GFD 2006 Lecture 2: Diffusion-controlled solidification

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1 Finishing off Lecture 1

As shown in Lecture 1, an approximation for the diffusion time is

$$t = \frac{a^2}{\kappa}. \tag{1}$$

An experiment was conducted using a commercial hand warmer. This is a plastic bag containing a liquid (an aqueous solution of sodium acetate) in a metastable state i.e. at a temperature below its freezing point. Crystallisation is initiated by flexing a thin metal disk contained in the bag and was observed to proceed at a rate of about 1 cm s^{-1}. Taking $a = 10\mathrm{cm}$, $\kappa = 10^{-2}\mathrm{cm}^2/\mathrm{s}$ gives $t \approx 10^4\mathrm{s} \approx 3\mathrm{hrs}$ using equation (1). A different mechanism must operate in the heat pack than was analysed in Lecture 1. We will return to this later.

2 Diffusion-Controlled Solidification into a Supercooled Liquid

Instead of considering a solid cooled from a boundary, we now consider a solid, assumed to be at T_m, surrounded by a liquid with far-field temperature given by $T_\infty < T_m$ so that the liquid is supercooled. Again, we only consider a one-dimensional problem, with $x = 0$ at the center of the solid and $x = a(t)$ at the solid–liquid interface. We solve the diffusion equation (in the liquid) with the Stefan condition and with appropriate temperature boundary conditions ($T(a) = T_m$ and $T(\infty) = T_\infty$):

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial x^2}, \tag{2}$$

$$\rho L \dot{a} = -k \frac{\partial T}{\partial x} \big|_{a^+} . \tag{3}$$

As before, we scale the equations and arrive at the similarity solution

$$\eta = \frac{x}{2\sqrt{\kappa t}}, \tag{4}$$

$$T = T_\infty + (T_m - T_\infty)\frac{\mathrm{erfc}(\eta)}{\mathrm{erfc}(\mu)}, \tag{5}$$

$$a = 2\mu\sqrt{\kappa t}, \tag{6}$$

$$\frac{1}{S} = F(\mu), \tag{7}$$

where

$$F(x) = \sqrt{\pi} x e^{x^2} \mathrm{erfc}(x). \tag{8}$$

Plotting $F(x)$, we find that $F(0) = 0$, and $F(x)$ has a maximum of 1 as $x \to \infty$ (see figure 10b of Lecture 1). Thus, no similarity solution exists for $1/S > 1$ or $S < 1$. In fact, all solutions become unbounded for $S < 1$. This inconsistency is remedied by relaxing the assumption of $T = T_m$ at the interface since this is strictly only true in equilibrium. For $S < 1$, however, growth is rapid, we are far from equilibrium, and molecular attachment kinetics are important. For ice, it is typically observed that attachment and detachment occur at a rate of approximately 1000 molecular layers per second. Below 0°C attachment is faster than detachment and above $0°C$ attachment is slower than detachment. The velocity of the boundary $\dot{a}$ is proportional to the difference between attachment and detachment. Thus, our revised problem is given by: Diffusion equation (2) in $x \geq a$; Stefan condition (3) at $x = a$; $T(\infty) = T_\infty$; $T(a) = T_i$; and $\dot{a} = \mathcal{G}(T_m - T_i)$, where $\mathcal{G}$ is a constant.

We again scale length with λ, time with τ and temperature difference with $\Delta T = T_m - T_\infty$. This results in

$$\lambda \sim \frac{\kappa}{\mathcal{G}\Delta T}, \tag{9}$$

$$\tau \sim \frac{\kappa}{\mathcal{G}^2 \Delta T^2}. \tag{10}$$

Using the scaling $a = \lambda a'$, $x = \lambda x'$, $T = T_\infty + \Delta T \cdot \theta$, substituting and dropping primed notation results in

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial x^2}, \tag{11}$$

$$S\dot{a} = -\frac{\partial \theta}{\partial x} \mid_{a^+}, \tag{12}$$

$$\dot{a} = 1 - \theta_i, \tag{13}$$

$$\theta(\infty) = 0 \qquad \theta(a) = \theta_i. \tag{14}$$

We now consider two limits. If $S \gg 1$, then (12) gives $\dot{a} \ll 1$ so $\theta_i = 1 + O(S^{-1})$ or dimensionally, $T_i \approx T_m$, the analysis from lecture 1 holds and we recover the similarity solution presented there. If $S \ll 1$, then (12) does not constrain $\dot{a}$ which is instead determined by the kinetic equation (13), which suggests looking for a solution of the form $\dot{a} = V$ where V is constant. Hence, we try $\theta = \theta(\eta)$, where $\eta = x - Vt$. Substitution leads to

$$\theta = \theta_i e^{-V\eta}, \tag{15}$$

$$a = Vt, \tag{16}$$

$$\theta_i = S, \tag{17}$$

and

$$V = 1 - \theta_i = 1 - S, \tag{18}$$

which is valid (exactly) if $S < 1$.

Finally, we note that the discrepancy between applying kinetics and using the previous ($S > 1$) similarity solution is typically small, especially at large time when the kinetic solution asymptotes to the similarity solution. Therefore, kinetics can often be neglected in many problems involving sea ice, for example.

3 Generalized Clapeyron Equation for Interfaces in Equilibrium

For a planar interface and at some reference pressure, the melting temperature is set by a balance of the temperature-dependent rates of the attachment and detachment of the solid phase – this is the reference melting/freezing point. But modification of the system pressure or a pressure difference between the solid and liquid phase can cause changes in the equilibrium interfacial temperature. The relation governing this phenomenon is

$$\frac{\rho_s L \left(T_m - T_e\right)}{T_m} = (p_s - p_l) + (p_l - p_m)\left(1 - \frac{\rho_s}{\rho_l}\right), \tag{19}$$

where T_m, p_m are the reference melting point and pressure. There are several examples of this effect that will appear later in these proceedings, briefly mentioned below.

3.1 Change in system pressure

Across a planar interface, pressures will be equal when the system is in mechanical equilibrium. But the overall system pressure may be elevated (or decreased), for example by hydrostatic effects. In this case the second term on the right-hand side of the Clapeyron equation comes into effect, with p_l equal to p. It is easy to see that the rate of change of the melting point with respect to pressure is given by

$$\frac{dT_e}{dp} = -\frac{T_m}{\rho_s L}\left(1 - \frac{\rho_s}{\rho_l}\right). \tag{20}$$

For example, in the ocean this allows us to find the melting point at depth. Hydrostatic balance gives us

$$\frac{dT_e}{dz} = -\rho_l g \frac{dT_e}{dp} \approx 7.5 \times 10^{-4}\mathrm{K/m}. \tag{21}$$

3.2 Curved interface

At a curved interface, there is a force involved with the interfacial energy that factors into the force balance, and results in an imbalance between p_l and p_s. This is expressed by

$$p_s - p_l = \gamma(\nabla \cdot \mathbf{n}). \tag{22}$$

Here γ is the interfacial energy and $\mathbf{n}$ is the unit normal to the interface, directed into the liquid. With $p = p_l$, this gives

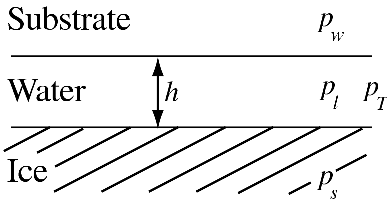

Figure 1: Interfacial premelting of a solid below the melting point. The hydrodynamic pressure (p_l) is lower than p_s because of the thermomolecular pressure p_T.

$$T_e = T_m - \Gamma(\nabla \cdot \mathbf{n}) \tag{23}$$

where

$$\Gamma \equiv \frac{\gamma T_m}{\rho_s L}. \tag{24}$$

Equation (23) is known as the Gibbs-Thomson equation.

3.3 Interfacial Premelting

When a solid near its bulk melting point is in contact with a gas or solid substrate, it is sometimes thermodynamically favorable for there to be a (very) thin liquid film between the solid and the substrate (figure 1). Among the determining factors are the interfacial energies per unit area between the solid and its liquid, the solid and the substrate, and the liquid and the substrate.

The liquid pressure in the film is actually lowered relative to the solid pressure, since intermolecular forces play a part in the mechanical equilibrium balance. This pressure difference is described as a Thermomolecular Pressure. A drop in interfacial temperature follows from the Clapeyron equation.

In thermodynamic terms, the chemical potential of the liquid – that is, the incremental change in free energy with respect to the addition of new material – is not equal to that of the solid, as it would be in a bulk equilibrium state, since intermolecular interaction potentials must be accounted for in minimizing the free energy of the system. The chemical potential is a state variable, and its change is accompanied by a change in hydrodynamic pressure.

4 Nucleation

The Gibbs-Thomson effect is nicely illustrated by a simple model of a solid particle nucleating into a supercooled liquid domain (figure 2). The dynamics of the initial formation of the particle are complex, but we will ignore such details and assume that the necessary events have already taken place for there to be a spherical solid particle with finite radius a at time t. The ambient temperature of the liquid is below its melting point, and furthermore, as before, we will assume that the Stefan number is large and make a quasi-stationary

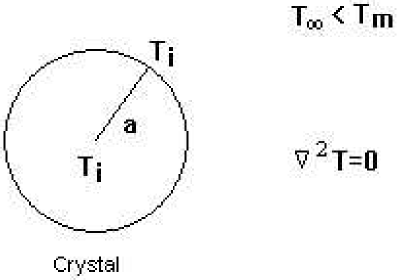

Figure 2: Nucleated spherical crystal in supercooled liquid with high Stefan number.

approximation, so that temperature is harmonic in the liquid and in the solid. Thus our system of equations is

$$\nabla^2 T = \begin{cases} 0 & r > a \\ 0 & r < a \end{cases}, \tag{25}$$

$$T = \begin{cases} T_\infty & r \to \infty \\ T_m - \Gamma(\nabla \cdot \mathbf{n}) & r = a \end{cases}. \tag{26}$$

This system is solvable for a given a, even though a is changing in time. Curvature is constant over the surface of the sphere (and is equal to $2/a$), so the equation and boundary conditions are spherically symmetric and we expect a symmetric solution. The temperature field in the solid is easy to diagnose: a harmonic function in a bounded domain with constant boundary condition is itself constant (and therefore the only flux at the interface is that on the liquid side). Our Stefan condition is then

$$\rho L \dot{a} = -k \frac{\partial T}{\partial r}|_{r=a+}. \tag{27}$$

Given the spherical symmetry of the problem, the temperature field in the liquid must have the form $A + Br^{-1}$. Using the boundary conditions, we can deduce that, for $r > a$,

$$T = T_\infty + (T_m - \frac{2\Gamma}{a} - T_\infty)\frac{a}{r}. \tag{28}$$

With an isothermal solid, the Stefan condition then gives us

$$\rho L \dot{a} = k a^{-1}(T_m - \frac{2\Gamma}{a} - T_\infty). \tag{29}$$

Rather than solve for $a(t)$ exactly, it is instructive to examine the sign of the R.H.S. of (29) and also to consider the limiting cases of small and large radii. First, note that a is increasing (decreasing) when it is larger (smaller) than a critical radius, $a_c \equiv 2\Gamma/(T_m - T_\infty)$. So a_c is an unstable fixed point; larger particles will grow, and smaller particles will shrink.

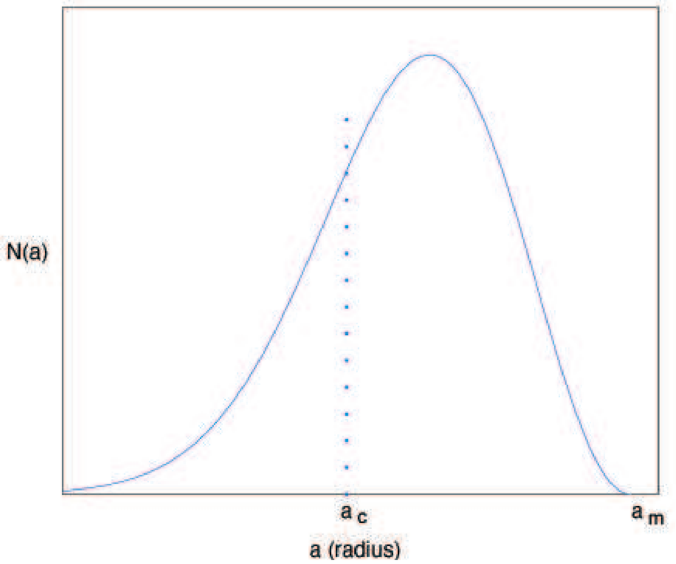

Figure 3: Scaled distribution of population of nucleating particles

(Note that this is just in our simple model – we are considering a single particle in a liquid whose far-field temperature does not change; see the discussion below.)

Furthermore, we can approximate the growth rate in the limit of large and small radii. For $a \gg a_c$, $\dot{a}$ is nearly proportional to a^{-1}, and we get

$$a(t) \approx \sqrt{\frac{2\kappa t}{S}}. \tag{30}$$

On the other hand, for $a \ll a_c$, (29) becomes

$$\rho L \dot{a} \approx \frac{-2k\Gamma}{a^2} \tag{31}$$

$$\Rightarrow a(t) \approx \sqrt[3]{a(0)^3 - \frac{6k\Gamma}{\rho L}}, \tag{32}$$

so the solid disappears in finite time.

Though we do not give the details, it is worth noting the case where there is an entire population of nucleating crystals, and the temperature of the system away from a crystal is not constrained (indeed, there is heat being given off by the solidification, and so the system temperature on the whole will be increasing). An interesting result is that the resulting distribution of particle size is self-similar, meaning that the probability distribution function, scaled by $t^{\frac{1}{3}}$ (**not** by $t^{\frac{1}{2}}$), remains constant in time. Such a distribution is shown in figure 3. Note that there is a finite cutoff (denoted by a_m) since particles will not grow to arbitrarily large size after finite time.

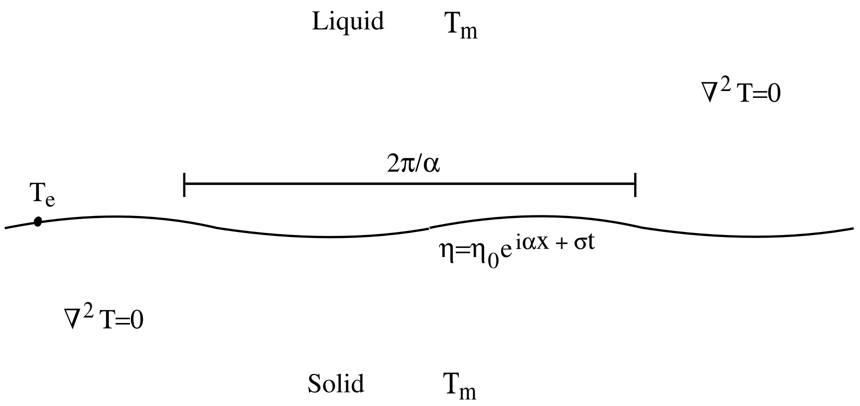

Figure 4: Student Problem

5 Student Problem

Consider perturbations to a 1-D planar interface in a 2-D system with large Stefan number and far-field temperature equal to the bulk melting point. The interface has an energy associated with it, and the disturbance has a small amplitude compared with its wavelength. For small times, and neglecting kinetics, how would the interface evolve?

Solution. Since the perturbation is small, this problem can be linearized, neglecting higher order terms in the small parameter $\eta_0\alpha$, where η_0 is the perturbation amplitude and α is its wavenumber. With large Stefan number we can make a quasi-stationary approximation and assume temperature is harmonic in both the liquid and solid domains (but not across the interface). Our equations are as follows:

$$\nabla^2 T = \begin{cases} 0 & z > \eta \\ 0 & z < \eta \end{cases}, \tag{33}$$

$$T = \begin{cases} T_m & z \to \pm\infty \\ T_m - \Gamma(\nabla \cdot \mathbf{n}) & z = \eta \end{cases}, \tag{34}$$

along with the Stefan condition

$$\dot{a} = -\frac{k}{\rho L}\frac{\partial T}{\partial n}|_{z=\eta+} + \frac{k}{\rho L}\frac{\partial T}{\partial n}|_{z=\eta-}, \tag{35}$$

where $\dot{a}$ is the normal velocity of the interface, which is equal to

$$(\sqrt{1+\eta_x^2})^{-1}\frac{\partial \eta}{\partial t}. \tag{36}$$

From the equation for the interface position $z - \eta(x,t) = 0$ we can determine

$$\mathbf{n} = \frac{(-\eta_x, 1)}{(1+\eta_x^2)^{1/2}} \tag{37}$$

and

$$\nabla \cdot \mathbf{n} = -\frac{\eta_{xx}}{(1+\eta_x^2)^{3/2}}. \tag{38}$$

Now we linearize, neglecting higher-order terms, and the problem simplifies. First of all, the smallness of the slope of the interface means that the normal derivative in (35) is a higher-order correction to the vertical derivative, and the smallness of η means that evaluation of the perturbed temperature field at η is a higher-order correction to its evaluation at zero. Likewise, the quadratic term in (36) is dropped, as is the one in (38). Our linearized system of equations is now

$$\nabla^2 T = \begin{cases} 0 & z > 0 \\ 0 & z < 0 \end{cases}, \tag{39}$$

$$T = T_m, \quad z \to \pm\infty, \tag{40}$$

$$T = T_m + \Gamma \eta_{xx}, \quad z = 0, \tag{41}$$

$$\eta_t = \frac{k}{\rho L}\left(-T_z|_{0+} + T_z|_{0-}\right). \tag{42}$$

Since this is a linear problem we can anticipate the form of the solution

$$\begin{aligned} \eta(x,t) &= \eta_0 e^{i\alpha x + \sigma t}, & (43) \\ T(x,z,t) &= T_m + \hat{T}(z) e^{i\alpha x + \sigma t}. & (44) \\ & & (45) \end{aligned}$$

Laplace's equation and the decay condition along with (41) give

$$\hat{T}(z) = -\alpha^2 \Gamma \eta_0 e^{\mp \alpha z}, \tag{46}$$

depending on whether z is positive or negative. The Stefan condition then shows that

$$\sigma = -\frac{2\alpha^3 \Gamma k}{\rho L}. \tag{47}$$

Thus the interface is stable for all wave numbers and the decay constant is proportional to α^3. The stabilizing effect is intuitive: "positive" bumps (areas where the solid protrudes into the liquid) have a lowered melting point due to Gibbs-Thomson, while "negative" bumps have elevated melting point. There is then a net heat flux from negative to positive bumps, which causes a melt/freeze pattern that counters the perturbation.