GFD 2006 Lecture 8: Interfacial pre-melting

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1 Interfacial Premelting

In the previous lectures, we have concentrated on solidification of ice on large scales. In the last two lectures, we will switch to microscopic scale and study a phenomenon of *premelting*: the existence of a thin liquid film on the surface of a solid below the bulk freezing temperature. Although the thickness of the films generated by premelting are typically of the order of 100 molecular diameters, we will see that they are highly relevant: for example premelting plays an important role in the generation of frost heave.

The existence of premelted films was first postulated by Faraday and Tyndall in the 19th century in order to explain the observation that snow sticks together when compacted, unlike most granular solids. The idea being that upon contact of two ice grains, the thin film will freeze at the contact line to join the two crystals (see Fig. 1). At the time however, it was accepted that an increase in pressure also caused melting and so in the absence of proof of the existence of premelted films, the pressure melting view prevailed. Recently however, experiments have delivered proof of the existence of the films, and this, coupled with the theoretical evidence showing that pressure melting can not possibly explain all observed effects has finally confirmed the validity of Faraday and Tyndall's ideas.

The presence of the film stems from a repulsive force between the solid and the air, due to van der Waals forces. As we will see, this force means that it is energetically favourable for some of the solid to melt, increasing the gap between the solid and the air. However, as the system is below the bulk freezing temperature of the liquid, the film is limited to microscopic thicknesses. It is this competition between repulsive force and freezing drive that determines the equilibrium thickness of the film.

2 van der Waals Forces

van der Waals forces are attractive forces arising from fluctuctions in the dipole field of molecules giving rise to fluctuations in nearby molecules. These fluctuations cause electrostatic forces to act between the molecules, giving rise to a potential between two molecules that takes the form

$$\phi = -\frac{k_{12}}{r^6}, \tag{1}$$

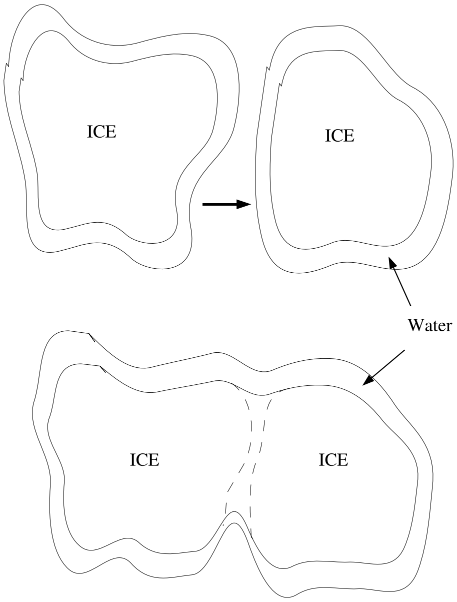


Figure 1: The sintering of two ice blocks upon contact by freezing of the premelted film.

where k_{12} is a constant depending on the properties of molecules 1 and 2, and r is the distance between the molecules.

2.1 Force between a molecule and an extended solid

From this expression, we can work out the attractive force between a molecule of phase 2, separated from a semi-infinite plane of phase 1 by a distance h (see Fig. 2(i)). Letting ρ_1 be the number density of molecules in phase 1 and D be the semi–infinite domain of phase 1, we can then integrate in cylindrical polar co–ordinates to yield the total potential

$$\phi = \int_{\mathcal{D}} \frac{-\rho_1 k_{12} dV}{[r^2 + (h+z)^2]^3} = -\frac{\pi}{6}\frac{k_{12}\rho_1}{h^3}. \tag{2}$$

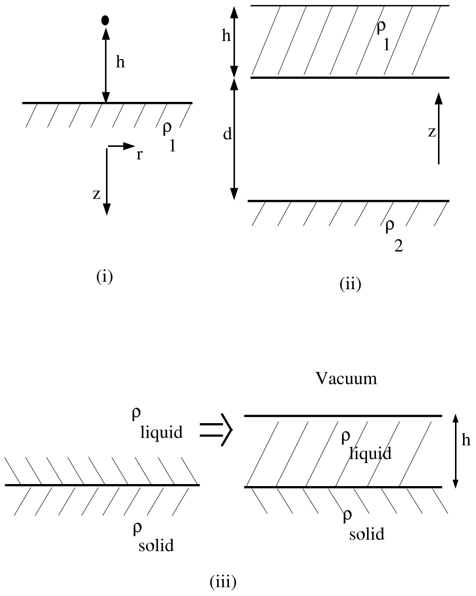
2.2 Interaction between a slab and a semi–infinite material

We can now use this potential to calculate the potential per unit area between an infinite slab of thickness h and a semi–infinite solid (Fig. 2(ii)), by integrating over the molecules that make up the infinite slab. Integrating equation (2) between $z = 0, h$, we find that the potential per unit area is

$$\phi = \int_0^h -\frac{\pi}{6}\frac{k_{12}\rho_1\rho_2}{(z+d)^3} dz = \frac{A_{12}}{12\pi}\left[\frac{1}{(h+d)^2} - \frac{1}{d^2}\right], \tag{3}$$

where $A_{12} = \rho_1\rho_2 k_{12}$ is the Hamaker constant for materials 1 and 2.

From this expression, we can obtain the surface energy when two infinite solids of phases 1 and 2 are in contact. By assuming that there is a molecular cutoff distance $d = \sigma_{12}$ that separates phases in contact, corresponding to the repulsive forces between molecules at



(i) (ii)

(iii)

Figure 2: (i) The potential between a molecule and a semi–infinite solid. (ii) The potential between a semi–infinite solid and a slab. (iii) The derivation of the potential for a liquid film. The reference state (LHS) is modified to achieve the desired potential (RHS).

short distances, when $h \to \infty$ in the above expression, we find that the potential per unit area between two semi–infinite phases separated by a gap of thickness d is

$$\phi = -\frac{A}{12\pi d^2}, \tag{4}$$

and letting $d \to \sigma_{12}$, we obtain the surface energy, given by

$$\gamma_{12} = -\phi = \frac{A_{12}}{12\pi\sigma_{12}^2}. \tag{5}$$

2.3 Thin liquid films

We are now in a position to calculate the potential of thin liquid film of thickness h on top of a semi–infinite solid. We will find the potential by starting with a reference state of known energy and then modify it, while tracking the energy changes associated with the modifications (Fig. 2(iii)). In this case, we start with a half–plane of solid underlying a half–plane of liquid. As we have seen, this has a surface–energy of γ_{sl}. We then remove the upper portion of liquid to leave the desired configuration. In doing so, we have removed the energy associated with the attractive forces between the removed chunk of liquid and the film, and the removed chunk of liquid and the underlying solid. Therefore the energy per unit area of the new state is

$$\phi = -\gamma_{sl} - \left[\frac{A_{sl}}{12\pi h^2} + \frac{A_{ll}}{12\pi}\left(\frac{1}{(h+\sigma_{ll})^2} - \frac{1}{\sigma_{ll}^2}\right)\right], \tag{6}$$

which (as $h \gg \sigma_{ll}$) gives

$$\phi = \text{const.} - \frac{A}{12\pi h^2}, \tag{7}$$

where $A = A_{sl} - A_{ll}$. We note that A can have either sign depending on the magnitude of A_{sl} and A_{ll}, so the force acting on the liquid can be either attractive or repulsive, leading to film rupture or wetting respectively. This force is known as the *disjoining pressure* and is given by

$$p_T = \frac{A}{6\pi h^3} = -\frac{\partial \phi}{\partial h}, \tag{8}$$

so that the force is attractive when $A < 0$, and repulsive when $A > 0$.

2.4 Two materials with an intervening liquid layer

As we will see, in real situations the liquid layer tends to be in between two phases, such as vapour and solid, or substrate and solid. Therefore, by using a similar argument to that of the previous section, it is possible to build the potential for a liquid layer of thickness h between two semi–infinite materials of phases 1,2 to find that

$$\phi = const - \frac{A}{12\pi h^2}, \tag{9}$$

where $A = A_{1l} + A_{2l} - A_{12} - A_{ll}$ can take both signs, so that the film can also either be wetting, or be unstable leading to rupture.

3 Premelting

Imagine a liquid film of water sandwiched between a semi-infinite block of ice and another substrate (e.g. water vapour or a solid wall). In equilibrium, the Clausius-Clapeyron equation gives

$$\frac{\rho_s L(T_m - T)}{T_m} = p_s - p_l + (p_l - p_m)\big(1 - \rho_s/\rho_l\big). \tag{10}$$

Here we shall assume, for simplicity, that $\rho_s = \rho_l$ so that the last term on the right-hand side of (10) disappears. This term is associated with pressure melting (since it includes the difference between the liquid pressure and the reference pressure, p_m) and so we are neglecting pressure melting in the calculation that follows. Now, $p_s - p_l = p_T$, the disjoining pressure, which is given in terms of the film thickness h by (8). Equation (10) therefore simplifies further to:

$$\frac{\rho_s L(T_m - T)}{T_m} = p_T = \frac{A}{6\pi h^3}, \tag{11}$$

where h is the thickness of the melt layer above the ice.

If $A > 0$, so that the layer is wetting, then we find immediately that

$$h \propto (T_m - T)^{-1/3}, \tag{12}$$

provided that $T < T_m$. Notice from (12) that as $T \nearrow T_m$, $h \to \infty$ so that the film thickness diverges as the temperature approaches the equilibrium melting temperature. Physically,

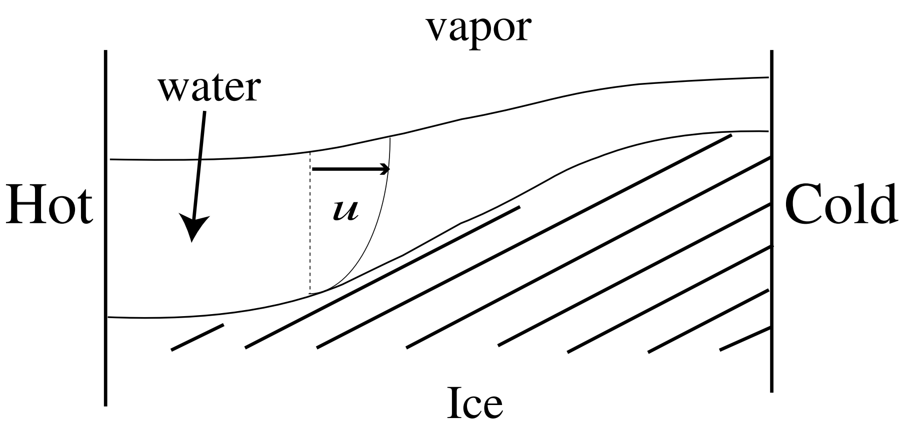


Figure 3: Diagram showing an ice block and its premelted film in a horizontal temperature gradient.

this is as expected because at the equilibrium melting temperature, we can have bulk liquid in coexistence with ice.

Equation (12) shows that below its equilibrium melting temperature, ice can coexist with a thin layer of water. This thin layer of water has important consequences that we shall investigate further in the last lecture. We begin by considering a simple mechanism by which flow can be driven in a premelted layer and compare this to a more conventional thin layer flow.

3.1 Premelting driven flow

Consider a semi-infinite block of ice between two vertical walls with a liquid film sitting between the ice and its vapour as shown in Fig. 3. If the walls are maintained at different temperatures (both with $T < T_m$) then a temperature gradient is set up across the width of the system. For the liquid film to remain in thermodynamic equilibrium, the film must be thicker at the hotter end of the experiment and so the ice melts a little here. However, this means that the thermomolecular pressure p_T is lower here and so, since $p_l = p_s - p_T$, the liquid pressure is higher. Therefore there is flow in the premelted film from hot to cold (i.e. from left to right in the setup shown in Fig. 3).

Here we neglect gradients in the surface tension coefficient resulting from the temperature change and so there is no traction on the interface. The pressure in the liquid film is therefore given by

$$p_l = -\gamma_{lv} H_{xx} - \frac{A}{6\pi h^3}, \tag{13}$$

where $H(x)$ is the interface position and *not* the film thickness $h(x)$. Here the Hamaker constant $A = A_{sl} + A_{lv} - A_{ll} - A_{sv}$ depends on the Hamaker constants of the different pairs of materials in the system.

The flow in the liquid layer is driven by the gradient in p_l and acts to eliminate this gradient. Eventually a static situation is reached with $p_l = \text{const.}$ everywhere but with the

	Premelting	**Marangoni**
Driving force	Disjoining Pressure (normal to interface)	Surface tension gradient (tangent to interface)
Direction of mass transport	Hot to cold	Hot to cold
Morphology of underlying solid	Yes	No
Equilibrium	Stationary	Dynamic
Film Thickness Determined:	Thermodynamically	Dynamically

Table 1: Comparison of main characteristics of the Premelting- and Marangoni-driven film flow problems.

interface deformed. Here the curvature force (surface tension) balances the thermomolecular forces. This means that in regions of high disjoining pressure (thin films), we expect to see large interfacial curvatures in steady state.

3.2 Marangoni driven flow

We now contrast this with the case of a thin wetting film on a rigid, solid substrate, such as glass. Again a temperature gradient is imposed across the system but now we account for the gradients in surface tension caused by the temperature gradient. In particular, we note that for water, the surface tension is higher at the cold end than at the warm end and so there is a surface tension gradient from warm to cold. This exerts a surface traction, $\tau = \mu \partial u / \partial n$, which balances the surface tension gradient. We therefore have

$$\mu \frac{\partial u}{\partial n} = \frac{\partial \gamma_{lv}}{\partial s}, \tag{14}$$

where s denotes the arc length measured along the interface. Unlike the previous case, at equilibrium the liquid is not quiescent (see figure (4)). The gradient in surface tension will drive a flow along the surface of the liquid from hot to cold, while the pressure reduction under the cold region of high curvature will drive a return flow underneath the surface flow. The equilibrium shape of the surface in this situation is controlled by a dynamic flow balance.

Although the flow of the two liquid films are similar in many respects, there are also several differences. These differences are summarized in table 1. In addition to these differences, we also note that when the vapour phase is replaced with a deformable solid, the Marangoni effect disappears but the premelting flow remains. We will consider such deformations in the final lecture.

Student Problem *Consider a thin disk of weight W, radius R and against which ice premelts, just ahead of an interface that is solidifying at a speed V (see Fig. 5). Find the maximum speed for which there is a steady state in which the disk translates ahead of the ice.*

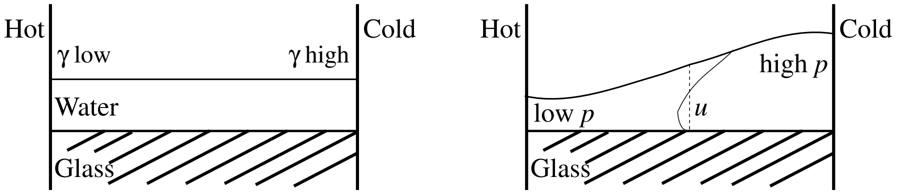


Figure 4: Diagram showing a thin film of water wetting a rigid substrate in a horizontal temperature gradient. Left: The initial configuration in which a layer of liquid lies above the solid. Right: The steady state in which flow in the layer continues because of the surface tension gradient.

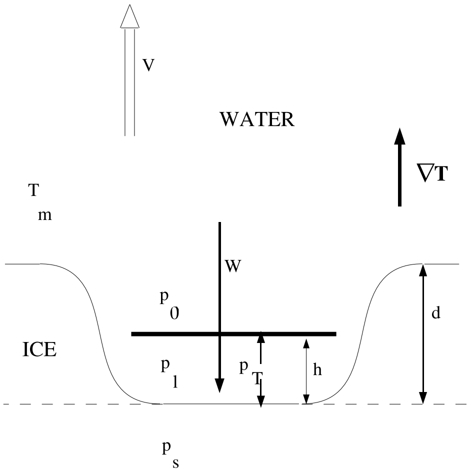


Figure 5: Diagram for the student problem: a disc of radius R is pushed ahead of a steadily translating ice–liquid interface.

Solution Because of the presence of the disk, there will be a pre-melted liquid layer, of constant thickness h, separating the disk from the solid interface. Assuming that $h \ll R$ so that the gap is 'thin', we can neglect effects associated with the edges of the disk. The liquid film exerts a disjoining pressure

$$p_T = \frac{A}{6\pi h^3}$$

on the disk, where A is the Hamaker constant. The disjoining force $p_T \times \pi R^2$ repels the disk from the ice phase.

Two forces are acting to move the disk in the direction of the ice. The first of these is the disk's weight W, while the second force is a suction force resulting from the inward flow of liquid beneath the disk. This force can be calculated using lubrication theory, as follows.

In the thin gap, the horizontal fluid velocity is

$$u = \frac{1}{2\mu} z(z-h)\frac{\partial p}{\partial r}, \tag{15}$$

where $p(r)$ is the unknown fluid pressure. The depth integrated radial fluid flux is then

$$Q = \int_0^h u \ \mathrm{d}z = -\frac{h^3}{12\mu}\frac{\partial p}{\partial r}. \tag{16}$$

Using the continuity equation $h_t + \nabla \cdot \mathbf{Q} = 0$, we then have

$$V = \frac{h^3}{12\mu}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial p}{\partial r}\right), \tag{17}$$

which can immediately be integrated twice to give

$$p = \frac{3\mu V}{h^3}(r^2 - R^2) \tag{18}$$

where we have defined zero pressure to be at $r = R$. This pressure force can be integrated to give the value of the lubrication induced adhesion between the disk and the ice:

$$F_{adh} = \int_0^R 2\pi r p(r) \ \mathrm{d}r = -\frac{3\pi\mu V R^4}{2h^3}. \tag{19}$$

Balancing the three forces acting on the disk we have

$$0 = \pi p_T R^2 - W + F_{adh}, \tag{20}$$

which can be rearranged to give the velocity of interface advance V in terms of the gap thickness, h:

$$V = \frac{A}{9\pi\mu R^2} - \frac{2h^3 W}{3\pi\mu R^4}. \tag{21}$$

Of course in an experiment V is likely to be the control parameter, rather than h. In this case (21) can be rearranged to give $h(V)$. However, the form in (21) is more convenient for our purposes since it demonstrates immediately that the steady state we have supposed can exist only if

$$V - \frac{A}{9\pi\mu R^2} < 0, \tag{22}$$

so that

$$V < V_{\max} \equiv \frac{A}{9\pi\mu R^2}. \tag{23}$$

If $V > V_{\max}$ this equilibrium configuration no longer exists and we conclude that the disk is engulfed by the ice.

It is interesting to calculate the temperature of the ice–water interface beneath the disc, T_i. From (11) we have that

$$\frac{A}{6\pi h^3} = \frac{\rho_s L(T_m - T_i)}{T_m}. \tag{24}$$

Using this expression to eliminate h from (21) and rearranging we find that

$$T_m - T_i = \frac{A}{6\pi}\frac{T_m}{\rho_s L}\frac{2}{3\pi\mu R^4}\left(\frac{A}{9\pi\mu R^2} - V\right)^{-1} \tag{25}$$

so that as $V \to V_{\max}$, $T_i \to -\infty$. In other words the disk is well below the undisturbed phase boundary.