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Dispersion-force effects in interfacial premelting of ice

L. A. Wilen
Department of Physics, Box 351560, University of Washington, Seattle, Washington 98195-1560

J. S. Wettlaufer
Applied Physics Laboratory, Box 355640, University of Washington, Seattle, Washington 98105

M. Elbaum*
Department of Physics, Technion–Israel Institute of Technology, Haifa 32000, Israel

M. Schick
Department of Physics, Box 351560, University of Washington, Seattle, Washington 98195-1560

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We calculate the van der Waals contribution to the surface free energy of ice-water-substrate systems as a model for interfacial melting. The result for each substrate is the excess surface free energy per unit area $F(L)$ as a function of the thickness L of a hypothetical water layer between the ice and the substrate. A minimum in this function as $L \to \infty$ is a necessary condition for complete interfacial melting, equivalent to complete wetting at the melting point. Retarded potential effects ensure that this condition is fulfilled for large L, a consequence of the relative refractive indices of ice, water, and the substrates in the visible. Whether or not complete melting occurs for a given substrate depends on the interactions at short range. When taken alone, the van der Waals interaction predicts incomplete melting, via a global minimum at finite L, for some substrates and complete melting for others. We have carried out the calculation for cases in which the materials in contact with ice are conductors (gold, copper, silver, tungsten, and silicon), dielectric crystals (MgO, sapphire, and fused quartz), and polymers (polyvinylchloride, Teflon, and polystyrene, among others) and find examples of both behaviors. Where complete melting is indicated, the interfacial interactions will stabilize a finite thickness liquid film at temperatures below the melting point. We find that these thicknesses are small at temperatures below $-0.1\,^\circ$C, and we compare our results to experimental observations. Using a simple model, we find that electrical interactions, if present, can be much stronger than the van der Waals interaction.

I. INTRODUCTION

Complete interfacial melting of a solid denotes the thickening, without limit, of a liquid film at the interface between the solid and a dissimilar substrate as the bulk melting line is approached. If the "substrate" is the vapor phase, the process is commonly referred to as surface melting. This process is accepted as an explanation for the absence of a nucleation barrier to melting,[1] in contrast to bulk solidification. In parallel with the terminology of wetting, incomplete interfacial melting refers to the situation in which the liquid film thickness saturates at a finite value, possibly zero, at bulk phase coexistence. A case of special interest is that of ice, whose melting has practical implications for a wide range of natural phenomena including frost heave, the charging of thunderclouds, the breakdown of rock and concrete, the sintering of snow, and the flow of glaciers.[2]

In recent years, the existence of a liquidlike layer at solid-vapor interfaces has been demonstrated unequivocally for metals and noble-gas solids using the techniques of ion backscattering,[3] x-ray scattering,[4] low-energy electron diffraction,[5] neutron scattering,[6] He atom scattering,[7] scanning tunneling microscopy,[8] and calorimetry.[9]

It has also been been shown that a fluid layer exists at the interface between ice and its vapor at temperatures near the triple point, although it is not clear whether or not the film thickness saturates as the melting temperature is approached. Furthermore, the studies disagree on the thickness of the melted layer as a function of temperature.[10–12] The situation is complicated by the fact that the different crystal facets exhibit different melting behavior and that the prism facet undergoes a roughening transition at a temperature below but close to the bulk melting temperature.[13] A recent experiment[14] using x-ray scattering provides evidence that a disordered layer persists at the ice surface down to temperatures as low as $-12\,^\circ$C.

Interfacial melting presents a more substantial experimental challenge because direct access to the interface is limited. Using a variety of techniques, numerous groups have attempted to elucidate the interfacial melting of ice. Because many of these experiments were motivated by the study of unfrozen liquids in porous media, particularly in soils for the case of water, their results were

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complicated by curvature and impurity effects.[2] Only a few studies have been performed to look at interfacial melting against a substrate with a planar geometry.[15–20]

In a classic experiment, Gilpin[16] measured the regelation of fine metal wires through ice and interpreted the results in terms of the properties of a melted layer at the ice-wire interface. More recently, several experiments have studied the melting of ice at various planar insulating interfaces.[17–20] Gilpin's work and these later experiments motivated the present calculation.

Theoretically, a layer of liquid will appear at the interface between ice and a substrate if its presence lowers the interfacial free energy. In general, this free energy is determined by all of the interactions present in the system. For a flat neutrally charged surface and in the absence of impurities, it is reasonable to expect that van der Waals (vdW) forces dominate at large distances and will determine whether it is favorable for a thick film to grow without limit as the melting line is approached. Such behavior is a necessary condition for interfacial melting. It is not sufficient because the lowest free energy may be attained when the film is thin.

The van der Waals contribution to the free energy of a surface consisting of a liquid layer of thickness L between bulk ice and a substrate can be obtained from the theory of Dzyaloshinskii, Lifshitz, and Pitaevskii.[21] The result of this theory is an integral expression for the interfacial free energy per unit area in terms of the frequency-dependent dielectric polarizabilities of the three media: ice (i), water (w), and substrate (s). The interfacial free energy per unit area is written as $\gamma_{is}(L) = \gamma_{iw} + \gamma_{ws} + F(L)$, where γ_{iw} and γ_{ws} are the interfacial free energies per unit area of the ice-water and water-substrate interfaces, with implicit reference to the crystallographic orientations present at an interface. Since the interactions decay with distance, $F(L) \to 0$ for $L \to \infty$. The ice-substrate interfacial free energy γ_{is} is given by the minimum, over L, of $\gamma_{is}(L)$. Complete interfacial melting is indicated by a global minimum of this function at $L \to \infty$ so that $\gamma_{is} = \gamma_{iw} + \gamma_{ws}$ at bulk coexistence. Incomplete interfacial melting is indicated by a minimum at finite L, with $F(L)$ negative there.

Loosely speaking, melting at an ice-substrate interface is favorable when the polarizability of the water lies between that of the ice and the substrate. The novelty of the ice-water system stems from the fact that the appropriately-transformed polarizability of ice is greater than that of water at frequencies higher than approximately 2×10^{16} rad s^{-1}, while at lower frequencies it is smaller. For thin films, the polarizabilities at all frequencies contribute additively to $F(L)$. As a film thickens, however, the effect of retardation (attenuation from travel time delays) is to reduce the high-frequency contribution to the excess free energy and therefore to bias the overall sum to the regime where the polarizability of water is greater than that of ice. From the criterion above, we expect complete interfacial melting to be possible in the case of ice against a substrate with low-frequency polarizability greater than water and forbidden in the case of a substrate with a low-frequency polarizability less than water. The former is true for most solids while the latter is certainly the case when the substrate is the system's own vapor, i.e., the case of surface melting. Indeed, Elbaum and Schick[22] found in this case that the thickness of the liquid layer saturated at a finite value, so that complete surface melting should not occur. Their calculation is consistent with the observation of droplets on the ice surface at the triple point.[10] Bar-Ziv and Safran[23] extended the calculation to include the effect of placing a hydrocarbon layer of variable thickness between the vapor and the water. They found that as the hydrocarbon layer thickens, a first-order surface transition occurs from incomplete to complete interfacial melting.

II. CALCULATION

The Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) expression for $F(L)$ has appeared in the literature in a variety of forms[21–25] and we present it here in order to clarify the connection between the dielectric response of the substrate (ϵ_s) and those of ice (ϵ_i) and water (ϵ_w),

$$F(L) = \frac{kT}{8\pi L^2} \times \sum_{n=0}^{\infty}{}' \int_{r_n}^{\infty} dx\, x \left[\ln\left(1 - \frac{(x-x_i)(x-x_s)}{(x+x_i)(x+x_s)} e^{-x}\right) + \ln\left(1 - \frac{(\epsilon_s x - \epsilon_w x_s)(\epsilon_i x - \epsilon_w x_i)}{(\epsilon_s x + \epsilon_w x_s)(\epsilon_i x + \epsilon_w x_i)} e^{-x}\right)\right], \quad (1)$$

where

$$x_j = \left[x^2 - r_n^2\left(1 - \frac{\epsilon_j}{\epsilon_w}\right)\right]^{1/2} \quad (j = i, s), \quad (2)$$

and the material (i, w, s) dielectric functions (corresponding to ice, water, and substrate) are evaluated at the sequence of imaginary frequencies $i\xi_n = i(2\pi kT/\hbar)n$. The prime on the sum indicates that the $n = 0$ term is weighted by 1/2. The lower limit of integration is $r_n = 2L(\epsilon_\ell)^{1/2}\xi_n/c$ and k, $\hbar$, and c have their usual meaning. The dielectric function required in the integral $\epsilon(i\xi)$ is the analytic continuation of the material dielectric function $\epsilon(\omega)$ to imaginary frequencies. This is most easily generated by fitting the dielectric response of the material to a damped-oscillator model of the form

$$\epsilon(\omega) = 1 + \sum_j \frac{f_j}{e_j^2 - i\hbar\omega g_j - (\hbar\omega)^2}, \quad (3)$$

where e_j, f_j, and g_j are fitting parameters.[24] Each term in the sum corresponds to an absorption band of frequency, width, and oscillator strength e_j, g_j, and f_j, respectively. Substitution of $i\xi$ for ω gives $\epsilon(i\xi)$, a well behaved, monotonically decreasing, real function of ξ.

Equation (1) assumes implicitly that ϵ_i is isotropic. The vdW result for materials with anisotropic polarizability functions has recently been worked out.[26] We neglect anisotropy in the ice polarizability in this work. It has not been measured over the full frequency range, but judging from known values at optical frequencies,[27] it is likely to be small.

The subtle effect of the frequency-dependent contributions of all the materials to the free energy of the water layer becomes more transparent when inspecting the following approximate[22–24] representation of Eq. (1):

$$F(L) \approx \frac{kT}{8\pi L^2} \sum_{n=0}^{\infty}{}' \left(\frac{\epsilon_i - \epsilon_w}{\epsilon_i + \epsilon_w} \right) \left(\frac{\epsilon_w - \epsilon_s}{\epsilon_w + \epsilon_s} \right) (1 + r_n) e^{-r_n}. \tag{4}$$

The approximation holds for $\epsilon_w \approx \epsilon_i \approx \epsilon_s \approx 1$. The term e^{-r_n}, due to retardation, acts as a high-frequency cutoff to the sum. The cutoff frequency is inversely proportional to L.

When the substrate is pure water vapor, ϵ_s may be taken equal to 1. In this case, it is clear that if $\epsilon_i - \epsilon_w < 0$ at all frequencies, $F(L)$ would be a monotonically *increasing* function of L and the film would not grow. Conversely, if $\epsilon_i - \epsilon_w > 0$ at all frequencies, then $F(L)$ would be a monotonically *decreasing* function and the film thickness would diverge as the melting temperature is approached. The functions ϵ_w and ϵ_i are shown in Fig. 1. Because $\epsilon_i - \epsilon_w$ changes sign at a frequency we denote by ξ_c, the melting behavior that results is intermediate between these cases. In particular, for sufficiently large L, where the sum is dominated by the low-frequency terms, surface melting is inhibited, as discussed earlier.

When the substrate is a solid material with arbitrary dielectric properties, the results are more complicated. The function ϵ_s now depends on frequency ξ and $\epsilon_w(i\xi) - \epsilon_s(i\xi)$ may change sign. However, one general conclusion may still be made upon examination of the dielectric curves. For all of the materials studied, we observe that $\epsilon_s > \epsilon_{i,w}$ in the frequency range $\xi < \xi_c$. We can say with certainty that for L large enough (approximately 30 Å) to allow retardation to come into play, $F(L)$ will be a positive monotonically decreasing function of L. Thus the necessary condition for complete interfacial melting to occur is fulfilled. To determine whether there is another, deeper, minimum in the free energy at small film thicknesses requires implementation of the full calculation.

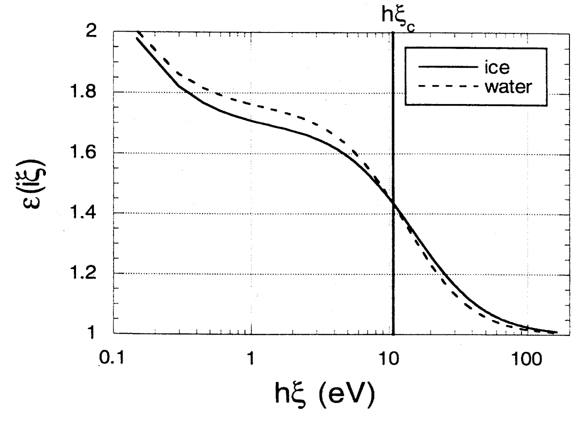

FIG. 1. Appropriately transformed dielectric constants of ice $\epsilon_i(i\xi)$ and water $\epsilon_w(i\xi)$, plotted against frequency. Note that $\epsilon_w(i\xi) > \epsilon_i(i\xi)$ for $\xi < \xi_c$ and $\epsilon_w(i\xi) < \epsilon_i(i\xi)$ for $\xi > \xi_c$.

III. NUMERICAL PROCEDURE

The integral in Eq. (1) is calculated by dividing the range into three regions with each evaluated by a five-point Gaussian quadrature integration routine. The sum over n was performed explicitly from $n = 0$ to 30 and the remainder was approximated by an integral again using Gaussian integration. Standard checks were performed to ensure that the numerical procedure gave correct results, including increasing the number of points in the domain and changing the limits of integration. We also checked the accuracy of the technique by integrating functions similar in form to those in Eq. (1), but for which the result could be determined analytically.

The dielectric fits came from several different sources. For ice and water, we have used the fits to the dielectric data found in Ref. 28 determined by Elbaum and Schick.[22] The dielectric functions for gold, copper, silver, polystyrene, and tetradecane were taken from Parsegian and Weiss.[29] These were fits to data from Ref. 30, covering a wide frequency range using multiple absorption bands. Data for silicon and MgO were taken from Sabisky and Anderson[25] and were based on a single and a double band, respectively. Data for all of the polymer materials, sapphire, and fused quartz were obtained from Hough and White.[31] These were fits to the available dielectric data[32] using two principal absorption bands: one in the ir and one in the uv. In addition, we have fit the data of Weaver, Lynch, and Olsen for tungsten.[33] Finally, one last material, labeled "hypothetical," is a material for which we used dielectric properties that emphasize interfacial melting in a maximal way. For this material, we took $\epsilon_s \to \infty$ for $\xi < \xi_c$ and $\epsilon_s = 1$ for $\xi > \xi_c$. An examination of Eq. (4) suggests that this choice yields the largest positive result possible for $F(L)$.[34] This will serve as a useful upper limit in comparisons with experiments.

IV. RESULTS

The results of the calculation are shown in Fig. 2. For convenience, the materials are divided into three groups: conductors, polymers, and dielectrics. For each material, we have plotted the dielectric curve as well as the result for $F(L)$. The results may be summarized as follows. For large L, $F(L)$ is a positive monotonically decreasing function of L. Depending on the substrate, we find two cases as $L \to 0$: (i) the free energy diverges to positive infinity or (ii) the free energy reaches a maximum and then diverges to negative infinity. The theory is not applicable to films smaller than a few molecular layers. The singularity at $L = 0$ is avoided by cutting off $F(L)$ at $L = D$, where D is approximately one molecular layer.

At bulk coexistence, the film thickness is determined by the global minimum of $F(L)$. Hence, in the absence

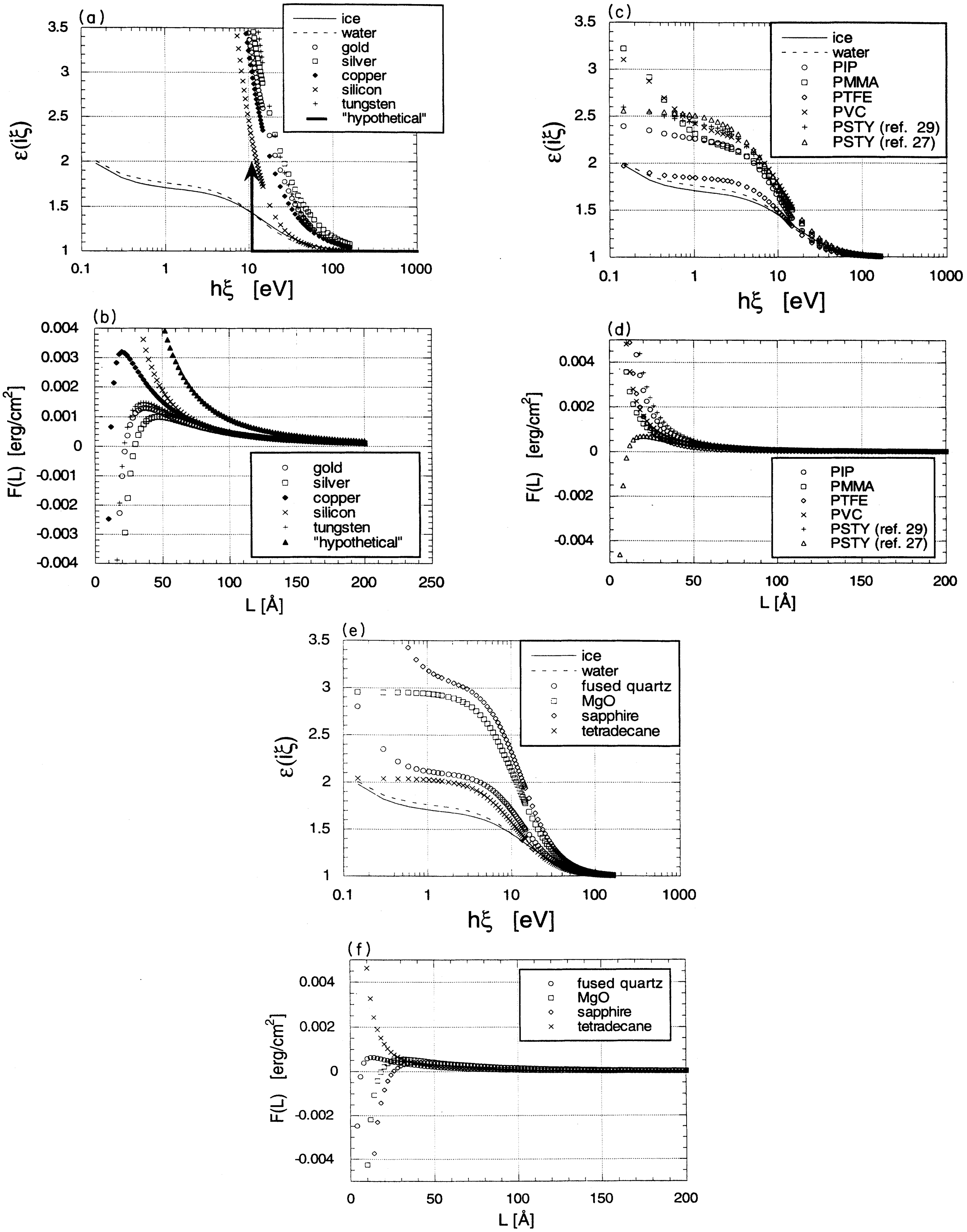

FIG. 2. Top: the dielectric function $\epsilon(i\xi)$ vs frequency. Bottom: $F(L)$ vs L. (a) and (b) Gold, silver, copper, silicon, tungsten, and "hypothetical" substrate. (c) and (d) Polyisoprene (PIP), polymethylmethacrylate (PMMA), polytetraflouroethylene (PTFE), polyvinylchloride (PVC), and polystyrene (PSTY). (e) and (f) Fused quartz, magnesium oxide (MgO), sapphire, and tetradecane.

of any additional forces, case (i) implies *complete* interfacial melting while case (ii) implies *incomplete* interfacial melting. The qualification of no additional forces is an important one. Below thicknesses of several molecular layers, short-range forces commonly observed in water will add to the vdW interaction and can influence the melting behavior. Our intention here is simply to exhibit the vdW result and indicate what behavior it implies if taken alone. Later, we will comment briefly on the influence of additional interactions.

An interesting possibility for the incomplete melting case is the following. If the surface were initially covered with water at the melting temperature, a metastable melted layer could persist down to lower temperatures because a transition to the global minimum at small thickness would require activation over the maximum in $F(L)$. Under certain conditions this might entail the nucleation of a "negative droplet." Such a scenario has been recently described for the wetting of helium films on transition-metal substrates[35] and also in a recent experiment on evaporation.[36] Another possibility that has been considered recently is that surface roughness would modify the short-range part of $F(L)$ in a way that results in complete melting.[37]

Because of the unusual crossover in dielectric properties of ice and water, retardation plays a more important role here as compared to other systems. When retardation is neglected, $F(L) \approx L^{-2}$ for *any* system. The usual effect of retardation is to cause the power-law dependence of $F(L)$ to decrease monotonically from -2 as L increases. For example, this is the behavior predicted for the case of the wetting of substrates by liquid helium.

Here the effect of retardation is more exotic; $F(L)$ changes sign in some cases, while for others $F(L)$ may fall off more slowly than L^{-2} in some range of L. Although the former possibility is obvious upon examination of the curves, the latter may be seen by plotting the logarithmic derivative of $F(L)$ against L.[24] Figure 3 shows such a plot for three of the materials. For comparison, the same quantity is plotted for the case of a Si-He-vapor interface, which exhibits the more common power-law behavior.

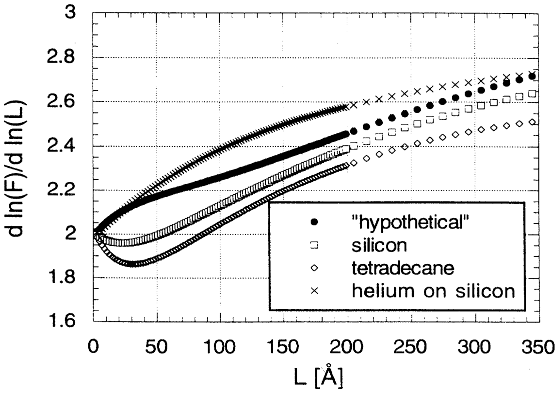

FIG. 3. Logarithmic derivative of $F(L)$ vs L, plotted for three ice-water-substrate interfaces. For comparison, the same quantity is also plotted for the silicon-helium-vapor interface.

The vdW interaction for the interfacial melting geometry is notably weak compared to typical vdW interactions for arbitrary interfaces. The reason for this is twofold. First, since $\epsilon_i \approx \epsilon_w$, the terms depending on $\epsilon_i - \epsilon_w$ in the sum are small. Moreover, for thin films, where the sum is evaluated over all frequencies, the range where $\epsilon_i < \epsilon_w$ partially cancels that where $\epsilon_i > \epsilon_w$. Another consequence of this near cancellation is that the details of the interaction for small L are very sensitive to the dielectric data. A small error in the material dielectric data can modify the weighting in the sum and change the sign of the result. As a case in point, we found that the data for polystyrene from Hough and White,[31] who used a simple two-band model, indicates complete melting, while the data from Parsegian and Weiss[29] indicates incomplete melting. The result due to Parsegian and Weiss is likely to be a closer representation of the actual dielectric properties of polystyrene because it is a precise fit to data taken over a large frequency range. In this instance, a two-band model is insufficient to achieve accurate results.

The Hamaker constant A_H is a common measure for comparing the strength of the vdW interaction for different interfaces. From it, one obtains the nonretarded vdW result by the definition $F(L)_{\text{nonretarded}} = -(A_H/12\pi L^2)$. The nonretarded result coincides with the full result at small L and gives an estimate of its magnitude over a wider range. We can easily extract A_H from our calculation of the full interaction by the definition $A_H = \lim_{L\to 0}\left[-12\pi L^2 F(L)\right]$.

Table I lists the Hamaker constants for various interfaces. The typical Hamaker constant for two planar surfaces separated by a water layer is an order of magnitude larger than the corresponding value for an interface between ice and a substrate.

At temperatures below the phase coexistence line a finite liquid layer thickness may be favored by the extra term in the chemical potential due to the interfacial interactions. The layer is opposed by the penalty to supercool the liquid. The thickness as a function of temperature is thus found by minimizing the quantity $G(L) = F(L) + (q_m/v_i T_0)(T_0 - T)L$, where q_m, v_i, and T_0 are the latent heat of melting, specific volume, and melting temperature of ice. In Fig. 4 we plot the layer thickness against temperature for a few substrates. Note that, at temperatures below $-0.1\,^\circ$C, the thicknesses are already less than 15 Å, even for the hypothetical substrate.

We compare our results with measurements from several experiments. Gilpin[16] performed detailed studies of ice premelting against tungsten and the alloys chromel and constantan by measuring the regelation rate of thin wires through ice as a function of temperature. With the assumption that the viscosity of the interfacially melted layer is the same as that of bulk (supercooled) water, the regelation rate yields the layer thickness. The actual viscosity of the layer may in fact be larger than the bulk value due to a proximity effect. If this is the case, then the film thicknesses that Gilpin calculates are smaller than the actual values. Over three decades of temperature he found evidence of a melted layer at the ice-metal

TABLE I. Hamaker constants for various interfaces.

Interface	Hamaker constant (10^{-14} ergs)
ice-water-gold	1.573
gold-water-gold	250.96
ice-water-silicon	-1.66
silicon-water-silicon	119.7
ice-water-polystyrene	0.122
polystyrene-water-polystyrene	13.4
ice-water-polyvinylchloride	-0.13
polyvinylchloride-water-polyvinylchloride	12.22
ice-water–fused quartz	0.03
fused quartz–water–fused quartz	7.46
ice-water-sapphire	0.63
sapphire-water-sapphire	51.2

interface whose thickness was independent of the wire material.[38] Gilpin's results for the film thickness are consistent with a form for $F(L)$ that is proportional to L^{-2}, suggesting a nonretarded van der Waals interaction.[39] However, the result of the full DLP calculation predicts the absence of interfacial melting for tungsten and the film thicknesses that Gilpin finds are even much larger than that produced by our hypothetical substrate (see Fig. 4). For example, Gilpin finds a thickness of about 35 Å at $T = -1\,^\circ$C, while the calculation yields 6 Å at the same temperature for the hypothetical substrate. Hence dispersion forces alone cannot account for the melting in Gilpin's experiment.

Two recent experiments have investigated planar ice-glass interfaces using ellipsometry. Below $-1\,^\circ$C, Furukawa and Ishikawa[18] ascribed a signal, corresponding to a water layer of approximately 100 Å, to the roughness of the glass substrate and above this temperature they observed the thickness to increase rapidly with temperature. Beaglehole and Wilson[19] observed no liquid film when ice was against smooth, impurity-free glass, but against roughened glass they found films at temperatures down to $-5\,^\circ$C. The effect of surface roughness on wetting has been treated in numerous contexts[37,40–44] and a complete understanding is still evolving.

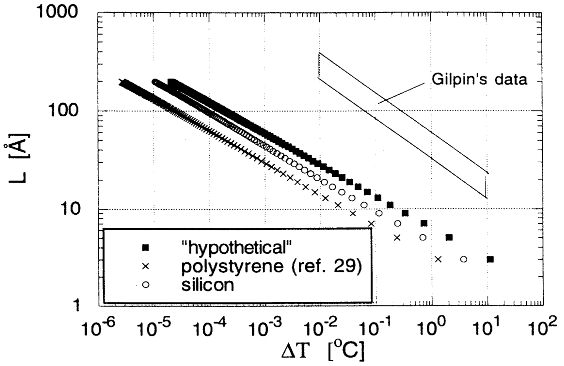

FIG. 4. Layer thickness vs temperature for various materials for which interface melting is indicated. Gilpin's data fall within the region shown.

Beaglehole and Wilson's results for a smooth substrate are consistent with the predictions of our calculation, which shows that the minimum of the surface free energy is at zero film thickness for all of the dielectric crystals studied. (The dielectric properties of fused silica are practically identical to those of fused quartz.) However, we point out that the results for these materials were calculated using a simple two-band model of the dielectric behavior. The same type of model gave an incorrect result for polystyrene, as discussed above. Slightly different dielectric data for quartz could give a result indicating complete interfacial melting, but with a film thickness of less than 10 Å at temperatures below $-0.1\,^\circ$C. Given Beaglehole's temperature and thickness resolution, this would still be consistent with his observations.[45]

Wilen and Dash[20] found a melted film of about 15–35 Å at the ice-polyvinylidenechloride interface for temperatures in the range from -0.03 to $-0.01\,^\circ$C with indications of an abrupt transition to smaller thicknesses below this range. Although dielectric data for polyvinylidenechloride were not available, we expect that it would give results similar to the other polymers. Again, the full van der Waals result predicts either extremely thin or no melted films in the temperature range where films were detected experimentally.

V. ADDITIONAL INTERACTIONS

Our main objective in this paper is to calculate the vdW interaction at ice-water-substrate interfaces. However, we would like to mention briefly the possible role that other forces may play in this system. Short-ranged interactions due to solvation or hydration forces may dominate for small layer thicknesses, but are difficult to calculate. Solvation forces are usually (spatially) oscillatory in nature while hydration forces can be either repulsive or attractive. When these short-range interactions are added to the vdW forces, they can change the overall melting behavior from incomplete to complete or vice versa. On the other hand, if melting is indicated, the thicknesses predicted by the vdW interaction will be fairly accurate if they are larger than the range of the short-range interactions present. Electrostatic forces will be present if the substrate becomes charged either by the ionization of surface groups or by the adsorption of ions,[46] resulting in an electrical double layer. We can estimate the strength of the electrical interaction if we make certain simplifying assumptions. First, we assume that there is no background electrolyte present in the liquid layer. In other words, all ions in the layer result from ionization of the substrate. This is not unreasonable if the water used in a given experiment is initially very pure. The degree of ionization of the substrate will be left as a parameter to be varied. Second, we assume that the ice-water interface is uncharged. This assumption is not as well motivated, but it simplifies the calculation and is unlikely to affect the order of magnitude of the estimate. With these caveats, we proceed along the lines developed by Israelachvili[46] for the analogous case of the wetting of ionizable substrates by water films.

The solution of the Poisson-Boltzmann equation gives the pressure P between two surfaces, each with surface charge density σ, separated by a medium of thickness d and dielectric constant ϵ as

$$P = 2\epsilon\epsilon_0 \left(\frac{kT}{ze}\right)^2 K^2, \tag{5}$$

where z is the valence of the ions in solution and K is found by solving

$$K \tan\left(\frac{Kd}{2}\right) = \frac{-ze}{2kT}\frac{\sigma}{\epsilon\epsilon_0}. \tag{6}$$

The assumption of no (surface) charge at the ice-water interface allows one to identify the above result for two charged surfaces to that expected for a water layer of thickness $L = \frac{d}{2}$ sandwiched between a single charged substrate and ice.[46] Equation (5) is solved numerically for many values of $d = 2L$ and the results are integrated to give $F_{\rm elec}(L)$

$$F_{\rm elec}(L) = \int_L^\infty P(x')dx'. \tag{7}$$

In Fig. 5 we have plotted the results for the electrical interaction, using three different surface charge densities, along with that expected from the vdW interaction for the hypothetical substrate. A charge density of $0.3\ \mathrm{C\,m^{-2}}$ is assumed to be typical of a fully ionized surface. For simplicity we have taken $z = 1$. Note that the electrical interaction is far stronger than that due to dispersion forces at distances greater than 25 Å, even for surface charge densities as small as 0.1% that of a fully ionized surface.

The electrical interaction in this example has a very long range, with $F_{\rm elec}(L)$ going as L^{-1} for large L. This fact depends explicitly on our assumption of no background electrolyte. In fact, electrolytes are always present, even for pure water. When these are taken into account, the range of the interaction is given by the usual Debye length, which depends inversely on the square root of electrolyte concentration and is about 1 μm for a concentration of $10^{-7}M$. Consequently, one can identify two situations where the effect of electrical interactions can be neglected. The first is in a pure system where little or no ionization of the substrate occurs and the second is when the concentration of electrolytes is high enough that the interaction dies out very quickly. (In the latter case, the electrical interaction may still need to be considered for its effect at short range.) In the absence of these special conditions, we see that electrical interactions can possibly outweigh the weak vdW forces that we have calculated for this system.

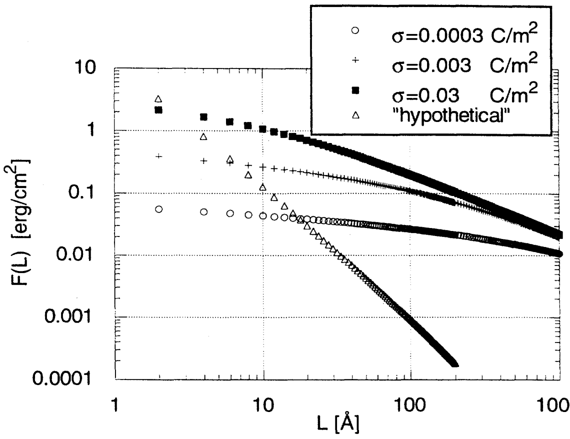

FIG. 5. Results of a simple electrical interaction for various surface charge densities compared to the vdW interaction of the hypothetical substrate.

VI. CONCLUSION

Within the framework of the full frequency-dependent theory of dispersion forces, we have investigated the conditions under which a variety of ice-substrate interfaces undergo complete interfacial melting. The calculations provide the van der Waals contribution to the surface free energy $F(L)$ of ice at interfaces with conductors, dielectric crystals, and polymers.

Retardation always results in a positive, monotonic decrease in $F(L)$ with L, as $L \to \infty$. Consequently, dispersion forces will never prevent the occurrence of complete melting of ice at dissimilar substrates. In the absence of all but van der Waals interactions, the predictions differ among the materials considered; both complete and incomplete melting occur. Subtle and unusual effects are observed in the sign and slope of $F(L)$, which originate in the frequency dependence of the polarizabilities of the materials. An intriguing result for some interfaces is the existence of a local free-energy maximum, which poses a barrier to the asymptotic behavior in $F(L)$ and could possibly lead to hysteretic freezing or melting phenomena. The similarity in the dielectric properties of ice and water results in a weak overall vdW interaction. Interfacial melting is a marginal case of wetting in that the vdW interaction is minimized for similar dielectric media such as the solid and liquid phases of a single material. Using a simple model to estimate the magnitude of electrical forces, we find that such forces, if present, may dominate the melting behavior.

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* Present address: Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel.

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