

The Surface of Ice

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The theoretical arguments and experimental evidence which suggest that the surface of ice possesses an anomalous quasi-liquid transition layer at temperatures a little below the melting point are reviewed and it is concluded that there is persuasive, though not decisive reason to accept the proposal. A revised calculation attempting to establish plausible limits for the thickness of the layer as a function of temperature is presented. Finally the possibility that such a layer exists on some other materials is examined. It is concluded that ice is one of a small group of materials where this may occur and several other cases are suggested for further study.

1. Introduction

The possibility that there is a quasi-liquid transition layer upon the surface of ice crystals in equilibrium at temperatures appreciably below the melting point has received attention and excited controversy since Faraday first put forward such a proposal in 1850. The history of this hypothesis, together with some of the experimental evidence in support of it, has been documented recently by Jellinek.¹

The first steps towards developing the hypothesis into a theory were made by Weyl,² who suggested a plausible physical driving energy which could lead to the stability of such a surface film. The semi-quantitative development of these ideas and their consequences rests almost entirely upon three papers by the present author.³⁻⁵ Although these papers have been subject to some justified criticism,⁶ which has been incorporated into the most recent version,⁵ there has been a general tentative acceptance rather than a rejection of the somewhat speculative theoretical treatment.

The purpose of the present paper is fourfold: to expound briefly the physical basis of the theory, to correct an error in the 1968 version and present revised calculations, to examine the most recent experimental evidence bearing on the problem, and finally to speculate on the possible existence of similar quasi-liquid transition layers on the surfaces of other materials.

2. Surface Orientation in Liquids

Water is an associated liquid in which association occurs through intermolecular hydrogen bonds. Several conflicting models for the structure of water have been proposed (for review and bibliography see Refs. 7-9). Some regard water as an almost completely bonded structure with distorted bonds, while others picture it in terms of clusters of molecules of

one bonding pattern in a matrix of molecules with a different bonding pattern. In either case, the coherence length for bonding, defined as the distance over which information about bond direction becomes lost, is about 10 Å for temperatures near the freezing point.^{8,9} One might expect a similar situation to occur in other hydrogen-bonded liquids, although perhaps water is an extreme case.

In the surface layers of a liquid whose molecules are nonspherical there is a tendency for molecular orientation relative to the plane of the surface.¹⁰ In simple liquids this orientation may be confined to the surface monolayer, but in associated liquids we should expect it to decay away from the surface with a characteristic length related to the coherence length for bonding.

Good¹¹ has examined the molar surface entropy for a large number of liquids and has found that, while simple liquids with quasi-spherical molecules have surface entropies around 24 J mol⁻¹ deg⁻¹, the surface entropies of hydrogen-bonded liquids are much lower, as shown in Table 1.

If the orientations of molecules in a monolayer are restricted to a solid angle of 2π , this reduces their molar entropy by $R \ln 2 = 5.8$ J mol⁻¹ deg⁻¹, so that it seems that the equivalent of 2 to 3 molecular layers near the surface of these liquids suffers orientation.

TABLE 1. Molar surface entropies (J mol⁻¹ deg⁻¹)

Water	9.8
Formic acid	11.3
Methanol	10.0
Formamide	9.1
Methyl amine	10.8
Hydrogen cyanide	13.5
Mean for simple liquids	24.0 ± 4

In water a molecular layer is about 3 Å, so this conclusion is in quite good agreement with the coherence length derived from theories of bulk water.

Jhon et al.¹² have applied significant structure theory to the calculation of the surface tension of water and find that they can reproduce the observed temperature variations by assuming an orienting field normal to the water surface such that the energy difference between favored and unfavored orientations is -2.8×10^{-13} erg per molecule. Both Stillinger and Ben-Naim,¹³ in a discussion of the interface potential of water near the critical point, and Fletcher⁵ showed that this energy arises from the asymmetry of the water molecule as expressed by its non-vanishing dipole and quadrupole moments, the orientation energy being of order

$$\epsilon_1 \sim -\mu_z \theta_{zz} c^{-4} (K_v^{-1} - K_l^{-1}), \quad (1)$$

where μ is the dipole- and θ the quadrupole-moment tensor, c is an exclusion radius associated with the molecule, and K_v and K_l are the dielectric constants of vapor and liquid respectively. The sign of ϵ_1 , and hence the favored orientation, depends upon the sign of θ_{zz} and this depends in turn upon the choice of origin for the exclusion sphere, a choice which should be made to minimize higher moments. This point has not yet been clarified but a choice of $c = 1.4 \times 10^{-8}$ cm (i.e. half the intermolecular distance in ice) suggests that $|\epsilon_1| \sim 10^{-13}$ erg, which agrees with other estimates.

To determine the equilibrium configuration of a liquid-water surface one must write down an expression for the free energy, taking into account the gain in energy and loss in entropy caused by the orientation, of the electrostatic interaction between molecular dipoles and of the differential adsorption of ions H_3O^+ and OH^- at the interface. This was done in the 1968 version of the theory⁵ but, as pointed out by R. J. Elliott (personal communication), the spherically symmetric part \bar{Q} of the quadrupole moment was wrongly included. This should be omitted or set to zero where it occurs in the treatment. Provided that ϵ_1 occurs with about the magnitude given by Eq. (1) above, this has little effect on the final numerical results. Although application has been made only to the case of water, the treatment for the other liquids listed in Table 1 should be very similar.

Since the theory does not give a definite prediction about the preferred surface orientation in water, we must rely upon experiment. Direct surface-potential measurements are equivocal, though they do sug-

gest an interfacial potential of the same order as the 0.1 V predicted by the theory. The observation, however, that negative atmospheric ions are much more efficient nuclei for water droplets in a cloud chamber than are positive ions^{14,15} indicates unambiguously that the low-energy configuration is that in which surface molecules have their protons buried in the liquid. This agrees with the original discussion³ but reverses the conclusion reached in 1968⁵ which was erroneous on this point because of the inclusion of \bar{Q} .

We may hope ultimately that direct quantum-mechanical calculations with clusters of molecules might elucidate this point and give an ab initio value for the energy. Unfortunately this cannot be done from any of the existing cluster calculations.^{16,17}

3. Surface Structure of Ice

There is no reason to think that the surface of ice is at all unusual, in our present sense, at temperatures below about -35°C . Between -35°C and the melting point, however, ice surfaces exhibit a variety of anomalies which we shall examine in the next section. For the present we seek a picture of the equilibrium surface structure by setting up a sufficiently flexible model and varying its parameters to minimize the free energy.

The thermodynamic driving force for a surface phase transition arises once again from the electrical asymmetry of the water molecule and its consequent preferred orientation in an interfacial situation. The natural coherence length for bond orientation in ice is set by the equilibrium concentration of L and D defects and is of the order of a millimeter at 0°C . The entropy loss associated with orientation over such a distance is prohibitive and, if orientation occurs, some other mechanism must be found.

The model supposes the existence of a highly disordered surface layer, so that surface orientation can relax over a short distance to a normal ice structure. The surface layer is not necessarily physically liquid, though the broken bonds make this likely. It also probably joins smoothly to the ice substrate by way of intermediate structures, but this is hard to model. We therefore assume a layer of definite thickness d with thermodynamic properties similar to those of the surface of liquid water. An intermediate or transitional structure should have a lower free energy so that, if the model predicts stability for the layer, this stability is true a fortiori for a more realistic model.

The analysis of this model⁵ is very similar to that

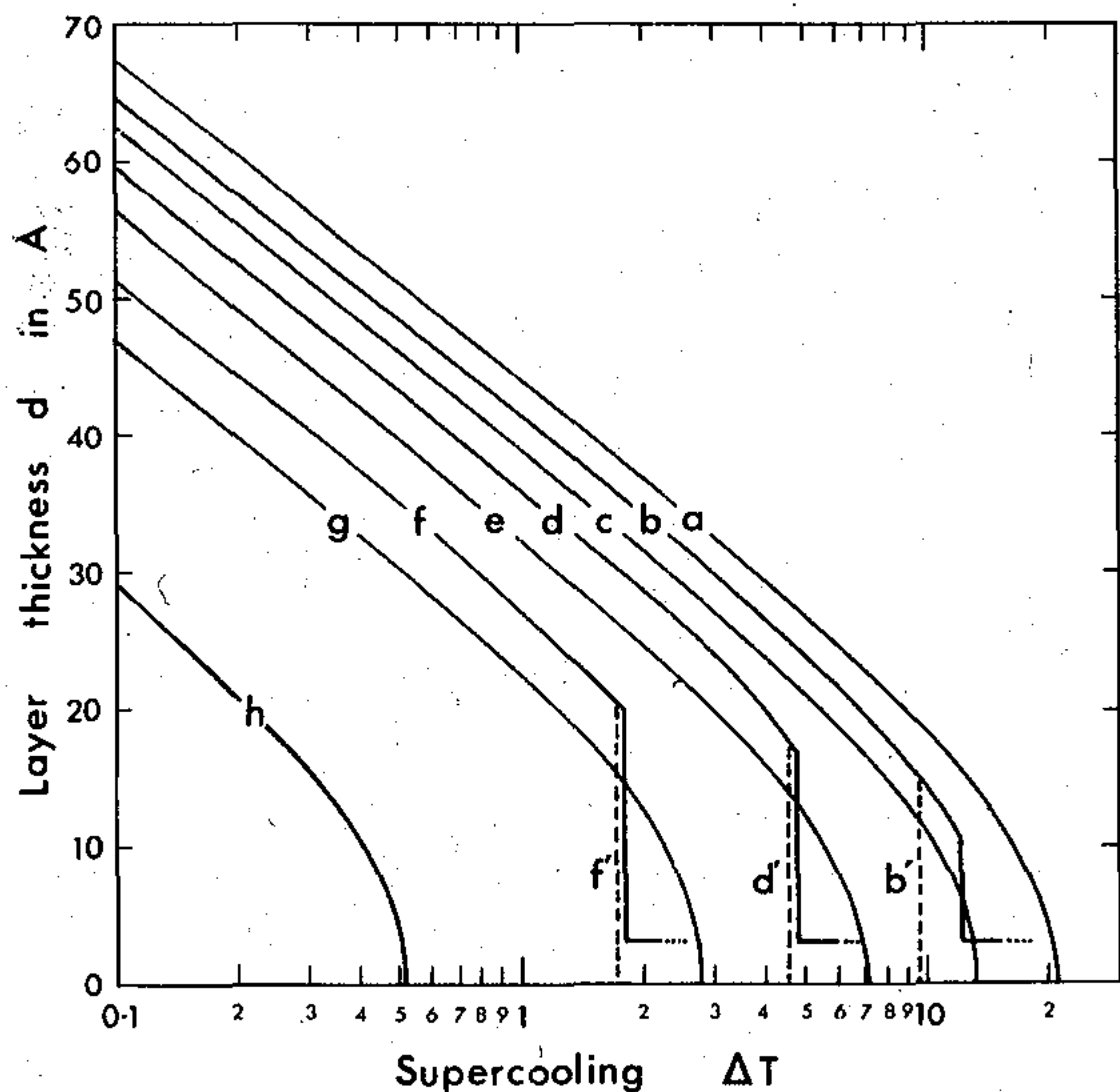


FIG. 1. Thickness a of the liquid transition layer on ice as a function of supercooling ΔT as predicted by the theory for the following values of ϵ_1 and ϵ_2 (in units of 10^{-13} erg): a: $\epsilon_1 = -2.5$, $\epsilon_2 = 2.5$; b: $\epsilon_1 = -2.5$, $\epsilon_2 = 2.0$; b': $\epsilon_1 = -2.0$, $\epsilon_2 = 2.5$; c: $\epsilon_1 = -2.0$, $\epsilon_2 = 2.0$; d: $\epsilon_1 = -2.0$, $\epsilon_2 = 1.5$; d': $\epsilon_1 = -1.5$, $\epsilon_2 = 2.0$; e: $\epsilon_1 = -1.5$, $\epsilon_2 = 1.5$; f: $\epsilon_1 = -1.5$, $\epsilon_2 = 1.0$; f': $\epsilon_1 = -1.0$, $\epsilon_2 = 1.5$; g: $\epsilon_1 = -1.0$, $\epsilon_2 = 1.0$; h: $\epsilon_1 = -0.5$, $\epsilon_2 = 0.5$.

given for a liquid water surface (with the correction noted above) but must take into account two further destabilizing effects. The temperature is below 0°C , so that water has a free energy higher than ice by an amount $\Delta S \Delta T$ where ΔS is the entropy of fusion and ΔT the supercooling. In addition, since the transition layer is of finite thickness, there will be an abrupt change in bonding orientation and therefore a concentration of L or D defects where it joins the ice structure. Each of these defects contributes a positive energy ϵ_2 , which is also of order 10^{-13} erg but should be less than the L or D defect energy in ice, which is about 4×10^{-13} erg.

Minimization of the free-energy function with respect to layer thickness shows that such a quasi-liquid film always leads to a lower free energy than that of a crystalline surface if the temperature is close enough to 0°C . The range of supercooling over which the film persists stably depends upon the values of ϵ_1 and ϵ_2 . Since we know these in order of magnitude only, it is best to carry out calculations for a range of possible values and this has been done in Fig. 1. Note that the liquid film persists to lowest temperature if $\epsilon_2 = -\epsilon_1$. If $\epsilon_2 > -\epsilon_1$, the film vanishes abruptly at a particular temperature, while if $\epsilon_2 < -\epsilon_1$ it collapses to an oriented monolayer below

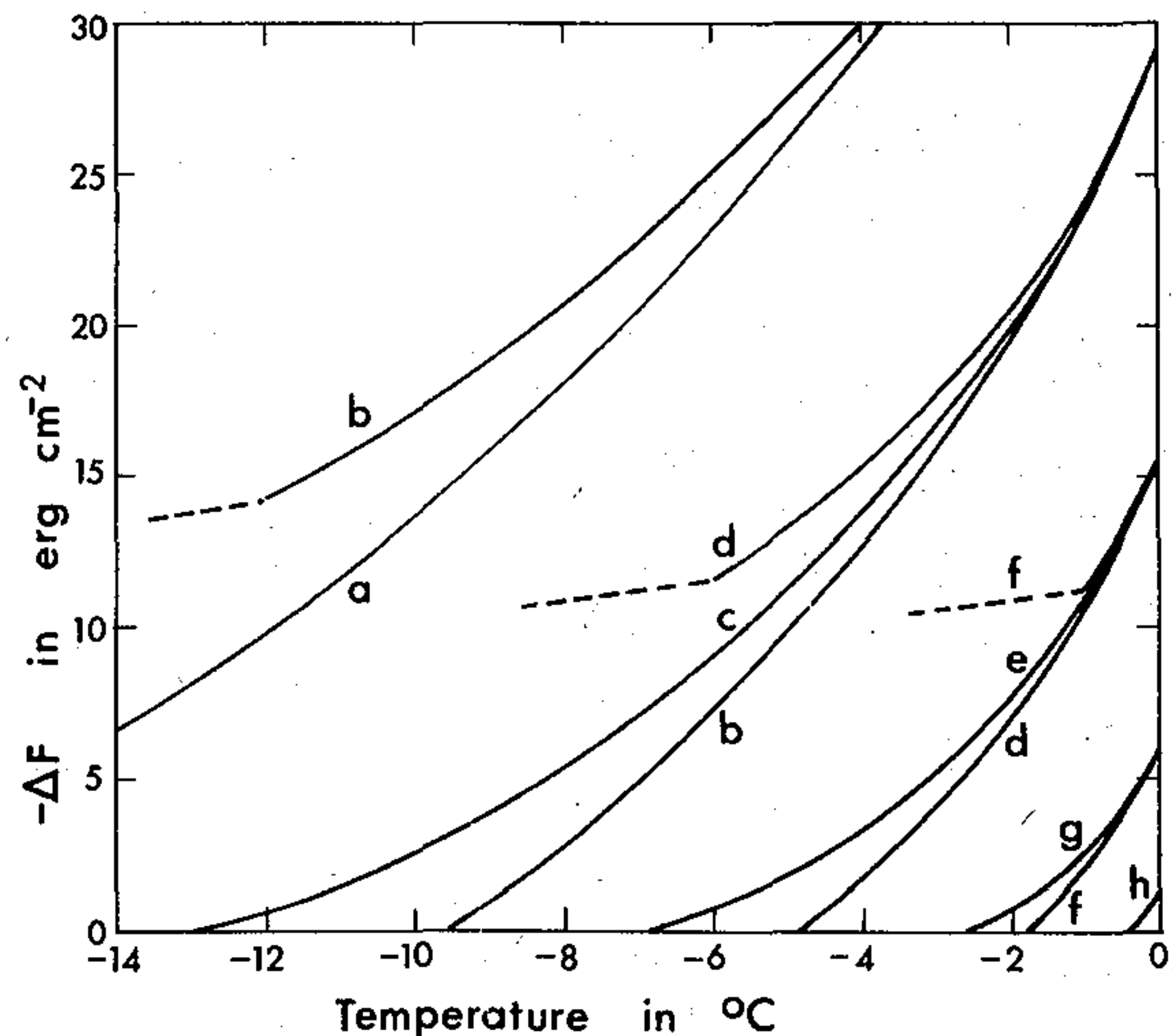


FIG. 2. The lowering $-\Delta F$ of the free energy per unit area of an ice surface by the presence of a quasi-liquid transition film as calculated from the theory for various values of ϵ_1 and ϵ_2 . Curve labels correspond to those in Fig. 1.

a particular temperature. The lowering of surface free energy achieved by the existence of the film for various ϵ_1 , ϵ_2 values is shown in Fig. 2.

From consideration of likely ranges for ϵ_1 and ϵ_2 we conclude that the liquid surface is the stable configuration above a temperature T^* which probably lies between -2 and -15°C . The dependence of T^* on ϵ_1 and ϵ_2 is shown in Fig. 3.

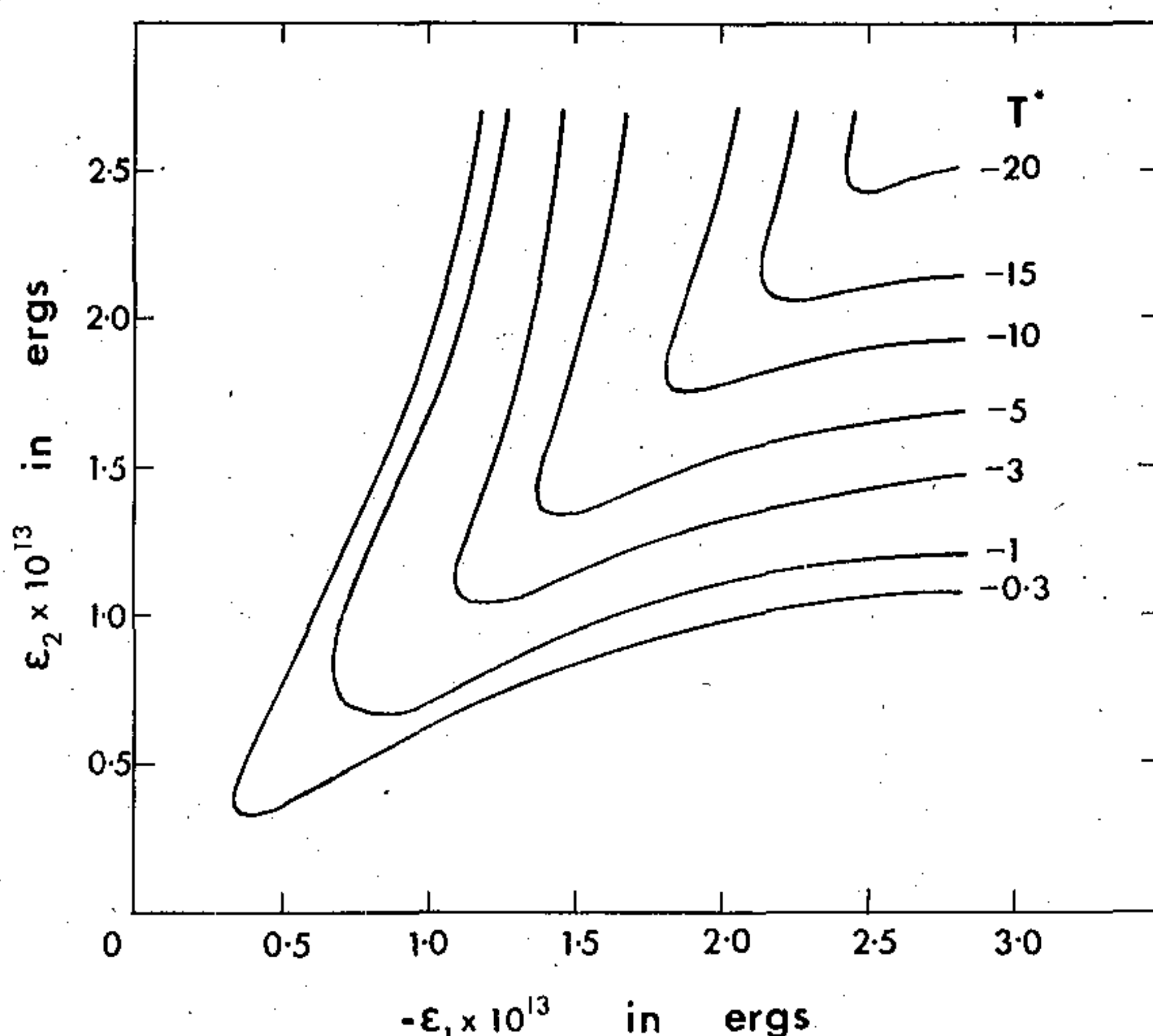


FIG. 3. Contours giving the temperature T^* above which a stable quasi-liquid surface film is present on the surface of ice, as calculated from the theory for a range of values of ϵ_1 and ϵ_2 .

The thickness of the quasi-liquid film is not given by a simple expression, but an approximate relation can be derived graphically. This has the form, for supercooling ΔT degrees and film thickness d Å,

$$d \simeq (20 \text{ to } 50) - 25 \log_{10} \Delta T. \quad (2)$$

4. Experimental Evidence on Ice Surfaces

It is difficult to obtain direct and unambiguous evidence for the existence of a liquid surface film for several reasons: (i) the segregation coefficient for most impurities in ice is very small, with the result that these are concentrated at surfaces and grain boundaries and may cause local lowering of the melting point; (ii) the phase diagram of ice shows the phenomenon of "pressure melting," which may confuse any mechanical measurements; (iii) measurements under nonequilibrium conditions are suspect and may not give a true indication of the equilibrium situation; (iv) there are few properties of ice and water which differ sharply enough for film detection to be easy.

Most of the classical "demonstrations" of the existence of a liquid layer on ice, as reviewed by Jellinek,¹ suffer from at least one of the difficulties (i) – (iii). We shall not repeat the discussion of these here but concentrate on more recent and more direct evidence.

Studies of ice-crystal habit and of step propagation in crystal growth by Mason and others¹⁸ show a somewhat unexpected temperature trend above -30°C and evidence for what appears to be a surface phase change above about -10°C . These studies were necessarily carried out under supersaturated conditions, however, and may not reflect the equilibrium situation.

Closer to equilibrium, Adamson et al.^{19,20} found a change in the character of adsorption of nitrogen and *n*-alkanes onto ice above -35°C towards a behavior more closely resembling that onto liquid water. Below -35°C the adsorption was like that of a low-energy surface such as Teflon. Various workers^{21–23} have also reported a great increase in the surface electrical conductivity of ice, which dominates its bulk conductivity above -10°C and may begin to be anomalously high above -35°C . This behavior is to be expected as a result of the theory because of the very large concentration and reasonable mobility of adsorbed ions in the liquid layer.⁵

Perhaps the most convincing experimental evidence comes from a proton magnetic resonance experiment on finely divided ice frost by Kvlividze et al.²⁴ Preparation of the ice specimen by vapor

deposition reduced the possibility of impurity contamination, while the small particle size ($40\text{--}60\ \mu\text{m}$ radius) and the considerable difference in the n.m.r. behavior of protons in water and ice, observed as a narrow liquid line superposed on a broad ice line, makes the experiment relatively sensitive. The quasi-liquid line was detected at temperatures above -10°C and its temperature variation was similar to that predicted by the theory.

Other sensitive tests are possible. One is photoelectric emission from ice surfaces, a technique that is being employed in our laboratory and on which we hope to report soon. We can, however, only sum up the available experimental evidence by the statement that it is encouraging but not yet conclusive.

5. Surfaces of Other Materials

Faraday is reported¹ to have carried out experiments on a variety of substances at their melting points without finding one with anomalous properties like those of ice. He cannot have examined many substances, however, and might easily have chosen the wrong ones. It is therefore useful to examine the question on the basis of our theory and to suggest materials which might be expected to be anomalous.

The prime requirements are three: that molecules of the material should have large electrical asymmetry leading to preferred orientation at a surface, that bonding in the liquid should be such that there is appreciable extension of any surface orientation to molecular layers below the surface, and that the crystal structure of the solid should be such that the low-energy orientation is not automatically produced at its surface.

The first two requirements are best fulfilled by hydrogen-bonded associated liquids and suitable possibilities can be recognized from surface entropy data. The liquids listed in Table 1 satisfy these conditions.

Crystal Structures of these materials are detailed by Wyckoff.²⁵ Methyl alcohol is orthorhombic and consists of H-bonded chains $\cdots\text{O—H}\cdots\text{O—H}\cdots$ running parallel to the *c* axis. This structure could lead to a transition layer on (001) faces but probably not on (100) or (010). Methyl amine also has an orthorhombic structure whose atom positions suggest H-bonded chains $\cdots\text{N—H}\cdots\text{N—H}\cdots$ running parallel to both *a* and *b* axes. We might expect a transition layer on (100) and (010) in this case, but not on (001). Similarly formic acid is orthorhombic with H-bonded chains $\cdots\text{O—H}\cdots\text{O—H}\cdots$ running in [011] and [0 $\bar{1}$ 1] directions so that (001) and

(010) should be the anomalous surface planes. Hydrogen cyanide is tetragonal²⁶ and has linear $\cdots\text{H}-\text{C}\equiv\text{N}\cdots\text{H}-\text{C}\equiv\text{N}\cdots$ chains parallel to the c axis, but in this case the crystal is polar so that surface molecules on one face, say (001), are in the low-energy configuration while those on (00 $\bar{1}$) are in the high-energy one. A transition film might therefore exist on the (001) face, but (00 $\bar{1}$), (010), and (100) should be normal. Finally formamide has a monoclinic structure involving $\text{O}-\text{H}\cdots\text{N}$ or $\text{O}\cdots\text{H}-\text{N}$ links in sheets parallel to (101) planes. This could lead to a transition film on any crystal face except (101) habit faces.

All these materials are worth further study in this connection and their differing properties may possibly make available some additional methods of study. The problems associated with achieving a firm conclusion in the case of ice, however, make it unlikely that an easy answer will be found. Among substances for comparison which should have normal surfaces we might include simple metals, alkali halides, and organic materials like benzene and cyclohexane.

6. Conclusion

The theoretical treatment, together with the somewhat inadequate experimental evidence so far available, suggests that ice is one of a small family of solids which may exhibit anomalous surface properties in the sense that a quasi-liquid transition layer exists on at least some crystal faces at temperatures a little below the melting point. It will be interesting to see what related evidence can be adduced from further studies of ice, or the other materials suggested, over the next few years.

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