

Solidification of Single Phase Metals and Alloys (I)

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In this chapter we will be concerned with the effect of the different solidification variables (e.g. growth rate and temperature gradient in the liquid) on the structure and composition of the growing solid. In particular, when we consider single-phase alloys, the way in which the solute redistributed during solidification will be examined as will the effects of this redistribution on the micro and macro structure of the solidifying alloy. Before examining the solidification process it is essential to define clearly a terminology.

Terminology

- **Growth Rate (R):** is a measure of the rate of advance of the interface between the liquid and the solid.

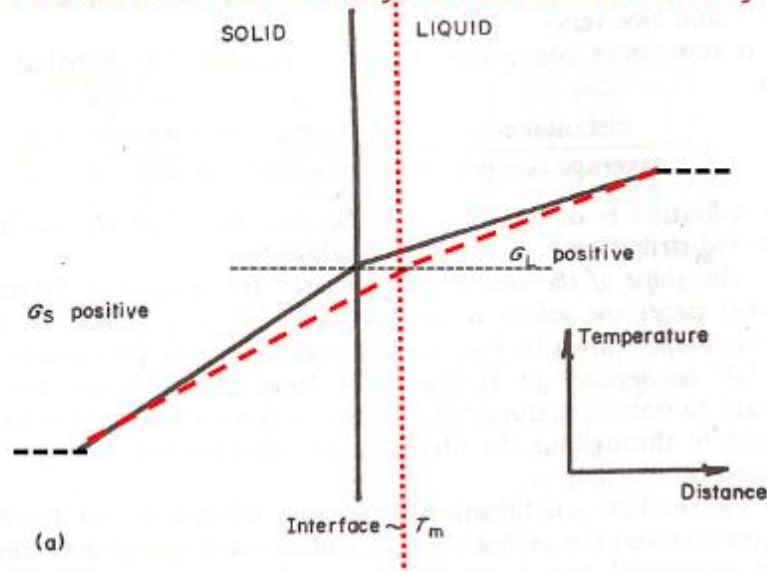
TYPICAL GROWTH RATES FOR DIFFERENT SOLIDIFICATION PROCESSES

<i>Process</i>	<i>Growth rate, cm sec⁻¹</i>
Growth of metal single crystals	10^{-3}
Directional growth studies in research	10^{-2}
Ingot solidification	10^{-2}
Initial dendritic growth ($\Delta T \sim 0.02 T_m$)	5
Initial dendritic growth ($\Delta T \sim 0.2 T_m$)	5 000

- **Temperature Gradient (G) (in the liquid)** is usually taken to refer to the gradient in the liquid away from the interface in the direction of growth. If the temperature increases as we go into the liquid, the temperature gradient is considered to be positive and vice versa. Commonly, temperature gradients vary from a few degrees centigrade per centimetre during the growth of single crystals, to tens of degrees centigrade per centimetre in castings and ingots, and to hundreds of degrees centigrade per centimetre during weld-pool solidification.

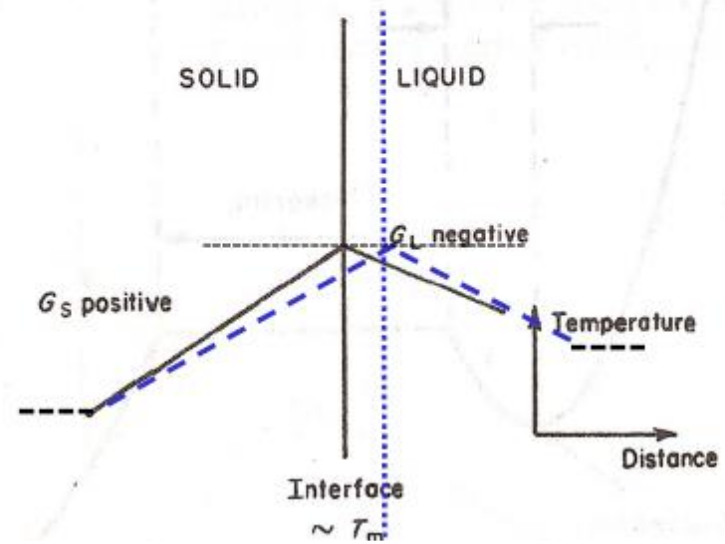
1) Superheated liquid

: Extraction of latent heat by conduction in the crystal



2) Supercooled liquid

: conduction of latent heat into the liquid



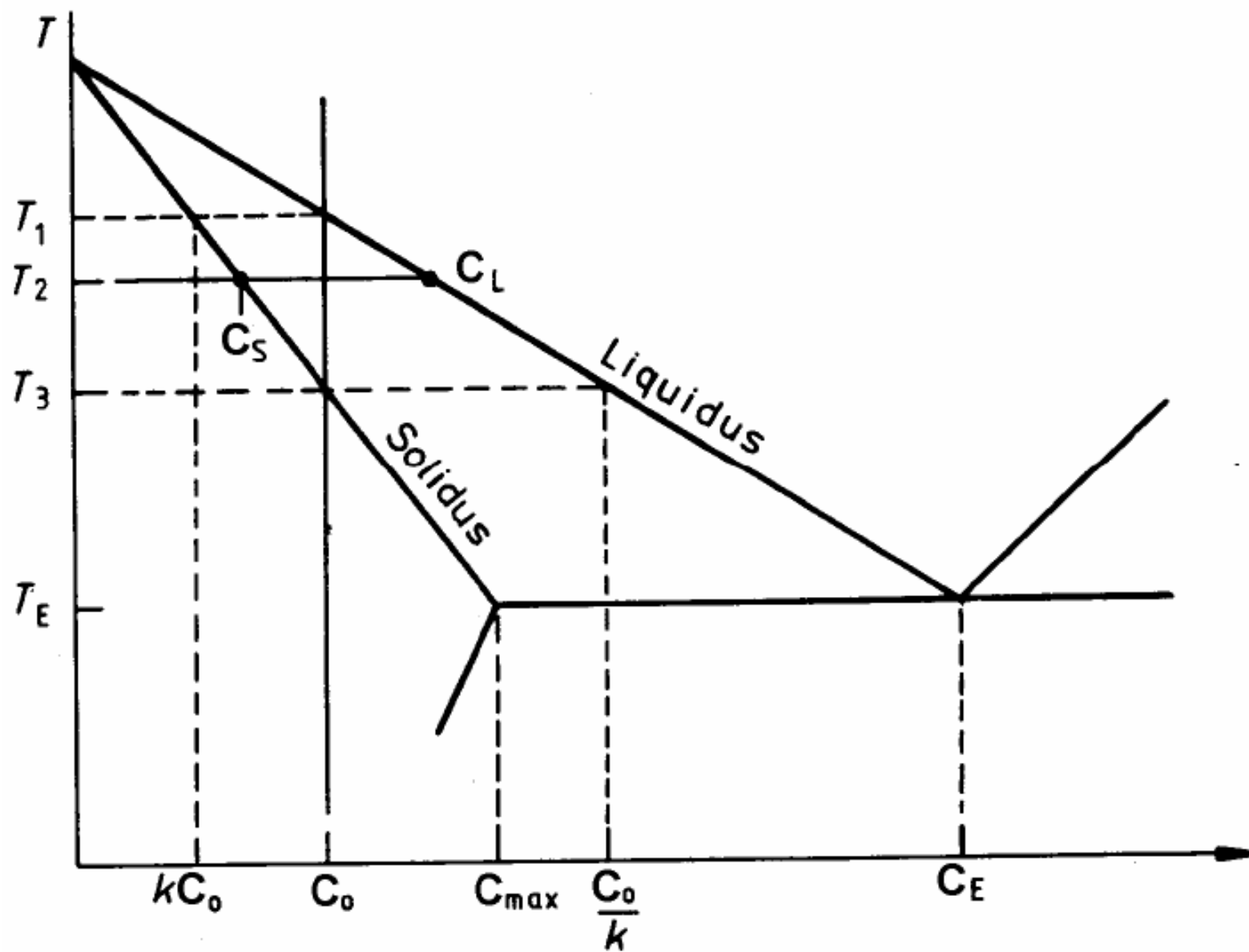
- **Diffusivity (Diffusion Coefficient, D):**

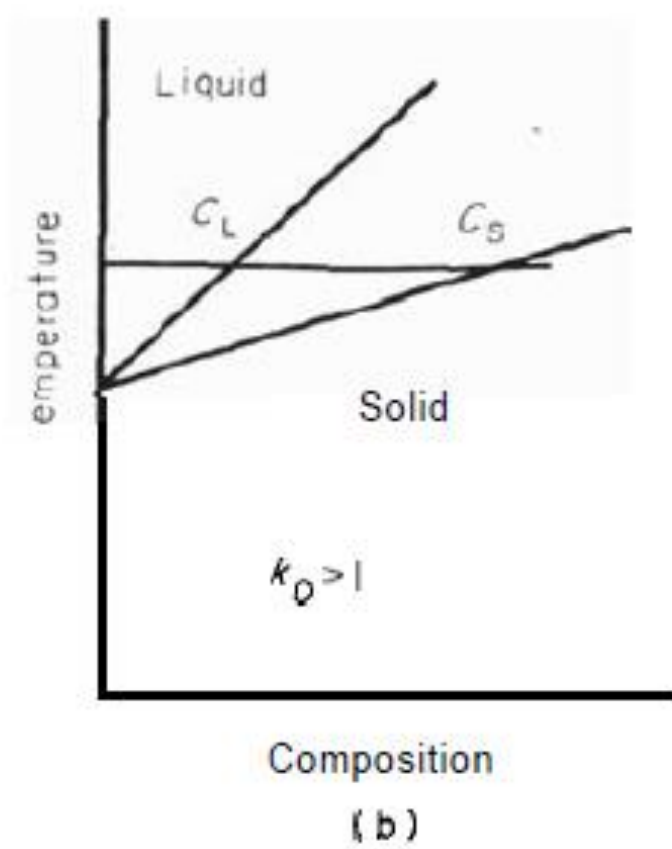
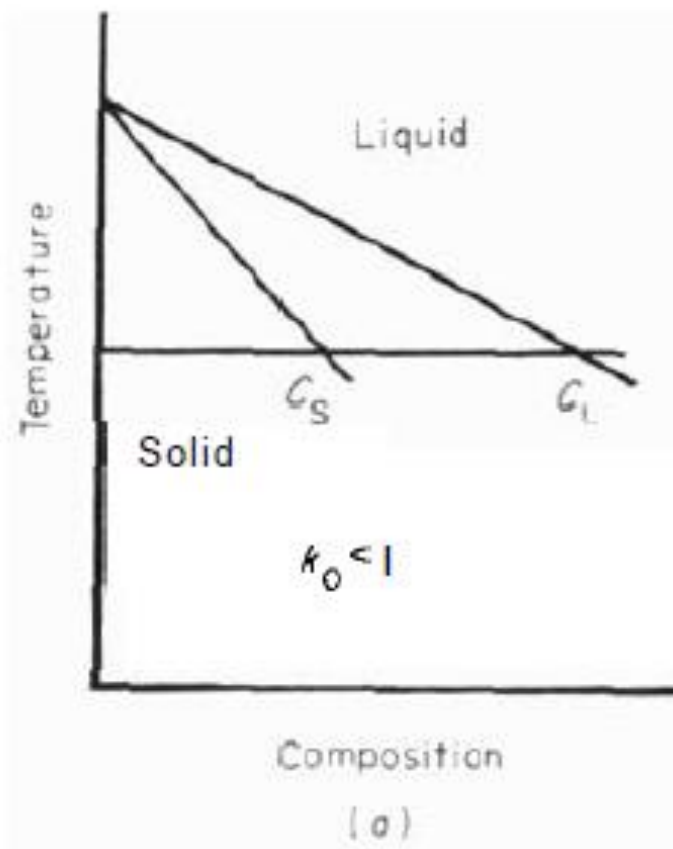
Determines the rate at which atoms can move in the liquid. For virtually all metallic liquids D is of the order of $5 \times 10^{-5} \text{ cm}^2/\text{sec}$. Diffusion rates in the solid are much smaller $\sim 10^{-8} \text{ cm}^2/\text{sec}$. for common metals just below their melting points. Thus solute redistribution in the solid is usually ignored in comparison to solute redistribution in the liquid.

- **The equilibrium distribution coefficient, k_0**

is defined by the phase diagram, assuming the liquidus and solidus lines to be straight. The equilibrium distribution coefficient is given by the ratio:

$$k_0 = \frac{\text{solute concentration in the solid at temperature } T}{\text{solute concentration in the liquid at the same temperature}}$$
$$= \frac{C_S}{C_L}$$





If the effect of the solute is to lower the liquidus temperature then $k_0 < 1$ and vice versa.

It is sometimes convenient to define an effective distribution, k_E as

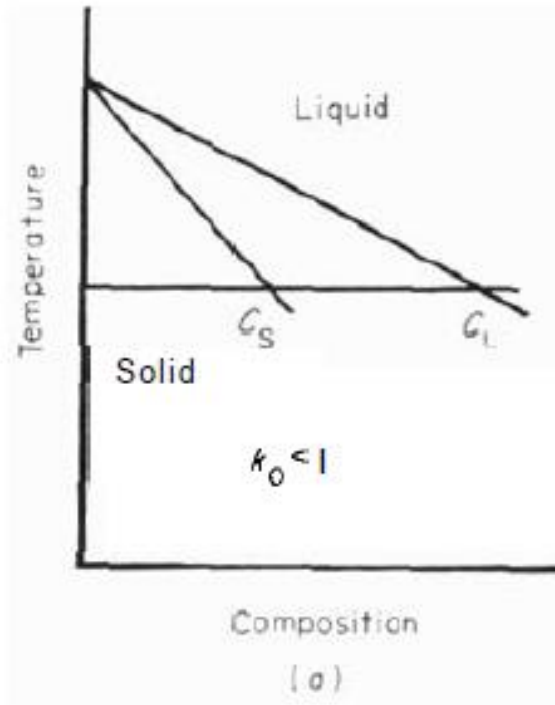
$$k_E = \frac{\text{instantaneous composition of solid formed}}{\text{average composition of the liquid at that time}}$$

Scheil Equation

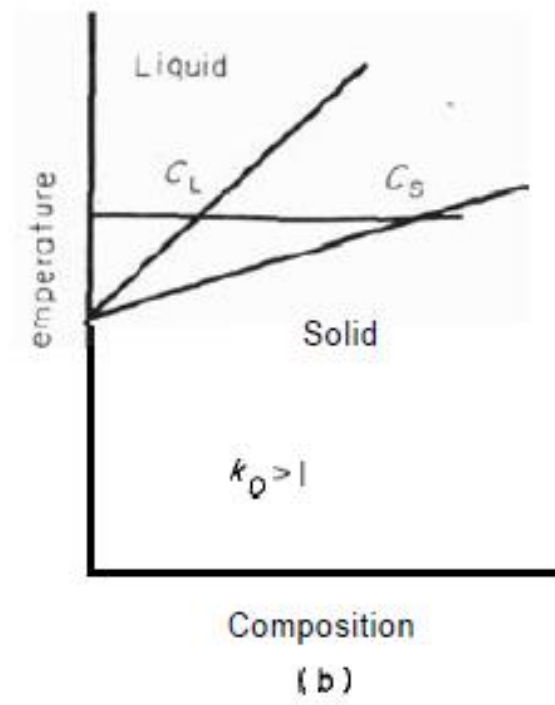
$$C_s = k_0 C_0 (1 - f_s)^{k_0 - 1}$$

f_s : fraction solidified

- Slope of the liquidus line (m)



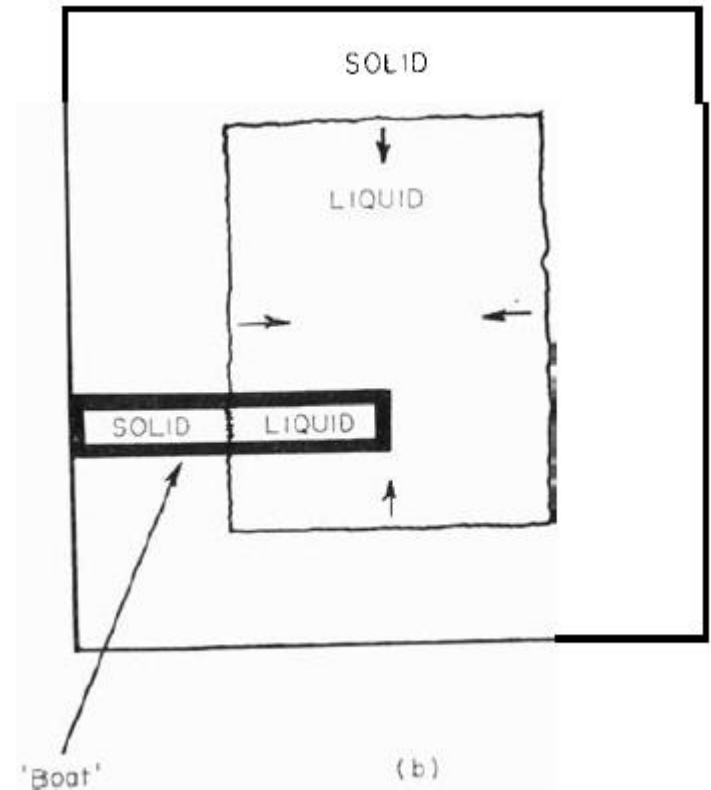
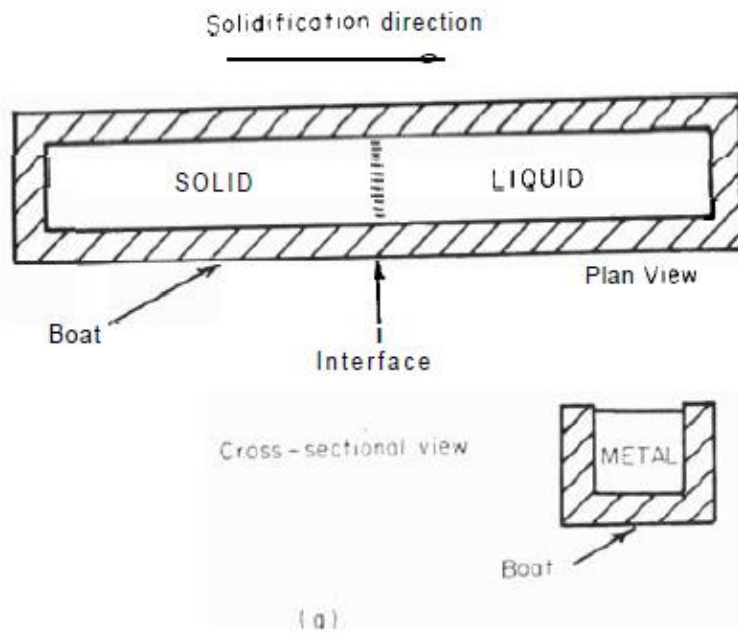
Positive (m)



Negative (m)

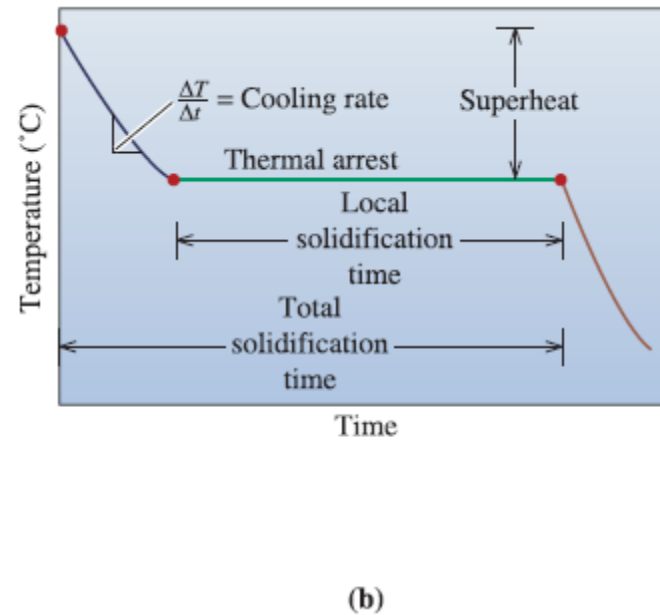
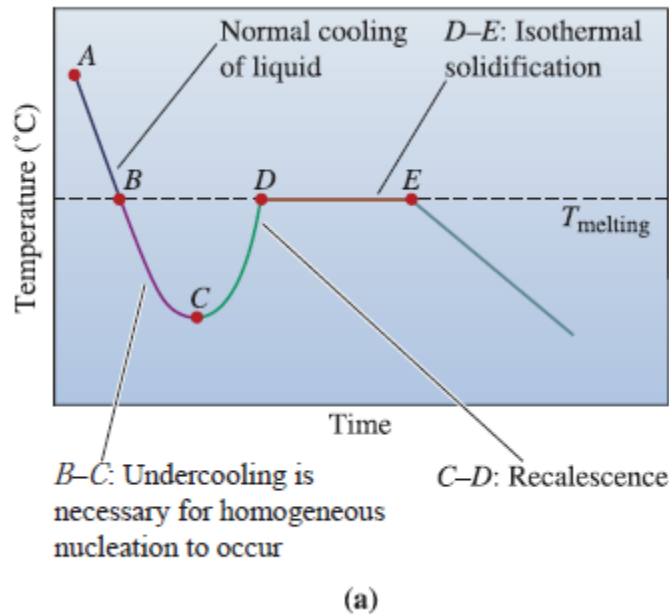
Although this is contrary to normal mathematical practice, this convention has been adhered to throughout the literature on solidification.

- **Unidirectional Solidification**



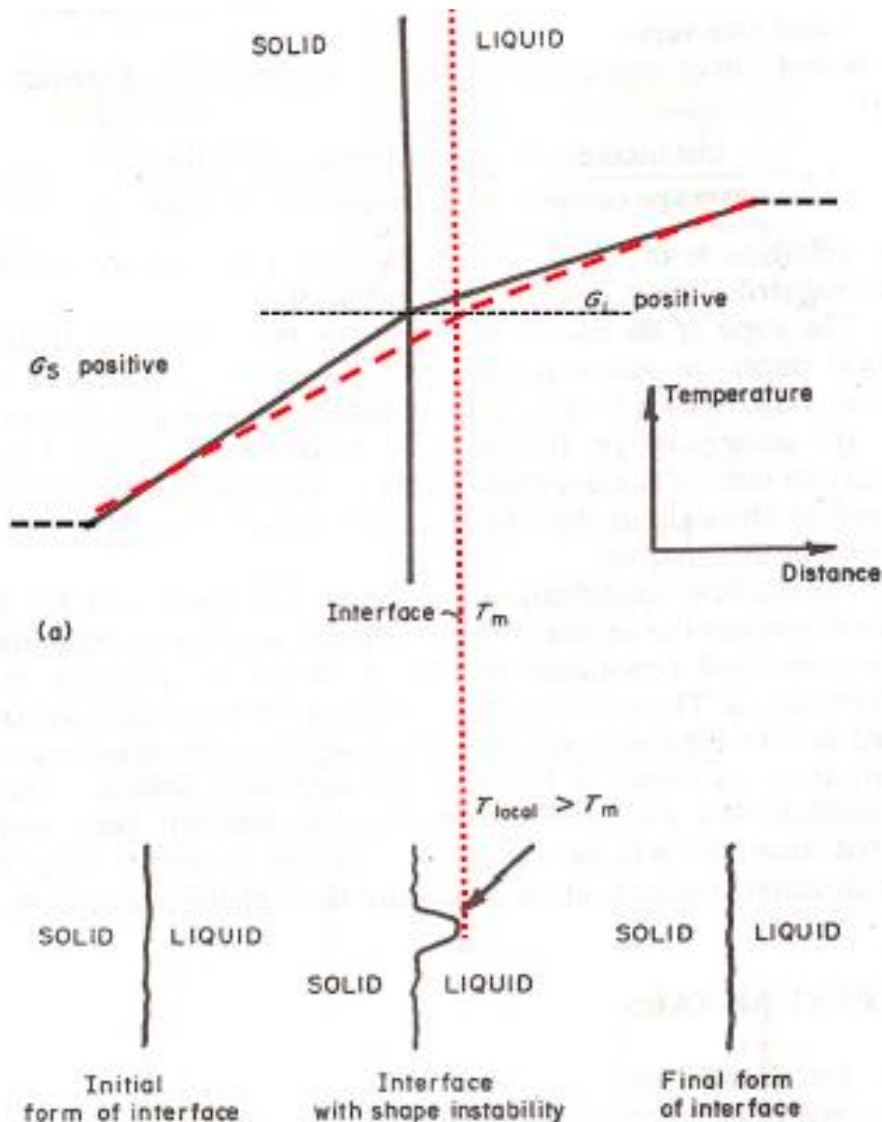
- (a) A casting boat (graphite) used for controlled directional solidification (schematic). The metal is shown as partially solidified.
- (b) Schematic view of the cross section of a partially solidified ingot showing how the casting boat can be considered as a section of the ingot.

- **Cooling curves**

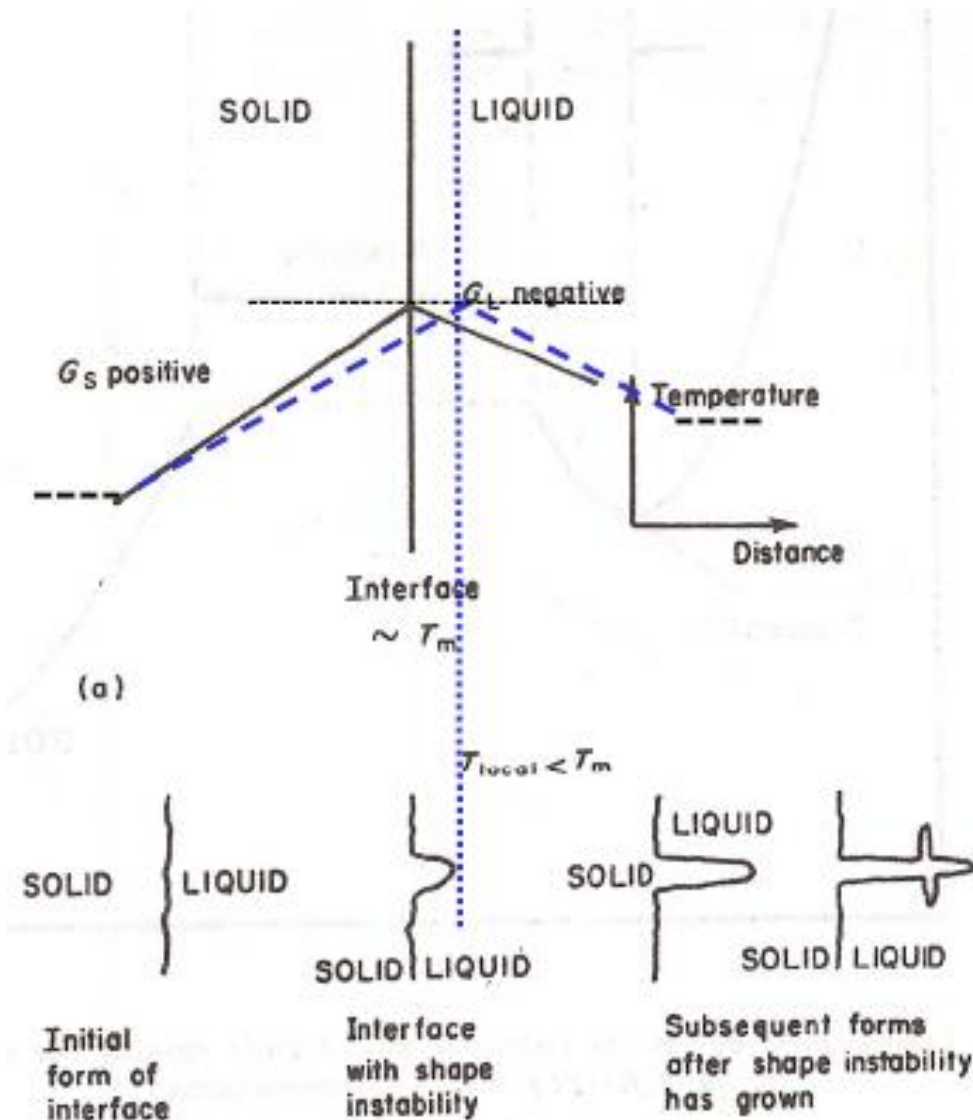


(a) Cooling curve for a pure metal that has not been well-inoculated. The liquid cools as specific heat is removed (between points A and B). Undercooling is thus necessary (between points B and C). As the nucleation begins (point C), latent heat of fusion is released causing an increase in the temperature of the liquid. This process is known as recalescence (point C to point D). The metal continues to solidify at a constant temperature (T_{melting}). At point E, solidification is complete. The solid casting continues to cool from this point. (b) Cooling curve for a well-inoculated, but otherwise pure, metal. No undercooling is needed. Recalescence is not observed. Solidification begins at the melting temperature.

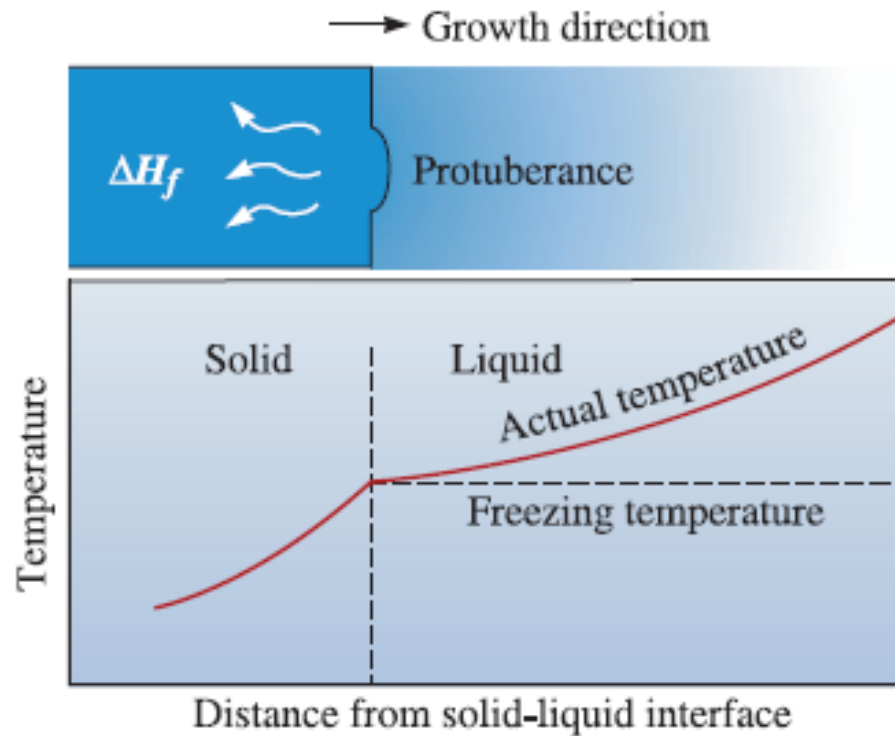
Pure metals: Interface forms (in macro scale)



(a) Area of solid and liquid adjacent to the interface showing positive temperature gradients in the liquid and solid (schematic). G_{solid} is steeper than G_{liquid} because of the higher thermal conductivity of the solid. (b) Schematic sequence showing the formation of an unstable protuberance which melts because the local tip temperature exceeds the melting temperature.

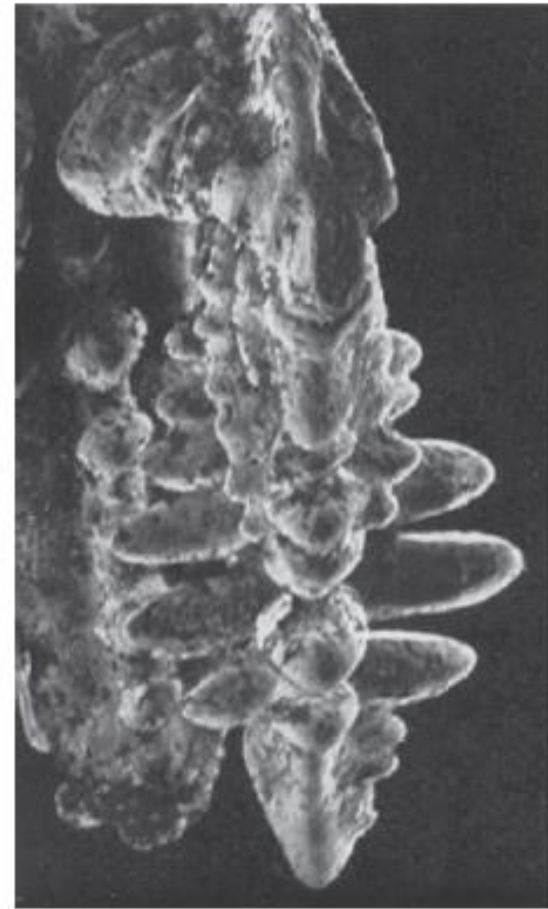
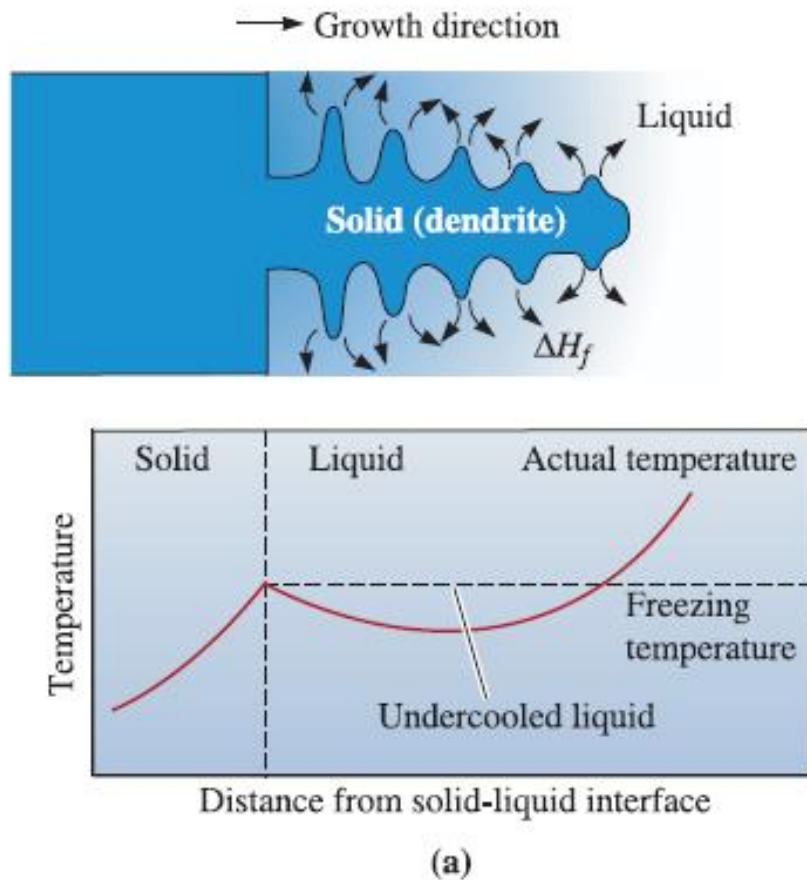


(a) Area of solid and liquid adjacent to the interface showing a negative temperature gradient in the liquid and a positive temperature gradient in the solid (schematic.) (b) Schematic sequence showing the formation and stabilisation of a protuberance on the interface when it projects into a region where the local tip temperature is below the melting temperature.



When the temperature of the liquid is above the freezing temperature, a protuberance on the solid-liquid interface will not grow, leading to maintenance of a planar interface. Latent heat is removed from the interface through the solid.

Planar Growth: When a well-inoculated liquid (i.e., a liquid containing nucleating agents) cools under equilibrium conditions, there is no need for undercooling since heterogeneous nucleation can occur. Therefore, the temperature of the liquid ahead of the solidification front (i.e., solid-liquid interface) is greater than the freezing temperature. The temperature of the solid is at or below the freezing temperature. During solidification, the latent heat of fusion is removed by conduction from the solid liquid interface. Any small protuberance that begins to grow on the interface is surrounded by liquid above the freezing temperature. The growth of the protuberance then stops until the remainder of the interface catches up. This growth mechanism, known as planar growth, occurs by the movement of a smooth solid-liquid interface into the liquid.



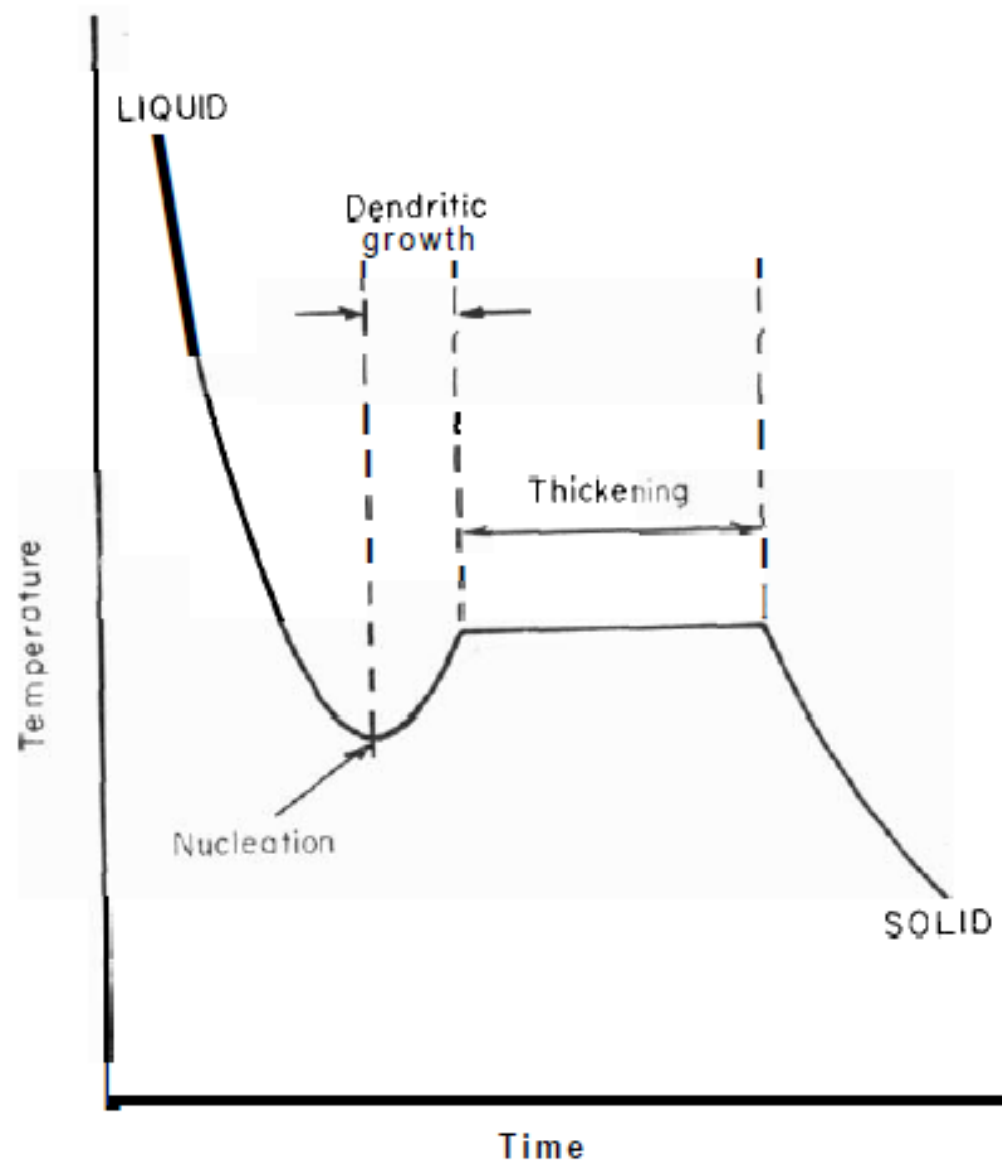
(a) If the liquid is undercooled, a protuberance on the solid-liquid interface can grow rapidly as a dendrite. The latent heat of fusion is removed by raising the temperature of the liquid back to the freezing temperature. (b) Scanning electron micrograph of dendrites in steel (x15).

Dendritic Growth: When the liquid is not inoculated and the nucleation is poor, the liquid has to be undercooled before the solid forms. Under these conditions, a small solid protuberance called a dendrite, which forms at the interface, is encouraged to grow since the liquid ahead of the solidification front is undercooled. The word dendrite comes from the Greek word dendron that means tree. As the solid dendrite grows, the latent heat of fusion is conducted into the undercooled liquid, raising the temperature of the liquid toward the freezing temperature. Secondary and tertiary dendrite arms can also form on the primary stalks to speed the evolution of the latent heat. Dendritic growth continues until the undercooled liquid warms to the freezing temperature. Any remaining liquid then solidifies by planar growth.

The difference between planar and dendritic growth arises because of the different sinks for the latent heat of fusion. The container or mold must absorb the heat in planar growth, but the undercooled liquid absorbs the heat in dendritic growth. In pure metals, dendritic growth normally represents only a small fraction of the total growth and is given by

$$\text{Dendritic fraction} = f = \frac{c\Delta T}{\Delta H_f} \quad (\Delta H_f = L_m)$$

where c is the specific heat of the liquid. The numerator represents the heat that the undercooled liquid can absorb, and the latent heat in the denominator represents the total heat that must be given up during solidification. As the undercooling ΔT increases, more dendritic growth occurs. If the liquid is well-inoculated, undercooling is almost zero and growth would be mainly via the planar front solidification mechanism.



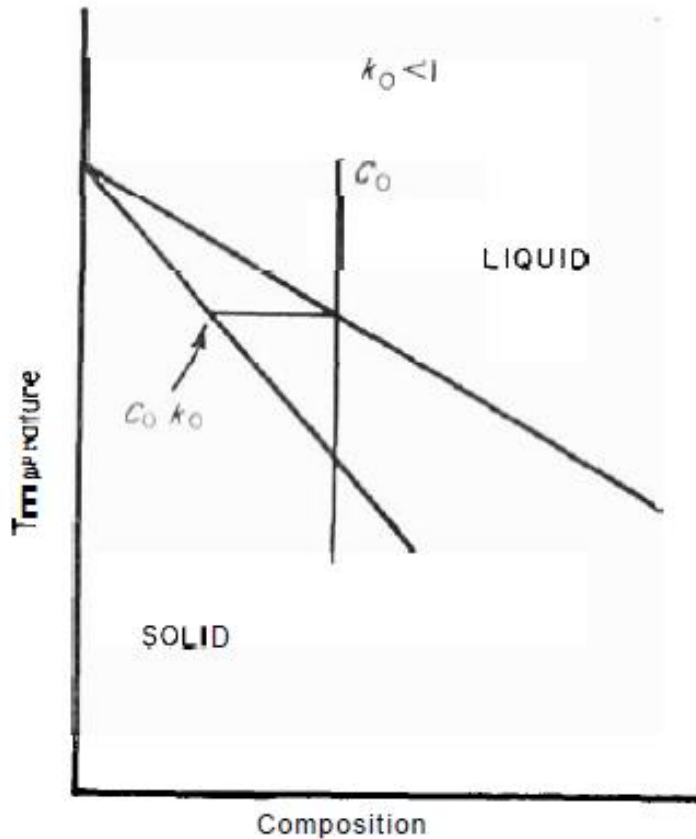
Typical form of cooling curve for pure metals showing the regions in which the different growth phenomena occur.

Solute Redistribution Effects in Alloys

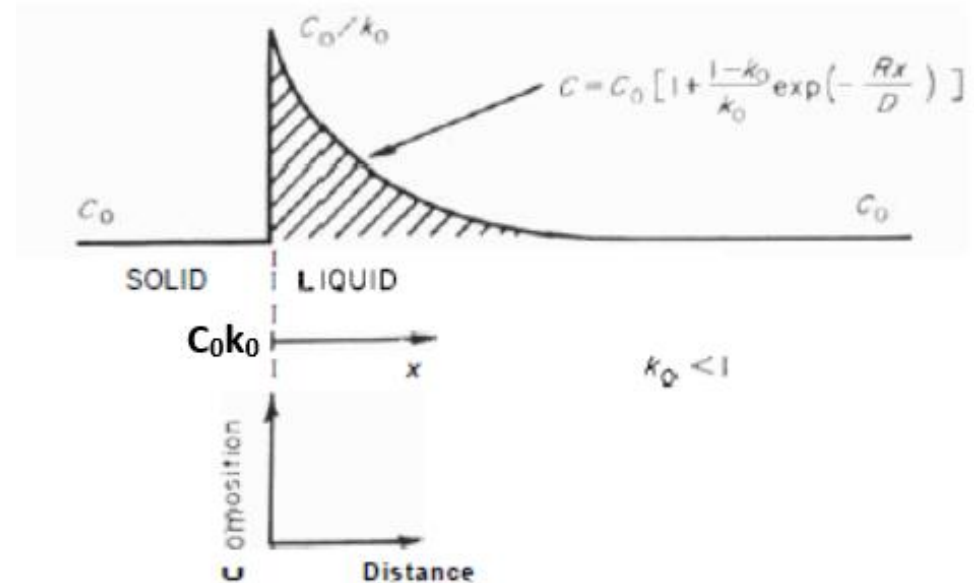
The growth of impure metals is much more complex because of the redistribution of solute that occurs during solidification. This can produce changes in the growth morphology and lead to solute segregation on both a microscale and a macroscale. If we consider the initial sequence of events during the solidification of an alloy of composition C_0 , with distribution coefficient $k_0 < 1$, it is clear from the phase diagram that the first solid to form will have composition of $C_0 k_0$. Since $k_0 < 1$ is a small localised increase in the solute content of the liquid. First, the solute increase may disperse in the liquid by diffusion only. Alternatively, conditions of complete mixing in the liquid which rapidly spread the excess solute throughout the bulk of the liquid.

- For solute concentrations (C_0) higher than about 0.5 % the solute pile-up effects are very marked and the physical nature of the interface alters to a non-planar configuration.

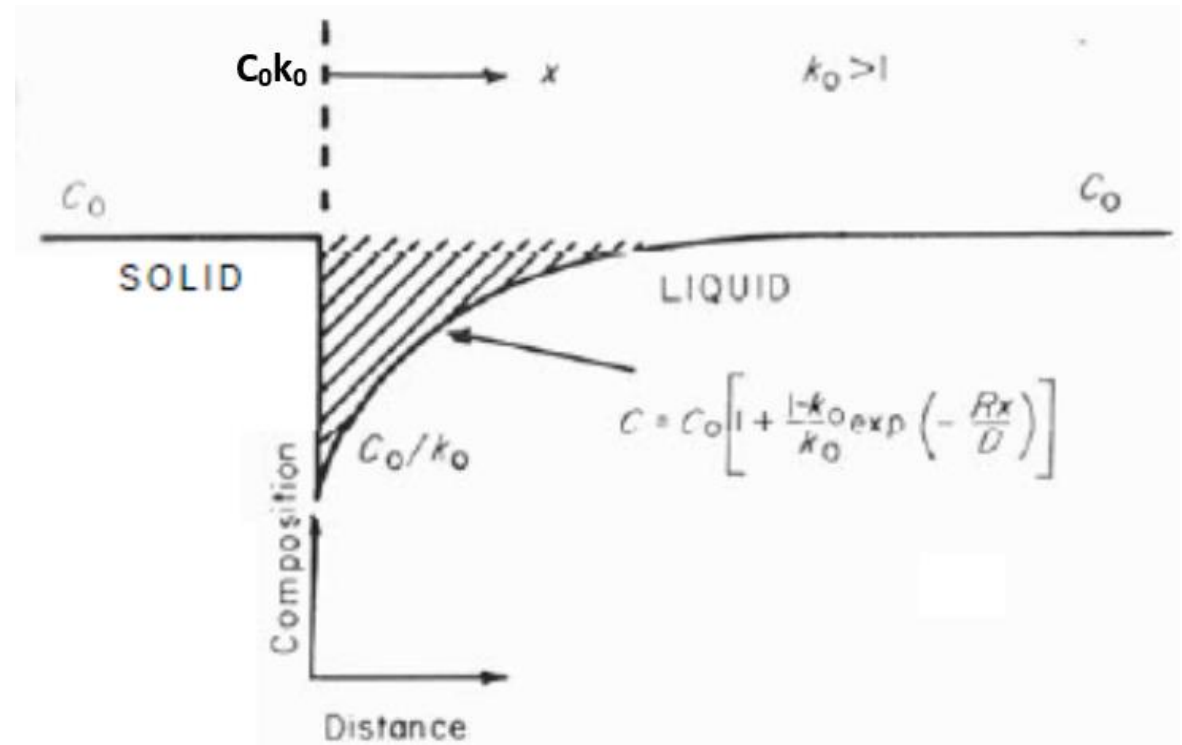
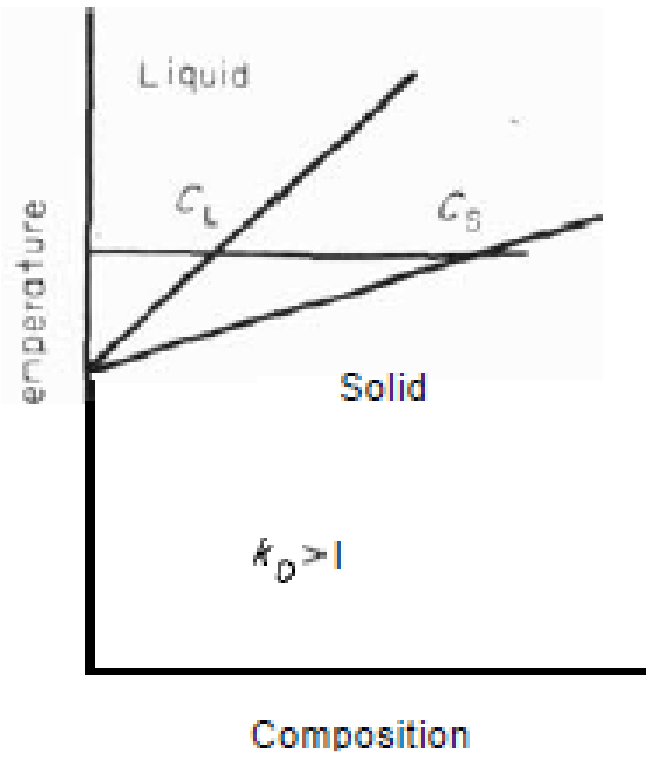
Solute redistribution by diffusion

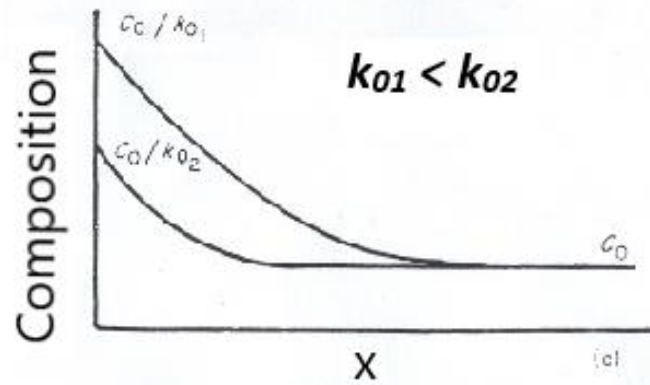
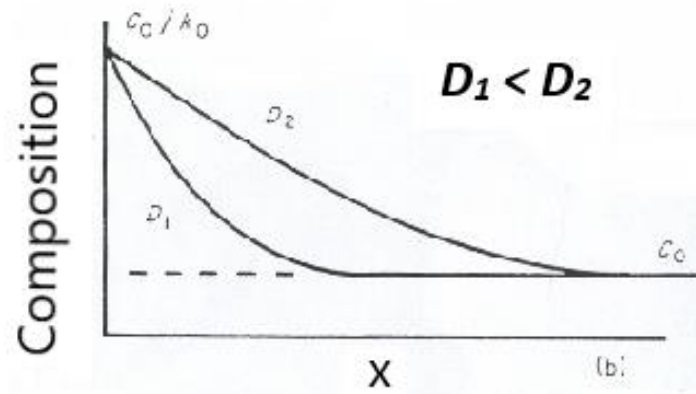
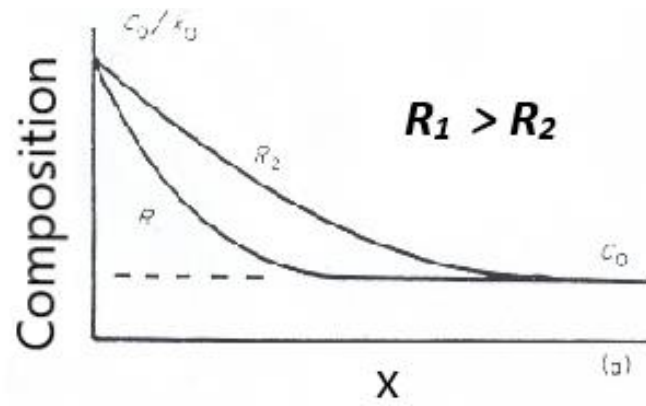


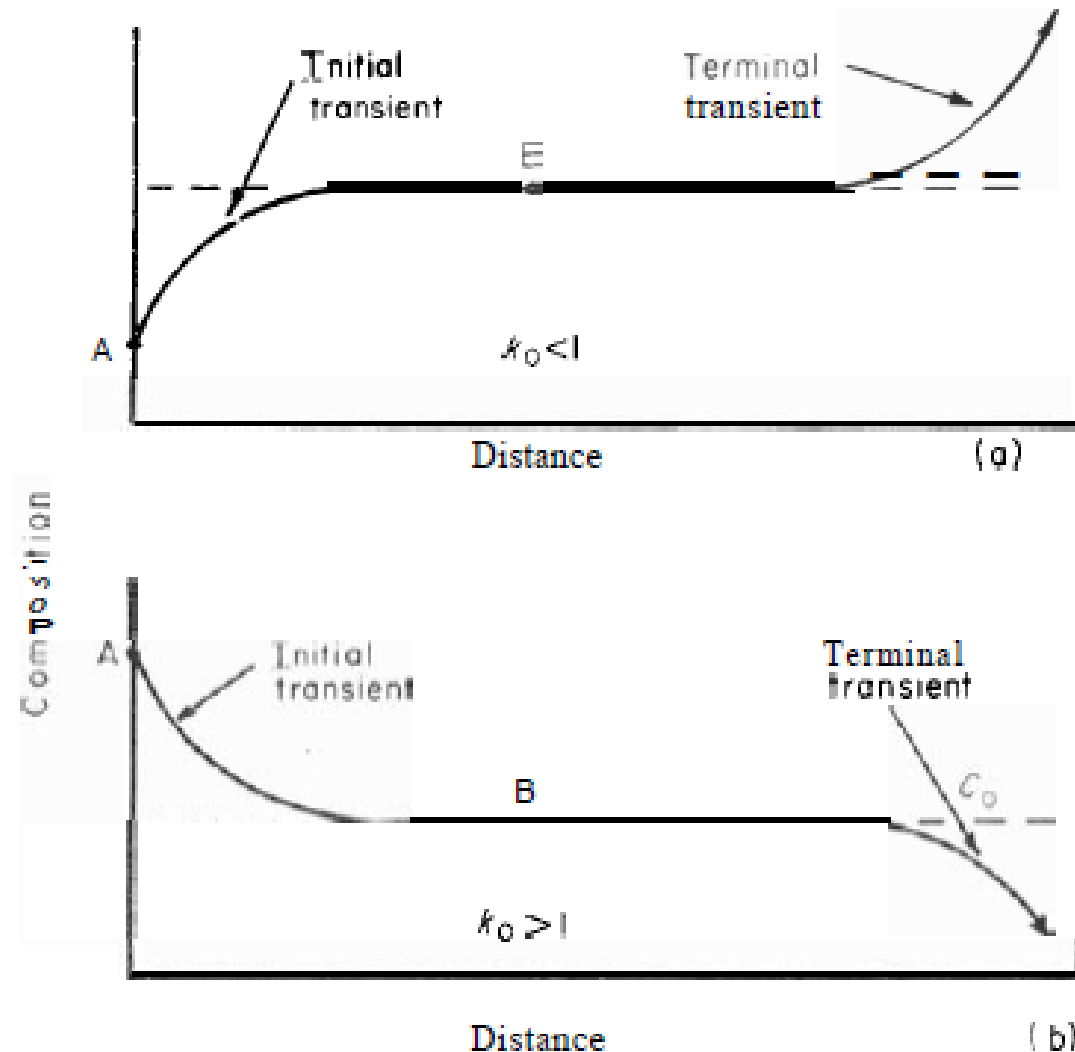
Portion of a phase diagram for an alloy of composition C_0 , with $k_0 < 1$ showing initial compositional changes.



The solute profile ahead of the interface during steady-state solidification with solute redistribution by diffusion only ($k_0 < 1$)







Concentration-distance profiles for a bar solidified under condition where solute transport in the liquid is by diffusion only. (a) $k_0 < 1$; (b) $k_0 > 1$.