

Application of the Theory of Dispersion Forces to the Surface Melting of Ice

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We apply the theory of Dzyaloshinskii, Lifshitz, and Pitaevskii to ice, water, and vapor at the triple point and find that electromagnetic interactions do not permit a liquid film of macroscopic thickness at the ice-vapor interface. Hence the surface melting of ice is at most incomplete. However, the thickness of the film which is permitted is surprisingly large, with retardation effects setting the scale. Our estimate is about 30 Å. Further liquid appears as droplets with a contact angle of about 0.2°. The film thickness decreases rapidly with temperature.

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Surface melting is the process by which a film of liquid forms at the interface between a solid and its vapor, and grows without limit as the triple temperature is approached. As a result, the solid is observed to melt from its surface inward. Although hypothesized for a long time,¹ it is only recently that the predicted divergence in the thickness of liquid has been subjected to experimental test.² Concurrently, there has been much theoretical activity elucidating the thermodynamic singularities associated with surface melting,³ but almost none predicting the systems which would or would not undergo this process. It is the purpose of this paper to carry out such a calculation on a system of particular interest, ice.⁴

A necessary condition for a system to undergo surface melting is that the liquid phase wet the solid-vapor interface at the triple point. In order to predict whether this will be so, one must take into account the interactions between particles in the solid, the vapor, and the liquid film. Because of the inherent many-body nature of such interactions in condensed matter, their effect is most conveniently treated by considering all phases as isotropic continuous media characterized by frequency-dependent dielectric functions. This is the approach taken by Dzyaloshinskii, Lifshitz, and Pitaevskii⁵ (DLP). Their result, Eq. (1) below, makes precise the intuition that a fluid less polarizable than its solid will be attracted to it, causing a thin liquid film to grow at the solid-vapor in-

terface. Conversely, a liquid more polarizable than its solid will not. For the case of ice, we find a very interesting result. While it is true that water is more polarizable than ice at frequencies in the visible, the appropriate dielectric response of ice is greater than that of water at frequencies higher than $\omega_0 \approx 2 \times 10^{16}$ rad/s, in the ultraviolet. For thin films for which retardation can be ignored, the dielectric response at all frequencies is important, and the net effect is that water is attracted to ice. Thus a thin layer of liquid will tend to thicken. As it does so, however, the effects of retardation become increasingly important, weakening first the dielectric contributions at high frequencies, just the ones tending to thicken the film. At some finite thickness the film ceases to grow. Hence surface melting is incomplete.⁶ As retardation is the cause, the scale of the finite film thickness is set by $c/\omega_0 \approx 150$ Å. The possibility of this unusual scenario was hypothesized by DLP in the context of the wetting of a wall, though we are aware of no other such observation.

The central result of the DLP theory is an expression for the excess Helmholtz free energy per unit area of a film of one medium and of thickness L at the interface between two other media. For the system of interest to us, water (W) at the interface of ice (I) and vapor (V), this excess free energy is $F(L) + \sigma_{IW} + \sigma_{WV}$, where the last two terms are the ice-water and water-vapor interfacial tensions and

$$F(L) = \left(\frac{kT}{8\pi L^2} \right) \sum'_{n=0} \int_{r_n}^{\infty} dx x \left[\ln \left(1 - \frac{(x-x_I)(x-x_V)}{(x+x_I)(x+x_V)} e^{-x} \right) + \ln \left(1 - \frac{(\epsilon_V x - \epsilon_W x_V)(\epsilon_I x - \epsilon_W x_I)}{(\epsilon_V x + \epsilon_W x_V)(\epsilon_I x + \epsilon_W x_I)} e^{-x} \right) \right], \quad (1)$$

with

$$x_M = \left[x^2 - r_n^2 \left(1 - \frac{\epsilon_M}{\epsilon_W} \right) \right]^{1/2} \quad (M=I, V).$$

In this expression, the dielectric functions ϵ of water, ice, and vapor are evaluated at the sequence of imaginary frequencies $i\xi_n = i(2\pi kT/\hbar)n$, the prime on the sum

means that the term $n=0$ receives a weight of $\frac{1}{2}$, and $r_n = 2L\xi_n(\epsilon_W)^{1/2}/c$, with k , \hbar , and c the usual fundamental constants. We take the dielectric function of vapor to be unity. An approximation to Eq. (1),

$$F(L) \approx \left(\frac{kT}{8\pi L^2} \right) \sum'_{n=0} \left(\frac{\epsilon_I - \epsilon_W}{\epsilon_I + \epsilon_W} \right) \left(\frac{\epsilon_W - 1}{\epsilon_W + 1} \right) (1 + r_n) e^{-r_n},$$

valid for $\epsilon_W \approx \epsilon_I \approx 1$, makes clear that were $\epsilon_I - \epsilon_W < 0$ over the whole frequency range, $F(L)$ would be a monotonically increasing function of L and the film would not grow. Conversely, were $\epsilon_I - \epsilon_W > 0$ over the whole range, the minimum free energy would correspond to a film thickening without limit. However, as noted above $\epsilon_I - \epsilon_W$ changes sign as a function of frequency at ω_0 in the ultraviolet.

The dielectric functions are constructed from measurements of the complex dielectric functions $\epsilon(\omega)$ of ice and water. The data are used to generate a damped-oscillator model of the dielectric response,

$$\epsilon(\omega) = 1 + \sum_j \frac{f_j}{e_j^2 - i\hbar\omega g_j - (\hbar\omega)^2}, \quad (2)$$

where e_j , f_j , and g_j are fitting parameters. The static dielectric constants are treated separately. Note that the functions required in Eq. (1), $\epsilon(i\xi_n)$, are real, defined at all frequencies, and are monotonically decreasing functions of ξ_n . This latter property permits simple interpolation between regimes in which measured data are available.

Data at zero frequency were taken from Buckley and Maryott⁷ for water at 0°C, $\epsilon_W(0) = 88.2$, and from Auty and Cole⁸ for ice at 0.1°C, $\epsilon_I(0) = 91.5$.⁹ For infrared frequencies, we used the data of Kislovskii and the compilation of Irvine and Pollack.¹⁰ In the visible, refractive indices are well known and were taken from handbooks. Ultraviolet data for water were taken from Heller *et al.*¹¹ and for ice from Daniels¹² and Seki, Kobayashi, and Nakahara.¹³ Fits of the form of Eq. (2) were obtained for water and checked with those of Parsegian¹⁴ for consistency, and were generated for ice using both sets of ultraviolet data. Parsegian has also pointed out the importance of constraining the fits to match the refractive-index data in the visible, which we have done; this ensures a measure of reliability in comparing data from different laboratories. All fitting parameters are presented in Table I. The resulting dielectric functions of imaginary frequency are shown in Fig. 1. In a region of zero absorption, this function is equal to the real part of ϵ at real frequencies.¹⁵ Hence, the fact that $\epsilon_W(i\xi) - \epsilon_I(i\xi) > 0$ in the visible is in agreement with the refractive indices. When these functions for water and ice (using the data of Daniels¹²) are substituted into Eq. (1), a result for $F(L)$ is obtained which is shown in Fig. 2. At the triple temperature the equilibrium thickness of the film is that value which minimizes $F(L)$. For small thicknesses, this function is positive. If retardation were ignored [i.e., $c \rightarrow \infty$ so $r_n \rightarrow 0$ in Eq. (1)], $F(L)$ would decrease with thickness like L^{-2} shown by the dotted line, a behavior which would lead to surface melting; the minimum is reached only as the film thickness diverges. However, when retardation is included, one obtains the full curve which shows a minimum at finite L of about 36 Å. (With the data of Seki, Kobayashi, and

TABLE I. Parameters used to model dielectric response according to the damped-oscillator model of Eq. (2). The generated functions $\epsilon(\omega)$ are fitted to experimental data available from the listed references. The entry marked with an asterisk corrects an error in Ref. 14.

e_j (eV)	f_j (eV ²)	g_j (eV)
Water ^{a,b}		
2.1×10^{-2}	6.3×10^{-4}	1.5×10^{-2}
6.9×10^{-2}	3.5×10^{-3}	3.8×10^{-2}
9.2×10^{-2}	1.3×10^{-3}	2.8×10^{-2}
0.20	5.4×10^{-4} *	2.5×10^{-2}
0.42	1.3×10^{-2}	5.6×10^{-2}
8.293	2.156	0.5248
10.02	5.184	0.8132
11.46	11.66	1.768
13.15	25.38	2.497
14.74	33.65	3.922
18.18	95.86	7.192
ir parameters for ice ^a		
1.716×10^{-2}	2.110×10^{-3}	8.553×10^{-2}
0.1140	6.754×10^{-3}	5.881×10^{-2}
0.4003	1.089×10^{-2}	2.594×10^{-2}
UV parameters for ice ^c		
8.740	3.081	0.7672
11.55	11.25	2.666
14.49	43.12	4.374
17.54	47.93	5.291
21.81	41.25	8.066
32.83	144.8	22.80
UV parameters for ice ^d		
8.603	5.027	0.7308
10.43	5.124	1.342
12.79	8.885	1.968
15.06	48.44	3.701
18.07	54.57	4.688
22.82	39.92	6.876
32.97	85.35	15.93

^aReference 10.

^bReference 11.

^cReference 12.

^dReference 13.

Nakahara,¹³ the minimum is at 22 Å.) Beyond this thickness, the liquid will not grow; hence surface melting is incomplete.

At the triple temperature, additional liquid appears as drops with a contact angle which can be estimated¹⁶ from the Young-Dupr es condition as

$$\cos(\theta) = (\sigma_{IV} - \sigma_{IW})/\sigma_{WV} = 1 + F(L_0)/\sigma_{WV}. \quad (3)$$

Using the generated $F(L_0)$ and $\sigma_{WV} = 75.7$ ergs/cm², we obtain $\theta = 0.2^\circ$. Indirect measurement of the contact angle has been attempted with an angle of 1° inferred in one case¹⁷ and “. . . zero or very near zero. . .” in the other.¹⁸ Our result indicates the order of precision needed in any such measurement.

The decrease in the thickness of this film as temperature is reduced along the sublimation line T - $p(T)$ is ob-

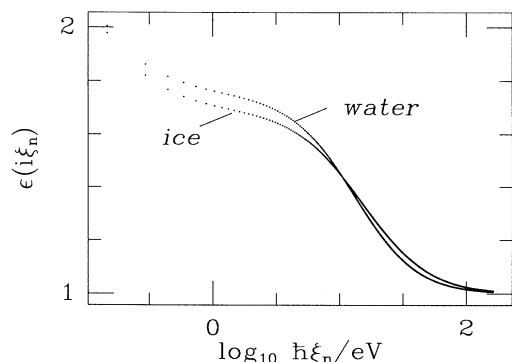


FIG. 1. Fits of the dielectric functions of water and of ice, evaluated at the discrete imaginary frequencies $i\xi_n$ used in Eq. (1). For the case of ice, the fits using data of Refs. 12 and 13 are indistinguishable on this scale.

tained from

$$\frac{dF(L)}{d\Gamma} = \mu(T, p(T)) - \mu(T_t, p(T_t)), \quad (4)$$

where T_t is the triple temperature and Γ is the excess adsorption.¹⁹ Expanding the right-hand side of the above according to the Gibbs-Duhem equation and relating the adsorption Γ to the thickness L we obtain

$$\begin{aligned} \frac{dF(L)}{dL} &= \rho_L q_{\text{fus}} \left(1 + \frac{\rho_V (\rho_L - \rho_I) q_{\text{sub}}}{\rho_L (\rho_I - \rho_V) q_{\text{fus}}} \right) \left(\frac{T - T_t}{T_t} \right) \\ &\approx \rho_L q_{\text{fus}} \left(\frac{T - T_t}{T_t} \right), \end{aligned} \quad (5)$$

where ρ_I is the number density of ice, etc., and q_{fus} and q_{sub} are the latent heats per particle of fusion and of sublimation. For a given temperature, this equation can be solved numerically for the corresponding thickness L . The results are presented in Fig. 3. For films which are not too thick, one sees that the film thickness increases with temperature as $L \propto (T_t - T)^{-1/3}$. Given that the film does grow at small thicknesses for which retardation is not important, this is the temperature dependence expected for dispersion forces.

In summary, we have calculated that the surface melting of ice is incomplete. We obtained a minimum in the surface free energy corresponding to a rather thick film of water at the ice-vapor interface, 36 or 22 Å depending on the experimental data chosen as input. These particular values should not be overemphasized, as the calculated minimum in the free energy is extremely shallow, as seen in Fig. 2, and is also subject to the assumptions of the DPL theory that all media can be treated as continuous and isotropic, and all interfaces as solely providing appropriate boundary conditions for the electromagnetic fields. Of more importance is the result that the calculated film thicknesses, though finite, are large, as

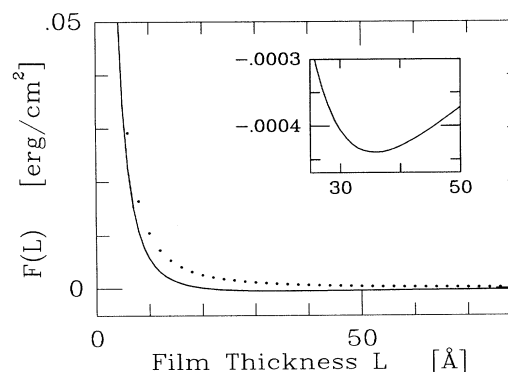


FIG. 2. The contribution $F(L)$ to the surface Helmholtz free energy per unit area as a function of film thickness L . The dotted line shows the result without retardation, and the solid line with retardation. Axes on the inset have the same units as those on the main graph.

this is due only to the crossover at high frequencies of the appropriate dielectric responses of ice and water. Fluctuations could induce a larger thickness, but cannot cause complete surface melting because dispersion forces dominate at large distances. Provided that there is no deeper minimum in the free energy at molecular distances, a minimum whose presence would not be revealed by this calculation, we would expect a thick film of water to be observed at the ice-vapor interface at the triple point. Further deposition of water on top of this film must result in bulk droplets whose contact angle we estimated as 0.2° . The thickness of the film decreases rapidly with temperature.

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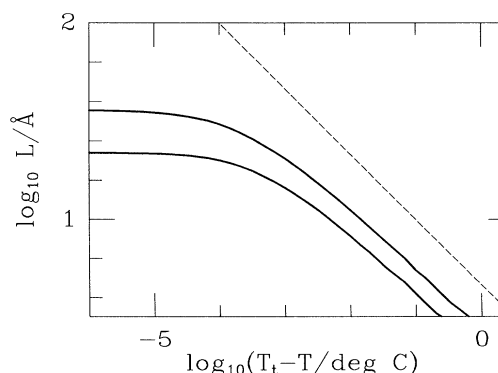


FIG. 3. Calculated film thickness vs $T_t - T$, with T_t the triple temperature. Upper (lower) curve uses the data of Ref. 12 (Ref. 13). The dashed line shows $(T_t - T)^{-1/3}$ power law expected when retardation is unimportant.

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