CHAPTER 5

ANALYTICAL SOLUTIONS FOR SOLIDIFICATION

5.1 INTRODUCTION

This chapter describes how the governing equations developed in Chap. 4 and the thermodynamic principles introduced in Chaps. 2 and 3 are applied to model the solidification process. For the time being, we consider only problems that have analytical solutions, reserving the discussion concerning computational approaches to a subsequent chapter. These problems provide valuable insight into the behavior of solidifying systems, as well as into the roles of various parameters. In particular, the analytical solutions demonstrate how the solidification front moves over time, and how solute boundary layers build up ahead of the interface.

For example, we will find that the thickness of a solidified layer growing from a fixed-temperature wall increases in proportion to $\sqrt{t}$ and that consequently the characteristic growth velocity of the interface $v^*$ is proportional to $1/\sqrt{t}$. In alloys, there is a solute boundary layer in the liquid ahead of the interface with a thickness of order $D_\ell/v^*$, where $D_\ell$ is the diffusion coefficient. These characteristics will be very important later on when we consider the development of microstructure. Our study begins with solidification of a superheated melt from a cold wall. Subsequently, we consider solidification in an undercooled melt, developing solutions for planar, paraboloidal and spherical front growth.

5.2 SOLIDIFICATION IN A SUPERHEATED MELT

5.2.1 Pure materials

Consider the one-dimensional solidification of a pure material in a mold, as depicted in Fig. 5.1. The initial condition is a pure liquid at uniform temperature $T_\infty$ greater than the melting point $T_f$, and filling the semi-infinite domain $x \geq 0$. A semi-infinite mold, initially at uniform temperature
Fig. 5.1 A schematic drawing of the temperature distribution in the mold, solid and liquid at a certain time after solidification begins.

$T_0 < T_f$, occupies the domain $x < 0$. Solidification begins at time $t = 0$ by conduction of heat into the mold. At some point in time, the temperature distributions in the mold, solid and liquid will correspond to the schematic depicted in Fig. 5.1. The position of the solid-liquid interface is designated $x^*(t)$, and part of the problem will be to find an analytical expression for $x^*$. We have assumed perfect contact between the solid and the mold, and the interface temperature $T_{ms}$ is thus identical in both materials. (This assumption is necessary in order to obtain an analytical solution for the movement of the interface.)

The goal in this section is to compute the temperature distributions in all regions at all times, as well as the movement of the solid-liquid interface. To accomplish this task, we will solve the equation for heat conduction in each material, subject to appropriate boundary conditions. Assume that all material properties are constant, that there is no liquid flow ($v_t = 0$), which also implies that there is no viscous dissipation, and that there is no internal heat generation. The energy balance (Eq. (4.127)) for each material takes the reduced form

$$\frac{\partial T_\nu}{\partial t} = \alpha_\nu \frac{\partial^2 T_\nu}{\partial x^2}$$

(5.1)

where $\nu = m, s, l$ refers to the mold, solid or liquid, respectively, and $\alpha_\nu = k_\nu/\rho_\nu c_\nu$ is the thermal diffusivity of the material or phase $\nu$. The thermal diffusivities of the solid and liquid are normally within approximately 10% of each other. However, $\alpha_m$ may be much smaller than $\alpha_s$ and $\alpha_l$, for example when casting metals in sand molds. In other cases, $\alpha_m$ may be much larger than $\alpha_s$ and $\alpha_l$, such as for polymers freezing in metal molds. We will first solve the problem in its general form, and consider these special cases afterward. Since we intend to keep all the terms without making any judgments regarding their magnitude, there is no particular advantage to be gained from scaling the equations in the general form. Accordingly, the solution is presented in dimensional form. Nevertheless, the solution is naturally expressed in terms of dimensionless groups, which will appear in due course.
Key Concept 5.1: Analytical solutions

In this chapter, we will find analytical solutions to solidification problems by solving Eq. (5.1) in the mold, solid and liquid. The solid and mold temperature solutions will be coupled by matching the temperature and heat fluxes at their boundary. At the solid-liquid interface, the temperature in both phases will be set equal to the equilibrium freezing temperature $T_f$, and the heat fluxes will be coupled to the motion of the interface, using Eq. (4.133).

The governing equation, boundary and initial conditions for the mold domain are

$$\frac{\partial T_m}{\partial t} = \alpha_m \frac{\partial^2 T_m}{\partial x^2} \quad -\infty < x \leq 0 \quad (5.2)$$

$$T_m = T_0 \quad x \to -\infty \quad (5.3)$$

$$T_m = T_{ms} \quad x = 0 \quad (5.4)$$

$$k_m \frac{\partial T_m}{\partial x} = k_s \frac{\partial T_s}{\partial x} \quad x = 0 \quad (5.5)$$

$$T_m = T_0 \quad t = 0 \quad (5.6)$$

Note that there are two boundary conditions at $x = 0$ as a result of the mold-solid interface temperature $T_{ms}$ not actually being known at this point. The heat flux must be continuous across the interface, as stated in Eq. (5.5). The governing equations for the solid are

$$\frac{\partial T_s}{\partial t} = \alpha_s \frac{\partial^2 T_s}{\partial x^2} \quad 0 \leq x \leq x^*(t) \quad (5.7)$$

$$T_s = T_{ms} \quad x = 0 \quad (5.8)$$

$$k_m \frac{\partial T_m}{\partial x} = k_s \frac{\partial T_s}{\partial x} \quad x = 0 \quad (5.9)$$

$$T_s = T_f \quad x = x^*(t) \quad (5.10)$$

$$\rho_s L_f \frac{dx^*}{dt} = k_s \frac{\partial T_s}{\partial x} - k_l \frac{\partial T_l}{\partial x} \quad x = x^*(t) \quad (5.11)$$

There is no initial condition for the solid, because the solidifying material is initially entirely liquid. Two boundary conditions are required at the solid-liquid interface because, although the temperature $T_f$ is known, the position of the interface $x^*(t)$ is not. The second boundary condition, Eq. (5.11), is called the Stefan condition, first introduced as Eq. (4.133).
Finally, for the liquid, we have
\[ \frac{\partial T_l}{\partial t} = \alpha_l \frac{\partial^2 T_l}{\partial x^2} \quad x^* \leq x < \infty \quad (5.12) \]
\[ T_l = T_\infty \quad x \to \infty \quad (5.13) \]
\[ T_l = T_f \quad x = x^*(t) \quad (5.14) \]
\[ \rho_s L_f \frac{dx^*}{dt} = k_s \frac{\partial T_s}{\partial x} - k_l \frac{\partial T_l}{\partial x} \quad x = x^*(t) \quad (5.15) \]
\[ T_l = T_\infty \quad t = 0 \quad (5.16) \]

We have repeated the Stefan condition for the sake of clarity, because it applies to both the liquid and the solid.

Equation (5.1) admits the possibility of a similarity solution, where the partial differential equation reduces to an ordinary differential equation in terms of a new variable that combines both \( x \) and \( t \). One can show by substitution into Eq. (5.1) that the following expression is a solution to the equation:
\[ T_\nu(x, t) = A_\nu + B_\nu \text{erf} \left( \frac{x}{2\sqrt{\alpha_\nu t}} \right) \quad (5.17) \]
where the error function \( \text{erf} (u) \) is defined as
\[ \text{erf} (u) = \frac{2}{\sqrt{\pi}} \int_0^u e^{-r^2} dr; \quad \frac{\partial (\text{erf} (u))}{\partial x} = \frac{2}{\sqrt{\pi}} e^{-u^2} \frac{\partial u}{\partial x} \quad (5.18) \]

Note that \( \text{erf} (0) = 0 \) and \( \text{erf} (\pm \infty) = \pm 1 \). We will also occasionally use the complementary error function, \( \text{erfc} (u) = 1 - \text{erf} (u) \). If coefficients \( A_\nu \) and \( B_\nu \) can be determined such that all of the boundary and initial conditions are satisfied, then Eq. (5.17) is a valid solution to the problem at hand. Such is the case for all three media (mold, solid and liquid) in this problem.

It is easy to demonstrate that the solution for the mold temperature that satisfies the boundary and initial conditions is
\[ T_m(x, t) = T_{ms} + (T_{ms} - T_0) \text{erf} \left( \frac{x}{2\sqrt{\alpha_m t}} \right) \quad -\infty < x \leq 0 \quad (5.19) \]
Recall that, at this point, \( T_{ms} \) is still unknown. Proceeding in a similar fashion to construct the solution for the temperature in the solid, substitution of the boundary conditions at \( x = 0 \) and \( x = x^*(t) \) into Eq. (5.17) yields
\[ T_f = T_{ms} + B_s \text{erf} \left( \frac{x^*(t)}{2\sqrt{\alpha_s t}} \right) \quad (5.20) \]
This equation leads to the following very important key concept.
Key Concept 5.2: Square root of time behavior

In media of infinite or semi-infinite extent, a similarity solution in terms of the error function satisfies the heat conduction equation. Since the left hand side of Eq. (5.20) is constant and $T_{ms}$ has been assumed to be constant also, then $x^*(t)$ must be proportional to $\sqrt{t}$ for a solution to exist, i.e.,

$$x^*(t) = 2\phi\sqrt{\alpha_s}t$$  \hspace{1cm} (5.21)

Here, $\phi$ is an as yet unknown constant. Note that the interface speed is given by

$$dx^*/dt = \frac{\phi\sqrt{\alpha_s}}{\sqrt{t}}$$  \hspace{1cm} (5.22)

The infinite speed at time zero arises from the discontinuity of the boundary and initial conditions, and is obviously not physical.

We can now determine $B_s$ in terms of $\phi$, with the result

$$T_s(x,t) = T_{ms} + \frac{T_f - T_{ms}}{\text{erf}(\phi)}\text{erf}\left(\frac{x}{2\sqrt{\alpha_s}t}\right) \quad 0 \leq x \leq x^*(t)$$  \hspace{1cm} (5.23)

By equating the heat fluxes in the solid and the mold at $x = 0$, Eq. (5.23) can be solved for $T_{ms}$

$$T_{ms} = \frac{T_0\sqrt{k_m\rho_m c_{pm}}\text{erf}(\phi) + T_f\sqrt{k_s\rho_s c_{ps}}}{\sqrt{k_m\rho_m c_{pm}}\text{erf}(\phi) + \sqrt{k_s\rho_s c_{ps}}}$$  \hspace{1cm} (5.24)

The product $\sqrt{k_\nu\rho_\nu c_{\nu\nu}}$ is called the effusivity of material $\nu$. Note that $T_{ms}$ is indeed constant, which is consistent with the assumptions made at the start of the problem. The constant $\phi$ is still unknown, and will be determined next.

The solution for the temperature in the liquid is determined after substituting Eq. (5.21) into Eq. (5.15) for the interface position $x^*(t)$, and then using the boundary and initial conditions to obtain

$$T_\ell = T_\infty - \frac{T_\infty - T_f}{\text{erfc}\left(\frac{x}{2\sqrt{\alpha_\ell}t}\right)}\text{erfc}\left(\frac{x}{2\sqrt{\alpha_s}t}\right) \quad x^*(t) < x < \infty$$  \hspace{1cm} (5.25)

Next, the substitution of the expressions for $T_s$ from Eq. (5.23) and $T_\ell$ from Eq. (5.25) into the Stefan condition, Eq. (5.11), produces the following transcendental equation for $\phi$

$$\left\{ \begin{aligned} 
&\phi \exp(\phi^2) - \frac{c_{ps}(T_\infty - T_f)}{L_f\sqrt{\pi}} \exp\left(\frac{[1 - \alpha_s/\alpha_\ell]\phi^2}{2}\right) \frac{k_\ell\rho_\ell c_{pl}}{k_s\rho_s c_{ps}} \times \\
&\text{erf}(\phi) + \sqrt{\frac{k_s\rho_s c_{ps}}{k_m\rho_m c_{pm}}} = \frac{c_{ps}(T_f - T_0)}{L_f\sqrt{\pi}} = \text{Ste} 
\end{aligned} \right.$$

\hspace{1cm} (5.26)
Analytical solutions for solidification

where we have identified the Stefan number, \( \text{Ste} = \frac{c_p s(T_f - T_0)}{L_f} \). Although this expression appears rather complicated, everything in Eq. (5.26) is known except \( \phi \). The left hand side of Eq. (5.26) is a monotonic function of \( \phi \), thus the solution is easily found, for example, by graphical methods. (See Example 5.1 below.)

**Key Concept 5.3: Solidification in infinite media**

Taken together, Eqs. (5.19) and (5.21-5.26) constitute the solution for the temperature and interface position for solidification in infinite media. Notice that the solution has developed naturally in terms of dimensionless groups: the Stefan number, and the ratios of the effusivities and thermal diffusivities.

**Example 5.1: Solidification of aluminum in a graphite mold**

Consider the solidification of pure aluminum in a graphite mold. The material properties for the mold, solid and liquid are tabulated below. The mold and liquid are assumed to be sufficiently thick for the assumption that the media are semi-infinite to be valid. The initial temperature for the liquid is 700°C, and the mold has an initial temperature of 25°C. The freezing point for Al is \( T_f = 660°C \).

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (kg m(^{-3}))</th>
<th>Specific heat (J kg(^{-1}) K(^{-1}))</th>
<th>Thermal conductivity (W m(^{-1}) K(^{-1}))</th>
<th>Heat of fusion (J kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>2200</td>
<td>1700</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>Aluminum (solid)</td>
<td>2555</td>
<td>1190</td>
<td>211</td>
<td>3.98 \times 10^5</td>
</tr>
<tr>
<td>Aluminum (liquid)</td>
<td>2368</td>
<td>1090</td>
<td>91</td>
<td>–</td>
</tr>
</tbody>
</table>

Begin by finding \( \phi \). Substituting the appropriate values for this example problem into Eq. (5.26) yields

\[
\left\{ \phi \exp \left( \phi^2 \right) - 0.041 \frac{\exp \left( -0.968\phi^2 \right)}{\text{erfc} \left( 1.403\phi \right)} \right\} \cdot \left\{ \text{erf} \left( \phi \right) + 1.304 \right\} = f(\phi) = 1.071
\]

The solution \( \phi = 0.522 \) can be obtained graphically with the aid of the plot of \( f(\phi) \) given below. Next, find the interface temperature \( T_{ms} = 474°C \) by substituting the problem parameters and newly found value for \( \phi \) into Eq. (5.24). Finally, when using these two values, the interface position and temperatures in the various materials at any
time are

\[ x^*(t) = 8.7 \times 10^{-3} \sqrt{t} \]

\[ T_m = 474 + 449 \text{erf} \left( 97.13 \frac{x}{\sqrt{t}} \right) \]

\[ T_s = 474 + 344.4 \text{erf} \left( 60.02 \frac{x}{\sqrt{t}} \right) \]

\[ T_{\ell} = 700 - 133.3 \text{erfc} \left( 84.17 \frac{x}{\sqrt{t}} \right) \]

with all lengths given in m, the time in s and the temperature in °C. The result is shown for \( t = 10 \) s in the figure below.

Notice that the slopes in the different materials do not match at the interfaces. This is due to the difference in conductivities between the mold and solid, and also to the liberation of latent heat at the solid-liquid interface. The temperature of the interface between the mold and the solid \( T_{ms} \) is also closer to the melting point of aluminum than to the initial temperature of the mold. This is mainly due to the fact that the effusivity of solid aluminum is large as compared to that of graphite.

Several dimensionless groups appear in the solution. There exist certain special cases of the general form that are useful to consider, corresponding to asymptotic values of these dimensionless groups. Often, metals are cast with low superheat, in which case we can take \( T_\infty \approx T_f \). One can partially compensate for the error in such an approximation by defining an effective latent heat \( L_{eff} \), given by

\[ L_{eff} = L_f + c_p \ell (T_\infty - T_f) \]  

(5.27)

The general problem just considered can thus be somewhat simplified. Equation (5.24) remains unchanged. However, the solution for the temperature in the liquid is just \( T_{\ell} = T_f \), and Eq. (5.26) also takes on a simpler