Lambda_L(n,N)$. Divide the chain (row) into two pieces with N_1 vertices in the first part, N_2 in the second, and $N_1+N_2=N$. In an obvious notation, consider the following trial function for the full chain $\bar\Psi(n,N)=\Psi(n_1,N_1)\Psi(n_2,N_2)$, with $n_1+n_2=n$. The reason for considering Λ_L alone now becomes apparent, for

$$(\bar\Psi,A_L\bar\Psi)/(\bar\Psi,\bar\Psi)=\Lambda_L(n_1,N_1)\Lambda_L(n_2,N_2)\,. \qquad \text{(A23)}$$

The proof of (A23) follows from the observation that the only part of A_L which contributes to $(\bar\Psi,A_L\bar\Psi)$ is that part which conserves both n_1 and n_2 separately. Also, when we go from the broken chain to the full chain we must add the H bond connecting N_1 to N_1+1 and N to 1. But we must also delete the H bonds connecting N_1 to 1 and N to N_1+1. The crux of the matter is that for those terms in $(\bar\Psi,A_L\bar\Psi)$ that do not vanish, the arrows along the two added H bonds are exactly the same as they would be along the two deleted H bonds of the broken chain. If we now define $g(\rho,N)=f_L(n,N)$ with $\rho=n/N$, we have from (A23)

$$g(\rho,N)\geq\omega_1 g(\rho_1,N_1)+\omega_2 g(\rho_2,N_2)\,, \qquad \text{(A24)}$$

with $\omega_j=N_j/N$ and $\rho=\omega_1\rho_1+\omega_2\rho_2$. We can define g for nonintegral values of n by linear interpolation: If $\rho=(n+\eta)/N$ with $0\leq\eta\leq1$, then

$$g(\rho,N)\equiv(1-\eta)g(n/N,N)+\eta g((n+1)/N,\,N)\,. \qquad \text{(A25)}$$

With this definition, it is possible to show that (A24) is *a fortiori* true for arbitrary ρ_1 and ρ_2 (cf. Ref. 11, footnote 25).

(f) From (A18) and (A19), we have the following large N bounds on g (valid for $\rho\neq0$, i.e., $n\neq0$): For antiferroelectrics

$$g(\rho,N)\leq\rho\ln[b_1^2(1-\rho)/b_3^2\rho]+\ln[b_3/(1-\rho)]\,,$$
$$g(\rho,N)\geq2\rho\ln[b_1/b_3]+\ln b_3\,. \qquad \text{(A26a)}$$

For ferroelectrics

$$g(\rho,N)\leq\rho\ln[(1-\rho)/\rho]+\ln[b_3/(1-\rho)]\,,$$
$$g(\rho,N)\geq\ln b_3\,. \qquad \text{(A26b)}$$

(g) Pick some $N_0>0$ and consider the sequence $N_j=2^jN_0$ with ρ fixed. Define $g_j\equiv g(\rho,N_j)$. Then (A24) states that g_j forms an increasing sequence. Since it has an upper bound (A26), it must have a limit. Call this limit $G(\rho,N_0)$. Now set $N_1=N_2=N_02^j$ and $N=2N_02^j$ in (A24) and take the limit $j\to\infty$. We thereby establish the concavity of $G(\rho,N_0)$. This function is, moreover, continuous, since a concave function bounded from below is necessarily continuous.

(h) We now wish to show that $G(\rho,N_0)$ is the common limit for an arbitrary sequence $\rho(N)=n(N)/N$ satisfying the conditions of the theorem. This will be done by showing that $\lim_{N\to\infty}\inf g(\rho(N),N)\geq G(\rho,N_0)$ and $\lim_{N\to\infty}\sup g(\rho(N),N)\leq G(\rho,N_0)$.

Lower bound: Obviously, the inequality (A24) can be iterated any number of times. In particular, let j be fixed and let $L=N_02^j$. Break the chain up into C subchains of length L plus a remainder of length M ($CL\leq N$ and $M=N-CL$). Then

$$g(\rho(N),N)\geq(CL/N)g(\rho,L)+(1-CL/N)g(\rho',\,N-CL)\,, \qquad \text{(A27)}$$

with $\rho'=[N\rho(N)-\rho CL][N-CL]^{-1}$. We wish to insure that $0<\rho'\leq\frac{1}{2}$, which means that $CL/N\leq[\frac{1}{2}-\rho(N)]\times[\frac{1}{2}-\rho]^{-1}$ and $CL/N<\rho(N)/\rho$. If C is always chosen to be the maximum integer satisfying these requirements then, as $N\to\infty$, $1-CL/N\to0$. But $g(\rho',N-CL)$ is bounded by (A18). Thus, letting $N\to\infty$ in (A27) yields $\lim_{N\to\infty}\inf g(\rho(N),N)\geq g(\rho,L)$. This is true for all j. Now let $j\to\infty$, whence $\lim_{N\to\infty}\inf g(\rho(N),N)\geq G(\rho,N_0)$.

Upper bound: L is defined as above. For each N let k be the smallest integer such that $U=N_02^k\geq2N$. Consider a chain of length U broken up into a piece of length N, C pieces of length L and a remainder of length $M=U-N-CL$. Then (A24) states that

$$g(\rho,U)\geq(N/U)g(\rho(N),N)+(CL/U)g(\rho,L)+(M/U)g(\rho',M)\,,$$

where $\rho'=[\rho U-\rho CL-N\rho(N)][U-CL]^{-1}$. In order to have $0<\rho'\leq\frac{1}{2}$ we require $CL/U<1-N\rho(N)/U\rho$. If C is the maximum possible integer for each N then, as $N\to\infty$, $U^{-1}(N+CL)\to1$. Therefore, $(M/U)g(\rho',M)\to0$. Hence

$$\limsup_{N\to\infty}g(\rho(N),N)\leq\lim_{N\to\infty}g(\rho,U)+(-1+U/N)g(\rho,U)$$
$$-(CL/N)g(\rho,L)\leq G(\rho,N_0)+3\,|G(\rho,N_0)-g(\rho,L)|\,.$$

(We have used the fact that $U/N<4$.) Now let $j\to\infty$, so that the last quantity, $|\ |$, goes to zero. Q.E.D.

[11] See, for example, M. E. Fisher, Arch. Rat. Mech. Analysis **17**, 377 (1964). It is to this paper that we are most indebted.