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AN ORIGIN OF THE EQUILIBRIUM LIQUID-LIKE LAYER ON ICE

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Abstract - Mechanism of liquid-like layer formation on ice was pursued by examining the nature of the surface layer. It was found that the hydrogen bond of ice which makes water expand upon freezing and the compression in the normal direction within the surface layer are responsible to cause the pressure melting effect on the ice surface. Assuming a rigid sphere model with $(-i)$-th power intermolecular potential and the additivity, a scheme was developed to compute the distribution of the total potential and that of the integrated force across the surface. It was shown that the total integrated pressure is approximately proportional to the $(-i+4)$-th power of the depth and the temperature of the liquid-like layer is proportional to this power. The relationship was shown for $i=6$ case. Based on this treatment, specific existence of the liquid-like layer was predicted on pressure-melting solids.

I - INTRODUCTION

Existence of equilibrium liquid-like layer on the surface of ice has been a subject of investigation ever since Michael Faraday became engaged in experiments for adhesive properties of ice in 1842 /1/. A number of experimental evidences, though mostly indirect, have accumulated ever since /2, 3, 4, 5, 6, 7, 8, 9, 10, 11/. It appears that this phenomenon is rather unique with the solid phase of water, i.e., ice.

To explain existence of the liquid-like layer, a number of attempts have been made: Gurney /12/ tried to reason that it is based on vacancies that appear in the stress-free surface layer of ice which is believed to collapse into the liquid form. However, the vacancies are no more favorable with the liquid than with the solid because ice holds more volume than water. Weyl /13/ presented a different view based on an electrical double layer which he assumed to possess the characteristics of liquid layer. His contention lacked conviction why the layer has to be liquid-like. Fletcher /14, 15, 16/ formulated a theory of liquid-like layer based on interactions...
of various molecular electric fields and described quantitatively the relationship between the layer thickness and the temperature. Lacmann and Stranski /17/ handled the liquid-like layer based on complete wettability of water on ice, which was not experimentally substantiated /1/. These treatments do not lead to the possible and exclusive existence of the surface layer on the solid phase of water substance. In the meantime, based on the treatment of Römkens and Miller /18/, which considered pressure melting in ice at the interface between mineral particles, Gilpin /19/ estimated the temperature dependency of the layer thickness at the interface between ice and a substrate but not in the free ice surface.

In this paper, we shall first examine the force balance and the relationship among various thermodynamic energies within the surface layer of ice. Then, applying an intermolecular potential to an idealized surface, we shall describe the force or the pressure acting normal to the surface and the potential arising from it. Finally, this pressure distribution will be used to estimate the pressure melting effect of ice in the surface layer or the relationship between the thickness of the liquid-like layer and the temperature.

II - THE SURFACE LAYER

A surface carries an energy and a surface energy is the energy to form the surface. The surface may be created by separating a bulk. After the separation, the surface normally relaxes to settle in a lowest possible energy state. A free energy to form such a surface is called a surface free energy or surface tension.

Let us consider an unrelaxed surface of isotropic condensed phase with density discontinuity for simplicity. Place the x-axis and the y-axis in the plane involving centers of the surface molecules and the z-axis in the direction perpendicular to the plane pointing inside the condensed phase. The bulk of a condensed phase holds a state of lowered intermolecular potentials in three directions. In the bulk, since it is isotropic the potential lowering is the same in every direction. In the surface layer, half of the total lowering is lost. The surface energy here, therefore, is this increase of energy due to formation of the unrelaxed surface with the increase equally assigned to each direction. According to Bikerman /20/, two-thirds of this total surface energy corresponds to the surface free energy. When this surface is created by separation, the force previously balanced in all directions becomes unbalanced in the z-direction and this force imbalance leads to compression within the surface layer, being countered by the intermolecular repulsive force due to overlapping of molecular electronic shells.

Water is a rather special substance in view of the fact that it expands during freezing due to bulky hydrogen bond formation in the solid. Because of this nature, according to Le Chatelier-Braun's law, ice melts under pressure. This suggests a possibility of describing the seemingly unique existence of the liquid-like layer on ice from the pressure melting effect. So, introducing an intermolecular potential, we shall evaluate the pressure in the surface layer of ice.

Intermolecular attractive potentials are given in a sum of the form

$$\phi = -A r^{-i}$$  \hspace{1cm} (1)

where A and i are constants, and $\phi$ sometimes depends on other factors such as dipole orientation. Here for simplicity, we disregard all factors other than the distance between the molecular centers, $r$, and assume rigid spheres for molecules and additivity of the attractive potentials. Since additivity of the potential is assumed, summation of different potentials can be carried out without any difficulty. So, we consider here the most dominant attractive potential only and proceed.

The force arising from the potential is given by its derivative, or

$$f = -\frac{d\phi}{dr} = -A i r^{-i-1}$$  \hspace{1cm} (2)
We now have to sum the z-component of the force in the half space within the condensed phase. Figure 1 illustrates the computational system. The origin of a cylindrical coordinate is placed at the center of one of the surface molecules and the radial distance in the x-y plane is expressed by $\rho$, and the distance between the nearest two molecules by $d$.

We take the following scheme of force integration. First, the x-component of the force acting on the molecule at the coordinate origin will be integrated with respect to $\rho$ in the entire space in the condensed phase and expressed as a function of $z$. The same procedure will be repeated for the succeeding molecules on the $z$-axis. Then, these forces will again be projected into the $z$-axis or integrated in the $\rho$-direction, to express the force distribution in the $z$-direction. Finally, by integration of the distribution, we obtain the integral distribution of the total force or the pressure. Integration of this force at the top of the surface layer gives the total energy due to the total force in the $z$-direction. As stated above, this energy should correspond to the surface tension, the constant in the expression can be estimated, and this constant will be used to describe the integral force or pressure distribution in the $z$-direction. Finally, the pressure term of the pressure melting will be applied to this distribution to obtain the height and temperature relationship of the liquid-like layer.

III - ESTIMATION OF THE LIQUID-LIKE LAYER

For the purpose of force integration, the space inside the condensed phase is divided into two parts; a column of radius $d$ with center on the $z$-axis and the rest of the space. Since contribution to the force from this column is small, this space will be ignored for the rest of this treatment. As already mentioned, at the end of this computation, the constant term will be evaluated in comparison with the surface free energy, only the variable parts of integration will be handled.

By describing the position of the molecule on the $z$-axis with the first subscript and the direction of integration with the following ones, the total force acting on the molecule at the coordinate origin is given as (see Fig. 1)
where $n$ is the number of molecules in a unit volume. The integrand of expression (3) gives the force distribution as a function of $z$. As can be seen in Fig. 1, the distribution $F_\text{opz}$, which is the same as $F_\text{opz}$, begins at $\theta = z/d = 3$ position starting from $\theta = z/d$ value of basic $F_\text{opz}$ distribution, and so on.

Projection of the variable part of this distribution into the $z$-axis gives a distribution

$$F_\text{opz} = \int \int f_z 2\pi \rho d\rho dz = 2\pi A \int z \int_{d}^{\infty} (\rho^2 + z^2)^{-\frac{1}{2}} \frac{1}{2} \rho d\rho$$

$$= \int_{d}^{\infty} z (d^2 + z^2)^{-\frac{1}{2}} \frac{1}{2} dz,$$

(3)

Changing the summation into integration from an average lower limit of $(2e + 3)/4$ and taking the variable part only, expression (4) becomes

$$\theta = \frac{\theta + 1}{2} \text{ or } \frac{\theta + 2}{2}$$

$$k = \theta + \frac{1}{2} \text{ or } \theta + \frac{2}{2}$$

$$\sum_{k} k(1 + k^2)^{-\frac{1}{2}} + \frac{1}{2}$$

(4)

The total integral force in the $z$-direction becomes, by integrating expression (5) for large $\theta$ or $1 << \theta$ and replacing $\theta$ with $z/d$

$$F_T = (z + \frac{d}{2})^{-i} + 4 - 2(\frac{z}{2} + \frac{3d}{4})^{-i} + 4$$

(5)

This is to say that, for $z >> d$,

$$F_T = Bz^{-i} + 4$$

(6)

where $B$ is a constant. $F_T$ distribution by double numerical integration of expression (4) shows that expression (7) holds well with the layer for $\theta = z/d > 4$ but when $\theta$ approaches unity, the numerically integrated values become smaller than expression (7).

The total potential arising from the force given by expression (7) may be obtained by integration of the expression to the top-most layer;

$$E_T = -\frac{B}{-i + 5} z^{-i} + 5$$

(7)

As already discussed above, this $E_T$ is supposed to correspond to the surface free energy of ice or $\sigma_{SG}$, where subscripts $S$ and $G$ stand for solid and gas, we have

$$B = \frac{(i - 5)}{2} \sigma_{SG} d^i - 5$$

(8)

Since $\sigma_{SG}$ is an energy per unit area, application of equation (9) to equation (7) leads to a relationship,

$$F_T = p$$

(9)

IV - PRESSURE MELTING

From the well-known thermodynamic treatment, the pressure that lowers the melting
point of ice by $\Delta T$ is given as

$$\Delta p = \left( \frac{dp}{dT} \right) \Delta T,$$  

(11)

where $dp/dT = -1.35 \times 10^7$ N/m²K. Among intermolecular attractive potentials, the one represented by $i = 6$ is often dominant. So, leaving detailed computation involving more appropriate potentials for the future, we estimate the relationship between the thickness of the liquid-like layer and the freezing point depression applying this $i = 6$ potential. Substituting $p$ in equation (11) with that in equation (7) under the condition given by equation (10) and using equation (9) with $d = 2.76 \times 10^{-10}$ m and $\sigma_{SG} = 0.109$ N/m, we have

$$\Delta T = -2.22 \times 10^{-18} z^{-2}$$  

(12)

where $z$ is in meters. Figure 2 shows this relationship in comparison with that estimated by Fletcher /16/. In the figure, it is apparent that the thickness of the liquid-like layer, $z$, estimated in the present work and that of Fletcher show
a reasonable agreement. The former is slightly smaller than the latter and drops more rapidly as the temperature lowers. However, the numerically estimated value of the integral force or the pressure is lower than the value of equation (12) which uses i = 6 condition. In addition, there are attractive potentials in hydrogen bond of ice with i < 6 [21]. This suggests that the tendency of the curve representing equation (12) is likely to move towards that of Fletcher's curves.

Being based on our present viewpoint of pressure melting, existence of the liquid-like layer is predicted just below the melting point on the solid phase of substances which expand during freezing. Such substances are not common and water belongs to the category. For normal substances which shrink during freezing, liquid-like layer formation should not happen and simple assignment of the excessive free energy at the surface to the phase equilibrium may produce a misleading result of the liquid-like layer formation on any solid surface.

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COMMENTS

V.F. PETRENKO

I did not understand what kind of space charge distribution did you used calculating the acting force?

Answer:

Space charge distribution was not considered as I stated in the condition of the present treatment. However, I can say that both the charge effect and the present...
pressure melting effect come from the energy of initial unrelaxed surface formation. I cannot tell how they are related each other.

E. GAFFNEY

If this is an important mechanism for formation of a liquid-layer, then we should be able to see such a layer on bismuth just below its melting point (which should be at low enough temperatures to permit such observation).

Answer :

I agree. That is what I have been saying these days. Of course, as I said in the conclusion, we have to be careful about the surface purity of the sample to avoid alloy formation and oxide film.

R. GAGNON

Is there an explanation as to why the refractive index of the liquid-like layer is less than that of water at 0°C.

Answer :

I don't know why it is but the observation presented in this symposium earlier shawed it was closer to water than to ice.