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## The configurational entropy in the Jaccard theory of the electrical properties of ice

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**Abstract.** The Jaccard theory of the electrical properties of ice includes a parameter  $\Phi$ , which relates the change in configurational entropy to the configuration vector  $\Omega$ . We show by an analytic mean-field type of calculation that  $\Phi \approx (8/\sqrt{3})ak_B T$ , where  $a$  is the oxygen–oxygen separation. The Jaccard theory is then fully compatible with the existing theories of the static permittivity of pure ice in which the key dimensionless parameter is given the value  $G \approx 3.0$ .

### 1. Introduction

The disorder of the protons in ice Ih is subject to the Bernal–Fowler [1] rules and gives rise to the Pauling entropy  $k_B \ln(\frac{3}{2})$  per molecule [2]. If the ice is polarized to some extent by the motion of electrical point defects, e.g. under the influence of an electric field, the arrangement of the protons will no longer be completely random and the configurational entropy is reduced. This reduction in entropy is an essential feature of the standard theory of the electrical properties of ice as formulated by Jaccard [3].

In this theory the ordering effect of the motion of point defects is described by a configuration vector  $\Omega$  defined by the equation

$$\Omega = \int_0^t (j_1 - j_2 - j_3 + j_4) dt' \quad (1)$$

in which  $j_1$ ,  $j_2$ ,  $j_3$  and  $j_4$  are the fluxes (per unit area) of  $\text{H}_3\text{O}^+$  ions,  $\text{OH}^-$  ions, D defects and L defects, respectively, and the proton system is fully disordered according to the Bernal–Fowler rules at  $t = 0$ . It is then assumed that for small  $\Omega = |\Omega|$  the change in the entropy  $S$  per unit volume due to the ordering can be expressed in the form

$$T \delta S(\Omega) = T(S(\Omega) - S(0)) = -\frac{1}{2} \Phi \Omega^2. \quad (2)$$

The constant  $\Phi$  introduced here plays a fundamental role in the Jaccard theory, entering directly in the equations for the permittivity and dielectric relaxation time of ice. To estimate  $\Phi$  Jaccard treated the ice as a system of bonds but took no account of the Bernal–Fowler rule that there are two protons adjacent to each oxygen atom. This gave the value

$$\Phi_J = \frac{16}{\sqrt{3}} ak_B T \quad (3)$$

in which  $a$  is the distance between adjacent oxygen sites (denoted by Jaccard as  $r_{\text{OO}}$ ).

For pure ice in which the polarization is produced by Bjerrum defects (i.e.  $\sigma_{DL} \gg \sigma_{\pm}$ ) the Jaccard theory gives the contribution to the relative permittivity

$$\epsilon_s - \epsilon_{\infty} = \frac{e_{DL}^2}{\epsilon_0 \Phi} \quad (4)$$

where  $e_{DL}$  is the charge on a Bjerrum defect and  $\epsilon_0$  is the permittivity of free space. Nagle [4, 5] has discussed the same problem from the viewpoint of the equilibrium thermodynamics of molecular dipoles of moment  $\mu$  in an electric field, giving

$$\epsilon_s - \epsilon_{\infty} = \frac{N}{V} \frac{G\mu^2}{3\epsilon_0 k_B T} \quad (5)$$

in which  $N/V = 3\sqrt{3}/8a^3$  is the number of dipoles per unit volume and  $G$  is a dimensionless constant. A simple argument due to Onsager and Dupuis [6] shows that  $\mu = e_{DL}a/\sqrt{3}$ , and to make equations (4) and (5) equivalent it is therefore necessary that

$$\Phi = \frac{8\sqrt{3}ak_B T}{G}. \quad (6)$$

Nagle [4] has shown by a combinatorial procedure involving the summation of a weakly convergent series that  $G \approx 3.0$ , and this has been confirmed by Adams [7] using a Monte Carlo procedure. However, this result has not been generally adopted in papers using the Jaccard theory (see, e.g., [8–10]).

In this paper we present a very different approach to the calculation of  $S(\Omega)$  within the framework of the Bernal–Fowler rules and confirm that to our level of approximation  $\Phi$  is given by equation (6) with  $G \approx 3.0$ . Our aim has been to establish that this is the appropriate theoretical value to use in the Jaccard model, and hence to resolve the confusion that exists on this point.

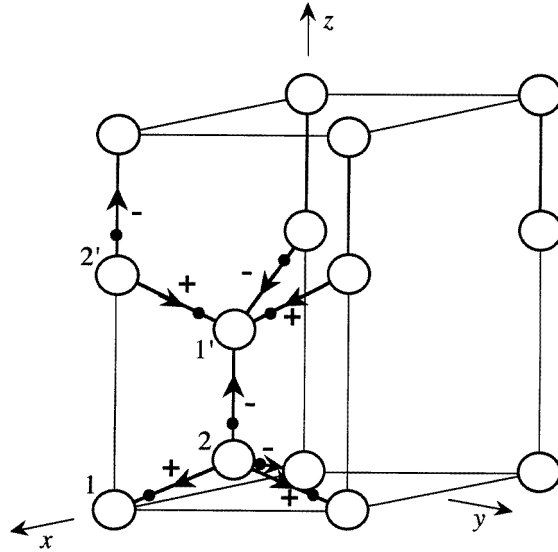
## 2. Theory

### 2.1. The basic model

Although Jaccard has defined the configuration vector by equation (1), the value of  $\Omega$  is a function of the state of the crystal and does not depend on the process by which the crystal reached that state. In our model we describe the state of the crystal, and hence define  $\Omega$ , by denoting the orientations of the bonds by pseudo-spin variables. We divide the oxygen lattice into two interpenetrating sublattices labelled 1,1' and 2,2' as shown in figure 1. Then we ascribe a spin variable  $s_i$  to each hydrogen bond such that  $s_i = +1$  if the proton is near a type 1 oxygen atom and  $s_i = -1$  if the proton is near to a type 2 oxygen atom. This formalism automatically satisfies the first Bernal–Fowler rule that there is one proton per bond. The second rule is introduced via the Hamiltonian [11]

$$H = J \sum_{i,j} s_i s_j \quad (7)$$

where the sum is over all pairs of nearest-neighbour bonds. For two protons close to a given oxygen atom the contribution to the sum is  $-2$ , for one or three protons it is 0 and for no protons or four protons it is  $+6$ . Thus, if  $J > 0$ , the minimum value of  $H$  is obtained when every oxygen atom is associated with two protons, and we shall take the limit  $J \rightarrow \infty$  to select only these lowest-energy configurations.



**Figure 1.** Unit cell of ice Ih. Large circles represent oxygen atoms of types 1, 1', 2 and 2'. Small spots represent protons at sites on bonds satisfying the Bernal–Fowler rules. Arrows show the directions of the unit vectors  $e_i$ , and the signs of  $s_i$  for this particular configuration are marked.

For each hydrogen bond we shall define a unit vector  $e_i$  directed along the bond from the type 2 to the type 1 oxygen as shown in figure 1; the components of these unit vectors are listed in the appendix. The configuration vector for  $N$  molecules can then be written as

$$\Omega_N = -\frac{a}{2} \sum_i s_i e_i \quad (8)$$

where the summation is over the  $2N$  bonds linking the molecules. If these  $N$  molecules occupy a volume  $V$  the configuration vector  $\Omega$  defined by equation (1) is given by  $\Omega_N/V$ , but we shall find it simpler to write the following theory in terms of  $\Omega_N$ . This quantity will clearly be zero in unpolarized ice. If the ice is polarized by the movement of some  $\text{H}_3\text{O}^+$  ions, then the arrangement defined in figure 1 is such that, for each bond traversed in the  $+e_i$  direction  $s_i$  changes from  $-1$  to  $+1$  while for bonds traversed in the  $-e_i$  direction the change in  $s_i$  is reversed. The right-hand side of equation (8) then yields the vector sum of the displacements of all the ions. Considering a specific volume, equation (1) yields the same result, and similar arguments apply to  $\text{OH}^-$  ions and Bjerrum defects.

## 2.2. The partition function

To calculate the entropy as a function of  $\Omega_N$  we shall use the restricted partition function

$$Z(\Omega_N) = \sum_{\{s\}} \exp(-\beta H) \delta\left(\Omega_N + \frac{1}{2}a \sum_i s_i e_i\right) \quad (9)$$

where  $\beta = 1/k_B T$ . The sum over  $\{s\}$  is over all  $2^{2N}$  configurations of the spin variables  $s_i$ ,  $H$  is defined by equation (7), and  $\delta$  is the three-dimensional delta function. With  $J \rightarrow \infty$  this partition function represents a sum over all states consistent with the specified  $\Omega_N$  and the Bernal–Fowler rules. We note that the vector  $\Omega_N$  and hence the argument of the

delta function are discrete variables. If we concentrate attention on one oxygen atom of type  $\alpha$ , labelled 1, 2, 1' or 2' in figure 1, and require that there are only two neighbouring protons, the contribution to  $\Omega_N$  from the bonds around this molecule will have the form  $(2a/\sqrt{3})\mathbf{n}_{\alpha j}$ , where the  $\mathbf{n}_{\alpha j}$  ( $j = 1-3$ ) are the unit vectors listed in the appendix. These unit vectors are linear combinations of the  $\mathbf{e}_i$ , and  $\pm\mathbf{n}_{\alpha j}$  represent the six possible orientations of a molecule of type  $\alpha$ . The discrete nature of  $\Omega_N$  is then represented by

$$\Omega_N = \sum_{\alpha} \sum_j \frac{2}{\sqrt{3}} am_{\alpha j} \mathbf{n}_{\alpha j} \quad (10)$$

in which the  $m_{\alpha j}$  are positive or negative integers.

We now represent the delta function in (9) as a Fourier transform

$$\delta\left(\Omega_N + \frac{1}{2}a \sum_i s_i \mathbf{e}_i\right) = \frac{8a^3}{3\sqrt{3}} \int_B \frac{d^3\mathbf{k}}{(2\pi)^3} \exp\left[\mathbf{i}\mathbf{k} \cdot \left(\Omega_N + \frac{1}{2}a \sum_i s_i \mathbf{e}_i\right)\right] \quad (11)$$

where the integral is over a suitable Brillouin zone, but the exact boundary of the zone is not important in this analysis because, as we shall see, the main contribution to the integral in the partition function (equation 18) will come from small  $\mathbf{k}$ . Inserting (11) into (9) and performing some algebraic rearrangement we obtain

$$Z(\Omega_N) = \frac{8a^3}{3\sqrt{3}} \int_B \frac{d^3\mathbf{k}}{(2\pi)^3} Z_{\mathbf{k}} \exp(\mathbf{i}\mathbf{k} \cdot \Omega_N) \quad (12)$$

where

$$Z_{\mathbf{k}} = \sum_{\{s\}} \exp\left(-\beta H + \sum_i h_i s_i\right) \quad (13)$$

in which

$$h_i = \mathbf{i}\frac{1}{2}a\mathbf{k} \cdot \mathbf{e}_i. \quad (14)$$

These equations have the standard form for a partition function in an applied field with component  $h_i$  along  $\mathbf{e}_i$ , except that  $h_i$  is imaginary.

### 2.3. The mean-field cluster approximation

The partition function  $Z_{\mathbf{k}}$  will be calculated by considering a cluster of the four bonds (or spins) around a single oxygen atom of type  $\alpha$ , and including the effect of the other bonds as a mean-field correction. The method is based on that of Blinc and Svetina [12].

The Hamiltonians for the cluster and for a single bond  $i$  are

$$H_{\alpha} = J \sum_{i,j \in \alpha} s_i s_j + \frac{1}{\beta} \sum_{i \in \alpha} \left(1 + \frac{1}{2}x\right) h_i s_i \quad (15)$$

$$H_i = \frac{1}{\beta} \sum_{i \in \alpha} (1+x) h_i s_i. \quad (16)$$

The quantities  $h_i$  are the 'applied fields' in equation (13) and we have added the effective mean fields  $\frac{1}{2}xh_i$  and  $xh_i$ . Because these terms take account of the effect of more distant bonds, they must vanish when the applied fields are zero; we are not looking for spontaneous ordering. In what follows the main contributions arise from small  $\mathbf{k}$  and thus small  $h_i$ , and it is therefore natural to assume that the mean field depends linearly on the applied field. The multiplier  $\frac{1}{2}$  in front of  $x$  in (15) takes account of the fact that a single spin within a cluster has three neighbours outside the cluster, whereas the single spin considered in (16)

has six neighbours. The parameter  $x$  which determines the strength of the mean field will be chosen by minimizing the free energy.

Using these Hamiltonians we find the partition functions for a four-spin cluster and for a single bond,  $Z_{k\alpha}^c$  and  $Z_{ki}$ , respectively, and then according to the four-spin cluster theory the partition function for a single molecule is

$$Z_{k\alpha} = \frac{Z_{k\alpha}^c}{(Z_{k1}Z_{k2}Z_{k3}Z_{k4})^{1/2}} = \frac{\sum_{j=1}^3 \cos[(2a/\sqrt{3})(1 + \frac{1}{2}x)\mathbf{k} \cdot \mathbf{n}_{\alpha j}]}{2 \prod_{i=1}^4 \cos[(a/2)(1+x)\mathbf{k} \cdot \mathbf{e}_i]} \quad (17)$$

As an approximation to the whole partition function  $Z_k$  we use the product of these  $Z_{k\alpha}$  for the  $N$  oxygen sites.

Evaluating  $Z(\Omega_N)$  from (12) gives

$$Z(\Omega_N) = \left(\frac{3}{2}\right)^N \int_B \frac{d^3\mathbf{q}}{(2\pi)^3} \exp\left[-N\varphi(\mathbf{q}) + i\left(\frac{\sqrt{3}}{2a}\right)\mathbf{q} \cdot \Omega_N\right] \quad (18)$$

where

$$\varphi(\mathbf{q}) = \frac{1}{4} \ln\left(\frac{\prod_{\alpha=1}^4 [\sum_{j=1}^3 \frac{1}{3} \cos[(1 + \frac{1}{2}x)\mathbf{q} \cdot \mathbf{n}_{\alpha j}]]}{\prod_{\alpha=1}^4 \prod_{i=1}^4 \cos^{1/2}[(\sqrt{3}/4)(1+x)\mathbf{q} \cdot \mathbf{e}_{i\alpha}]}\right) \quad (19)$$

and  $\mathbf{q} = (2a/\sqrt{3})\mathbf{k}$  with  $-\pi \leq q_x, q_y, q_z \leq \pi$ . When  $N \rightarrow \infty$  we can use the saddle-point approximation to evaluate this integral, with  $\varphi(\mathbf{q})$  expanded to second order as a Taylor expansion about the extremal point  $\mathbf{q} = \mathbf{0}$ . In this approximation the contribution from each type of oxygen atom  $\alpha$  is the same, and using expressions for the unit vectors  $\mathbf{e}_i$  and  $\mathbf{n}_{\alpha j}$  from the appendix we get

$$Z(\Omega_N) = \left(\frac{3}{2}\right)^N \int_B \frac{d^3\mathbf{q}}{(2\pi)^3} \exp\left[-\frac{N}{6}\mathbf{q}^2\lambda(x) + i\frac{\sqrt{3}}{2a}\mathbf{q} \cdot \Omega_N\right] \quad (20)$$

where  $\lambda(x) = (1 + \frac{1}{2}x)^2 - \frac{3}{8}(1+x)^2$ . Performing the integration gives

$$Z(\Omega_N) = \left(\frac{3}{\pi N}\right)^{3/2} \left(\frac{3}{2}\right)^N \exp\left(-\frac{9\Omega_N^2}{8Na^2\lambda(x)}\right). \quad (21)$$

Considering unit volume ( $N = 3\sqrt{3}/8a^3$ ) and small degrees of polarization the entropy given by  $k_B \ln Z$  is

$$S(\Omega) = S(0) - \frac{\sqrt{3}k_B a}{\lambda(x)} \Omega^2. \quad (22)$$

The optimum value of  $x$  is obtained by minimizing the free energy (i.e. maximizing  $\lambda(x)$ ), which occurs at  $x = 1$  with  $\lambda = \frac{3}{4}$ . In this case, equation (22) gives

$$\Phi = \frac{8}{\sqrt{3}}ak_B T. \quad (23)$$

This is half Jaccard's value (equation (3)) and corresponds to  $G = 3$ . Ignoring the mean-field correction would be equivalent to putting  $x = 0$ , giving  $\lambda = \frac{5}{8}$  or  $G = \frac{5}{2}$ .

### 3. Discussion

Although our theory has been formulated for the ice Ih structure, requiring summation over four oxygen sites, the symmetry of each four-spin cluster is tetrahedral and the result must be isotropic. The same answer would be obtained for ice Ic. Our calculation has established

a value for  $G$  at a level of approximation which is equivalent to the static permittivity calculations of Hollins [13] or Minagawa [14]. Nagle [4] and Adams [7] include the effects of longer range correlations, but with no significant effect on  $G$ , and no anisotropy apparent for ice Ih.

In his treatment of the Jaccard model, Hubmann [15] introduces a dimensionless parameter  $\Gamma$  which has the same status in the Jaccard theory as  $G$  in the theory of dielectric permittivity of pure ice. However,  $\Gamma$  was defined in terms of a polarization variable that is specific to polarization along the  $c$  axis, and this has led to some confusion over the relationship between  $\Gamma$  and  $G$ . It is now clear that Nagle's [5] conclusion that  $\Gamma = G/4$  is correct.

Hubmann [15] describes detailed experiments on pure and doped ice from which he deduced that  $e_{DL} = (0.38 \pm 0.01)e$  and hence, using data with the field along the  $c$  axis, he obtained  $\Gamma = 0.90 \pm 0.05$ . This is commonly quoted as the experimental value for  $\Gamma$  [10]. However, many experiments [16–18] indicate that  $\epsilon_s$  is larger when the electric field is parallel to the  $c$  axis (though one particularly careful experiment [19] designed to test this point showed no anisotropy) and, if such experimental anisotropy exists, care is need in interpreting these measurements.

Some experiments over a wide range of temperatures [17, 18] indicate that anisotropy arises primarily from a Curie–Weiss temperature dependence as  $1/(T - \Delta)$  of the  $c$  axis permittivity in anticipation of a ferroelectric ordering at low temperatures [20, 21]. An interaction leading to such ordering is included in the theory of Minagawa [14, 22] but does not affect the slope of a plot of  $(\epsilon_s - \epsilon_\infty)^{-1}$  versus  $T$ . For comparison with the present theories it is therefore appropriate to use either this slope or a permittivity measured perpendicular to the  $c$  axis. A typical value of  $\epsilon_s - \epsilon_\infty$  is then 100 at 250 K, and with  $G$  now established as about 3.0 it seems appropriate to use the data to calculate  $e_{DL}$ , giving  $0.39e$ . This is compatible with Hubmann's experimental value.

We may test the range of applicability of equation (21) by calculating the entropy of ice which is fully polarized along the  $c$  axis but disordered in the plane perpendicular to this. The corresponding value of  $\Omega_N$  is  $aN/3$  which gives

$$Z(\Omega_{Nmax}) = (3/2e^{1/6})^N = 1.270^N$$

and the entropy per molecule is  $k_B \ln(1.270)$ . Auvert and Villain [23] have shown by an exact calculation that this entropy should be  $k_B \ln(1.175)$ , but it is not surprising that our approximation does not work well in this limit.

#### 4. Conclusion

Our purpose in undertaking this study was to clarify the relationship between the Jaccard theory of the electrical properties of ice and the very detailed theoretical studies that exist on the static permittivity of pure ice. The Jaccard theory is essential for the extension of the theory to more complicated processes such as dielectric relaxation, conductivity, doped ice and space-charge effects [10]. We confirm that both theories involve a single dimensionless parameter, which can be the quantity  $G$  in equation (5). In the theory of the static permittivity it is well established that  $G = 3.0$  to a very close approximation, and we have confirmed this by a very different analysis more clearly applicable to the Jaccard model. This result is shown to be consistent with the experimental data without having to assume a value for the dipole moment of a molecule in the ice structure.

The theoretical value of the Jaccard constant  $\Phi$  is given by equation (23):

$$\Phi \approx \frac{8}{\sqrt{3}}ak_B T$$

where  $a$  is the oxygen–oxygen spacing. Hubmann's constant  $\Gamma$  has the theoretical value of about 3/4, but because of the way that it is defined and confusion about its value in earlier work we recommend that it is not used.

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### Appendix

For a molecule of type 2 in figure 1 the unit vectors  $e_i$  along the bonds are

$$\begin{aligned} e_1 &= \sqrt{\frac{2}{3}}e_x - \frac{\sqrt{2}}{3}e_y - \frac{1}{3}e_z \\ e_2 &= \frac{2\sqrt{2}}{3}e_y - \frac{1}{3}e_z \\ e_3 &= -\sqrt{\frac{2}{3}}e_x - \frac{\sqrt{2}}{3}e_y - \frac{1}{3}e_z \\ e_4 &= e_z. \end{aligned}$$

The unit vectors  $n_{\alpha j}$  for a molecule of type  $\alpha = 2$  are

$$\begin{aligned} n_{21} &= \frac{1}{\sqrt{2}}e_x - \frac{1}{\sqrt{6}}e_y + \frac{1}{\sqrt{3}}e_z \\ n_{22} &= \sqrt{\frac{2}{3}}e_y + \frac{1}{\sqrt{3}}e_z \\ n_{23} &= -\frac{1}{\sqrt{2}}e_x - \frac{1}{\sqrt{6}}e_y + \frac{1}{\sqrt{3}}e_z. \end{aligned}$$

The unit vectors for other molecular sites are obtained by interchanging the signs of appropriate components.

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