Electrostatics of proton arrangements in ice Ic

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Abstract

Possible proton configurations in cubic ice Ic are explored. In a unit cell of eight water molecules there are 90 possible arrangements of the protons, but degeneracy of the Coulomb energy reduces these to four different classes, of which the antiferroelectric structure has the lowest energy, and the fully ferroelectric structure the highest energy. The energy differences per water molecule are in the meV range. There is a one-to-one correspondence between the dipole moment of the unit cell and the electrostatic energy. The energy increments from the antiferroelectric configuration are proportional to the square of the dipole moment. In the 8-molecule cell there are four dipole types. In a cell with 16 oxygens and 32 hydrogens there are 15 dipole types. In both, the degeneracies of the weakly ferroelectric states are high.

Keywords: Ice; Proton order; Electrostatics

1. Introduction

Cubic ice Ic and hexagonal ice Ih are both tetrahedrally hydrogen-bonded, with very similar densities and other physical properties [1,2]. In both, the protons are disordered, each hydrogen nucleus being placed at about 1 Å from the nearer oxygen nucleus along the line joining two neighbouring oxygens. Pauling [3] proposed the proton disorder to explain the low-temperature entropy of ice. The agreement between experiment and theoretical entropy calculations based on completely random proton positions is excellent [1,2]. However, ice Ih doped with KOH has been found to undergo a first-order transition to a ferroelectrically ordered phase of ice, named ice XI, at 72 K [4–6]. A recent neutron diffraction study of D_2O ice Ih doped with KOD [7] shows that below the corresponding transition at 76 K the transformed sample is a mixture of an orthorhombic phase and of hexagonal untransformed ice.

In this paper we calculate the Coulomb energies of various proton arrangements in a cubic superlattice composed of a periodically repeated cubic unit cell containing 8 oxygens and 16 hydrogens, with the oxygens in the diamond lattice structure. The Bernal–Fowler [8] rules (two protons near each oxygen, one proton on each O–O bond) are obeyed, and it is assumed that each proton is at the same fraction f of the oxygen–oxygen distance R, i.e. the O–H distances in each HOH unit are fR. If it is also assumed that the net charge q on each proton and $-2q$ on each oxygen, as well as the chemical bonding of the structure, are not affected by proton rearrangement provided the Bernal–Fowler rules are obeyed, the energy differences between the various proton arrangements will be purely electrostatic. It is these energy differences that we calculate.

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The intention here is not to try to explain the proton or deuteron ordering in doped hexagonal ices, but rather to present a detailed and exact analysis of the most basic model, in the much simpler case of pure cubic ice. The model assumptions were made explicit in the previous paragraph. No account is taken of the possibility that the hydrogen nuclei may lie slightly off the O–O lines, or that the local dipole arrangement may affect the bonding, as is suggested by inelastic neutron scattering spectra in ice Ih [9]. Three main results come from the simple model: the oxygen–hydrogen Coulomb energy is independent of hydrogen placement; the hydrogen–hydrogen energies are in one-to-one correspondence with the squares of the cell dipole moments; and the antiferroelectric (zero dipole) proton arrangement has the lowest energy.

The Coulomb energies can be expressed at q^2/R times a function of f. While R is quoted in a narrow range (2.75–2.76 Å), the oxygen–hydrogen distance $r \equiv fR$ has been determined as low as 0.85 Å by X-ray diffraction [10], and as high as 1.008 Å by neutron diffraction [11], giving a spread of f values from 0.31 to 0.37. An even larger range exists for the charge q on the hydrogen nuclei (with corresponding charge $-2q$ on each oxygen nucleus): if we take the O–H distance (0.9572 Å) and HOH angle (104.52°) together with the dipole moment (0.7296 a.u.) for the bare water molecule [12], the charge giving this dipole moment is $q = 0.3295|e|$. (This charge gives quadrupole moment elements about 6% too high for the lone molecule.) Coulson and Eisenberg [13] have estimated, however, that the dipole moment in ice is about 40% larger than in the isolated molecule. The HOH angle is also slightly larger, being close to the tetrahedral angle $\arccos(-\frac{1}{3}) = 109.47°$; the resulting charge q is $1.4 \times 0.3493|e| = 0.489|e|$, if the lone molecule O–H distance is assumed. Values ranging from $0.41|e|$ to $0.865|e|$ [14, 15] have been used in computer simulations of water and ice.

Given the wide range in the values of f, and the even wider spread in the charge q, we emphasize that our calculations depend only on the assumptions listed in the second paragraph above, and that the deduced energy differences scale as q^2/R. We will accordingly give theoretical expressions for the multiplier of q^2/R, and plots of this multiplier as a function of f, as well as energy differences in electron volts for the mid-range of the parameters f and q.

2. Possible proton arrangements in bulk Ic

Fig. 1 shows a unit cell of cubic ice Ic, containing 8 oxygens. The figure is adapted from Kamb [16]; it has been reproduced as Fig. 3.2 of [1]. The 16 protons are arranged on the numbered O–O bonds, at distance fR from the nearer oxygen and $(1-f)R$ from the other. Consider protons 1, 2, 3 and 4. Each of these has two positions on its bond, "up" and "down", which we represent by 1 and 0, respectively. Each configuration of these four hydrogen nuclei can be coded as a binary number of four digits. Of the 16 proton arrangements, the following six are allowed by the Bernal–Fowler rules (or "ice rules"):

$$
\begin{array}{cccccc}
[0] & [1] & [2] & [3] & [4] & [5] \\
0000 & 0101 & 0110 & 1001 & 1010 & 1111
\end{array}
\tag{1}
$$

Similarly protons $(5, 6, 7, 8)$, $(9, 10, 11, 12)$, $(13, 14, 15, 16)$ must be in one of these allowed configurations. Further, because the unit cell is periodically repeated in all three spatial directions, the proton groups $(1, 6, 11, 16)$, $(2, 5, 12, 15)$, $(3, 8, 9, 14)$ and $(4, 7, 13, 10)$ must also be chosen from the allowed configurations given in (1). It follows that in the 4×4 matrix of proton numbers

$$
\begin{array}{cccc}
1 & 2 & 3 & 4 \\
5 & 6 & 7 & 8 \\
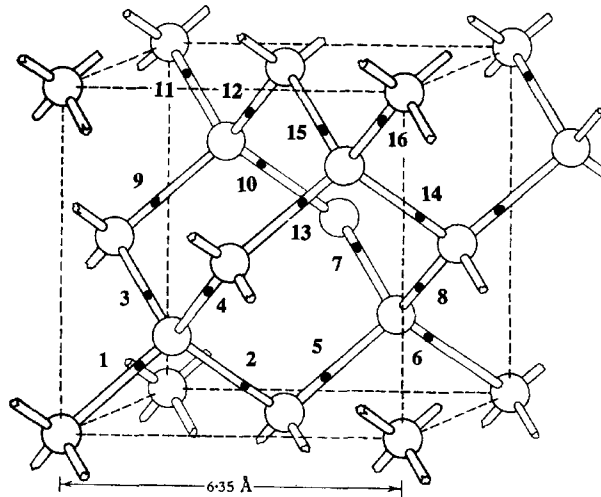9 & 10 & 11 & 12 \\
13 & 14 & 15 & 16
\end{array}
\tag{2}
$$

Fig. 1. One possible proton configuration in an 8-molecule unit cell of ice Ic. The 16 protons within the cell, and two outside it, are indicated by black dots. The configuration shown is [3223], one of 12 antiferroelectric arrangements. In total, 90 configurations are allowed by the ice rules.

each row, both diagonals and both broken diagonals $(2,5,12,15)$ and $(3,8,9,14)$ must be chosen from the set (1). There are 90 configurations which obey the constraints imposed by the ice rules. We shall see that there is a lot of degeneracy, and in fact that the 90 configurations give only four different Coulomb energies.

First we define a shorthand notation for the 16 proton positions in terms of the numbers [0] to [5] of the allowed arrangements in any given row, as labelled in (1). Thus, $[r1, r2, r3, r4]$ defines the 16 proton positions in terms of the four row numbers $r1$ to $r4$; for example:

$$
[0000] \equiv \begin{matrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{matrix}
\qquad
[0101] \equiv \begin{matrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 \end{matrix}
$$

$$
[0140] \equiv \begin{matrix} 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \end{matrix}
\qquad
[3223] \equiv \begin{matrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 1 & 0 & 0 & 1 \end{matrix}
\qquad (3)
$$

Of these four examples, [0000] is fully ferroelectric, with all the protons in the down position, [3223] is antiferroelectric, with half the protons up and half down, and the other two states are partially ferroelectric, with four protons up and twelve down.

It is clear that for any allowed state there will be an allowed inverse, with up and down (1 and 0) interchanged: thus [5555] is just [0000] with the diagram turned upside down, etc. We can accordingly deal just with the 45 states which have $r1 = 0, 1$ or 2.

3. Dipole and quadrupole moments

To classify the possible proton arrangements, we calculate the dipole and quadrupole moments of the unit cell, for each arrangement. The dipole and quadrupole moments of the oxygens are identically zero.

For the protons we first define position in terms of the binary digits b_i (zero or unity) which specify whether proton i is in the up ($b_i = 1$) or down ($b_i = 0$) state. Let $\boldsymbol{u}_i$ and $\boldsymbol{d}_i$ be the oxygen positions at the upper and lower ends of the bond which contains proton i. For example, $\boldsymbol{u}_2 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})L$, $\boldsymbol{d}_2 = (\frac{1}{2}, \frac{1}{2}, 0)L$, where $L = 4R/\sqrt{3}$ is the edge length of the cubic cell (this is 6.35 Å for $R = 2.75$ Å) and the origin of coordinates is at the near bottom corner of the cell. The position vector of proton i is then

$$\boldsymbol{r}_i = [1 - f - b_i(1 - 2f)]\boldsymbol{d}_i + [f + b_i(1 - 2f)]\boldsymbol{u}_i. \tag{4}$$

The dipole moment for the cell, which is centered at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})L$, is

$$\boldsymbol{D} = q\left[\sum \boldsymbol{r}_i - (8, 8, 8)L\right]$$

$$= q(1 - 2f)\left[\sum b_i(\boldsymbol{u}_i - \boldsymbol{d}_i) - (0, 0, 2)L\right]. \tag{5}$$

The vectors $\boldsymbol{u}_i - \boldsymbol{d}_i$ are of four types, according to which column of the array (2) the proton i is in:

$$\boldsymbol{u}_i - \boldsymbol{d}_i = \begin{cases} (1, 1, 1)L/4, & \text{(column 1)}, \\ (-1, -1, 1)L/4, & \text{(column 2)}, \\ (-1, 1, 1)L/4, & \text{(column 3)}, \\ (1, -1, 1)L/4, & \text{(column 4)}. \end{cases} \tag{6}$$

Thus, the dipole moment of a given configuration has components

$$D_x = \tfrac{1}{4}qL(1 - 2f)\left(\sum_{c1} - \sum_{c2} - \sum_{c3} + \sum_{c4}\right)b_i,$$

$$D_y = \tfrac{1}{4}qL(1 - 2f)\left(\sum_{c1} - \sum_{c2} + \sum_{c3} - \sum_{c4}\right)b_i, \tag{7}$$

$$D_z = \tfrac{1}{4}qL(1 - 2f)\left(\sum b_i - 8\right),$$

where $\sum_{c1} b_i$ means the sum of the four b_i entries in column 1 of the array in (2), etc.

We note that all components of the dipole moment of the cell are identically zero when $f = \frac{1}{2}$, that is when the protons are half-way along the oxygen–oxygen bond line. We also note that the z (vertical) component of the dipole moment is zero for all configurations in which half the protons are up and half are down (so that $\sum b_i = 8$), but that only some of these are antiferroelectric, with all dipole components zero.

All of the 45 proton configurations with entries $r1 = 0, 1$ or 2 fall into four categories of dipole moment. These are listed below, the dipoles being the listed components times $qL(1 - 2f)$:

Dipole components	Number of configurations	Prototype	
$(-2, 0, 0)$ or $(0, -2, 0)$ or $(0, 0, -2)$	3	[0000]	
$(0, \pm 1, \pm 1)$ or $(\pm 1, 0, \pm 1)$ or $(\pm 1, \pm 1, 0)$	12	[0101]	(8)
$(\pm 1, 0, 0)$ or $(0, \pm 1, 0)$ or $(0, 0, \pm 1)$	24	[0140]	
$(0, 0, 0)$	6	[3223]	

The six configurations with zero dipole moment are antiferroelectric, the others are partially or fully ferro-electric.

It happens that the dipole classification has one-to-one correspondence with the energy degeneracy, as we shall see in the next section. Nevertheless, we give the quadrupole moment results as well, for completeness: we find that all the allowed proton configurations have zero diagonal components of the quadrupole tensor, and one non-zero off-diagonal element equal to $\pm\frac{3}{2}qL^2(1-2f)$. No configuration has the quadrupole moment identically zero; on the other hand when $f \to \frac{1}{2}$ all configurations become equivalent, and have null quadrupole as well as dipole moments.

4. Coulomb energies

We wish to evaluate the electrostatic energy of a superlattice composed of the cubic unit cell of Fig. 1, for various proton arrangements within the unit cell. There is a large literature dealing with such problems, most of it relating to Ewald's method. The author [17] developed a method which is more compact, and also is faster in situations where the charges within a cell are well spaced out [18]. We quote the essential results here: the potential energy of a pair of charges q_1 and q_2, and of their repetition to infinity in identical cubic cells in all three dimensions, is given by

$$\frac{q_1 q_2}{L^2}[V(\xi,\eta,\zeta) + C],$$ (9)

where $\xi = (x_1 - x_2)/L$, $\eta = (y_1 - y_2)/L$, $\zeta = (z_1 - z_2)/L$, $C = 3.19134\ldots$ and V involves a sum over modified Bessel functions K_0:

$$V(\xi,\eta,\zeta) = 4 \sum_{\ell=1}^{\infty} \cos(2\pi\ell\xi) \sum_{m,n=-\infty}^{\infty} K_0(2\pi\ell[(\eta+m)^2 + (\zeta+n)^2]^{1/2})$$

$$+ 2\pi\eta^2 - \log \lim_{M\to\infty} \prod_{-M}^{M} \frac{\cosh[2\pi(\eta+m)] - \cos(2\pi\zeta)}{\cosh(2\pi m)}.$$ (10)

The total energy per cell of the Coulomb interactions of all the particles within a cell, and of all of their periodic repetitions, is given by a sum over all pairs of terms like (9). The cell must be neutral, otherwise the total energy would diverge. Neutrality is assumed in the derivation of (9), as it is in the Ewald method: see the first and last paragraphs in Section 4 of [17].

We note that only relative displacements enter into the Coulomb energy, but that these enter as vectors rather than as distances in the Coulomb energy of a pair of isolated charges q_1 and q_2, which is $q_1 q_2/r_{12}$. Because of the translational and cubic symmetries, many potential terms are equal. Although this is not obvious from (10), the potential V is invariant with respect to any permutation of ξ, η and ζ, and is periodic in all three variables, with period 1. It is clear from (10) that V is even in all three variables.

The total electrostatic energy per cell containing 8 oxygen and 16 hydrogen nuclei is

$$U = \frac{(2q)^2}{L}(V_{OO} + 28C) + \frac{q^2}{L}(V_{HH} + 120C) - \frac{2q^2}{L}(V_{OH} + 128C)$$

$$= \frac{q^2}{L}\{4V_{OO} + V_{HH} - 2V_{OH} - 24C\},$$ (11)

where each of V_{OO}, V_{HH} and V_{OH} is a sum over all pairs of the relevant particles. For example, there are 28 oxygen–oxygen interactions. With the oxygens at L times

$$000, \quad 0\tfrac{1}{2}\tfrac{1}{2}, \quad \tfrac{1}{2}0\tfrac{1}{2}, \quad \tfrac{1}{2}\tfrac{1}{2}0,$$
$$\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4}, \quad \tfrac{1}{4}\tfrac{3}{4}\tfrac{3}{4}, \quad \tfrac{3}{4}\tfrac{1}{4}\tfrac{3}{4}, \quad \tfrac{3}{4}\tfrac{3}{4}\tfrac{1}{4}, \tag{12}$$

the displacements reduce, by the symmetries discussed above, to 16 of type $\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4}$ and 12 of type $0\tfrac{1}{2}\tfrac{1}{2}$, so only two values of (10) are needed:

$$V_{OO} = 16V(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}) + 12V(0, \tfrac{1}{2}, \tfrac{1}{2}). \tag{13}$$

The simplest proton arrangement is that of the fully ferroelectric states [0000] and [5555], for which we find

$$V_{OH} = 16V(\tfrac{f}{4}, \tfrac{f}{4}, \tfrac{f}{4}) + 16V(\tfrac{1}{4} - \tfrac{f}{4}, \tfrac{1}{4} - \tfrac{f}{4}, \tfrac{1}{4} - \tfrac{f}{4})$$
$$\quad + 48V(\tfrac{f}{4}, \tfrac{1}{2} - \tfrac{f}{4}, \tfrac{1}{2} - \tfrac{f}{4}) + 48V(\tfrac{1}{4} - \tfrac{f}{4}, \tfrac{1}{4} + \tfrac{f}{4}, \tfrac{1}{4} + \tfrac{f}{4}), \tag{14}$$

$$V_{HH}^{002} = 24V(0, \tfrac{1}{2}, \tfrac{1}{2}) + 8V(0, \tfrac{f}{2}, \tfrac{f}{2}) + 8V(0, \tfrac{1}{2} - \tfrac{f}{2}, \tfrac{1}{2} - \tfrac{f}{2})$$
$$\quad + 16V(\tfrac{f}{2}, \tfrac{1}{2} - \tfrac{f}{2}, \tfrac{1}{2}) + 32V(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4} - \tfrac{f}{2}) + 32V(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4} + \tfrac{f}{2}). \tag{15}$$

It is shown in the appendix that expression (14) gives the oxygen–hydrogen Coulomb interactions for *all* possible proton arrangements; hence, we have omitted the dipole type 002 on V_{OH}. On the other hand, there are four different values of V_{HH}, corresponding to the four dipole classifications:

$$V_{HH}^{011} = V_{HH}^{002} + 8\varDelta,$$
$$V_{HH}^{001} = V_{HH}^{002} + 12\varDelta, \tag{16}$$
$$V_{HH}^{000} = V_{HH}^{002} + 16\varDelta,$$

where the energy difference for hydrogen–hydrogen interactions in the [0101] and [0000] arrangements, per HOH unit, is given by q^2/L times $\varDelta$, with

$$\varDelta(f) = \{V_{HH}^{001}[0101] - V_{HH}^{002}[0000]\}/8$$
$$\quad = V(\tfrac{f}{2}, \tfrac{1}{2} - \tfrac{f}{2}, \tfrac{1}{2}) + V(\tfrac{1}{4} - \tfrac{f}{2}, \tfrac{1}{4} + \tfrac{f}{2}, \tfrac{1}{4} + \tfrac{f}{2}) - V(0, \tfrac{1}{2}, \tfrac{1}{2}) - V(\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4} + \tfrac{f}{2}). \tag{17}$$

Thus, the degeneracy among the Coulomb energies of the possible proton arrangements is such that there are only four different energies, and further, the energy differences are all multiples of $\varDelta$, in proportion to square of the associated dipole moment.

The function $\varDelta(f)$ is symmetric about $f = \tfrac{1}{2}$ (at which value the protons each lie half-way between their two oxygen bonding neighbours). Note that $\varDelta$ is zero at $f = 0$ and $f = \tfrac{1}{2}$, as expected on physical grounds.

5. Numerical results and discussion

The oxygen–oxygen Coulomb energy, per water molecule, is
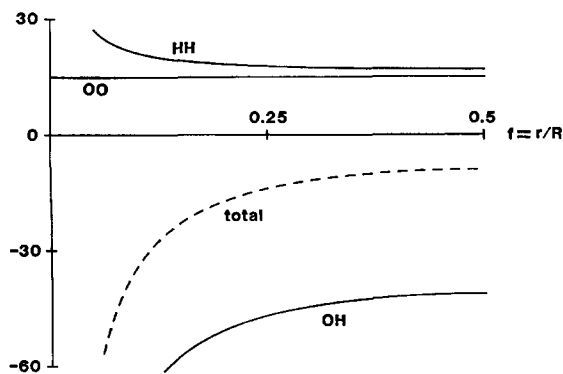
$$u_{OO} = \frac{4q^2}{L}(V_{OO} + 28C)/8. \tag{18}$$

Fig. 2. Coulomb energies as a function of $f = r/R$ ($r = $ O–H distance, $R = $ O–O distance), in units of q^2/R, per molecule. The oxygen–hydrogen, hydrogen–hydrogen and total curves are labelled. The oxygen–oxygen Coulomb energy ($14.992q^2/R$) is represented by the horizontal line. The differences between the various proton configurations are not visible on the HH curve at this scale.

This evaluates to $34.623q^2/L$ or $14.992q^2/R$ (since $L = 4R/\sqrt{3}$). The oxygen–hydrogen and hydrogen–hydrogen Coulomb energies, per HOH unit, are

$$u_{OH} = \frac{-2q^2}{L}(V_{OH} + 128C)/8, \tag{19}$$

$$u_{HH}^{002} = \frac{q^2}{L}(V_{HH}^{002} + 120C)/8. \tag{20}$$

These vary with the ratio $f = r/R$ which gives the proton positions along the O–O bond lines. Fig. 2 shows the coefficients of q^2/R for the O–H and H–H energies, as well as of the total energy. In the range $f = 0.31$–0.37 which is of physical interest, there is a decrease of about 5% in the Coulomb binding energy. At $f = 0.35$ the coefficients of q^2/R in u_{OH} and u_{HH}^{002} are -42.52 and 17.12; the coefficient of q^2/R in the total Coulomb energy is -10.40. For $q = 0.5|e|$ and $R = 2.75$ Å, this gives a binding energy per molecule of -13.62 eV, since q^2/R is then 1.309 eV. We can compare this with the Coulomb energy of an isolated molecule with the same charges and the O–H distance $r = 0.35R$, and with the angle HOH taken as the tetrahedral angle arccos $(-\frac{1}{3})$. This energy is

$$E = \frac{-4q^2}{r}\left(1 - \frac{1}{8}\sqrt{\frac{3}{2}}\right), \tag{21}$$

which evaluates to -12.67 eV, giving lattice electrostatic binding of 0.95 eV per molecule. The charge $q = 0.39|e|$ would give 0.58 eV per molecule, in agreement with the experimental lattice energy [2, p. 39].

Our main interest lies in the energy differences between the various proton arrangements. These are all multiples of $\Delta(f)$, which is given in (17) and plotted in Fig. 3. We see that Δ is never positive; it reaches a minimum of $\Delta_m \approx -0.013q^2/L$ at $f \approx 0.22$. It follows that (for all possible values of f) the antiferroelectric states, of which [3223] is the prototype, have the lowest energy in bulk cubic ice. For $f = 0.35$ Δ, takes the value $-0.007q^2/L \approx -0.003q^2/R$, which evaluates to -0.004 eV for the q and R values used above. The energy difference between the completely ferroelectric proton arrangement and the antiferroelectric state is twice this, namely 8 meV per molecule.

As the unit cell is enlarged, we expect the number of energetically distinct configurations to increase, with new levels appearing but with the antiferroelectric states still having the lowest energy. Doubling the cell size
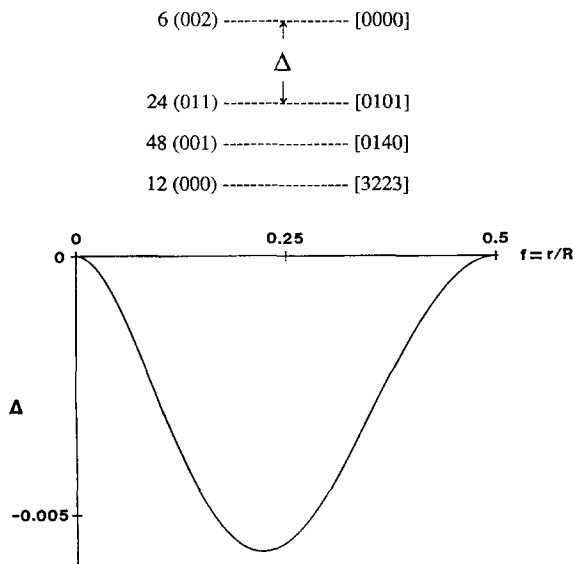
Fig. 3. Energy level diagram, and the energy difference Δ between the [0000] configuration (all protons down) and the [0101] configuration (four protons up), as a function of $f = r/R$. In the energy level diagram, the first column gives the degeneracy, the second gives the dipole moment in units of $qL(1 - 2f)$, and the third a representative configuration. The energy difference Δ is shown in units of q^2/R; note the scale compared to that in Fig. 2. Since Δ is negative, the fully ferroelectric proton configurations have the highest energy, and the antiferroelectric configurations have the lowest energy.

by doubling one of its dimensions gives 6426 possible configurations for the 32 protons. These configurations are of 15 dipole types, listed below:

000	001	$\frac{1}{2}\frac{1}{2}1$	011	$\frac{1}{2}1\frac{3}{2}$	002	012	$1\frac{3}{2}\frac{3}{2}$	112	$\frac{1}{2}1\frac{5}{2}$	022	003	$\frac{1}{2}\frac{1}{2}3$	013	004
0	2	3	4	7	8	10	11	12	15	16	18	19	20	32
210	576	720	384	496	268	328	48	48	48	20	32	16	16	3

The first row denotes the type of dipole components, with entry abc standing for dipole values $qL(1 - 2f)$ times any permutation of $(\pm a, \pm b, \pm c)$. The second row entries are proportional to the square of the dipole moment; the numbers given are $2(a^2 + b^2 + c^2)$. The last row gives half of the number of proton configurations with the given type of dipole moment; the entries add to 3213.

We see that there are large numbers of weakly ferroelectric states with small cell dipole moments, relative to both the antiferroelectric states and the strongly ferroelectric states with large dipole moment. The zero-moment antiferroelectric states are 6.5% of the total; in the 8-molecule cell they were 13.3% of the total.

It seems likely that Coulomb energies of larger cells will continue to be correlated with cell dipole moment. If so, the trends shown above indicate that while energetics favour the antiferroelectric proton configurations, entropy favours those that are weakly ferroelectric. An order–disorder phase transition, if it exists in pure ice, would then be from an antiferroelectric low-temperature ordered phase to a disordered weakly ferroelectric phase. This is in agreement with a recent simulation [15], but not with earlier theoretical predictions [19, 20], which did not sum the Coulomb interactions exactly.

Acknowledgements

Appendix. Invariance of V_{OH}

We wish to show that the oxygen–hydrogen Coulomb interactions are unaffected by proton rearrangement, provided the protons stay on the oxygen–oxygen lines and move from a position at $r = fR$ from the nearest oxygen to a position at fR from the other oxygen.

With reference to Fig. 1, we note that a legal move (one obeying the ice rules) can be made up from a chain of illegal moves. For example, from the fully ferroelectric arrangement, with all protons down, we can form another allowed configuration by moving protons 1, 4, 13 and 16 up on their bonds.

Again with reference of Fig. 1, it is apparent that there are just two different types of proton position in the unit cell: between a corner oxygen and an inside oxygen, and between a face oxygen and an inside oxygen. Protons 1 and 2 are of these two types, respectively.

Consider the single illegal move in which proton 1 moves from $r/L = (g, g, g)$ to $r'/L = (\frac{1}{4} - g, \frac{1}{4} - g, \frac{1}{4} - g)$, where $g = f/4$. The eight displacements from proton 1 to the oxygens are all changed, but in such a way that there is a one-to-one equivalence between the original set of eight displacements and the new set. (The displacements are calculated from r, r' and the oxygen coordinates given in (12).) For example

$$(-g, \tfrac{1}{2} - g, \tfrac{1}{2} - g) \equiv (g, \tfrac{1}{2} + g, \tfrac{1}{2} + g) \tag{A1}$$

from the fact that potential $V(\xi, \eta, \zeta)$ is invariant with respect to change of sign of any of the variables, and is also periodic (with unit period) in all three variables. With reference to (12), we find that the displacement between r and an oxygen in the top row is equivalent to displacement between r' and the oxygen directly below, and vice versa.

The same result holds for an illegal move made with proton 2, from $r/L = (\frac{1}{2} - g, \frac{1}{2} - g, g)$ to $r'/L = (\frac{1}{4} + g, \frac{1}{4} + g, \frac{1}{4} - g)$. In this case the equivalence is between displacements relative to oxygens designated by coordinates in the top row of (12), and those with coordinates in the bottom row in reversed order.

Since any legal move is made up from a chain of illegal moves, it follows that the oxygen–hydrogen Coulomb energy is independent of the hydrogen placement. This result has been obtained for a unit cell containing 8 oxygens and 16 hydrogens, in cubic ice Ic, but we suspect that it is more general.

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