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(Transition)
Layer on Ice

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by

H. H. G. Jellinek

PREFACE

This report was prepared by Dr. H. H. G. Jellinek, under contract DA-ENG-27-021-62-G1 with the University of Windsor, Windsor, Ontario, Canada, for the Research Division, Mr. James A. Bender, chief.

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SUMMARY

A survey of the literature covering about the last hundred years is presented concerning the existence of a liquid-like transition layer on ice below its melting point. The conclusion is reached that the available evidence is very strongly in favor of the existence of such a layer. However, more direct measurements of the properties of such a layer are needed and possible methods for obtaining such information are indicated.

LIQUID-LIKE (TRANSITION) LAYER ON ICE

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Introduction

The concept of a liquid-like layer on ice even below the freezing point of water has become of increasing importance because it can account for the surprising surface properties of ice. This concept has a very interesting history involving many famous scientists of the last century such as Faraday, Lord Kelvin, J. Thomson, Helmholtz, and Tyndall. Actually, an appreciable amount of research was carried out about 100 years ago. A survey of the concept of the liquid-like layer covering approximately the last hundred years is given here.

Early work

In 1850, M. Faraday[1]*described a phenomenon shown by ice, which soon became the object of a lively controversy between such famous scientists as Faraday and Tyndall on the one side and J. Thomson, his brother W. Thomson (later Lord Kelvin), and Helmholtz on the other side. Faraday's observation was a very simple one: If two pieces of ice at 0C or higher ambient temperature are brought into slight contact, they freeze together. Faraday points out in various papers that water can be supercooled and superheated. However, when an ice crystal is placed into supercooled water, crystallization takes place at once. He ascribes this freezing to the effect of "cohesive" forces exerted on the neighboring water "particles." This effect is intensified, according to him, if a water film is situated between two ice surfaces - a situation which is brought about by contacting two pieces of ice; the cohesive forces are then so effective that freezing takes place even when the ambient temperature is above 0C. This property of ice was a very remarkable one at that time and Faraday carried out a number of experiments with other substances at their melting points, but they did not show this behavior.

It may be appropriate to quote Faraday[2]: "Two pieces of ice, if put together, adhere and become one; at a place where liquifaction was proceeding, congelation suddenly occurs. The effect will take place in air, or in water, or in vacuo. It will occur at every point where the two pieces of ice touch but not with ice below the freezing point, i. e., with dry ice, or it be so cold as to be everywhere in the solid state. When first observed in 1850, I explained it by supposing that a particle of water, which could retain the liquid state whilst touching ice only on one side, could not retain the liquid state if it were touched by ice on both sides, but became solid, the general temperature remaining the same." He also remarked[2]: "The next point may be considered as an assumption: it is that many particles in a given state exert a greater sum of their peculiar cohesive force upon a given particle of the like substance in another state than few can do; and that as a consequence a water particle with ice on one side and water on the other is not so apt to become solid as with ice on both sides; also that a particle of ice at the surface of a mass in water is not so apt to remain ice as when, being within the mass, there is ice on all sides, temperature remaining the same. If that be admitted, then regelation is sufficiently accounted for. Difference of temperature above or below that of the changing points of water is not alone sufficient to cause change of state, the change being independent of temperature throughout a large range. At such times, the particles appear to be governed by cohesion. Cohesion resolves itself into the forces exerted on one particle by its neighbours, and this force seems to me sufficient under the circumstances to account for regelation."

Tyndall accepted Faraday's view and the term regelation (refreezing) was first coined by him in a paper with Huxley[3]. Tyndall attempted to explain the "flow" of

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*Numbers refer to references.
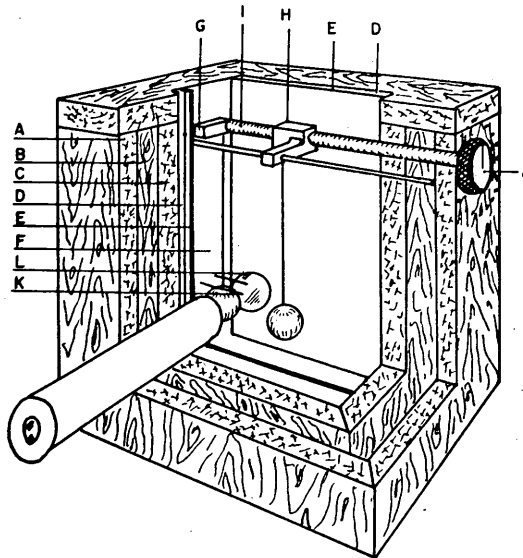
Figure 2. Apparatus for measuring force of separation of ice spheres. A outer cell of insulated box, B glassfiber, C inner shell, F apparatus chamber, D cooling chamber packed with dry ice, E copper plates, G and H brass clips holding the ice spheres, I wormscrew, J knob for turning screw measuring linear movement of H (minimum 1×10^{-3}), K thermocouple, L Lucite rod windows.[11, 12]
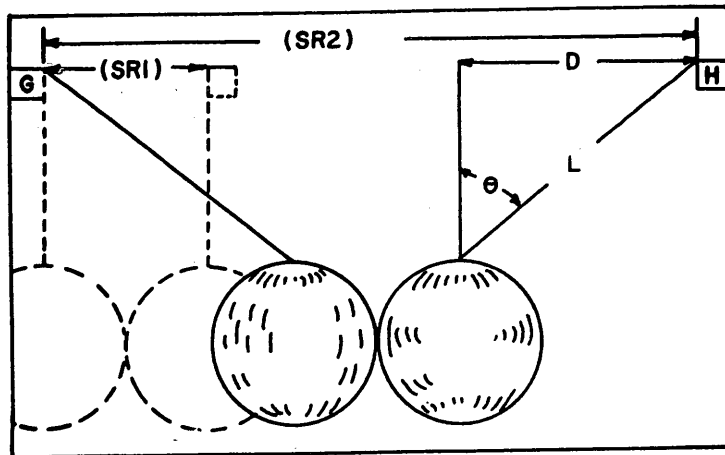
Figure 3. Initial and final positions of spheres. Force of separation F = weight of sphere x tan θ; horizontal distance one sphere has moved = (SR 2 - SR 1)/2 = D, L = length of suspending thread, hence tan θ = D/L.[11, 12]

Figure 4. Separation force as a function
of temperature. A, water-vapor-saturated
atmosphere; B, dry atmosphere.[11, 12]

The data gives a good straight line by plotting the logarithms of the separation force
against the reciprocal absolute temperature T, yielding an apparent energy of activation
$E = 10.6$ Kcal; R is the ideal gas constant and A' is a constant. If the assumption is
now made that the contact area A where freezing is taking place is proportional to some
power n of the transition layer thickness d, we have:

$$F = F_1 A = kF_1 \cdot d^n \tag{2}$$
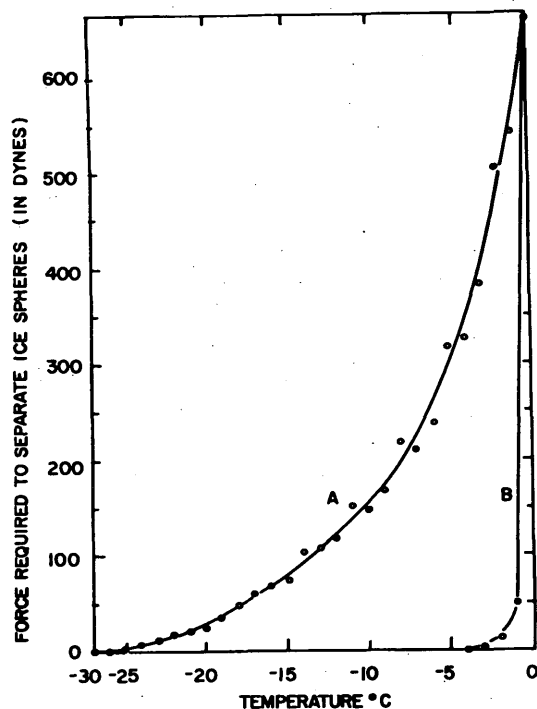
where F is the tensile strength of the bond and k is a constant of proportionality. From
eq 1 and 2 we obtain:

$$d^n = \frac{A'}{kF_1} \; e^{-E/RT}$$

$$\text{or} \quad \log d = \frac{-E'}{2.303 RT} + \frac{1}{n} \log \frac{A'}{kF_1} \tag{3}$$

where $E' = E/n$.

Hence the logarithm of the layer thickness plotted against the reciprocal absolute
temperature should also give a straight line, with an energy of activation E' differing
by a factor $1/n$ from the apparent energy of activation E for the separating force. That
this is actually the case will be discussed subsequently.

It would be very difficult to account for these experimental results on the basis of
the pressure melting theory. Some simple calculations were performed by Jensen[12] to
illustrate this. For instance, if the spheres were brought together at -5C, a pressure
P_{-5} of about 600 atm is needed to achieve pressure melting. This would occur if the
contact area between the spheres is A_{-5} cm². If the spheres were brought together with

the same force at -20C, the pressure P_{-20} for melting would have to be 1910 atm. The corresponding contact area would be A_{-20} cm². Hence, the separating forces at these two temperatures would be given by $F_{-5} = P_{-5} A_{-5}$ and $F_{-20} = P_{-20} A_{-20}$ or, since $F_{-5} = F_{-20}$,

$$\frac{A_{-5}}{A_{-20}} = \frac{P_{-20}}{P_{-5}}.$$

The contact area at -5C would have to be 3.2 times that at -20C if the same force were used in both cases for contacting. If the tensile strength were the same in both cases, the force of separation should be 3.2 times as great at -5C as at -20C. These separating forces can be obtained from experimental data. The actual ratio is 10.5. One should expect that the tensile strength decreases somewhat with increasing temperatures.

Jensen also computed the actual contact areas from his experimental data, taking 17.4 kg/cm² as the tensile strength of ice. The result is that the actual pressures on the contact areas are 3000 to 10,000 times smaller than those which are required for melting.

The differences observed in the saturated and dry environments also contradict the pressure melting theory. The environment should have a negligible influence in the case of pressure melting.

Thus, these experiments overwhelmingly support the transition layer theory. Experiments on the aggregation of ice crystals carried out by the same authors also support this theory, but are not as exact as the experiments using ice spheres.

Jellinek[13, 14] investigated the adhesive properties of ice by carrying out tensile and shear experiments with ice frozen to various surfaces such as stainless steel optical flat quartz, and various polymers. He observed that only cohesive breaks occurred with tensile experiments, however finely polished the surface was. But shear experiments gave adhesive breaks; the strength depended on the rate of shear, surface finish, and temperature. The temperature relationship is shown in Figure 5, where the adhesive strength is plotted as a function of temperature. Down to -13C, this relationship is linear, the adhesive strength increasing with decreasing temperature. A sharp change occurs at -13C; below this temperature only cohesive breaks are observed, the tensile strength being practically independent of temperature. Adhesive strength as a function of surface finish is shown in Figure 6. The adhesive strength decreases with decreasing roughness of the surface. Figures 7 and 8 show the adhesive strength as a function of rate of shear for mirror-polished stainless steel and optically flat quartz surfaces respectively; linear relationships are found.

Some adhesion experiments were also carried out by Raraty and Tabor[15] which are substantially in agreement with Jellinek's data. The latter has made use of Weyl's postulate of a liquid-like or transition layer at the ice/solid interface. This provides the only reasonable explanation for the observed phenomena. The situation is indicated in Figure 9, where the solid is completely wettable by water. In such a case there is a pressure difference across the curved surface given by the following equation:

$$\Delta p = \frac{2\gamma}{L} \tag{4}$$

where γ is the interfacial tension at the liquid-like layer/air interface and $\underline{L}$ is the thickness of the layer. Supposing that $L = 2 \times 10^{-6}$cm and $\gamma = 76.4$ dyne/cm, the pressure Δp becomes 7×10^7 dynes/cm², a value far above the bulk tensile strength of ice. Hence only cohesive breaks will take place for tensile experiments. The situation becomes more complicated if the surface of the solid is not completely wetted by the liquid-like layer, since in such a case the contact angle is greater than zero.

The situation is quite different for shear experiments. If the surface of the solid were ideally flat, the smallest shear force should start the solid moving across the ice, provided the transition layer has no yield point. (There are, however, indications of a small yield point, see Figures 7 and 8.) Experimental data indicate that this is actually the case for fused quartz optical flats. The ratio of the viscosity to the thickness of the

Figure 5. Strength as a function of temperature for snow-ice sandwiched between stainless steel disks, obtained by shear. Cross-sectional area 1.54 cm², height 0.2 to 0.4 cm. Adhesive breaks down to -13C; cohesive breaks below -13C. Each point represents the average of at least 12 tests.[13, 14]
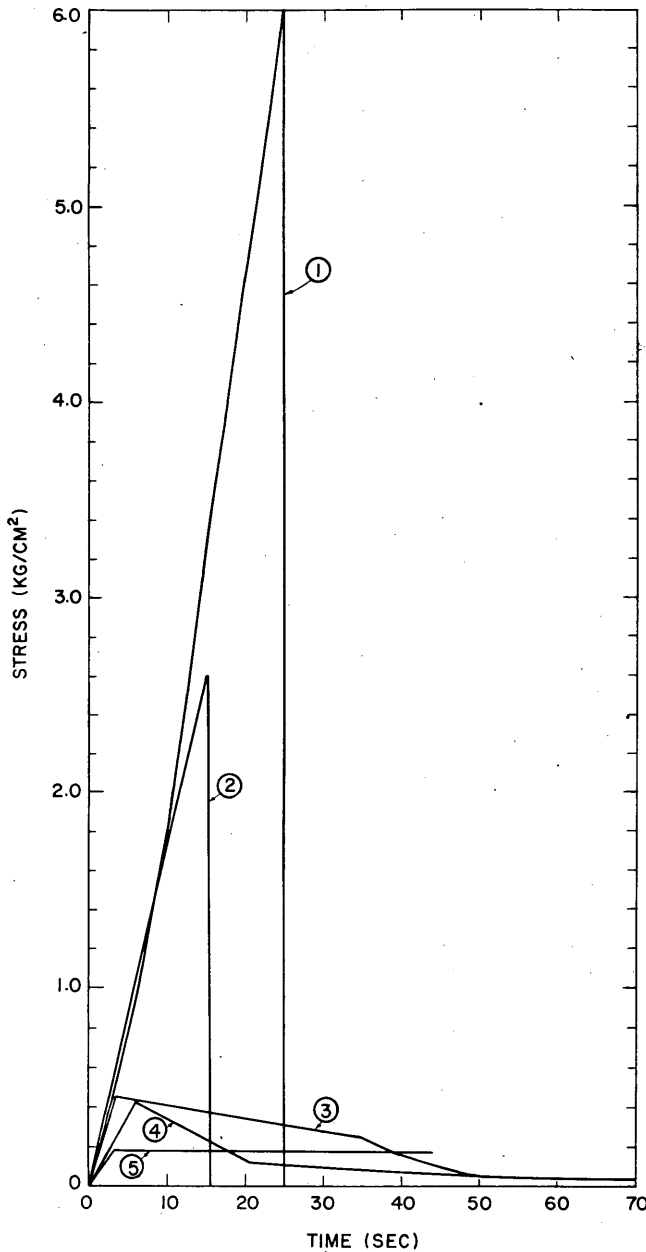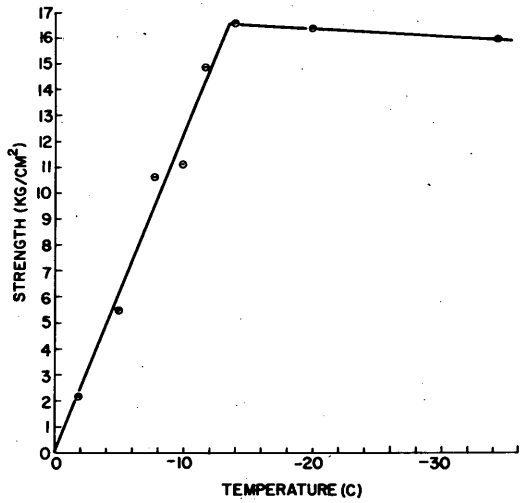
Figure 6. Typical stress vs time curves for stainless steel disks of different roughness and for a fused quartz optical flat (rates of shear are similar in all cases).[14]

(1) Snow-ice - stainless steel, steel surface finished on lathe

(2) Snow-ice - stainless steel, mat polish

(3) Snow-ice - stainless steel, mirror polish

(4) Snow-ice - stainless steel, mirror polish

(5) Snow-ice - fused quartz optical flat (flat to within 1/5 waveband), temperature -4.5C.
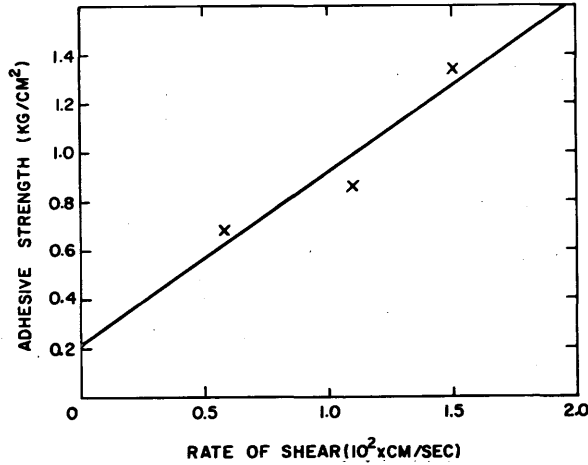
Figure 7. Relationship between average adhesive strength and rate of shear for snow-ice - stainless steel (mirror polish). Temperature -4.5C.[14]
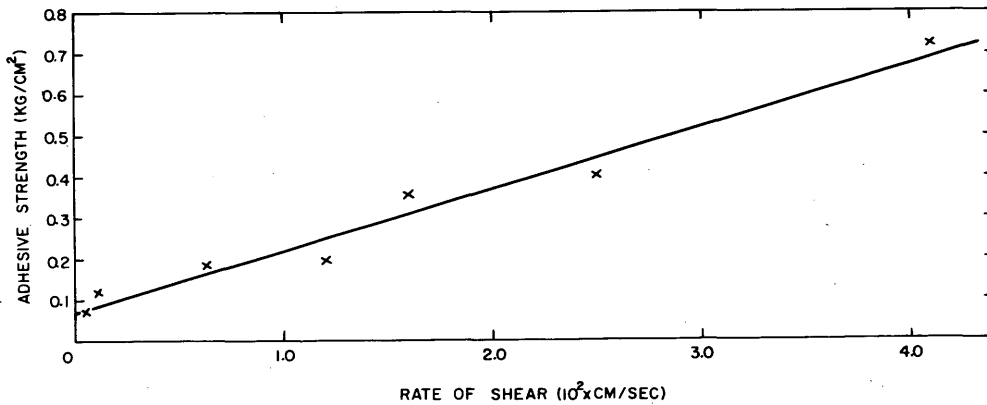
Figure 8. Relationship between average adhesive strength and rate of shear for snow-ice - fused quartz optical flat. Temperature -4.5C.[14]

Figure 9. Liquid-like transition layer sandwiched between ice and stainless steel. Pressure difference Δp across curved surface is $\Delta p = \dfrac{2\gamma}{L}$ where γ is the surface tension of the liquid-like layer and $\overline{V}$ is the velocity of the stainless steel disk for shear experiments.[13]

liquid-like layer is given by:

$$\eta/L = dS/dV \qquad (5)$$

assuming as a first approximation that the transition layer is Newtonian. Here η is the viscosity, $\underline{S}$ the shear strength, and $\underline{V}$ the velocity of shear. It has also to be remembered that $\overline{\eta}$ is an average value as the properties of the layer change continually from the solid/liquid layer interface until the proper ice crystal lattice is reached. The relationship between cohesive strength and rate of shear was found to be linear:

$$\text{for ice/stainless steel: } dS/dV = \eta/L = 69.9 \ \frac{\text{kg sec}}{\text{cm}}$$

$$\text{for ice/quartz: } \qquad dS/dV = \eta/L = 15.1 \ \frac{\text{kg sec}}{\text{cm}}$$

A reasonable assumption, considering the roughness of the various surfaces involved, gives an estimate for $\underline{L}$, and approximate values for the viscosity can then be obtained. For $\underline{L}$ varying from 10^{-5} to 10^{-6} cm at -4.5C one obtains 70 to 700 poises for η at an ice/steel interface and 15 to 150 for ice/quartz. Of course it is quite possible that both η and $\underline{L}$ are different for the two interfaces. However, this is the first rough estimate of th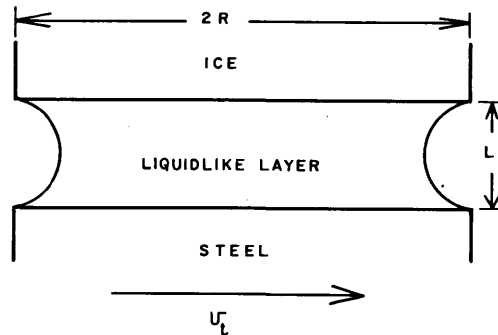e viscosity of the liquid-like layer and it does not seem to be unreasonable, lying between the viscosity of supercooled water (2.1×10^{-2} poises at -5C) and ice (about 10^{14} poises).

T. E. Ford and O. D. Nichols[16] reported that cohesional breaks took place on shearing of ice frozen to various solids. The apparent discrepancy between Jellinek's results[13, 14] and those of Ford and Nichols is probably due to the high rate of pressure application (20 psi/sec) used by the latter. This rate is so high that the liquid-like layer cannot accommodate the change in pressures rapidly enough.

Kingery[17] carried out some interesting experiments on the growing together of ice spheres. Growing together of particles, or sintering, is a general phenomenon taking place at temperatures not too far below the melting point of a substance. The driving force for the sintering is the decrease in surface free energy. Ice, of course, is usually studied very near the melting point and sintering should be readily apparent. However, ice seems to have a special position due to the dipole nature of the water molecule, and the disturbance (transition layer) in its surface is particularly pronounced. The general relationship between the radius $\underline{X}$ of the neck between two spheres and the radius of the spheres is given by the following equation (see Fig. 10):

$$\left(\frac{X}{R}\right)^n = \frac{F(T)}{R^{n-m}} \qquad (6)$$

where $F(T)$ is a function of the surface free energy and $\underline{n}$ and $\underline{m}$ are exponents which are characteristic of the respective growth process:

$$n = 2, \ m = 1 \qquad \text{Viscous flow}$$
$$n = 3, \ m = 1 \qquad \text{Evaporation-condensation}$$
$$n = 5, \ m = 2 \qquad \text{Volume diffusion}$$
$$n = 7, \ m = 3 \qquad \text{Surface diffusion.}$$

Kingery carried out growth experiments with ice spheres having radii varying from 0.011 to 0.328 cm over a temperature range from -2.2C to -25.1C. In all cases, the average values for $\underline{n}$ were near 7 and those for $\underline{m}$ about 3, indicating surface diffusion. Two remarkable features were noted: the diffusion coefficient ($D_0 = 10^{22}$) was several magnitudes larger than expected and the energy of activation was very high:

$$D_s = 10^{22} \exp (-27500/RT)$$

(no dimensions were given for D_s).

The energy of activation (27,500 cal/mole/deg) suggested to Kingery that the rate-determining process was that of diffusion of water molecules from the ice into the

surface layer. The above relationship may be compared with that obtained by Murphy[18] for the bipedal walk of a water molecule on an ideal ice surface. In this case, only one hydrogen bond has to be broken at the time:

$$D_s = 3.5 \times 10^{-4} \exp(-5200/RT) \ cm^2/sec.$$

The energy of activation for this process is about half that for the heat of evaporation of water (strength of hydrogen bond).

Kingery does not think it necessary to assume a transition film on ice, but only a very highly mobile surface layer, one or two molecules thick. However, in view of all the evidence presented here for the existence of a liquid-like layer on ice, it is clear that Kingery's results agree very well with the assumption of such a transition layer[19]. He also remarks that, if such a film were present, a discontinuity in the surface diffusion properties should become apparent with change of temperature. As a matter of fact, the rate of diffusion as a function of the reciprocal absolute temperature suggests such a discontinuity. If the two points corresponding to the two highest temperatures are considered, an energy of activation of about 180 Kcal/mole/deg is derived.

Kuroiwa[20] also carried out experiments on the growing together of ice spheres. His ice spheres had radii smaller than 10^{-2} cm (20 to 80 μ) over a range of temperatures from -15.5 to -2C. However, no attempt was made to calculate diffusion coefficients and energies of activation. Experiments carried out under kerosine indicated that volume and surface diffusion were involved. Evaporation-condensation was definitely excluded in the experiments under kerosine.

Fletcher[21] was the first to attempt to show quantitatively that a transition layer exists on an ice surface and also on a water surface. His arguments are partly thermodynamic and partly statistical. The main point is to show that ice having such a transition layer on its surface has a lower free energy than ice with an ordinary surface and no disturbance in the surface layer; in fact, the equilibrium state is given when G shows a minimum. Suppose there is a definite amount of ice with an ideal ice surface at a given temperature T; this means it has a perfect ice crystal lattice throughout. The free energy G of the system is given by:

$$G = H - TS \tag{7}$$

where H is the enthalpy, T the absolute temperature, and S the entropy of the system. The essential point is the following: Suppose all the water molecules in the first surface layer are oriented in such a way that all oxygen atoms are pointing outward and all hydrogen atoms inward. This, of course, creates a disturbance in the crystal lattice and there will be a decreasing orientation in neighboring layers until eventually the proper ice structure is reached. If this process is connected with a decrease in G then ice will have such a transition layer. This decrease can be brought about by a decrease in enthalpy and an increase in entropy or any combination of changes in both as long as:

$$\Delta G = \Delta H - T \Delta S$$

is negative; an equilibrium state will be reached when G is at a minimum. This is essentially the basis of Fletcher's paper.
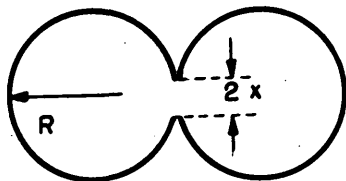
Figure 10. Growing together of ice spheres. [17]

Fletcher points out that the treatment is only an approximate one, since the structure of polar liquids is not yet well understood; however, he maintains that his results are at least of a semiquantitative nature.

The surface structure of water is considered first. Supercooled water or water near the freezing point has a short-range "ice-like" structure. This means that there are small domains which have the structure of ice and which continually fluctuate and change in space and time. This mobility is largely due to the fact that about 13% of the possible hydrogen bonds are

broken. It should also be mentioned that evidence for liquids having surface transition layers was collected by Henniker[22].

The surface molecules of water are supposed to have their oxygen atoms pointing outward whereas the hydrogen atoms are pointing inward. The energy gained (negative ΔH) per molecule by changing from a random orientation to the orientation indicated above is about $\varepsilon \simeq 10^{-12}$ erg/molecule or 14.34 kcal/mole. This value can be estimated in the following ways: (a) The energy gained by orienting one proton in a water surface from pointing outward to the opposite direction is approximately equal to the energy of formation of a hydrogen bond. This leads to a value for ε of about 4×10^{-13} ergs; (b) Estimates using electrostatic energies lead to $\varepsilon \approx 10^{-12}$ erg; (c) Measurements of the surface entropy of water[26] showed that this was lower by 1.7 k (k is Boltzmann's constant) per molecule than the entropy expected from a randomly oriented surface. In a random surface, half of the molecules are oriented inward, the other half outward. For the oriented surface to be stable, this decrease in entropy must be compensated by the enthalpy ε per molecule gained for the process, hence:

$$\varepsilon/2 > 1.7 \, kT$$

which gives for T = 273K,

$$\varepsilon > 1.2 \times 10^{-13} \text{ erg.}$$

Although the orientation decreases the enthalpy of the surface, it does not necessarily follow that the free energy will be decreased, since, because of the orientation, a diminution of the entropy takes place. As long as the decrease of $T\Delta S$ is smaller than that of the enthalpy, a decrease in ΔG occurs. Fletcher's calculations lead to an approximate expression for the change in free energy per molecule resulting from changing the surface and underlying layers from a random orientation to a preferred orientation of the outermost layer with decreasing orientation of the underlying layers:

$$\Delta G \approx -(a_0 - \tfrac{1}{2}) \, \varepsilon + \delta \gamma \, (a_0 - \tfrac{1}{2})^2 + kT \, (a_0 - \tfrac{1}{2})^2 / 2\gamma \qquad (8)$$

where a_0 is a measure of the degree of orientation ($a_0 = 1$ for complete orientation and $a_0 = \tfrac{1}{2}$ for random orientation), ε is the change in enthalpy per molecule, δ is a factor connected with the fraction of time each molecule remains in the oriented state, k is Boltzmann's constant, and γ is a constant. This equation has a minimum for a positive value of $(a_0 - \tfrac{1}{2})$. By choosing reasonable values for ε, γ and δ, and taking $a_0 = 1$ (complete orientation of the uppermost layer), Fletcher comes to the conclusion that, at equilibrium, near the freezing point, water has a transition layer of about 13 molecules (26A) with the outermost layer oriented in such a way that the oxygen atoms point outward.

The structure of the ice surface is treated similarly to that of water. The free energy would not be decreased by just orienting the outermost layer because of the large decrease in entropy. The disturbance has to go very much deeper than that. Fletcher treated the case of a transition layer on ice as envisaged by Weyl[8]. The transition starts with one oriented layer of water molecules at the top, decreasing in orientation until eventually the random arrangement of the ice crystal lattice is reached. The change in enthalpy per molecule for the water/air interface is $\varepsilon_1 \approx 5 \times 10^{-13}$ erg, and ε_2 is the change in enthalpy for the breaking of a single hydrogen bond. As before, he obtains an expression for the change in free energy from an ideal ice surface to a transition layer of thickness $\underline{d}$,

$$\Delta G \approx S_F \cdot \Delta T d = \frac{kT}{2\gamma} \, (a_0 - \tfrac{1}{2})^2 \, [1 - \exp(-2\gamma d)] + \delta \gamma \, (a_0 - \tfrac{1}{2})^2$$

$$-(a_0 - \tfrac{1}{2}) [\varepsilon_1 - \varepsilon_2 \exp(-\gamma d)]. \qquad (9)$$

ΔS_F is the entropy of fusion which is connected with the free energy of fusion for water supercooled by ΔT as follows:

$$\Delta G_F = \Delta S_F \Delta T.$$

Minimization is more complicated than for the previous case but it can be approximately carried out numerically. Figure 11 shows an upper limit for ΔG as a function of temperature. ΔG is definitely negative for a temperature range from 0 to -13C; at lower temperatures ΔG becomes very slightly positive. In actual fact, however, even in the range from -13 to -30C, ΔG may be negative as the calculations are only approximate. The thickness of the transition layer is given by

$$d \approx 2.8 \times 10^{-7} \log \frac{40}{\Delta t} - 0.4 \text{ cm} \tag{10}$$

where Δt is in centigrade. This relationship is depicted in Figure 12. Log d as a function of the reciprocal absolute temperature actually gives a straight line between -2C and -24C with an apparent energy of activation of about 14 kcal/mole/deg. This relationship may be compared with the results of Hosler et al. where the separation force for two ice spheres decreased exponentially with temperature. The ratio of the energies of activation for Hosler's data[11] and Fletcher's theoretical results is given by

$$n = \frac{10.6}{14.0} = 0.75 .$$

Although Fletcher's theoretical considerations contain uncertainties and approximations, as clearly pointed out by him, his results seem to be reasonable and fit in well with all the experimental evidence presented previously.

In a note, Watts-Tobin[23] criticizes Fletcher's paper for neglecting the dipole-dipole interaction between water molecules, which would produce a strong depolarizing effect; however, Fletcher himself has pointed out that his results are at best semiquantitative. It is the first attempt of a quantitative treatment and is therefore of great importance in spite of its shortcomings.

In a recent reply to Watts-Tobin's criticism Fletcher[23a] points out that taking into account the dipole-dipole interaction will not alter the whole picture essentially, but will only affect the quantitative aspects.

He also points out an error in eq 26 (eq 9 in this report) of his paper: "The third term on the right hand side should contain an additional factor $[1 - \exp(-2\gamma d)]$. Minimization of this free energy expression by numerical methods gives a curve closely similar to that of Figure 2 (our Figure 12) above -5C, but below this temperature the film thickness decreases more rapidly and the film vanishes at -12C."

Recently, Telford and Turner[24] made a very careful study of the passage of a thin steel wire through a block of ice over a range of temperatures from -0.5C to -3.5C. Similar experiments were carried out previously by various other workers, but not under well defined and controlled conditions. The older experiments were all explained in terms of pressure melting. Telford and Turner worked with a steel wire 0.045 cm in diameter, polycrystalline ice blocks of about 1 cm thickness, a fixed load of 2.1 kg, and a temperature control of about ± 0.02C. The movement of the wire was recorded; a sensitivity of 1 cm on the chart for a movement of .004 cm was achieved. The migration of the wire in four blocks was measured. The mean velocities as a function of temperature are shown in Figure 13. Between -3.5C and -0.7C a straight line relationship is obtained for the logarithms of the velocity as a function of the logarithms of the temperature in centigrade, the velocities ranging from about 10^{-7} cm/sec to 10^{-6} cm/sec. Above -0.7C the velocity increased enormously, by a factor of about 200 at -0.5C. This increased velocity is attributed to pressure melting. A pressure of about 45 atm is exerted by the wire, which is enough to depress the melting point of ice by about 0.5C. The migration of the wire at temperatures lower than -0.5C, which was completely missed by other workers, cannot be attributed to pressure melting. The authors accept the assumption of a transition layer between the wire and the ice, and consider the movement to be due to the flow of this viscous layer around the wire. The flow is assumed to be Newtonian as a first approximation. Such movement is described by the following equation:

$$V = \frac{F}{12\pi\eta} \left(\frac{d}{a}\right)^3 \tag{10}$$
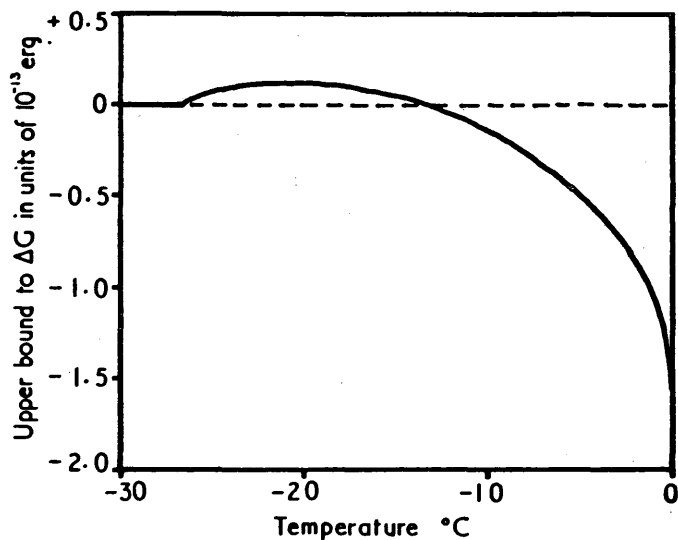
Figure 11. Upper bound to the amount
ΔG by which the free energy of the equi-
librium liquid film surface exceeds that
of a solid crystalline ice surface. ΔG
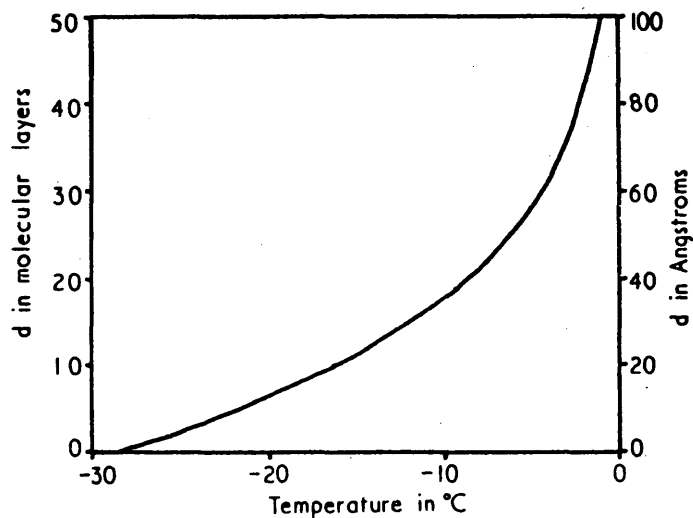is given per surface molecule.[21]

Figure 12. Thickness d of the equi-
librium liquid film on the surface of
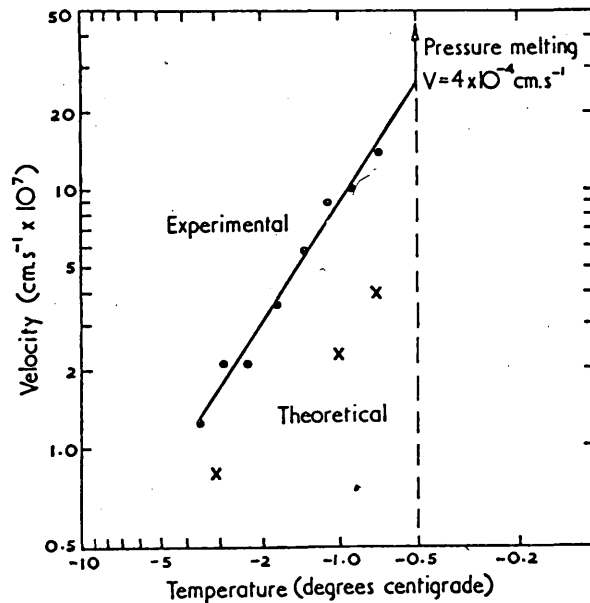ice as a function of temperature.[21]

Figure 13. Velocity of a wire mov-
ing through ice as a function of temp-
erature.[24]

where $\underline{V}$ is the velocity of the wire, $\underline{F}$ the load per unit length of the wire, $\underline{d}$ the thickness of the transition layer, η its viscosity and $\underline{a}$ the radius of the wire. The authors inserted Fletcher's values for the appropriate temperatures and corresponding viscosities for supercooled water into eq 10. The values thus obtained for the velocities are indicated in Figure 13. This, of course, is only a very approximate treatment; the authors are aware of this, since they ascertained that the rate of travel increased with the cube of the load.

An alternative to the above explanation of a liquid-like layer would be that the movement of the wire is due to creep of ice. However, a plot of the logarithm of the rate of travel as a function of the reciprocal absolute temperature gives a straight line; the energy of activation derived from this plot is 180 kcal/mole/deg. This is a very much higher value than that for creep, which amounts at the most to 31.8 kcal/mole/deg. Thus the experimental results are in substantial agreement with the assumption of a transition layer at the ice/metal interface.

It is of interest to note that Mason, Bryant and Van den Heuvel[25] studied the growth of ice crystals and pointed out the importance of surface migration. They suggest that some of their results may be explained in terms of a liquid-like layer on the surface of ice crystals.

It would lead too far here to discuss all the phenomena which are related to the present topic of a transition layer on ice. Into this category fall all the experimental data for systems where the surface or interfacial properties are predominant, such as freezing of droplets, freezing in capillaries or porous systems, frictional properties of ice, properties of thin water films, etc. Some relevant papers are noted in reference 19.

Conclusion and outlook

The experimental and theoretical evidence presented in this report make the existence of a transition layer on ice very likely. What is needed now is more information about the actual properties of such a transition layer. At present, there are only very rough estimates available. From the adhesion measurements we know that the thickness of the layer at an ice/metal and ice/quartz interface is approximately between 10^{-5} to 10^{-6} cm and its viscosity several hundred poises at about -4C. From theoretical considerations, the thickness is known to be about 100A near the melting point, decreasing

exponentially with decreasing temperature until it vanishes at about -30C. It is not known whether the layer is Newtonian as far as viscosity is concerned. Probably it is not. Moreover, all its properties will vary continuously from one side of the film to the other.

Some of the methods which may yield more direct information about the properties of the transition layer will now be considered briefly:

(a) A direct method of measuring film thickness is that of ellipsometry. Plane polarized light reflected from a surface which is coated with a thin layer or a transition layer shows an elliptic component in its reflected beam. The amount of ellipticity, which can be measured, is a function of the film thickness; however, the refractive indexes of the two boundaries or the refractive index as a function of surface layer depth have to be known to obtain actual values for the layer thickness. The effect is quite pronounced for opaque substances but transparent media such as glass, water, and ice are expected to show much smaller effects (see reference 26). Some ellipsometry has been carried out on water surfaces[27]. The least possible thickness which could be calculated from the data was 2.26A. This was calculated with a refractive index $1.1558 = (\mu_1\mu_2)^{\frac{1}{2}}$ where $\mu_1 = 1.0000$ is the refractive index for air and $\mu_2 = 1.3359$ is that for water at 20.0C. However, this is a fairly arbitrary way of choosing the refractive indexes, especially if the layer is a transition layer, and hence a large number of layer thicknesses could be calculated choosing other combinations for the refractive indexes. No data are as yet available for ice.

(b) Electron diffraction should prove a useful tool in this connection, especially low angle diffraction as the electron beam does not penetrate the material deeply in contrast to X-rays.[28]

(c) Infrared spectra, especially reflection spectra, should be of help as their sensitivity for hydrogen bonds is very great.[29]

(d) Nuclear magnetic resonance spectra (NMR) may also be of help.[30]

(e) Surface potentials are also of interest but are not very reproducible.[31]

(f) Surface conductance[32] and surface diffusion would constitute indirect methods which would be of value. Surface diffusion of radioactive molecules such as tritiated water would not be suitable for an ice/air (gas) interface because of exchange reactions, vaporization, and condensation; the same holds true for H_2O^{18} or D_2O. A study of surface diffusion of large molecules tagged with radioactive isotopes would be more feasible.

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