2017 Fall

"Phase Transformation *in* Materials"

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Contents for today's class

Solidification: Liquid ⟶ Solid

< Nucleation >
&
< Growth >

- Nucleation in Pure Metals

- Equilibrium Shape and Interface Structure on an Atomic Scale
- Growth of a pure solid
- Heat Flow and Interface Stability

4.3 Alloy solidification

- Solidification of single-phase alloys
- Eutectic solidification
- Off-eutectic alloys
- Peritectic solidification

1. Solidification of single-phase alloys

- Three limiting cases
  1) Equilibrium Solidification (perfect mixing in solid & liquid)
  2) No Diffusion in Solid, Perfect Mixing in Liquid
  3) No Diffusion on Solid, Diffusional Mixing in the Liquid

1) Equilibrium Solidification

(perfect mixing in solid & liquid)

→ low cooling rate

: infinitely slow solidification

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

partition coefficient

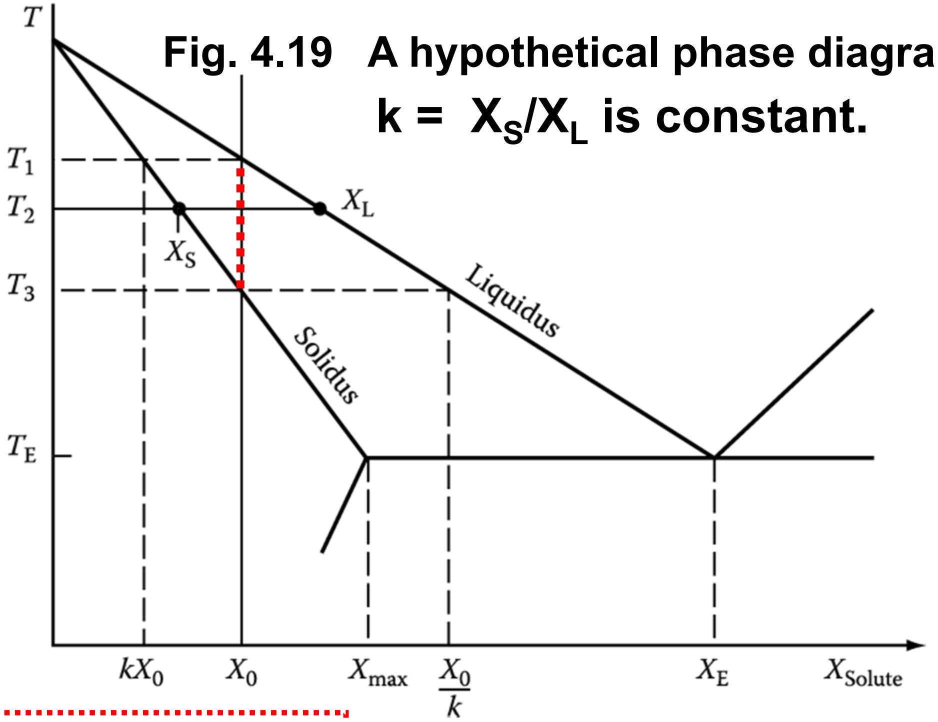
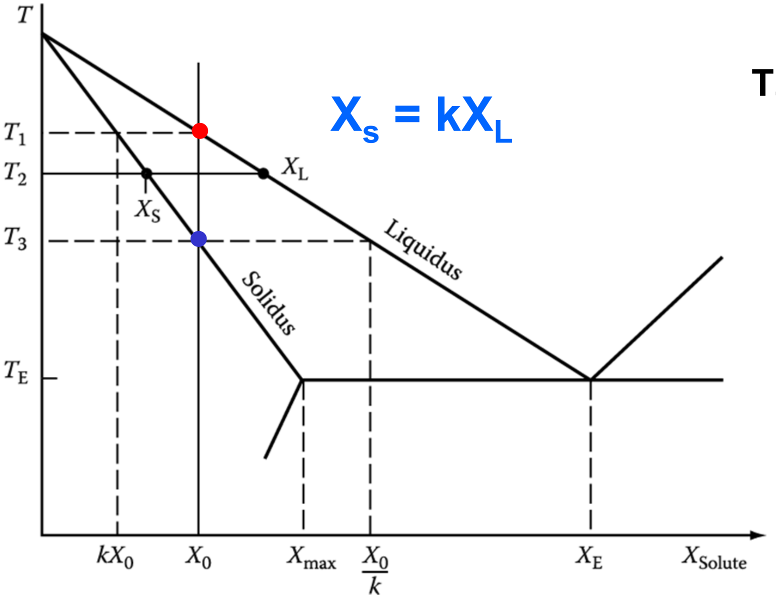


Fig. 4.19 A hypothetical phase diagram.

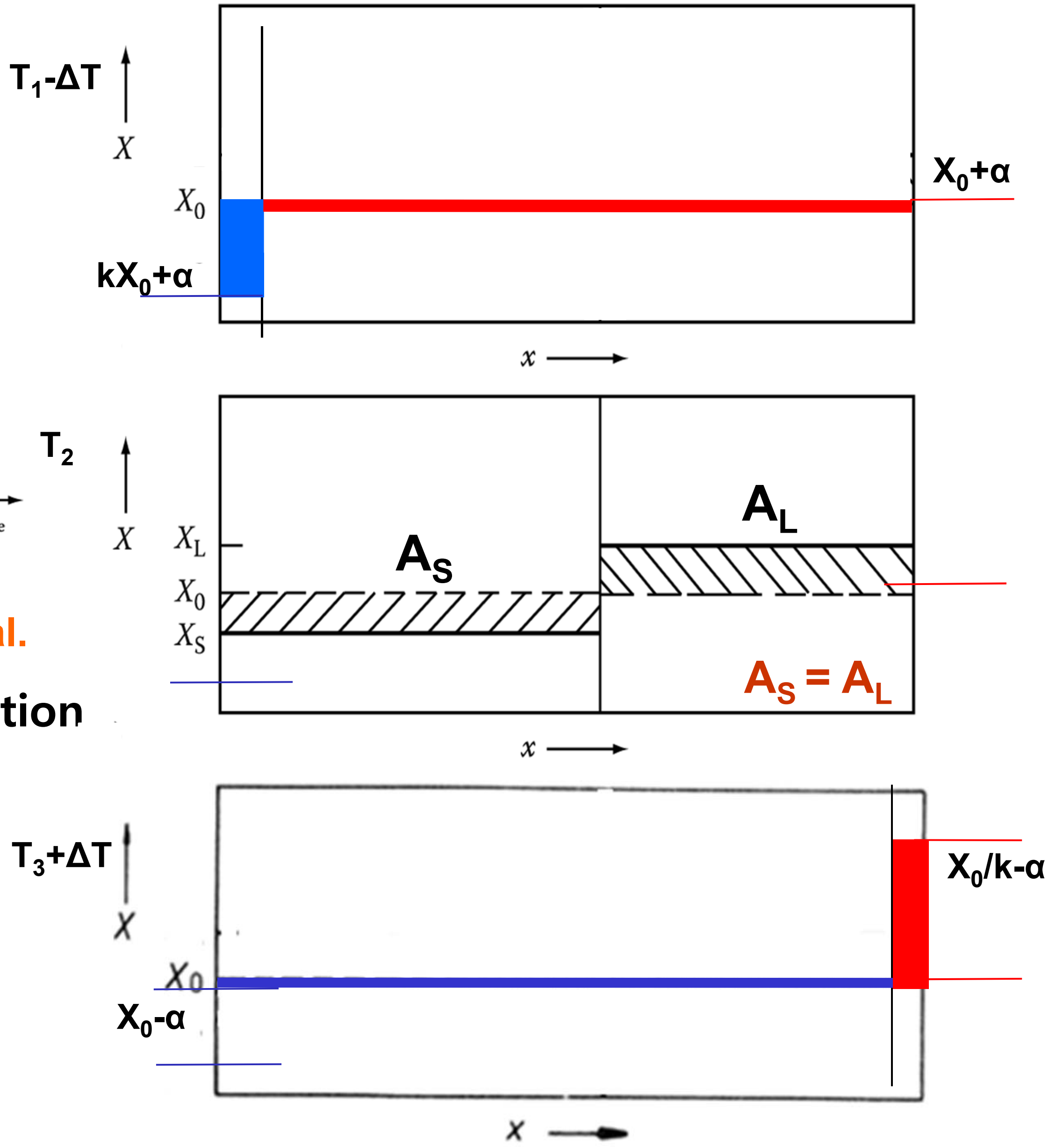
k = X_S/X_L is constant.

- Sufficient time for diffusion in solid & liquid
- Relative amount of solid and liquid : lever rule
- Solidification starts at T_1 ($X_s = kX_0$) and ends at T_3 ($X_L = X_0/k$).

1) Equilibrium Solidification : perfect mixing in solid and liquid



$X_s = kX_L$



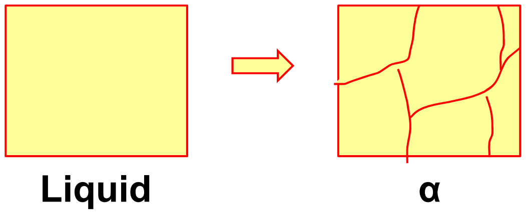
$A_S = A_L$

Conservation of solute requires the two shaded areas to be equal.

* Equilibrium solute concentration

$kX_0 \leq X_s \leq X_0$

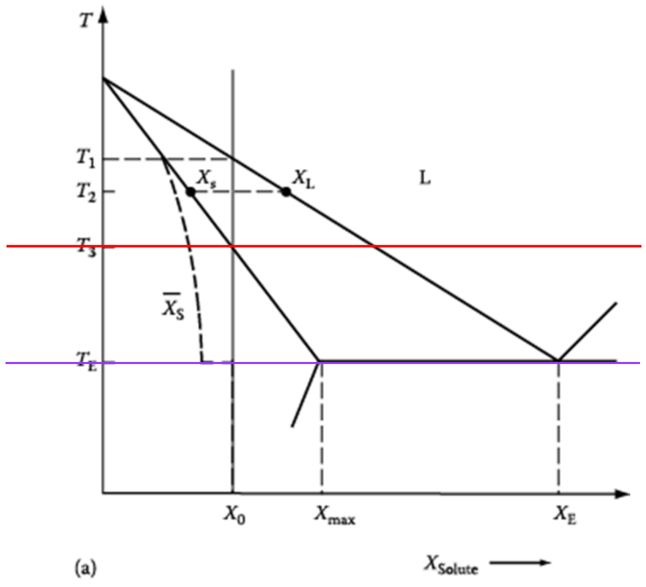
$X_0 \leq X_L \leq X_0/k < X_E$



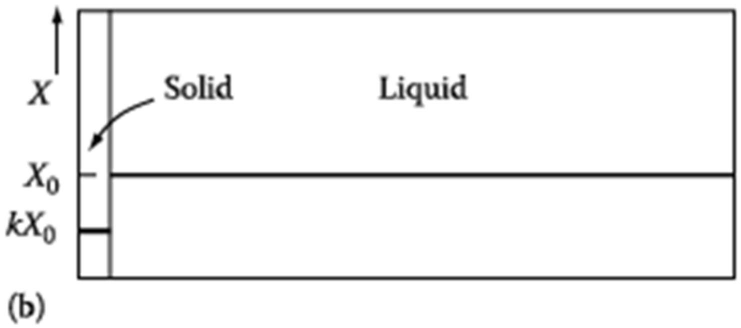
2) No Diffusion in Solid, Perfect Mixing in Liquid

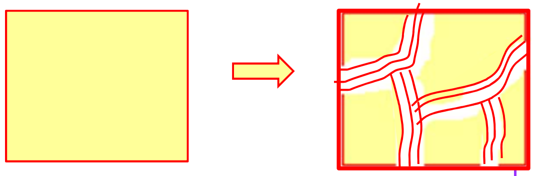
: high cooling rate, efficient stirring

- **Separate layers of solid retain their original compositions**
- **mean comp. of the solid ($\overline{X}_S$) < X_s**



T_1-ΔT

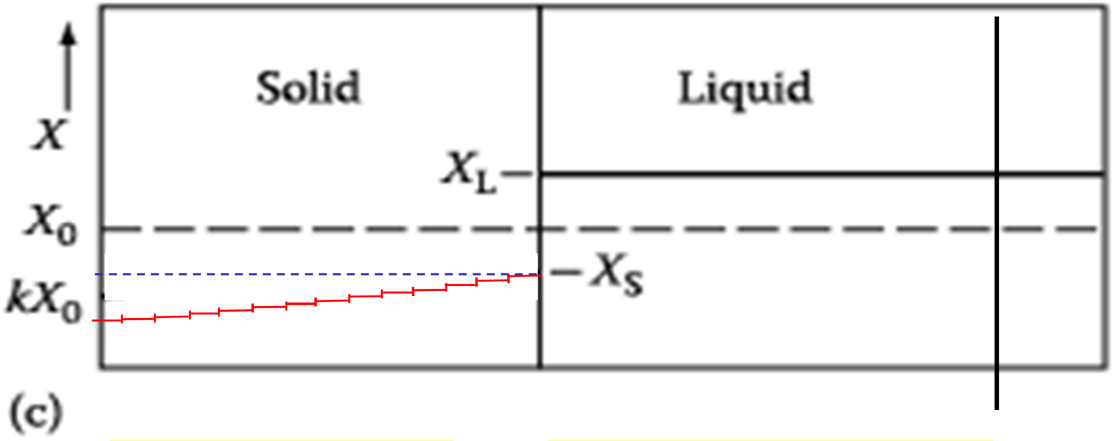


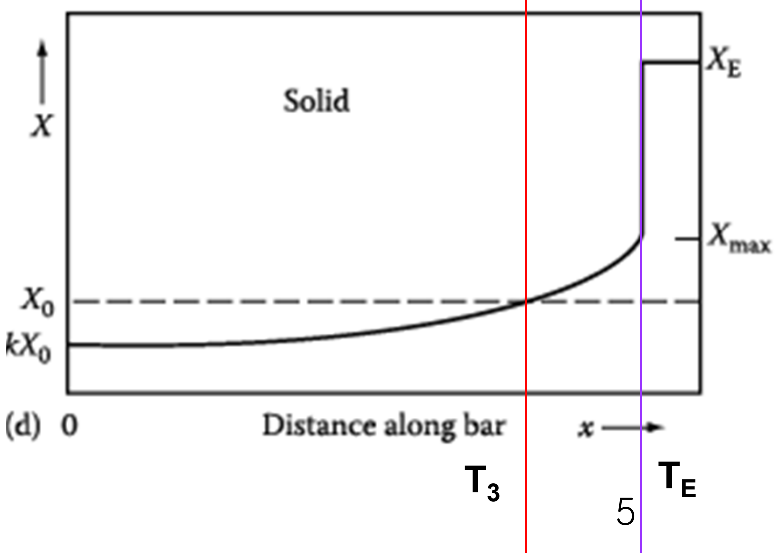


Liquid

Primary α + Eutectic

T_2





$solid \rightarrow \overline{x}_s < x_s$

$liquid > X_0/k \rightarrow X_E$

$$\int_0^{f_S} \frac{df_S}{1-f_S} = \int_{X_0}^{X_L} \frac{dX_L}{X_L - X_S} = \int_{X_0}^{X_L} \frac{dX_L}{X_L - kX_L} = \int_{X_0}^{X_L} \frac{dX_L}{X_L(1-k)}$$

$$\int_0^{f_S} (1-k)(-1)d\ln(1-f_S) = \int_{X_O}^{X_L} d\ln X_L$$

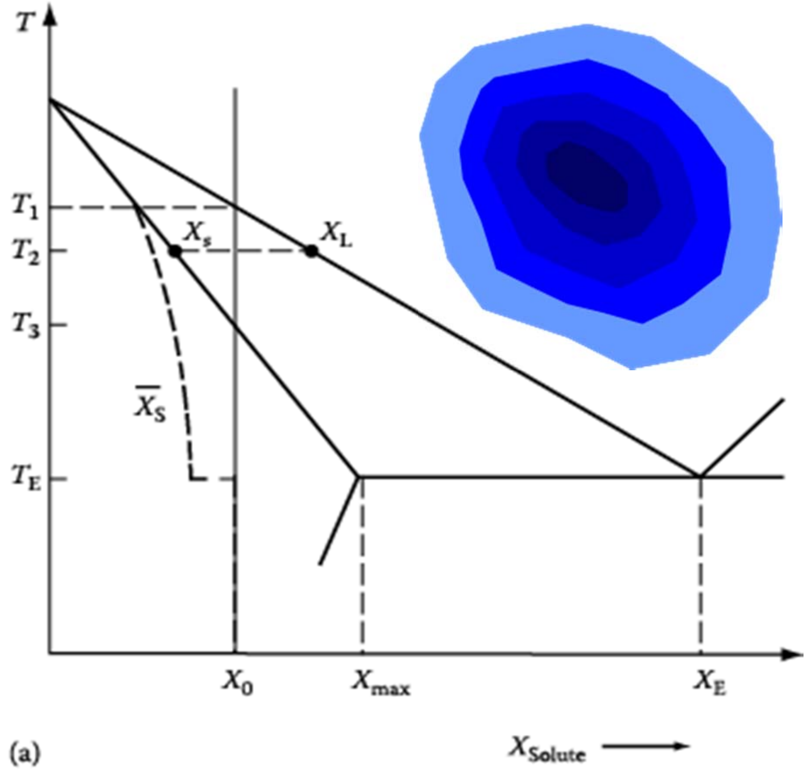
$$\ln\frac{X_L}{X_O} = (k-1)\ln(1-f_S)$$

$$\therefore X_L = X_O f_L^{(k-1)}$$

$X_s = kX_L$

$$X_S = kX_O(1-f_S)^{(k-1)}$$

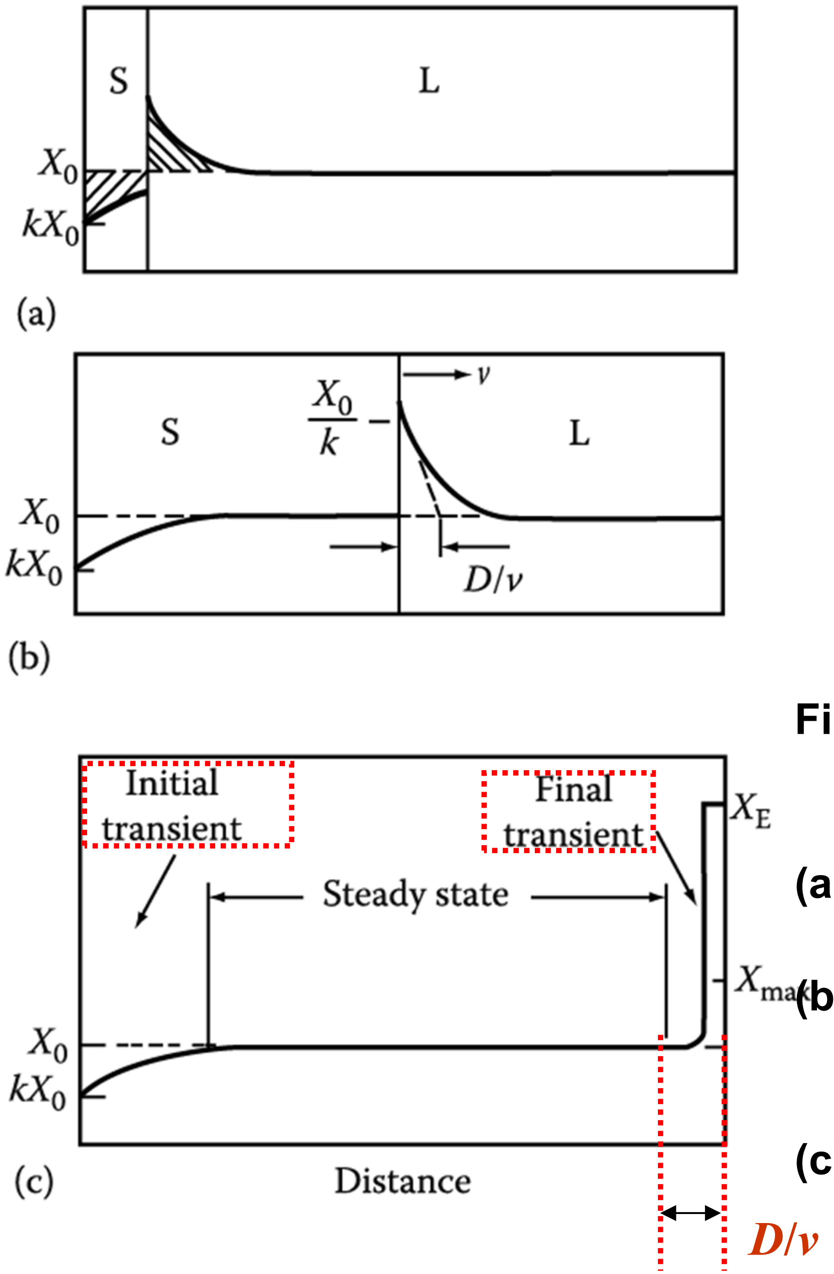
: non-equilibrium lever rule (Scheil equation)



→ **quite generally applicable even for nonplanar solid/liquid interfaces provided here, the liquid composition is uniform and that the Gibbs-Thomson effect is negligible.**

"If k<1: predicts that if no diff. in solid, some eutectic always exist to solidify."
($X_s < X_L$)

No Diffusion on Solid, Diffusional Mixing in the Liquid



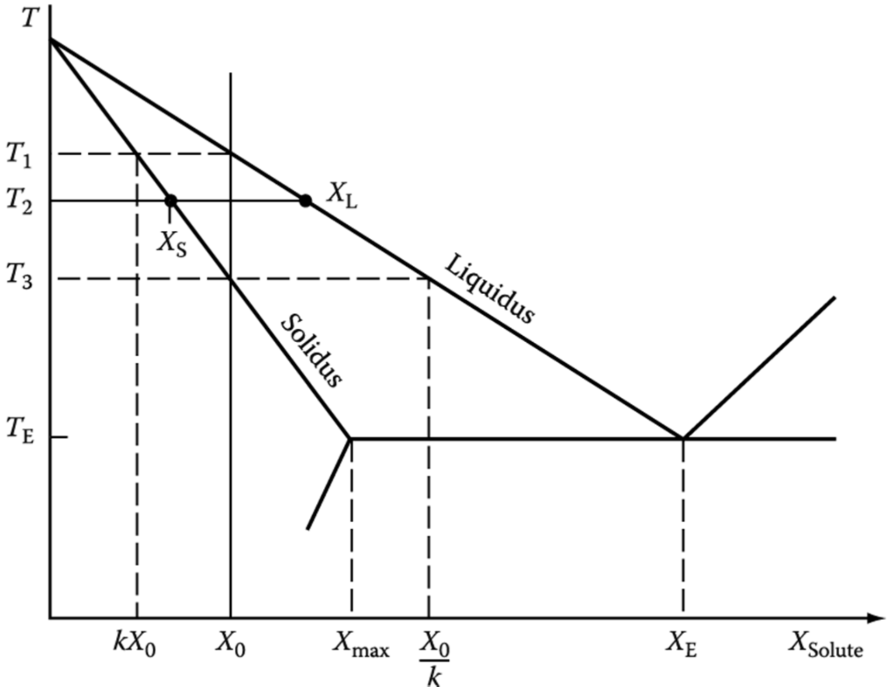


Fig. 4.22 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in solid and no stirring in the liquid.

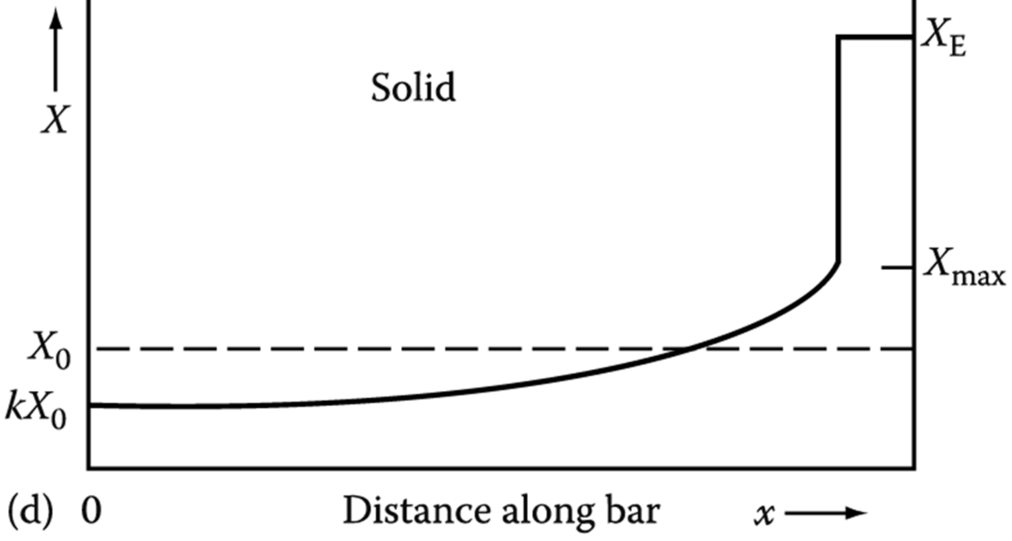
(a) Composition profile when S/L temperature is between T_2 and T_3 in Fig. 4.19.

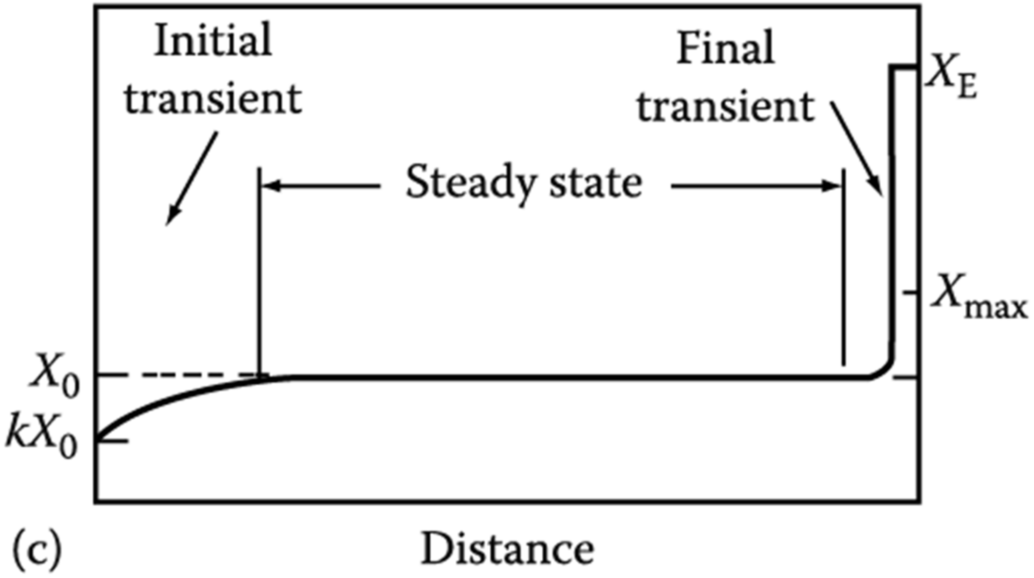
(b) Steady-state at T_3. The composition solidifying equals the composition of liquid far ahead of the solid (X_0).

(c) Composition profile at T_E and below, showing the final transient.

Concentration profiles in practice

: exhibit features between two cases



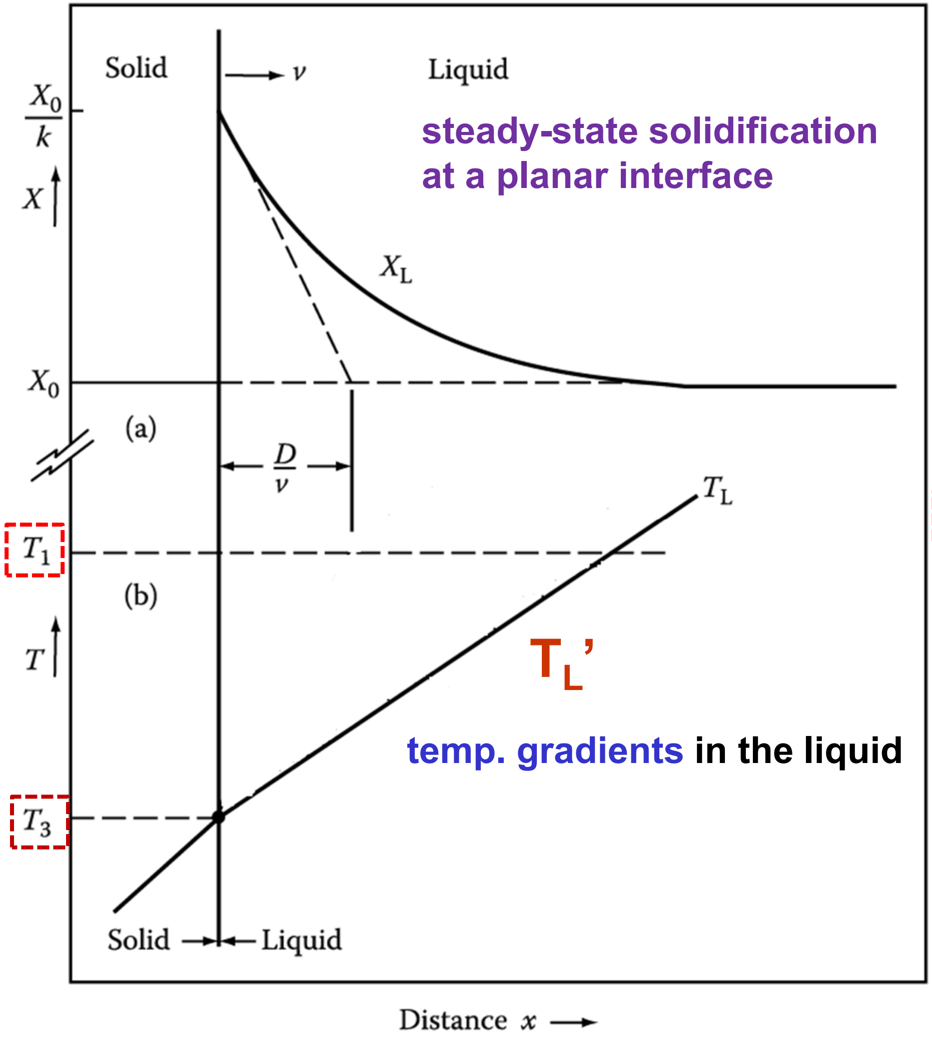


➡ **Zone Refining**

2. Cellular and Dendritic Solidification

Fast Solute diffusion similar to the conduction of latent heat in pure metal, possible to break up the planar front into dendrites.

→ complicated, however, by the possibility of temp. gradients in the liquid.

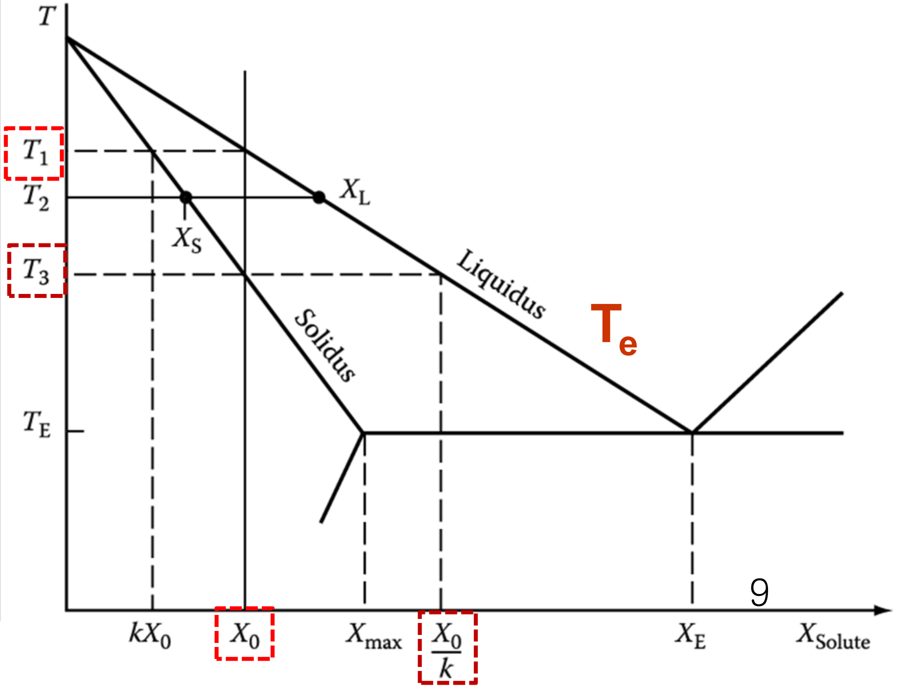


steady-state solidification at a planar interface

T_L'

temp. gradients in the liquid

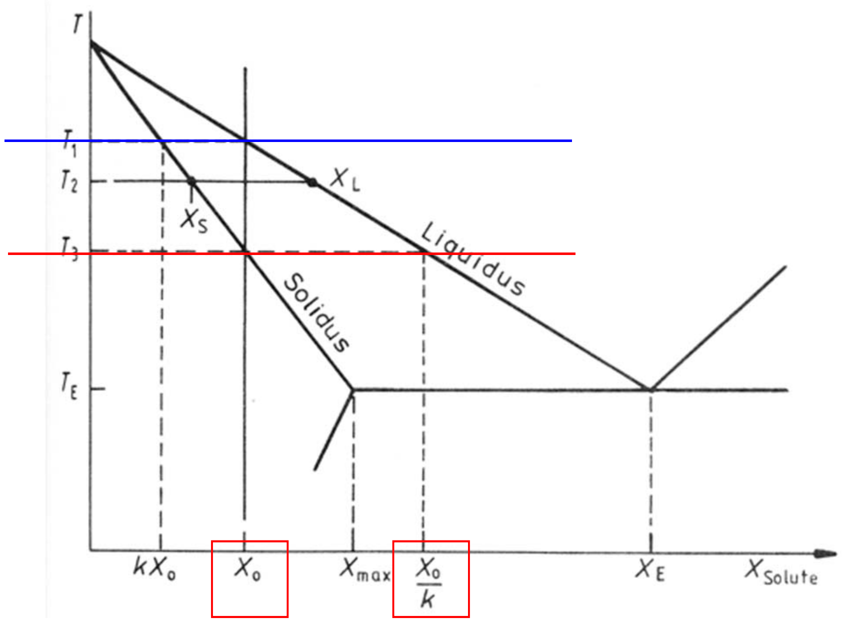
What would be T_e along the concentration profile ahead of the growth front during steady-state solidification?



T_e

* Constitutional Supercooling

**No Diffusion on Solid,
Diffusional Mixing in the Liquid** ➡ **Steady State**

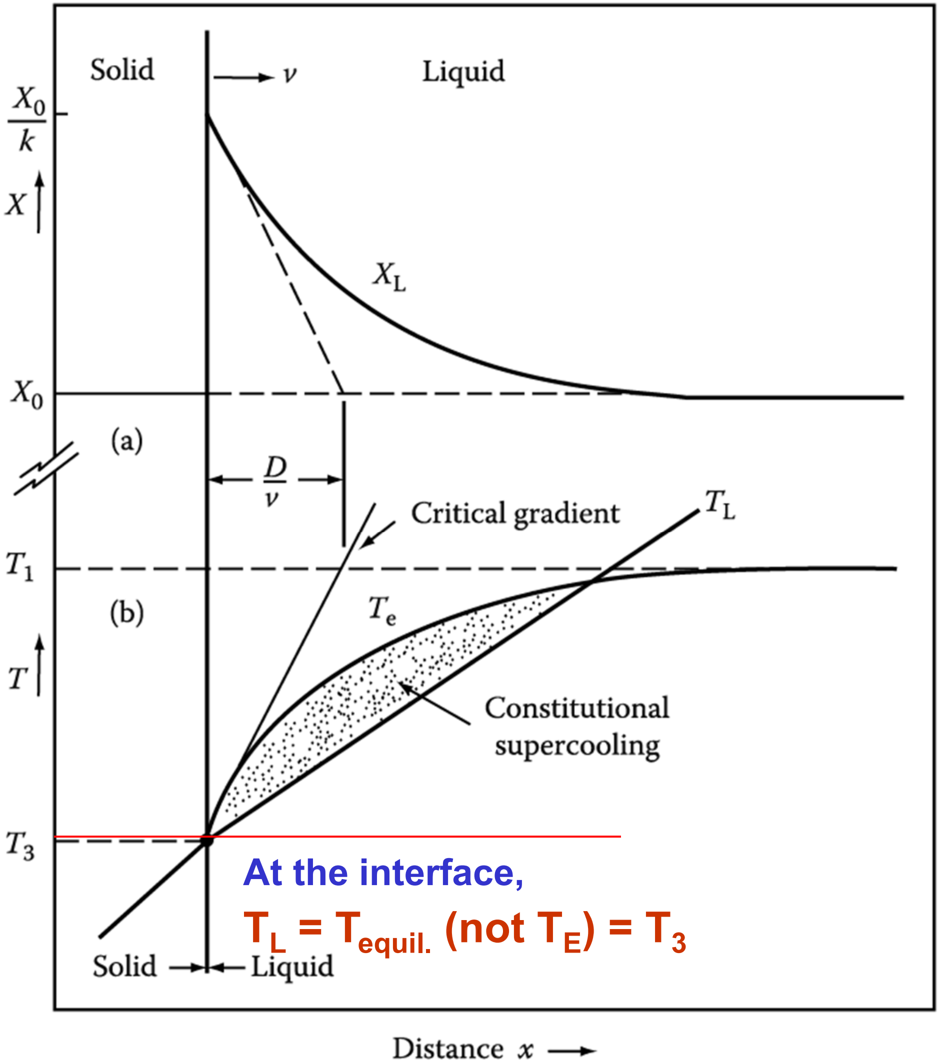


*** Actual temperature gradient in Liquid**

T_L'

*** equilibrium solidification temp. change**

$T_{equil.}$



At the interface,

$T_L = T_{equil.}$ (not T_E) $= T_3$

$T_L' > (T_1-T_3)/(D/v)$: **the protrusion melts back** ➡ **Planar interface: stable**

$T_L'/v < (T_1-T_3)/D$: **Constitutional supercooling→ cellular/ dendritic growth**

Solidification of Pure Metal : Thermal gradient dominant

⇕

Solidification of single phase alloy: Solute redistribution dominant

a) Constitutional supercooling

Planar → Cellular growth → cellular dendritic growth → Free dendritic growth

Cellular growth: 응고계면에 조성적 과냉의 thin zone 형성에 의함
Dome 형태 선단 / 주변에 hexagonal array

cellular dendritic growth: T↓ → 조성적 과냉영역 증가
Cell 선단의 피라미드형상/ 가지들의 square array/ Dendrite 성장방향쪽으로 성장방향 변화

Free dendritic growth: 성장하는 crystal로 부터 발생한 잠열을 과냉각 액상쪽으로 방출함에 의해 형성
Dendrite 성장 방향/ Branched rod-type dendrite

→ "Nucleation of new crystal in liquid"

성장이 일어나는 interface 보다 높은 온도

b) Segregation

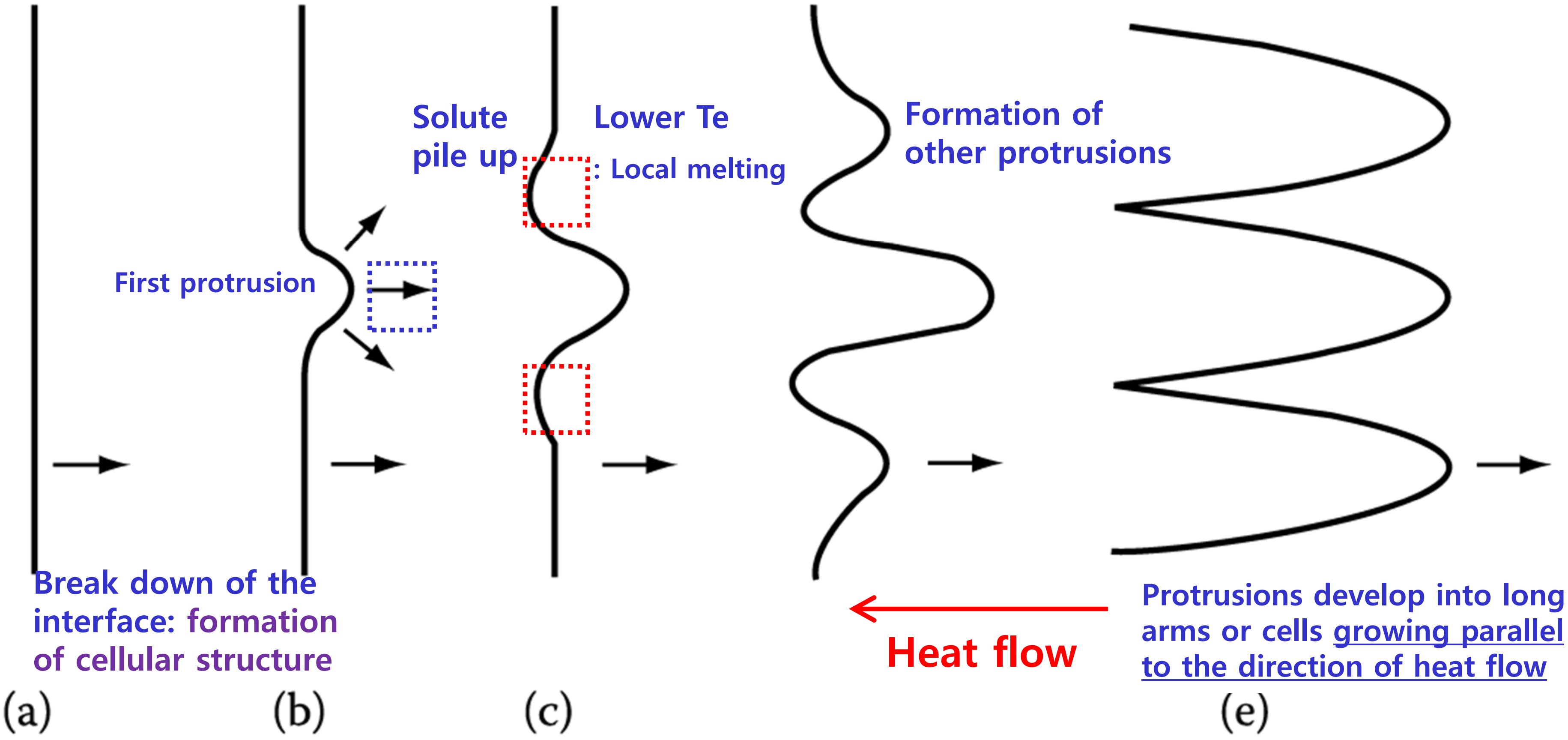
: normal segregation, grain boundary segregation, cellular segregation, dendritic segregation, inversegregation, coring and intercrystalline segregation, gravity segregation

Q: Planer → Cell structure → Dendrite?

by constitutional supercooling in superheated liquid

Cellular Solidification: formation by constitutional supercooling in "superheated liquid"

If temperature gradient ahead of an initially planar interface is gradually reduced below the critical value, (constitutional supercooling at solid/liquid interface)



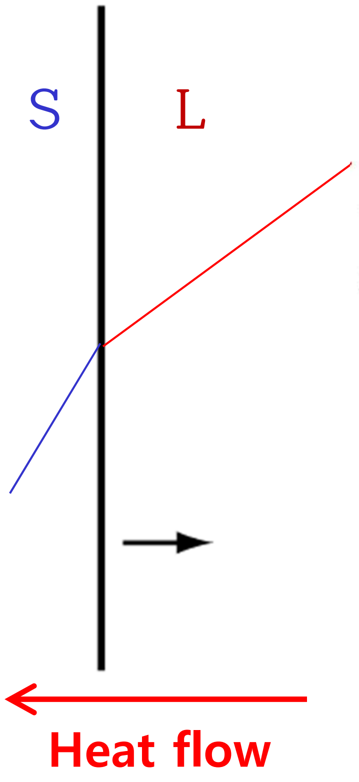
Break down of the interface: formation of cellular structure

Protrusions develop into long arms or cells growing parallel to the direction of heat flow

Fig. 4.24 The breakdown of an initially planar solidification front into cells

Cellular Solidification: formation by constitutional supercooling in "superheated liquid"

If temperature gradient ahead of an initially planar interface is gradually reduced below the critical value, (constitutional supercooling at solid/liquid interface)



(a)

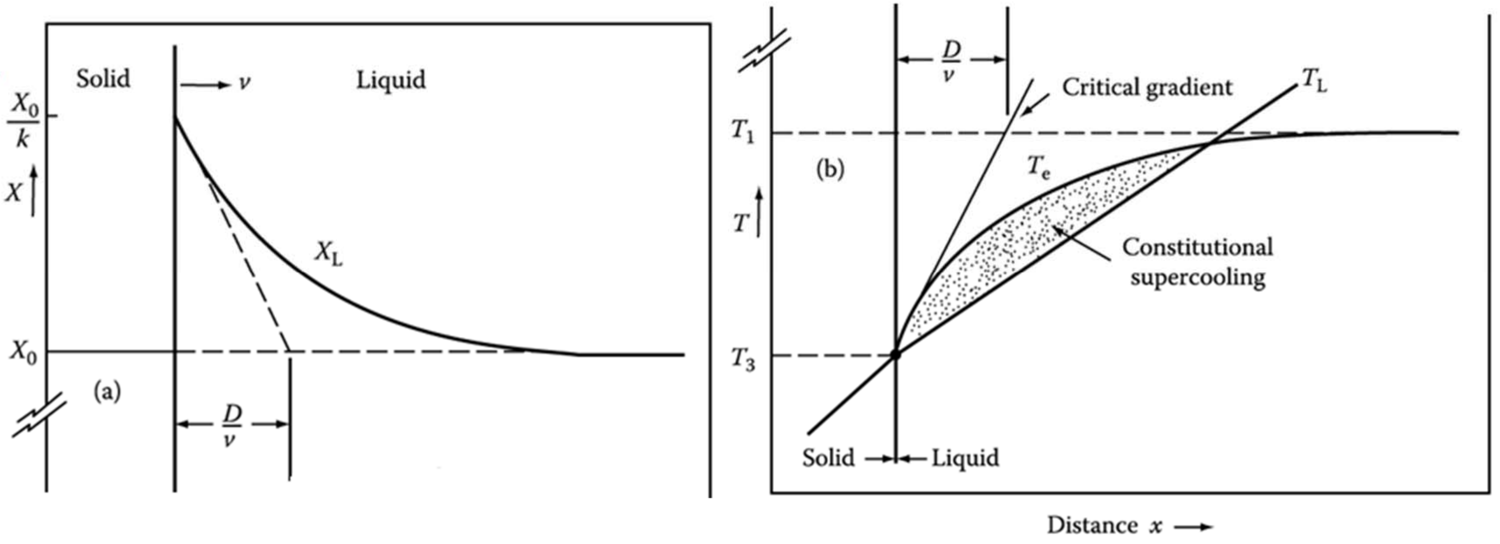
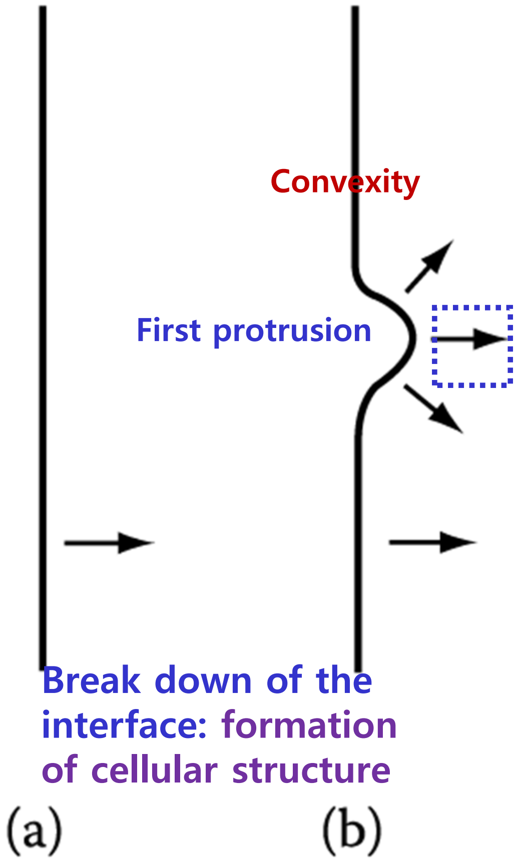


Fig. 5.30. Supercooling ahead of planar interface

<The breakdown of an initially planar solidification front into cells>

Cellular Solidification: formation by constitutional supercooling in “superheated liquid”

If temperature gradient ahead of an initially planar interface is gradually reduced below the critical value, (constitutional supercooling at solid/liquid interface)



Break down of the interface: formation of cellular structure

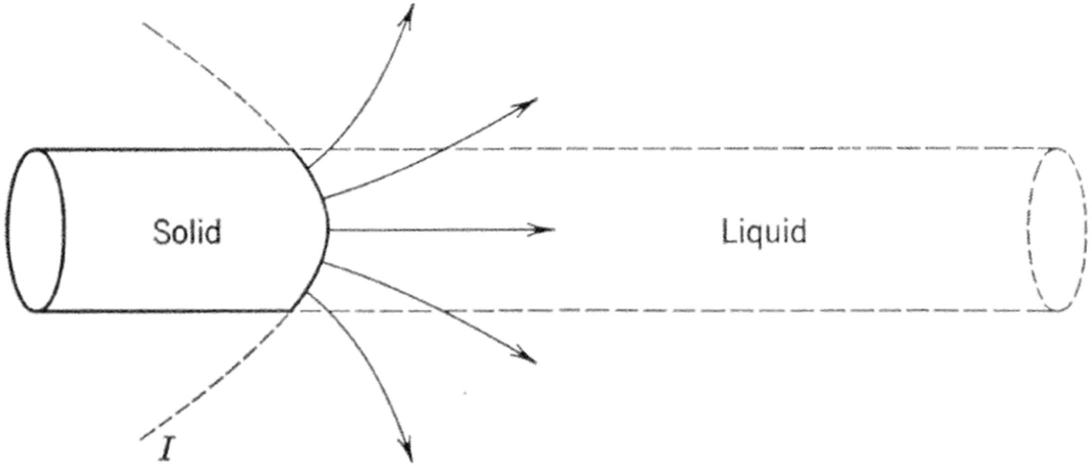


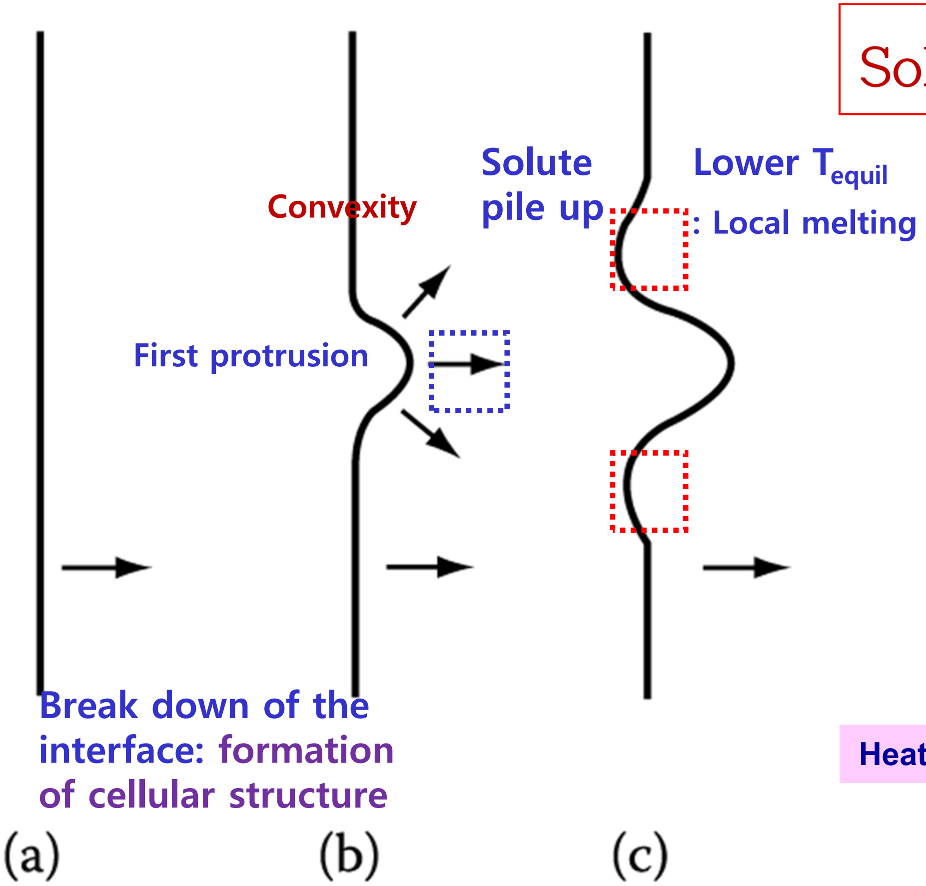
Fig. 5.14. Solute diffusion ahead of a convex interface

<The breakdown of an initially planar solidification front into cells>

Cellular Solidification: formation by constitutional supercooling in “superheated liquid”

If temperature gradient ahead of an initially planar interface is gradually reduced below the critical value, (constitutional supercooling at solid/liquid interface)

Solute pile up→ T_e ↓ → T_L' ↑ → v ↓



Convexity

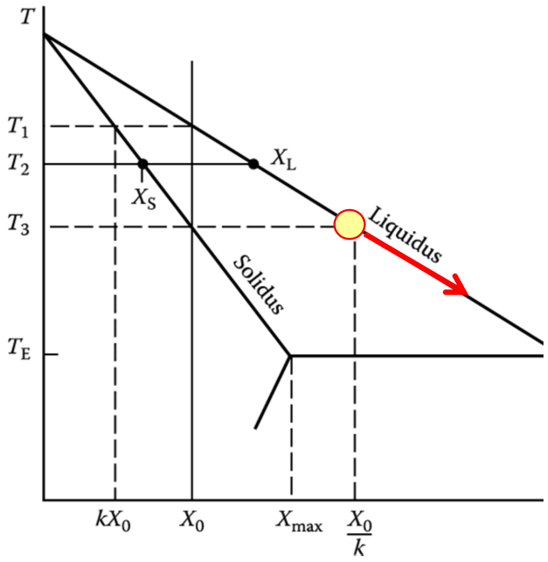
First protrusion

Solute pile up

Lower T_{equil} : Local melting

Break down of the interface: formation of cellular structure

<The breakdown of an initially planar solidification front into cells>



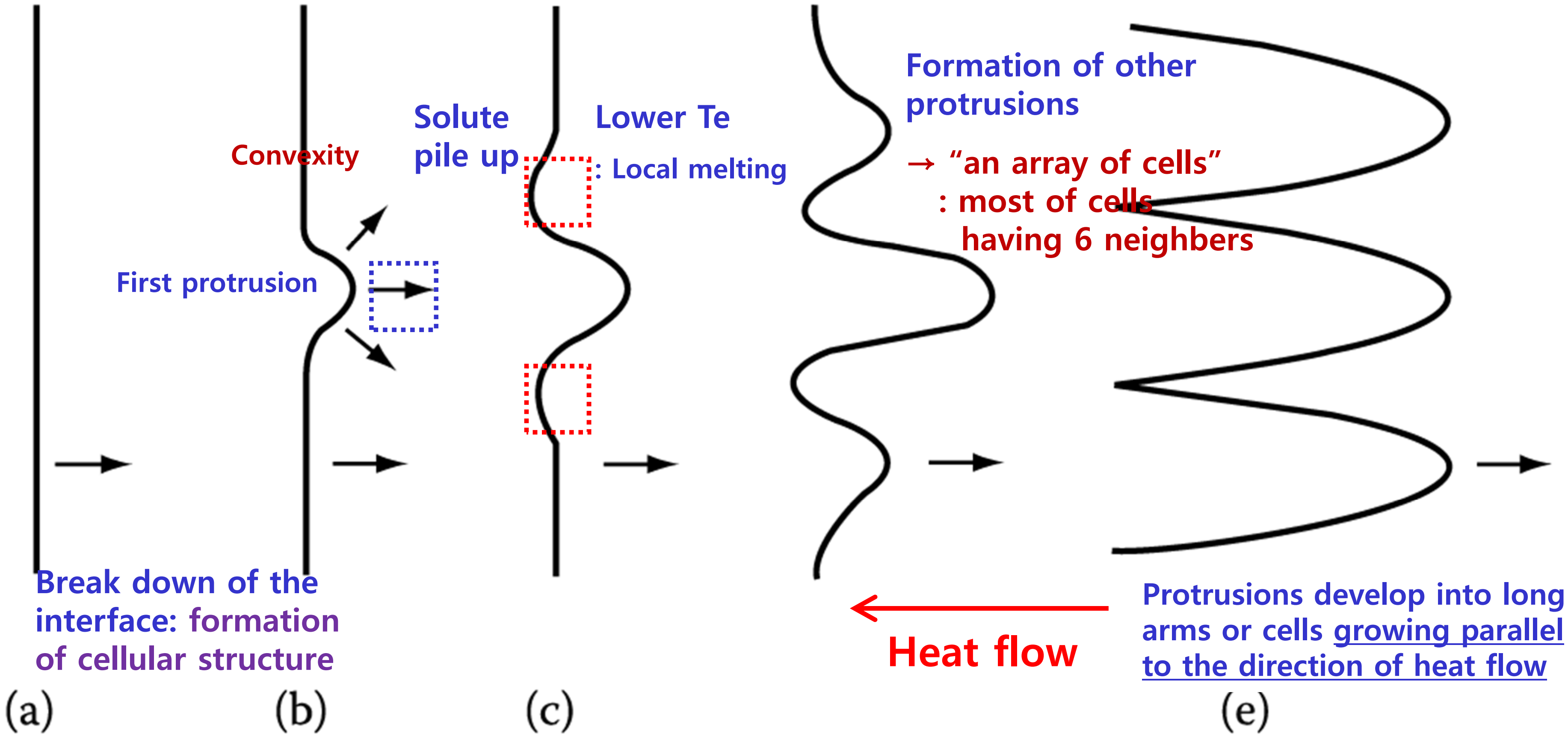
Heat Balance Equation

$$K_S T_S' = K_L T_L' + vL_V$$

K: thermal conductivity

Cellular Solidification: formation by constitutional supercooling in “superheated liquid”

If temperature gradient ahead of an initially planar interface is gradually reduced below the critical value, (constitutional supercooling at solid/liquid interface)



Convexity

First protrusion

Solute pile up

Lower Te : Local melting

Formation of other protrusions

→ “an array of cells” : most of cells having 6 neighbors

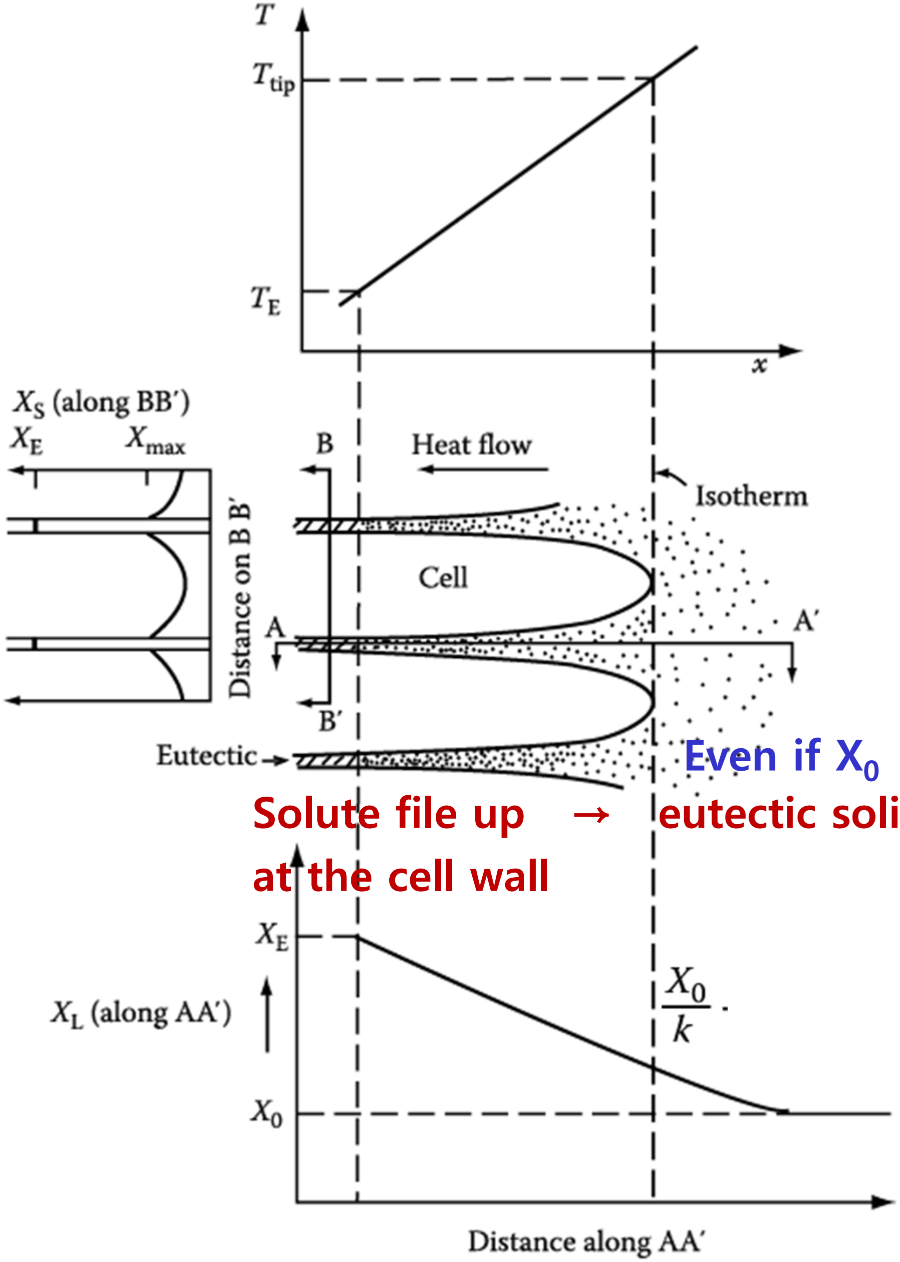
Break down of the interface: formation of cellular structure

Heat flow

Protrusions develop into long arms or cells growing parallel to the direction of heat flow

<The breakdown of an initially planar solidification front into cells>

Tips of the cells grow into the hottest liquid and therefore contain the least solute.



Even if $X_0 << X_{max}$

Solute file up → eutectic solidification → formation of 2nd phases
at the cell wall

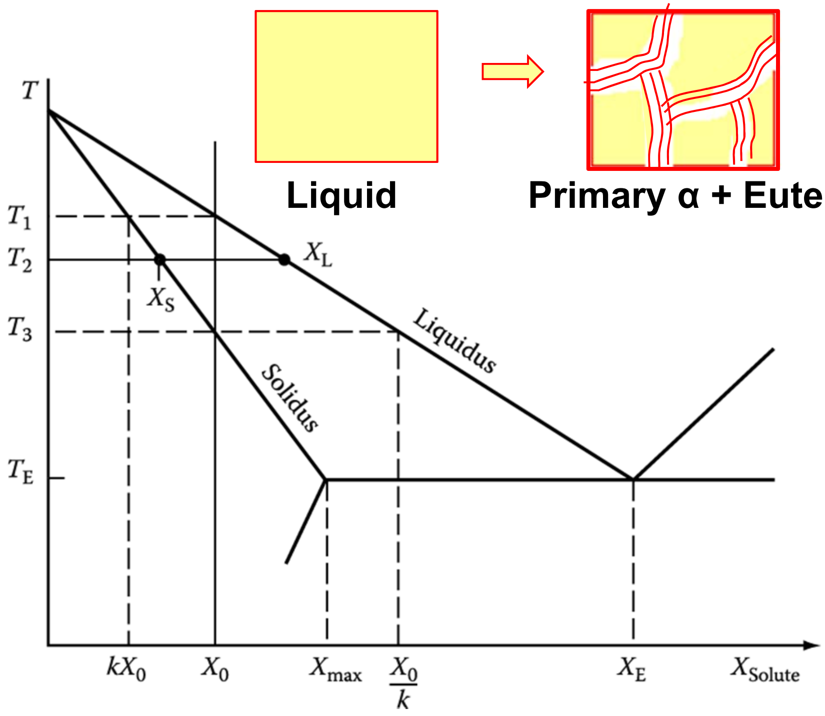
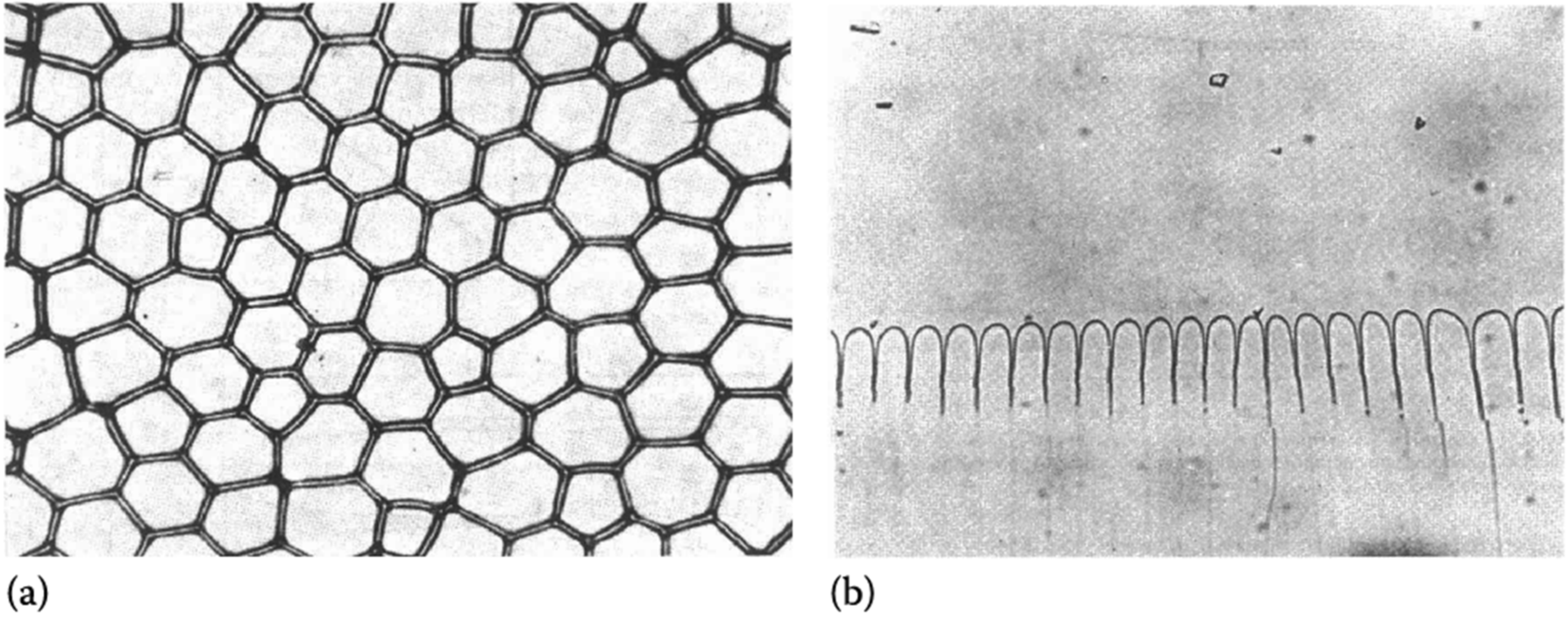


Fig. 4.25 **Temperature and solute distributions associated with cellular solidification. Note that solute enrichment in the liquid between the cells, and coring in the cells with eutectic in the cell walls.**



*** Cellular microstructures**

Note that each cell has virtually the same orientation as its neighbors and together they form a single grain.

(a) A decanted interface of a cellularly solidified Pb-Sn alloy (x 120)

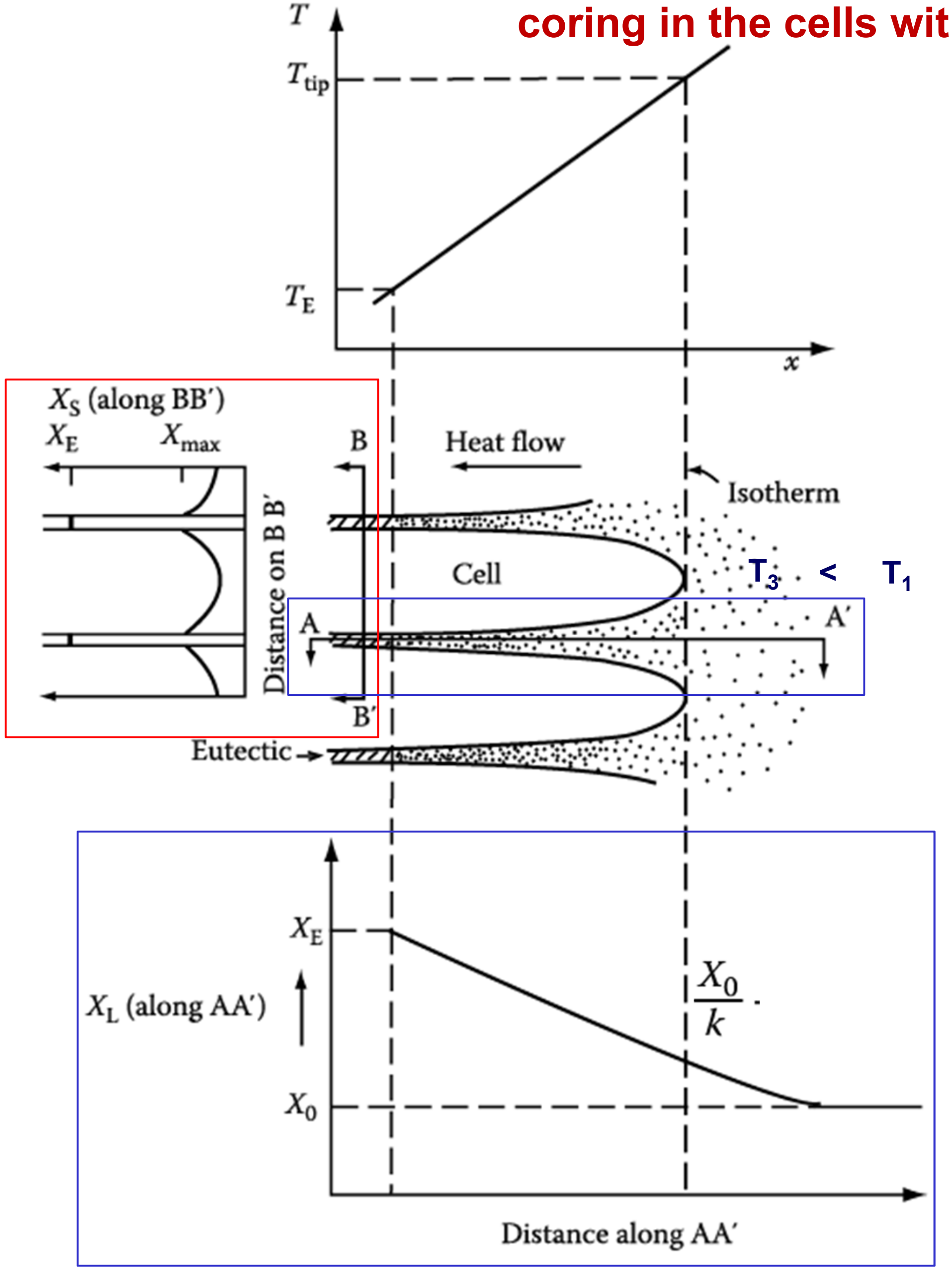
(after J.W. Rutter in Liquid Metals and Solidification, American Society for Metals, 1958, p. 243).

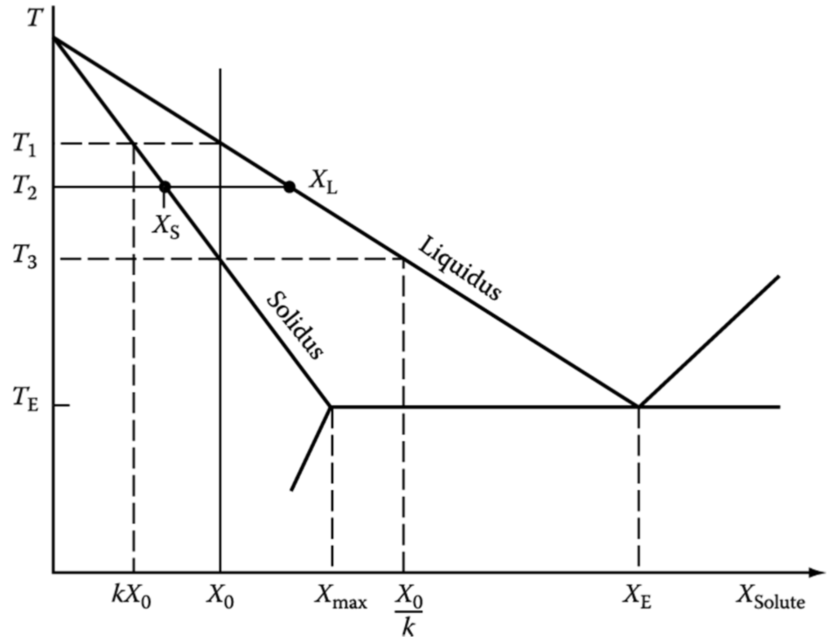
(b) Longitudinal view of cells in carbon tetrabromide (x 100)

(after K.A. Jackson and J.D. Hunt, Acta Metallurgica 13 (1965) 1212).

* Temp. and solute distributions associated with cellular solidification.

1) Note that solute enrichment in the liquid between the cells, and coring in the cells with eutectic in the cell walls.





2) Tips of the cells grow into the hottest liquid and therefore contain the least solute.

3) Even if $X_0 << X_{max}$

Solute file up → eutectic solidification

→ formation of 2nd phases at the cell wall

The change in morphology from cells to dendrites

* Cellular microstructures are only stable for a certain range of temp. gradients.

→ Sufficiently low temp. gradients → **Creation of constitutional supercooling in the liquid between the cells causing interface instabilities in the transverse direction (although, No temp. gradient perpendicular to the growth direction)**

→ Develop arms, i.e. dendrites form & Change in the direction of the primary arms away from the direction of heat flow into the crystallographically preferred directions i.e. (100) for cubic metals.

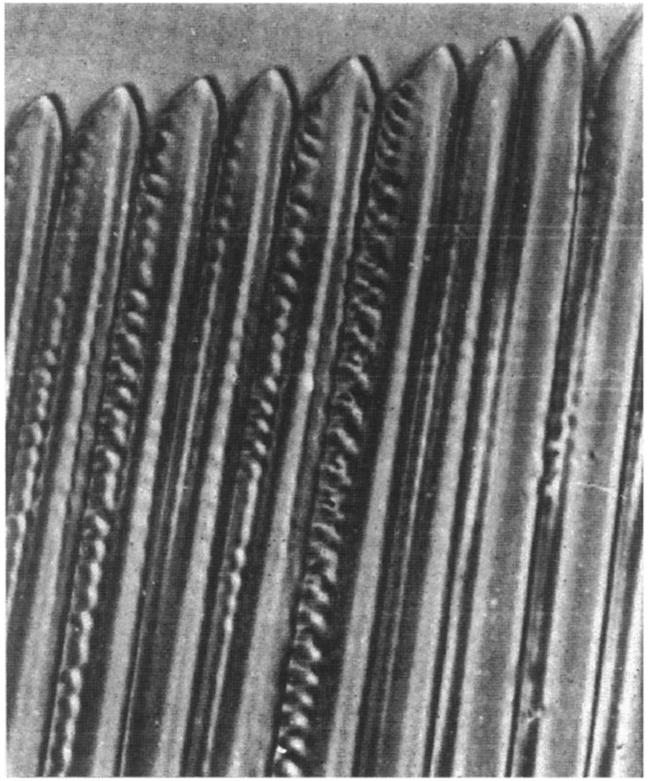


Fig. 4.27 Cellular dendrites in carbon tetrabromide.

(After L.R. Morris and W.C. Winegard, Journal of Crystal Growth 6 (1969) 61.)

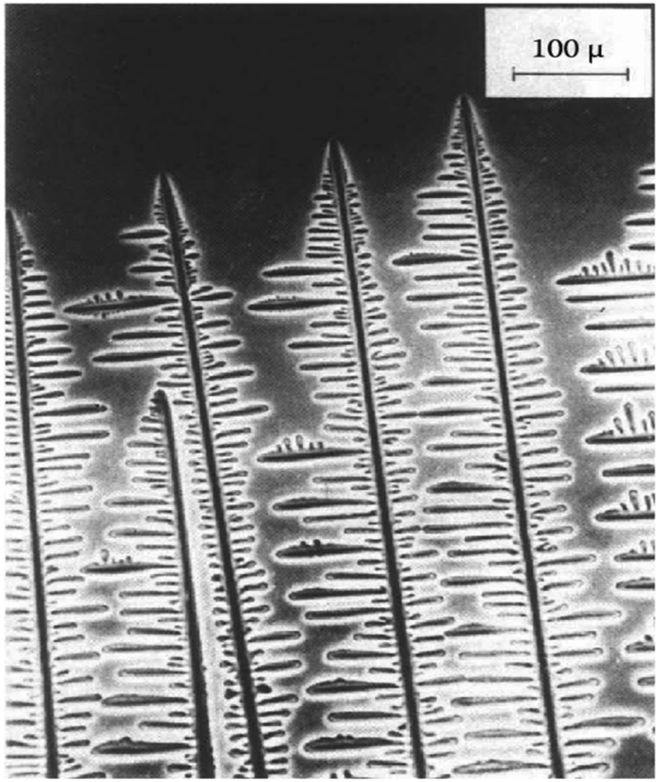


Fig. 4.28 Columnar dendrites in a transparent organic alloy.

(After K.A. Jackson in Solidification, American Society for Metals, 1971, p. 121.)

Cellular and Dendritic Solidification

At the interface, $T_L = T_e$ (not T_E) $= T_3 \rightarrow T_{L,\ liquid} = T_1 : T' = T_1 - T_3$ (superheating)

- **Criterion for the stable planar interface:**

$T_L' > (T_1-T_3)/(D/v)$: the protrusion melts back_steeper than the critical gradient

$T_L'/v > (T_1-T_3)/D$ (T_1-T_3 : Equilibrium freezing range of alloy)

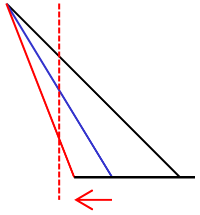
⟶ **Large solidification range of T_1-T_3 or high v promotes protrusions.**

⇨ **need to well-controlled experimental conditions (temp. gradient & growth rate)**

- **Constitutional supercooling:** **$T_L'/v < (T_1-T_3)/D$**

➡ **Formation of Cell and Dendrites Structures**

Solute effect : addition of a very small fraction of a percent solute with very small k ($k = \frac{X_S}{X_L}$) → (T_1-T_3) ↑ promotes dendrites.



Cooling rate effect : Higher cooling rate allow less time for lateral diffusion of the rejected solute and therefore require smaller cell or dendrite arm spacings to avoid constitutional supercooling.

Solidification of Pure Metal : Thermal gradient dominant

⇕

Solidification of single phase alloy: Solute redistribution dominant

a) Constitutional supercooling

Planar → Cellular growth → cellular dendritic growth → Free dendritic growth

응고계면에 조성적 과냉의
thin zone 형성에 의함
Dome 형태 선단 / 주변에
hexagonal array

T↓ → 조성적 과냉영역 증가
Cell 선단의 피라미드형상/ 가지
들의 square array/ Dendrite
성장방향쪽으로 성장방향 변화

성장하는 crystal로 부터 발생한 잠
열을 과냉각 액상쪽으로 방출함에
의해 형성
Dendrite 성장 방향/ Branched
rod-type dendrite

→ "Nucleation of new crystal in liquid"

성장이 일어나는 interface 보다 높은 온도

b) Segregation

: normal segregation, grain boundary segregation, cellular segregation, dendritic segregation, inversegregation, coring and intercrystalline segregation, gravity segregation

Q: Various different types of eutectic solidification ($L \rightarrow \alpha + \beta$) ?

4.3.2 Eutectic Solidification: L→α + β

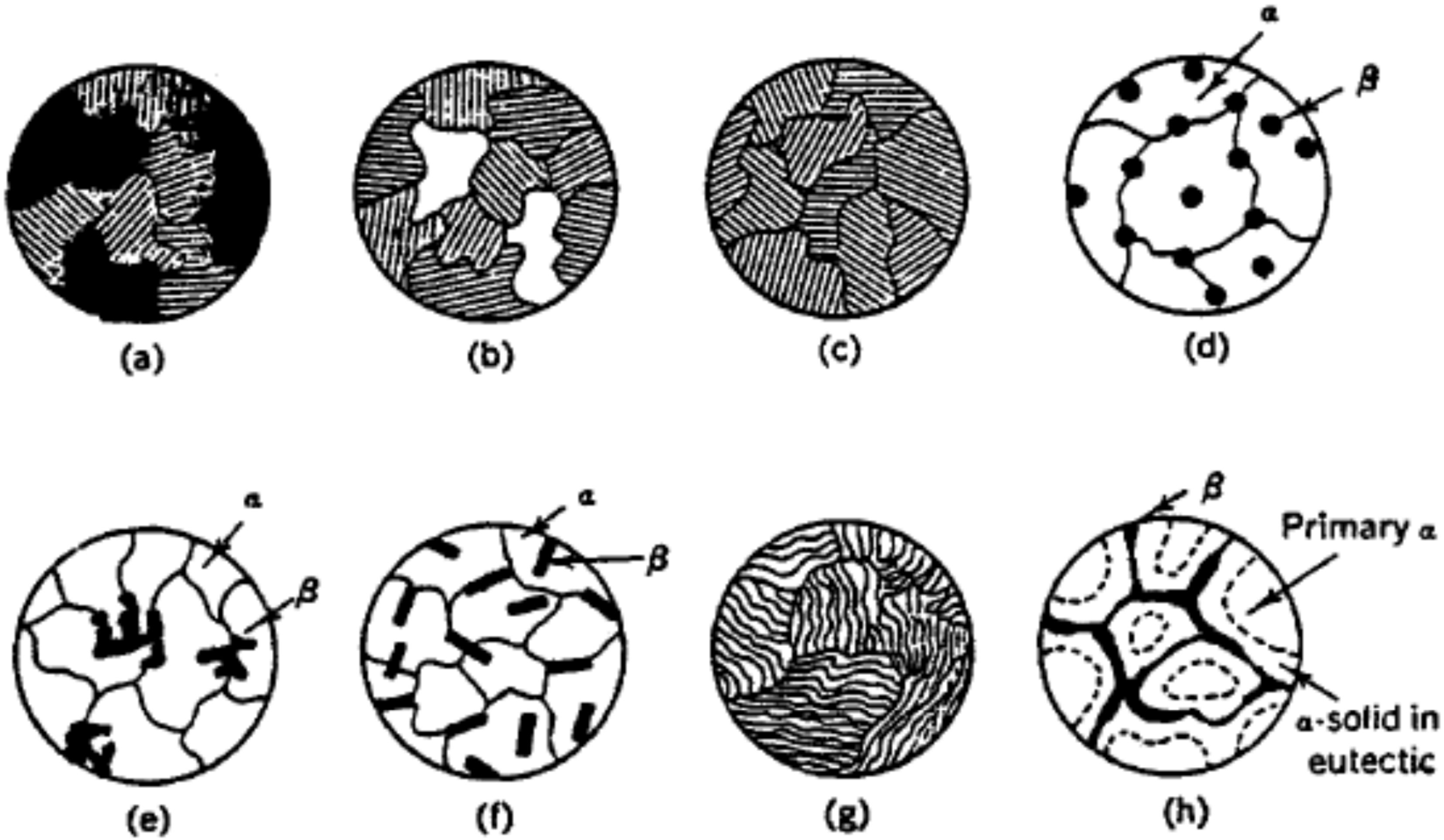


Fig. 14 Schematic representation possible in various eutectic structures. (a), (b) and (c) are alloys shown in fig. 13; (d) nodular; (e) Chinese script; (f) acicular; (g) lamellar; and (h) divorced.

4.3.2 Eutectic Solidification

Various different types of eutectic solidification → Both phases grow simultaneously.

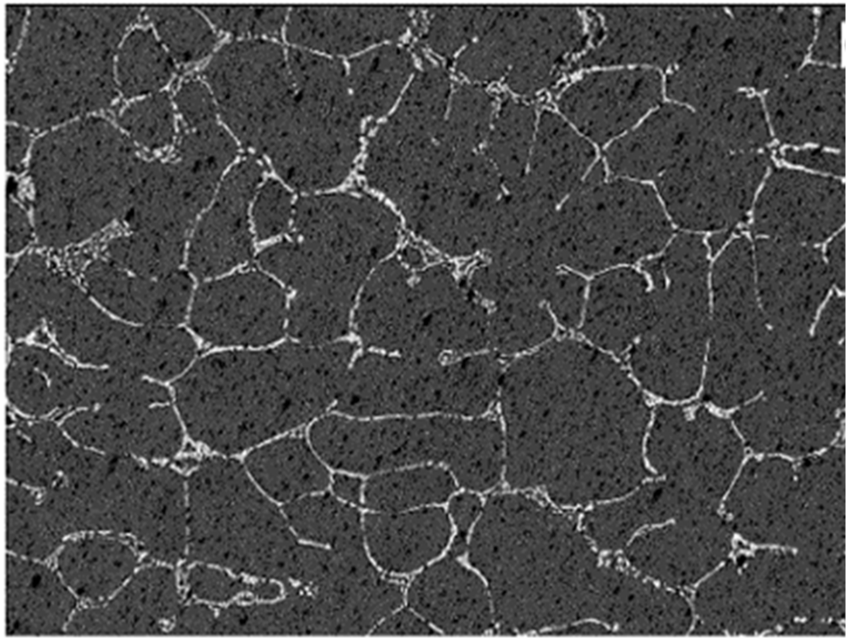
Normal eutectic

both phases have low entropies of fusion.

Fig. 4.30 Rod-like eutectic. Al_6Fe rods in Al matrix. Transverse section. Transmission electron micrograph (x 70000).

Anomalous eutectic

One of the solid phases is capable of faceting, i.e., has a high entropy or melting.

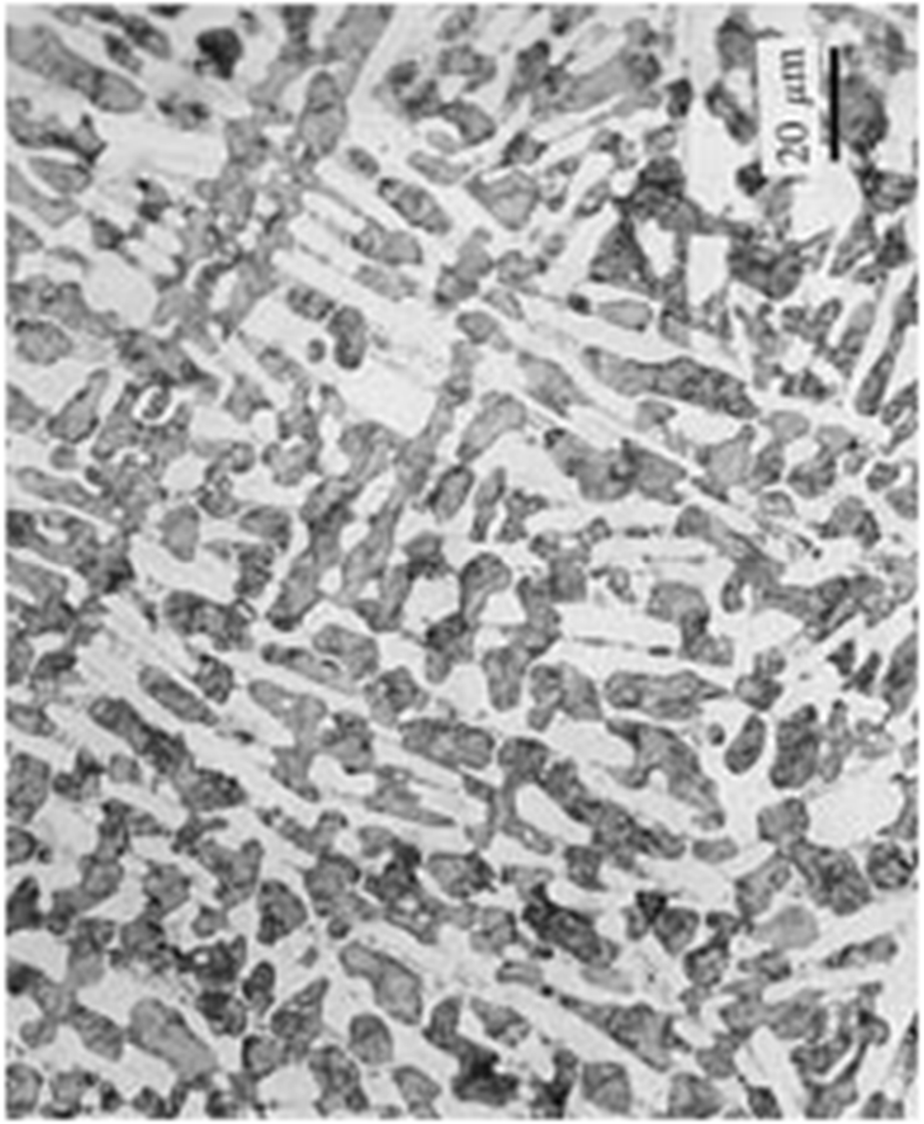


The microstructure of the Pb-61.9%Sn (eutectic) alloy presented a coupled growth of the (Pb)/βSn eutectic. There is a remarkable change in morphology increasing the degree of undercooling with transition from regular lamellar to anomalous eutectic.

http://www.matter.org.uk/solidification/eutectic/anomalous_eutectics.htm

Eutectic

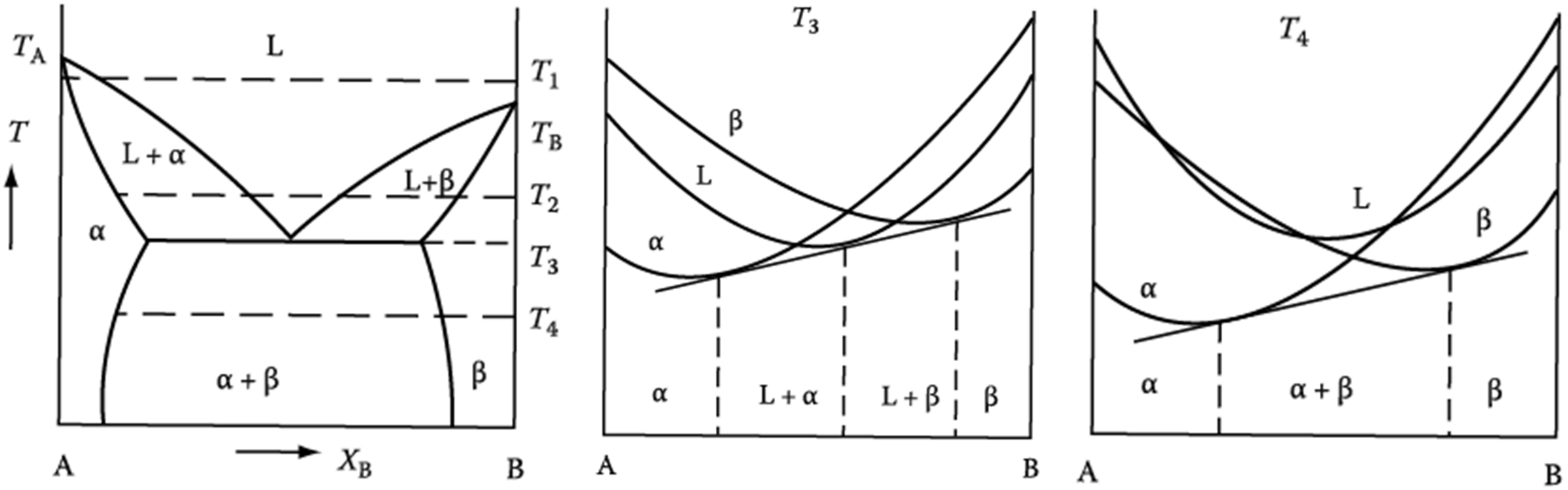
Divorced Eutectic



Q: Thermodynamics and Kinetics of eutectic solidification (L→α + β) ?

This section will only be concerned with normal structures, and deal mainly with lamellar morphologies.

2. Eutectic Solidification (Thermodynamics)



Plot the diagram of Gibbs free energy vs. composition at T_3 and T_4.

What is the driving force for the eutectic reaction (L →α + β) at T_4 at C_{eut}?

What is the driving force for nucleation of α and β? " ΔT "

Eutectic Solidification (Kinetics)

: ΔT→ formation of interface + solute redistribution

If α is nucleated from liquid and starts to grow, what would be the composition at the interface of α/L determined?

→ rough interface (diffusion interface) & local equilibrium

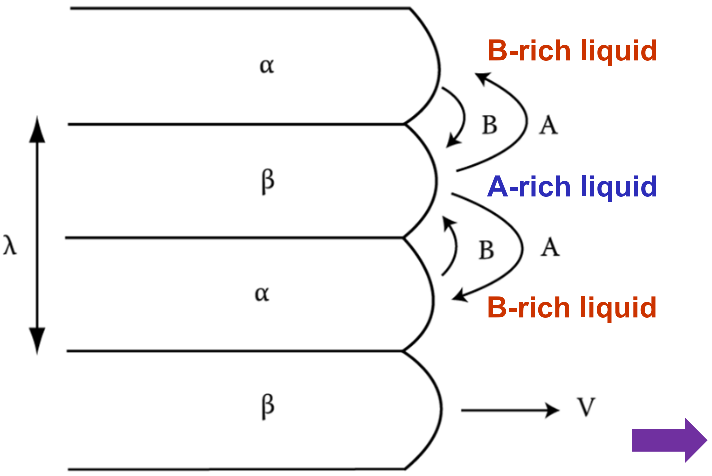
How about at β/L? Nature's choice? Lamellar structure

$$\rightarrow \quad G = G_{bulk} + G_{interface} = G_0 + \gamma A$$

$$\sum A_i\gamma_i + \Delta G_S = minimum$$

Interface energy + Misfit strain energy

interlamellar spacing →



Eutectic solidification

: diffusion controlled process

1) λ ↓→ eutectic growth rate ↑

but 2) λ ↓→ α/β interfacial E, $\gamma_{\alpha\beta}$↑

→ lower limit of λ

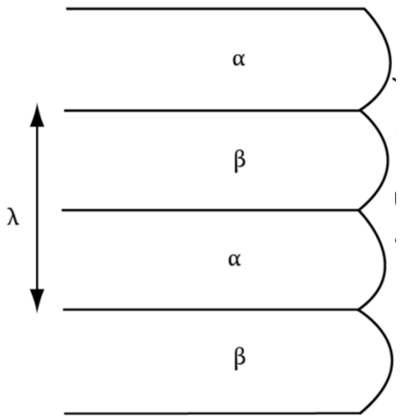
➡ fastest growth rate at a certain λ

What would be a role of the curvature at the tip?

→ Gibbs-Thomson Effect

Eutectic Solidification (Kinetics)

: ΔT→ a) formation of interface + b) solute redistribution



How many α/β interfaces per unit length? $\rightarrow 1/\lambda \times 2$

a) Formation of interface: **ΔG**

For an interlamellar spacing, λ, there is a total of (2/ λ) m^2 of α/β interface per m^3 of eutectic.

$$\Delta G = \Delta\mu \cong \frac{L\Delta T}{T_m} \qquad \rightarrow \Delta G = \Delta\mu = \boxed{\frac{2\gamma}{\lambda}\times V_m}$$

Molar volume

Driving force for nucleation = Total interfacial E of eutectic phase

For very large values of λ, interfacial E~ 0

Total undercooling

$$\lambda \rightarrow \infty\,, \quad \Delta G(\infty) = \Delta\mu = \frac{\Delta H\,\Delta T_0}{T_E}$$

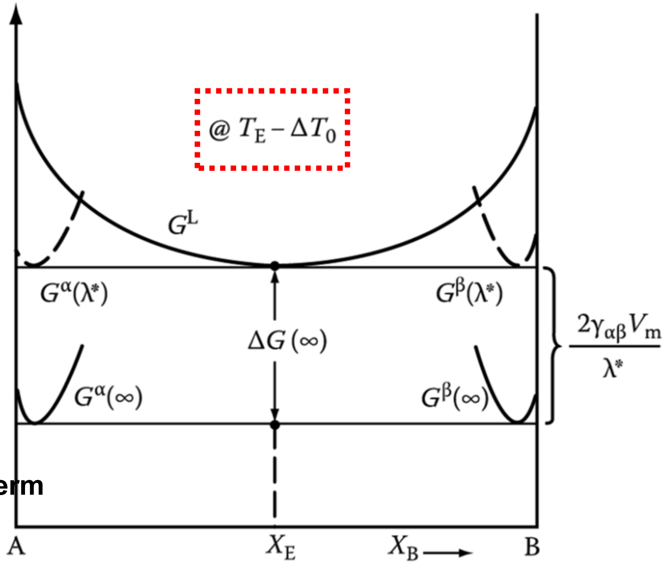
No interface (ideal case)

$$\Delta G(\lambda) = ? = -\Delta G(\infty) + \boxed{\frac{2\gamma V_m}{\lambda}}$$

Interfacial E term

With interface (real case)

Solidification will take place if ΔG is negative (-).



a) All **ΔT→ use for interface formation=** min. **λ**

What would be the minimum λ?

Critical spacing, $\lambda^* : \Delta G(\lambda^*) = 0$

최소 층상 간격

$$\Delta G(\infty) = \frac{2\gamma V_m}{\lambda^*} \qquad \lambda^* = +\frac{2T_E\gamma V_m}{\Delta H\,\Delta T_0}$$

$$\lambda^* = -\frac{2T_E\gamma V_m}{\Delta H \Delta T_0} \rightarrow$$ *identical to critical radius of dendrite tip in pure metal*

Gibbs-Thomson effect

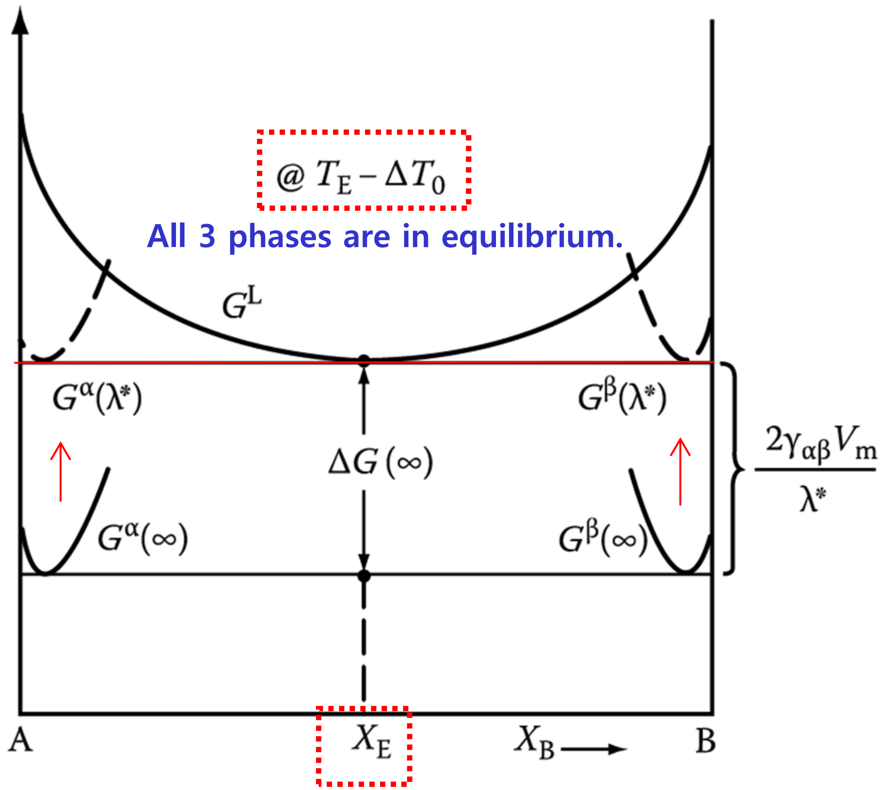
$$cf)\ r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL}T_m}{L_V}\right)\frac{1}{\Delta T}$$

L_v : *latent heat per unit volume*

$L = \Delta H = H^L - H^S$

* Growth Mechanism: Gibbs-Thomson effect in a ΔG-composition diagram?

1) At λ=λ* (<∞),

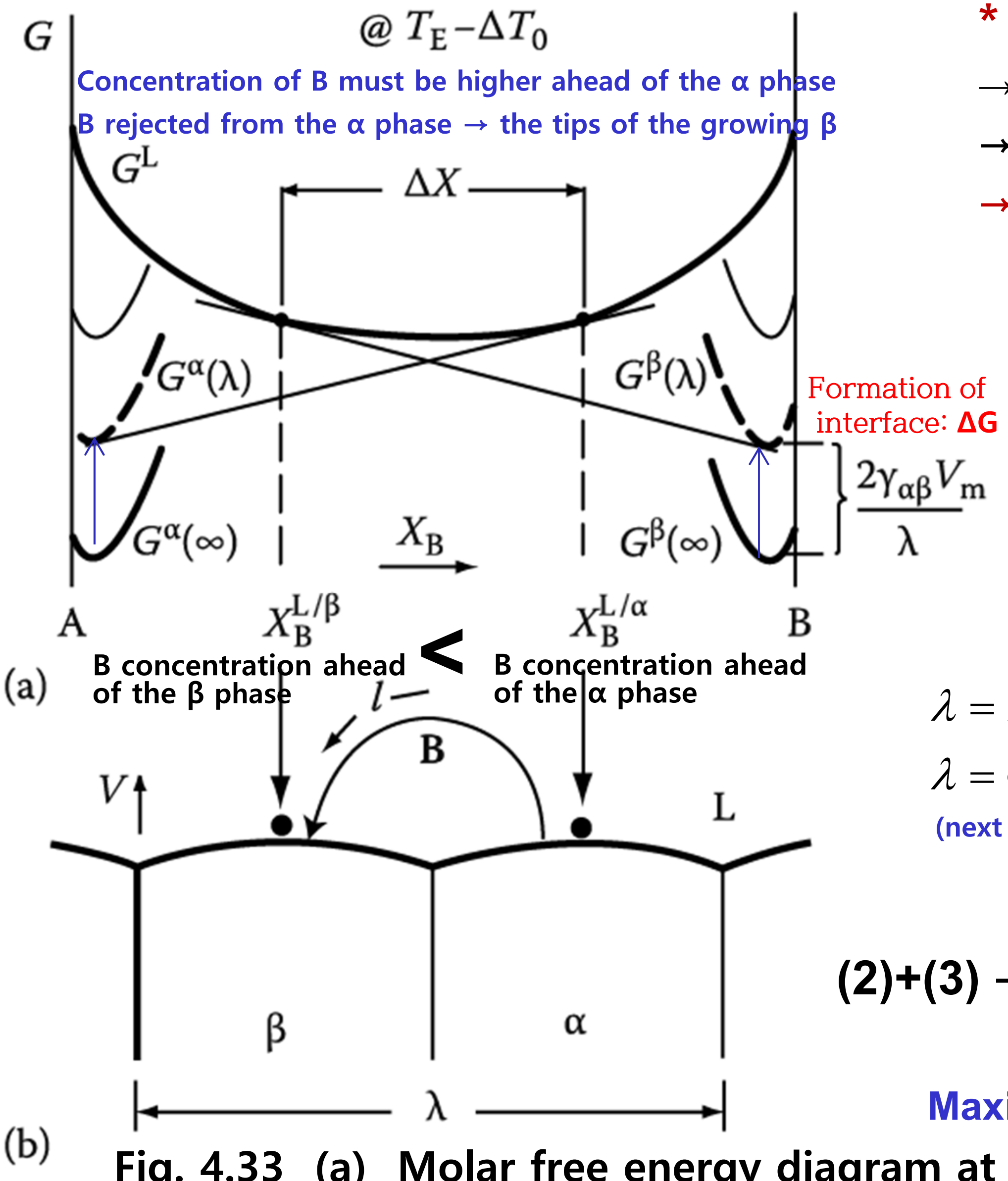


The cause of G increase is the curvature of the α/L and β/L interfaces arising from the need to balance the interfacial tensions at the α/ β/L triple point, therefore the increase will be different for the two phases, but for simple cases it can be shown to be $\frac{2\gamma_{\alpha\beta}V_m}{\lambda}$ **for both.**

1) If λ=λ*, growth rate will be *infinitely slow* because the liquid in contact with both phases has the same composition, X_E in Figure 4.32.

2) At λ= (∞>) λ (>λ*),

If ∞> λ > λ*, G_α and G_β are correspondingly reduced because less free energy is locked in the interfaces. → $X_B^{L/\alpha} > X_B^{L/\beta}$



Concentration of B must be higher ahead of the α phase

B rejected from the α phase → the tips of the growing β

Formation of interface: **ΔG**

B concentration ahead of the β phase **<** B concentration ahead of the α phase

* Eutectic growth rate, v

→ if α/L and β/L interfaces are highly mobile

→ proportional to flux of solute through liquid

→ diffusion controlled process

$$\boxed{v \propto D\frac{dC}{dl} \propto (X_B^{L/\alpha} - X_B^{L/\beta})}$$

$\propto$ 1/effective diffusion distance.. 1/λ

$$\boxed{v = k_1 D\frac{\Delta X}{\lambda}} \qquad \textbf{(1)}$$

$\lambda = \lambda^*, \Delta X = 0$

$\lambda = \infty, \Delta X = \Delta X_0$

(next page)

$$\boxed{\Delta X = \Delta X_0\left(1 - \frac{\lambda^*}{\lambda}\right)} \qquad \textbf{(2)}$$

$$\boxed{\Delta X_0 \propto \Delta T_0} \qquad \textbf{(3)}$$

(2)+(3) → (1)
$$\boxed{v = k_2 D\frac{\Delta T_0}{\lambda}\left(1 - \frac{\lambda^*}{\lambda}\right)}$$

Maximum growth rate at a fixed ΔT_0→ $\boxed{\lambda = 2\lambda^*}$

Fig. 4.33 (a) Molar free energy diagram at (T_E - ΔT_0) for the case λ* < λ < ∞, showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

ΔX will it self depend on λ. ~ maximum value, ΔX_0

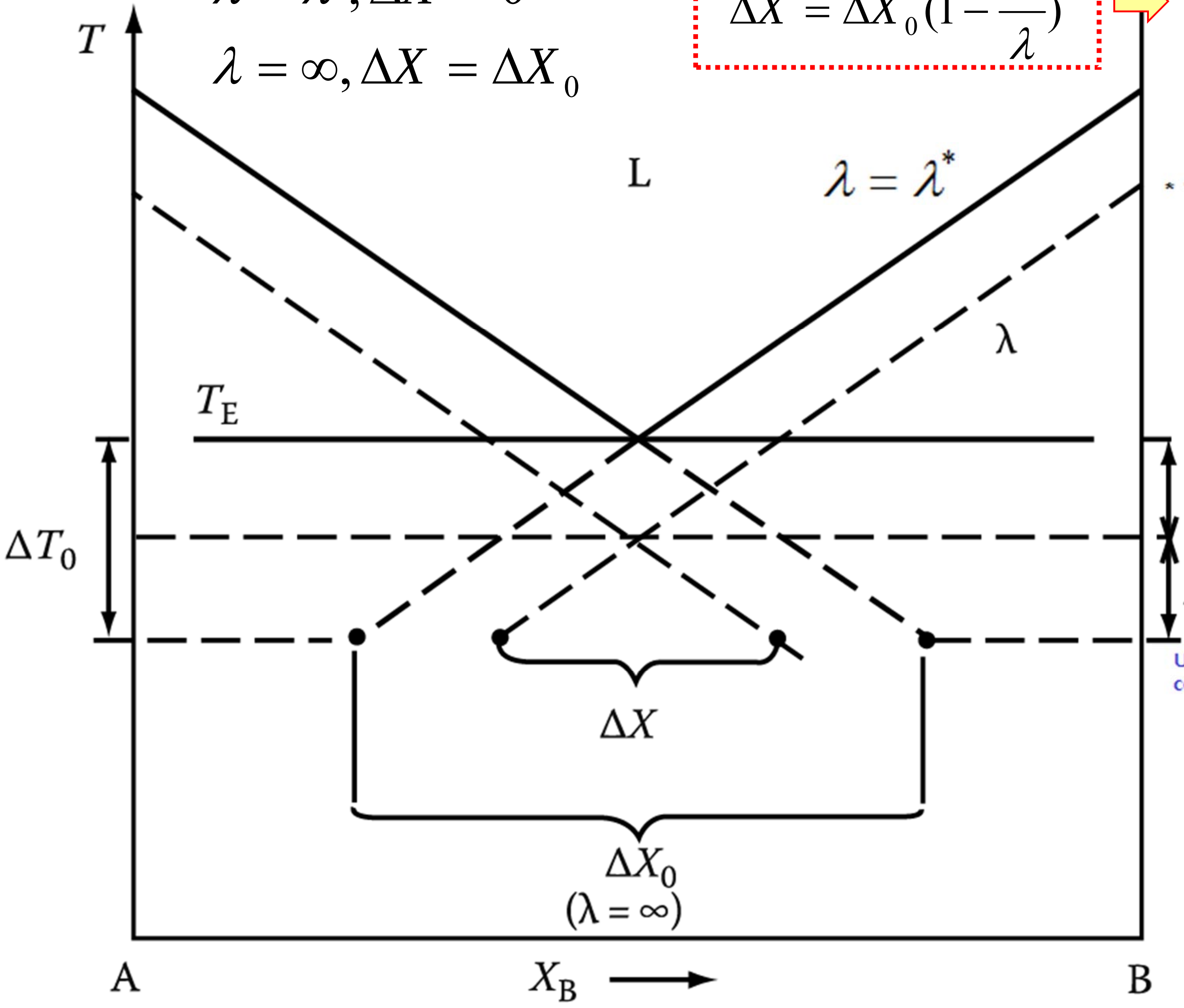
$$\lambda = \lambda^*, \Delta X = 0$$

$$\lambda = \infty, \Delta X = \Delta X_0$$

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

If undercooling is small,

$$\Delta X_0 \propto \Delta T_0$$



* Total Undercooling

$$\Delta T_0 = \Delta T_r + \Delta T_D$$

Undercooling required to overcome the interfacial curvature effects

ΔT_r Undercooling for curvature, r

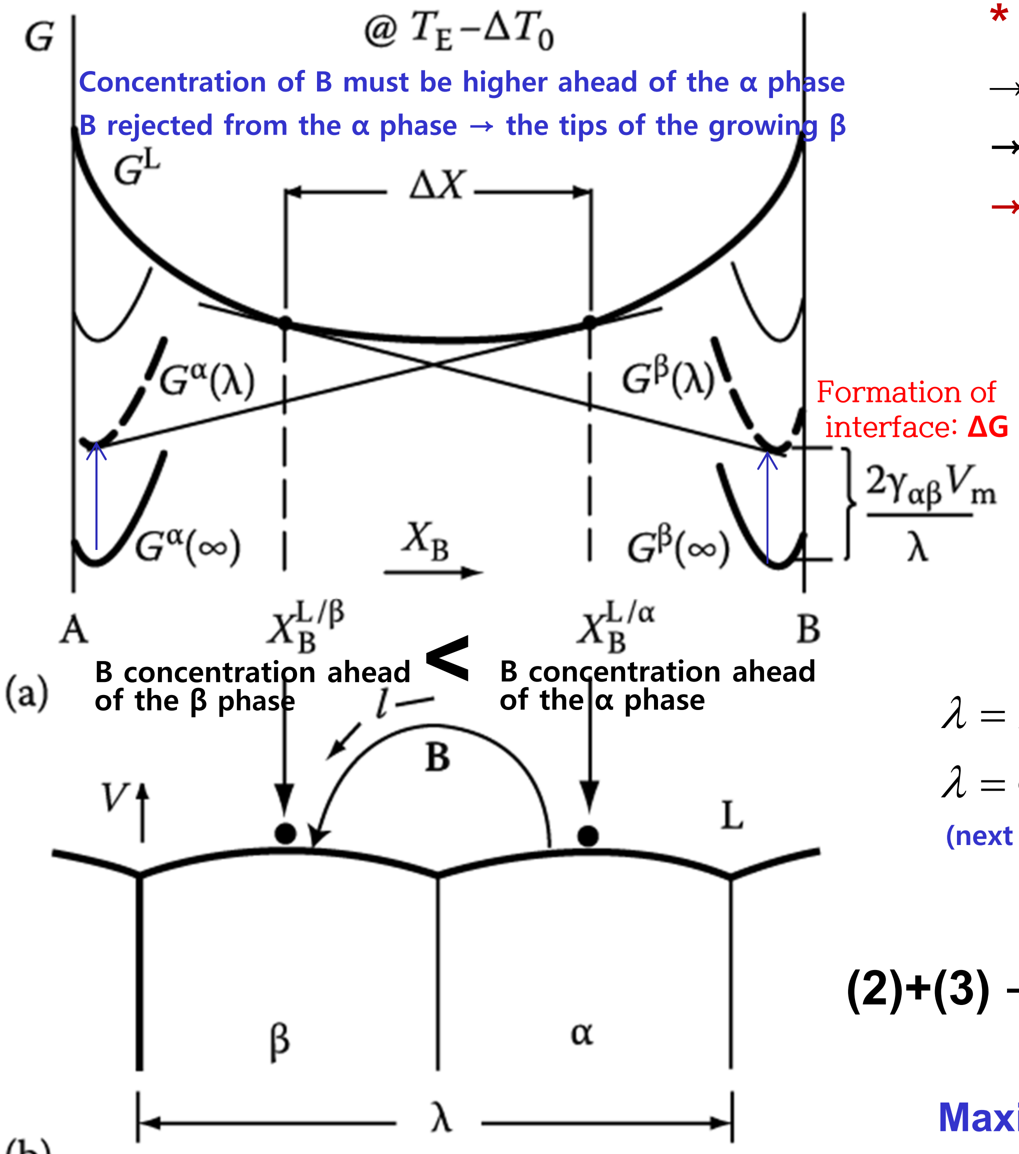
ΔT_D Undercooling for Diffusion

Undercooling required to give a sufficient composition difference to drive the diffusion

Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and ΔX_0 (exaggerated for clarity)

2) At λ= (∞>) λ (>λ*),

If ∞> λ > λ*, G_α and G_β are correspondingly reduced because less free energy is locked in the interfaces. → $X_B^{L/\alpha} > X_B^{L/\beta}$



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$$v \propto D\frac{dC}{dl} \propto (X_B^{L/\alpha} - X_B^{L/\beta})$$

$\propto$ 1/effective diffusion distance.. 1/λ

$$v = k_1 D\frac{\Delta X}{\lambda} \qquad \textbf{(1)}$$

$\lambda = \lambda^*, \Delta X = 0$

$\lambda = \infty, \Delta X = \Delta X_0$

(next page)

$$\Delta X = \Delta X_0\left(1 - \frac{\lambda^*}{\lambda}\right) \qquad \textbf{(2)}$$

$$\Delta X_0 \propto \Delta T_0 \qquad \textbf{(3)}$$

(2)+(3) → (1) $$v = k_2 D\frac{\Delta T_0}{\lambda}\left(1 - \frac{\lambda^*}{\lambda}\right)$$

Maximum growth rate at a fixed ΔT_0 → $\boxed{\lambda = 2\lambda^*}$

Fig. 4.33 (a) Molar free energy diagram at (T_E - ΔT_0) for the case λ* < λ < ∞, showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

Closer look at the tip of a growing dendrite

different from a planar interface because heat can be conducted away from the tip in three dimensions.

Assume the solid is isothermal $\left(T_S' = 0\right)$

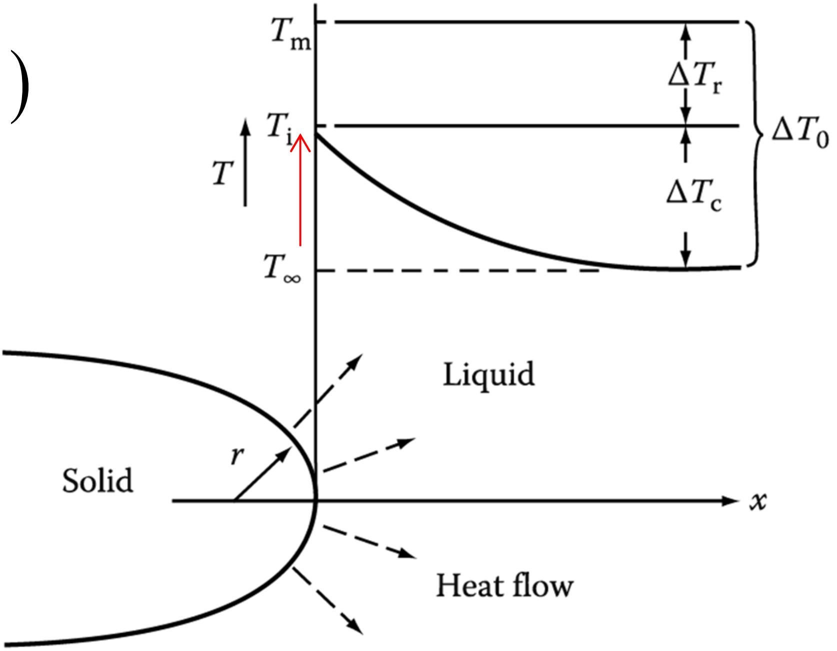
From $K_S T_S' = K_L T_L' + vL_V$

$$\text{If } T_S' = 0, \boxed{v = \frac{-K_L T_L'}{L_V}}$$

A solution to the heat-flow equation for a hemispherical tip:

$$T_L'(negative) \cong \frac{\Delta T_C}{r} \quad \Delta T_C = T_i - T_\infty$$

$$v = \frac{-K_L T_L'}{L_V} \cong \frac{K_L}{L_V} \cdot \frac{\Delta T_C}{r} \qquad v \propto \frac{1}{r}$$



However, ΔT also depends on r. How?

Thermodynamics at the tip?

Gibbs-Thomson effect: melting point depression

$$\Delta G = \frac{L_V}{T_m} \Delta T_r = \frac{2\gamma}{r} \qquad \Delta T_r = \frac{2\gamma T_m}{L_V r}$$

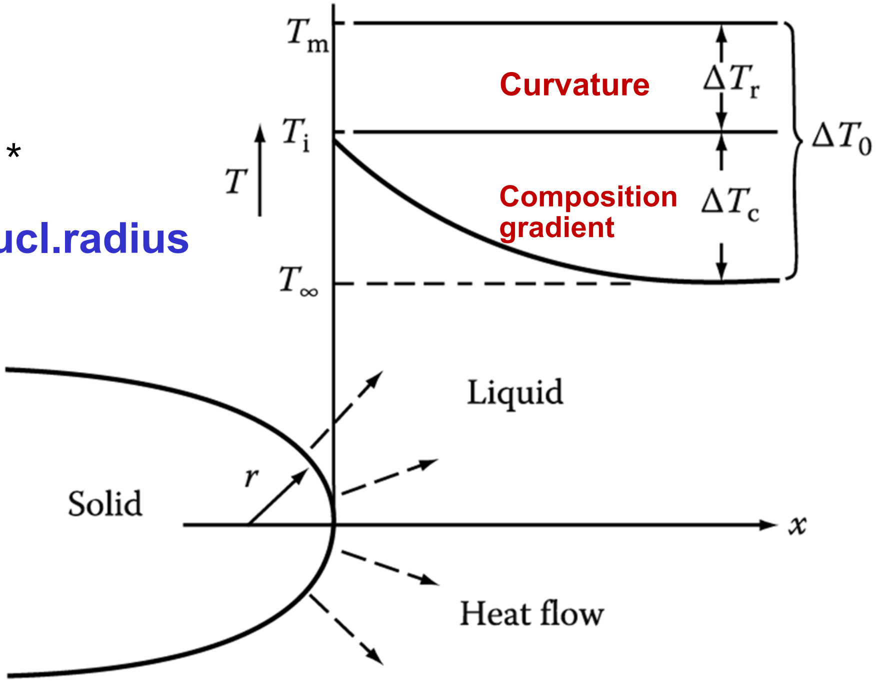
Minimum possible radius (r)?

$$r_{min} : \Delta T_r \to \Delta T_0 = T_m - T_\infty \to r^*$$

The crit.nucl.radius

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

$$\Delta T_r = \frac{2\gamma T_m}{L_V r}$$



Express ΔT_r by r, r^* and ΔT_o.

$$\Delta T_r = \frac{r^*}{r} \Delta T_o$$

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

$v \to 0$ as $r \to r^*$ due to Gibbs-Thomson effect

as $r \to \infty$ due to slower heat condution

Maximum velocity?

$$\boxed{\to \ r = 2r^*}$$

Undercooling ΔT_0

$$\Delta T_0 = \boxed{\Delta T_r} + \boxed{\Delta T_D} \quad \Rightarrow \quad \Delta G_{total} = \boxed{\Delta G_r} + \boxed{\Delta G_D} \quad \Rightarrow \quad \boxed{v = k_2 D \frac{\Delta T_0}{\lambda}(1 - \frac{\lambda^*}{\lambda})}$$

Curvature **Composition gradient**

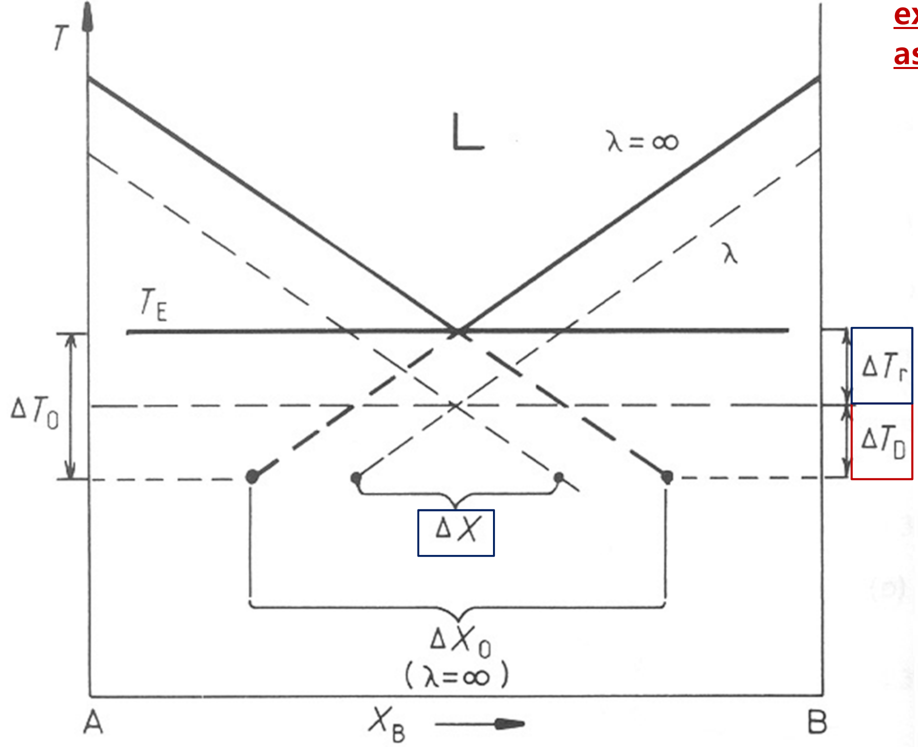
$$\Delta G_r = \frac{2\gamma_{\alpha\gamma} V_m}{\lambda}$$

→ *free energy dissipated in forming α/β interfaces*

ΔG_D → *free energy dissipated in diffusion*

By varying the interface undercooling (ΔT_0) it is possible to vary the growth rate (v) and spacing (λ) independently.

Therefore, it is impossible to predict the spacing that will be observed for a given growth rate. However, controlled growth experiments show that a specific value of λ Is always associated with a given growth rate.



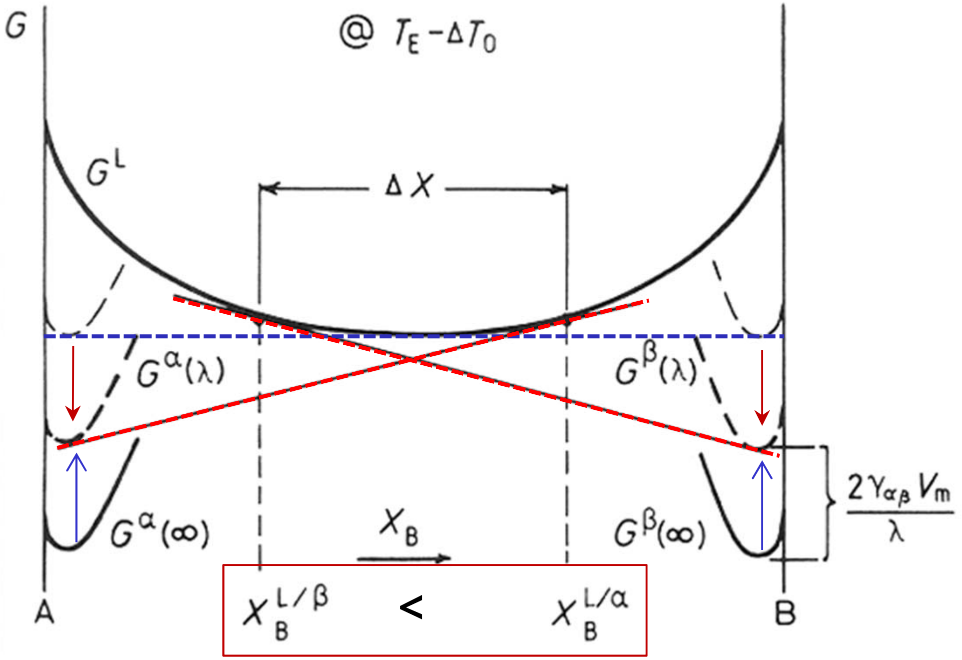


Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and ΔX_0 (exaggerated for clarity)

Undercooling ΔT_0

$$\Delta T_0 = \boxed{\Delta T_r} + \boxed{\Delta T_D}$$

Curvature　Composition gradient

$$\Rightarrow \quad \Delta G_{total} = \boxed{\Delta G_r} + \boxed{\Delta G_D} \quad \Rightarrow \quad v = k_2 D \frac{\Delta T_0}{\lambda}\left(1 - \frac{\lambda^*}{\lambda}\right)$$

$$\Delta G_r = \frac{2\gamma_{\alpha\gamma} V_m}{\lambda}$$

$\rightarrow$ *free energy dissipated in forming α/β interfaces*

$\Delta G_D \rightarrow$ *free energy dissipated in diffusion*

By varying the interface undercooling (ΔT_0) it is possible to vary the growth rate (v) and spacing (λ) independently.

Therefore, it is impossible to predict the spacing that will be observed for a given growth rate. However, controlled growth experiments show that a specific value of λ Is always associated with a given growth rate.

*** For example,**

Maximum growth rate at a fixed ΔT_0 $\rightarrow \boxed{\lambda_0 = 2\lambda^*}$

(4) $$v = k_2 D \frac{\Delta T_0}{\lambda}\left(1 - \frac{\lambda^*}{\lambda}\right) \quad \Rightarrow \quad \boxed{v_0 = k_2 D \Delta T_0 / 4\lambda^*} \quad \textbf{(5)}$$

From Eq. 4.39

$$\lambda^* = + \frac{2T_E \gamma V_m}{\Delta H \Delta T_0} \quad \Rightarrow \quad \boxed{\Delta T_0 \propto 1/\lambda^*} \quad \textbf{(6)}$$

So that the following relationships are predicted:

(5) + (6) $\rightarrow$

$$v_0 \lambda_0^2 = k_3 \ \textbf{(constant)}$$

$$\frac{v_0}{(\Delta T_0)^2} = k_4$$

Ex) Lamellar eutectic in the Pb-Sn system

k_3~ 33 μm^3/s and k_4~ 1 μm/s·K^2

⇒ v = 1 μm/s, λ_0 = 5 μm and ΔT_0 = 1 K

* Total Undercooling

$$\Delta T_0 = \Delta T_r + \Delta T_D$$

Undercooling required to overcome the interfacial curvature effects

Undercooling required to give a sufficient composition difference to drive the diffusion

Strictly speaking,

ΔT_i term should be added but, negligible for high mobility interfaces

Driving force for atom migration across the interfaces

$\Delta T_D \rightarrow$ Vary continuously from the middle of the α to the middle of the β lamellae

$\Delta T_0 = const$ ← Interface is essentially isothermal.

$\Delta T_D \rightarrow \boxed{\Delta T_r}$ The interface curvature will change across the interface.

Should be compensated

* A planar eutectic front is not always stable.

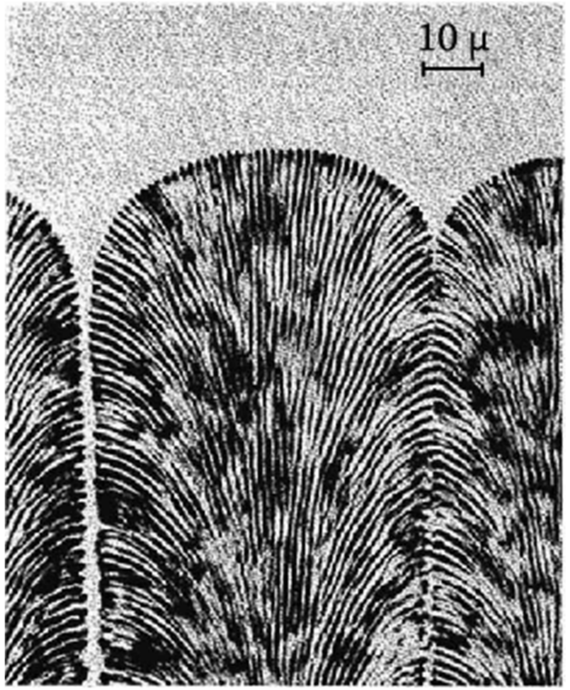
Binary eutectic alloys contains impurities or other alloying elements ➡ "Form a cellular morphology"

analogous to single phase solidification

restrict in a sufficiently high temp. gradient.

➡ The solidification direction changes as the cell walls are approached and the lamellar or rod structure fans out and may even change to an irregular structure.

➡ Impurity elements (here, mainly copper) concentrate at the cell walls.



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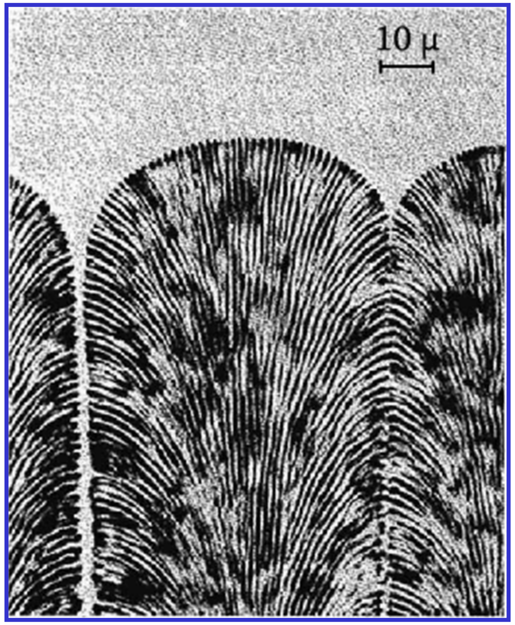

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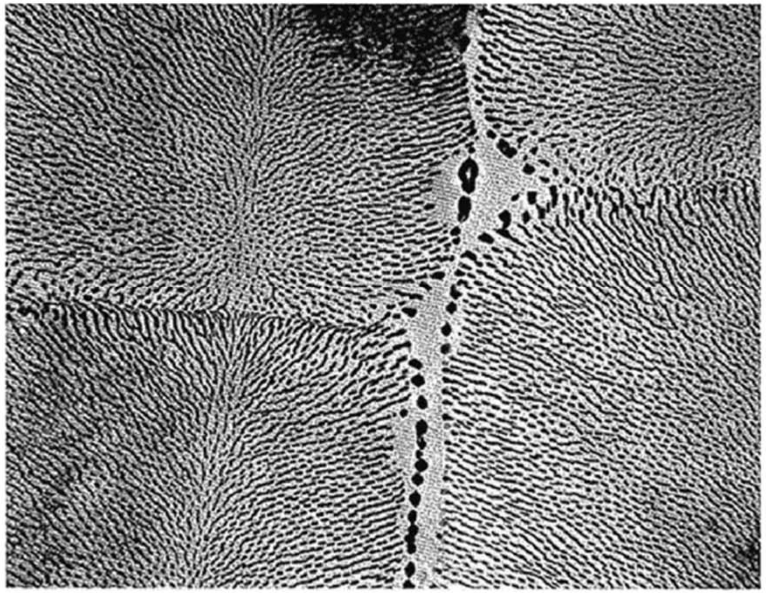

Fig. 4.35 Transverse section through the cellular structure of an Al-Al$_6$Fe rod eutectic (x3500).

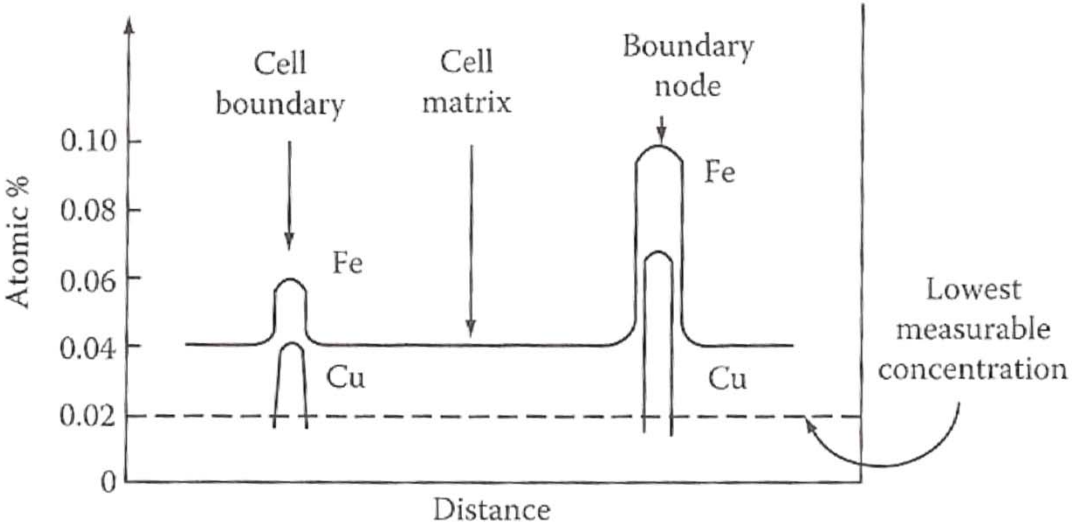

Fig. 4.36 Composition profiles across the cells in Fig. 4.35b.

재료상변태 남은 주요 일정 (eTL 공지 참고)

1. 12월 2일 9시 - 1시 재료설계 발표

   각조 당 20분씩 (15분 발표, 5분 질의응답)
   관련 발표자료는 해당 주제에 대해서 학생들이 기본적인 개념/특징/ 응용처 등을 가장 잘 이해할 수 있도록 발표자료를 만들면 되고, 그 재료를 이해하기 쉽도록 독창적인 아이디어를 가지고 발표자료를 구성하는 것을 권장합니다.

2. 기말고사 12월 19일 9시-1시