2009 fall

Phase Transformation of Materials

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Contents for previous class

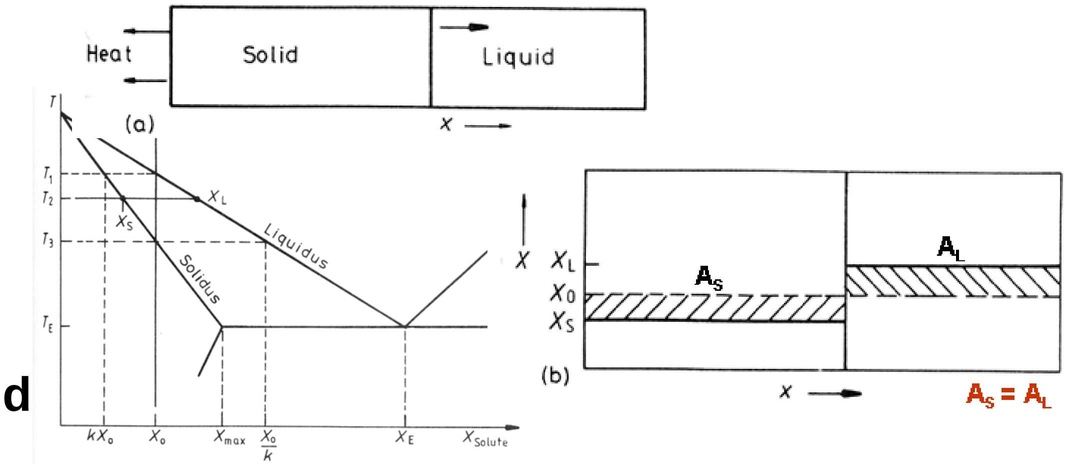
"Alloy solidification"- Solidification of single-phase alloys

Planar S/L interface
→ unidirectional solidification

- **Three limiting cases**

1) Equilibrium Solidification

: perfect mixing in solid and liquid



- Sufficient time for diffusion in solid & liquid (low cooling rate)

- Relative amount of solid and liquid : lever rule

2) No Diffusion in Solid, Perfect Mixing in Liquid

: high cooling rate, efficient stirring

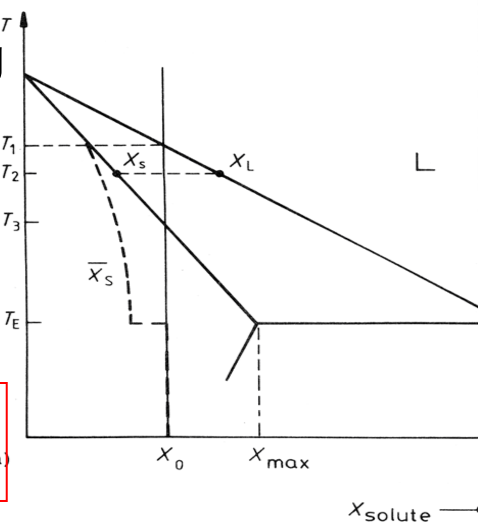
- Separate layers of solid retain their original compositions

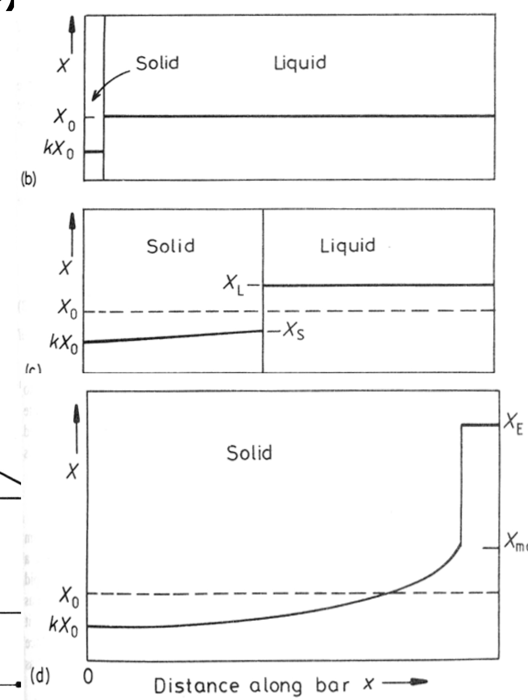
mean comp. of the solid ($\overline{X}_S$) < X_S

Scheil equation

: non-equilibrium lever rule

$$X_L = X_O f_L^{(k-1)} \quad X_S = kX_O \left(1 - f_S\right)^{(k-1)}$$

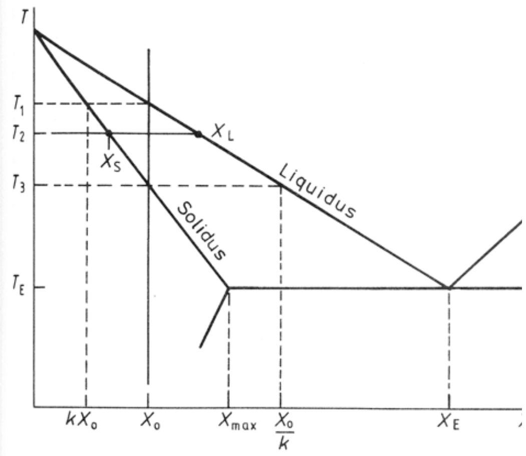


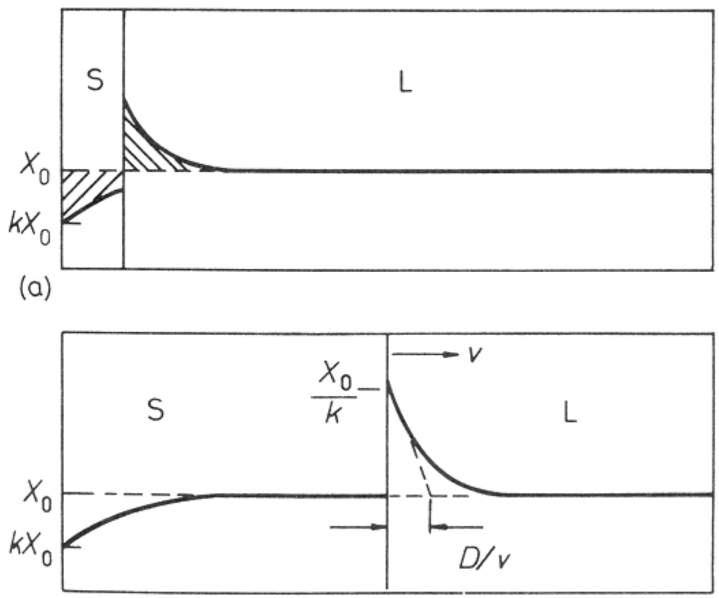


Contents for previous class

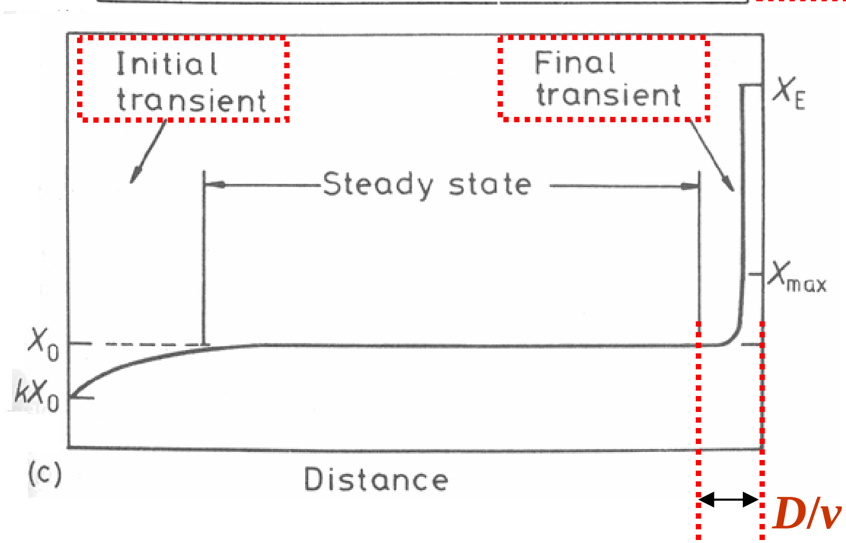
"Alloy solidification"- Solidification of single-phase alloys

3) No Diffusion on Solid, Diffusional Mixing in the Liquid



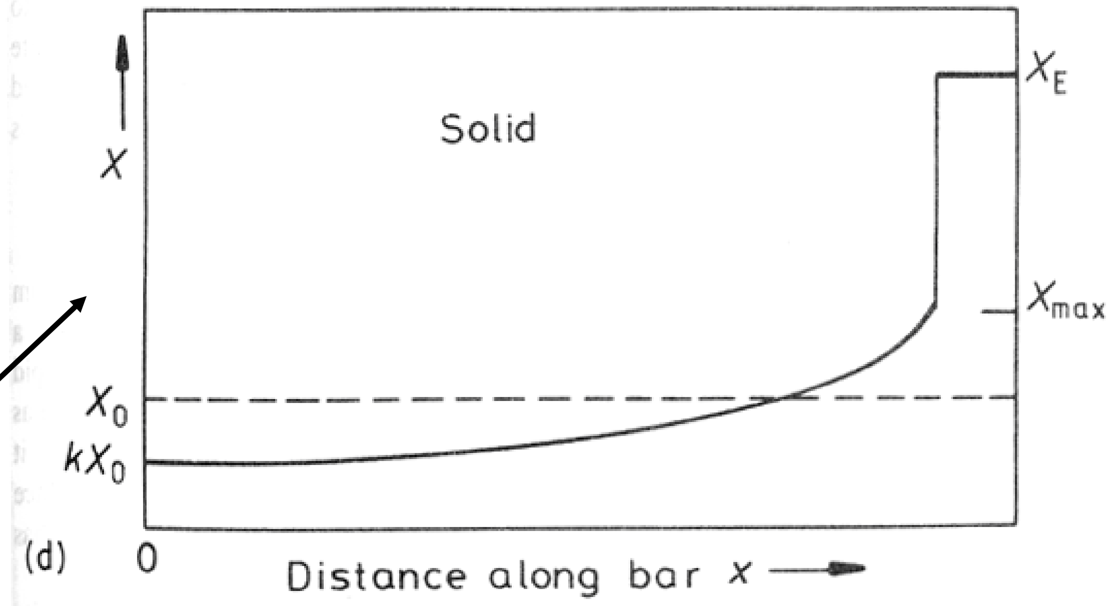


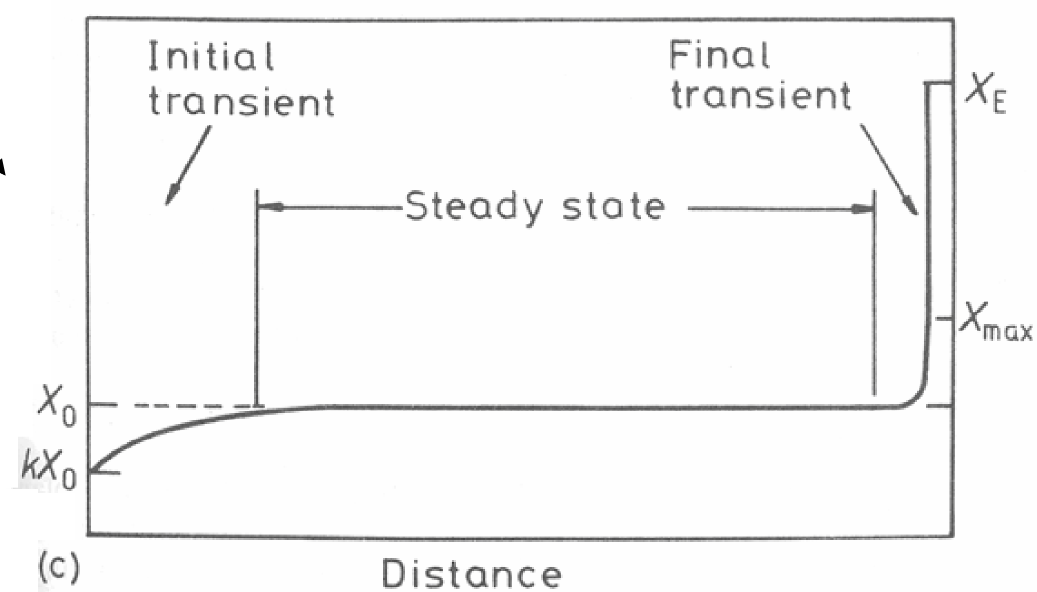
$$X_L = X_O[1 + \frac{1-k}{k}\exp(-\frac{x}{(D/v)})]$$



실제의 농도분포

두 가지 경우의 중간형태





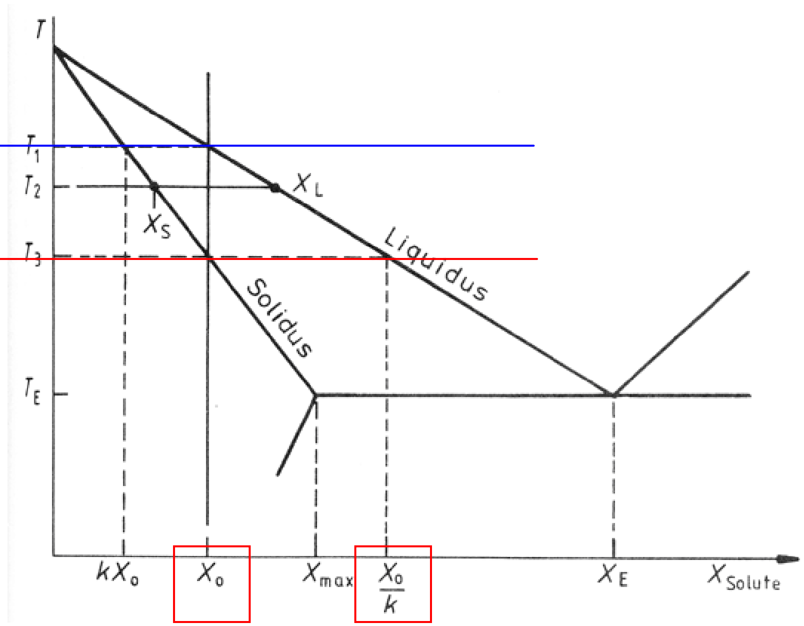
➡ **Zone Refining**

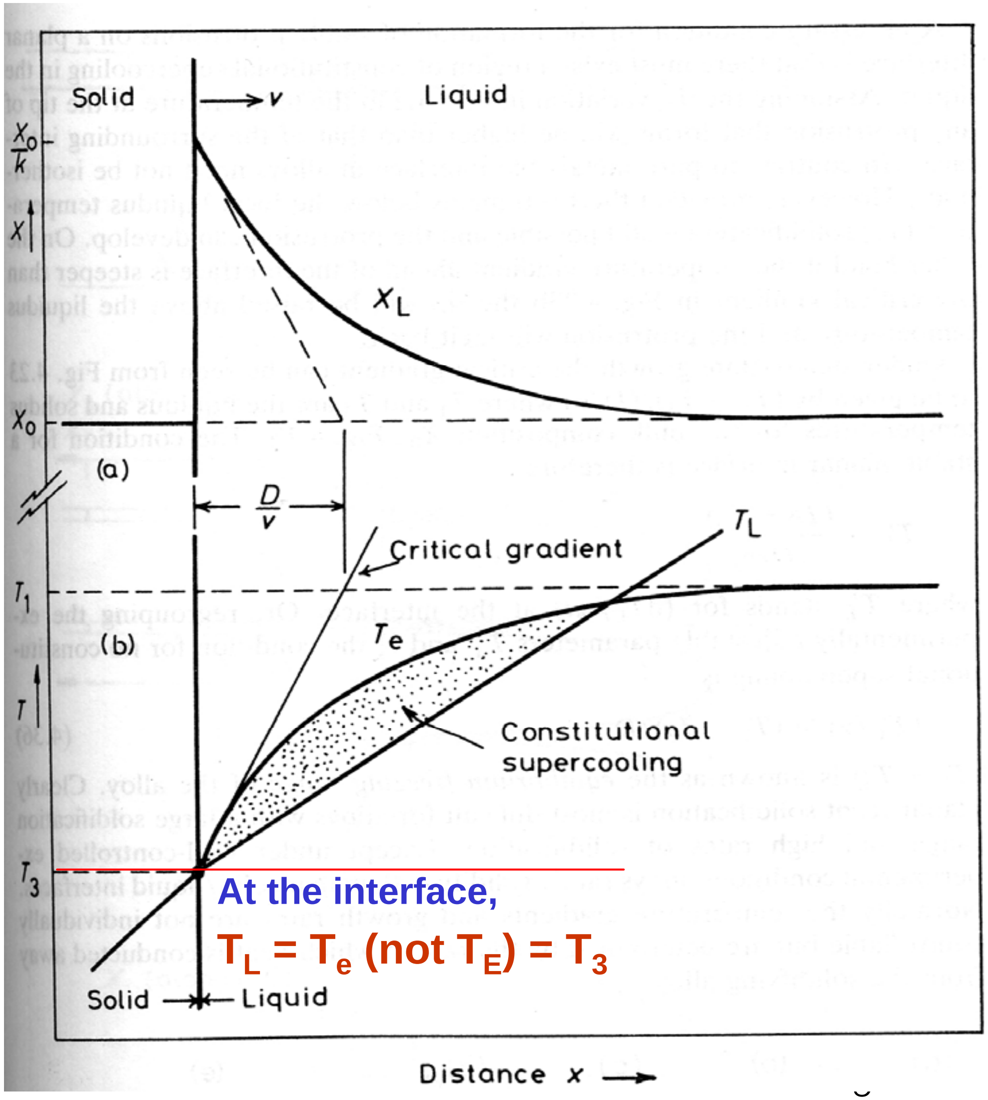
Contents for previous class

"Alloy solidification"

Constitutional Supercooling

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





*** Temperature gradient in Liquid**

T_L'

*** equilibrium solidification temp. change**

T_e

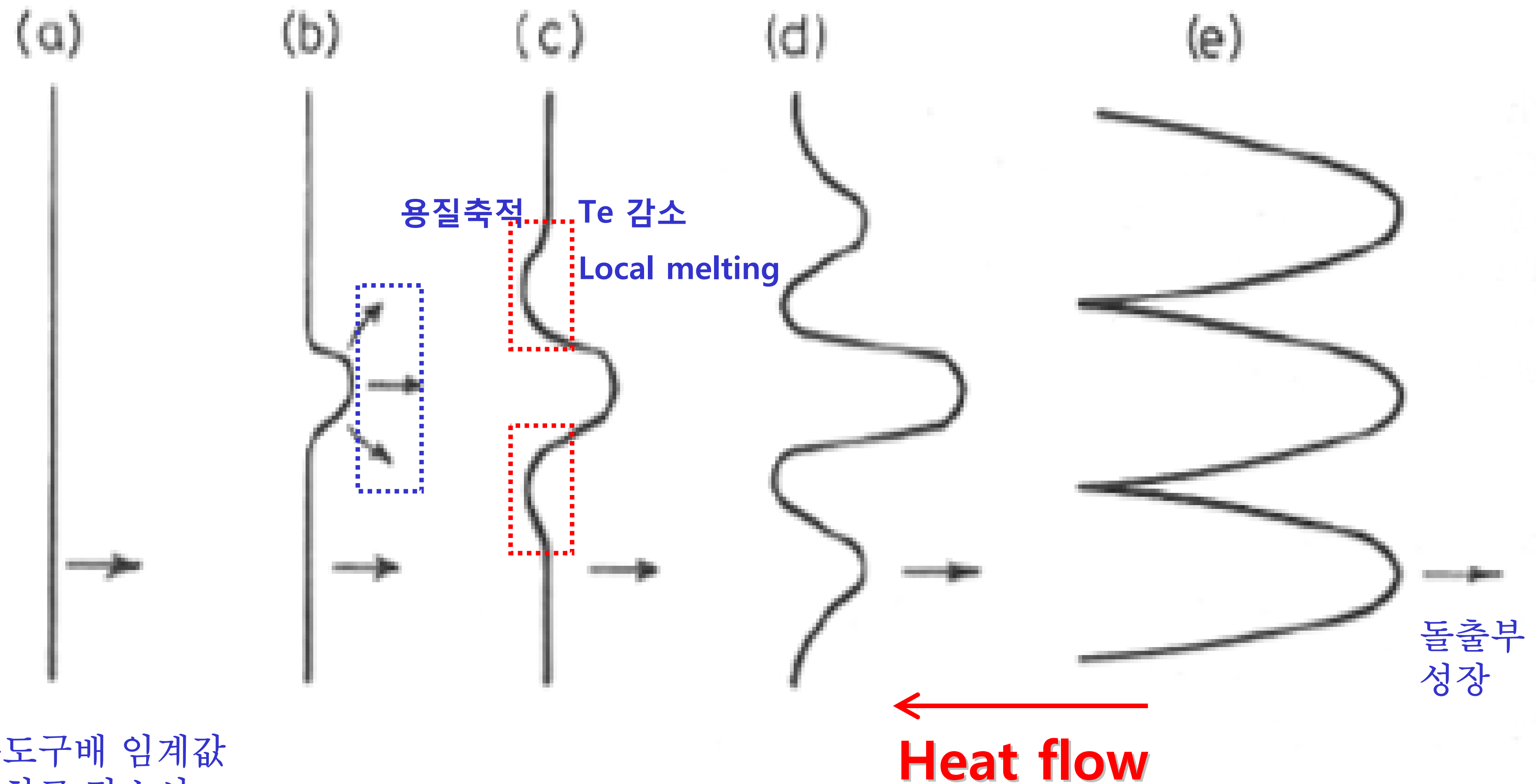
At the interface,

$T_L = T_e$ (not T_E) $= T_3$

$T_L' / v < (T_1 - T_3)/D$

Cellular Solidification

$T_L' / v < (T_1 - T_3)/D$



온도구배 임계값
이하로 감소시
평면계면 불안정

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

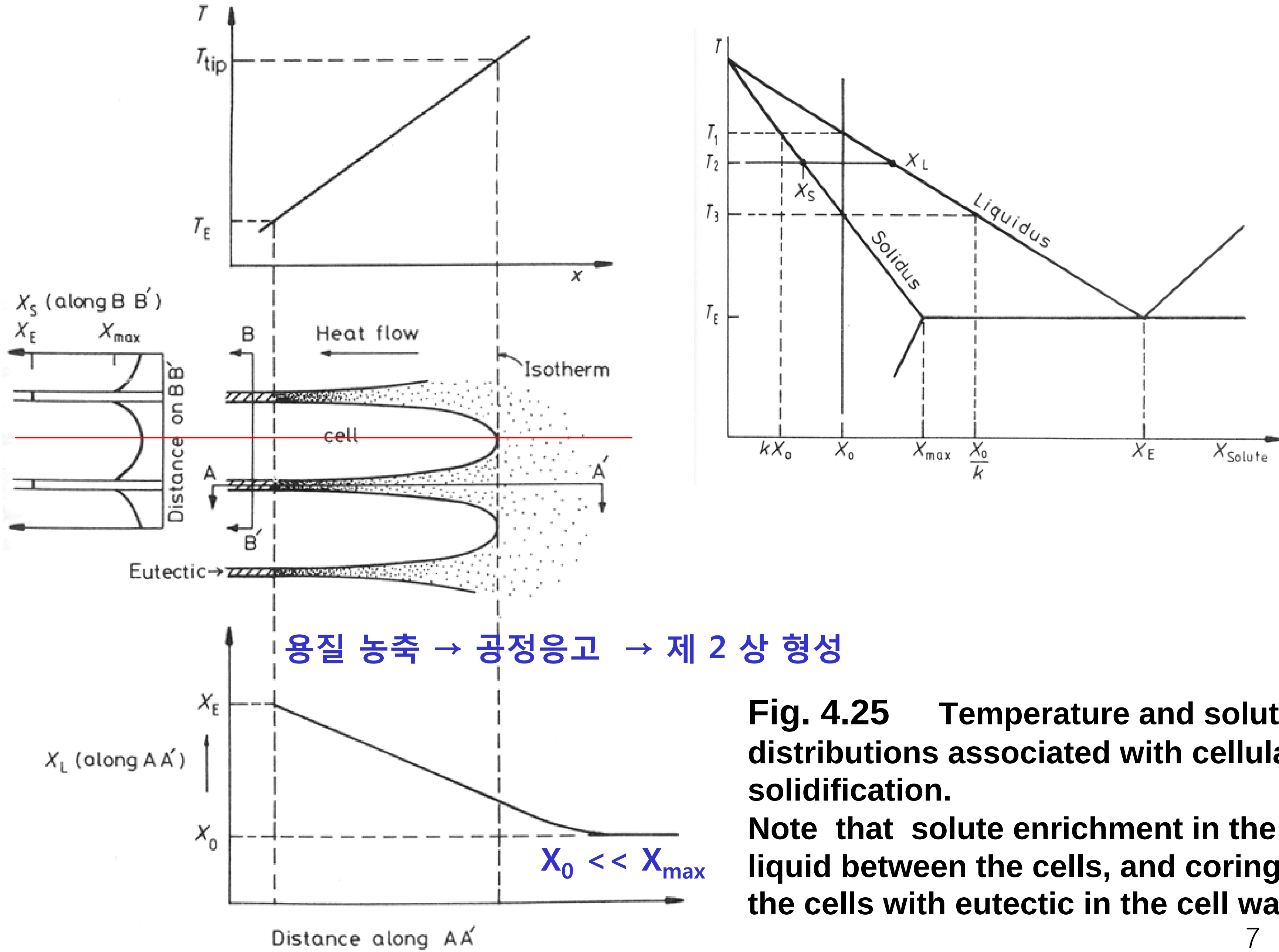


Fig. 4.25 **Temperature and solute distributions associated with cellular solidification.**

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

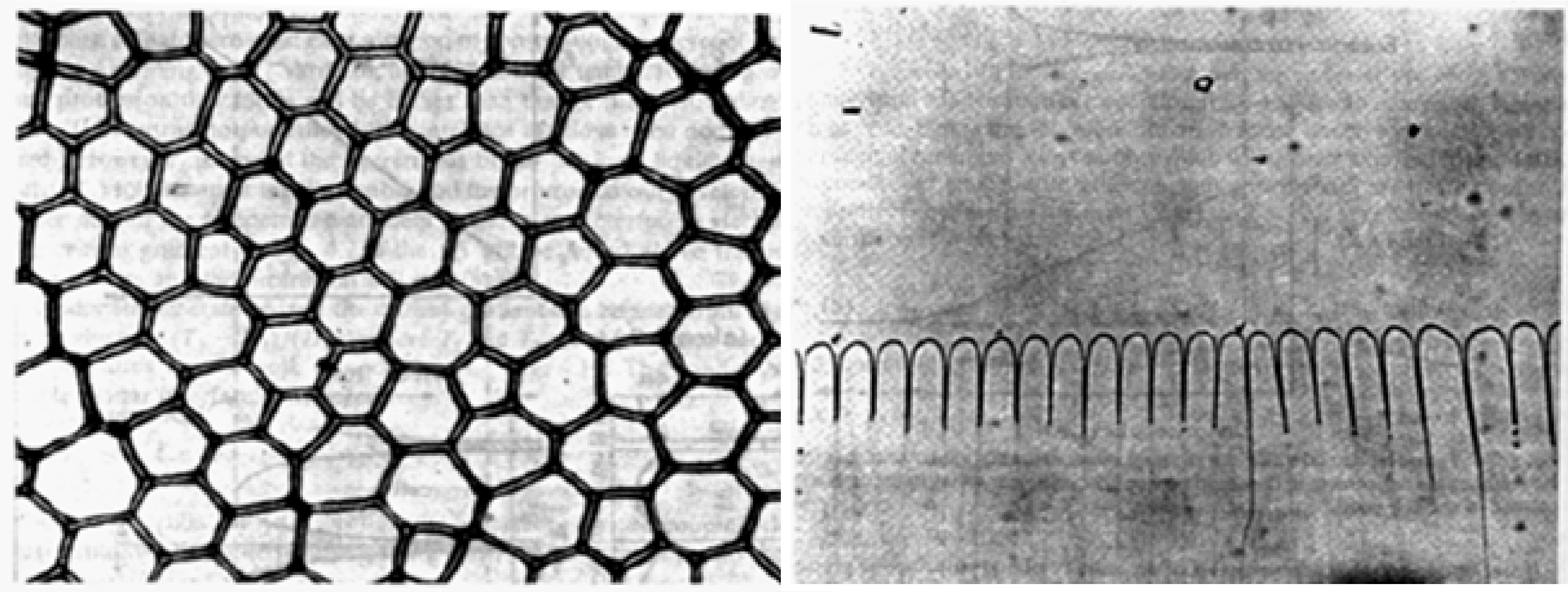


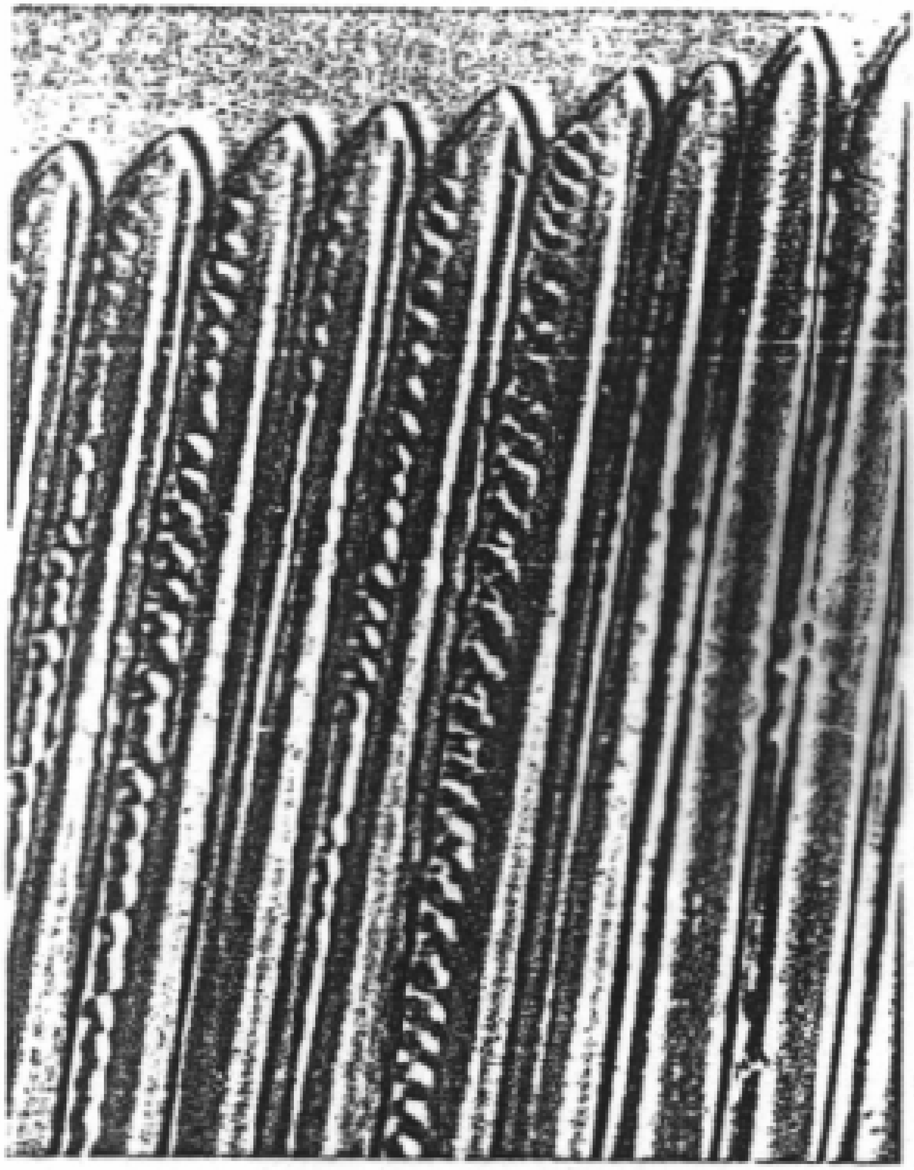
Fig. 4.26 Cellular microstructures.

(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).



형태 변화

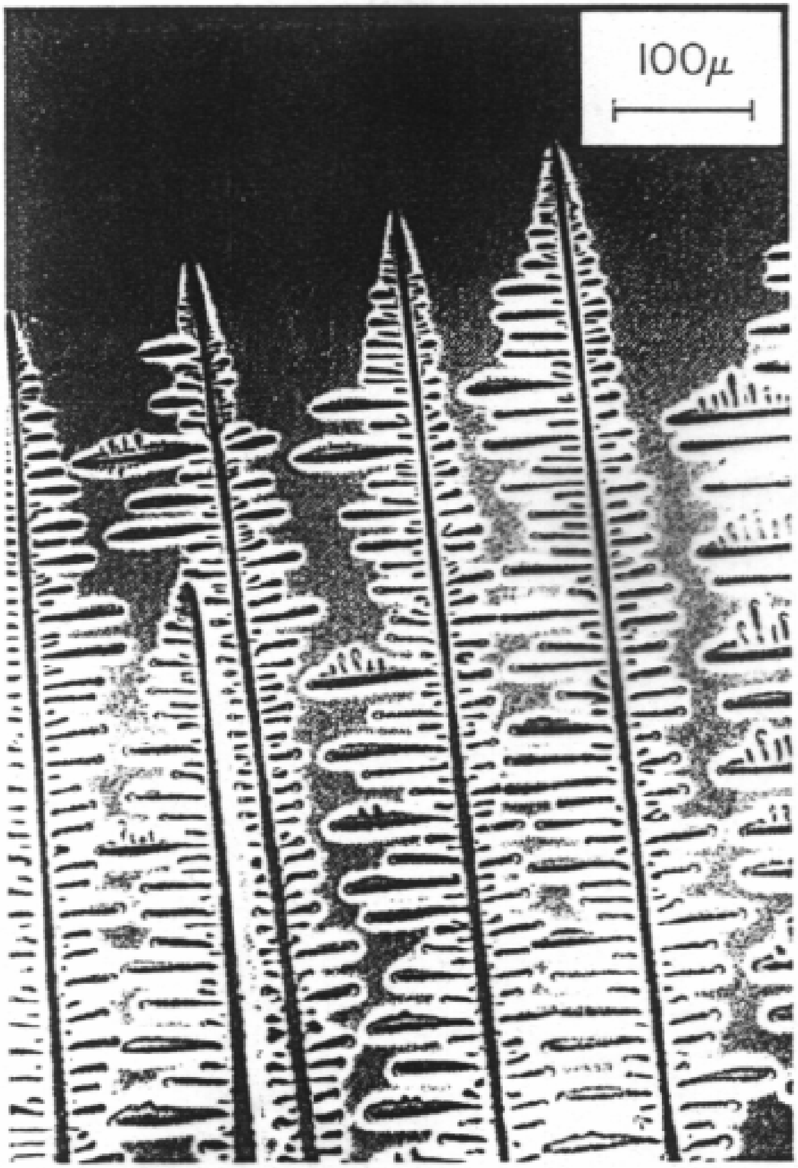
세포상 조직 과 수지상 조직의 천이

온도구배가
특정한 범위로
유지될 때 안정

온도구배 ↓ 면
수지상 형성

Fig. 4.27 Cellular dendrites in carbon tetrabromide.

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



1차 가지 성장 방향 변화

열전도 방향 → 결정학적 우선 방향

Fig. 4.28 Columnar dendrites in a transparent organic alloy.

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

Contents for today's class

4.3 Alloy solidification

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

4.4 Solidification of ingots and castings

- Ingot structure
- Segregation in ingot and castings
- Continuous casting

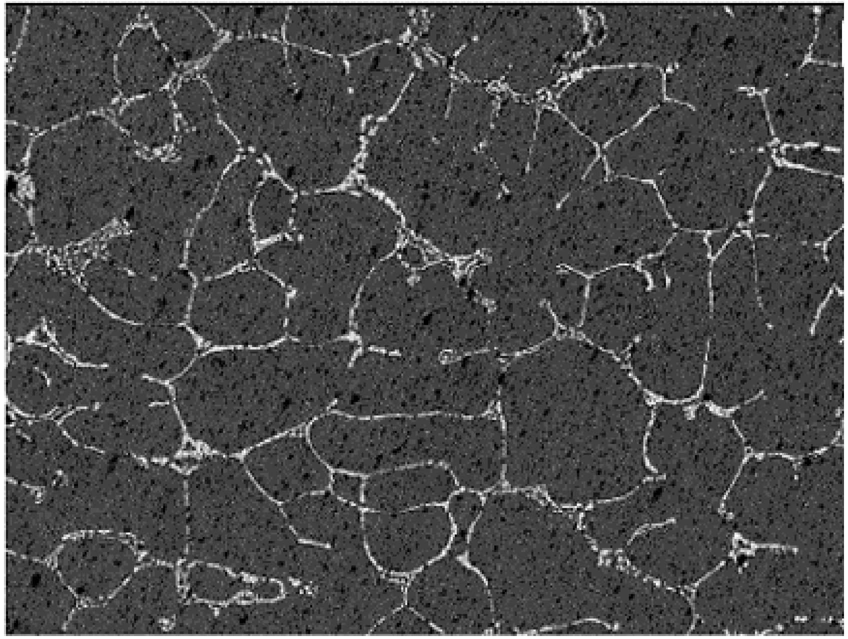
4.6 Solidification during quenching from the melt

4.3.2 Eutectic Solidification

Normal eutectic

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

Anomalous eutectic



The microstructure of the Pb-61.9%Sn (eutectic) alloy presented a coupled growth of the (Pb)/bSn 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

4.3.2 Eutectic Solidification

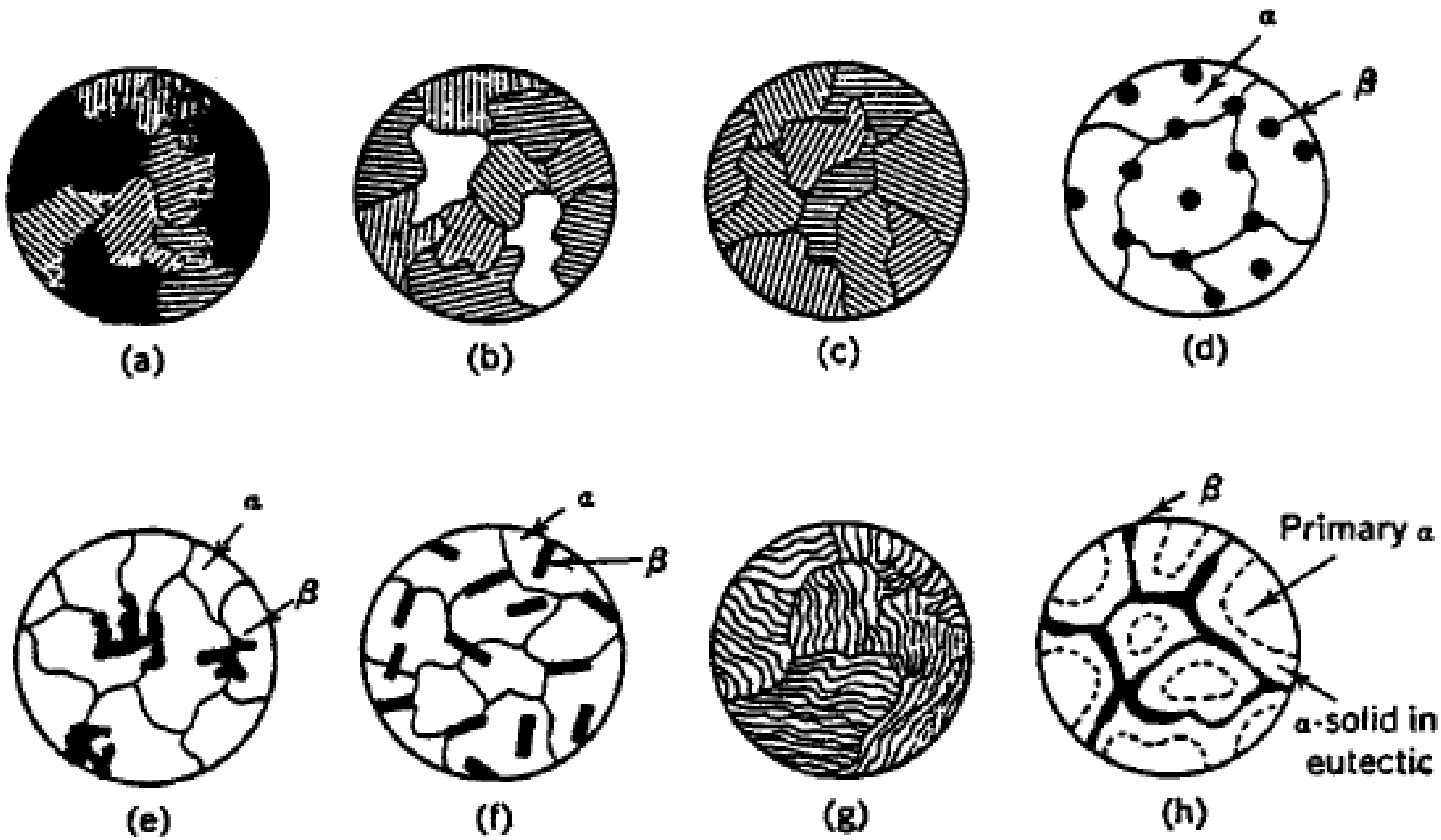
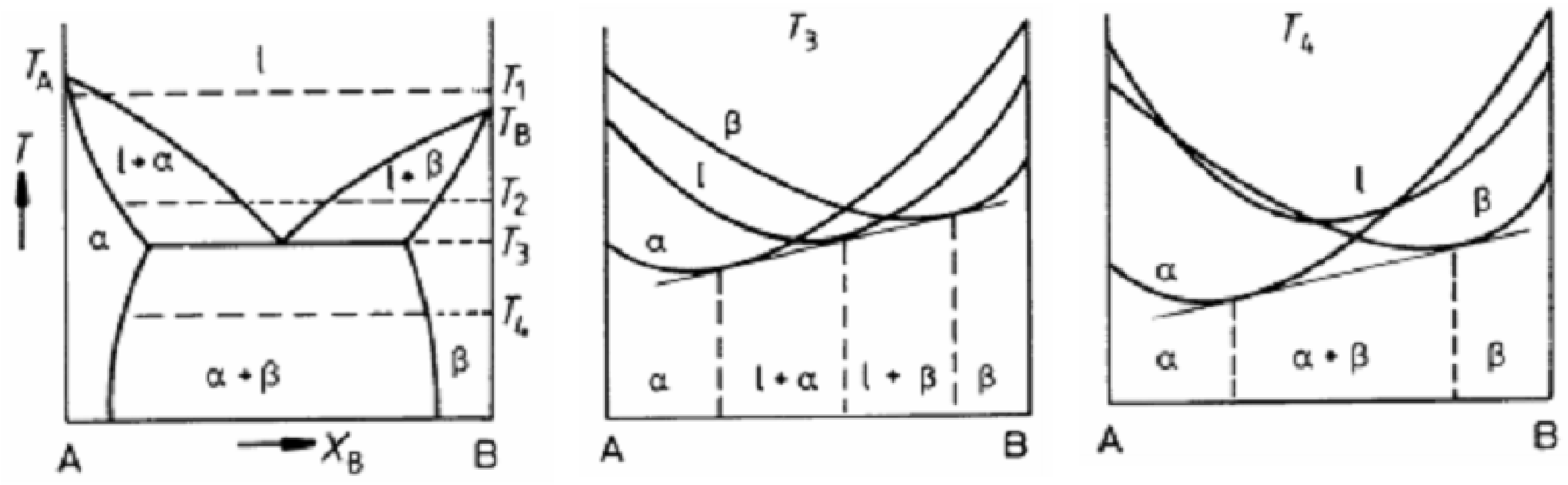


Fig. 14 Schematic representation possible in eutectic structures. (a), (b) and (c) are alloys shown in fig. 13; (d) nodular; (e) Chinese script; (f) acicular; (g) lamellar; and (h) divorced.

4.3.2 Eutectic Solidification (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 ($L \rightarrow \alpha + \beta$) at T_4 at C_{eut}?

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

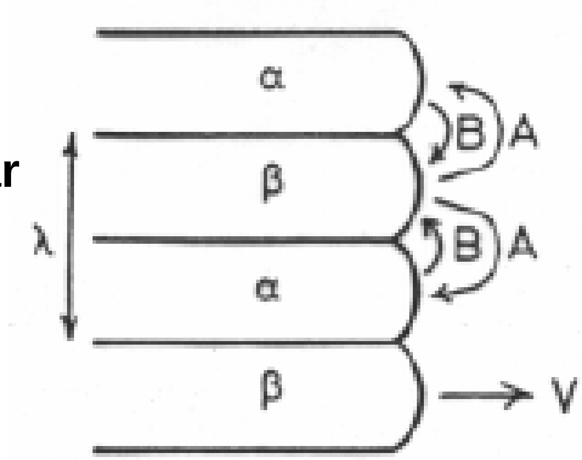
Eutectic Solidification (Kinetics)

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?

interlamellar spacing →



1) λ ↓ → 성장속도 ↑

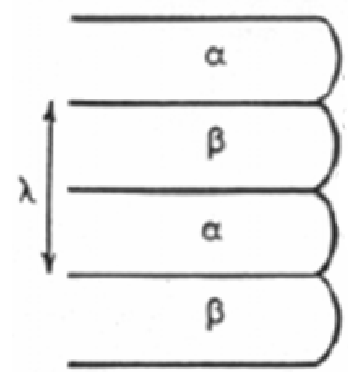
2) λ ↓ → $\gamma_{\alpha\beta}$ ↑ 로 계의 계면 E ↑
최소 λ 존재

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

→ Gibbs-Thomson Effect

Eutectic Solidification

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

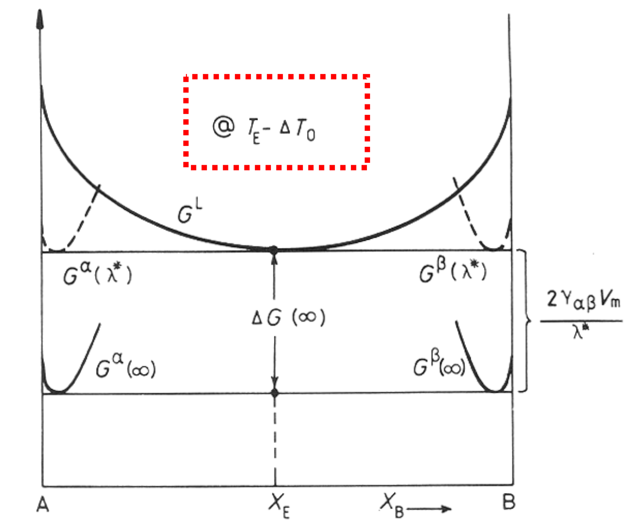


For an interlamellar spacing, λ, there is a total of $(2/\lambda)$ m^2 of α/β interface per m^3 of eutectic.

$$\Delta G = \Delta\mu \cong \frac{L\Delta T}{T_m}$$

Driving force for nucleation

$$\rightarrow \Delta G = \Delta\mu = \frac{2\gamma}{\lambda} \times V_m$$



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

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

What would be the minimum λ?

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

$$\Delta G(\infty) = \frac{2\gamma V_m}{\lambda^*}$$

$$\lambda^* = +\frac{2T_E \gamma V_m}{\Delta H\, \Delta T_0}$$

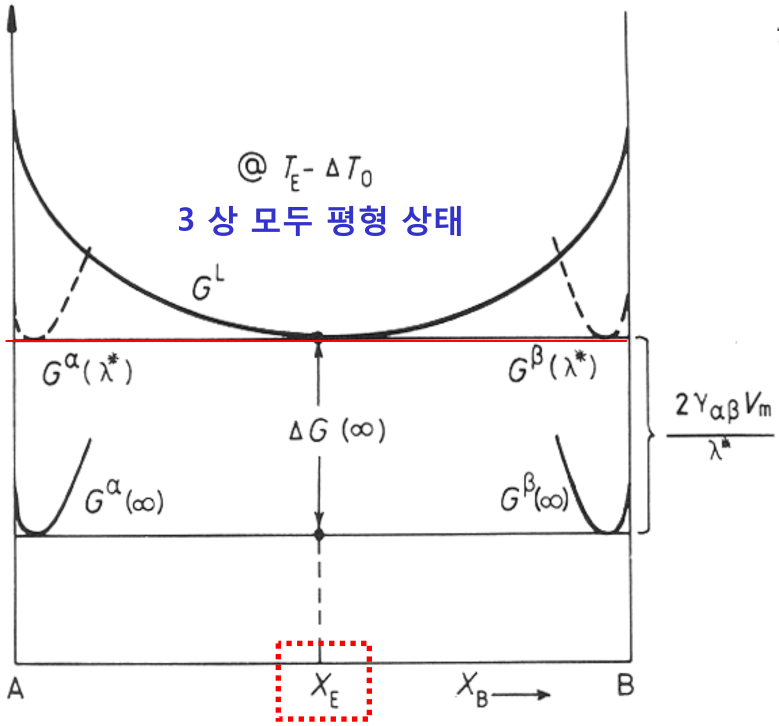
$$cf)\ r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL} T_m}{L_V}\right)\frac{1}{\Delta T}$$

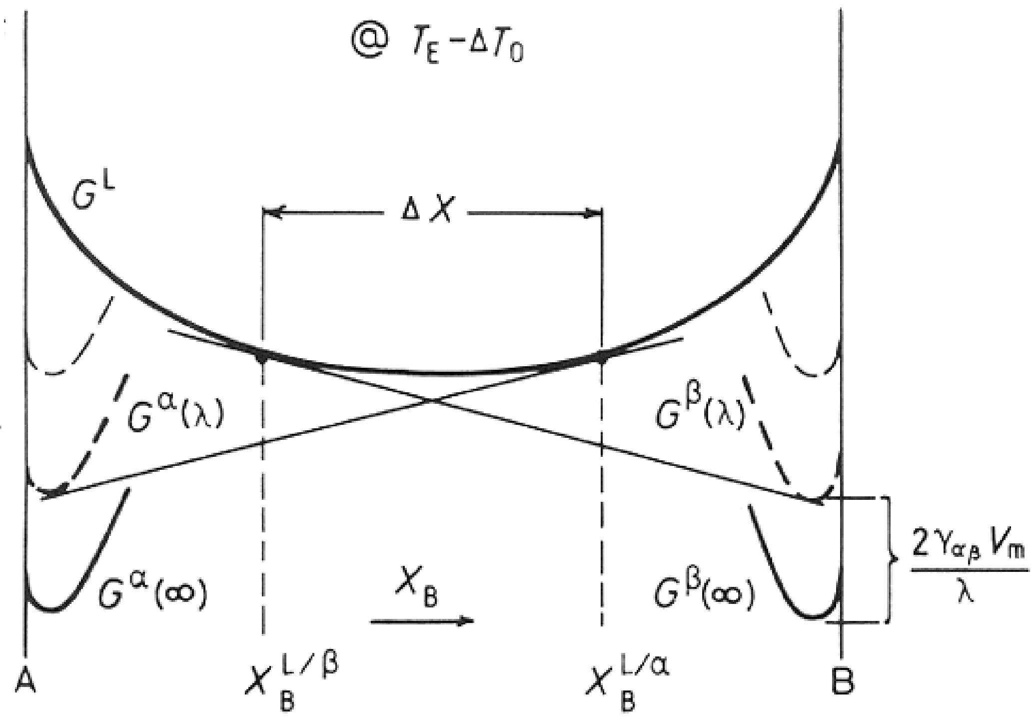
L_v : *latent heat per unit volume*

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

$$\lambda^* = +\frac{2T_E \gamma V_m}{\Delta H \Delta T_0} \rightarrow \textit{identical to critical radius}$$

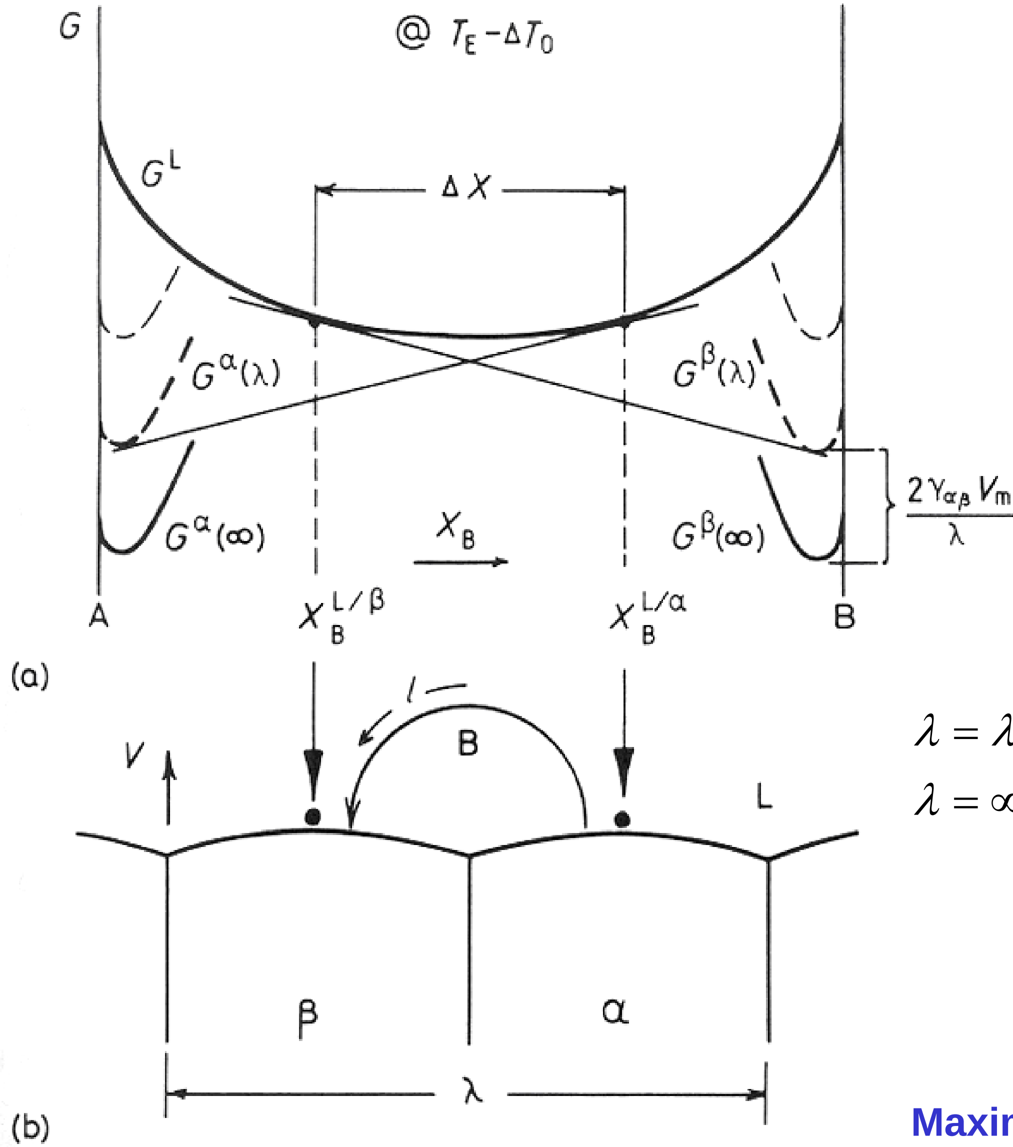
Gibbs-Thomson effect in a ΔG-composition diagram?





G 증가의 원인은 α/β/L의 3중점에서 계면장력이 균형을 유지하기 위하여 α/L 계면과 β/L 계면이 곡률을 갖기 때문

β 상과 국부적 평형 이루는 액상의 B 조성 < α 상과 국부적 평형 이루는 액상의 B 조성



공정의 성장속도 v

→ α/L와 β/L 계면의 이동도가 커서 액상을 통한 용질이동과 비례

→ 성장 확산 제어

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

$\propto$ 1/유효확산거리 … 1/λ

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

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

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

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

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

$$v = k_2 D\frac{\Delta T_0}{\lambda}(1 - \frac{\lambda^*}{\lambda})$$

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 $\lambda^* < \lambda < \infty$, showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

계면 과냉 변화시킴에 따라 성장속도와 간격 서로 독립적으로 변화시킬 수 있음.

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 $\left(T_S' = 0\right)$

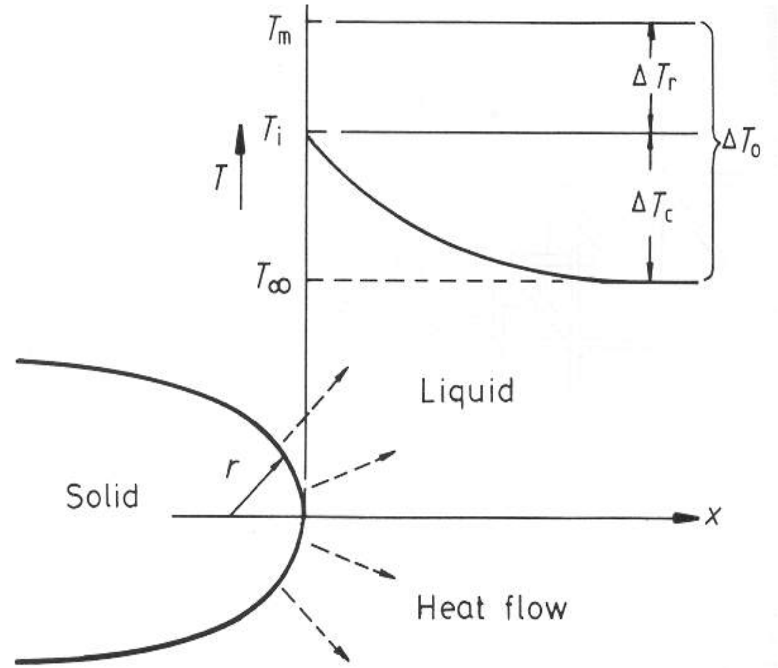
From $K_S T_S' = K_L T_L' + v L_V$

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

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

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

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



However, ΔT also depends on r. How?

Thermodynamics at the tip?

Gibbs-Thomson effect: melting point depression

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

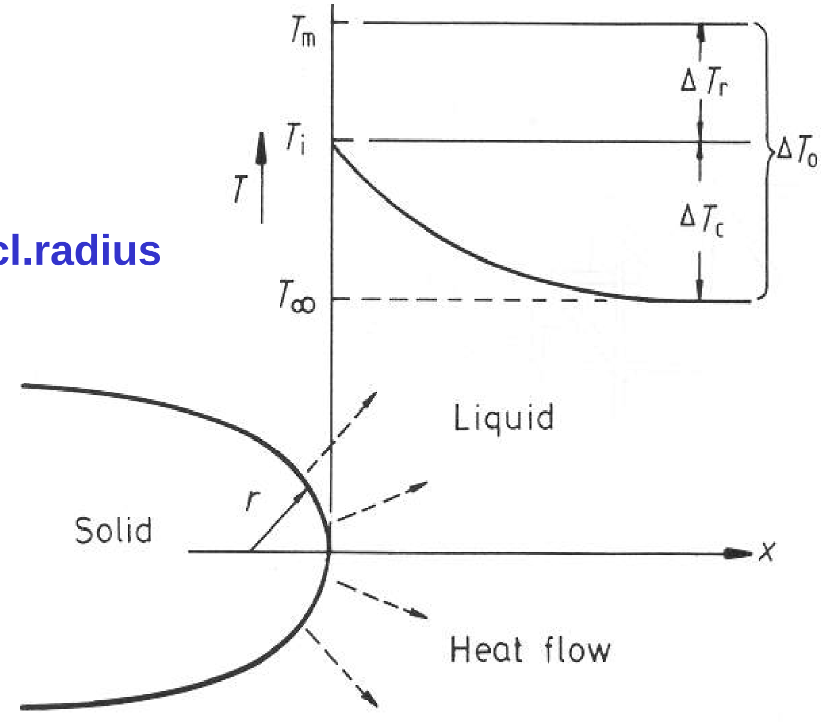
Minimum possible radius (r)?

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

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.

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

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

$v \rightarrow 0$ as $r \rightarrow r^*$ due to Gibbs-Thomson effect
as $r \rightarrow \infty$ due to slower heat condution

Maximum velocity?

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

Corresponding location at phase diagram?

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

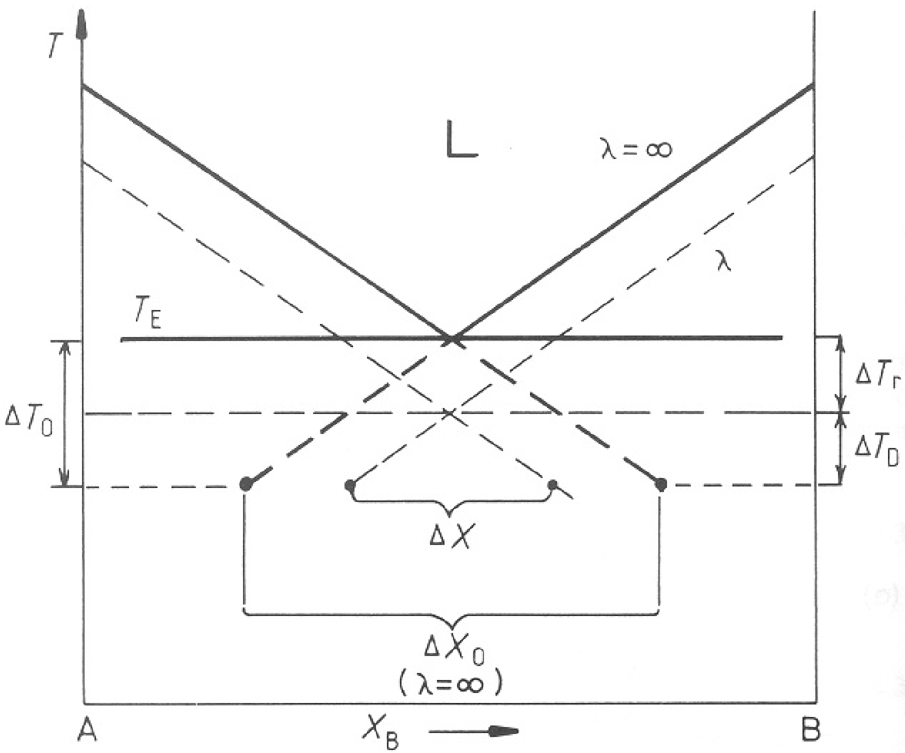
curvature composition gradient

$$\Delta G_{total} = \Delta G_r + \Delta G_D$$

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

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

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



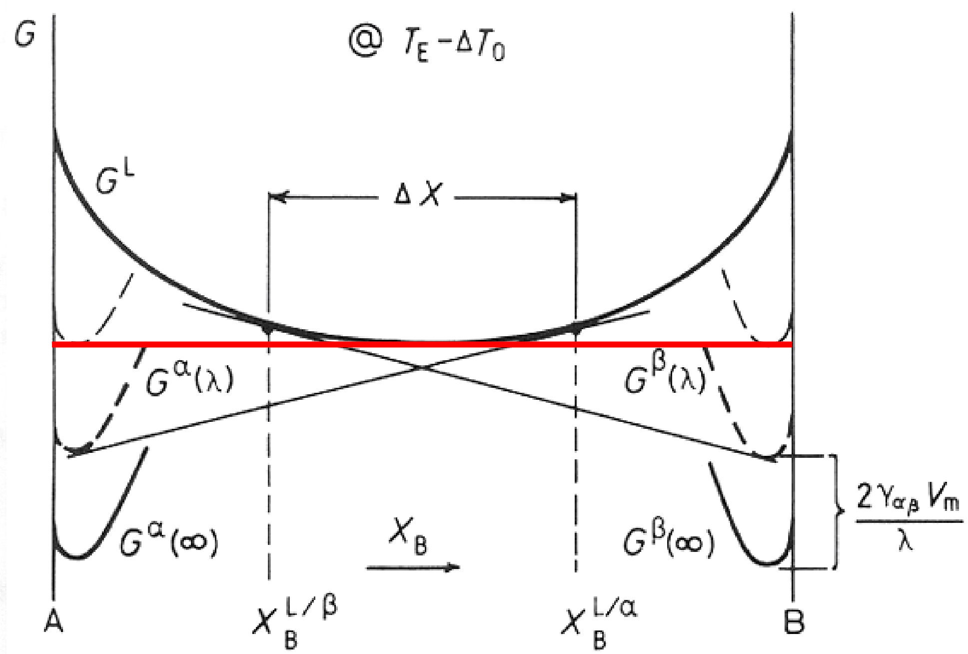


Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and ΔX_0 (exaggerated for clarity)

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

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

$$v_0 = k_2 D \Delta T_0 / 4\lambda^*$$

$$\lambda^* = + \frac{2T_E \gamma V_m}{\Delta H \Delta T_0}$$ 로 부터, $\Delta T_0 \propto 1/\lambda^*$

$\lambda = \lambda_0$ 인 경우,

$$v_0 \lambda_0^2 = k_3$$

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

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

계면 곡률효과 극복 과냉도 — **확산 위한 충분한 조성차주기 위한 과냉**

$\Delta T_D \rightarrow$ **α층의 중간부터 β층의 중간까지 연속적으로 변화**

$\Delta T_0 = const$ **계면은 항상 등온**

ΔT_r **로 극복해야 함 → 계면의 곡률을 따라 변화**