

Proton Distribution in Ice and the Kirkwood Correlation Factor*

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4096 molecules of water forming an ice Ic structure and 2048 molecules forming an ice Ih structure, with standard periodic boundary conditions in each case, have been used to calculate the dipole correlations which arise from proton allocation to the oxygen nuclei according to the Bernal-Fowler ice rules. The calculations reveal a substantial antiparallel correlation in the coordination shells at about twice the distance of the nearest neighbors in the lattice. The value of g_K , the Kirkwood correlation factor, is found to be 2.07 ± 0.02 for ice Ih. For ice Ic the value, determined with less precision, is 2.11 ± 0.10 . In connection with Kirkwood's dielectric formula the value of g_K implies an effective dipole moment, μ_s , of the molecule in the solid ice Ih phase equal to 2.92 D.

I. INTRODUCTION

A knowledge of the distribution of protons along the hydrogen bonds in an ice crystal is of importance in understanding the low temperature residual entropy of ice on the one hand and the dielectric properties of the crystal on the other. Bernal and Fowler's¹ theory of this distribution has been tested successfully by an accurate experimental determination of the residual entropy of ice. The elements of this theory are simply expressed:

- (i) Ice consists of intact water molecules.
- (ii) The oxygens form a lattice with tetrahedral coordination.
- (iii) The bond between two neighboring oxygens can accommodate one and only one proton belonging [as a consequence of (i)] explicitly to one of the two oxygens.
- (iv) All proton configurations satisfying the above 3 conditions are equally probable.

On the basis of these Bernal-Fowler "rules," it is possible to work out the number of possible proton configurations and hence to calculate the residual entropy of ice. A fair amount of work has gone into a refinement of Pauling's² original and rather accurate estimate of this quantity. It is not the purpose of this paper to treat this elegant problem of combinatorial analysis.

It is easy to see that the ice rules imply certain angular correlations between the dipole direction of one molecule and that of its immediate neighbors but research on the quantitative aspects of these correlations seems to have attracted rather little attention. The importance of this aspect of the problem of proton distribution arises from the fact that the static dielectric constant of polar liquids and solids depends precisely on the nature of angular correlations between the dipoles. The central quantity is the Kirkwood correlation factor, g_K , defined as follows (for an N -molecule

system):

$$g_K = 1 + \sum_{j=2}^{N_0} \langle \mu_1 \cdot \mu_j \rangle, \quad 1 \ll N_0 \ll N,$$

where μ_j is the unit vector in the direction of the dipole of molecule j and $\langle \dots \rangle$ implies an appropriate average.

Hollins³ has attempted to calculate g_K and his calculation appears conclusive *provided* one grants his assumption about the "dendritic," or "ever-opening," nature of the dipole distribution. Under this assumption Hollins calculates g_K , finding the value 3. However, Powles⁴ had already attempted a more exact analysis but on a very limited scale; taking account of the presence of closed rings of hydrogen bonds but going only partially beyond the second shell of molecules he had found g_K to be less than 3; his estimate for polycrystalline hexagonal ice is 2.65 for g_K . It is, therefore, a plausible conjecture that the "dendritic" assumption overestimates the values of g_K .

In this paper we are reporting on a fairly thorough computer analysis of this problem in which we have attempted to calculate g_K for the hexagonal and for the cubic form of ice usually referred to as ice Ih and ice Ic, respectively. For further details on these two structures, the reader is referred to Eisenberg and Kauzmann.⁵

II. STATEMENT OF THE PROBLEM

Here we shall outline in general terms the logical procedure that we have followed, amounting almost to a verbal flow chart of our computer program. Since it applies equally well to ice Ih and to ice Ic, no distinction will be made between them in this section.

A lattice of N points is constructed to represent the positions of oxygens, and extended to infinity in the usual way through periodic boundary conditions. Each point is thus connected to exactly four nearest neighbors. Along the four directions emanating from point A say, to its neighbors B, C, D, E , two are given a

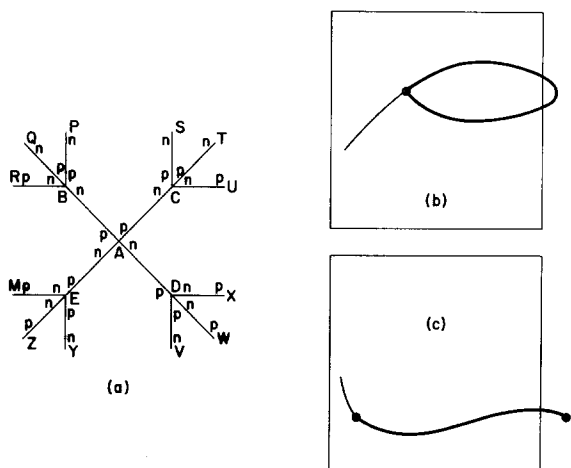


FIG. 1. Diagram to illustrate the computational logic used for generating proton configurations. In (b) and (c) the square outline of the system is totally fictitious because of periodic boundary conditions. The thick line indicates a chain. Open chains as in (c) are extremely improbable for a system consisting of a few thousand particles.

label p and two a label n . This is done for the entire lattice in such a way that the ice rules are totally satisfied everywhere in the infinite system generated by the periodic boundary conditions. Diagrammatically, around A we have the situation shown in Fig. 1(a).

The dipole direction on A is then the direction of the vector sum $\mathbf{AB} + \mathbf{AC}$. Similarly for B it is the direction given by $\mathbf{BP} + \mathbf{BQ}$. We shall denote the unit vector in the direction of the dipole at point i by μ_i .

The initial configuration of hydrogen bonds is chosen to satisfy not only the ice rules but also the additional constraint

$$\sum_{i=1}^N \mu_i = 0.$$

Of course, a subset of the N particles will not necessarily have a vanishing moment. It is perhaps useful to remind ourselves that periodic boundary conditions give an infinite system in which any N particles, lying inside a cell whose edges are of appropriate lengths and are parallel to the direction of periodicity, will have a vanishing total moment.

Using a pseudorandom number generator a particle is picked from among the N particles of the system. Let this be A (we shall use the sketch in Fig. 1(a) to explain the procedure we have followed). One of the four neighbors of A is now picked randomly. Let this be D . This implies that we have, without bias, decided to make

$$A\underline{n} \underline{p}D \text{ into } A\underline{p} \underline{n}D.$$

Then among the two neighbors W and X of D one, say X , is chosen randomly to make

$$D\underline{n} \underline{p}X \text{ into } D\underline{p} \underline{n}X.$$

These jumps are continued until one returns to A via BA or CA .

Obviously a "return" to a point on the path other than the initial point of the chain is not excluded; see Fig. 1(b). If this happens then only the looping part of the chain is retained. This is shown as a thick line in Fig. 1(b).

This does not yet make the chain acceptable. Periodicity implies that the chain, as it develops, may encounter the periodic image of one of the points already on the chain; see Fig. 1(c). This will give the impression that one has "returned" to a point already on the chain. Obviously such an event becomes rather rare as the size of the system increases. Shift of protons along the chain (thick line) shown in Fig. 1(c) will produce a new configuration, acceptable under the ice rules, but one which has an altered value of

$$\sum_{i=1}^N \mu_i.$$

Since we want to investigate the properties of the system of N particles under the constraint

$$\sum_{i=1}^N \mu_i = 0,$$

we have to reject such open chains.

Once a closed chain has been found, Fig. 1(b), thick line, the flipping of the relevant p 's and n 's produces a new configuration while conserving the vanishing value of

$$\sum_{i=1}^N \mu_i.$$

After several hundred such operations of flipping protons along closed chains have been performed, the correlations of interest are calculated. This is continued as long as is necessary for accumulating good statistical data regarding these correlations.

III. SPECIFIC DETAILS OF THE SYSTEMS INVESTIGATED

In the cubic case of ice Ic, we took 4096 molecules with oxygens occupying the sites of a diamond type lattice arranged in a cubic periodic box. If the first neighbor distance is taken as the unit of length, the cubic box containing 4096 particles has an edge length of $32/\sqrt{3}$.

In the hexagonal case, of ice Ih, we took 2048 molecules with oxygens occupying the sites of a hexagonal wurtzite type structure in which the basal plane has oblique axes x and y at an angle of 120° , the z axis being the "c direction," perpendicular to the xy plane. The parallelepiped cell, containing 2048 particles, to which periodic boundary conditions are applied, is thus a right prism with a rhombus for the base. The edge of the rhombus is $16(2/3)^{1/2}$ and the height $64/3$ [thus c/a has the ideal value $(8/3)^{1/2}$]. In these units the first neighbor distance is again unity.

TABLE I. Square of distance r , of ν th coordination shell and its population n_ν .
(A suitable multiple of r_ν^2 is used to reduce all entries to integers.)

Hexagonal Ice Ih																												
ν	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	$\sum_{\nu=0}^{26} n_\nu$
$9(r_\nu^2/r_1^2)$	0	9	24	25	33	48	49	57	64	72	81	88	89	96	97	105	113	120	121	129	136	137	144	145	152	153	160	1
n_ν	1	4	12	1	9	6	6	9	2	18	9	12	3	6	6	18	3	12	7	3	12	6	6	6	6	12	12	206

Cubic Ice Ic																												
ν	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	$\sum_{\nu=0}^{26} n_\nu$
$3(r_\nu^2/r_1^2)$	0	3	8	11	16	19	24	27	32	35	40	43	48	51	56	59	64	67	72	75	80	83	88	91	96	99	1	
n_ν	1	4	12	12	6	12	24	16	12	24	24	12	8	24	48	36	6	12	36	28	24	36	24	24	24	36	524	

In both these structures each oxygen is surrounded by four others, and is at the center of the perfect tetrahedron formed by these four neighbors. The second coordination shell contains 12 neighbors in both cases. The two structures start to have differences from the third coordination shell onwards. Table I gives the values of n_ν , the population of the coordination shell ν , and its distance r_ν .

(A) The statistics of the lengths of chains generated in the manner explained above has been collected for these two structures.

(B) The cubic system of 4096 molecules can be divided into cubic regions containing 8, 64, and 512 molecules, the number of such regions being 512, 64, and 8, respectively. In the hexagonal case the subregions contain 4, 32, and 256 particles, there being 512, 64, and 8 of them, respectively; each region is, of course, a right prism with the base in the shape of a rhombus. We have studied the fluctuation of the dipole moments of these subsets of the total system in each case.

(C) Let $g_K^{(\nu)}$ denote the contribution of the ν th

coordination shell to the Kirkwood g_K . Then, by definition,

$$g_K^{(\nu)} = N^{-1} \sum_{i=1}^N \sum_{j=1}^{n_\nu} \langle \mu_i \cdot \mu_j \rangle,$$

where ν is the label for a particular coordination shell of molecule i and the summation over j extends over the ν th shell of the i th molecule.

In the cubic case, the symmetry allows only the three values, 0, ± 1 , for the product $\mu_i \cdot \mu_j$ for any pair i, j . However, in the hexagonal case there are seven possible values; namely, 0, $\pm 1/3$, $\pm 2/3$, ± 1 . In each case we have determined the statistics of occurrence of the possible values of $\mu_i \cdot \mu_j$ when the pair belongs to a particular mutual coordination shell.

(D) Finally, $g_K = \sum g_K^{(\nu)}$ has been calculated for the two systems. In this summation $\nu=0$ stands for the particle itself, giving a contribution 1 to g_K (see the definition of g_K in the Introduction).

IV. DISTRIBUTION OF CHAIN LENGTHS

In Fig. 2 we have shown the probability of occurrence of closed chains of lengths 6, 8, 10, ...etc.; these are

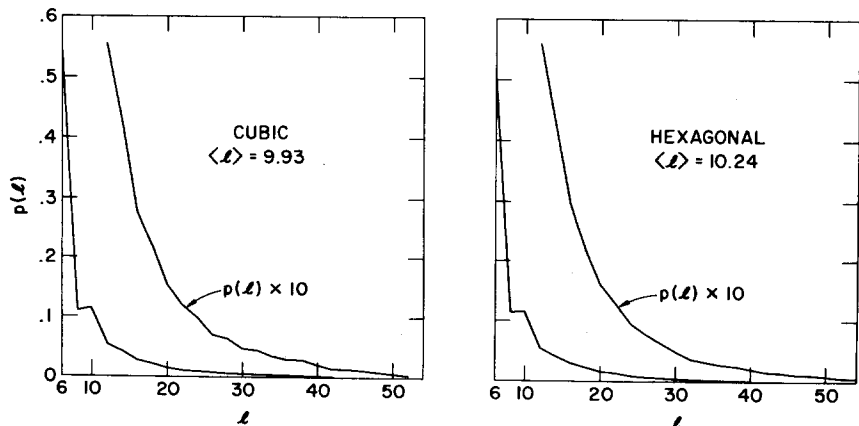


FIG. 2. The probability of occurrence of lengths of chains along which protons are switched to get new configurations. In the cubic case 50 000 chains were used to construct the probability distribution and 140 000 in the hexagonal case.

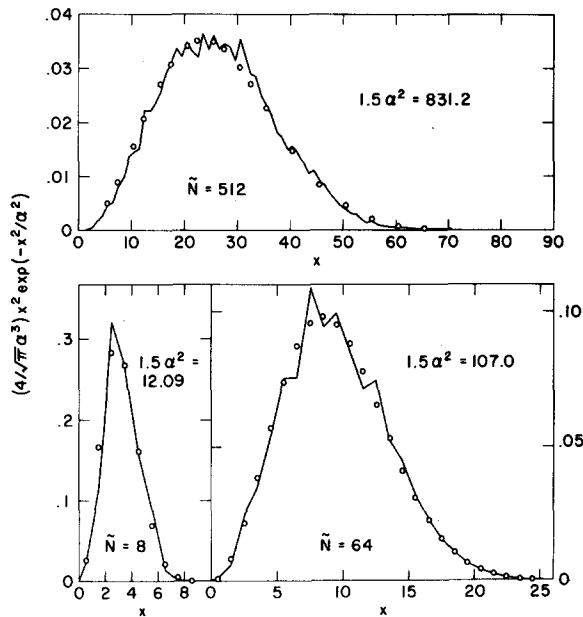


FIG. 3. The probability density for the magnitude of the moment of a subset of 4096 molecules in the cubic case. Observed values are shown by the solid line while calculated normal distributions are shown as by open circles. The size of the subset \tilde{N} as well as the width α of the normal distribution (last entry in Table II) is indicated on each graph separately. The sample consists of $50\,400 \times 4\,096/\tilde{N}$ members in each case.

generated following the method already described. The figure shows the statistics for both the cubic and the hexagonal cases.

The remarkable feature is firstly the similarity of the two distributions and secondly the overwhelming frequency of occurrence of $l=6$. The first feature is not unexpected. However, the second feature; namely, the high frequency with which $l=6$ occurs, already indicates that the dendritic hypothesis is hopelessly off the mark.

In Fig. 2, both for the cubic and the hexagonal case, the probability of occurrence of chains of lengths 8 and 10 is almost equal (~ 0.11). It is pertinent to note that this equality is not due to insufficient statistics but is quite definitely a quantitative feature of these probability distributions.

V. DISTRIBUTION OF REGIONAL MOMENTS

In the cubic case, the 4096 particle system can be composed out of 512 regions of 8 particles each. The probability distribution of the magnitude of the moments of these regions is shown in Fig. 3. Since we are using the moment of each particle as a unit vector, the moment of an 8 particle set cannot exceed 8. However, the probability of total alignment is rather small. Sets of 64 particles, of course, can have a large variety of values of their total moment and the broad distribution is shown in Fig. 3. This distribution for sets of

512 particles is of course even broader as can be seen in Fig. 3.

Let

$$\tilde{\mathbf{M}} = \sum_{i=1}^{\tilde{N}} \boldsymbol{\mu}_i$$

denote the moment of a subset containing \tilde{N} molecules. Figure 3 shows that the vector sum of the dipoles of a cluster of contiguous particles in the system is normally distributed with zero mean. (Note that Fig. 3 is a plot of the distribution of the magnitude of $\tilde{\mathbf{M}}$.)

The values of $\langle \tilde{M}^2 \rangle / \tilde{N}$ were found to be 1.51 for $\tilde{N}=8$, 1.7 for $\tilde{N}=64$, and 1.6 for $\tilde{N}=512$. However, the constraint of zero total moment for the entire system prevents the moments of the subsets from varying quite independently. To correct for this constraint one needs a factor $S/(S-1)$ where $S=4096/\tilde{N}$. Because of the limited statistical accuracy of the results quoted, this correction is negligible except for $\tilde{N}=512$. After this correction is applied we get $\langle \tilde{M}^2 \rangle / \tilde{N} = 1.51, 1.7,$ and 1.8 for $\tilde{N}=8, 64, 512$, respectively.

We now note that $\langle \tilde{M}^2 \rangle / \tilde{N}$ may be identified with g_K provided we keep in mind the important reservation that the former will certainly contain important surface effects. We shall argue later that the value of $\langle \tilde{M}^2 \rangle / \tilde{N}$ is indicative of a lower bound for the correct value of g_K . Thus for ice Ic, in view of the values of $\langle \tilde{M}^2 \rangle / \tilde{N}$ mentioned above, g_K cannot be less than 1.8.

In Table II we have shown the manner in which the values of $\langle \tilde{M}^2 \rangle / \tilde{N}$ converge to the values mentioned as the statistics become more abundant. It is seen from the table that even after 50 000 configurations have been averaged over, the values of $\langle \tilde{M}^2 \rangle$ for $\tilde{N}=512$ are not quite stable. This is the most difficult case of the three since each configuration provides 8 values of \tilde{M}^2 for $\tilde{N}=512$, 64 values for $\tilde{N}=64$, and 512 values for $\tilde{N}=8$.

In the hexagonal case the 2048 particle system was broken into sets of 4, 32, and 256 particles. The prob-

TABLE II. Ice Ic: Values of $\langle \tilde{M}^2 \rangle$ for subsets containing \tilde{N} molecules is shown as a function of the number (*in thousands*) of configurations over which the averaging has been performed.

	\tilde{N}		
	8	64	512
5	12.09	108.9	900.5
10	12.01	106.8	974.3
15	12.01	104.1	902.9
20	12.01	103.7	878.8
25	12.05	104.7	861.7
30	12.08	106.7	869.6
35	12.08	107.8	839.2
40	12.08	107.4	832.0
45	12.06	107.1	821.4
50	12.09	107.0	831.2

ability distribution of the magnitude of the moments of these sets is shown in Fig. 4.

The values of $\langle \tilde{M}^2 \rangle / \tilde{N}$, after correcting with the factor $S/(S-1)$ mentioned above, were found to be 1.43 for $\tilde{N}=4$, 1.6 for $\tilde{N}=32$ and 1.8 for $\tilde{N}=256$. The difficulty of convergence is shown in Table III. Looking at Tables II and III together, we notice that when the subset is larger the convergence problem becomes more acute because the values of \tilde{M}^2 for larger subsets can vary over a wider range of values. However, the convergence is convincing enough to conclude that 1.8 is a lower bound for g_K in Ice Ih as well.

VI. ANGULAR CORRELATIONS $g_K^{(\nu)}$

The quantity $g_K^{(\nu)}$ defined in Sec. III.(C) is calculated for a given configuration by taking each particle (say i) in the system and adding up the value of $\mu_i \cdot \mu_j$ for all j belonging to the ν th coordination shell of particle i .

On the average a chain has been shown to consist of about 10 particles so that two consecutive configurations are only slightly different. Hence the angular correlations giving $g_K^{(\nu)}$ were calculated only after executing 200 chains. Thus the total number of "central" particles around which the correlations were cal-

TABLE III. Ice Ih: Values of $\langle \tilde{M}^2 \rangle$ for subsets containing \tilde{N} molecules is shown as a function of the number (in thousands) of configurations over which the averaging has been performed.

	\tilde{N}		
	4	32	256
5	5.776	50.53	415.4
10	5.758	52.14	389.3
15	5.762	52.36	414.3
20	5.764	52.53	418.0
25	5.780	52.51	422.0
30	5.777	52.69	411.0
35	5.770	52.65	405.5
40	5.753	52.22	396.8
45	5.754	52.67	409.9
50	5.754	52.75	411.7
55	5.754	52.83	413.0
60	5.749	52.78	410.5
65	5.749	52.66	410.0
70	5.744	52.66	408.6
75	5.746	52.67	407.7
80	5.745	52.67	410.9
85	5.741	52.56	408.3
90	5.737	52.48	407.8
95	5.738	52.37	407.3
100	5.744	52.30	405.3
105	5.741	52.30	404.9
110	5.740	52.29	402.3
115	5.737	52.26	403.0
120	5.734	52.22	402.8
125	5.733	52.13	402.7
130	5.734	52.20	402.8
135	5.734	52.29	402.9
140	5.733	52.35	404.9
140 200	5.733	52.35	405.2

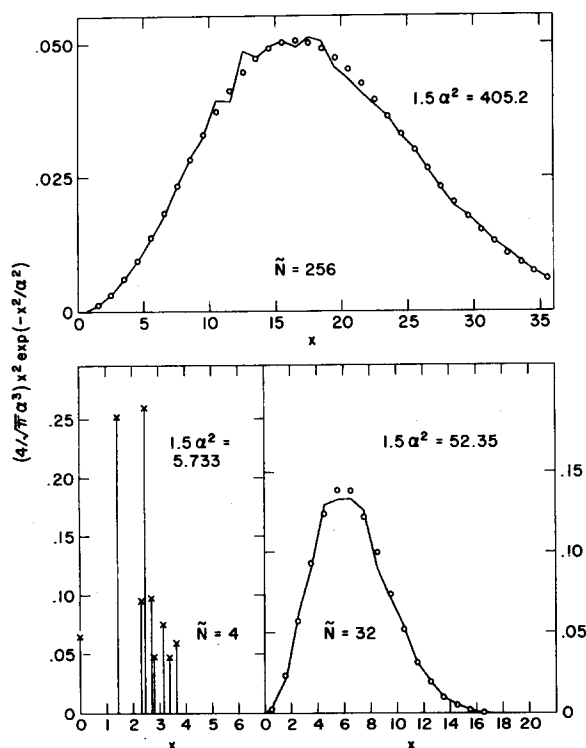


FIG. 4. The same as Fig. 3 except that we have 2048 molecules in an appropriately shaped right prism for the hexagonal case. For $\tilde{N}=4$ there are only nine allowed values of the moment and the probability of each value is shown. For $\tilde{N}=32$ and 256, the probability density is shown as in Fig. 3. The values of α are taken from last entry in Table III. The size of the sample is $140\,200 \times 2\,048 / \tilde{N}$.

culated is given by the number of particles in the system times total number of chains executed divided by 200. But $\mu_i \cdot \mu_j \equiv \mu_j \cdot \mu_i$, and hence the number of independent readings is in fact half this number.

As previously remarked, the cubic symmetry of the ice Ic structure allows only three values; namely, 0, ± 1 , for $\mu_i \cdot \mu_j$. However, the nearest-neighbor pairs are slightly exceptional in that their dipoles cannot be antiparallel. As already explained in Sec. III.(C), if $g_K^{(\nu)}$ denotes the contribution of the ν th coordination shell, at distance r_ν , to the Kirkwood g_K , then $g_K^{(\nu)} = n_\nu (p_{+1}^{(\nu)} - p_{-1}^{(\nu)})$, where $p_{0,\pm 1}^{(\nu)}$ are the probabilities of occurrence of the values 0, ± 1 of $\mu_i \cdot \mu_j$ when i, j belong to the ν th mutual coordination shell; n_ν is shown in Table I. Instead of displaying $p_{0,\pm 1}^{(\nu)}$, Table IV actually shows the counts, $C_{0,\pm 1}^\nu$, registered for the three values of $\mu_i \cdot \mu_j$; it is obvious that the count given for the 0th shell is the appropriate normalization factor to obtain the normalized probabilities $p_{0,\pm 1}^{(\nu)}$; in other words $n_\nu \times p_{0,\pm 1}^{(\nu)} = C_{0,\pm 1}^\nu / C_{+1}^0$.

In the absence of all correlations, we should have

TABLE IV. Ice Ic: Detail of counts registered for the three possible values of $\mu_i \cdot \mu_j$ for pairs belonging to various mutual coordination shells. Last two columns show four significant figures.

ν	Counts					n_ν	$g_k^{(\nu)} \times 10^4$	$\sum_{k=0}^{\nu} g_k^{(k)} \times 10^4$
	$3r_\nu^2/r_1^2$	C_{-1}^ν	C_0^ν	C_{+1}^ν	$C_{+1}^\nu - C_{-1}^\nu$			
0	0	0	0	1 032 192	1 032 192	1	10 000	10 000
1	3	0	2 823 758	1 305 010	1 305 010	4	12 643	22 643
2	8	2 044 908	8 293 184	2 048 212	3 304	12	32	22 675
3	11	2 317 656	8 219 386	1 849 262	-468 394	12	-4 537	18 137
4	16	1 031 042	4 125 904	1 036 206	5 164	6	50	18 187
5	19	1 914 264	8 260 320	2 211 720	297 456	12	2 881	21 069
6	24	4 134 394	16 515 456	4 122 758	-11 636	24	-112	20 956
7	27	2 796 884	11 006 528	2 711 660	-85 224	16	-825	20 130
8	32	2 066 842	8 256 656	2 062 806	-4 036	12	-39	20 091
9	35	4 172 984	16 515 572	4 084 052	-88 932	24	-861	19 229
10	40	4 132 372	16 517 612	4 122 624	-9 748	24	-94	19 135
11	43	2 032 672	8 258 896	2 094 736	62 064	12	601	19 736
12	48	1 374 768	5 508 932	1 373 836	-932	8	-9	19 727
13	51	4 124 738	16 517 308	4 130 562	5 824	24	56	19 784
14	56	8 265 204	33 033 936	8 246 076	-19 128	48	-185	19 598
15	59	6 206 644	24 779 746	6 172 522	-34 122	36	-330	19 268
16	64	1 034 316	4 126 992	1 031 844	-2 472	6	-23	19 244
17	67	2 072 714	8 256 938	2 056 652	-16 062	12	-155	19 088
18	72	6 203 374	24 767 420	6 188 118	-15 256	36	-147	18 940
19	75	4 830 872	19 265 492	4 805 012	-25 860	28	-250	18 690
20	80	4 139 092	16 507 812	4 125 704	-13 388	24	-129	18 560
21	83	6 180 712	24 775 850	6 202 350	21 638	36	209	18 770
22	88	4 135 802	16 516 460	4 120 346	-15 456	24	-149	18 620
23	91	4 135 458	16 516 166	4 120 984	-14 474	24	-140	18 480
24	96	4 128 662	16 511 668	4 132 278	3 616	24	35	18 515
25	99	6 200 810	24 771 760	6 186 342	-14 468	36	-140	18 375

$p_{\pm 1}^{(\nu)} = \frac{1}{6}$ and $p_0^{(\nu)} = \frac{2}{3}$; for large ν , this behavior is apparent in the values shown in Table IV.

In Fig. 5 $g_K^{(\nu)}$ is plotted as a function of ν^2 . We notice the strong negative correlation of the third shell and then a considerable positive value for the fifth.

The hexagonal symmetry of ice Ih allows seven values for $\mu_i \cdot \mu_j$, as already mentioned. Table V gives the counts registered at various coordination shells for the possible values of $\mu_i \cdot \mu_j$. Figure 6 shows $g_K^{(\nu)}$ as a function of ν^2 .

A comparison of Figs. 5 and 6 shows the qualitative similarity between the two cases; however, the quantitative differences are quite apparent and show that from the point of view of $g_K^{(\nu)}$ the two lattices do not behave in the same manner.

The dendritic hypothesis³ gives the $g_K^{(1)} = 4/3$ and $g_K^{(2)} = 4/9$. It is now clear that only $g_K^{(1)}$ is approximately correct. For other coordination shells, the dendritic assumption gives quite wrong values. The fact that the $g_K^{(1)}$ we have obtained is less than $4/3$ is obviously due to the fact that closed chains of length 6 dominate the configurations (Fig. 1) and do not allow a complete absence of correlation between the first-neighbor dipole directions.

VII. THE KIRKWOOD CORRELATION FACTOR

Before we discuss the various features of the angular correlations which have been displayed in the foregoing sections, we show in Fig. 7 the manner in which the value of g_K fluctuates as the statistics become more abundant.

In the case of hexagonal ice Ih we ran a total of 140 200 chains and hence 701 configurations were used for getting the value of g_K shown in Fig. 7. Each configuration has 2048 "central" particles around each of which 206 neighbors belonging to the first 26 shells were included. After this degree of averaging, the apparent value of g_K was found to be 1.86 (last entry in right most column of Table V). But the total system of 2048 particles is constrained to have zero moment. Hence if around each "central" particle we had drawn an appropriate parallelepiped containing 2047 neighbors, we would formally have found $g_K = 0$. In other words, each of the 2047 neighbors contributes a bias of amount $-1/2047$ to g_K . We conclude that for ice Ih the value of g_K , as given by these calculations is $1.86[1 - (206/2047)]^{-1}$ or $g_K = 2.07$. We believe that the error is not more than ± 0.02 .

Since ice Ih is not isotropic we have included in our calculations a breakup of the quantity $\mu_i \cdot \mu_j$ into products of the type $xx, xy, yx, yy,$ and zz . The results briefly stated are as follows. The contributions of the five quantities listed above are, in that order, 0.833, $-0.207, -0.218, 0.862,$ and $0.587,$ respectively. The fact that $xx \neq yy$ and $xy \neq yx$ is indicative of statistical fluctuations. After smoothing such differences and applying the correction factor mentioned above, one gets $g_{K^+} = 2.12$ and $g_{K^{\parallel}} = 1.96$. Powles⁶ has shown that the angle averaged g_K is obtained by taking $(2g_{K^+} + g^{\parallel})/3$.

In the cubic case of ice Ic, Fig. 7 shows a greater uncertainty. Using the last entry at the bottom of Table IV, the value of g_K can be stated to be $1.84[1 - (524/4095)]^{-1} = 2.11$ with an error of as much as ± 0.10 . It is possible that with improved statistics the agreement between the value of g_K for ice Ic and for ice Ih will be found to be even closer.

It is now clear why the values of $\langle \bar{M}^2 \rangle / \bar{N}$ discussed in detail in Sec. V are lower than the value of g_K . In a subset of the system the quantity $\langle \bar{M}^2 \rangle / \bar{N}$, which is

$$\bar{N}^{-1} \sum_{i=1}^{\bar{N}} \mu_i \cdot \sum_{j=1}^{\bar{N}} \mu_j,$$

does not contain all the first neighbors of the "surface"

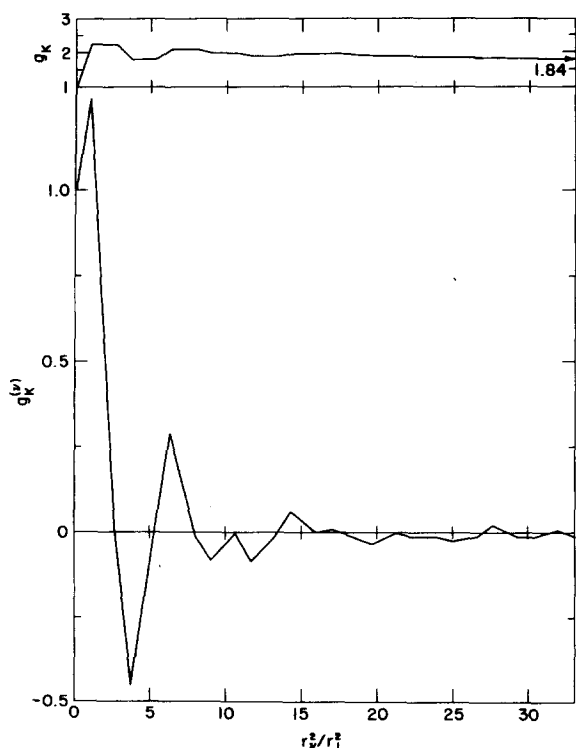


FIG. 5. The contribution $g_K^{(v)}$ of the v th shell, for $v = 1, 2, \dots, 25,$ to the Kirkwood g_K in the cubic case. The top part of the figure shows the value of g_K as coordination shells are progressively included in the sum $\sum g_K^{(v)}$. The total number of neighbors up to the 25th shell is 524.

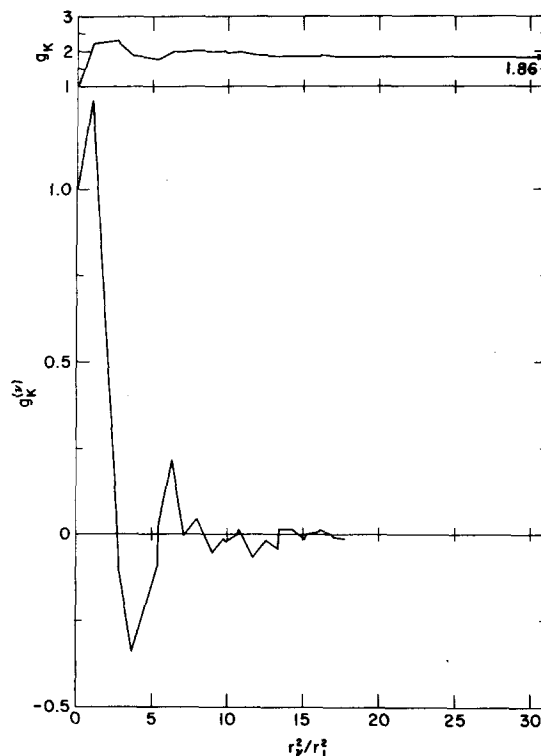


FIG. 6. Same as Fig. 4 but for hexagonal ice Ih. The 26 shells have a total of 206 neighbors (see Table I).

particles and thus, for small subsets a major positive contribution to g_K is excluded in $\langle \bar{M}^2 \rangle / \bar{N}$, the effect being larger for smaller \bar{N} . It is, however, surprising that the values ranging from 1.43 to 1.8 (\bar{N} from 4 to 512) were found for $\langle \bar{M}^2 \rangle / \bar{N}$; indeed $\langle \bar{M}^2 \rangle / \bar{N}$, say for $\bar{N} = 32$, in spite of the surface effects, is 1.6, closer to the value 2.07 of g_K than that given by the dendritic assumption.³

VIII. DISCUSSION

It emerges clearly from these calculations that the Bernal-Fowler ice rules exclude the possibility of uncorrelated dipole directions for pairs of first neighbors. The value 1.26 instead of $4/3$ for $g_K^{(1)}$ implies a certain depletion in the probability of these dipoles being parallel. This small change is magnified enormously by the time one comes to the third shell in ice Ic and the fourth in ice Ih where $g_K^{(v)}$ actually becomes negative to the order of -0.4 .

This bias towards negative values of $g_K^{(v)}$ in the region where $r_v^2/r^2 \sim 4$ has been observed in molecular dynamics simulation of arrangements and motion of molecules in liquid water. Let $g_K(r)$ denote the contribution to g_K of particles at distance r from each other [in other words $g_K = (N/V) \int g_K(r) d\bar{r}$]. The dependence of $g_K(r)$ on the distance r is shown in Fig. 8 for water⁷ at 265°K. As we have mentioned in another place, this behavior in the liquid is the consequence of

TABLE V. Ice Ih: Detail of counts registered for the seven possible values of $\mathbf{u}_i \cdot \mathbf{u}_j$ for pairs belonging to various mutual coordination shells. Last two columns show four significant figures.

ν	$9r_s^2/r_1^2$	Counts							n_s	$g_h^{(\nu)} \times 10^4$	$\sum_{s=0}^{\nu} g_h^{(s)} \times 10^4$
		C_{-1}^{ν}	$C_{-2/3}^{\nu}$	$C_{-1/3}^{\nu}$	C_0^{ν}	$C_{1/3}^{\nu}$	$C_{2/3}^{\nu}$	C_1^{ν}			
0	0	0	0	0	0	0	0	1 435 648	1	10 000	10 000
1	9	0	0	514 730	2 944 228	0	920 918	1 362 716	4	12 573	22 573
2	24	1 423 764	2 718 298	1 642 194	5 760 288	1 210 926	3 042 470	1 429 836	12	546	23 119
3	25	0	530 804	331 422	0	164 188	409 234	0	1	-952	22 166
4	33	805 742	3 175 016	1 331 318	2 858 058	1 512 008	2 595 546	643 144	9	-3 403	18 762
5	48	0	2 939 886	1 499 544	0	1 372 818	2 801 640	0	6	-936	17 826
6	49	0	2 835 010	1 454 508	0	1 418 382	2 905 988	0	6	245	18 072
7	57	1 997 324	0	0	8 619 172	0	0	2 304 336	9	2 138	20 210
8	64	481 120	0	0	1 912 660	0	0	477 516	2	-25	20 185
9	72	1 433 652	5 721 320	2 818 562	5 746 748	2 926 176	5 761 718	1 433 488	18	436	20 622
10	81	727 240	2 930 292	1 404 672	2 871 956	1 466 068	2 812 856	707 748	9	-538	20 083
11	88	2 880 630	0	0	11 486 040	0	0	2 861 106	12	-135	19 947
12	89	733 112	0	0	2 871 948	0	0	701 884	3	-217	19 730
13	96	1 436 892	0	0	5 743 748	0	0	1 433 248	6	-25	19 704
14	97	0	2 860 506	1 426 992	0	1 440 922	2 885 468	0	6	148	19 852
15	105	2 901 962	2 911 910	1 413 546	11 481 464	1 460 042	2 828 390	2 844 350	18	-681	19 171
16	113	730 368	0	0	2 872 184	0	0	704 392	3	-180	18 990
17	120	0	5 793 090	2 869 604	0	2 870 390	5 694 692	0	12	-455	18 535
18	121	0	3 331 606	1 678 066	0	1 673 978	3 365 886	0	7	149	18 685
19	129	707 732	0	0	2 871 746	0	0	727 466	3	137	18 822
20	136	2 879 850	0	0	11 488 272	0	0	2 859 654	12	-140	18 682
21	137	1 437 070	0	0	5 738 856	0	0	1 437 962	6	6	18 688
22	144	0	2 875 714	1 412 710	0	1 459 678	2 865 786	0	6	62	18 751
23	145	0	2 844 780	1 464 176	0	1 408 612	2 896 320	0	6	110	18 861
24	152	0	2 860 958	1 462 212	0	1 407 202	2 883 516	0	6	-22	18 838
25	153	2 879 046	0	0	11 485 584	0	0	2 863 146	12	-110	18 727
26	160	2 884 264	0	0	11 482 812	0	0	2 860 700	12	-164	18 563

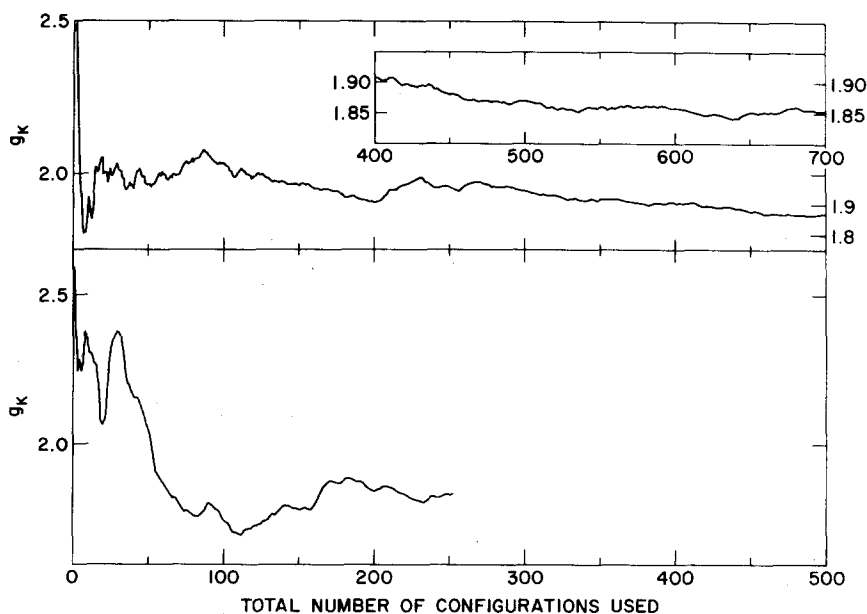


FIG. 7. The average value of g_K for ice Ih and ice Ic as a function of the number of configurations over which one has already averaged. For ice Ih a total of 700 configurations was reached. For ice Ic the calculation was terminated after averaging over 250 configurations.

strong tetrahedrality in the arrangement of neighboring molecules.

Implicit in this analysis of orientational correlation in ice is the assumption of equal *a priori* weights for all zero-moment configurations satisfying the ice rules. In principle, of course, there must exist some energy variation between acceptable configurations, with an associated Boltzmann-factor bias in occurrence probabilities. However, Pauling's² remarkable success in explaining the residual entropy of ice³ on a purely combinatorial basis strongly suggests that energy bias has minor influence. Nevertheless, this presumption deserves ultimately to be checked, and a generalization of the present project to include interaction energies explicitly is a desirable subsequent task.

The Kirkwood⁹ theory of polar dielectrics connects g_K specifically to the static dielectric constant ϵ_0 for the material (which is presumed to be isotropic), and to the mean value μ_s of the molecular dipole moment in that material. Its result may be displayed in the following form:

$$\mu_s^2 = (3k_B T / g_K) [(\epsilon_0 - 1)(2\epsilon_0 + 1) / 12\pi\rho\epsilon_0 - \bar{\alpha}],$$

where k_B is Boltzmann's constant, T is the absolute temperature, ρ is the number density, and $\bar{\alpha}$ is the mean molecular polarizability. As a result of molecular interactions in dense phases, one can reasonably expect μ_s to depart significantly from the vapor-phase dipole moment μ_0 . Unfortunately the estimates of μ_s for ice have been uncertain and scattered in magnitude.¹⁰

We are now in a position to provide an independent estimate for μ_s in ice. The Kirkwood formula above applies to cubic ice which, by virtue of its symmetry, is necessarily an isotropic dielectric. Unfortunately ϵ_0 has not been determined for this crystal modification. Ice Ih seems to be only moderately anisotropic, and thus it appears reasonable to suppose that the Kirkwood formula applies to polycrystalline ice Ih. Auty and Cole¹¹ have measured ϵ_0 for polycrystalline ice Ih; at 0°C they find the value 91.5. The number density at this temperature is

$$\rho = 0.03065 \times 10^{24} \text{ molecules/cm}^3,$$

while $\bar{\alpha}$ is¹⁰ $1.444 \times 10^{-24} \text{ cm}^3$. Thus at 0°C in ice Ih:

$$g_K \mu_s^2 = 17.653 \times 10^{-36} \text{ cgs.}$$

By inserting our g_K value 2.07 ± 0.02 in this expression, one concludes that

$$\mu_s = 2.92 \pm 0.02 \text{ D.}$$

This result is substantially larger than the isolated molecule moment $\mu_0 = 1.83 \text{ D.}$ ¹²

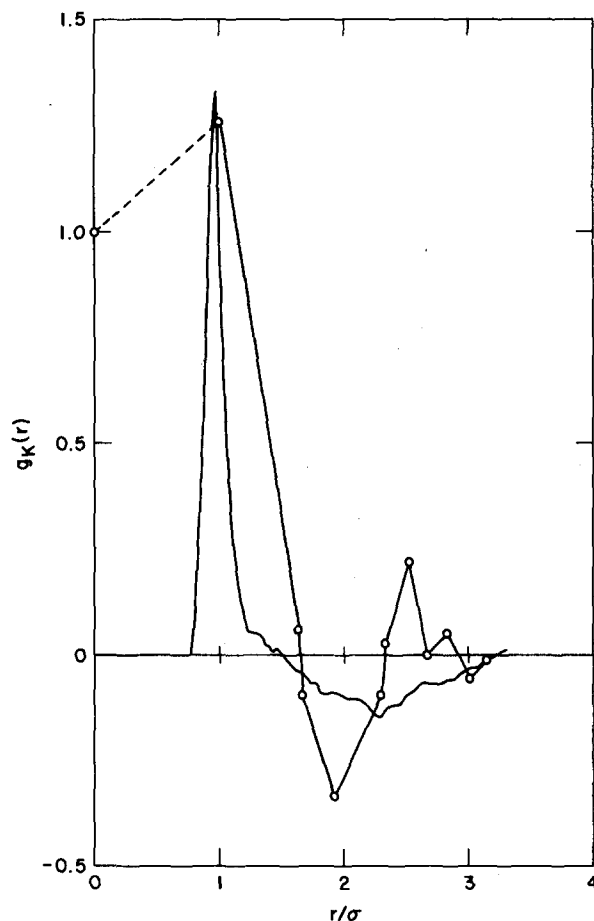


FIG. 8. $g_K(r)$ for liquid H_2O at 265°K compared with $g_K(r)$ for ice Ih. The distance r is expressed in terms of σ , the distance parameter mentioned in Ref. 7. The peak in the oxygen-oxygen pair correlation in the liquid occurs at $r/\sigma \sim 1$.

If one alternatively had used the Hollins "dendritic" value 3 for g_K , μ_s would have appeared to be only 2.49 D. Therefore it is clear that quantitative understanding of the molecular effects of hydrogen bonding in ice requires a very careful study of local orientational correlations.

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¹² Reference 5, p. 12.