Morphological instabilities of the solidification front induced by undercooling the liquid phase

This problem set is adapted from Chapter 18 of the monograph *Thermomechanics of Evolving Phase Boundaries in the Plane* by M. E. Gurtin (Clarendon Press, Oxford, 1993). In it, we tackle the problem of solidification of a pure substance (e.g., the transition from liquid water to solid ice as temperature is lowered) and investigate the morphological stability of the liquid-solid interface. Specifically, in Section 1, the free-boundary problem is **linearized** for small departures of the temperature from its melting value. Next, Section 2 is devoted to the **one-dimensional growth** of a solid phase from a zero-measure seed in an undercooled liquid. Finally, we analyze in Section 3 the onset of **morphological instabilities** in an initially flat solidification front in two space dimensions.

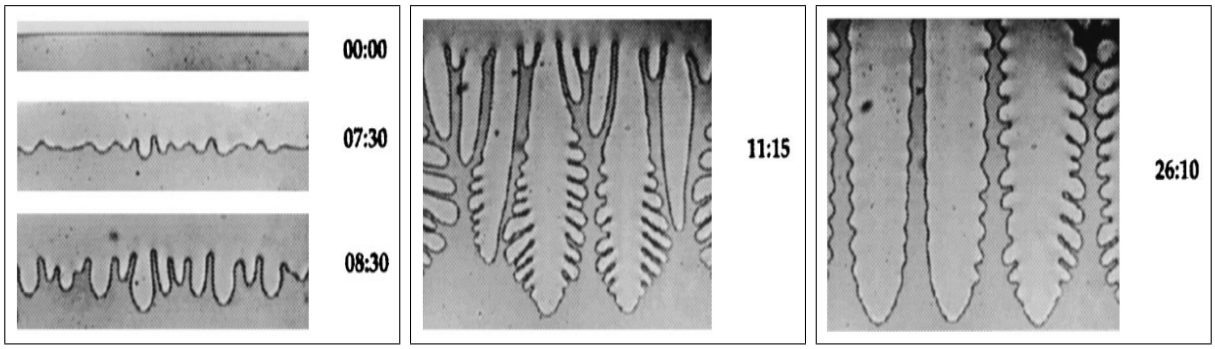

Figure 1: Morphological evolution of the liquid-solid interface during the directional solidification of a binary alloy consisting of organic crystal succinonitrile doped with the laser dye coumarin 152. [Reproduced from W. Losert, B. Q. Shi, and H. Z. Cummins. Evolution of dendritic patterns during alloy solidification: Onset of the initial instability. *Proc. Natl. Acad. Sci.*, **95**, 431–438 (1998).]

1 The linearized solidification free-boundary problem

In class, we derived the equations that make up the solidification free-boundary problem for a pure substance. Ignoring any source terms (e.g., heat radiation), the first of these equations are the energy balances

$$\frac{\partial e_\alpha}{\partial t} = -\mathrm{div}\boldsymbol{q}_\alpha \tag{1}$$

in each of the liquid and solid phases ($\alpha = \ell, s$), where $e_\alpha(T)$ is the temperature-dependent internal energy per unit area of the α phase and, assuming *isotropic* heat conduction, the heat flux in the α phase obeys Fourier's law, i.e., $\boldsymbol{q}_\alpha = -\mathsf{k}_\alpha(T)\nabla T$. Denoting by e^* the internal energy per unit length of the solidification front, the bulk energy balances (1) are complemented by the *interfacial energy balance*

$$\overset{\circ}{e^*} - (\llbracket e \rrbracket + e^*\kappa^*)\, v_n^* + \llbracket \boldsymbol{q} \rrbracket \cdot \boldsymbol{n}^* = 0, \tag{2}$$

where κ^* is the curvature of the interface and v_n^* is its velocity in the normal direction $\boldsymbol{n}^*$, and $\llbracket \varphi \rrbracket := \varphi_\ell^+ - \varphi_s^-$ denotes the jump in the limiting values of any bulk field φ at the solidification

front. Finally, a *linear kinetic relation*, linking the driving force $[\![\psi]\!] + \psi^*\kappa^*$ for solidification to the normal velocity v_n^* of the liquid-solid interface, is postulated:

$$[\![\psi]\!] + \psi^*\kappa^* = \beta^* v_n^*, \tag{3}$$

where $\psi^*(T)$ is the temperature-dependent Helmholtz free energy per unit length of the solidification front and $\beta^*(T)$ is its kinetic coefficient.

1.1. Let T_m be the *melting temperature* of the pure substance under consideration, i.e., T_m is the unique temperature at which the free-energy densities of the liquid and solid phases coincide, $\psi_\ell(T_m) = \psi_s(T_m)$. Define the *dimensionless temperature* as $u := (T - T_m)/T_m$. Finally, denote by $\mathsf{c}_\alpha(T) := \partial e_\alpha(T)/\partial T$ the *specific heat* of the α phase ($\alpha = \ell, s$).

Hereafter, we assume that the departures of the temperature from its melting value are small, i.e., $|u| \ll 1$, and that all derivatives of u are also small. By Taylor-expanding the temperature-dependent fields to first-order, show that the bulk energy balances (1) reduce to the *linear heat equation*

$$\mathsf{c}_\alpha \frac{\partial u}{\partial t} = \mathsf{k}_\alpha \nabla^2 u \tag{4}$$

in each of the liquid and solid phases ($\alpha = \ell, s$), where $\mathsf{c}_\alpha := \mathsf{c}_\alpha(T_m)$ denotes the specific heat and $\mathsf{k}_\alpha := \mathsf{k}_\alpha(T_m)$ the thermal conductivity in the α phase, both evaluated at the melting temperature.

1.2. Define the *latent heat* as $\mathcal{L} := e_\ell(T_m) - e_s(T_m)$. Show that $\mathcal{L}$ can be expressed as

$$\mathcal{L} = T_m [\![\eta(T_m)]\!] \tag{5}$$

and infer that the jump in free-energy density at the liquid-solid interface has the form

$$[\![\psi(T)]\!] = -\mathcal{L}u + \mathcal{O}(u^2). \tag{6}$$

It follows from (6) that $\mathcal{L} > 0$ is a necessary and sufficient condition for the solid phase to be more stable than the liquid phase at temperatures below the transition temperature, in the sense that $\psi_s(T) < \psi_\ell(T)$ whenever $T < T_m$.

Deduce that the kinetic relation (3) can be approximated by the *generalized Gibbs–Thomson relation*

$$u = \frac{\psi^*}{\mathcal{L}}\kappa^* - \frac{\beta^*}{\mathcal{L}} v_n^*, \tag{7}$$

where $\psi^* := \psi^*(T_m)$ and $\beta^* := \beta^*(T_m)$ denote the interfacial free-energy density and kinetic coefficient evaluated at the melting temperature. The generalized Gibbs–Thomson relation states that the temperature at the interface deviates from the melting temperature, the difference consisting of two contributions: a *capillary undercooling* proportional to the interfacial curvature κ^*, and a *kinetic undercooling* proportional to the solidification rate v_n^*.

1.3. Neglecting the contributions associated with the internal energy e^* per unit length of the solidification front, show that the interfacial energy balance (2) reduces to the *Stefan condition*

$$v_n^* = -\frac{T_m}{\mathcal{L}} (\mathsf{k}_\ell (\nabla u)^+ - \mathsf{k}_s (\nabla u)^-) \cdot \boldsymbol{n}^*, \tag{8}$$

which states that the rate $\mathcal{L}V^*$ at which heat is generated at the solidification front equals the rate $-(\mathsf{k}_\ell(\nabla T)^+ - \mathsf{k}_s(\nabla T)^-) \cdot \boldsymbol{n}^*$ at which it diffuses away from the interface and into the liquid and solid phases.

Thus, the unknown fields are u and v_n^*, and the free-boundary problem consists of the (linearized) heat equation (4) in each of the liquid and solid phases, supplemented by the generalized Gibbs–Thomson relation (7) and the Stefan condition (8) at the interface between them, as well as appropriate initial and boundary conditions. In what follows, we make two additional simplifying assumptions:

— The interfacial velocity v_n^* is *small* in comparison with the characteristic velocity for the conduction of heat in either bulk phase. The liquid and solid phases are therefore assumed to be in thermal equilibrium at all times. In this *quasistatic limit*, (4) is replaced by *Laplace's equation*

$$\nabla^2 u = 0. \tag{9}$$

— The liquid and solid are assumed to be in *phase equilibrium*, in the sense that the driving force vanishes everywhere along the solidification front. In the present linearized setting, this is equivalent to the assumption $\beta^* = 0$, so that (7) reduces to the *standard Gibbs–Thomson relation*

$$u = \frac{\psi^*}{\mathcal{L}} \kappa^*. \tag{10}$$

2 The one-dimensional problem: Growth of a solid phase from a zero-measure seed

We begin with the simple one-dimensional problem corresponding to a flat interface, restricting temperature variations to the direction normal to the propagating front. Taking the x-axis to be normal to the interface, the two-phase body may be, after a suitable rescaling, identified with the $[0, 1]$ interval.[1] The dimensionless temperature is then a function $u(x, t)$ defined on this interval and the position of the solidification front is given by $\xi(t) \in (0, 1)$. We assume that the solid occupies the interval $(0, \xi(t))$ and the liquid the interval $(\xi(t), 1)$.

2.1. Assuming that the endpoint $x = 0$ is *insulated* (i.e., no heat can flow through it) while the other endpoint $x = 1$ is in contact with a thermal reservoir at *fixed* temperature T_o, and assuming that the whole body is initially in the liquid phase, with the solid seed confined to the endpoint $x = 0$, write the free-boundary problem for the dimensionless temperature difference $u(x, t)$ and the interface position $\xi(t)$.

2.2. Show that the temperature field is given by

$$u(x,t) = \begin{cases} 0 & \forall\, x \in (0, \xi(t)], \\ \dfrac{u_\mathrm{o}(x - \xi(t))}{1 - \xi(t)} & \forall\, x \in [\xi(t), 1), \end{cases} \tag{11}$$

where $u_\mathrm{o} = (T_\mathrm{o} - T_m)/T_m$.

2.3. Show that if $T_\mathrm{o} \geqslant T_m$, the interface does not propagate. Hence, the solid seed cannot grow unless the liquid is *undercooled* ($T_\mathrm{o} < T_m$).

[1] We recover the same one-dimensional setting if we consider instead the solidification of a liquid that fills a narrow cylindrical tube, whose cross-sectional dimensions are small compared to its length. In such a tube, it is reasonable to neglect any lateral variations in the temperature field, so that it may be approximated by a segment of the x-axis.

2.4. Assuming that the liquid is undercooled, show that the position of the interface is given by

$$\xi(t) = 1 - \sqrt{1 + \frac{2\mathsf{k}_\ell u_\mathrm{o}}{\mathcal{L}} t} \quad \forall t \leqslant t_\mathrm{o}, \tag{12}$$

and determine the time t_o at which the entire body is solid. What happens for $t > t_\mathrm{o}$?

2.5. Solve the free-boundary problem for a one-dimensional body identified with the interval $[-1, 1]$ and consisting entirely of liquid except for a solid seed of zero measure placed at a point $\xi_\mathrm{o} \in (-1, 1)$, assuming that both endpoints are now kept at the same temperature T_o, i.e., $u(-1, t) = u(1, t) = u_\mathrm{o}$.

3 The two-dimensional problem: Instability of a flat solidification front

In this section, we investigate the stability with respect to infinitesimal perturbations of a flat solidification front that propagates into the liquid with constant speed. This problem illustrates the unstable nature of the free-boundary problem under consideration. In particular, it highlights the effects of capillarity, as encapsulated by the thermodynamic structure of the interface. Specifically, we proceed as follows:

— We first compute the *fundamental solution*, which corresponds to a flat interface that evolves with constant velocity.

— To study the stability of this solution, we introduce a perturbation of the flat interface, whose smallness allows us to *linearize* the free-boundary problem with respect to the perturbation.

— Finally, the resolution of the linearized equations yields the *growth rate* of the perturbation as a function of its wavenumber. The sign of the growth rate determines when the flat solidification front turns unstable, and provides insight into the competing mechanisms that govern its stability.

3.1. **Fundamental solution**: We assume that the body occupies the whole plane (endowed with Cartesian coordinates) and seek a solution such that a flat solidification front parallel to the x-axis propagates in the y-direction with constant velocity V_o and the temperature field in both liquid and solid phases is of the form $u(x, y, t) = \overline{u}(y - V_\mathrm{o} t)$, see Fig. 2.

In this setting, it is convenient to work in a frame that moves with the flat interface. We therefore make the change of variables $\tilde{x} = x$ and $\tilde{y} = y - V_\mathrm{o} t$, and in order to avoid cumbersome notation drop the tildes hereafter. Importantly, Laplace's equation (9), the standard Gibbs–Thomson relation (10), and the Stefan condition (8) remain *invariant* under this change of variables, and the temperature field associated with the fundamental solution reads $u(x, y, t) = \overline{u}(y)$.

Assuming that the heat fluxes are prescribed away from the interface, so that the far-field Neumann boundary conditions

$$\lim_{y \to -\infty} \frac{\partial u}{\partial y} = \mathsf{g}_s \quad \text{and} \quad \lim_{y \to +\infty} \frac{\partial u}{\partial y} = \mathsf{g}_\ell \tag{13}$$

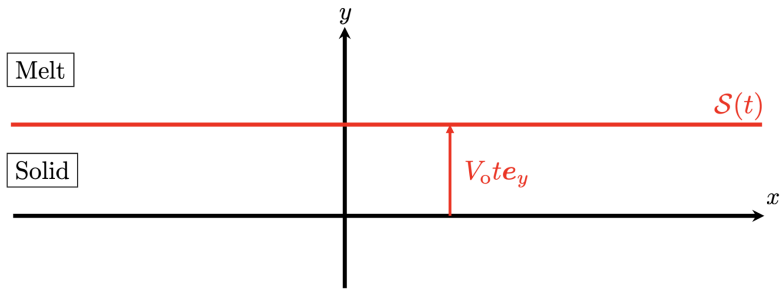

Figure 2: Schematic of a flat solidification front that moves with constant velocity $V_o \boldsymbol{e}_y$ relative to a fixed Cartesian reference frame.

hold, determine the temperature fields in the liquid and solid, and the velocity V_o with which the solidification front moves. Plot $\overline{u}(y)$ when (i) $0 < \mathsf{k}_\ell^* \mathsf{g}_\ell < \mathsf{k}_s^* \mathsf{g}_s$ and (ii) $\mathsf{k}_\ell^* \mathsf{g}_\ell < 0 < \mathsf{k}_s^* \mathsf{g}_s$, where $\mathsf{k}_\alpha^* = \mathsf{k}_\alpha / \mathcal{L}$ $(\alpha = \ell, s)$, and discuss the relative magnitude and direction of the heat fluxes at the interface.

3.2. **Small perturbation of the interface**: To study the (linear) stability of the fundamental solution, we introduce a small perturbation of the flat solidification front in the form of the graph of a function, i.e., the interface is parametrized by x according to

$$\boldsymbol{x}^*(x,t) = x\boldsymbol{e}_x + h(x,t)\boldsymbol{e}_y, \tag{14}$$

where

$$h(x,t) = \epsilon(t)\sin(\omega x), \tag{15}$$

with $\omega \in \mathbb{R}_+^*$ the wavenumber of the perturbation and $\epsilon(t)$ its time-dependent amplitude, assumed small: $|\epsilon(t)| \ll 1$. The purpose of the stability analysis is to determine $\epsilon(t)$.

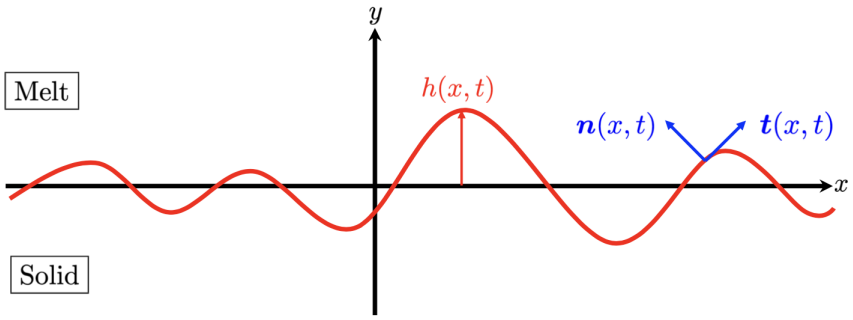

Figure 3: Schematic of a perturbed solidification front, represented by the graph of a function $h(x,t)$ in a Cartesian reference frame that moves with constant velocity $V_o \boldsymbol{e}_y$ (the flat interface of the fundamental solution coincides now with the x axis).

Compute the expressions of the interfacial unit tangent $\boldsymbol{t}^*(x,t)$ and normal $\boldsymbol{n}^*(x,t)$, curvature $\kappa^*(x,t)$, and normal velocity $v_n^*(x,t)$ to first order in ϵ.

3.3. **Perturbed temperature field**: Show that the perturbed temperature field

$$u(x,y,t) = \begin{cases} \mathsf{g}_s y + \mathsf{C}_s(t)\exp(\omega y)\sin(\omega x) & \forall\, y \leqslant h(x,t), \\ \mathsf{g}_\ell y + \mathsf{C}_\ell(t)\exp(-\omega y)\sin(\omega x) & \forall\, y \geqslant h(x,t), \end{cases} \tag{16}$$

satisfies Laplace's equation (9) in the solid and liquid phases, with $\mathsf{C}_s(t)$ and $\mathsf{C}_\ell(t)$ both $\mathcal{O}(\epsilon)$. Further, by enforcing the standard Gibbs–Thomson relation (10) to within terms of order $\mathcal{O}(\epsilon^2)$, express $\mathsf{C}_s(t)$ and $\mathsf{C}_\ell(t)$ in terms of $\epsilon(t)$.

3.4. **Dispersion relation**: By imposing the Stefan condition (8) to within terms of order $\mathcal{O}(\epsilon^2)$, show that the amplitude of the perturbation solves the differential equation

$$\dot{\epsilon}(t) = -\lambda(\omega)\epsilon(t), \tag{17}$$

where the superposed dot denotes differentiation with respect to time. In doing so, determine the expression of the growth rate $-\lambda$ in terms of the wavenumber ω.

3.5. **Linear stability analysis**: The flat solidification front is said to be (linearly) *stable* if $\lambda(\omega) \geqslant 0$ for all $\omega \in \mathbb{R}_+^*$. Otherwise, i.e., whenever $\lambda(\omega) < 0$, the perturbation whose wavenumber is ω grows exponentially with time, and the front is *unstable*.

Assuming that $\mathsf{g}_s > 0$, discuss the dependence of the stability of the solidification front on the sign of g_ℓ. In particular, when $\mathsf{g}_\ell < 0$, for which wavenumbers is the front unstable? Finally, provide a physical interpretation for your conclusions.