

Constitutional supercooling

Below is what you easily recognize as the directional growth equation:

$$C^L(z) = C_0^L + (C_i^L - C_0^L) \exp\left(-\frac{v}{D}z\right) \quad (1)$$

where z is a distance from the interface¹, D is the diffusion coefficient of the solute in the liquid phase, v is the interface velocity, C_0^L is an initial concentration of the solute in the melt prior to solidification, and C_i^L is the concentration of the solute in the liquid phase at the interface. Figure 1 a) gives you a fairly good idea about the shape of the dependence (1). Please realize that the situation shown in this figure corresponds to the case when $k_{\text{eff}} = 1$.

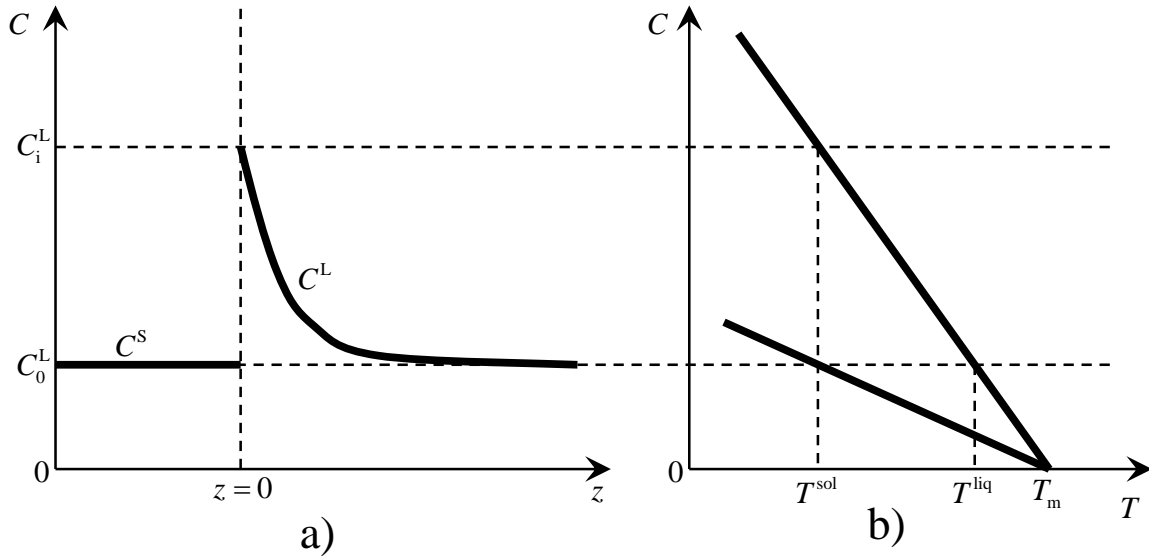


Figure 1

Figure 1 b) establishes a correspondence between C_0^L and C_i^L , on one hand, and between liquidus and solidus temperatures, on the other hand. It should be clear that temperature at the moving interface is to be associated with the solidus temperature, T^{sol} , corresponding to the given overall composition. When we move from the interface into the liquid phase, the concentration of solute is decreasing, which means that we are getting closer and closer to the

¹ the origin of the spatial axis is pinned to the S/L interface

component A. This, in turn, means that temperature is gradually increasing from T^{sol} to the liquidus temperature T^{liq} . This is clarified in Figure 2 (bold black lines).

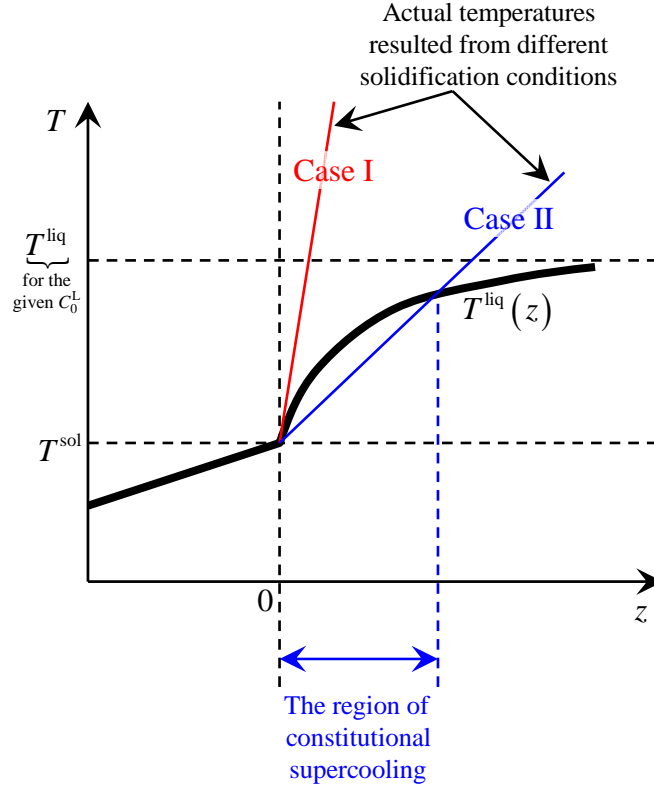


Figure 2

Imagine yourself sitting at the interface and looking straight into the liquid phase along the z axis. In the case of **Case I**, you see liquid, which temperature is always greater than the equilibrium liquidus temperature. It can be conjectured that the interface remains flat. In the second case, **Case II**, you see a certain region within which the actual temperature is less than the equilibrium liquidus temperature. This region is known as the region of constitutional supercooling. Within it, a morphological instability of the S/L interface can be expected, but not necessarily occur.

What is the fundamental difference between **Case I** and **Case II**?

$$\left(\frac{dT^{\text{liq}}}{dz} \right)_{z=0} < \underbrace{\left(\frac{dT}{dz} \right)_{z=0}}_{G^{\text{L}} - \text{temperature gradient in the liquid phase near the interface}}$$

$$\left(\frac{dT^{\text{liq}}}{dz} \right)_{z=0} > \underbrace{\left(\frac{dT}{dz} \right)_{z=0}}_{\substack{G^{\text{L}} - \text{temperature gradient} \\ \text{in the liquid phase near} \\ \text{the interface}}} \quad (2)$$

In order to make (2) more useful, let us employ a couple of tricks.

$$\left(\frac{dT^{\text{liq}}}{dz} \right)_{z=0} = \underbrace{\left(\frac{dT^{\text{liq}}}{dC^{\text{L}}} \right)_{z=0}}_{\text{liquidus slope}} \left(\frac{dC^{\text{L}}}{dz} \right)_{z=0} \quad (3)$$

It is trivial to calculate slope, because it is apparent from Figure 1 b) that:

$$\text{liquidus slope} = \frac{T^{\text{sol}} - T^{\text{liq}}}{C_i^{\text{L}} - C_0^{\text{L}}} = - \frac{T^{\text{liq}} - T^{\text{sol}}}{C_i^{\text{L}} - C_0^{\text{L}}} \quad (4)$$

It is equally easy to calculate $\left(dC^{\text{L}}/dz \right)_{z=0}$ in the RHS of (3), because (1) tells us what $C^{\text{L}}(z)$ is.

Differentiation gives:

$$\left(\frac{dC^{\text{L}}}{dz} \right)_{z=0} = (C_i^{\text{L}} - C_0^{\text{L}}) \left(-\frac{v}{D} \right) \exp\left(-\frac{v}{D} z \right) = -\frac{v}{D} (C_i^{\text{L}} - C_0^{\text{L}}) \quad (5)$$

By inserting (4) and (5) in (3) one gets:

$$\left(\frac{dT^{\text{liq}}}{dz} \right)_{z=0} = - \frac{T^{\text{liq}} - T^{\text{sol}}}{C_i^{\text{L}} - C_0^{\text{L}}} \left[-\frac{v}{D} (C_i^{\text{L}} - C_0^{\text{L}}) \right] = \frac{v(T^{\text{liq}} - T^{\text{sol}})}{D} \quad (6)$$

From (2) and (6) it is clear that the constitutional supercooling may occur if the following criterion is satisfied:

$$\frac{v(T^{\text{liq}} - T^{\text{sol}})}{D} > G^{\text{L}} \quad (7)$$

Usually, (7) is written as:

$$\frac{G^{\text{L}}}{v} < \frac{T^{\text{liq}} - T^{\text{sol}}}{D}$$