Surface Structure of Water and Ice
II. A Revised Model

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ABSTRACT

The author's 1962 treatment of the surface structure of water and ice is reconsidered in the light of new theoretical information on the quadrupole moment of the water molecule and on the structure of liquid water. Electrostatic effects are explicitly taken into account and it is concluded that the principal mechanism driving molecular orientation at a liquid water surface is the interaction between molecular dipole and quadrupole moments in the partially oriented region near the surface. The preferred molecular orientation is that with protons directed outwards from the liquid and the dipole layer so formed, modified by the presence of an equilibrium ionic atmosphere, leads to a calculated surface potential jump of about $0 \cdot 1$ v, the surface being positive with respect to the bulk liquid. In the case of an ice surface, the free energy available from surface polarization is sufficient to drive a surface phase change at temperatures a few degrees below the melting point. It is concluded that, at temperatures above about $-(5 \pm 3)°c$ the surface of ice is covered by a quasi-liquid layer whose thickness is of order 10 to 40 Å, increasing as the temperature approaches 0°c. The equilibrium ionic concentration in this layer accounts qualitatively for the large surface electrical conductivity of ice.

§ 1. INTRODUCTION

MORE than 100 years ago, Michael Faraday proposed that the surface of ice, when not too far below the melting point, is covered by a thin liquid-like layer. His proposal was put forward to account for surface phenomena like regelation and the abnormally low coefficient of friction of ice, some of which are now known to be accounted for by pressure melting or by frictional heating. More recently, however, Weyl (1951) revived these ideas and the present author (Fletcher 1962, to be referred to as I) attempted to justify a liquid-surface model from statistical and thermodynamic considerations and to make semi-quantitative estimates of some of the quantities involved.

This attempt was criticized by Watts-Tobin (1963) for its neglect of long-range electrostatic interactions, a criticism which was justified but, in the view of the present author (Fletcher 1963), too extreme—all that was required was a modification of the model rather than its complete abandonment.

In recent years, several writers have given serious attention to the liquid-surface model in interpreting some of the properties of ice and measurements of surface diffusion (Bryant, Hallett and Mason 1960,

Hallett 1961, Mason, Bryant and Van den Heuvel 1963) and of surface electrical conductivity (Jaccard 1967) have provided additional evidence for some sort of progressive phase change in ice surfaces within 10 or 20 degrees of the melting point. Because of this continuing interest and because new data are available upon which to base a significantly improved discussion, it now seems worth while to attempt a revision of the theory. It must be emphasized that the model, as applied both to liquid water and to ice, still remains speculative but it is hoped that the present more careful treatment will disclose additional approaches by which its validity can be checked theoretically or experimentally.

§ 2. Surface Orientation Energy

It was proposed in I that the driving force leading to a surface phase transition in ice is the electrical asymmetry of the water molecule. To a first approximation this molecule is tetrahedral, with two positive vertices at the proton positions and two negative vertices due to more or less hybridized lone-pair orbitals. It is obvious that positive and negative vertices are not equivalent, so that a surface molecule with vertices of one sign directed out of the liquid must have an energy different from that of a molecule of opposite orientation.

In I an oversimplified model was used for the water molecule and, on the basis of this, it was concluded that the low energy orientation at the surface of liquid water was that with the protons directed inwards. The energy difference between the two orientations was estimated as a few times 10^{-13} erg or about one hydrogen-bond equivalent. We will now show that this conclusion is incorrect: the low energy orientation is that with the protons directed outwards at the surface.

There are now available several reasonably consistent quantum mechanical treatments of the water molecule (Ellison and Shull 1953, 1955, McWeeny and Ohno 1960) which give quite good agreement with the experimental dipole moment (1.84×10^{-18} e.s.u.) and allow a calculation to be made of the quadrupole moments of the molecule. This has been done by Glaeser and Coulson (1965) who, with the definition

$$Q_{\alpha\beta} = \int r_\alpha r_\beta \rho(\mathbf{r})\, d\mathbf{r}, \qquad \cdots \cdots \cdots \quad (1)$$

where $\rho(\mathbf{r})$ is the electrical charge density at $\mathbf{r}$, find the different treatments to agree approximately on the values

$$Q_{xx} \simeq -6.5 \times 10^{-26}; \quad Q_{yy} \simeq -5.3 \times 10^{-26}; \quad Q_{zz} \simeq -5.6 \times 10^{-26}\, \text{e.s.u.,} \quad (2)$$

where the z axis is taken to bisect the H–O–H angle in the plane of the molecule and the x axis is perpendicular to this plane.

The important thing is that these moments are all negative and approximately equal in magnitude. In particular, the moment Q_{zz} differs in sign from that implied by the molecular model used in I—it is not the proton vertices but rather the lone-pair vertices which are the

most polar part of the molecule and it is for this reason that the lowest energy configuration is that with the protons directed outwards.

Estimation of the energy difference between the two configurations of surface molecules is a difficult problem which could, however, be solved by evaluating the energy in the electric field outside a surface consisting of outward-directed molecules on a lattice of spacing c and subtracting from this the energy outside a surface consisting of inward-directed molecules. The algebra involved in this calculation is formidable, but it can easily be seen that the order of magnitude of the result is the dipole–quadrupole interaction energy :

$$\epsilon \sim \frac{\mu Q_{zz}}{c^4} \sim -10^{-13}\,\mathrm{erg}. \qquad \ldots \ldots \quad (3)$$

In any real situation, however, this energy difference will be almost completely masked by the adsorption of non-polar gas molecules, of air for example, at the liquid surface. The effective value ϵ_1 of ϵ will then be considerably smaller than indicated by (3) and will, in fact, be too small to drive any major molecular orientation in the liquid surface. We shall, however, include the surface term formally in the total energy of the system for completeness. To do this, suppose that a fraction α_0 of the surface molecules have their dipoles directed out of the surface. Then if there are n surface molecules per unit area, the energy of the surface from this cause exceeds that of a random surface by :

$$\Delta U_1 = n(\alpha_0 - \tfrac{1}{2})\epsilon_1, \qquad \ldots \ldots \ldots \quad (4)$$

where $n \simeq 1 \times 10^{15}\,\mathrm{cm}^{-2}$ and $\epsilon_1 \sim -1 \times 10^{-14}\,\mathrm{erg}$.

Despite the small value of ϵ_1, surface orientation can still take place and the driving force turns out to be the long-range electrostatic interactions between water molecules through their dipole and quadrupole moments—the very interactions which were neglected in I. To see how this comes about we first consider the case of a liquid water surface and then apply our conclusions to ice surfaces.

§ 3. The Surface of Water

If molecular orientation is to occur at a liquid surface it must be because the free energy of the total system is lower when the surface molecules are oriented than when they are completely random. Because of the large amount of hydrogen bonding in liquid water, any orientation cannot be confined to surface molecules but will persist some small distance below the surface and the entropy loss associated with this ordering must be balanced against the energy gain at the surface. In addition, the dipole moments of oriented molecules will produce a net electric field normal to the surface and the interaction of molecular dipoles with this field and of molecular quadrupoles with its gradient must be included in the free energy balance. Finally we must recognize that water is

not a perfect dielectric but contains free ions. These ions will be partially separated in the electric field near the surface in such a way as to reduce its magnitude and this effect must also be included.

Discussion of the surface structure of liquid water is made difficult by lack of a generally accepted model for the structure of bulk water itself. Pople (1951) put forward a model in which the structure is uniform, completely bonded and ice-like, except that bond lengths and bond angles have a statistical distribution, the average bond angle distortion near 0°c being about 26°. This model gives good agreement with the radial distribution function at various temperatures but has not been extended to include detailed thermodynamic calculations. On the other hand, we have various cluster models in which water is pictured in terms of small groups of tetrahedrally bonded molecules separated from one another either by unbonded molecules or by some antagonistic bonding type. Among the best known cluster theories are those of Némethy and Scheraga (1962), who derived a cluster size of about 90 molecules near 0°c, and the various 'significant structure' approaches of Eyring and others (for example Jhon, Grosh, Ree and Eyring 1966) in which the cluster size is about 50 molecules.

We do not believe that either group of theories presents a completely true picture. Bond bending is completely omitted from cluster theories despite strong evidence for its occurrence in the high pressure ices and despite infra-red evidence that hydrogen bond strengths in water cover a continuous range of values, while the uniform theories neglect cooperative clustering, despite the fact that there are certainly cross terms in the polarizability tensor in tetrahedral fields, even if cooperative hybridization is not fully established. The truth undoubtedly lies somewhere in between.

We can, however, derive useful and consistent information from both groups of theories. In Pople's model the bond angle uncertainty is about 26° so that we must traverse four bonds or about 11 Å before the uncertainty amounts to half the bond angle. The coherence length in the structure is thus about 10^{-7} cm. Similarly, in the cluster theories, we must traverse a distance roughly equal to a cluster diameter before coherence is lost. For clusters of 50 to 100 molecules, this distance is again about 10^{-7} cm. We should therefore expect this coherence length to persist as a feature of any more realistic intermediate theory. There is a slight variation with temperature, the coherence length being reduced by about 30% at 100°c, but we need not consider this refinement here.

Because of this cooperative bonding within the liquid, any ordering imposed upon molecules at a surface or interface will decay away from the interface in a characteristic length, l, which is of the same order as the coherence length discussed above. This will apply, in particular, to molecular orientation, which is transmitted to neighbouring molecules by the conditions of hydrogen bonding. The analytic form of the decay of orientation away from the surface will be determined by details of the water structure but it is probably a good approximation to represent

it as exponential. Thus if α measures the orientation at a depth z below a surface of orientation α_0, we can write:

$$\alpha(z) = \tfrac{1}{2} + (\alpha_0 - \tfrac{1}{2}) \exp(-z/l), \quad \ldots \ldots \quad (5)$$

where $l = 10^{-7}$ cm.

In I we used an ice-like model for liquid water to calculate the entropy penalty of orientation, but this is not necessary. Indeed, for a layer containing n molecules per unit area, of which a fraction α are constrained to have their dipoles pointing outward, the entropy penalty is seen immediately to be:

$$-\delta S = nk[\alpha \ln \alpha + (1-\alpha) \ln(1-\alpha) + \ln 2]. \quad \ldots \quad (6)$$

If each molecular layer has a thickness $d \simeq 3 \times 10^{-8}$ cm, then the total entropy change produced by a surface ordering α_0 is:

$$\Delta S \simeq -2(\alpha_0 - \tfrac{1}{2})^2 nlk/d, \quad \ldots \ldots \ldots \quad (7)$$

provided $|\alpha_0 - \tfrac{1}{2}| \ll 1$. In this and other parts of the calculation we have treated most of the quantities involved as continuous functions of z, the justification being that they are really ensemble-average quantities over the microscopic configurations of the liquid.

Now let us consider electrostatic terms. The moment per unit area of a molecular layer of orientation α is:

$$M = 2(\alpha - \tfrac{1}{2})n\mu \overline{\cos \theta} = (\alpha - \tfrac{1}{2})n\mu, \quad \ldots \ldots \quad (8)$$

where μ is the magnitude of the molecular dipole and $\cos \theta$ is averaged over all orientations in which the dipole points out of the surface. The potential drop across this layer is $4\pi M/k$, where $K \simeq 3$ is the electronic and distortional part of the dielectric constant of water. The macroscopic electric field in the z direction in this layer is thus:

$$E_1(z) = \frac{4\pi M}{Kd} = \frac{4\pi(\alpha_0 - \tfrac{1}{2})n\mu}{Kd} \exp(-z/l) \quad \ldots \ldots \quad (9)$$

and, if $\alpha_0 > \tfrac{1}{2}$ so that protons are directed preferentially outward at the water surface, then E_1 is positive and the potential at the surface is higher than that within the bulk liquid.

Now in bulk water there is an equilibrium concentration $\rho_+(\infty) = \rho_-(\infty) \simeq 3 \times 10^{15}$ cm^{-3} of positive and negative ions. These will distribute themselves in the potential gradient near the surface in such a way as to shield the electrostatic effects of the oriented dipoles and thereby to reduce the total free energy of the system. The negative ions will thus form a concentrated layer just inside the surface where the electrostatic potential is highest, while a balancing excess of positive ions will form a more diffuse concentration slightly deeper into the liquid. If $\rho_+(z)$ and $\rho_-(z)$ are the ionic concentrations at a depth z below the surface, then the field which they produce will be:

$$E_2(z) = \frac{4\pi q}{K} \int_0^z (\rho_+ - \rho_-) dz, \quad \ldots \ldots \ldots \quad (10)$$

where $\pm q$ is the charge on an individual ion. In addition we have, for

self-consistency, the requirement that both positive and negative ions should obey a Boltzmann distribution in the total potential:

$$\rho_{\pm}(z) = \rho_{\pm}(\infty) \exp\left\{ \mp \frac{q}{kT} \int_z^\infty [E_1(z) + E_2(z)]\, dz \right\}. \qquad (11)$$

Solution of (9), (10) and (11) is difficult because they form a non-linear set and the usual linearizing approximation that the potential is everywhere small compared with kT cannot be applied. We must therefore be content with an approximation solution. To that end we note that the charge distribution in the double layer can be represented approximately by:

$$\rho(z) = \rho_+(z) - \rho_-(z) \simeq -a \exp(-z/\lambda) + (a\lambda/\eta) \exp(-z/\eta), \qquad (12)$$

provided $\lambda < \eta$. This expression shows the correct general behaviour and integrates to zero as required. It contains three parameters which can be determined to give best fit with the true charge distributions by requiring that (12) satisfy the Boltzmann condition (11) at three representative distances z. This is approximately equivalent to minimizing the free energy associated with the charge distribution (12) in the potential generated by the self-consistent field $E_1(z) + E_2(z)$.

From (11) in the limit as $z \to \infty$ we find:

$$\eta = l, \qquad \ldots \ldots \ldots \ldots \qquad (13)$$

while from (11) evaluated at the point where the potential passes through zero so that $\rho(z) = 0$:

$$\lambda a = (\alpha_0 - \tfrac{1}{2}) n\mu/qd . \qquad \ldots \ldots \ldots \qquad (14)$$

Finally, from the behaviour at $z = 0$ and the approximation $\lambda \ll l$, together with the results (13) and (14), we find:

$$a \ln[a/\rho(\infty)] \simeq \frac{4\pi(\alpha_0 - \tfrac{1}{2})^2 n^2 \mu^2}{Kd^2 kT}. \qquad \ldots \ldots \qquad (15)$$

This equation can easily be solved graphically for a given value of α_0 so that all the parameters in (12) can be determined. The calculated value of a is shown in fig. 1 as a function of α_0. The effective value of λ is less than 10^{-8} cm over most of the range of α_0 so that the assumption $\lambda \ll l$ is justified. Since this length is so small, all the negative ions are effectively localized in the surface monolayer. The total surface concentration λa of ions of one sign is also plotted in fig. 1. We shall return to discuss the significance of this plot later.

Turning now to evaluate the electrostatic part of the energy associated with molecular orientation, we recall that it consists of two parts: the interaction of molecular dipoles with the total field $E = E_1 + E_2$ and the interaction of molecular quadrupoles with the gradient of this field.

Taking the quadrupole energy first, we note that since $Q_{xx} \simeq Q_{yy} \simeq Q_{zz}$ the interaction is almost independent of molecular orientation and we may use an average isotropic quadrupole moment $\bar{Q} \simeq -6 \times 10^{-26}$. We note further that the part of the field, E_2, due to the ionic atmosphere

and given by (10) and (12) contributes nothing to the quadrupole energy when integrated over z. The total quadrupole energy of a surface of orientation α_0 is thus, from (9):

$$\Delta U_2 = \int_0^\infty \bar{Q} \frac{dE_1}{dz} d(z/d) = \frac{4\pi(\alpha_0 - \frac{1}{2})n^2\mu\bar{Q}}{Kd^2}, \quad \cdots \quad (16)$$

which is negative if $\alpha_0 > \frac{1}{2}$.

Fig. 1
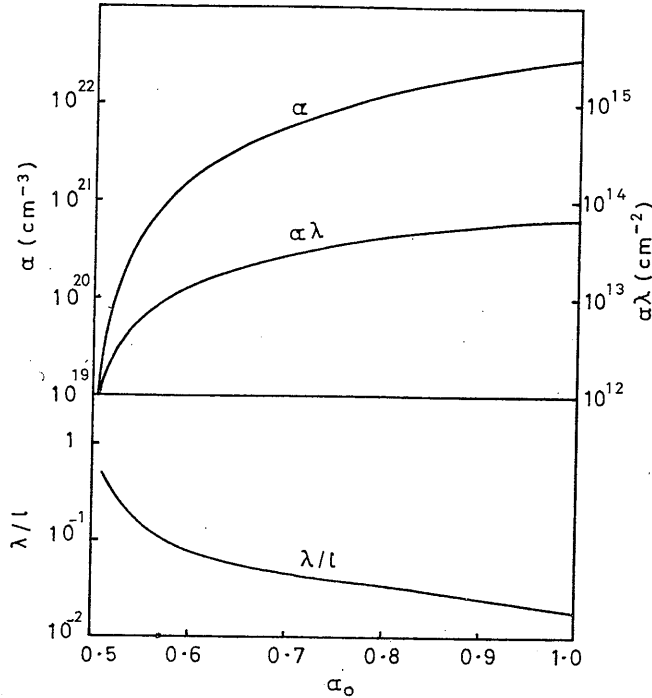
The concentration, a, and total number, $a\lambda$, of negative ions localized in the surface film, and the ratio, λ/l, of the characteristic length λ for the negative ion distribution to the coherence length l in the liquid, all as functions of surface orientation α_0.

The dipole energy can be evaluated similarly, but here both E_1 and E_2 contribute. Using equations (8) to (14) we find:

$$\Delta U_3 = \int_0^\infty M(z)E(z) d(z/d) = \frac{4\pi(\alpha_0 - \frac{1}{2})^2 n^2\mu^2}{Kd^2}\left(\frac{l\lambda}{l+\lambda}\right), \quad (17)$$

which is, of course, positive. The factor involving λ can be evaluated as a function of α_0 from the curve for λ/l given in fig. 1. To a very good approximation:

$$\lambda/l \simeq 9 \times 10^{-3}(\alpha_0 - \tfrac{1}{2})^{-1}, \quad \cdots \cdots \quad (18)$$

so that, since we shall be only concerned with values of α_0 greater than about 0·6, we can write :

$$\Delta U_3 \simeq \frac{3 \cdot 6 \times 10^{-2} \pi (\alpha_0 - \frac{1}{2}) n^2 \mu^2 l}{K d^2}. \qquad \dots \quad (19)$$

We now can write down the total free energy difference between a surface of orientation α_0 and a random surface as :

$$\Delta F = \Delta U_1 + \Delta U_2 + \Delta U_3 - T \Delta S, \qquad \dots \quad (20)$$

which, using (4), (7), (16) and (17), becomes :

$$\Delta F = n(\alpha_0 - \tfrac{1}{2})\epsilon_1 + \frac{\pi(\alpha_0 - \tfrac{1}{2})n^2\mu}{Kd^2}(\bar{Q} + 3\cdot 6 \times 10^{-2}\mu l) + 2(\alpha_0 - \tfrac{1}{2})^2 nlkT/d. \quad (21)$$

It is interesting to note that the first term is an order of magnitude smaller than the second so that its precise value, and even its sign, are in fact, relatively unimportant. The orientation processes are driven primarily by dipole–quadrupole interactions within the oriented layer, coupled through the agency of the macroscopic electric field.

It is now simple to minimize ΔF as a function of α_0 at a particular temperature T. This minimum occurs when

$$\alpha_0 = 0\cdot 5 - \frac{n\epsilon_1 + \pi n^2 \mu(\bar{Q} + 3\cdot 6 \times 10^{-2}\mu l)/Kd^2}{4nlkT/d}, \qquad \dots \quad (22)$$

which is $\alpha_0 = 0\cdot 74$ at 0°c. The value of ΔF at this minimum is about $-15\, \mathrm{erg\, cm^{-2}}$. Calculations at other temperatures are complicated by the temperature variation of the coherence length l and little can be gained by comparing the temperature variation of ΔF with that of surface tension for, though they are in the same sense, the latter quantity contains a large contribution from the changes which take place in water structure with changing temperature.

It is, however, useful to calculate the total potential drop ΔV across the surface layer by integrating the total electric field given by (9) and (10) which gives the result :

$$\Delta V \simeq -0\cdot 1\,\mathrm{v}, \qquad \dots \dots \quad (23)$$

the sign of the potential jump being such that the exterior of the liquid is positive relative to its bulk. This result is of the magnitude indicated by the most recent experimental work (Case and Parsons 1967), and since the sign is in doubt from much of the experimental evidence, may serve to define this. The result is, of course, of the sign and magnitude expected, since the ionic atmosphere will substantially compensate the field produced by the dipole orientations, but this compensation should be incomplete to the extent of a few times kT/q.

The absolute accuracy of our estimate of ΔV depends upon the assumed value of l in our model for water structure and upon the closeness with which the expression (12) can be made to approximate the exact solution of (10) and (11). Neither of these is likely to lead to an error as large as

a factor of 2 in ΔV and all other quantities are known to much higher precision. There is an additional uncertainty because of the graphical method used in solution of (15) so that the total error may approach a factor of 2 in either direction.

§ 4. The Surface of Ice

At the surface of crystalline ice any molecular orientation can relax only through the agency of L or D defects in the crystal. The equilibrium concentration of these is about 10^{16} cm^{-3} at $-10°$c so that the relaxation length is of the order of a millimetre. The entropy penalty for surface orientation at a crystalline surface is thus so severe that essentially no orientation can take place.

There is, however, the alternative possibility, discussed in I, that the surface may be covered by a thin, highly disordered layer, rather similar to the surface layer on water, in which relaxation can take place. Whilst it is obvious that this layer will not have exactly the structure and proper-ties of liquid water and will probably not be of well defined thickness but will merge gradually with the ice structure, a first-order estimate of its properties can be made by assuming it to be a uniform layer of thick-ness h, in which the molecules have the same chemical potential as in liquid water at the same temperature. To a good approximation (Fletcher 1966) the entropy of fusion of ice at a supercooling $\Delta T°$c is:

$$\Delta S_v \simeq (1\cdot13 - 0\cdot004\Delta T) \times 10^7 \, \text{erg deg}^{-1} \, \text{cm}^{-3}, \quad . \quad . \quad . \quad (24)$$

so that the free energy excess per unit area of surface due to the presence of the unoriented liquid film is:

$$\Delta F_1 = h\Delta S_v \Delta T = (1\cdot13 - 0\cdot004\Delta T) \times 10^7 \, h\Delta T \, \text{erg cm}^{-2}. \quad (25)$$

If the surface of the quasi-liquid film has orientation α_0, then the free energy due to orientation effects can be calculated by the methods of § 3, except that the integrals involved are all over the range $(0, h)$ instead of $(0, \infty)$. A more accurate recalculation than this should really be carried out for the ionic atmosphere but is not really justified in view of the other approximations involved. The ionic concentration $\rho_{\pm}(\infty)$ is correctly that for liquid water since we have assumed the film to approximate the liquid in structure.

There is, in addition, the energy of the water/ice interface to be con-sidered. As in I, we make the reasonable approximation that, in the absence of any orientation effects, the surface free energies $\sigma(\alpha)$ are related by:

$$\sigma(\tfrac{1}{2})_{\text{ice/vapour}} = \sigma(\tfrac{1}{2})_{\text{ice/water}} + \sigma(\tfrac{1}{2})_{\text{water/vapour}}. \quad . \quad . \quad (26)$$

The only term arising from this cause in the free energy difference between our model and a completely crystalline surface is thus that due to the sudden jump in α at the water/ice interface. The orientation in the water at the interface is $\alpha = \tfrac{1}{2} + (\alpha_0 - \tfrac{1}{2})\exp(-h/l)$ while that in the ice is $\alpha = \tfrac{1}{2}$ and the jump must be accomplished by a concentration of diffuse

L defects in the liquid. If ϵ_2 is the formation energy for such a defect then the energy excess from this cause is:

$$\Delta U_4 = n(\alpha_0 - \tfrac{1}{2})\epsilon_2 \exp(-h/l). \qquad \qquad (27)$$

Unfortunately it is very difficult to make any reliable estimate of the magnitude of ϵ_2. It is certainly very much less than the energy of an L defect in ice ($\simeq 4 \times 10^{-13}$ erg) because the two negative vertices involved need not be in line or even close to each other and there is no elastic strain implied in the surrounding structure. On the other hand, certainly $\epsilon_2 > 0$ and it may be as large as a few times 10^{-14} erg. As we shall see presently, the exact value is rather critical to some of our final conclusions so that we shall carry through the calculations for a range of values of ϵ_2.

Now, summing all these contributions, we have, for the free energy excess associated with the quasi-liquid surface:

$$\Delta F = \Delta U_1 + \Delta U_2' + \Delta U_3' + \Delta U_4 - T\Delta S' + \Delta F_1, \qquad (28)$$

where the primes indicate appropriately truncated forms of the expressions appearing in § 3. More explicitly, and by analogy with (21):

$$\Delta F = n(\alpha_0 - \tfrac{1}{2})\epsilon_1 + \frac{\pi(\alpha_0 - \tfrac{1}{2})n^2\mu}{Kd^2}(\bar{Q} + 3\cdot 6 \times 10^{-2}\mu l)[1 - \exp(-h/l)]$$

$$+ n(\alpha_0 - \tfrac{1}{2})\epsilon_2 \exp(-h/l) + \frac{2(\alpha_0 - \tfrac{1}{2})^2 nlkT}{d}[1 - \exp(-2h/l)]$$

$$+ h\Delta S_v \Delta T. \quad (29)$$

This expression can be minimized algebraically with respect to α_0 but the minimization with respect to h must be done numerically. The results of this calculation are shown in figs. 2 and 3 for a range of values of ϵ_2 from 1×10^{-14} erg to 3×10^{-13} erg, the probable value lying somewhere between these two extremes. For all values of ϵ_2 considered, the calculation indicates that, at temperatures within a few degrees of the melting point, the equilibrium state of the surface is one in which it is covered by a quasi-liquid layer a few tens of angstroms in thickness.

From fig. 2 it can be seen that at low temperatures a crystalline surface is stable but that, as the temperature is raised towards 0°C, a transition to a quasi-liquid surface takes place at a well defined temperature which, in the approximation of the present model, ranges from -6 to -3°C depending upon the value of ϵ_2. As the temperature is further raised, the liquid film thickness increases and tends towards infinity at the melting point. The film thickness at a given temperature depends only slightly upon ϵ_2 and at most temperatures is sufficiently much greater than the characteristic length l that our crude approximation in the treatment of the ionic atmosphere is reasonably well justified.

Figure 3 shows the free energy change at the surface produced by the presence of the liquid film. Since the free energy of the crystalline surface, taken as reference, varies relatively little with temperature, this calculation predicts that the total surface free energy of ice falls by about 15 erg cm^{-2} within a few degrees of the melting point.

Fig. 2
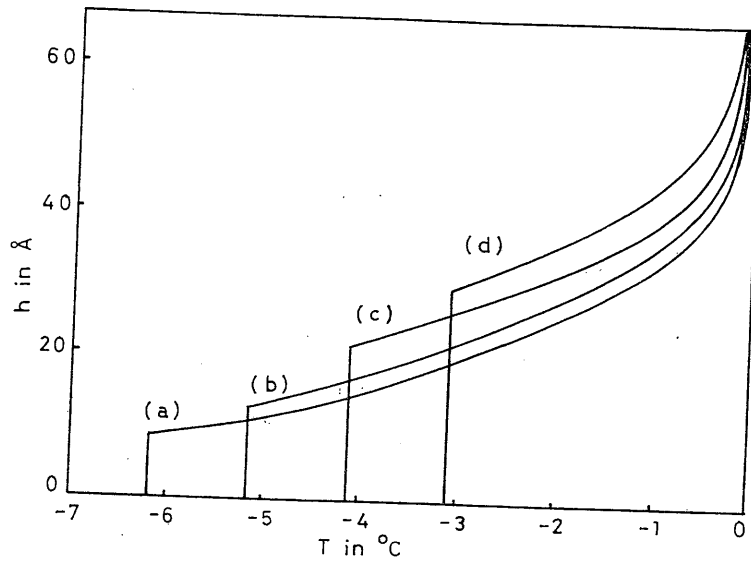
Calculated temperature dependence of the equilibrium thickness, h, of the quasi-liquid film on ice for various assumed values of ϵ_2, the energy of formation of diffuse L defects at the ice/water interface. (a) $\epsilon_2 = 1 \times 10^{-14}$, (b) $\epsilon_2 = 3 \times 10^{-14}$, (c) $\epsilon_2 = 1 \times 10^{-13}$, (d) $\epsilon_2 = 3 \times 10^{-13}$ erg.

Fig. 3
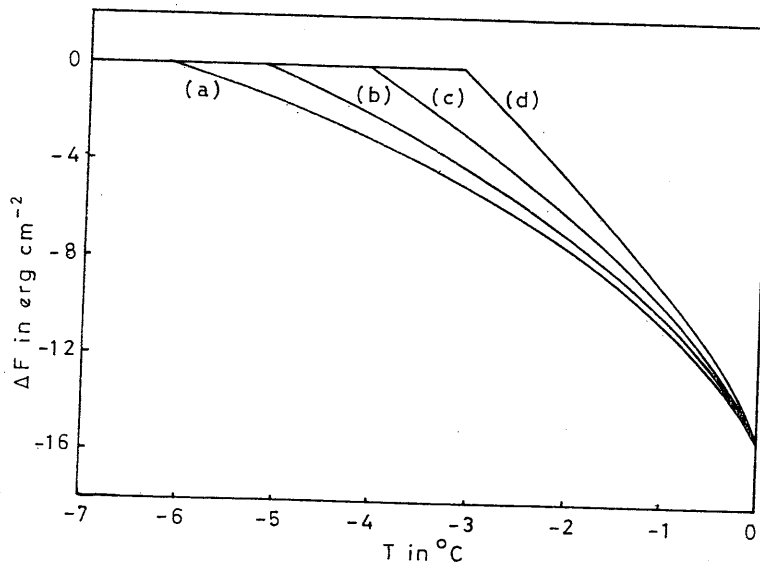
Calculated temperature dependence of the change ΔF in the free energy of an ice surface as a result of the surface phase change. Curves are for the same values of ϵ_2 as in fig. 2.

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In view of our crude treatment of the ionic atmosphere, we have not calculated the variation of the surface potential of ice with temperature, but the general trend and magnitude of the effect are clear. There is no surface potential component due to orientation effects at an ice surface at low temperature but, as the temperature is raised, a sudden jump in surface potential will occur as the quasi-liquid layer comes into existence, the surface dipole being so oriented that the exterior surface is positive with respect to the bulk. The magnitude of this potential jump will be, from the fact that α_0 is in the range 0·70 to 0·74 for most film thicknesses and from our calculations on liquid water, rather less than 0·1 v. As the temperature is further raised towards the melting point the surface potential jump will increase slightly towards the value for liquid water which is about 0·1 v.

The surface conductivity of ice can be estimated from the surface density of ions, $a\lambda$, plotted in fig. 1, together with some assumption about the mobility of the ions in the quasi-liquid layer. If this mobility is taken as equal to that of hydrogen ions in water, or about 3×10^{-3} cm^2/v sec, then, since $\alpha_0 \simeq 0·74$ for thick films, the surface conductivity of ice just below the melting point should be about 10^{-8} ohm^{-1}. This estimate represents an upper limit and the surface conductivity will certainly decrease as the temperature is lowered and the surface film becomes thinner. When the surface film vanishes, the surface conductivity from this cause should also vanish.

§ 5. Discussion

Our treatment of the surface structure of water has shown that an oriented surface layer is thermodynamically more stable than is a completely random surface. The preferred surface orientation of water molecules is that with protons directed out from the surface and the driving energy for the orientation comes primarily from dipole/quadrupole interactions within the oriented surface zone, rather than from asymmetry at the surface itself. Because of lack of a sufficiently detailed theory of the structure of liquid water, numerical calculations were based upon features common to most present theories of water structure and represent estimates only. They indicate, however, that a fraction near 0·74 of the surface molecules have their dipoles oriented with a positive component out of the liquid surface and that this orientation decays roughly exponentially below the surface with a characteristic length of order 10^{-7} cm.

The reliability of the surface potential calculations depends upon the assumed numerical values involved, but it seems likely that the calculated value of 0·1 v, with the surface more positive than the bulk liquid, is not in error by much more than a factor of 2 in either direction. It is therefore in good agreement with experiment.

The treatment of ice surfaces involved an additional assumption about the thermodynamic properties of the quasi-liquid surface layer upon which the model was built. The assumption that the chemical potential

of molecules in the layer is equal to that of molecules in water at the same temperature is reasonable, and the results would not have been greatly affected if we had assumed the chemical potential to be an extrapolation of that of the amorphous or glassy state of ice which can occur at low temperatures. A more artificial assumption was that the layer has a well-defined thickness instead of merging gradually with the ice structure. The latter is almost certain to be the case and would have the effect of smoothing out the sharp transition shown in the curves of fig. 2.

With these qualifications it seems reasonable to conclude that there is a transition from a crystalline to a quasi-liquid surface at some temperature between about $-2°$ and $-10°\mathrm{c}$ and that the thickness of the quasi-liquid layer is within about a factor of 2 either way from the values shown in fig. 2. This temperature range is close to that in which many of the anomalous surface properties of ice become apparent. In considering any experimental results, however, it must be borne in mind that any dissolved impurities, such as atmospheric CO_2, may concentrate in the surface layer and maintain its stability to lower temperatures, a complication which we have not considered here.

The surface electrical properties of ice require some further comment. One might hope to detect the change in surface potential with temperature by direct electrical measurement (though this is now a more difficult task than it appeared from the excessively large estimate of surface potential made in I) by photoelectric determination of work function. Experiments along these lines are proceeding.

The large surface conductivity predicted by the model is qualitatively well known from experiment and Jaccard (1967) has measured a value of $10^{-10}\,\mathrm{ohm}^{-1}$ at $-11°\mathrm{c}$. This is considerably smaller than our calculated value of $10^{-8}\,\mathrm{ohm}^{-1}$ just below $0°\mathrm{c}$ but the difference may arise either from the lower temperature of the experiments or from the effective ion mobility being less than the liquid water value, in addition to the uncertainties in our basic calculation. The experiment suggests that the liquid layer persists to at least $-11°\mathrm{c}$, which is below our estimate but within the range of uncertainty.

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