1 Introduction

In previous lectures we considered solidification at a planar boundary, and we found that in this case there was the possibility of constitutional supercooling in the liquid region ahead of the solidification front. Such constitutional supercooling causes morphological instability of the phase boundary, and the interface evolves until a ‘mushy layer’ (region of mixed phase) is formed. A mushy layer is modeled as a two-component, reactive porous medium. We have also seen that the growth of a mushy layer is governed by the rate of thermal diffusion.

The morphological instability of the interface, caused by constitutional supercooling, increases its specific surface area, and thereby enhances the latent heat release, leading to a temperature that is greater than that obtained for a planar boundary. Increased specific surface area also enhances the release of solute from the solid, which increases the concentration of the interstitial fluid; this increase in concentration acts to lower the liquidus temperature in the mushy layer.

Therefore, if a region of constitutional supercooling is present in a mushy layer, the liquidus temperature in the interstitial region decreases, due to enhanced release of solute, and the actual temperature increases, due to the enhanced release of latent heat. These temperature changes continue until the region of supercooling in the mushy layer has been eliminated (as shown in Figure 1); the temperature and the liquidus temperature in the mushy layer evolve until they are equal. We therefore assume that throughout the mushy layer the temperature is equal to the local liquidus temperature.

Our goal here is to establish the position of the interface between the liquid and the mushy region (and also the solid and the mushy region), and to do this we treat the mushy region separately as an inhomogeneous porous medium. We therefore have two unknown boundaries to determine as part of our solution.

2 Governing equations

From lecture 5, we have that the governing equations describing the evolution of the mean temperature $T(x,t)$, mean concentration of the liquid phase $C(x,t)$ and solid fraction $\phi(x,t)$
in a mushy layer are

\[
\nabla \cdot \mathbf{u} = (1 - r) \frac{\partial \phi}{\partial t}, \\
\frac{\rho c_p}{\partial T} + \rho \mathbf{u} \cdot \nabla T = \nabla \cdot (k \nabla T + \rho_s L \frac{\partial \phi}{\partial t}), \\
(1 - \phi) \frac{\partial \mathbf{C}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{C} = \nabla \cdot (\vec{D} \nabla \mathbf{C}) + r \mathbf{C} \frac{\partial \phi}{\partial t}, \\
T = T_L(C), \\
\mu \mathbf{u} = \Pi(-\nabla p + \rho \mathbf{g}),
\]

where \( r = \rho_s / \rho_l \) and the remaining symbols have their usual meaning (as described in previous lectures), and we have assumed that the solid phase is pure. Equations (1) – (3) arise from conserving mass, heat and solute. Equation (4) describes the assumption that the temperature and concentration of the interstitial liquid lie on the liquidus, and the final equation (5) is the transport equation for the Darcy velocity \( \mathbf{u} \).

If we consider the case in which the solid in the mushy layer (ice) is growing, then noting that \( \rho_s < \rho_l \), equation (1) shows that the velocity field will have a positive divergence. We have an advection-diffusion equation (2) to solve for the temperature, which is forced by latent heat release in the mushy layer. We also have an advection-diffusion equation for the
solute (3), which is modified by a source term to reflect the increase in concentration of the interstitial fluid as a result of the formation of pure ice crystals.

We are interested in dynamically generated fluid flows, particularly under the action of gravity, and therefore use Darcy’s law (5), which states that the fluid velocity is proportional to the negative pressure gradient.

Equations (1)–(5) are solved in the mushy layer; the Navier-Stokes equations coupled with advection-diffusion equations for heat and solute are solved in the liquid region, while we consider pure diffusion in the solid phase.

2.1 Internal Disequilibrium

In earlier lectures, we saw that for the kinetically driven solidification of a planar interface, the normal velocity of the phase boundary could be described by

\[ v_n = G(T_m - T), \]

where \( G \) is the kinetic coefficient, which is assumed constant. In the case of a mushy layer, equation (6) can be modified to

\[ \dot{\phi} = GA[T_L(C) - T], \]

where \( A \) denotes the specific surface area of the internal phase boundaries in the mushy layer. Thus if \( T \neq T_L(C) \) in the interior of the mushy layer, the surface area \( A \) increases and as the product \( GA \) becomes large \( T \simeq T_L(C) \).

3 Interfacial conditions

To generate boundary conditions for the governing equations, we apply the conservation laws at both interfaces. The first interfacial condition, derived from equation (1) is

\[ [u \cdot n] = -(1 - r)v_n[\phi]. \]

In most circumstances, \( \phi \) is continuous between the mushy layer and the liquid, and therefore \( [\phi] = 0 \). At the interface between the solid and the mushy layer, however, there may be a discontinuity in \( \phi \), and we would expect only to be able to impose continuity of \( \phi \) at one boundary as there is only one partial derivative of \( \phi \) in the governing equations.

The second boundary condition is analogous to the Stefan condition, and is given by

\[ \rho_s L[\phi]v_n = [k n \cdot \nabla T]. \]

Note that there is no advective term in condition (9) as the equations of mass and heat conservation imply that \( [T] = 0 \) at the interface; it is not obvious, however, that the same will be true for the mean concentration, \( C \).

The third condition, applied at the interface of the mushy layer and the liquid, is

\[ [(v_n - u \cdot n)C]'_m + C_m \phi v_n = [-D n \cdot \nabla C]'_m. \]

The subscript \( l \) denotes evaluation in the liquid; \( m \) denotes evaluation in the mushy layer.
As we have homogenized the mushy layer on some scale, we cannot interrogate it on a length scale that is smaller than this. In deriving these interfacial conditions we can therefore no longer consider the interface between the mushy layer and the solid or liquid phase to be a line; instead, we must consider it to be a region with a thickness that is comparable to the homogenization scale, $\delta$.

Boundary conditions (8) and (9) are robust in this sense; condition (10) is more controversial, and depends on the relative sizes of the homogenization length scale and the length scale of diffusion, $l_D$. The choice $\delta < l_D$ allows the retention of solute diffusion in equation (3), which means that the mean concentration of the liquid phase, $C$, is continuous. Boundary condition (10) may therefore be simplified to

$$C_m \phi v_n = [-D_n \nabla C]_m^n.$$

It is also possible to suppose $\delta \sim l_D$ and consider the limit where $D/\kappa \to 0$, but more slowly than $\delta \to 0$. In this case, the term representing diffusion of solute is removed from equation (3), meaning that we can no longer impose continuity of $C$. An analogous situation occurs in fluid mechanics if the viscosity of a fluid tends to zero. In this case it is no longer possible to enforce continuity of the velocity field, and it is therefore possible to obtain shear layers.

The three boundary conditions (8) – (10) come from the conservation of mass, heat and solute, equations (1) – (3). However, these must be supplemented due to the presence of the additional dependent variable $\phi$. Early work imposed $\phi = 0$ at the interface and required $\phi$ to be continuous, but for certain parameter regimes the problem is then mathematically ill-posed. There is also no good physical justification for this condition; again, it is not possible to interrogate the system on length scales which are smaller than $\delta$, which implies that a jump in $\phi$ is allowed.

Instead, we return to our earlier descriptions of a solid–liquid interface. In this case, we saw that there was the possibility of forming a region of constitutional supercooling, and this drove the morphological instability at the interface and thus the formation of the mushy layer. The criterion for formation of such a region of constitutional supercooling was

$$\frac{\partial T}{\partial n} < \frac{\partial T_L}{\partial n},$$

and as the mushy layer thickens, this inequality tends to an equality. We therefore make the assumption that the mushy layer grows just quickly enough that any residual supercooling in the liquid ahead of it is eliminated, which allows us to write the final boundary condition (assuming the interface is solidifying),

$$\frac{\partial T}{\partial n} = \frac{\partial T_L}{\partial n}.$$ 

The final boundary condition consists of a specified temperature at the solid–mushy layer interface. We now have a complete set of equations (1) – (5) with boundary conditions (8), (9), (10) and (13). This system has solutions for all parameter values.

4 ‘Ideal’ mushy layers

The aim of this section is to simplify the governing equations for the evolution of a mushy layer while retaining all the necessary interactions. To do this, we make the following
Figure 2: The trajectory of $T$ and $C$ in the phase diagram for a mushy layer (solid curve) compared with that when there is a planar solid liquid interface (dashed curve). The liquidus temperature $T_L(C)$ is given by $T = T_m - mC$ for some positive constant $m$. The temperature in the mushy layer follows the liquidus curve and thus there is no possibility of constitutional supercooling. Note that in this case the temperature field in the liquid region emerges at a tangent to the liquidus. In contrast, the temperature field in the solid–liquid system has a portion lying below the liquidus and thus constitutional supercooling is possible.

assumptions. Firstly, we assume that the densities of the solid and liquid phases are equal, i.e. $\rho_s = \rho_l$. Thus we have that $r = 1$, and conservation of mass, equation (1), gives that the velocity is solenoidal.

We next assume that $D \ll \kappa$, which allows us to eliminate the second derivative term in the conservation of solute equation. Although this may appear to be a singular perturbation, it is justified because we have a relationship between $T$ and $C$ in the mushy layer (equation (4)), and we retain the second derivative in the conservation of heat equation (2). Finally, we make the assumptions that properties are independent of phase and that the system is above the eutectic temperature.

Using these assumptions, the governing equations (1) – (5) become

$$\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T = \kappa \nabla^2 T + \frac{L}{c_p} \frac{\partial \phi}{\partial t},$$

(14)

$$(1 - \phi) \frac{\partial C}{\partial t} + \mathbf{u} \cdot \nabla C = C \frac{\partial \phi}{\partial t},$$

(15)

$$T = T_L(C),$$

(16)

$$\mu \mathbf{u} = \Pi_0 (\nabla p + \rho g),$$

(17)

$$\nabla \cdot \mathbf{u} = 0.$$  

(18)

Here we assume that $\kappa$ is constant in the ideal mushy layer and also that $\rho$ is constant; later we will consider $\rho = \rho(T, C)$.  

59
\[
\begin{align*}
T_\infty & \\
\text{Liquid layer} & \quad \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2} \\
\text{Mushy layer} & \quad c_p \text{eff} \frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2} \\
& \quad z = h \\
& \quad z = 0
\end{align*}
\]

Figure 3: Growth of a mushy layer from a cooled boundary at \( z = 0 \). The mush–liquid interface is at \( z = h(t) \) and the position of the cooled boundary is at \( z = 0 \).

The above assumptions can also be used to simplify the boundary conditions: during solidification, equations (8), (9) and (10) become

\[
[u \cdot n] = 0, \quad (19)
\]
\[
[\phi]^l_m = 0, \quad (20)
\]
\[
[n \cdot \nabla T]^l_m = 0. \quad (21)
\]

In this case there is no solid layer: only the mushy layer and the liquid region above it.

5 The case of no flow

When there is no pressure gradient in the mushy layer and convection is not possible because there is a stable density field, the Darcy velocity is zero. In this case there is no flow in the system and the advective part of the transport equations (14)–(18) can be eliminated to obtain

\[
\begin{align*}
\frac{\partial T}{\partial t} &= \kappa \nabla^2 T + \frac{L}{c_p} \frac{\partial \phi}{\partial t}, \\
(1 - \phi) \frac{\partial C}{\partial t} &= C \frac{\partial \phi}{\partial t}, \\
T &= T_L(C).
\end{align*}
\]

The second of these equations can be rearranged and integrated as follows

\[
\frac{\partial}{\partial t} [C (1 - \phi)] \Rightarrow (1 - \phi) C = \tilde{C} \text{(x)},
\]

implying that the total amount of species \( C \) is constant in time but variable in space according to the function \( \tilde{C} \text{(x)} \). If initially this function is constant in the liquid (\( \tilde{C} \text{(x)} = C_0 \)) then equation (25) reduces to

\[
\phi = 1 - \frac{C_0}{C},
\]

[60]
Figure 4: The plot on the left shows the normalized interface position for the solid-liquid interface, $\lambda_a$, and the mush-liquid interface, $\lambda_b$, as a function of $T_L(C_0) - T_B$ for experiments (crosses) and numerics (solid line). The plot on the right shows the solid fraction as a function of height for numerics (dashed line) and experiments (circles) corresponding to $r = 0.74$.

which effectively constrains the amount of solid by the deviation in concentration from its initial value. This equation can be differentiated with respect to time to obtain

$$ \frac{\partial \phi}{\partial t} = \frac{C_0}{C_L(T)^2} \frac{\partial C_L(T)}{\partial t} = \frac{C_0}{C_L^2} \frac{\partial T}{\partial t} \frac{\partial T}{\partial t}, $$

in which we assume that the concentration follows the liquidus line as a function of temperature. This new relationship for the void fraction provides closure to the temperature equation (22), which now becomes

$$ \frac{\partial T}{\partial t} = \frac{1}{C_L} \frac{\partial}{\partial z} \left[ C_L \frac{\partial T}{\partial z} \right] = \kappa \nabla^2 T - c_{\text{p,eff}} \frac{\partial T}{\partial t} = \kappa \nabla^2 T, $$

where $c_{\text{p,eff}}$ is the non-dimensional effective specific heat. This is a nonlinear diffusion equation for $T$ in which the effective heat capacity is enhanced by the internal release of latent heat.

In summary we have the setup shown in figure 3 with the following governing equations

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

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

for the temperature evolution in the liquid and mushy layers respectively. In the far field liquid we use the constant boundary condition $T(t, \infty) = T_\infty$ and at the base of the mushy layer we use $T(t, 0) = T_B$. As described previously we have the following interface conditions

$$ T = T_L(C_0), \quad \left[ \frac{\partial T}{\partial z} \right]_L^M = 0, \quad \left[ T \right]_M^L = 0, $$
<table>
<thead>
<tr>
<th>$C_\infty &lt; C_E$</th>
<th>Cooled from below</th>
<th>Cooled from above</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy fluid released</td>
<td>stable Temperature</td>
<td>unstable Temperature</td>
</tr>
<tr>
<td>No compositional effects</td>
<td>Mushy Layer</td>
<td>Thermal and</td>
</tr>
<tr>
<td></td>
<td>no convection</td>
<td>compositional convection</td>
</tr>
<tr>
<td>$C_\infty &gt; C_E$</td>
<td>5. Compositional convection</td>
<td>4. Mushy layer</td>
</tr>
<tr>
<td>light fluid released</td>
<td>in liquid and</td>
<td>thermal convection</td>
</tr>
<tr>
<td></td>
<td>mushy layer</td>
<td>in the liquid</td>
</tr>
</tbody>
</table>

Table 1: Organization of the different convective regimes as explained thoroughly in the text. In all cases we assume that the density of the fluid increases with the concentration, $C$ and increases with a decrease in the temperature, $T$. Here $C_E$ is the eutectic concentration and $C_\infty$ is the concentration far from the phase boundary.

In general these equations have a similarity solution with the similarity variable $\eta = z/2\sqrt{\kappa t}$ and interface position $h = 2\lambda\sqrt{\kappa t}$. Figure 4 shows the numerical solutions and experimental results for the normalized interface position $\lambda$ as a function of $T_L(C_0) - T_B$ and the solid fraction as a function of height scaled with the moving interface.

## 6 Solidification and convection

During the solidification of a binary melt there are some interesting physical features, such as the formation of mushy layers and the onset of convection, that depend on the properties of the released fluid and the solidification boundary. In table 6 we organize these features according to the location of the solidification boundary and the concentration, which increases with density, of the rejected fluid in comparison to the far field concentration, $C_\infty$. We now discuss each of these cases in turn.

1. In this case there is no excess solute produced by the solidifying front and the compositional density field remains uniform. Since the temperature is lowest at the bottom, and thus the density decreases with height the temperature field is stable as well. As a result convection will not occur and the growth rate will proceed as in the Stefan problem.

2. Here the concentration of the melt is less than that of the solid and in general a mushy layer will form. Since the rejected solute makes the fluid adjacent to the moving boundary denser the compositional density field is stable. In addition the thermal density field is stable, owing to the cold lower boundary, and convection will not occur.

3. Similar to case 1 except that now the temperature is higher at the top and therefore the density increases with height. The thermal density field is unstable and may lead
Figure 5: Schematic illustration of a solid growing into a binary melt, cooled from above. Since the density is larger at the top due to a lower temperature, there is thermal convection. Here $F$ is the flux of heat by thermal convection in the liquid.

to convection if the Rayleigh number is large enough.

4. In this case the residual melt adjacent to the phase boundary is lighter than the melt in the far field, resulting in a stable compositional density field. On the other hand, the thermal density field is unstable and thermal convection can occur. This convection will occur in the liquid only; the mush will remain stagnant.

5. In this case the thermal density field is stable, whereas the compositional density field is unstably stratified. Double-diffusive convection can occur in the liquid in the form of fingers but will not occur in the mushy layer as the temperature and concentration are constrained by the liquidus relationship and are therefore not independent. There may be convection in the mushy layer leading to the formation of dissolution channels.

6. Here the melt is cooled from above and heavy fluid is released from the phase boundary. The thermal and compositional density fields are both unstable and will act together to produce convection. In addition, convection will occur in the mushy layer, which may alter the micro-structure of this porous medium. This is the regime for the formation of sea ice.

Cases 3 and 4

For cases 3 and 4 of table 6 the convection generated in the liquid acts to transport heat from the bottom to the solidifying interface as illustrated in figure 5. The Rayleigh number for this situation was assumed to be large ($Ra \gg 1$) and therefore the interior of the liquid
is well mixed up to the thermal boundary layer. The Stefan condition will have the form

$$\rho_s L \dot{a} = -k \frac{\partial T}{\partial z} \bigg|_s - F,$$

where $F$ is the heat flux from the liquid to the solid. Naturally this heat flux will be a function of the temperature difference between the interface and far field liquid temperature and the strength of the fluid advection, given by

$$F = B \left( \frac{\rho c_p}{\nu} \right)^{\frac{1}{3}} [T - T_L(C_0)]^{\frac{4}{3}}.$$  \hspace{1cm} (33)

Here $B$ is an experimentally determined number, $\nu$ is the kinematic viscosity, $\alpha$ is the coefficient of thermal expansion and $g$ is the acceleration due to gravity. Since we must conserve energy, the liquid will cool down according to

$$\rho c_p (H - a) \frac{\partial T}{\partial t} = -F,$$  \hspace{1cm} (34)

due to the transfer of heat from the liquid to solid.

The position of the phase boundary as a function of time is shown in figure 6 with some distinct, quantitatively different regimes due to the onset and development of convection. We can make the quasi-stationary approximation

$$k \frac{T_L - T_B}{a} = \rho L \dot{a} + F.$$  \hspace{1cm} (35)

At early time, labeled 1 in figure 6, the solid thickness is small ($a \ll 1$), the growth rate is large ($\dot{a} \gg 1$) and the convective flux is negligible. The dominant balance is between the first and second terms in equation (35) and the solution proceeds as in the planar case with $a \propto \sqrt{t}$. Eventually buoyancy forces due to the unstable thermal gradient dominate viscous dissipation and convection ensues (region 2 in figure 6). At early times the advective transport of thermal energy from the bottom to the top is enough to balance the transfer of heat away into the solid and the growth rate slows. Later on, the liquid cools down, reducing the convective heat transfer in the liquid, according to equation (34) and the growth rate proceeds according to equation (35). At long time, indicated by region 3 in figure 6, the temperature of the liquid has cooled down sufficiently so that the convective heat transfer is much smaller than conduction in the solid. The dominant balance is again between the first and second terms in equation (35) and the solution proceeds as in the planar case with $a \propto \sqrt{t}$.

7 Student problem 6

Determine the position of the interface between the mushy layer and liquid for the constant solidification rate shown in figure 7. The governing equations and appropriate boundary conditions in the liquid region and the mushy layer respectively, are as follows

$$\frac{\partial T}{\partial t} = \kappa \frac{\partial^2 T}{\partial z^2}, \quad T(t, \infty) = T_\infty, \quad T(t, h) = T_L(C_0) \quad z > h,$$  \hspace{1cm} (36)

$$\frac{\partial T}{\partial t} = C(T) \kappa \frac{\partial^2 T}{\partial z^2}, \quad T(t, 0) = T_E, \quad T(t, h) = T_L(C_0) \quad 0 < z < h.$$  \hspace{1cm} (37)
Figure 6: Interface position of a solidifying binary melt as a function of time. There are
three distinct regimes, labeled 1, 2 and 3, which are distinguished by the relative strength
of convection occurring in the liquid region.

where \( C(T) = 1 - LC_L C_0/c_p C_L^2 \). Along the liquidus line we have the linear expression
\( C_L = C_0 + mT \), where \( m = (C_0 - C_E)/(T_L(C_0) - T_E) \) is the slope. In addition we have the
following interfacial condition

\[
\frac{\partial T}{\partial z} \bigg|_{\text{liquid}} = \frac{\partial T}{\partial z} \bigg|_{\text{mushy layer}}, \tag{38}
\]

at \( z = h \).

Answer

The non-dimensional version of the specific heat can be expressed as

\[
C(T) = 1 - \frac{S}{\xi} \left( 1 + \frac{1}{\xi} \frac{T}{T_L(C_0) - T_E} \right)^2, \tag{39}
\]

where \( S \) is the Stefan number and \( \xi = C_0/(C_0 - C_E) \) is a concentration ratio. In the limit
\( \xi \gg 1 \) and \( S \gg 1 \), while \( S/\xi = O(1) \) we obtain \( C(T) = 1 - S/\xi = \Omega \). Note that \( \Omega > 0 \).

For a constant growth rate \( V \) we can move the coordinate system by making a Galilean
transformation so that we are in a steady reference frame. Mathematically this is written
as, \( \tilde{x} = z - Vt \), so that \( \frac{\partial}{\partial t} = -V \frac{\partial}{\partial z} \). In addition it is convenient to non-dimensionalize the
equations using the following scales

\[
\theta = \frac{T - T_L}{T_E - T_L}, \quad \hat{z} = z \frac{\kappa}{V}, \tag{40}
\]

so that equations (36)–(37) become

\[
\theta'' + \theta' = 0, \quad \theta(\infty) = \theta_\infty, \quad \theta(\hat{h}) = 0 \quad z > h, \tag{41}
\]

\[
\theta'' + \Omega \theta' = 0, \quad \theta(0) = -1, \quad \theta(\hat{h}) = 0 \quad 0 < z < h. \tag{42}
\]
Figure 7: Setup for the student problem, showing the growth of a mushy layer into a liquid from a cooled boundary at \( z = 0 \). The apparatus is being pulled at a constant velocity through heat exchangers such that we are in a steady frame of reference.

The solutions of these equations are

\[
\theta = \theta_\infty - \theta_\infty e^{\hat{h} - \hat{z}} \quad z > h, \quad (43)
\]

\[
\theta = \frac{1}{1 - e^\Omega \hat{h}} \left[ e^{\Omega (\hat{h} - \hat{z})} - 1 \right] \quad 0 < z < h. \quad (44)
\]

The position of the interface is calculated by using the flux condition (38) \( \theta'|_{\text{liquid}} = \theta'|_{\text{mushy layer}} \) to obtain

\[
\hat{h} = \frac{1}{\Omega} \ln \left[ 1 + \frac{\Omega}{\theta_\infty} \right]. \quad (45)
\]