A Theory of Premelting Dynamics for all Power Law Forces

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We present a new theory for premelting dynamics valid for all power law interfacial free energies, and reexamine recent frost heave dynamics experiments in light of the predictions. We find a family of similarity solutions and examine a subset relevant to several types of interaction. The experimental frost heave data are best described in terms of an electrostatic interfacial free energy. The results are generally important in the dynamics of wetting under interfacial interactions.

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The stable existence of interfacial water below the bulk freezing point has been associated with frost heave for decades but the basic causes are only just now being addressed in the context of interfacial premelting [1]. Supercooled liquid of any material is metastable in bulk but may find a stable existence at interfaces. In the case of H2O, the mobility and pressure of this liquid can have dramatic effects in the polar and subpolar regions by controlling impurity redistribution within sea and glacier ice [1], weathering rocks and soils [2], and influencing structural design [3]. The main dynamical prediction of premelting thermodynamics [4,5] is that liquid motion in interfacial films is driven by a temperature gradient which induces a chemical potential gradient, driving liquid from high to low temperatures. The phenomenon is possible in any material in which interfacial interactions extend the equilibrium domain of the liquid phase into the solid region of the bulk phase diagram.

Frost heave studies have traditionally been conducted in porous media which have the advantage of greatly increased surface area of premelted liquid. Unfortunately the convolution of curvature, surface disorder, and the tortuosity of the medium obscures the fundamental flow behavior [1], which has only recently been revealed in experimental studies of isolated crystalline interfaces.

In the following we derive the theory germane to a recent experimental study of interfacial dynamics on single crystal facets of ice [6]. A liquid film of melt (ℓ), thickness d, and area Aℓ may disjoin a solid (s) from a wall at temperatures below the bulk freezing point as the result of the competition between a reduction of interfacial free energy and the expense of maintaining a layer of undercooled liquid [1]. It is properly thought of as a wetting phenomenon away from bulk coexistence (e.g., [7]). The free energy of the system

\[ \Omega = -P_\ell V_\ell - P_s V_s + I(d), \]  

is composed of bulk and surface terms, where P and V denote pressure and volume. The interfacial term \( I(d) = [\Delta \gamma f(d) + \gamma_{sw}]A_\ell \), where \( \Delta \gamma = \gamma_{s\ell} + \gamma_{\ell w} - \gamma_{sw} \), and the \( \gamma \)'s are the solid-liquid (sℓ), liquid-wall (ℓw), and solid-wall (sw) interfacial free energies, captures the film thickness dependence of the free energy [8]. Melting may be complete or incomplete [1,9]. Complete interfacial melting occurs when the film thickness diverges as the bulk melting point \( T_m \) is approached from below, in which case \( I(d) \) is a positive, monotonically decreasing function of \( d \) at long range. Power law interaction potentials have the form \( f(d) = 1 - (\sigma/d)^n \), where \( \sigma \) is on the order of a molecular diameter, and \( n \) depends on the nature of the interactions. In incomplete interfacial melting the film growth is truncated at finite undercooling. The minimization of \( \Omega \) at fixed temperature and chemical potential yields two results [8]. First, a pressure difference between the melt film and the solid,

\[ P_\ell - P_s = \Delta \gamma n \sigma d^{-(n+1)}, \]  

is a general result. Second, to first order in the reduced temperature \( t_r = (T_m - T)/T_m \), the film thickness is

\[ d = \left( \frac{\nu - 1}{\nu} \sigma \rho_s q_m \right)^{1/\nu} t_r^{-1/\nu} \equiv \lambda_p t_r^{-1/\nu}, \]  

where \( \nu = n + 1 \), \( \rho_s \) is the density of the solid, and \( q_m \) is the latent heat of fusion [10]. Equation (2) tells us that the pressure is uniform in each phase, but that interfacial interactions create a pressure difference between the melted layer and the bulk solid, and Eq. (3) shows that the film thickens with temperature. The essential idea of premelting dynamics can be described by combining these two results,

\[ P_\ell = P_s - \rho_s q_m t_r. \]  

Suppose we fix \( P_s \), then the pressure in the film, \( P_\ell \), must increase with temperature. Therefore, a temperature gradient parallel to a premelted interface will drive a flow in the film toward lower temperatures [11]. Because
the film thins as the temperature decreases, continuity demands that liquid will convert to solid as it moves toward lower temperatures.

Wilen and Dash [6] have studied the motion of a water layer in a temperature gradient, \( \mathcal{G} \), at the interface between a single crystal of ice and a flexible polymer membrane. Spatial gradients in the thin-film volume flux lead to the growth of the solid, causing changes in the height of the membrane, \( h = h(x,t) \), measured relative to an initial reference height \( h(x,t_0) \). They found that flow occurred in a narrow range of temperature near \( T_m \) toward lower temperatures. At lower temperatures, the relative lack of membrane deformation was interpreted as an abrupt decrease to \( d = 0 \), consistent with an interfacial free energy that decreases monotonically with film thickness at long range, but which possesses a local minimum at shorter range. The underlying dynamics of frost heave are controlled by the nature of the intermolecular interactions in the system and the mechanical interaction between the film and the membrane. Here, we uncover the relationship between these two controlling factors.

The radial cell configuration can be treated in a one-dimensional slab geometry (Fig. 1) since the membrane height deformations are much less than the disk radius. The flow is driven by a thermomolecular pressure gradient,

\[
\nabla P_\ell = -\rho_\ell q_m \nabla t_t + \frac{\rho_\ell}{\rho_s} \nabla P_s, 
\]

where \( P_s \) is the external pressure exerted on the solid by the membrane [1,6,8,12]. The relaxation time of the film to the thickness determined by Eq. (3) is negligible relative to that for heat conduction. Mass conservation is written as

\[
\partial_t h + \partial_x Q = 0, 
\]

where \( Q \) is the volume flux per unit breadth through the film of thickness given by Eq. (3), and for a lubrication flow it is

\[
Q = -\frac{d^3}{12\mu} \nabla P_\ell, 
\]

where \( \mu \) is the viscosity [8]. The membrane possesses a tension, \( \sigma \), and when distorted it exerts a pressure on the solid proportional to the curvature [13]. Combining Eqs. (3)-(7), and noting that \( t_t = \mathcal{G} x / T_m \), so that \( d^3 \propto x^{-3/\nu} \) yields the following dimensional equation for the evolution of the membrane height:

\[
\partial_t h + \Lambda_\nu \partial_x [x^{-3/\nu}(1 + \alpha h_{xx})] = 0, 
\]

where

\[
\alpha = \frac{\sigma T_m}{\rho_s q_m \mathcal{G}}, \quad \Lambda_\nu = \frac{\lambda_s^2 \rho_\ell q_m (T_m / \mathcal{G})^{(3-\nu) / \nu}}{12\mu}. 
\]

Analysis of Eq. (8) suggests the following similarity solution:

\[
h = \alpha^{-1}(\Lambda_\nu \alpha t)^{3\nu/(4\nu+3)} f(\eta), 
\]

with similarity variable

\[
\eta = x(\Lambda_\nu \alpha t)^{-\nu/(4\nu+3)}. 
\]

This leads to a family of fourth-order, dimensionless ordinary differential equations for the function \( f(\eta) \),

\[
f''' + \frac{3}{\nu} \frac{f'' + 1}{\eta} + \frac{\nu}{4\nu + 3} \eta^{(3/\nu)+1} f' = -\frac{3\nu}{4\nu + 3} \eta^{3/\nu} f, 
\]

where the primes denote \( d/d\eta \). Note that there are no free parameters in Eq. (12). The experimental cell is large enough so that the membrane height is unaffected by the edges [6], and the cell center (\( \eta = \eta_c \)) is far from the region of deformation, suggesting the following boundary conditions:

\[
f' = f'' = 0 \quad (\eta = 0) \quad \text{and} \quad f' = 0 \quad (\eta = \eta_c). 
\]

As \( \eta \to \infty \) asymptotic analysis of Eq. (12) reveals that the membrane height decays algebraically as

\[
f \sim \eta^{-[3/(\nu+1)]} \quad (\eta \to \infty). 
\]
Finally, a necessary condition on the solution is that
\[ f''' = -1 \quad (\eta = 0). \] (15)

Equation (12) subject to (13)–(15) was solved numerically using a finite-difference method that exploits an adaptive mesh and collocation at Gaussian points.

In Fig. 2 we show the cases where the premelting behavior was dominated by electrostatic ($\nu = 3/2, 2$), nonretarded ($\nu = 3$), and retarded ($\nu = 4$) van der Waals interactions. By electrostatic interfacial interactions we refer to a simple treatment in which the substrate possesses a surface charge density and the confinement of counterions present in the liquid layer creates a repulsive interaction [9]. We can approximate $I(d) \approx d^{-1/2}$, over a reasonable range for small $d$, and at long range $I(d) \approx d^{-1}$ [9].

Two features that are independent of the nature of the interactions are (a) the membrane deformation takes a maximum value in the region of the high temperatures where the film thickness and the gradient in the volume flux are maximal and (b) there is an infinite train of oscillations with an exponentially decaying amplitude about the algebraically decaying mean value of $f$ [cf. Eq. (14)]. The elasticity induced curvature, that was not considered in an earlier theory [8], is responsible for the secondary maxima as follows. The primary maximum creates a positive curvature which the elasticity of the membrane attempts to straighten out. As it does so it draws fluid in from both the high and low temperature regions. The fluid drawn from low temperatures creates the first trough, which the membrane again tries to straighten and thereby pushes fluid away toward both the high and low temperature regions. The fluid pushed toward low temperatures creates the second peak, and so on ad infinitum.

At any time Eqs. (10) and (11) show that $f'$ describes $dh/dx$ for a given interaction. The slope of the membrane is maximal in the ($\nu = 3/2$) electrostatic case, and the first minimum and secondary maximum are found at higher temperatures and are more localized in space. This can be understood by noting that the volume flux is a product of the film thickness cubed and the thermomolecular pressure gradient, seen as $x^{-3/\nu}$ and $1 + a h_{xx}$ in Eq. (8). The former depends on the nature of the interactions and, as has been shown previously (e.g., [1]), the latter is a universal thermodynamic statement. The membrane deformation is driven by the gradient of this product; as the exponent $\nu$ characterizing the interactions decreases, the decay in the volume flux increases, thereby localizing frost heave as is seen in Fig. 2.

The most robust experimental feature is the time evolution of the maximum height $h_{\text{max}}$ of the membrane. Equation (10) predicts the scaling
\[ h_{\text{max}} = \alpha^{-1}(\Lambda_x \alpha t)^{3\nu/(4\nu+3)} f_{\text{max}}. \] (16)

The coefficient depends only on material constants multiplied by $[(\nu - 1)\alpha^{\nu-1} \Delta y]^{-[9/(4\nu+3)]}$, which we fit to determine the slope of the interfacial potential $I(d)$. For example, when $\nu = 3$ we are estimating the Hamaker constant [10]. The fits span several decades in time (Fig. 3).

The coefficient for a given interaction then allows us to predict $h(x,t)$ by solving the relevant evolution equation [from Eqs. (12)]. The agreement between theory and experiment (Fig. 4) is best in the case of electrostatic interactions which always dominate van der Waals at long range and, depending on the surface charge density, may also dominate at short range [9].

It is clear that the van der Waals interaction does not dominate the melting behavior. Less certain is that an electrostatic interaction is solely responsible for the observed behavior. Since the latter dominates at long range [9], we have confidence in the calculation for the region where the heave is maximal, but this does not exclude the role of other interactions. A crossover with temperature from one type of interaction to another can be treated, but will not be describable by a similarity solution. Since the height
grows a thousand times faster than it spreads [Eqs. (10) and (11)], the relative deformation at lower temperatures is so small we expect that the secondary maxima, for any type of interaction, and distinctions between different interactions in that region will severely test experimental resolution. The scaling clearly exhibits that varying the temperature gradient may allow these subtle features to be extracted.

The most important result concerns a new interpretation of the experimental data. The relative lack of membrane deformation at lower temperatures was interpreted as an abrupt decrease to $d = 0$, consistent with an interfacial free energy that decreases monotonically with film thickness at long range, but which possesses a local minimum at shorter range. Here we have shown that the experimental data can be described with an interfacial free energy that decreases monotonically over the entire range of film thicknesses.

Interesting issues associated with proximity effects [1] await understanding. From the theoretical perspective the results are of fundamental interest in other lubrication flows where the equations of motion possess scaling behavior [14]. Since experimental verification of similarity solutions over the time scales shown here is rare, we hope that our theory stimulates further experimentation.

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[10] For $\nu = 3$, $\sigma^2 \Delta y = A/12\pi$; $A$ is the Hamaker constant (e.g., see Appendix of [8]), but clearly the coefficient of $\lambda_\nu$ depends on $\nu$.
[13] The membrane energy is dominated by surface tension: $\bar{\sigma} = 1$ psi $\text{cm}^{-1}$, Young’s modulus $E \approx 600$ psi and the membrane is 0.025 mm thick, so that the bending energy contributes only about 1% to the membrane energy. Furthermore, the radius of curvature is large compared to $d$, so the membrane exerts a pressure deep within the solid. Although the solid can maintain a shear stress, we assume that any plastic deformation is slow relative to the film dynamics.