Impurity Effects in the Premelting of Ice

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The effect of impurities on the surface and interfacial melting of ice is investigated in the context of the Derjaguin-Landau-Verwey-Overbeek theory by calculating van der Waals and Coulombic interactions within interfacial solution films. At high temperatures, the classical solute effect dominates the melting behavior. However, depending on the amount of impurity, as temperature decreases the slope of the film-thickness versus temperature curve changes in a manner that depends on the relative strengths of van der Waals and Coulombic interactions. The results explain the wide range of experimental discrepancies and hence impact a host of environmental phenomena. [S0031-9007(99)08716-5]

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The ice-water conversion is one of the most common first order transitions experienced by humanity and observed in the natural environment. Our basic understanding of the melting of ice involves the modern theory of premelting [1,2] which refers to the existence of liquid at temperatures and pressures in the solid region of the bulk phase diagram. The environmental importance of premelting in ice is great, playing a fundamental role in frost heave [3–5], the slip at glacier beds [6], and chemical uptake on atmospheric ice surfaces [7]. Here, we investigate the previously unquantified effect of soluble impurities on the interfacial premelting of ice.

Premelting occurs in most materials including metals, semiconductors, solid rare gases, and molecular solids and can be caused by a number of mechanisms. A familiar example is the Gibbs-Thomson shift in bulk coexistence due to curvature of the interface. *Surface* (*interfacial*) *premelting* refers to a less familiar, but no less common, process whereby a liquid, or a liquidlike, film is present at the surface of a crystal in contact with its vapor phase (a rigid wall) at temperatures below the bulk melting transition [8]. The process begins gradually at $T < 0.9\ T_m$, where T_m is the bulk transition temperature, with monolayer films that thicken with increasing T. Another variant of surface melting is *grain boundary melting* wherein premelting occurs at junctions between crystals of the same material. During *complete* melting the film thickens without limit as the melting line is approached from the solid region of the bulk phase diagram. In *incomplete* melting the film growth is truncated at finite undercooling, usually by retarded potential effects. Melting is driven by the tendency to reduce the interfacial free energy. The asymmetry of the surface phase change about T_m is the hallmark of surface melting: Most fluids can be deeply supercooled, but there is a complete absence of superheating of their solid phase.

Although the surface melting of ice is well documented (recent reviews are given in [2,9]), so is the great variation in the magnitude and temperature dependence of the melting behavior (see Figs. 1 of [10,11] and see also [12,13]). Therefore, the discrepancies in the existing experimental data on ice, and the fact that essentially all environmentally relevant phenomena will involve contaminants in some form, motivate an attempt to gain a simple understanding of how impurities can influence surface melting. In this Letter, a phenomenological model is proposed to gain insight into the problem.

We consider the thermodynamic conditions necessary for the stable existence of an impure film disjoining a solid from its vapor, from air, or from a foreign wall at temperatures below the bulk melting temperature. The film is an electrolyte solution containing, for example, a monovalent ionic species such as NaCl. In either surface or interfacial melting, the interfaces can be considered to have a finite charge density q_s, and hence any ions present in the film screen the Coulomb interaction with an efficiency that depends on their number density. Long ranged van der Waals interactions are always present, and they may influence the melting behavior [14]. Essentially the same physical phenomena underlie the forces that act between charged surfaces in solution, examples of which pervade technological and biological problems [15], and provide the basis of Derjaguin-Landau-Verwey-Overbeek (DLVO) theory which assesses the competition between the screened Coulomb and attractive van der Waals interactions [16]. For example, DLVO theory explains the flocculation or stabilization of charged colloidal particles. An essential distinction with the case of surface melting concerns the nature of the nonretarded van der Waals contribution to the total excess surface free energy per unit area, denoted by $F_{\mathrm{vdW}}(d) = -\frac{A_H}{12\pi d^2}$, where A_H is the Hamaker constant. For colloidal substrates in solution, d is their separation distance, while for interfacial melting d is the water film thickness. For identical colloids the Hamaker constant is positive producing an attraction. The screened Coulomb interactions are repulsive and suppress the flocculation of charged colloids. For dissimilar materials, the van der Waals contribution can be both attractive and repulsive. Such is the case of the interfacial melting of ice [14].

The screening of surface charges is described by calculating the electrostatic potential ψ created by the distribution of ions of number density $n(z)$ throughout the film, *viz.* the *Poisson-Boltzmann equation*

$$\frac{d^2\psi}{dz^2} = -\frac{Zen(z)}{\epsilon\epsilon_o} = -\frac{Zen_o}{\epsilon\epsilon_o}\, e^{-Ze\psi/k_bT}, \qquad (1)$$

where ϵ is the dielectric constant of the film, ϵ_o is the free space permittivity, z measures the distance normal to the plane of the film, and n_o is the ion density at its midplane. At very short ranges, the theory must be modified to account for steric effects [17], but we will not deal with these complications here (Israelachvili [15] provides a thorough review and discusses the limitations of the Poisson-Boltzmann equation). For a monovalent electrolyte, and a surface potential ψ_s less than 25 mV, Eq. (1) can be linearized in the so-called *Debye-Hückel* limit which yields

$$\psi(z) \approx \psi_s e^{-\kappa z}, \quad \text{where } \kappa^{-1} = \left(\frac{\epsilon\epsilon_o k_b T}{e^2 n_b}\right)^{1/2} \qquad (2)$$

is called the Debye length, which describes the characteristic falloff of the ion field adjacent to the surface, where n_b is the bulk ion density. A repulsive force between two charged surfaces originates in the restriction of the entropy of the ions as the surfaces are brought closer: Although ions of charge opposite to those of the surface are attracted to it, they are repelled from each other, and the increased proximity induced by decreasing the film thickness increases the free energy. In this limit, the excess interfacial free energy per unit area across a film of thickness d is written

$$F_{\rm DH} \approx \frac{2q_s^2}{\kappa\epsilon\epsilon_o}\, e^{-\kappa d}, \qquad (3)$$

and the total excess interfacial free energy of relevance to the interfacial melting of ice in the presence of electrolytes is the sum of $F_{\rm DH}(d)$ and $F_{\rm vdW}(d)$ which can be considered to be a special case of DLVO theory.

The experimental paradigm of surface force measurements [15] provides the film under scrutiny an infinite supply of solution at fixed concentration. Hence, an experiment can be prepared in which the Debye length is fixed for all values of the film thickness. In contrast, during surface melting we envisage the following experimental situation. A surface is prepared at a temperature where, in the absence of impurities, a film is present. N_i moles per unit area of a single species of monovalent nonvolatile impurities are deposited in the film. Because of their low volatility, and the fact that the ice-solution equilibrium segregation coefficient is extremely small, of order 10^{-6} (which we take to be zero), there are a fixed number of electroyte ions in the film, maintaining equilibrium with the interfacial charge. An increase (decrease) in film thickness is accommodated by melting (freezing) of the solid so that, up to the solubility limit, the impurity concentration is simply inversely proportional to the film volume. Hence, at low temperatures, a surface film will thin, increase in impurity concentration, and decrease the Debye screening length: $\kappa^{-1} \propto d^{1/2}$. Only at low temperatures, where the films are very thin and many of our approximations are violated, does the variation in κ^{-1} itself begin to be important. However, what is important here is how this variation influences the total *free energy* of the *system,* which is written as

$$\begin{aligned} G_T(T,P,d,N_i) = {} & \rho_\ell \mu_\ell(T,P)d + \mu_i(T,P)N_i \\ & + RTN_i \ln\frac{N_i}{\rho_\ell d} + \mu_s(T,P)N_s \\ & + F_T(d), \end{aligned} \qquad (4)$$

wherein, ρ_ℓ, μ_ℓ, and $N_\ell = \rho_\ell d$ are the molar density, chemical potential per mole, and the number of moles per unit area of the solvent, μ_i is the chemical potential of the impurity, R is the gas constant, μ_s and N_s are the chemical potential per mole and the number of moles per unit area of the solid, and F_T is the total effective interfacial free energy as discussed above. For simplicity of presentation, the entropic term, $RTN_i \ln\frac{N_i}{\rho_\ell d}$, is written in the dilute limit of ideal solution theory, but the analysis can proceed without these approximations if we replace the molar ratio by the activity coefficient for the impurity in the solvent. Such complications do not change the essential behavior of the system. The interfacial term captures the asymptotic behavior of the system within the context of DLVO theory as follows:

$$F_T(d) = \gamma_d + \Delta\gamma\left(1 - \frac{\sigma^2}{2d^2} - \frac{e^{-\kappa(d-\sigma)}}{2}\right), \qquad (5)$$

in which the dry interfacial energy, whether it be the solid/vapor or solid/wall interface, is represented by γ_d, $\Delta\gamma = \gamma_{s\ell} + \gamma_{\ell v(w)} - \gamma_d$ is the difference in free energy between the dry and wet interfaces, where s, ℓ, v, w denote solid, liquid, vapor, and wall, respectively. The second term describes the sum of the DLVO contributions to the free energy as a function of film thickness, where σ is a short range cutoff of the order of a molecular diameter. The coefficients can be related to those of DLVO theory [4].

Interfacial adsorption of impurities shifts the interfacial free energy in a manner described by the classical Gibbs-adsorption isotherm [18]. In contrast to the case of nonelectrolyte solutions, $\gamma_{\ell v}$ *increases* with electrolyte concentration due to an image charge effect. Although it is known that the difficulty of impurity incorporation influences surface structural phase transitions by reducing the surface energy [19], we only have experimental information for the water/vapor interface. Because the impurities are nonvolatile and insoluble in ice, each of the interfacial coefficients in $\Delta\gamma$ will be modified in a manner that depends on, among other things, the magnitude of the surface charge density and the bulk electrolyte concentration. An increase in $|\Delta\gamma|$ will enhance surface melting relative to the pure case, and there are some experimental indications that this occurs in ice against air [10,11]. Nonetheless, the exact dependencies of the constituents of $\Delta\gamma$ on N_i are presently unknown to us and hence to introduce further theoretical treatment risks an extension beyond the realm of firm evidence. The form of our result is amenable to an experimental estimate of this effect. A more sensitive impurity dependent effect resides in the film thickness dependence of the Debye length as discussed above. Equation (2) leads to $\kappa = c\sqrt{N_i/d}$, where $c = 7.237 \times 10^7\ \mathrm{m}^{1/2}\,\mathrm{mol}^{-1/2}$ is a constant.

As the temperature is raised or lowered isobarically, material is exchanged between the solid and the liquid, and the condition for equilibrium is

$$\frac{\partial G_T}{\partial N_\ell} = \frac{\partial G_T}{\partial N_s}, \tag{6}$$

which leads to the following relationship between the undercooling and the film thickness:

$$T_m - T = \frac{T_m}{\rho_\ell q_m}\left[\frac{RT_mN_i}{d} - \frac{\Delta\gamma\sigma^2}{d^3} - \frac{\Delta\gamma c}{2}\sqrt{\frac{N_i}{d}} \times \left(1 + \frac{\sigma}{d}\right)e^{-c\sqrt{N_i/d}\,(d-\sigma)}\right]. \tag{7}$$

The first term is the surface version of Raoult's law, and the second and third terms are the nonretarded van der Waals and the Coulombic contributions, respectively.

Figure 1 shows the film thickness versus undercooling at the interface between ice and a substrate of (a) silicon, (b) polyvinylidene chloride, and (c) water vapor, with different values of N_i. The Hamaker constant decreases from silicon to the water vapor interface. The dominance of the surface Raoult's law at high temperatures is clearly demonstrated: As N_i *increases*, (i) the film *thickens*, as expected, and (ii) the temperature at which this power law ($d \propto \Delta T^{-1}$) begins to dominate the melting behavior *decreases*. It is particularly sensitive in the case of the vapor interface where it may be strong enough to overwhelm the incomplete melting controlled by van der Waals interactions in the pure case [10,20] and drive complete surface melting, thereby reconciling the difference between experimental observations made by different groups [10–13]. For large enough contamination at any interface, the entire range of melting behavior is dominated by the surface Raoult's law. As the temperature decreases, the first crossover occurs to interfacial melting controlled by van der Waals interactions ($d \propto \Delta T^{-1/3}$) appearing at higher temperatures as the Hamaker constant increases.

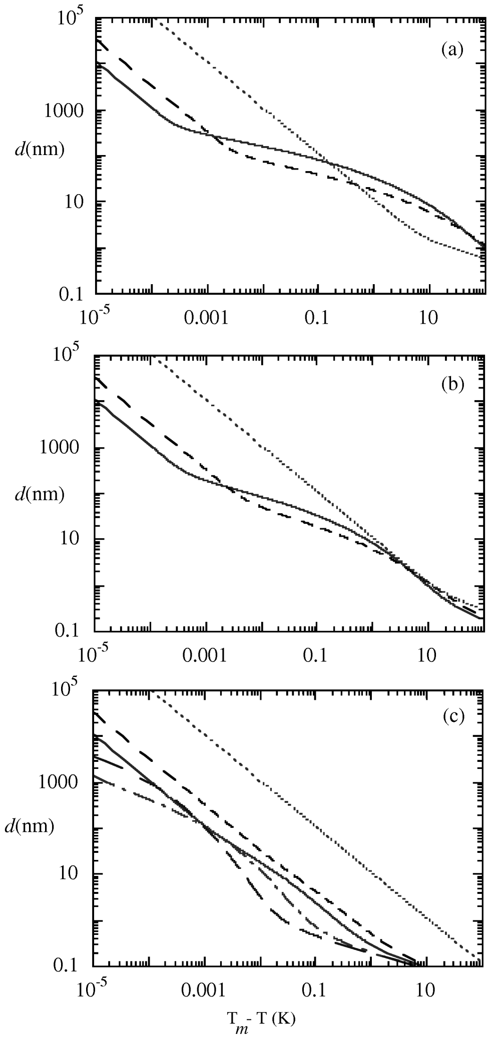

FIG. 1. Film thickness versus undercooling at the interface between ice and a substrate of (a) silicon, (b) polyvinylidene chloride, and (c) water vapor. In (a) and (b) $N_i = 0.06$ (solid line), 0.18 (small dashed line), and 6 (dotted line) μM NaCl per square meter. In (c) $N_i = 6 \times 10^{-4}$ (long dashed line), 6×10^{-3} (dash-dot line), 0.06 (solid line), 0.18 (small dashed line), and 6 (dotted line) μM NaCl per square meter. Depending on the sign convention taken for $F_{\mathrm{vdW}}(d)$, the Hamaker constant can be related to the interfacial coefficient $\Delta\gamma$, viz. $12\pi\sigma^2\Delta\gamma = A_H$ [4]. Hamaker constants can be calculated using the complete theory of dispersion forces [14,20], which requires as input, spectral data for the dielectric functions of ice, water, and the substrate of interest, or they can be taken from experimental measurements. In the former case, the results are often sensitive to the data set and fitting model used to incorporate them into dispersion force theory. Elbaum and Schick [20] used two data sets to calculate film thickness versus temperature, and here the data which produced the largest Hamaker constant [22] for the vapor interface was used, giving $A_H = -3.07 \times 10^{-22}$ J. For polyvinylidene chloride we use fits to experimental data $A_H = -1.50 \times 10^{-20}$ J [5] and increase this by 1 order of magnitude to describe Silicon [14]. The vapor interface is most sensitive to the impurity content. As its temperature increases, the lowest concentrations change slope twice (in this range), and above about a mK, the *lower* dopant level yields a *thicker* film. As the temperature increases further, there is another crossover (not seen on this scale). Clearly, the thickness is sensitive to small amounts of impurities, and hence it is quite dependent on factors that are extremely difficult to control in an experimental apparatus.

For sufficiently low concentrations the range of undercooling of this van der Waals plateau is limited, and a Coulombic shoulder appears which rapidly steepens the thinning; the slope exceeding that of the purely solutal effect. As noted above, for sufficiently large N_i the surface Raoult's law may dominate the melting behavior, but it should be stressed that there is a combination of effects that occur. First, the increasing strength of the solute effect extends the surface Raoult's law to lower temperature; second, it decreases in the range of the Coulombic interaction. In other words, as N_i *decreases*, the range of the Coulombic interaction *increases* and its strength can begin to dominate that of the van der Waals interaction of a film of a higher concentration. Hence, for a given material, we see the possibility of a crossover, within the van der Waals plateau, between films with two N_i values, the film of larger N_i having a smaller thickness at the same undercooling. This behavior should be unique to interfacial melting, wherein the Debye length depends on the film thickness.

Clearly, it is important to examine the nature of melting when the van der Waals interactions are attractive (nonmelting) and the Coulombic interactions (which can be short or long range) are repulsive, but we leave this, and additional effects [15], including the facet dependence of interfacial melting, for future research when the experimental data are refined. Finally, we note that Beaglehole [21] studied the effects of size and impurities on the melting of ice particles, but restricted interfacial interactions to a very short range and did not consider how the impurities extend the range of these interactions.

We have derived a phenomenological treatment of the role of impurities in surface and interfacial melting in the context of DLVO theory and have applied it to the phase behavior of ice doped with NaCl. Upon addition of a small amount of impurity three different dependencies of film thickness on temperature result. Within a given type of dependence, the magnitude of the film thickness is extremely sensitive to the amount of dopant, and at low concentrations the Coulomb interaction can effectively compete with the van der Waals interaction at long range. The surface melting of ice is well documented [2,9–13], as is the variation in the magnitude and slope of the film-thickness versus temperature relations wherein a given experiment often exhibits changes in slope [10–13]. Both the typical magnitude of the interexperimental variations and the changes in slope are easily bracketed by the behavior shown in Fig. 1. Therefore, the results provide a reasonable explanation for the differences observed among various experimental groups. Rather than attempting to prepare absolutely pure samples, it is hoped that the magnitude of the impurity sensitivity can be used as a guide for future experimental work toward an approach of systematic doping.

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