



## Solidification, casting and cast alloys

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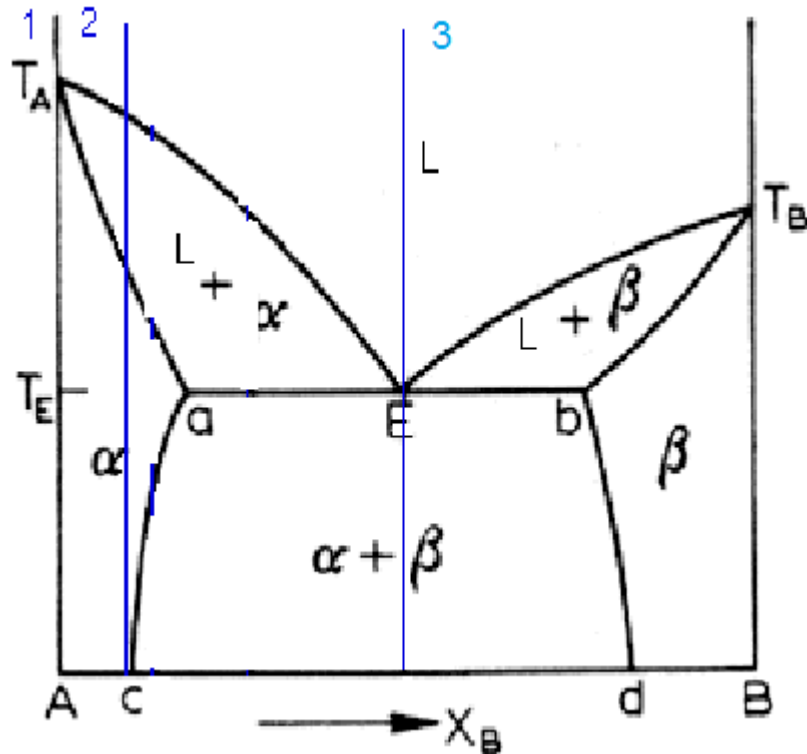
Solidification is important in metal processing:

- **Casting** (sand casting, die casting, etc.)
- **Welding**
- **Additive manufacturing** (3D printing)

Casting in metal production is a manufacturing process where a liquid metal is poured into a mold, which contains a hollow cavity of the desired shape, and then allowed to solidify. The solidified part, also known as the casting, is then ejected or broken out of the mold to complete the process. Casting is used to make complex shapes that would be difficult or uneconomical to make by other methods.



Solidification occurs by nucleation (heterogeneous) and growth. A substantial amount of heat must be removed. For pure elements (1) transformation is massive to a single phase. For alloys it can be primary with solute partitioning (2), eutectic (3), peritectic, ....



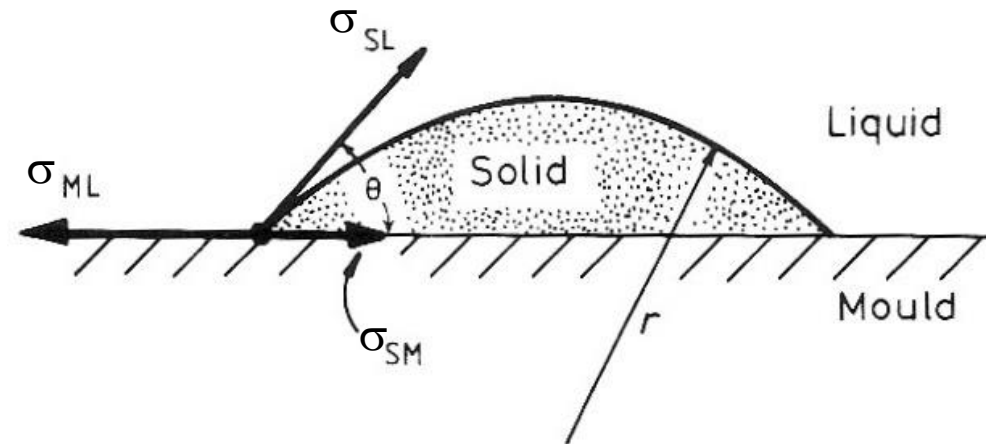
The driving force for nucleation is

$$\Delta G = (G_L - G_\alpha) = -V\Delta G_V + A\gamma_{het}$$

giving, as previously discussed

$$r^* = \frac{2\gamma}{(\Delta G_v)}$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$



Surface energy balance is  $\gamma_{ML} = \gamma_{SM} + \gamma_{SL} \cos \theta$

Free energy of formation of embryo

$$\Delta G_{het} = -V_S \Delta G_V + A_{SL} \gamma_{SL} + A_{SM} \gamma_{SM} - A_{SM} \gamma_{ML}$$

\*Using the geometrical formulas:

$$A_{SM} = \pi r^2 \sin^2 \theta$$

$$A_{SL} = 2\pi r^2 (1 - \cos \theta)$$

$$V_s = \frac{\pi r^3 (2 + \cos \theta)(1 - \cos \theta)^2}{3}$$

it can be shown that...

$$\Delta G_{het} = \left\{ -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL} \right\} S(\theta) \quad \text{with}$$

$$S(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2 / 4 \quad 0 \leq S(\theta) \leq 1$$

$$\Delta G_{het}^* = S(\theta) \Delta G_{hom}^*$$

For example:

$$\theta = 10^\circ \rightarrow S(\theta) \sim 10^{-4}$$

$$\theta = 30^\circ \rightarrow S(\theta) = 0.2$$

$$\theta = 90^\circ \rightarrow S(\theta) = 0.5$$

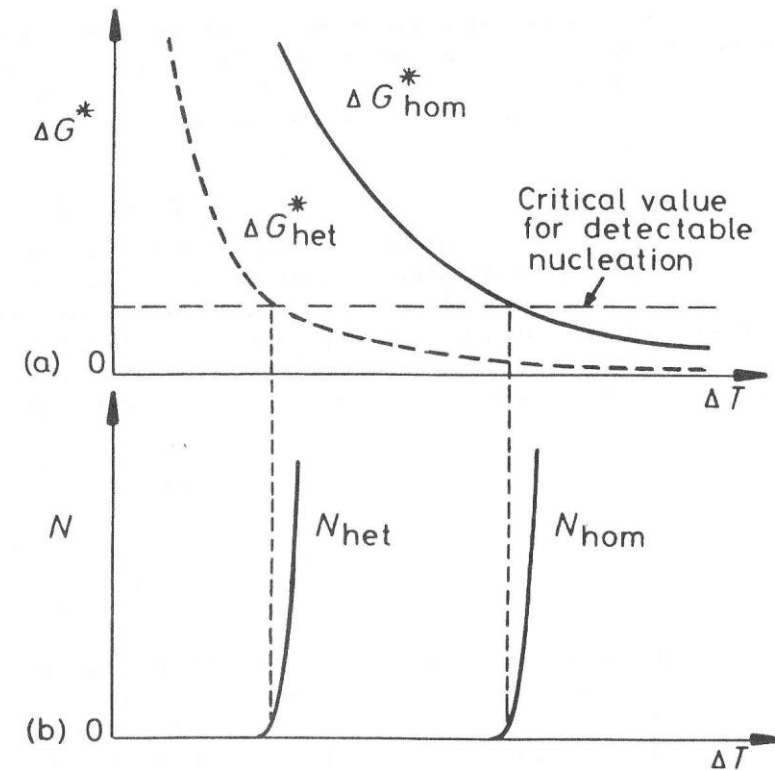
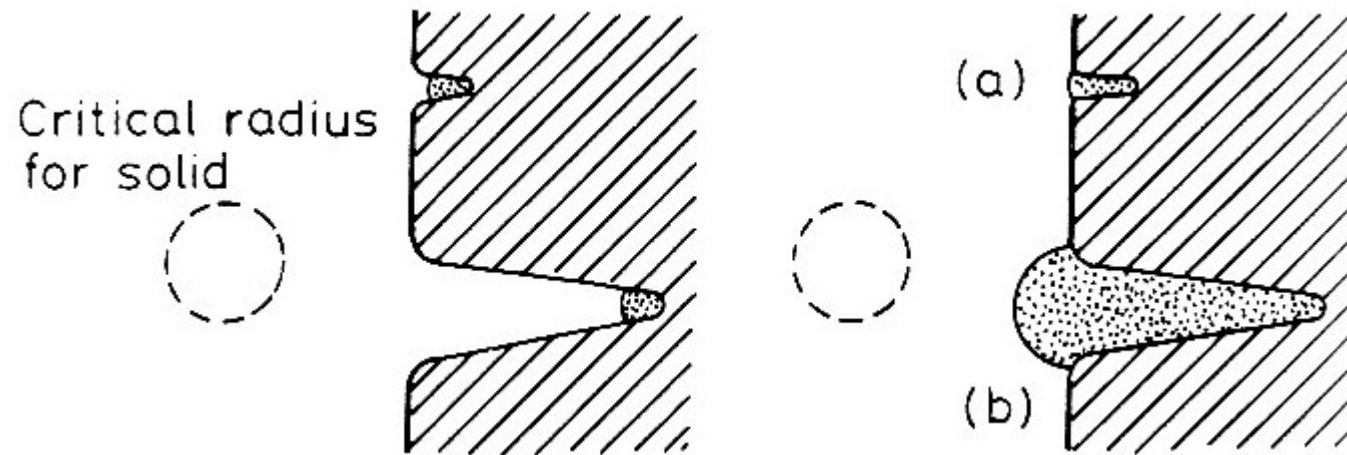


Fig. 4.9 (a) Variation of  $\Delta G^*$  with undercooling ( $\Delta T$ ) for homogeneous and heterogeneous nucleation. (b) The corresponding nucleation rates assuming the same critical value of  $\Delta G^*$ .

Nucleation most likely on crevices of mould wall (if not of size below  $r^*$ ).



Solid/liquid interfaces are of two types:

- a) Sharp (or faceted or smooth)
- b) Diffuse (or non-faceted or rough)

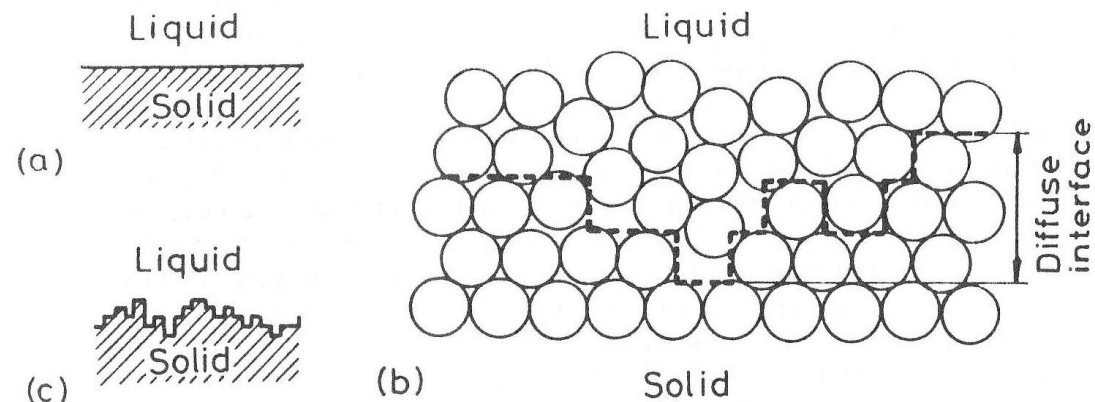


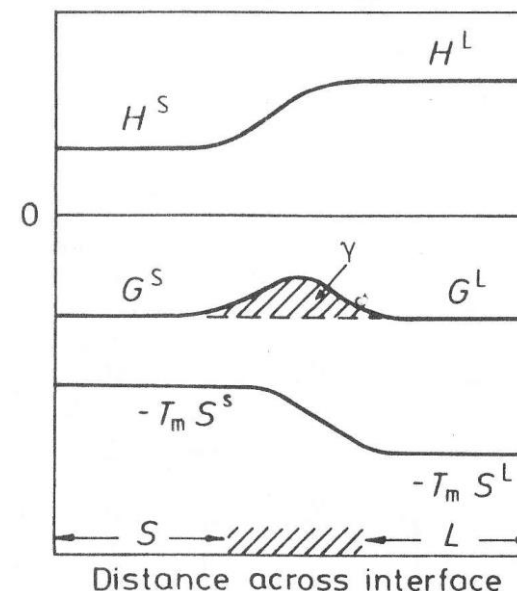
Fig. 3.63 Solid/liquid interfaces: (a) atomically smooth, (b) and (c) atomically rough, or diffuse interfaces. (After M.C. Flemings, *Solidification Processing*, McGraw-Hill, New York, 1974.)

In case a), the transition from liquid to solid occurs over a narrow zone (~one atomic layer).

In case b), the transition from liquid to solid occurs over several atomic layers, with increasing disorder.

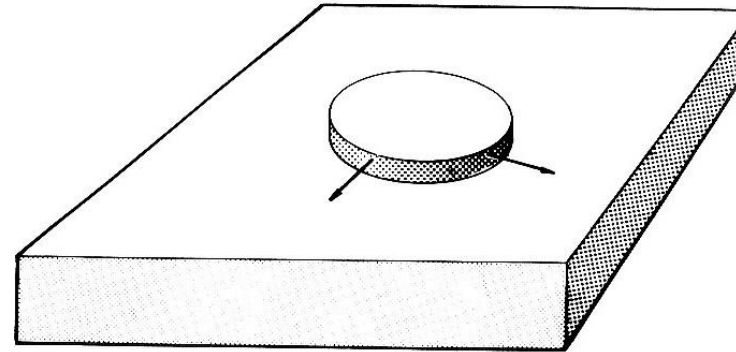
The type of interface in a particular system is that which minimizes the interfacial energy.

Most elemental metals/liquid interfaces are diffuse. Intermetallic compounds and non metallic elements have sharp S/L interfaces.

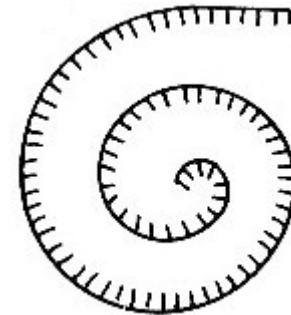
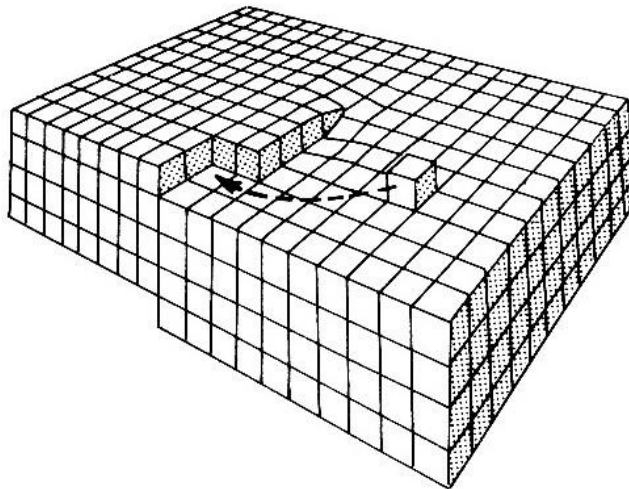




Surface nucleation has been documented. It is then followed by lateral growth.



Emerging screw dislocation can be sites for it, then spiral growth occurs.

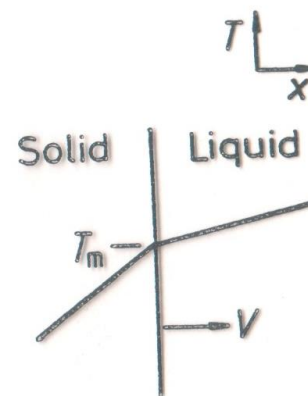




# 1) Solidification in pure elements

Rate and mechanism depend on heat extraction. Basic equation expressing heat flux balance in one dimension with  $K_i$  thermal conductivity,  $v$  interface rate,  $L_v$  latent heat per unit volume:

$$K_s \frac{dT_s}{dx} = K_L \frac{dT_L}{dx} + vL_v$$



Local equilibrium is assumed at the interface:  $T = T_m$ .

The temperature gradients determine **interface stability**: if heat is subtracted through the solid  $\rightarrow$  planar interface, if heat is subtracted through the liquid  $\rightarrow$  dendritic interface.

# 1) Solidification in pure elements

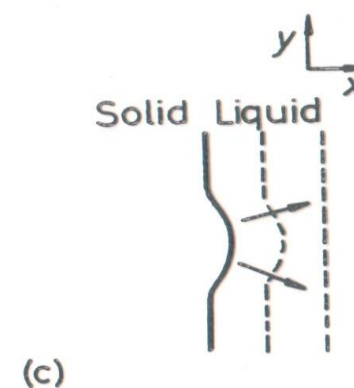
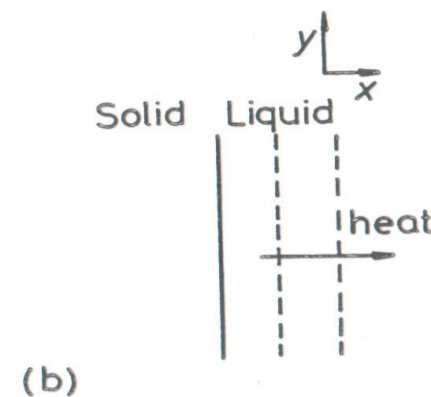
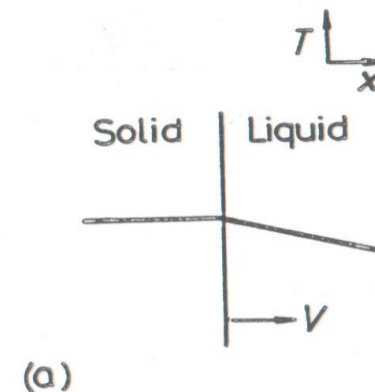
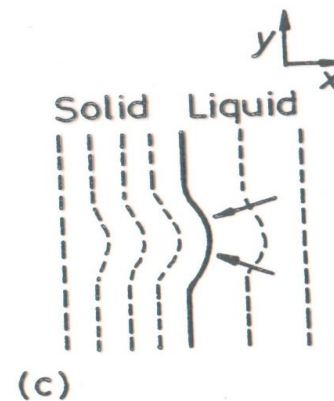
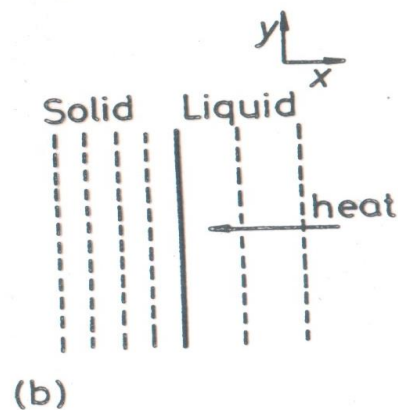
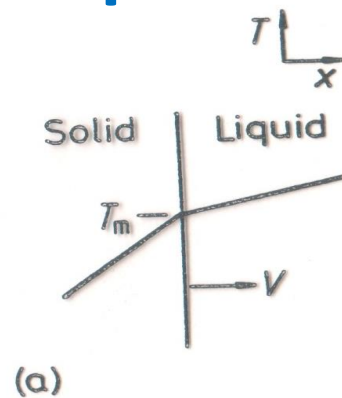
Left: a) temperature profile when heat is extracted through the solid phase

b) isotherms for planar interface

c) isotherms for protrusion.

Right: a) temperature profile when heat is extracted through the liquid phase

b) and c) as above.



# 1) Solidification in pure elements

Growth of **thermal dendrite** from protrusion.

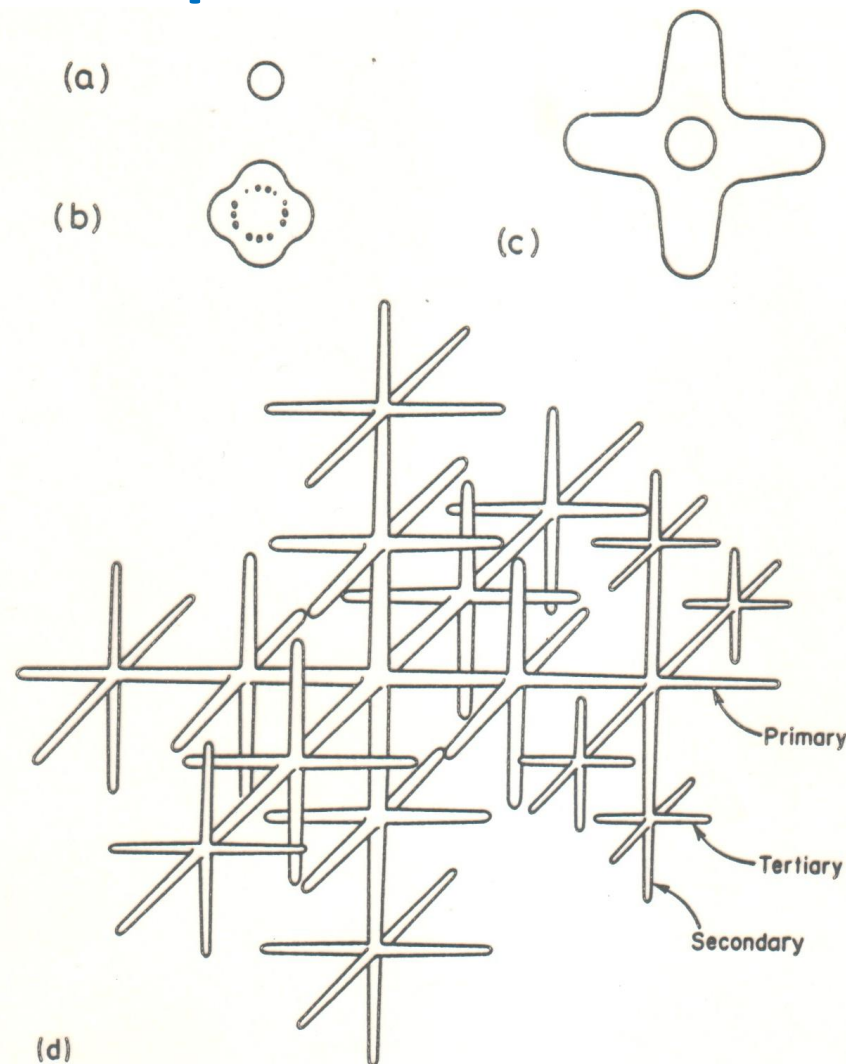


Fig. 4.17 The development of thermal dendrites: (a) a spherical nucleus; (b) the interface becomes unstable; (c) primary arms develop in crystallographic directions ( $\{100\}$  in cubic crystals); (d) secondary and tertiary arms develop

# 1) Solidification in pure elements

Dendrite growth rate

$$v = -\frac{K_L}{L_V} \frac{dT_L}{dx} \approx \frac{K_L}{L_V} \frac{\Delta T_C}{r}$$

Considering the Gibbs-Thomson effect ( $T_i$  is reduced melting temperature because of curvature,  $T_\infty$  is temperature of liquid far from interface,  $\Delta T$ s are undercoolings) the limiting radius is (note analogy with critical radius for nucleation)

$$r^* = \frac{2\gamma T_m}{L_V \Delta T_0}$$

therefore

$$v = \frac{K_L}{L_V} \frac{\Delta T_0}{r} \left( 1 - \frac{r^*}{r} \right)$$

(demonstration on next slides)

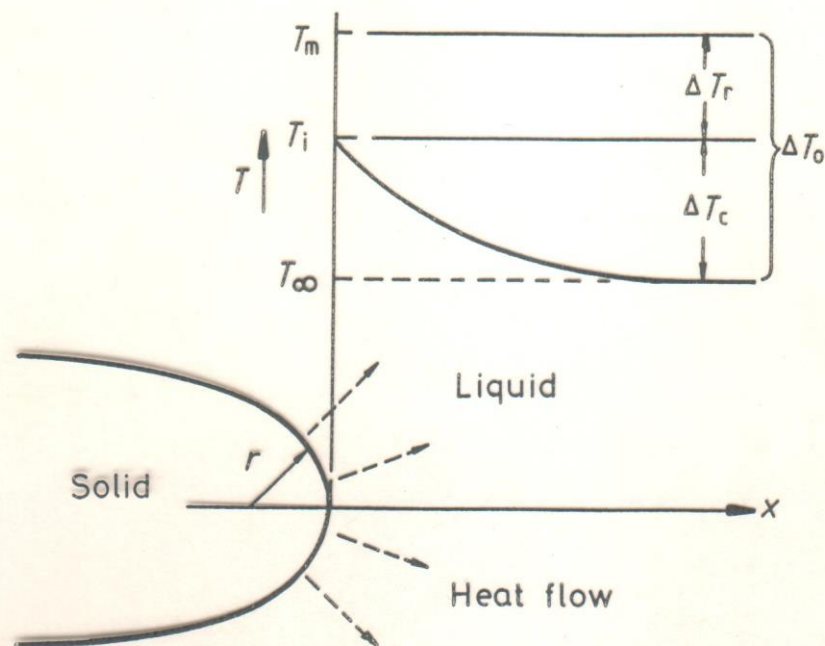


Fig. 4.18 Temperature distribution at the tip of a growing thermal dendrite.

# 1) Solidification in pure elements

Diff. between G of solid and liquid:

$$\Delta G_V = \Delta H_V - T\Delta S_V$$

Latent heat of melting:  $\Delta H_V = L_V$

At  $T_m$ :  $\Delta G_V = 0$



$$\Delta S_V = \frac{\Delta H_V}{T_m} = \frac{L_V}{T_m}$$

$$\Delta G_V = L_V - T\Delta S_V = L_V - T \frac{L_V}{T_m} = L_V \frac{\Delta T}{T_m}$$

critical radius for nucleation:



$$r^* = \frac{2\gamma}{\Delta G_V}$$



$$r^* = \frac{2\gamma T_m}{L_V \Delta T_0}$$

$$\Delta T_0 = \frac{2\gamma T_m}{L_V r^*}$$

# 1) Solidification in pure elements

From  $v \approx \frac{K_L}{L_V} \frac{\Delta T_C}{r}$

using  $\Delta T_C = \Delta T_0 - \Delta T_r$

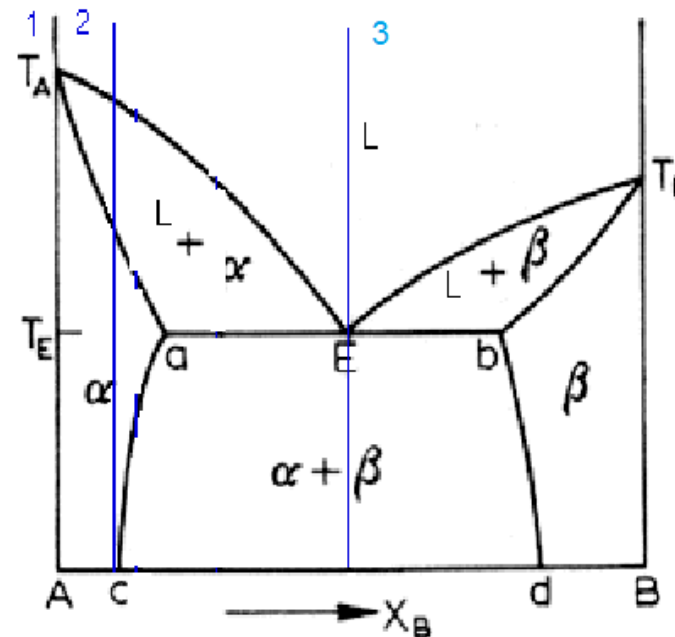
and  $\Delta T_0 = \frac{2\gamma T_m}{L_V r^*}$   $\Delta T_r = \frac{2\gamma T_m}{L_V r}$

$$v = \frac{K_L}{L_V} \frac{1}{r} (\Delta T_0 - \Delta T_r) = \frac{K_L}{L_V} \frac{1}{r} \left( \frac{2\gamma T_m}{r^* L_V} - \frac{2\gamma T_m}{r L_V} \right) = \frac{K_L}{L_V} \frac{1}{r} \left( \frac{2\gamma T_m}{L_V} \right) \left( \frac{1}{r^*} - \frac{1}{r} \right)$$

$$v = \frac{K_L}{L_V} \frac{1}{r} \left( \frac{2\gamma T_m}{r^* L_V} \right) \left( 1 - \frac{r^*}{r} \right) = \frac{K_L}{L_V} \frac{\Delta T_0}{r} \left( 1 - \frac{r^*}{r} \right)$$

## 2) Solidification in binary alloys

Solidification of a single solid phase  $\alpha$  from liquid (case 2)



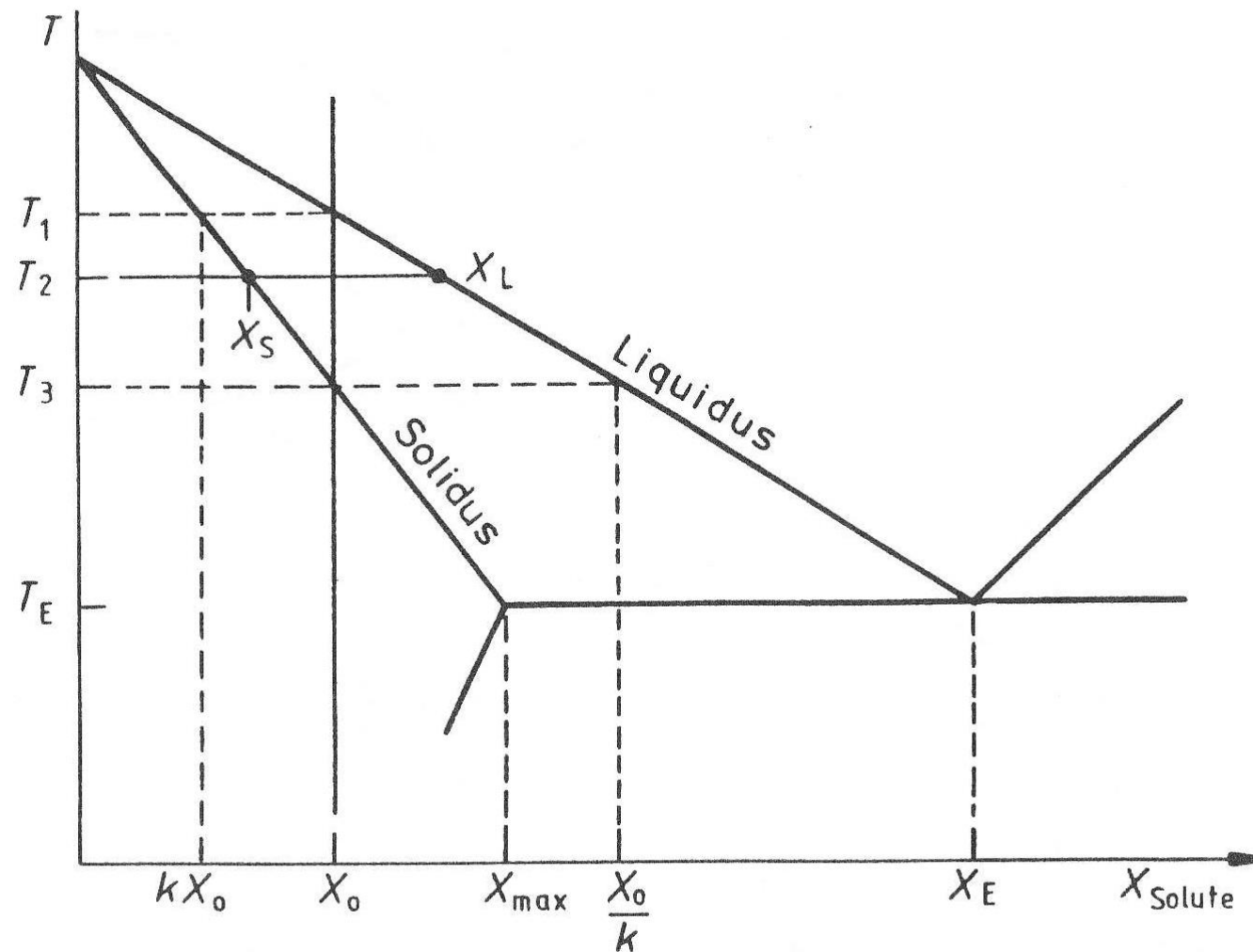
- Equilibrium solidification (infinitely slow)
- No diffusion in solid, perfect mixing in liquid (Scheil-Gulliver solidification)
- No diffusion in the solid, only diffusional mixing in the liquid



## 2a) Equilibrium solidification in binary alloys

Definition of partition coefficient,  $k$ , for linear solidus and liquidus:

$$k = \frac{X_S}{X_L}$$



## 2a) Equilibrium solidification in binary alloys

Equilibrium unidirectional solidification: profile of solute concentration.

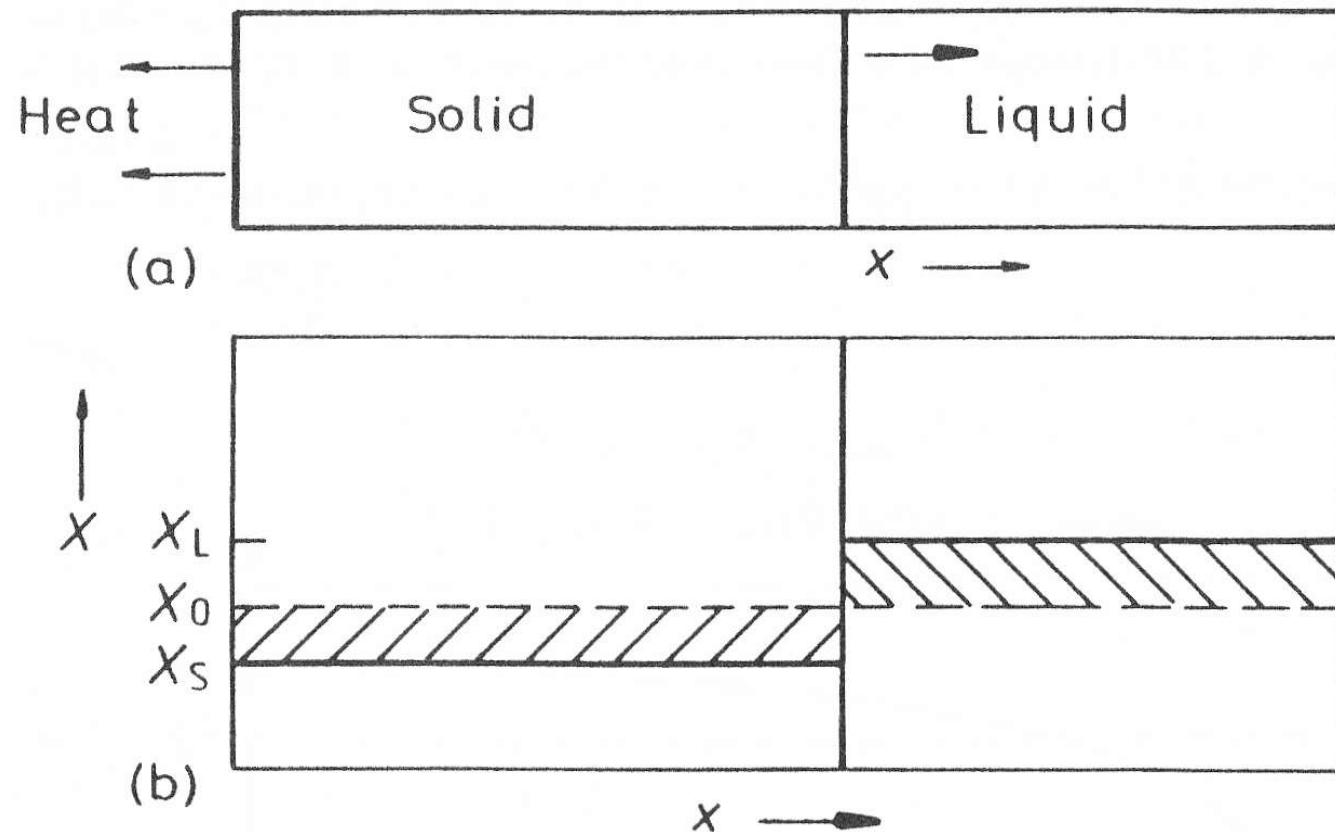
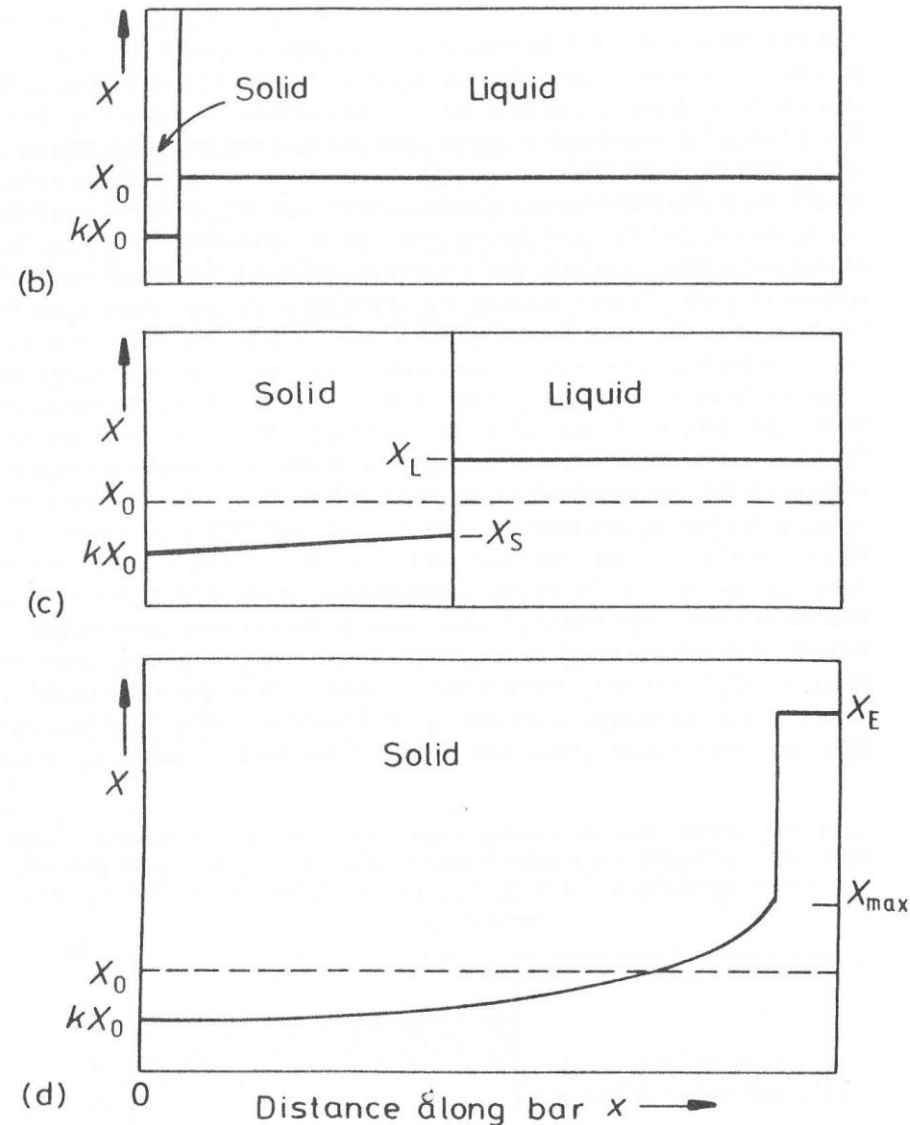


Fig. 4.20 Unidirectional solidification of alloy  $X_0$  in Fig. 4.19. (a) A planar S/L interface and axial heat flow. (b) Corresponding composition profile at  $T_2$  assuming complete equilibrium. Conservation of solute requires the two shaded areas to be equal.

## 2b) Scheil-Gulliver solidification in binary alloys

Unidirectional solidification  
out of equilibrium: no  
diffusion in the solid,  
complete mixing in the liquid  
(convection + stirring).

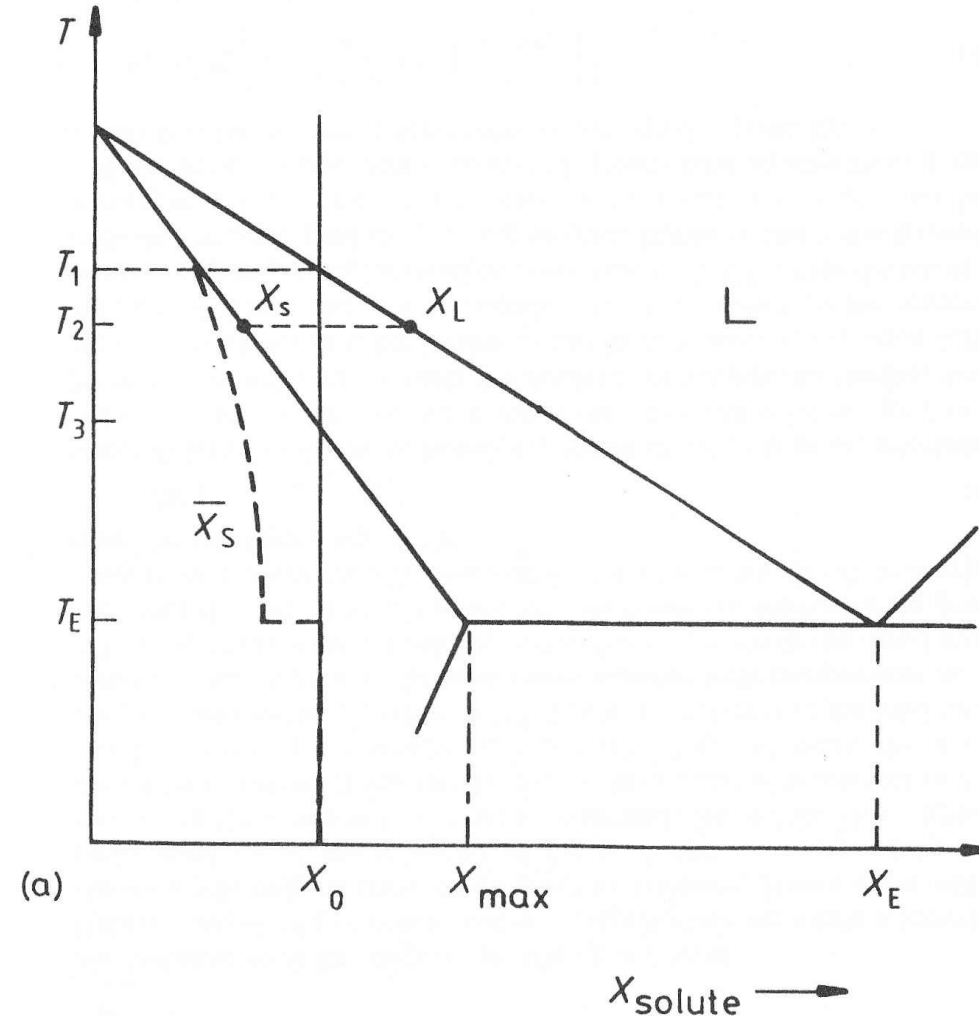
Concentration profile of  
solute in the bar due to  
rejection of solute into the  
liquid.



## 2b) Scheil-Gulliver solidification in binary alloys

Unidirectional solidification out of equilibrium: no diffusion in the solid, complete mixing in the liquid (convection + stirring).

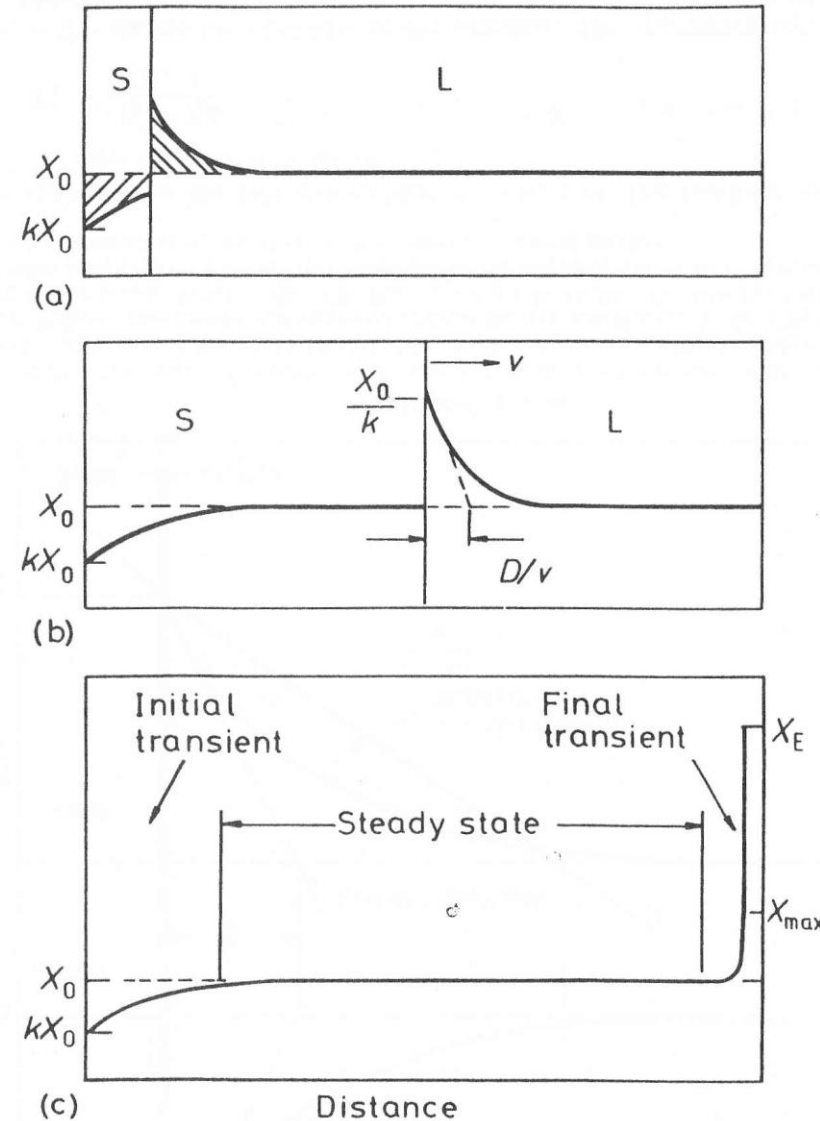
Phase diagram with the average solute concentration in the solid reported as dashed line.





Unidirectional solidification  
out of equilibrium: no  
diffusion in the solid, mixing  
in the liquid only by diffusion.

Concentration profile of solute in the bar is steady with initial and final effect of solute rejection.



The solid composition and local microstructure in the direction of solidification depends on atomic transport within the liquid by diffusion (no diffusion in the solid, nor mixing in the liquid). A balance of matter flux imposes

$$D \frac{dC_L}{dx} = -v(C_L - C_S)$$

Flux of solute in the liquid

Excess of solute rejected  
from the solid into the liquid

By solving the equation the concentration profile of solute in the liquid is obtained.

$$X_L = X_0 \left\{ 1 - \frac{1-k}{k} \exp \left[ -\frac{x}{D/v} \right] \right\}$$

## Constitutional supercooling:

difference between equilibrium liquidus and actual temperature along distance. Causes dendrite formation in alloys.

The instability of planar solid-liquid interface (implying formation of protrusions) is due to the diffusional concentration profile even if heat is subtracted through the solid (below a critical rate).

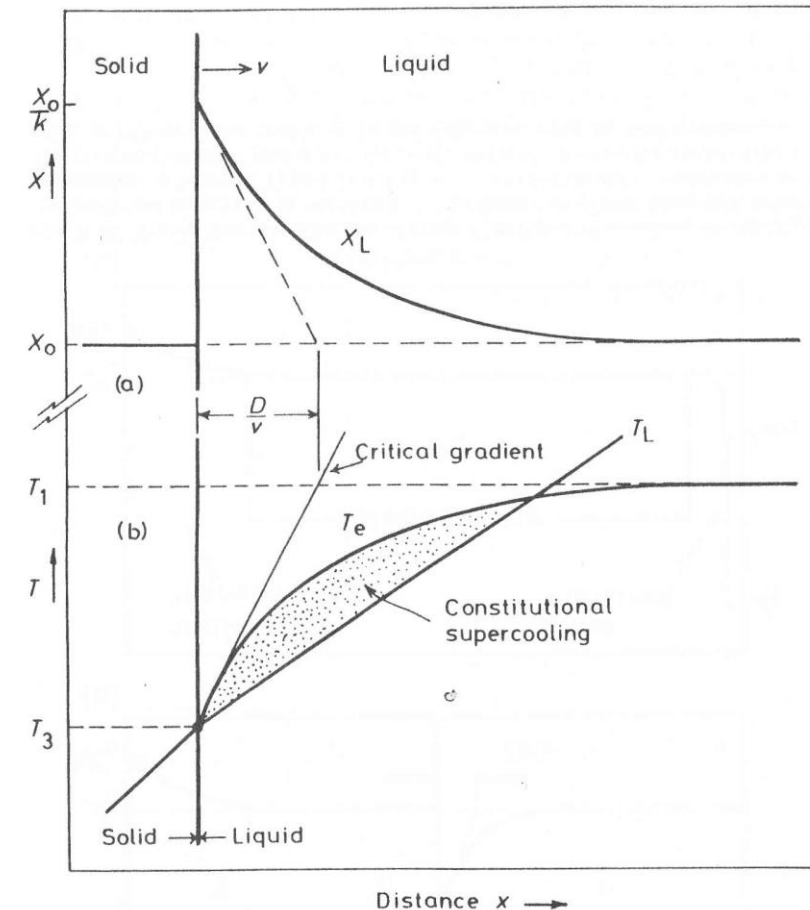
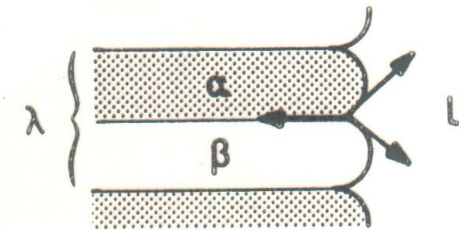
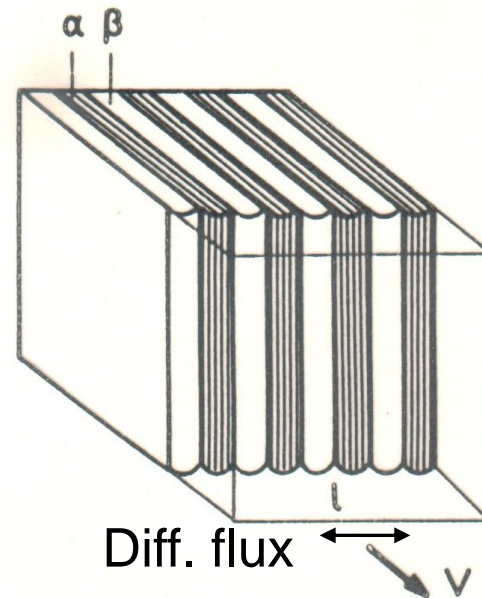
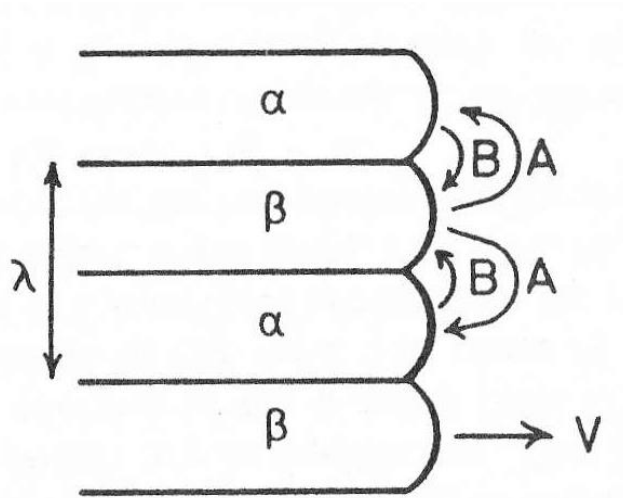


Fig. 4.23 The origin of constitutional supercooling ahead of a planar solidification front. (a) Composition profile across the solid/liquid interface during steady-state solidification. The dashed line shows  $dX_L/dx$  at the S/L interface. (b) The temperature of the liquid ahead of the solidification front follows line  $T_L$ . The equilibrium liquidus temperature for the liquid adjacent to the interface varies as  $T_e$ . Constitutional supercooling arises when  $T_L$  lies under the critical gradient.



### 3) Eutectic solidification

Assuming a lamellar eutectic the solidification front is planar. Growth is ruled by atomic transport (coupled growth and diffusion).



### 3) Eutectic solidification

Small lamellar spacing  $\lambda$  should lead to rapid growth.

However, there is a minimum possible value  $\lambda^*$  determined by the necessity to balance the interfacial energy  $\gamma_{\alpha\beta}$

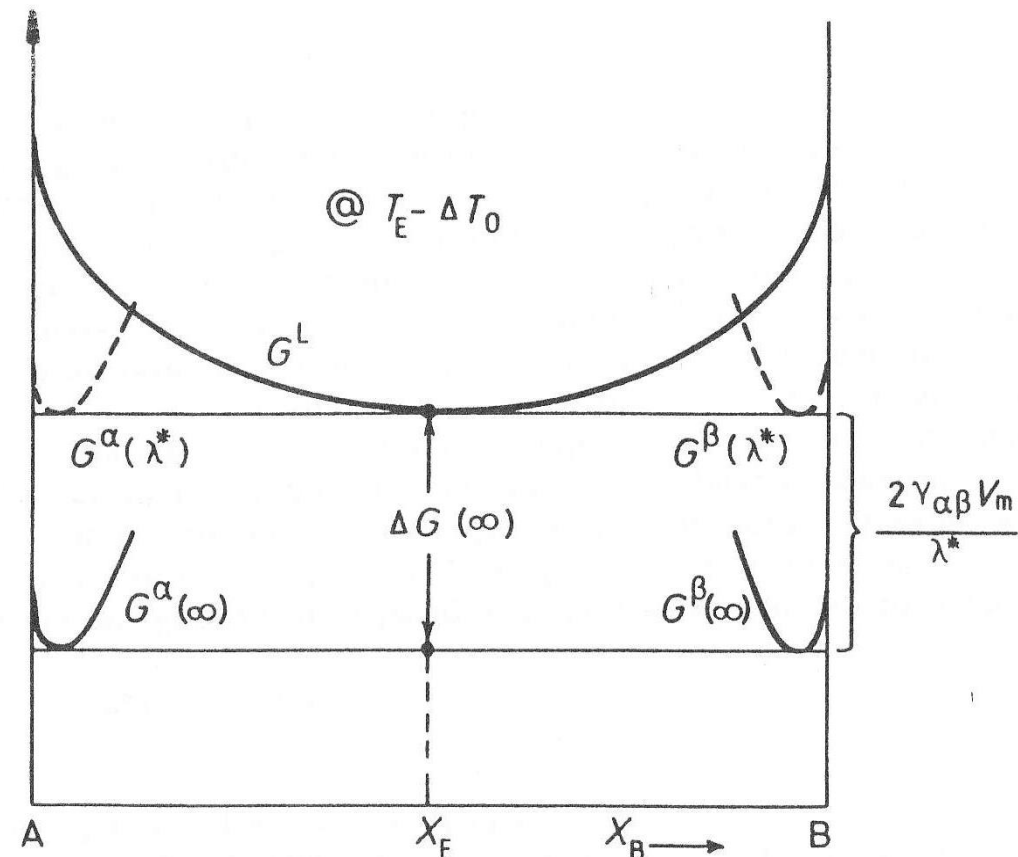
For a given  $\lambda$ , there is a total of  $2/\lambda$  m<sup>2</sup> of  $\alpha/\beta$  interface per m<sup>3</sup> of eutectic.

$$\Delta G(\lambda) = -\Delta G(\infty) + \frac{2\gamma_{\alpha\beta}V_m}{\lambda}$$

$$\Delta G(\infty) = k_0\Delta T_0$$

The minimum value  $\lambda^*$  is obtained at  $\Delta G(\lambda)=0$ , i.e.

$$\lambda^* = \frac{2\gamma_{\alpha\beta}V_m}{k_0\Delta T_0}$$



### 3) Eutectic solidification

For a given  $\lambda$ , growth rate  $v$  should be proportional to diffusion flux in the liquid:

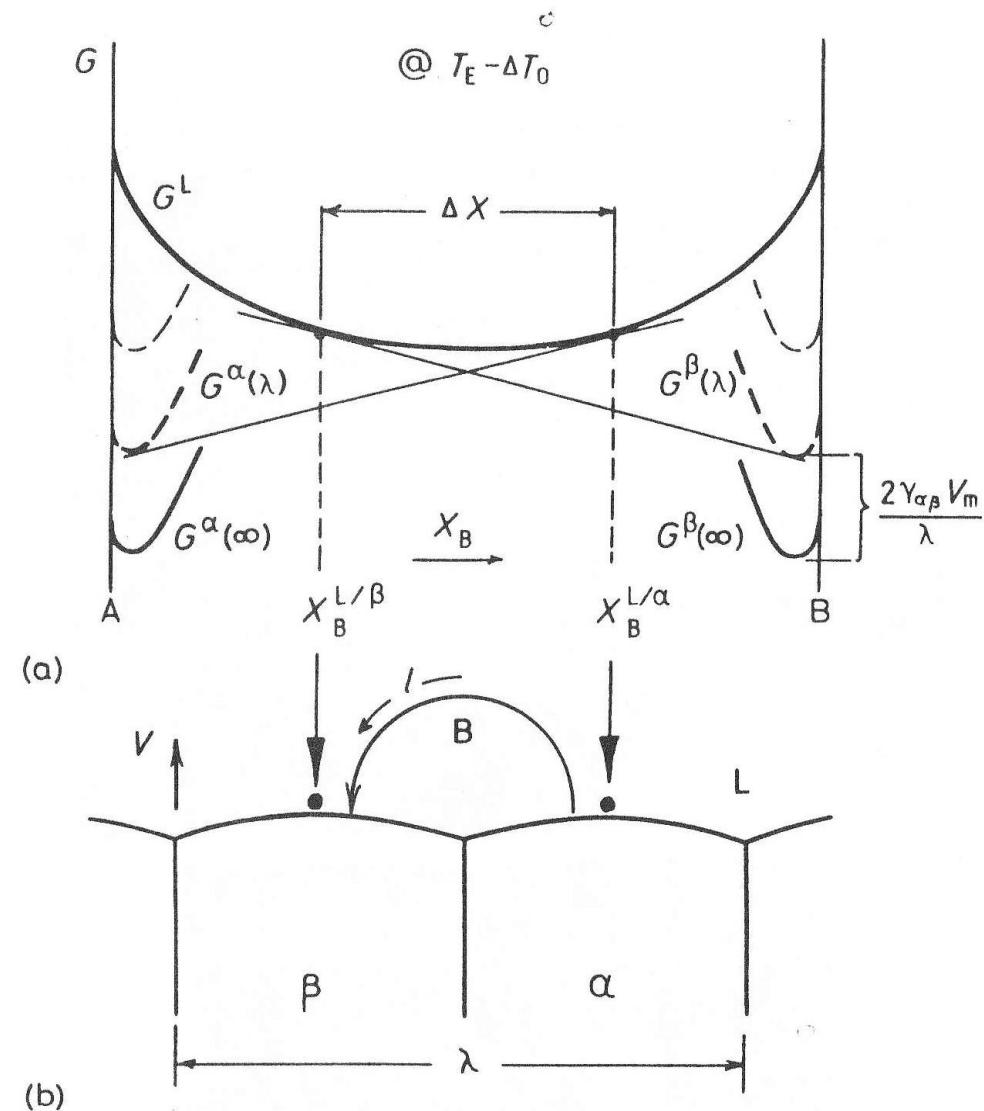
$$v = k_1 D \frac{dC_L}{dl} = k_1 D \frac{\Delta X}{\lambda}$$

$$dC_L \approx X_B^{L/\alpha} - X_B^{L/\beta} = \Delta X \quad dl \approx \lambda$$

$$\Delta X = \Delta X_0 \left( 1 - \frac{\lambda^*}{\lambda} \right)$$

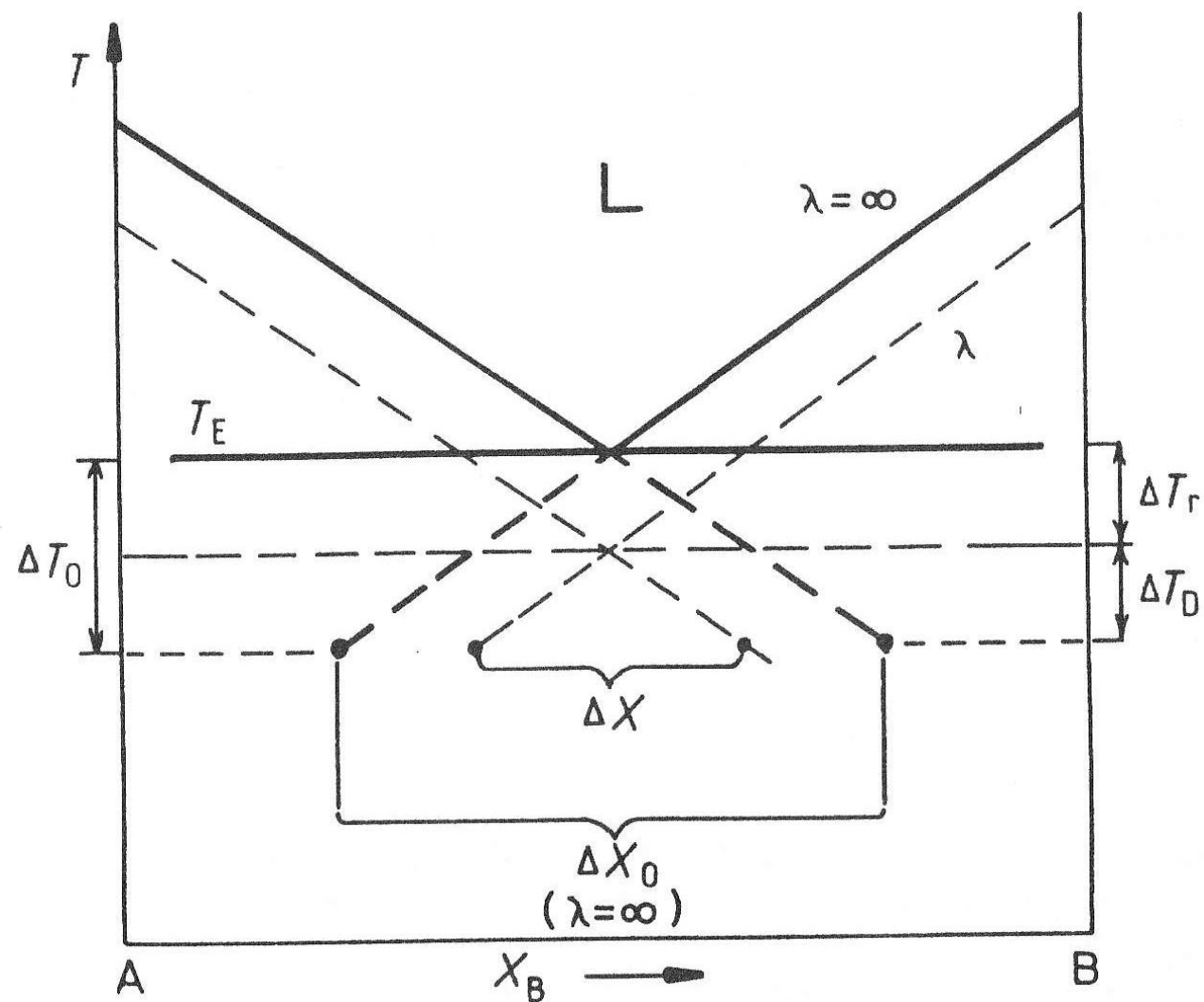
$$\Delta X_0 = k_2 \Delta T_0$$

$$v = k D \Delta T_0 \frac{1}{\lambda} \left( 1 - \frac{\lambda^*}{\lambda} \right)$$

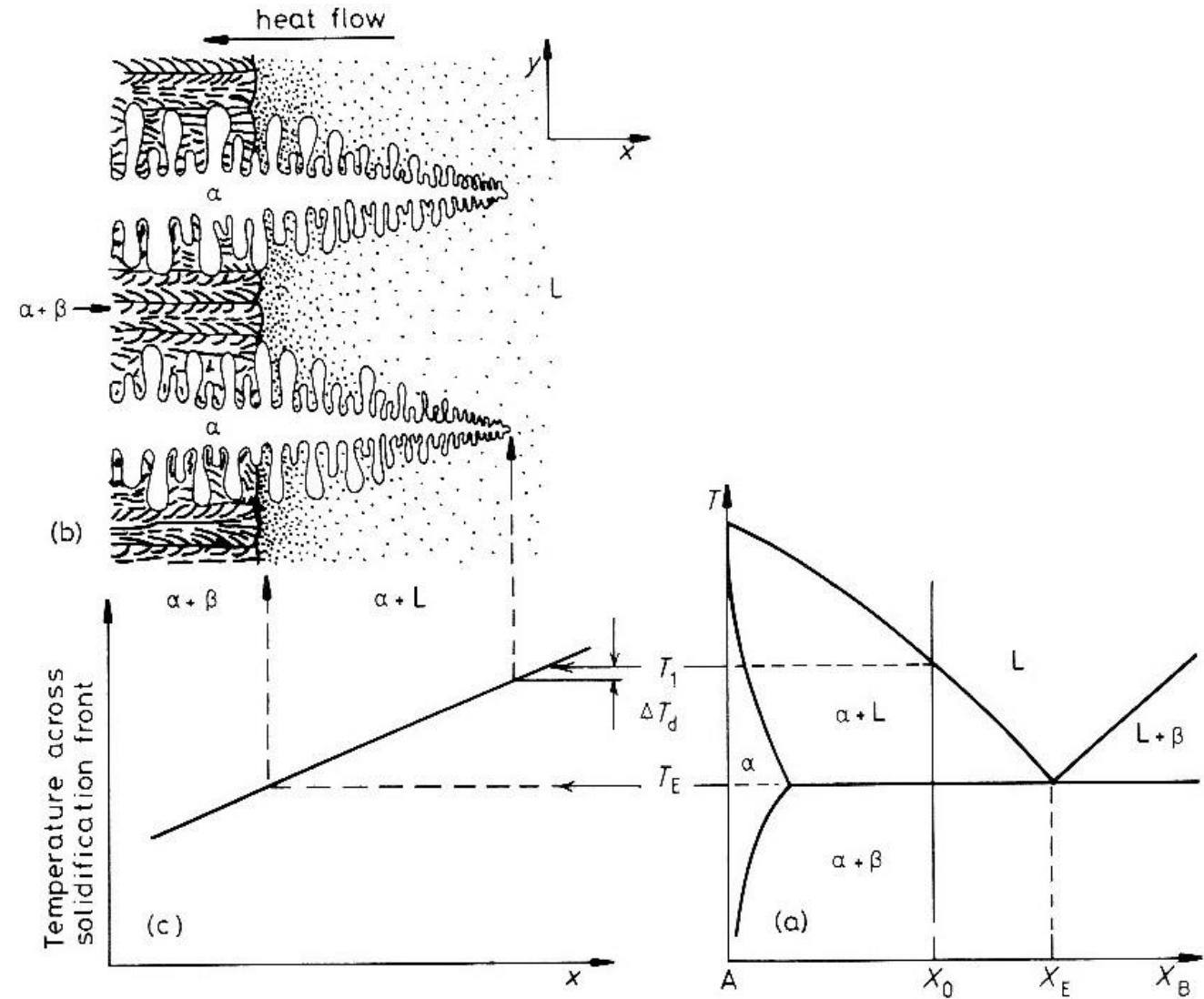


### 3) Eutectic solidification

The total undercooling ( $\Delta T_0 = \Delta T_r + \Delta T_D$ ) has two contributions:  $\Delta T_r$  is the undercooling required to overcome the interfacial curvature effects,  $\Delta T_D$  is the undercooling required to give a sufficient composition difference to drive diffusion.



A schematic description of dendrites and temperature gradients in solidification of an off-eutectic alloy.



A schematic description of dendrites and temperature gradients in solidification of a peritectic alloy.

