재료상변태

Phase Transformation of Materials

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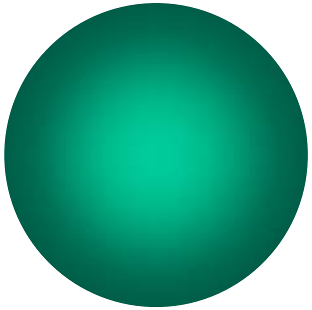
Contents for previous class

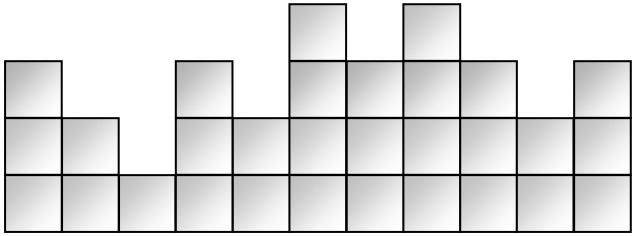
- **Equilibrium Shape and Interface Structure on an Atomic Scale**
- **Growth of a pure solid**
- **Heat Flow and Interface Stability**

Equilibrium Shape and Interface Structure on an Atomic Scale

rough interface

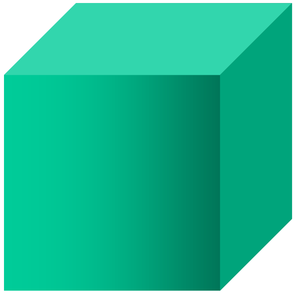
isotropic γ



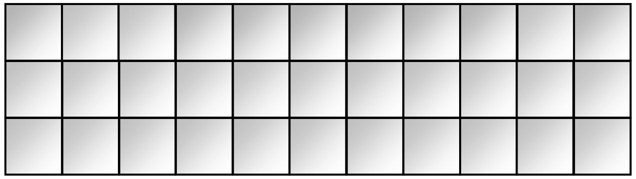


atomically-disordered

singular (smooth) interface



anisotropic γ



atomically-flat

Apply thermodynamics to this fact and derive more information.

Entropy-dominant

weak bonding energy

stable at high T

Enthalpy-dominant

strong bonding energy

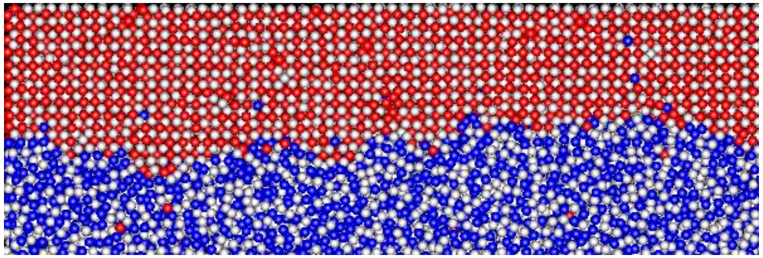
stable at low T

4.2 Growth of a pure solid

Two types of solid-liquid interface

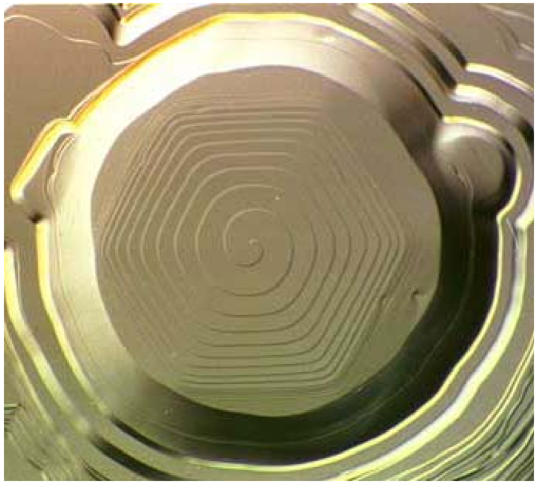
1. Continuous growth

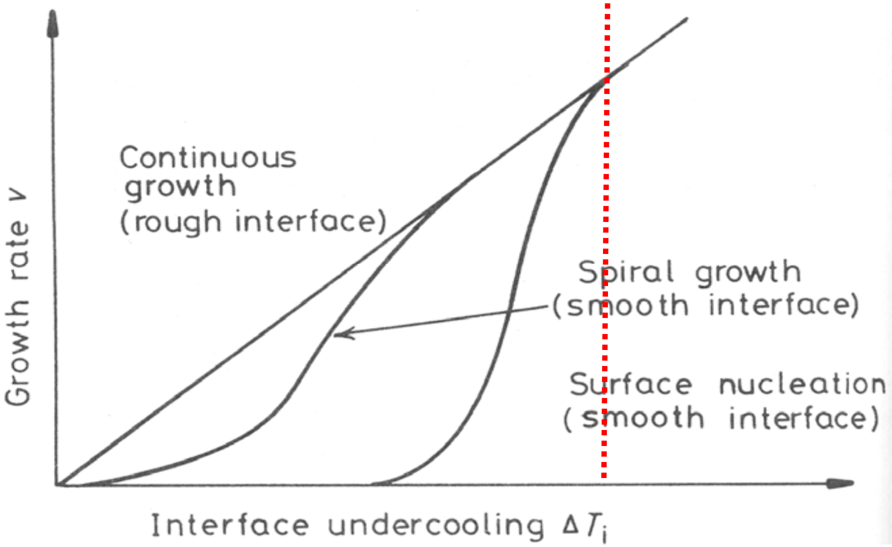
：Atomically rough or diffuse interface



2. Lateral growth

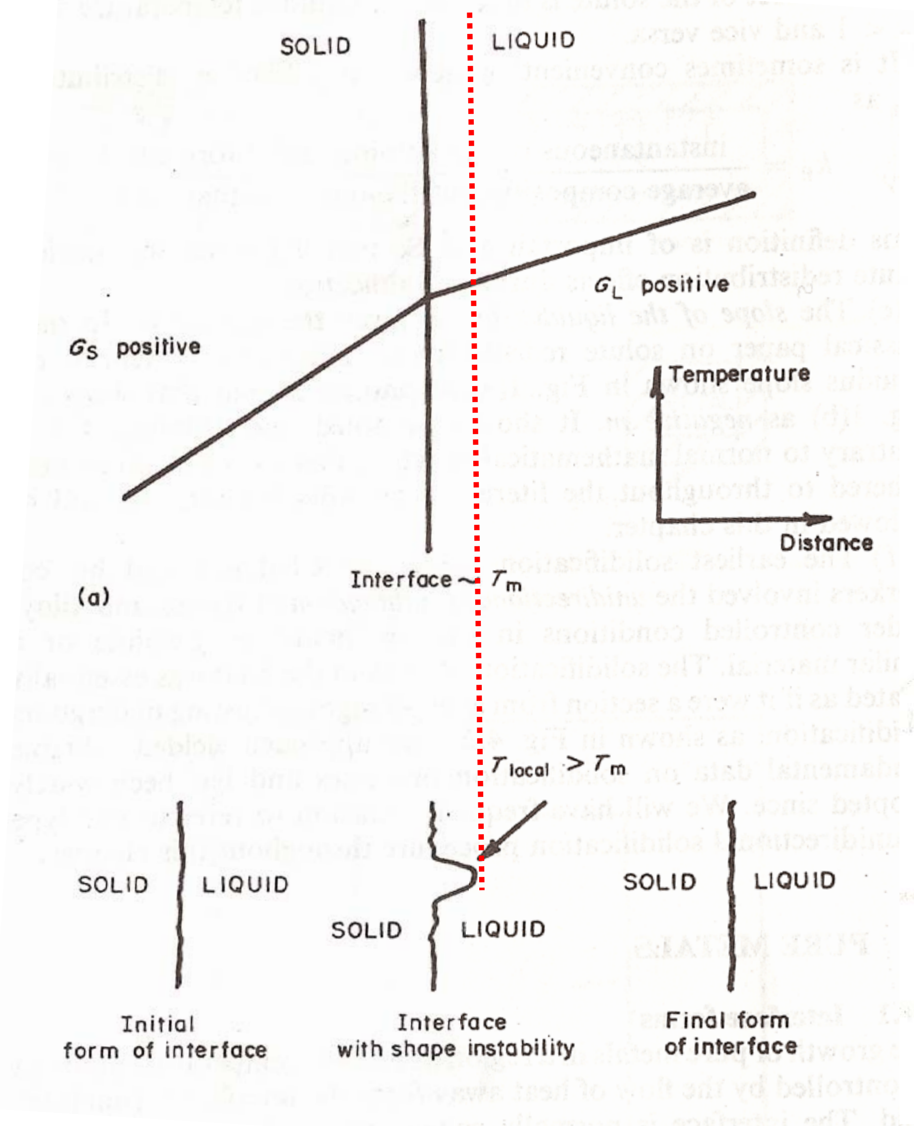
：Atomically flat of sharply defined interface



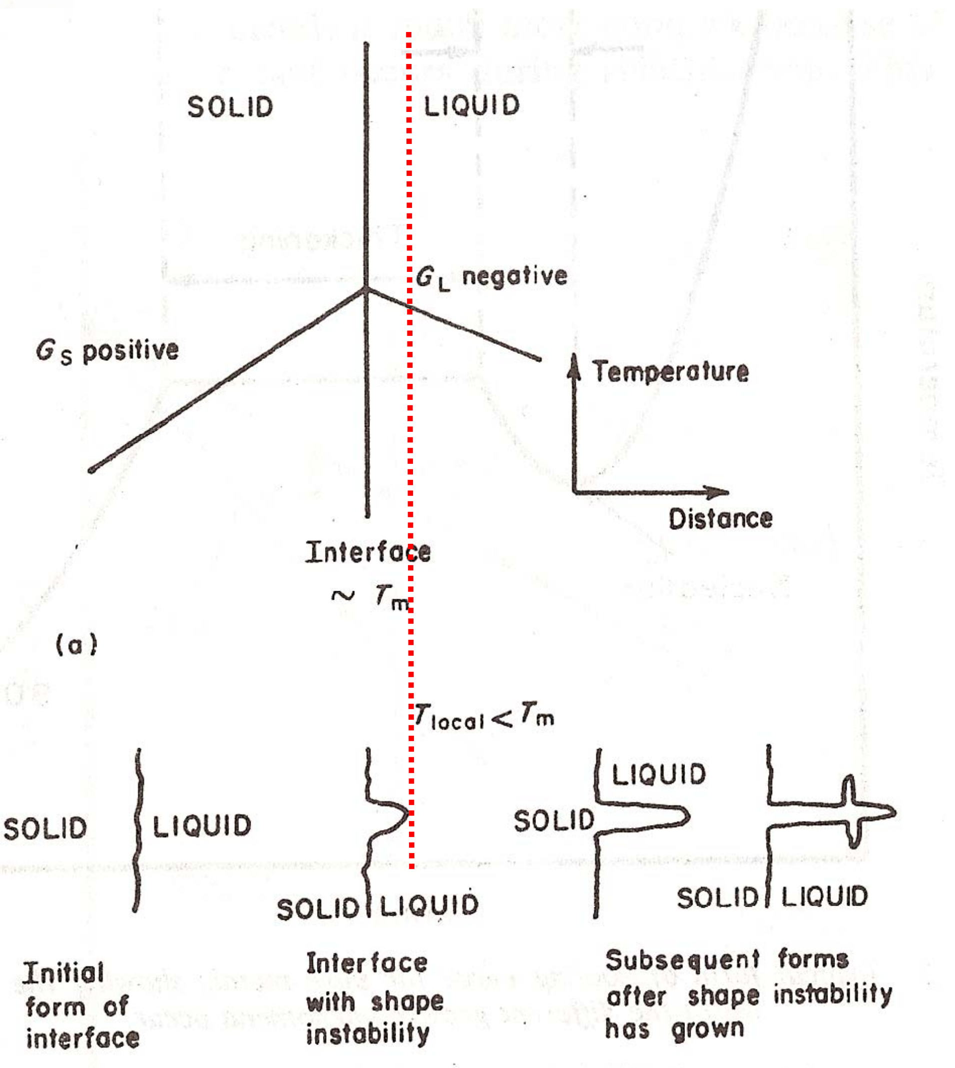


4.2.3 Heat Flow and Interface Stability - Planar interface

1) Superheated liquid



2) Supercooled liquid



Contents for today’s class

“Alloy solidification”

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

4.3.1 Solidification of single-phase alloys

$$k = \frac{X_S}{X_L} < 1$$

k **: partition coefficient**

X **: mole fraction of solute**

In this phase diagram of **straight solidus and liquidus**, ***k*** **is independent of** ***T*****.**

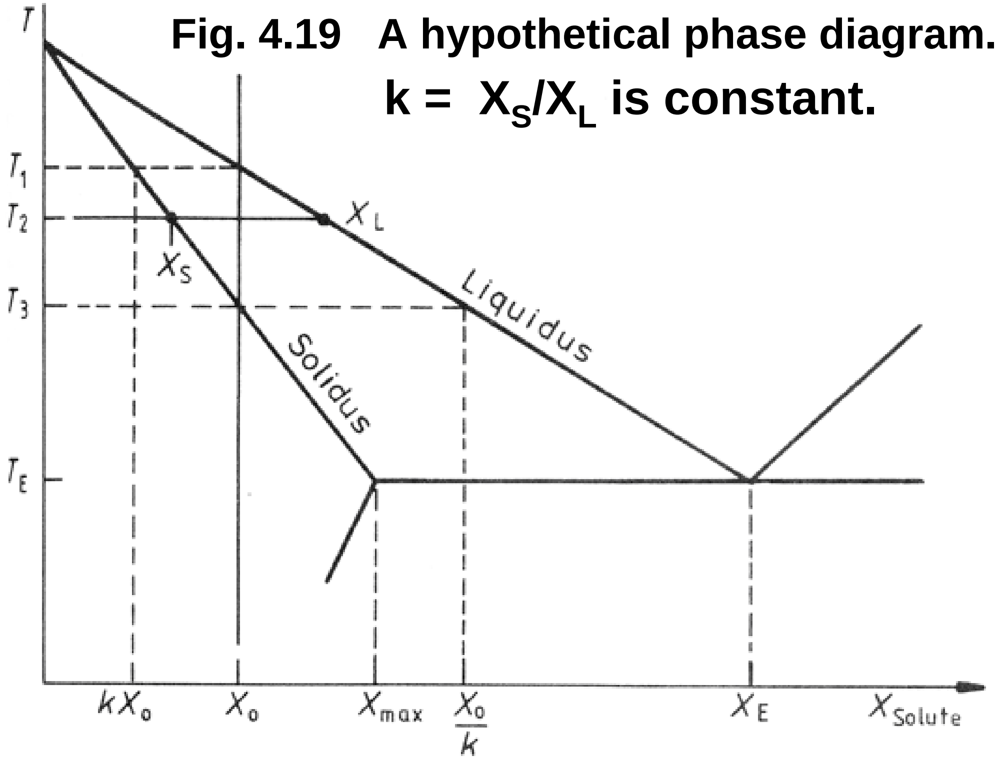
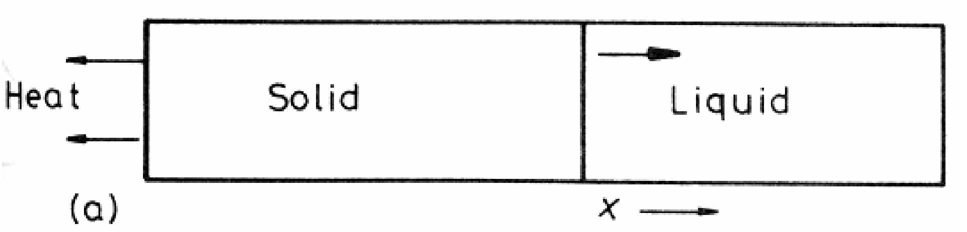


Fig. 4.19 A hypothetical phase diagram.

k = X_S/X_L is constant.

Planar S/L interface
→ unidirectional solidification



4.3.1 Solidification of single-phase alloys

- **Three limiting cases**

1) Equilibrium Solidification

2) No Diffusion in Solid, Perfect Mixing in Liquid

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

1) Equilibrium Solidification

→ **low cooling rate**

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

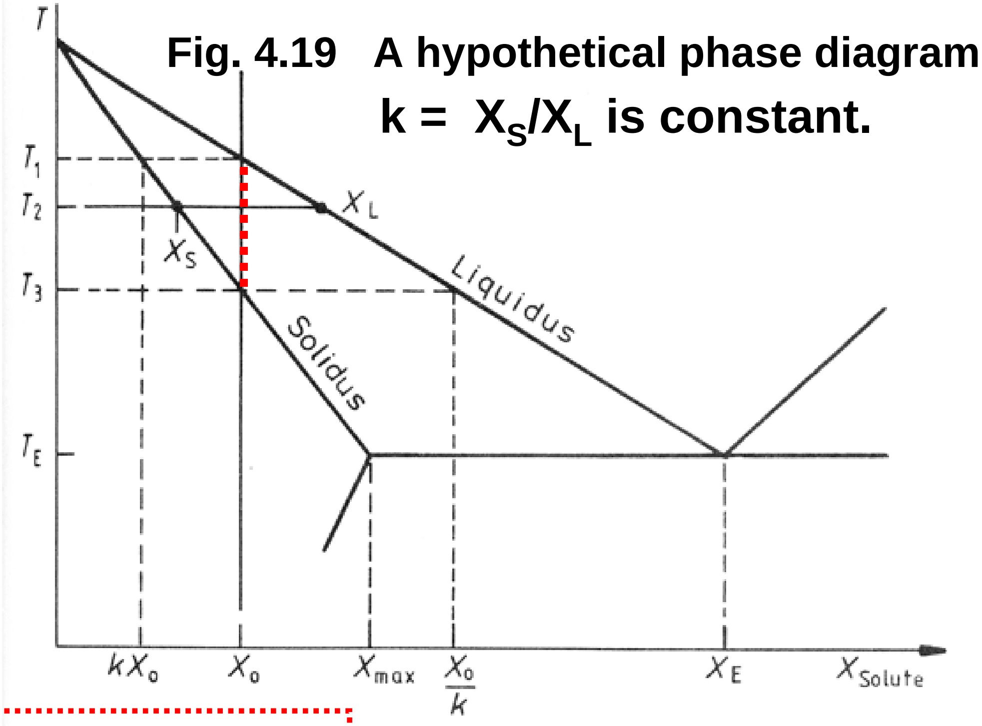
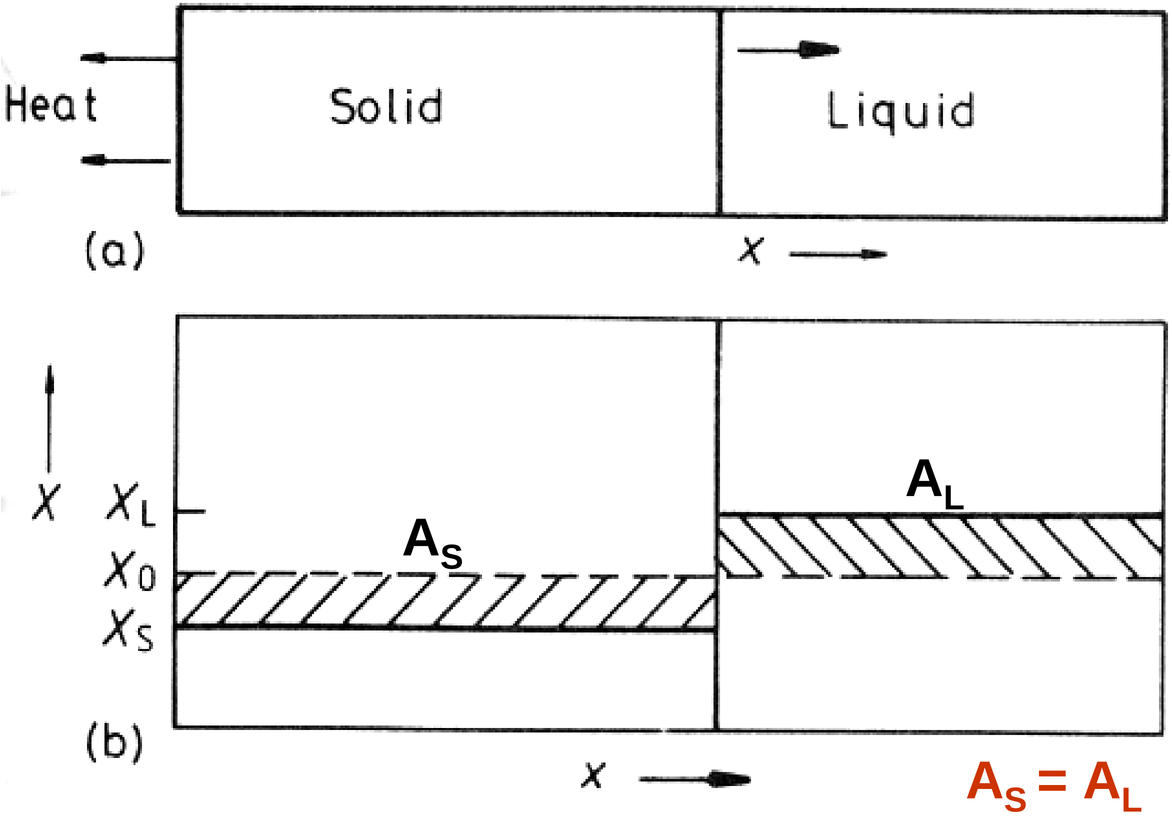


Fig. 4.19 A hypothetical phase diagram.

$k = X_S/X_L$ 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 ($X_L=X_0/k$).**

Composition vs **x at T_2**



$A_S = A_L$

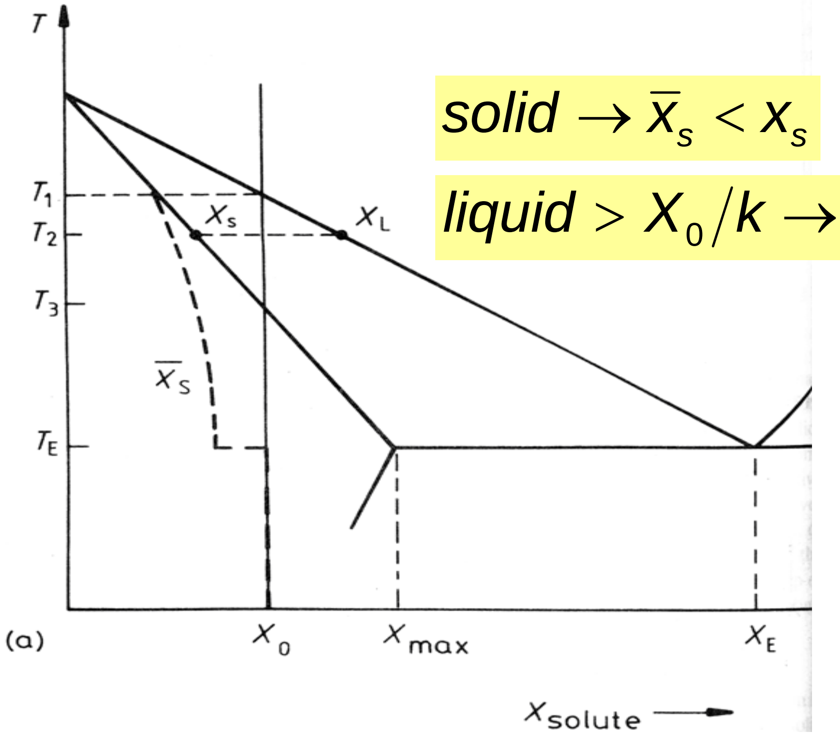
Fig. 4.20 Unidirectional solidification of alloy X_0 in Fig. 4.19. (a) A planar S/L interface and axial heat flow. (b) Corresponding composition profile at T_2 assuming complete equilibrium. Conservation of solute requires the two shaded areas to be equal.

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
- **Liquid become richer than X_0/K → X_E**
- **Variation of X_s: solute rejected to the liquid**



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

$$liquid > X_0/k \rightarrow X_E$$

local equil. at S/L interface

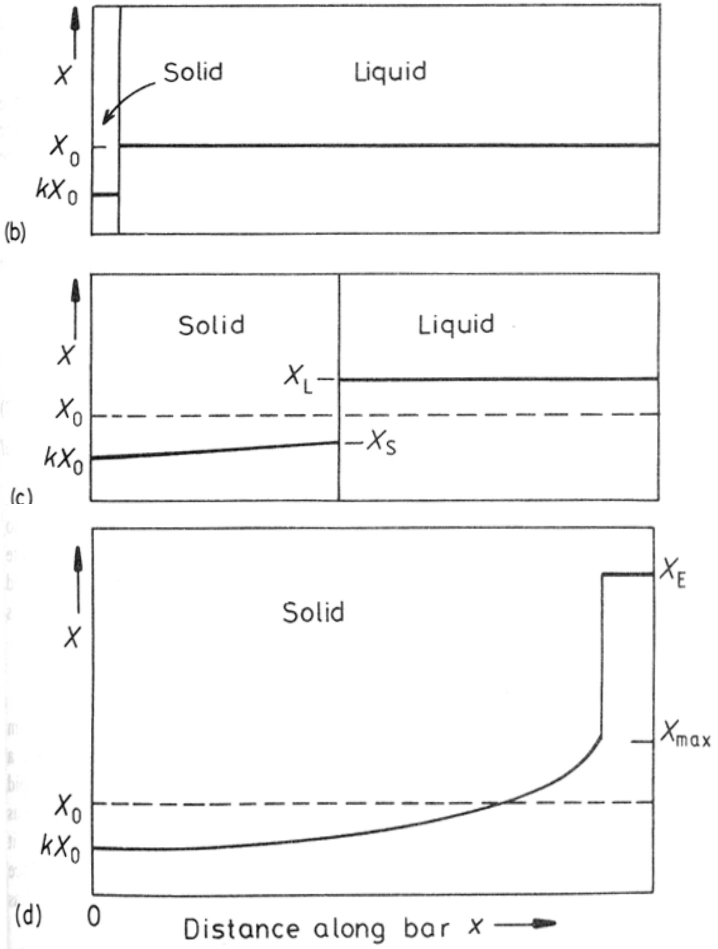


Fig. 4.21 Planar front solidification of alloy X_0 in fig. 4.19 assuming no diffusion in the solid, but complete mixing in the liquid. (a) As Fig. 4.19, but including the mean composition of the solid. (b) Composition profile just under T_1. (c) Composition profile at T_2 (compare with the profile and fraction solidified in Fig.4.20b) (d) Composition profile at the eutectic temperature and below.

Mass balance: non-equilibrium lever rule (coring structure)

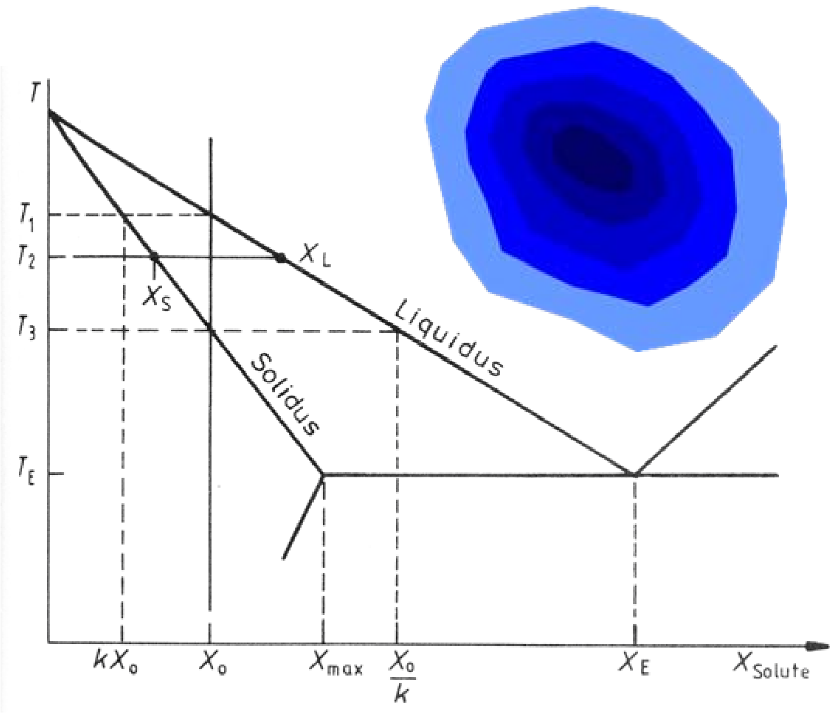
When cooled by dT from any arbitrary T, determine the followings.

solute ejected into the liquid = ?

→ **solute increase in the liquid**

Ignore the difference in molar volume between the solid and liquid.

f_S: **volume fraction solidified**



solute ejected into the liquid=? → **proportional to what?** **df_S** **$(X_L – X_S)$**

solute increase in the liquid=? → **proportional to what?** **$(1-f_S)$** **dX_L**

$$(X_L - X_S)df_S = (1-f_S)dX_L$$

Solve this equation.

when $f_S = 0$ → X_S, X_L?

$X_S = kX_0$ and $X_L = X_0$

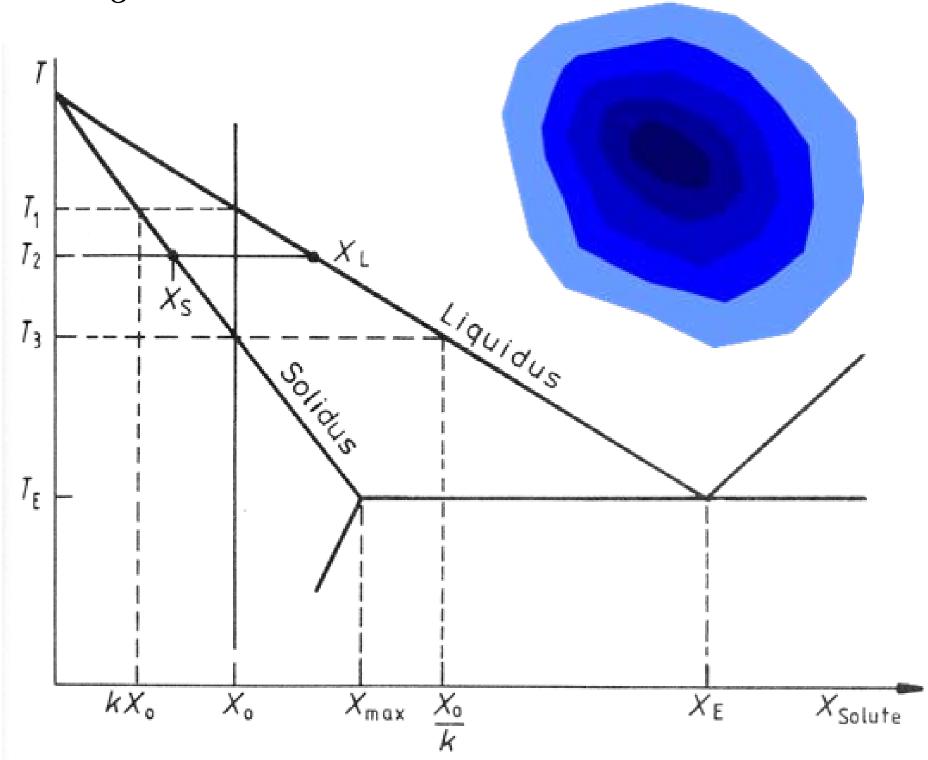
$$\int_0^{f_S}\frac{df_S}{1-f_S}=\int_{X_0}^{X_L}\frac{dX_L}{X_L-X_S}=\int_{X_0}^{X_L}\frac{dX_L}{X_L-kX_L}=\int_{X_0}^{X_L}\frac{dX_L}{X_L(1-k)}$$

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

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

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

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

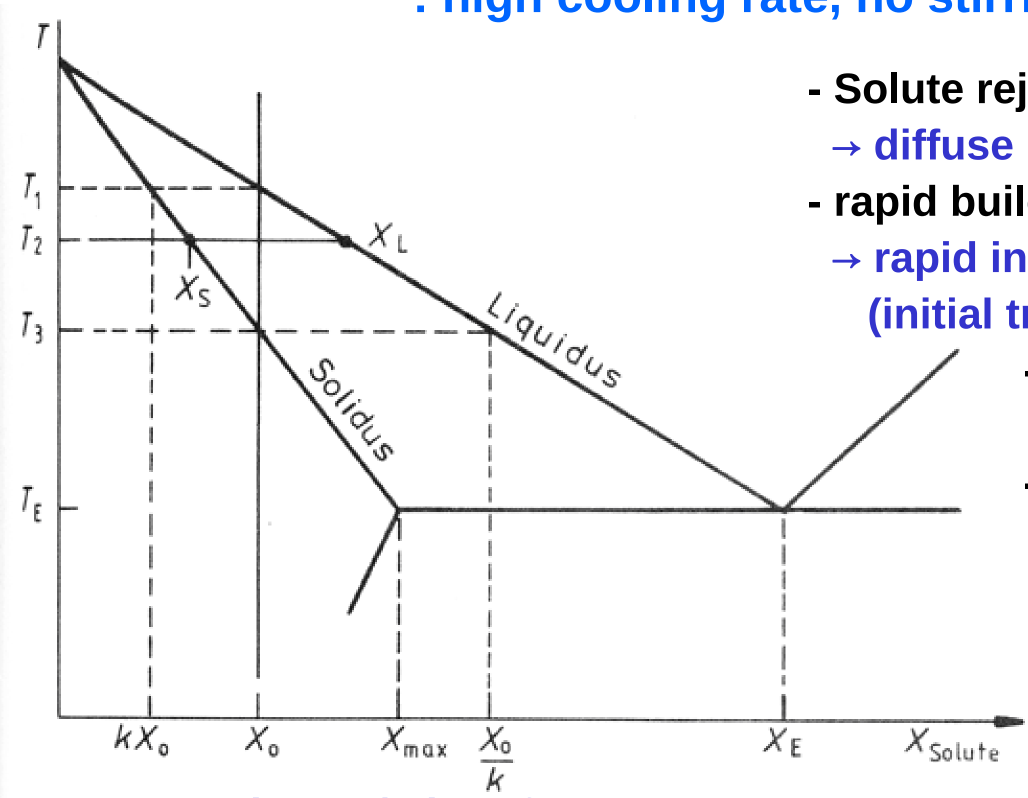


: non-equilibrium lever rule. (Scheil equation)

If K<1: predicts that if no diff. in solid, some eutectic always exist to solidify.

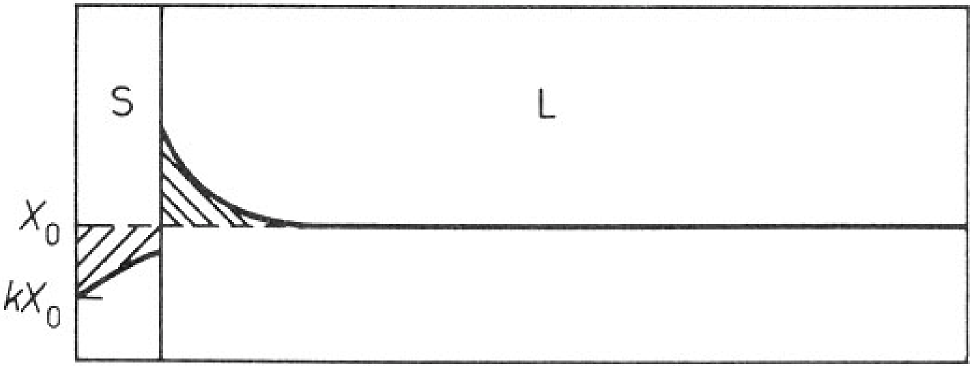
3) No Diffusion on Solid, Diffusional Mixing in the Liquid

: high cooling rate, no stirring→ diffusion



- **Solute rejected from solid**
  → diffuse into liquid with limitation
- **rapid build up solute in from of the solid**
  → rapid increase in the comp. of solid forming (initial transient)
- **if it solidifies at a const. rate, v, then a steady state is finally obtained at T_3**
- **liquid : X_0/k, solid: X_0**

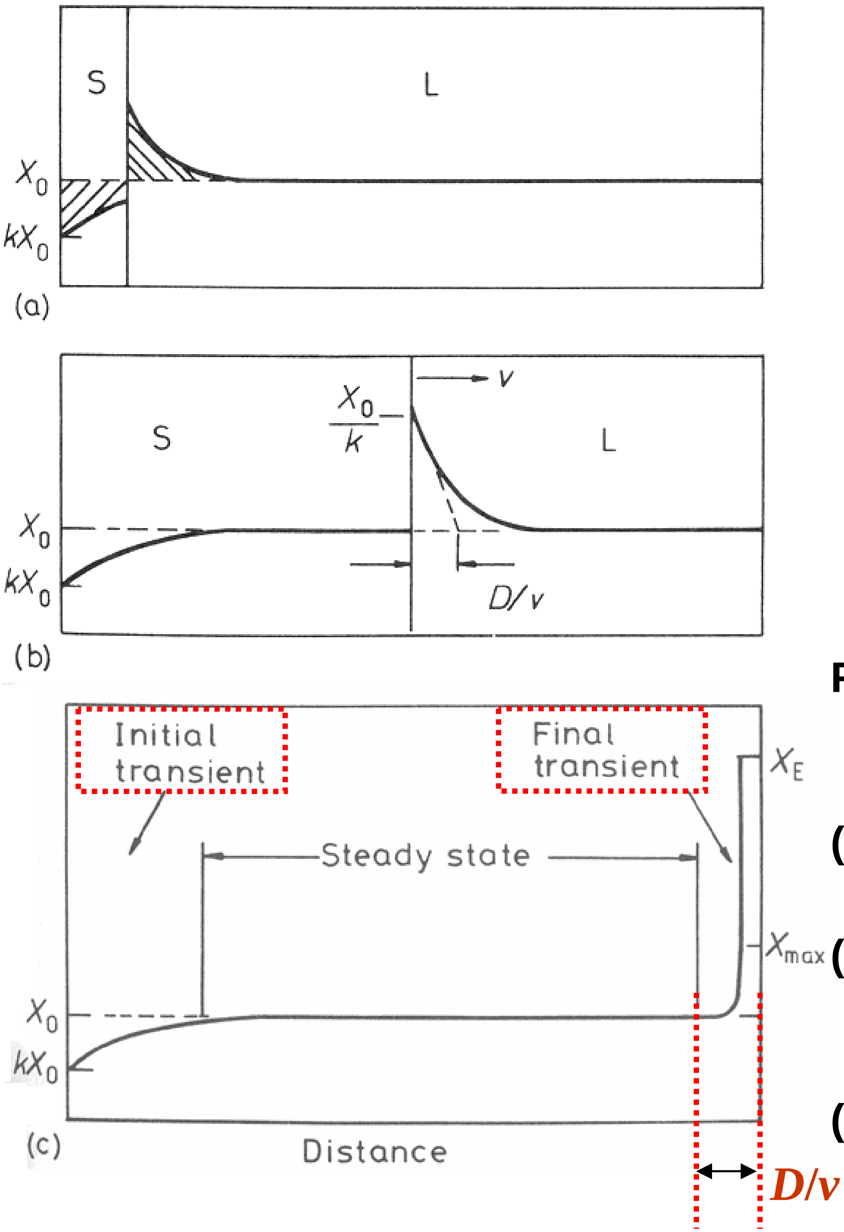
local equil. at S/L interface



Composition profile at $T_2 < T_{S/L} < T_3$?

Steady-state profile at T_3?
at T_E or below ?

No Diffusion on Solid, Diffusional Mixing in the Liquid



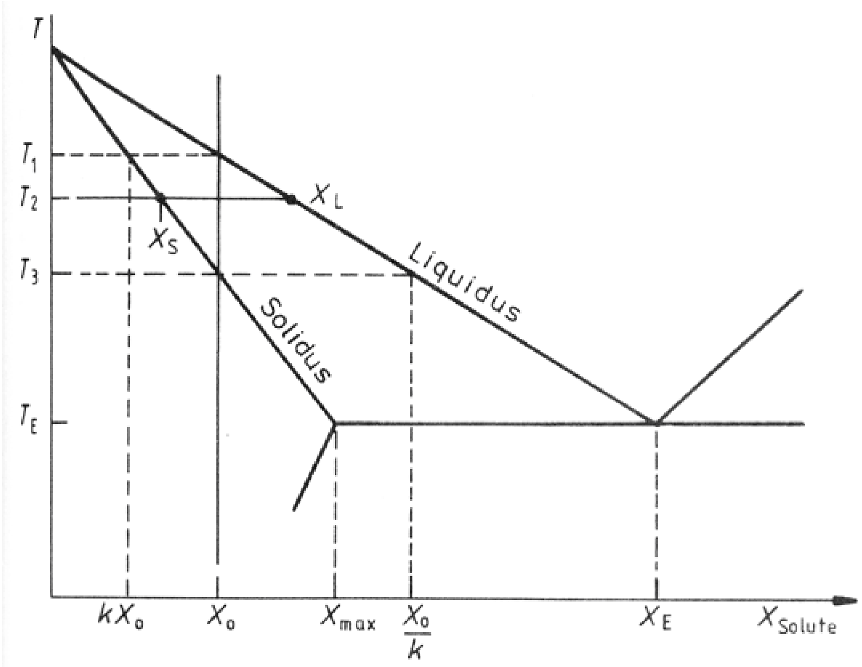


Fig. 4.22 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in solid and no stirring in the liquid.

(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.

No Diffusion on Solid, Diffusional Mixing in the Liquid

During steady-state growth

(Diffusion in solid)

Rate at which solute diffuses down the concentration gradient
= Rate at which solute is rejected from the solidifying liquid

(Liquid → Solid)

Set up the equation.

$$J = -DC_L' = v(C_L - C_S)$$

$$J = -D\frac{\partial X_L}{\partial x} = v\boxed{\left(X_L - X_S\right)}$$

(합금의 응고 속도: 과잉 용질 제어)

$$\Updownarrow$$

$$K_S T_S' = K_L T_L' \quad + v\boxed{L_V}$$

(순금속의 응고속도: 잠열 제어, 10^4 배 빠름)

Solve this equation.

$$X_S = X_o \ \text{for all}\ x \geq 0$$

$$\frac{dX_L}{X_L - X_o} = -\frac{v}{D}dx$$

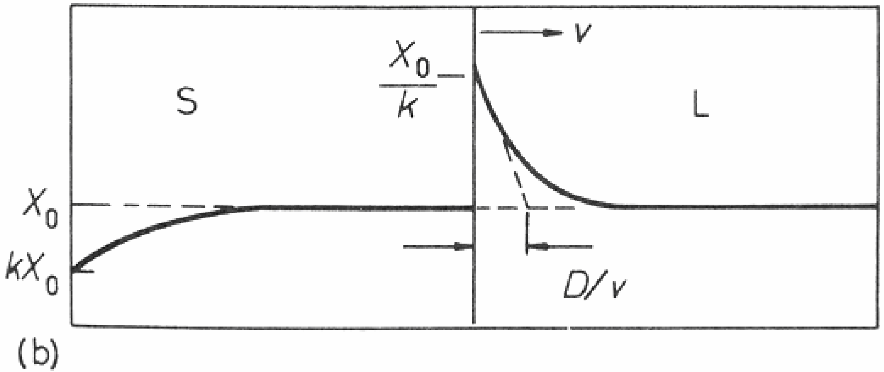
$$\ln\left(X_L - X_o\right) = -\frac{v}{D}x + c$$

$$x = 0;\ X_L = X_o / k$$

$$c = \ln\left(\frac{X_o}{k} - X_o\right)$$

$$\ln \frac{X_L - X_o}{X_o\left(\frac{1}{k} - 1\right)} = -\frac{v}{D}x$$

$$X_L - X_o = X_o\left(\frac{1-k}{k}\right)e^{-\frac{vx}{D}}$$



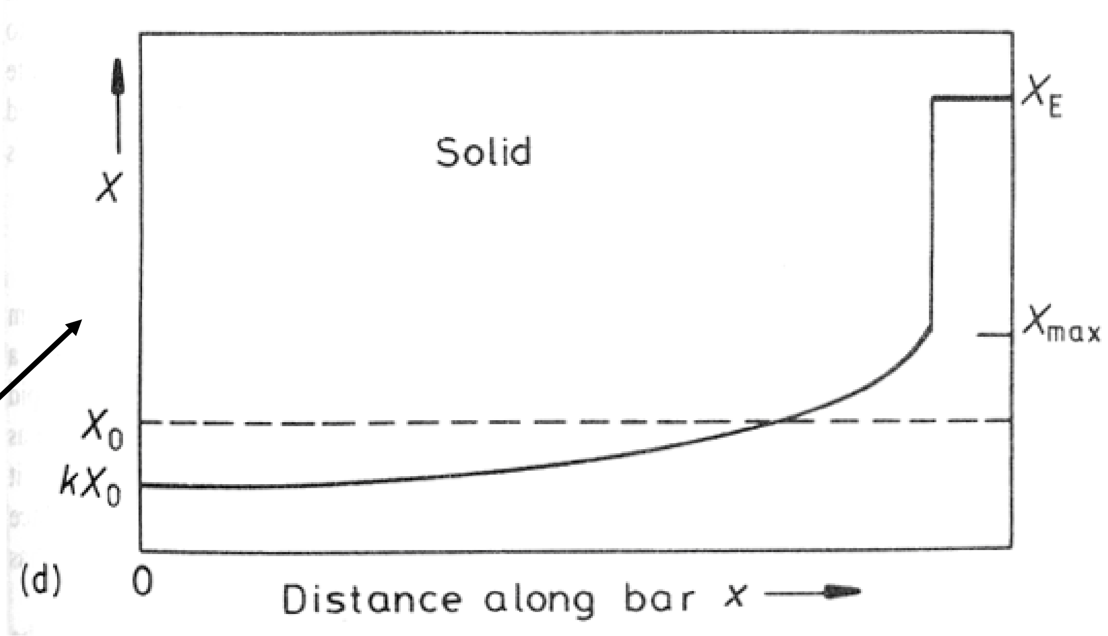
$$X_L = X_O\left[1 + \frac{1-k}{k}\exp\left(-\frac{x}{(D/v)}\right)\right]$$

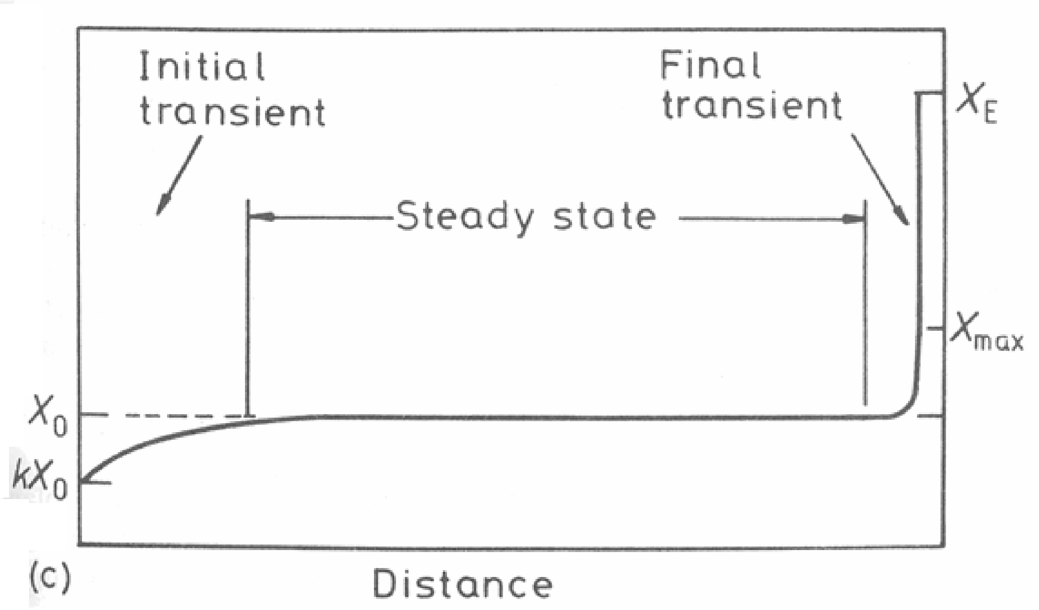
- The concentration gradient in liquid in contact with the solid :

$$J = -DX_L' = v\left(X_L - X_S\right) \qquad X_L' = -\frac{X_L - X_S}{D/v}$$

실제의 농도분포

두 가지 경우의 중간형태



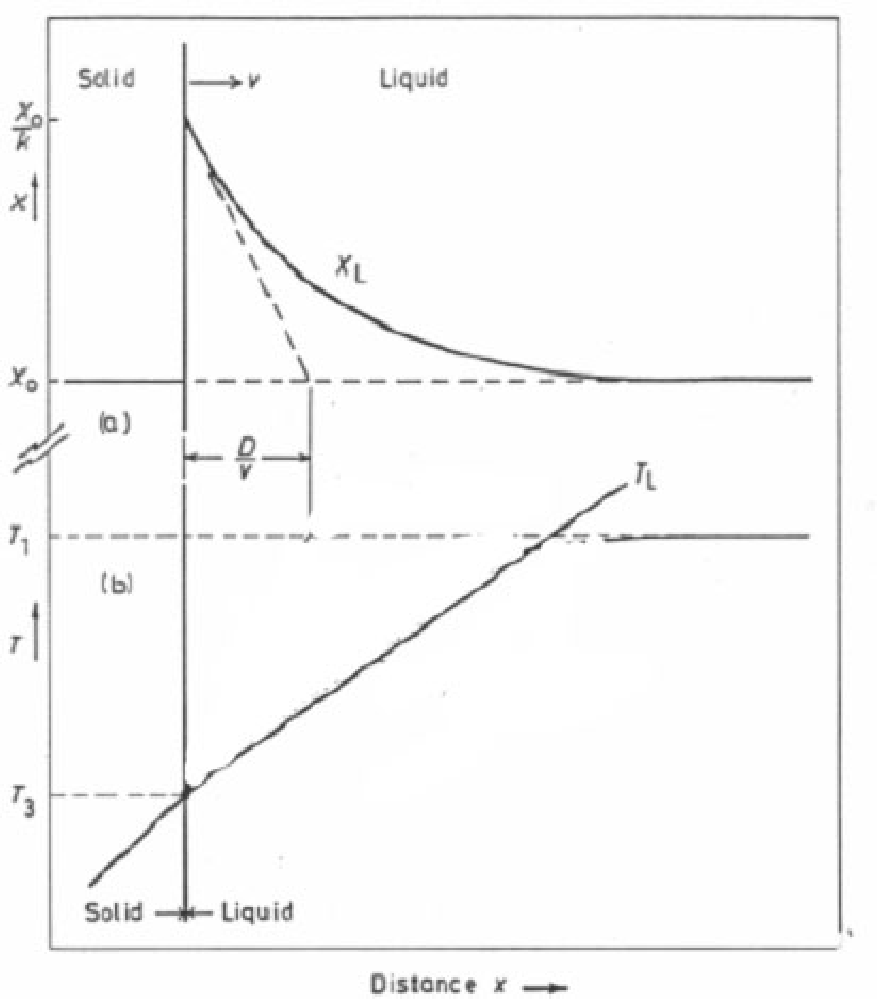


➡ **Zone Refining**

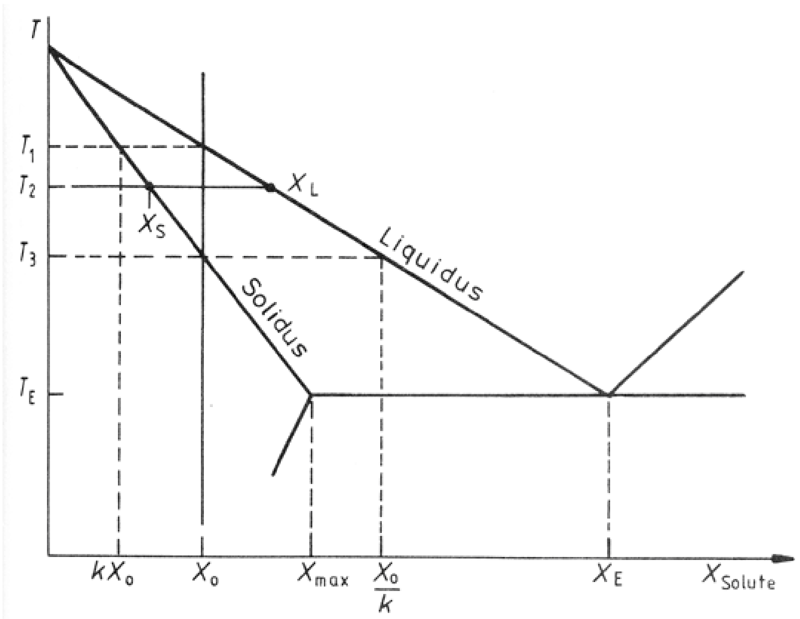
Cellular and Dendritic Solidification

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

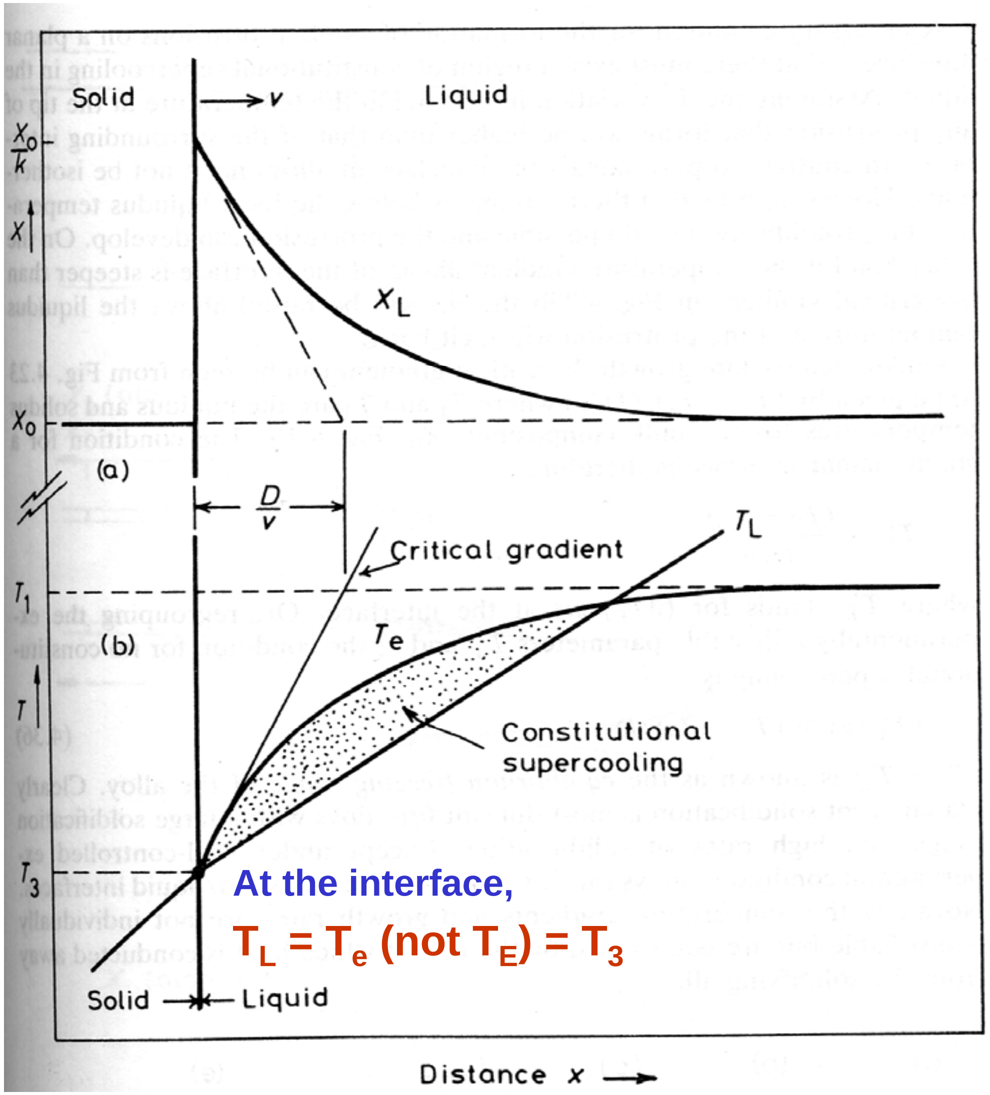
→ complicated by the possible temp. gradient in the liquid.



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



Constitutional Supercooling



At the interface,

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

Condition for a stable planar interface

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

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

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 Te. Constitutional supercooling arises when T_L lies under the critical gradient.

Cellular and Dendritic Solidification

- **Constitutional supercooling :**

  At the interface, $T_L = T_e$ (not T_E) $= T_3$.

- **Criterion for the planar interface :**

  $T_L'/v > (T_1-T_3)/D$: the protrusion melts back. 조성적 과냉 X

  (T_1-T_3 : Equilibrium freezing range of alloy)

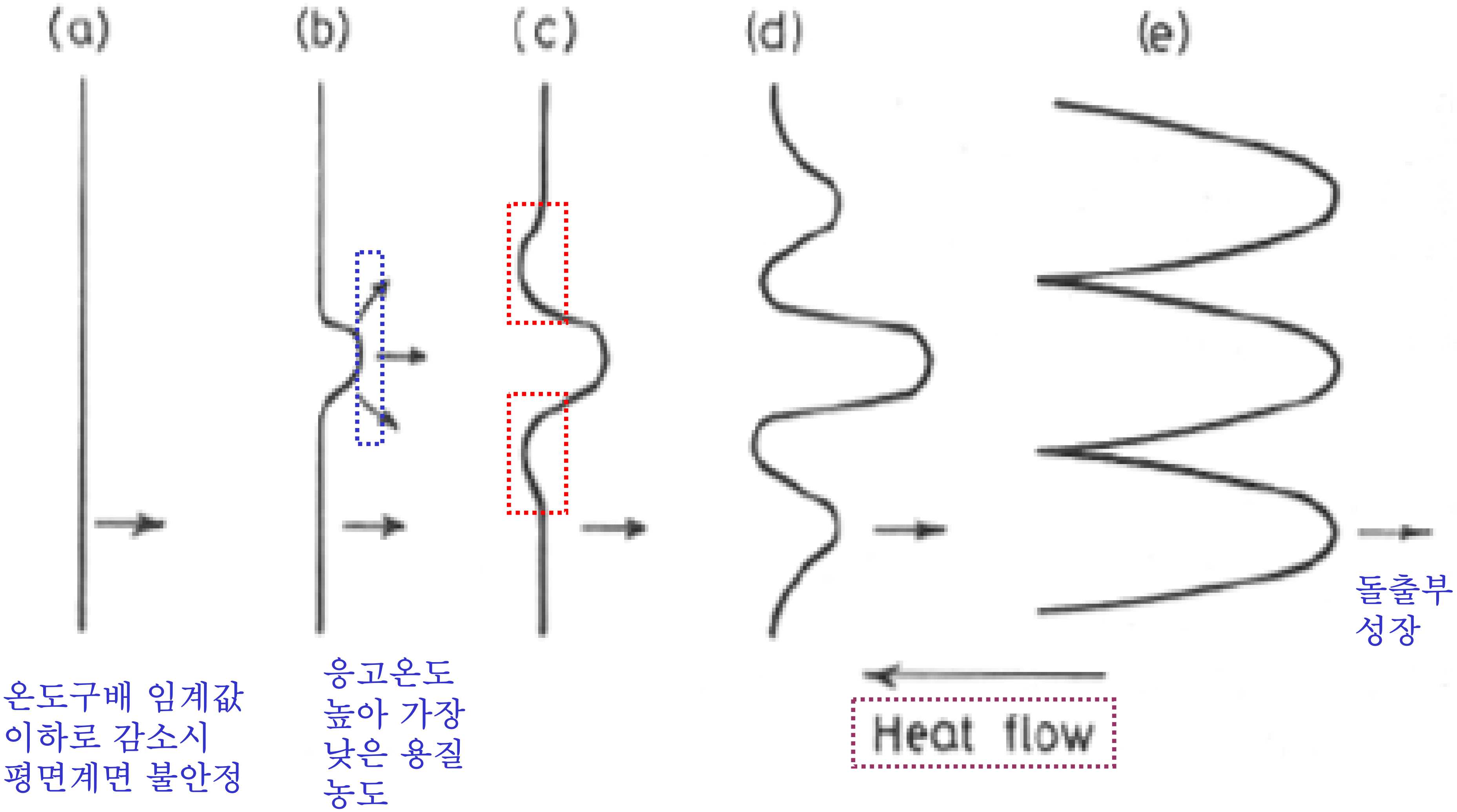
  → **Large range of T_1-T_3 or high v promotes protrusions.**

- **Dendrites**

  Solute effect : low k enlarges T_1-T_3 promotes dendrites.

  → **Development of secondary arms and tertiary arms: <100>**

  Cooling rate effect : Fast cooling makes lateral diffusion of the rejected solutes difficult and promotes cell formation of smaller cell spacing.

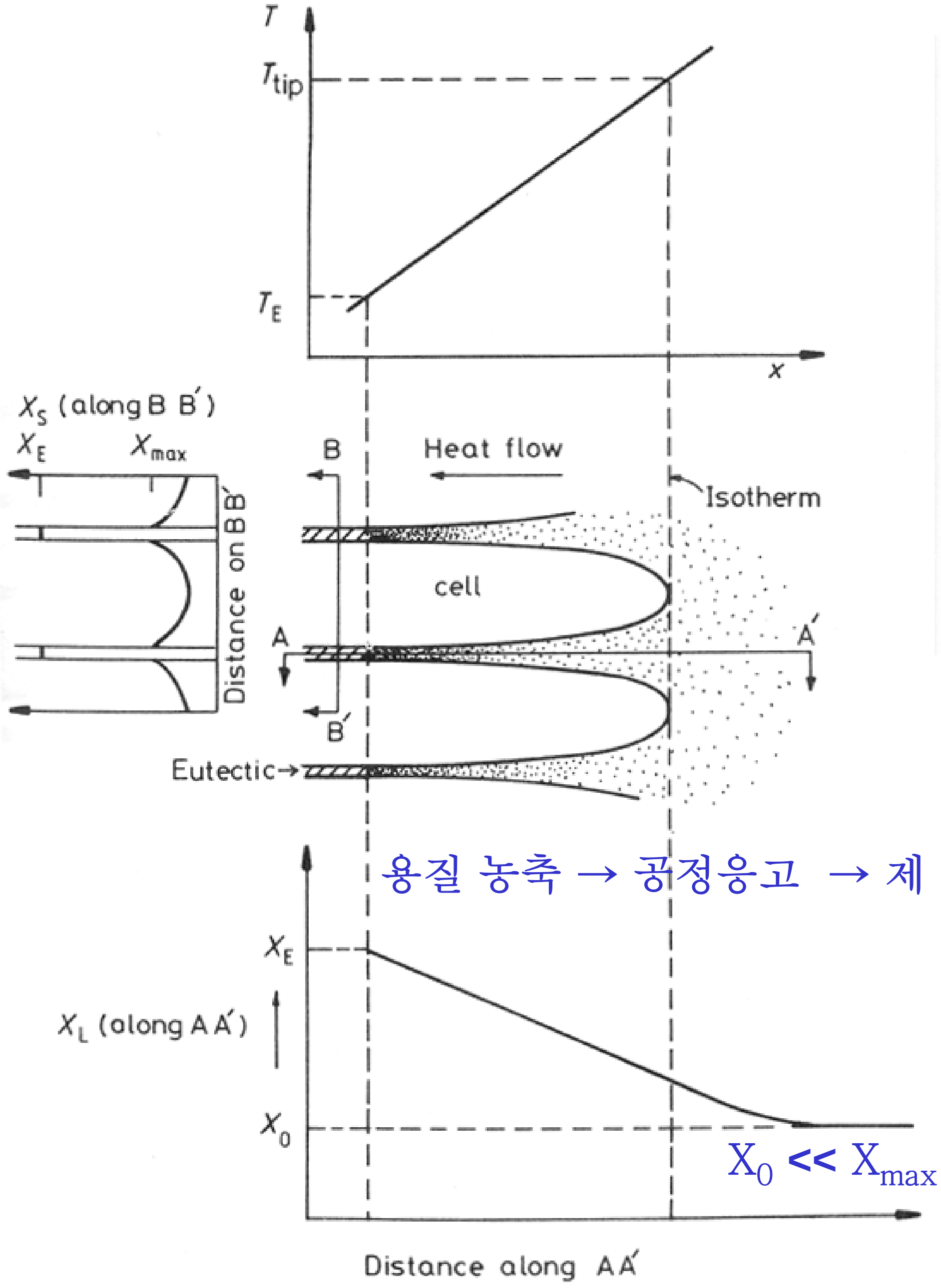


온도구배 임계값
이하로 감소시
평면계면 불안정

응고온도
높아 가장
낮은 용질
농도

돌출부
성장

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



용질 농축 → 공정응고 → 제 2 상 형성

$X_0 << X_{max}$

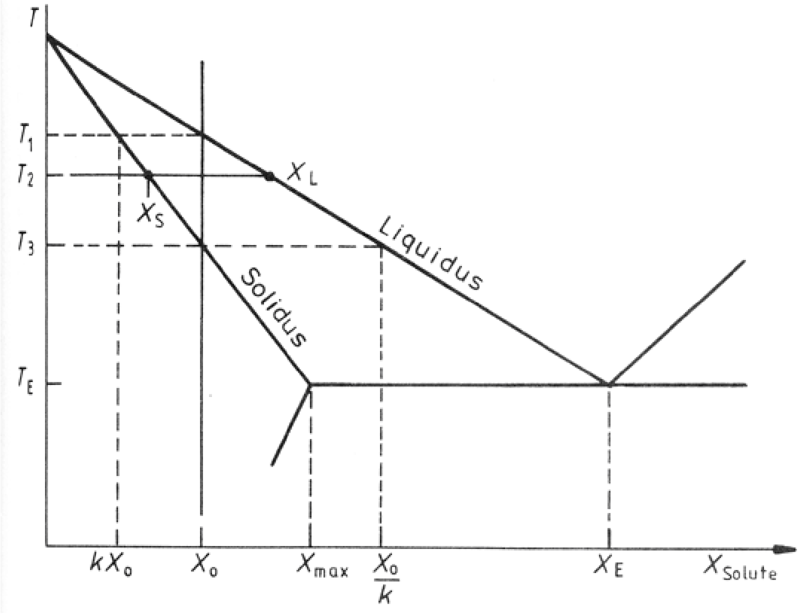


Fig. 4.25 **Temperature and solute distributions associated with cellular solidification.**

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

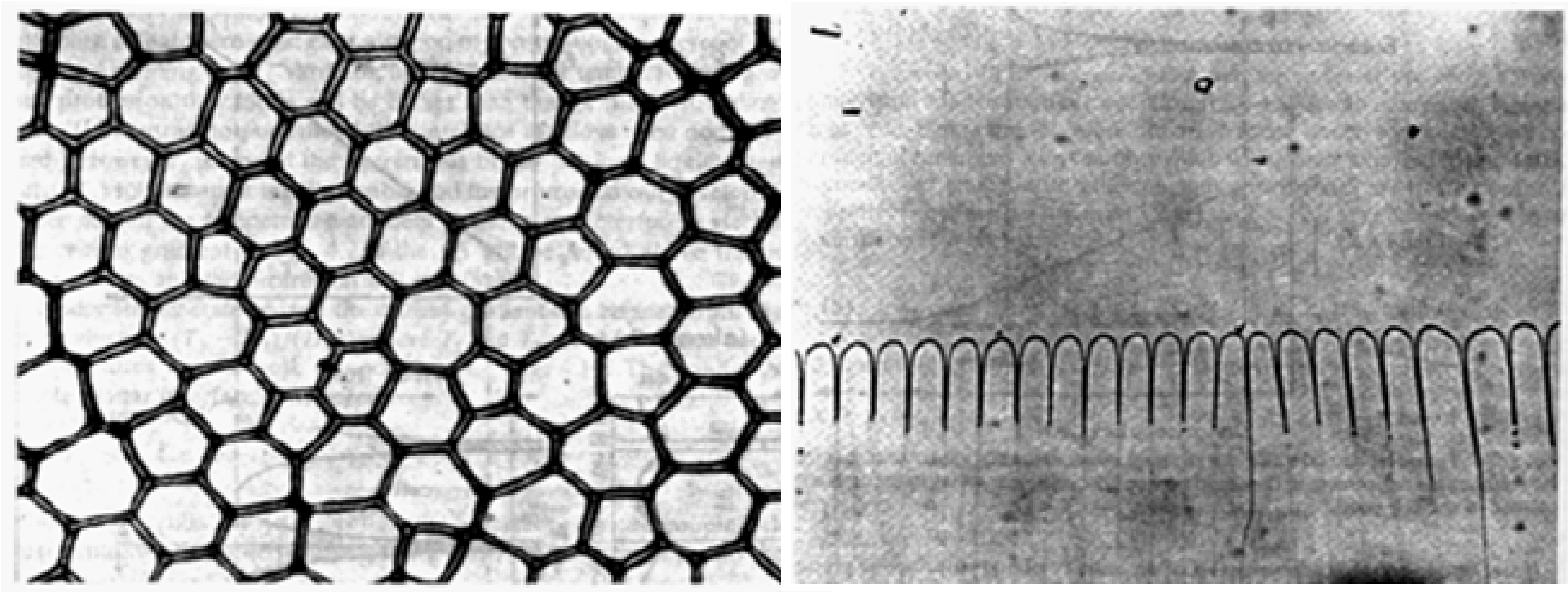


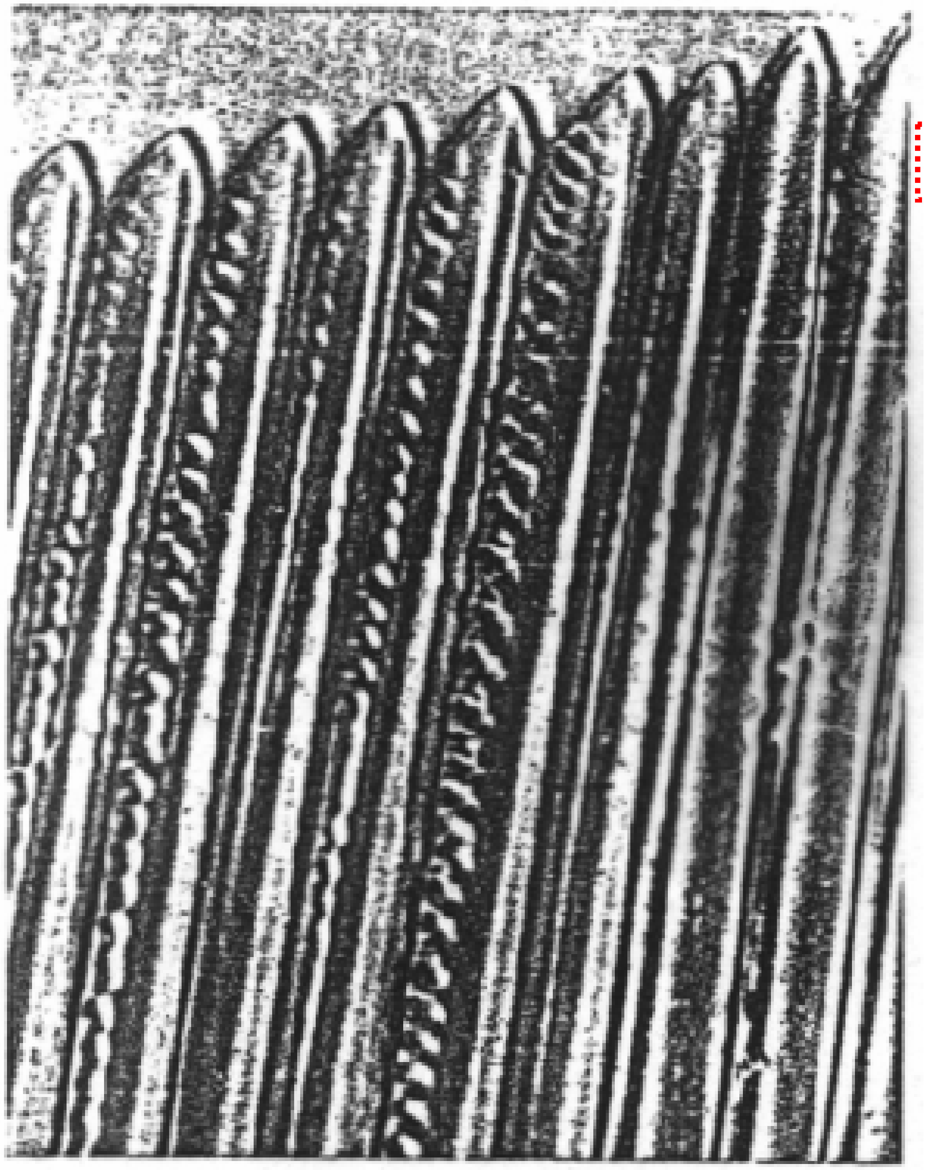
Fig. 4.26 Cellular microstructures.

(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

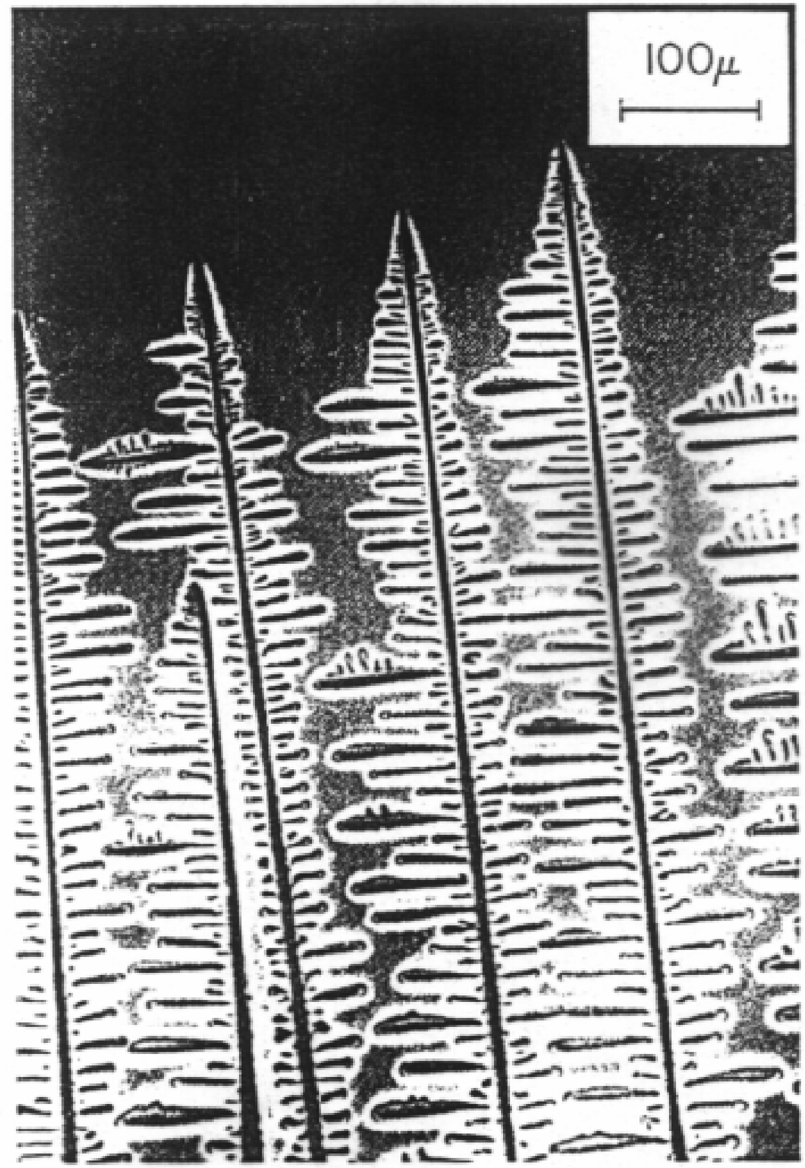
세포상 조직 과 수지상 조직의 천이

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.

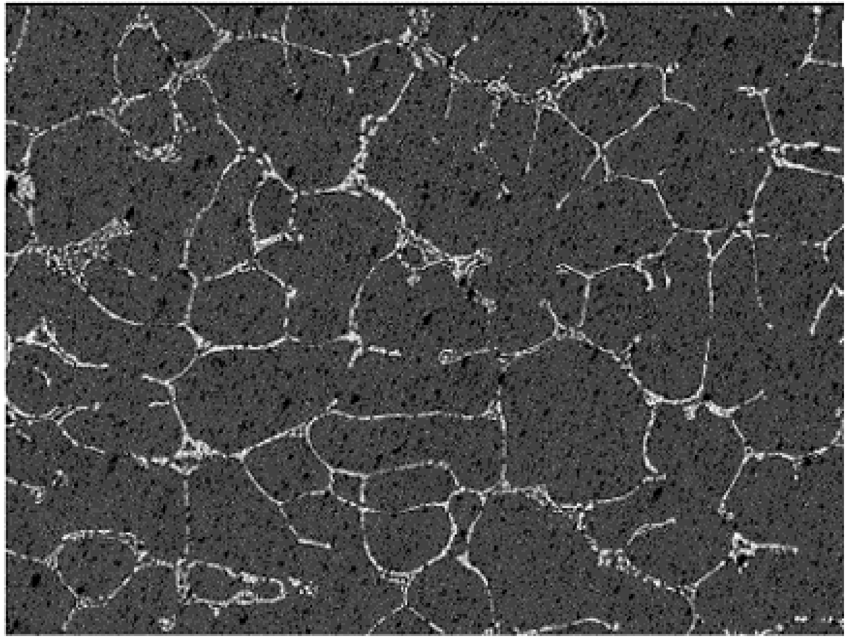
(After K.A. Jackson in Solidification, American Society for Metals, 1971, p. 121.)

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

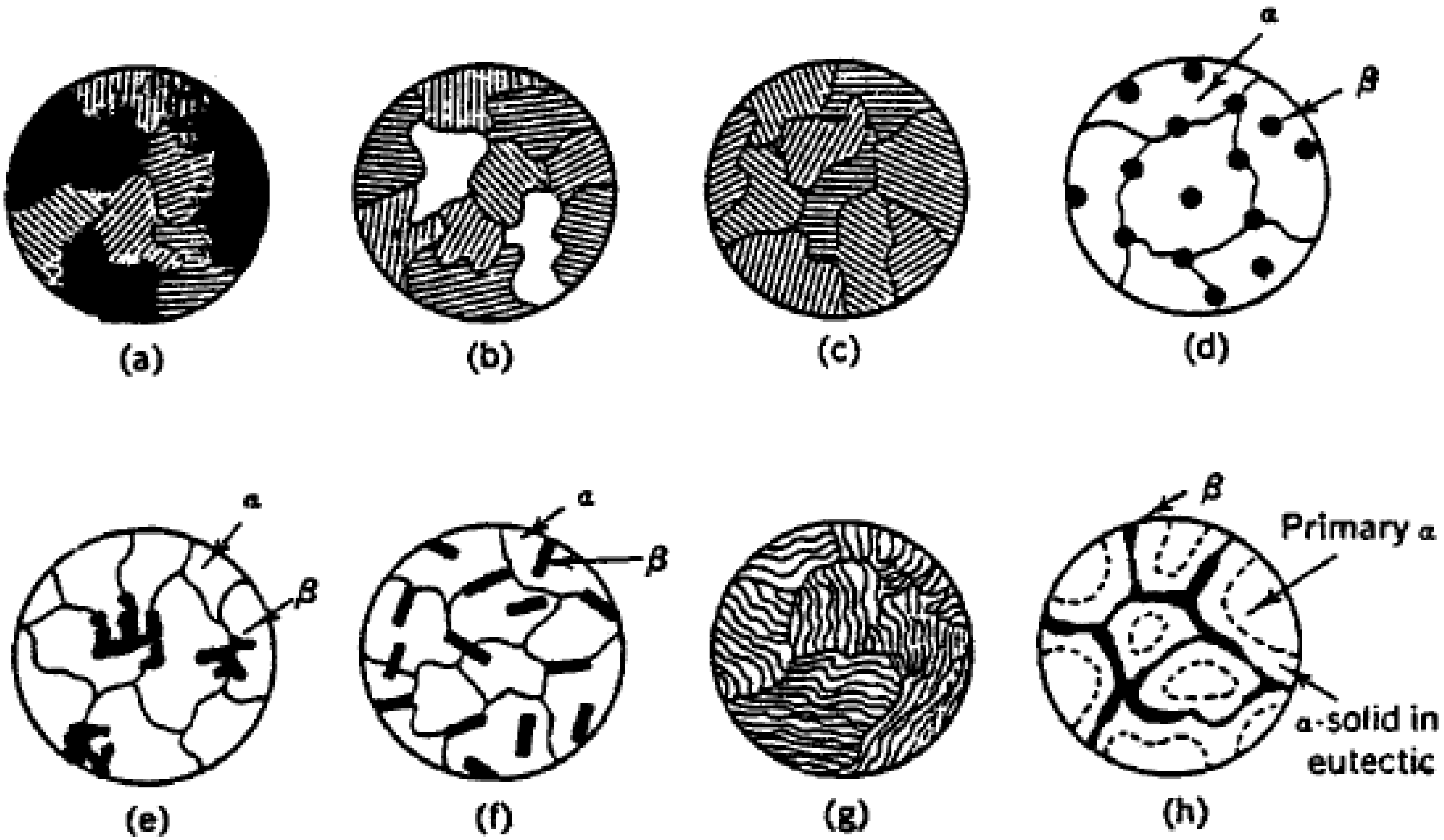
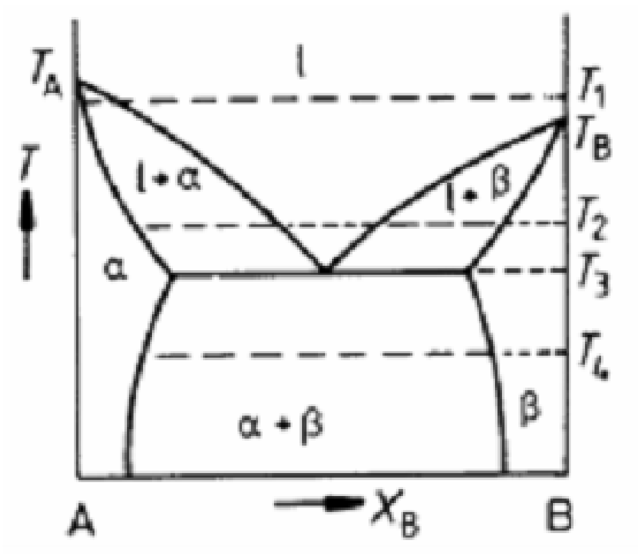
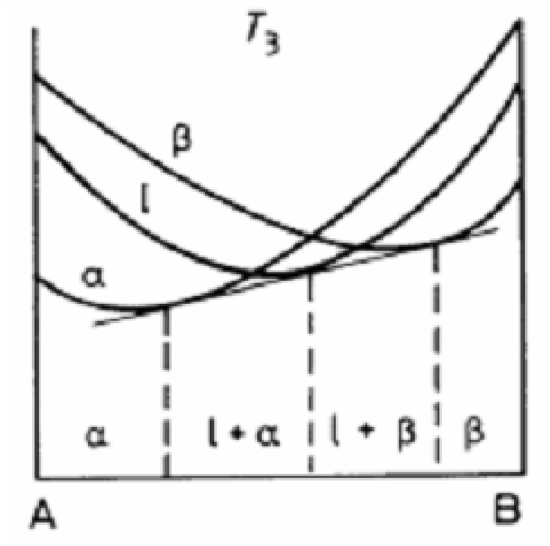
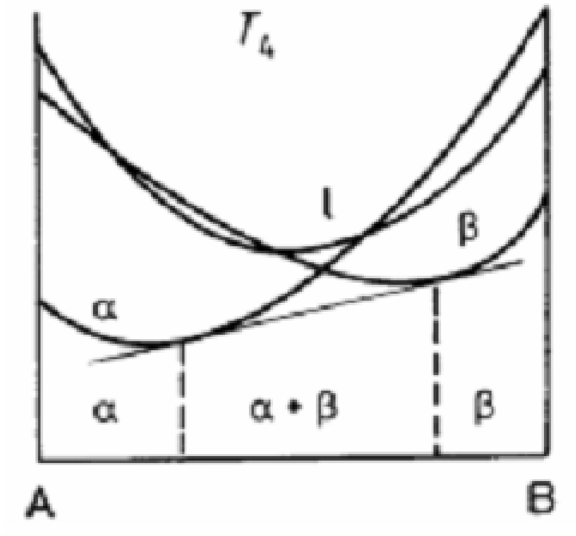


Fig. 14 Schematic representation possible in eutectic structures. (a), (b) and (c) are alloys shown in fig. 13; (d) nodular; (e) Chinese script; (f) acicular; (g) lamellar; and (h) divorced.

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?

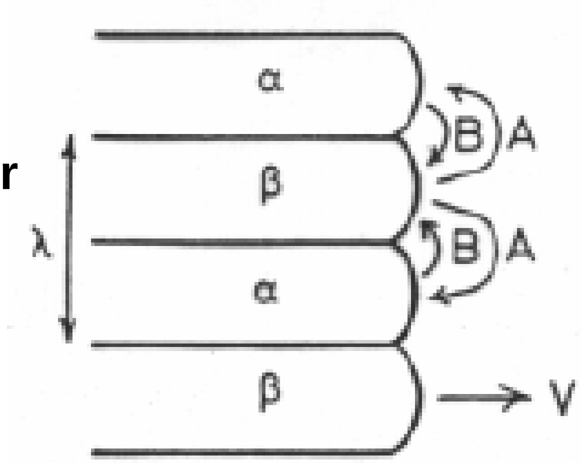
Eutectic Solidification (Kinetics)

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

→ rough interface & local equilibrium

How about at β/L? Nature's choice?

interlamellar spacing →



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

→ Gibbs-Thomson Effect

Eutectic Solidification

How many α/β interfaces per unit length?

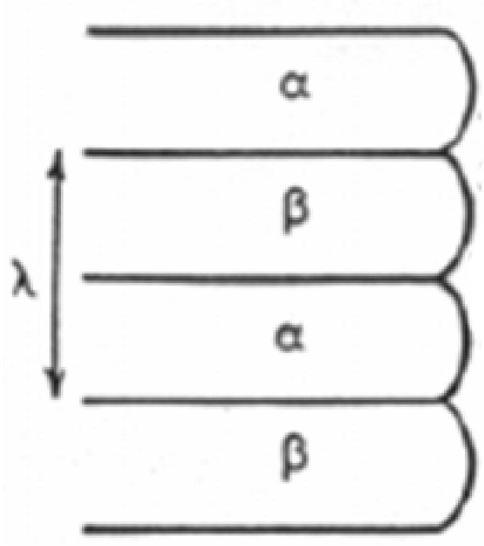
$$\rightarrow 1/\lambda \times 2$$

For an interlamellar spacing, λ, there is a total of (2/ λ) 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?

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

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

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

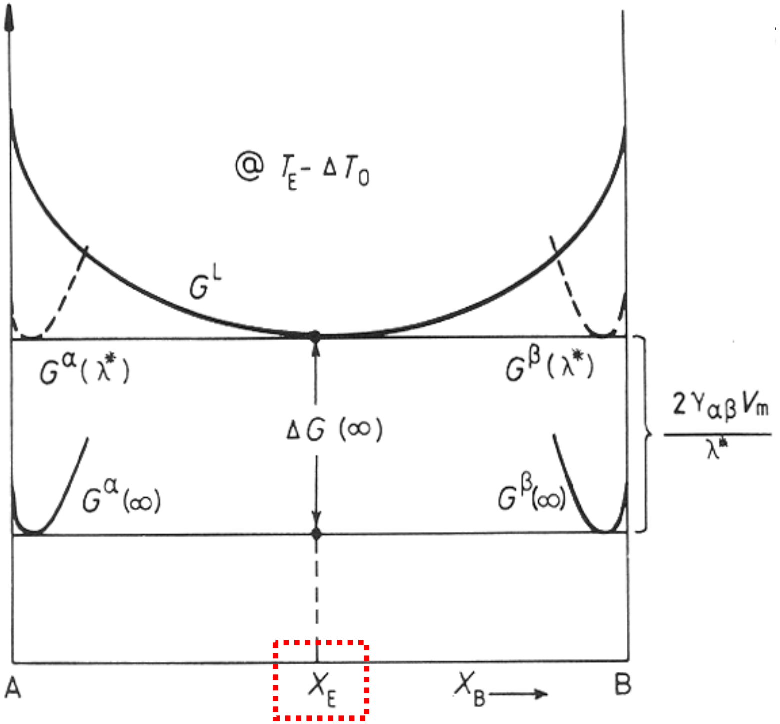
$$cf)\ r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL} T_m}{L_V}\right)\frac{1}{\Delta T}$$

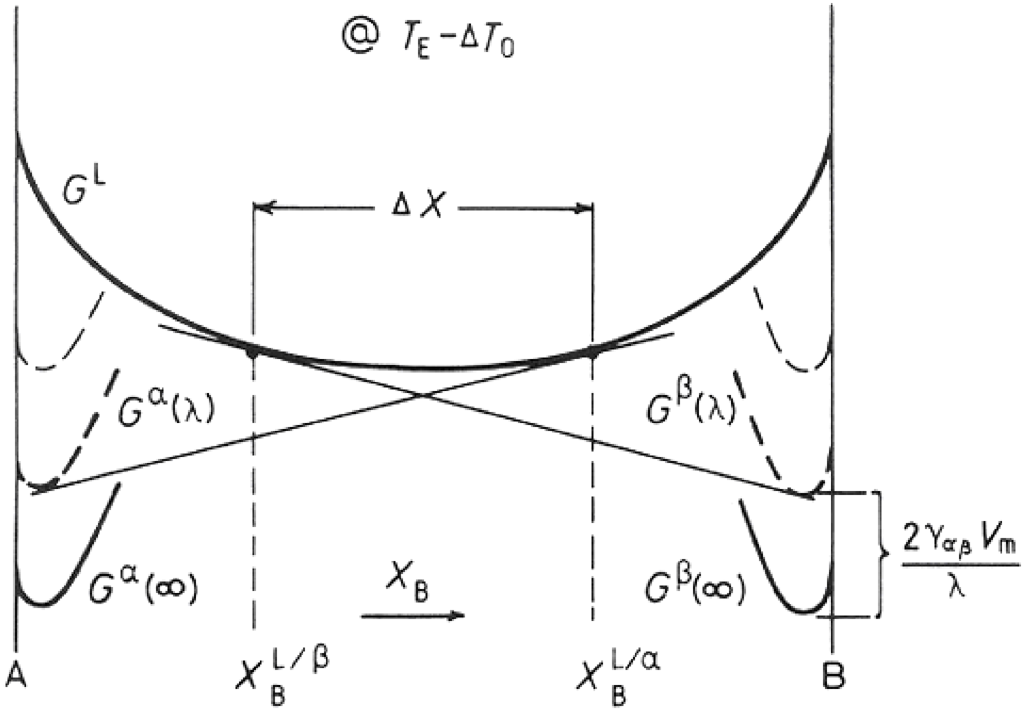
L_V : *latent heat per unit volume*

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

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

Gibbs-Thomson effect in a ΔG-composition diagram?





β 상과 국부적
평형 이루는
액상의 조성

<

α 상과 국부적
평형 이루는
액상의 조성

공정의 성장속도 ***v***

→ 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 → $\boxed{\lambda = 2\lambda^*}$

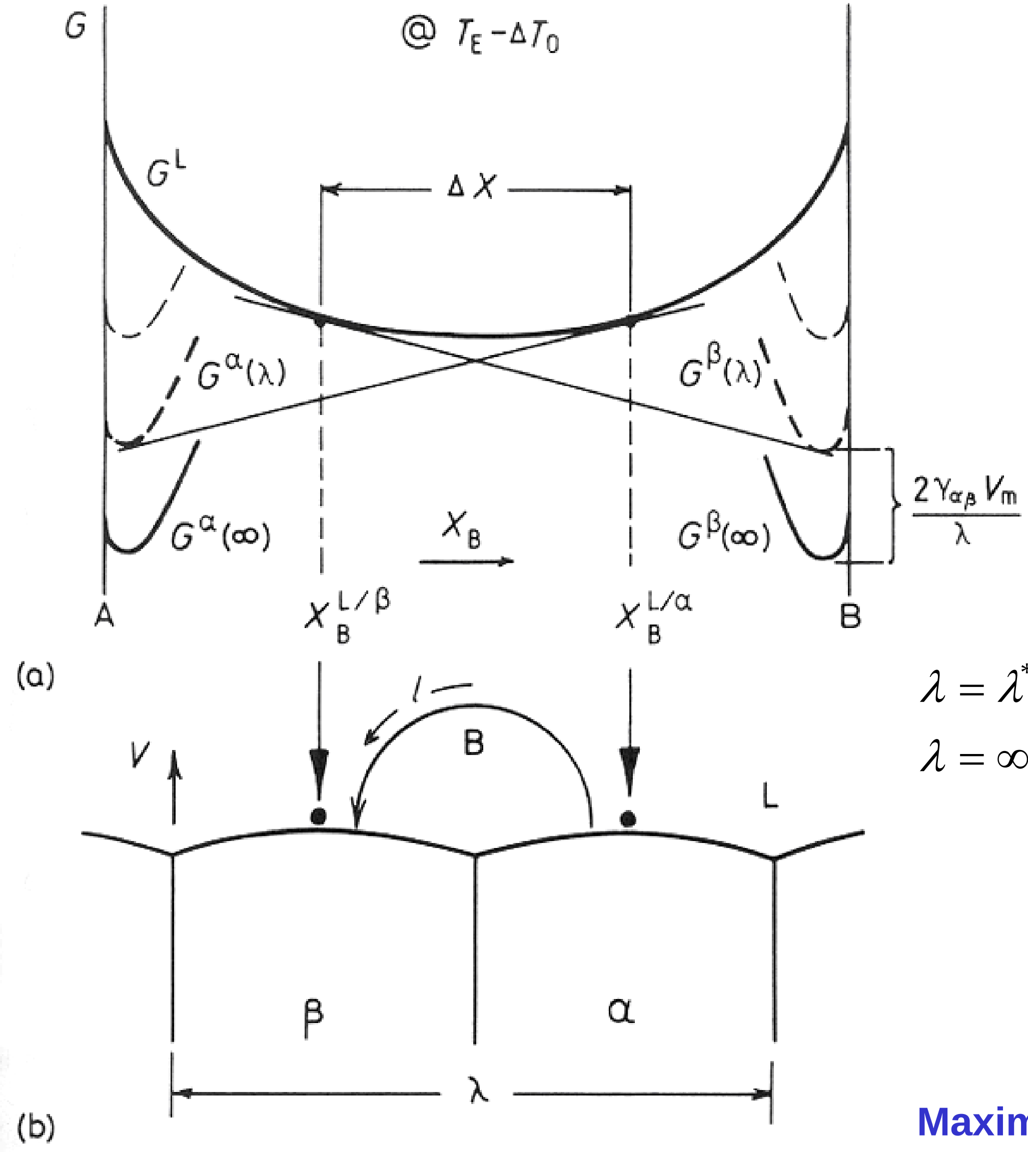


Fig. 4.33 (a) Molar free energy diagram at (T_E - ΔT_0) for the case λ * < λ < ∞ , showing the composition difference available to drive diffusion through the liquid (ΔX). (b) Model used to calculate the growth rate.

Corresponding location at phase diagram?

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

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

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

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

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

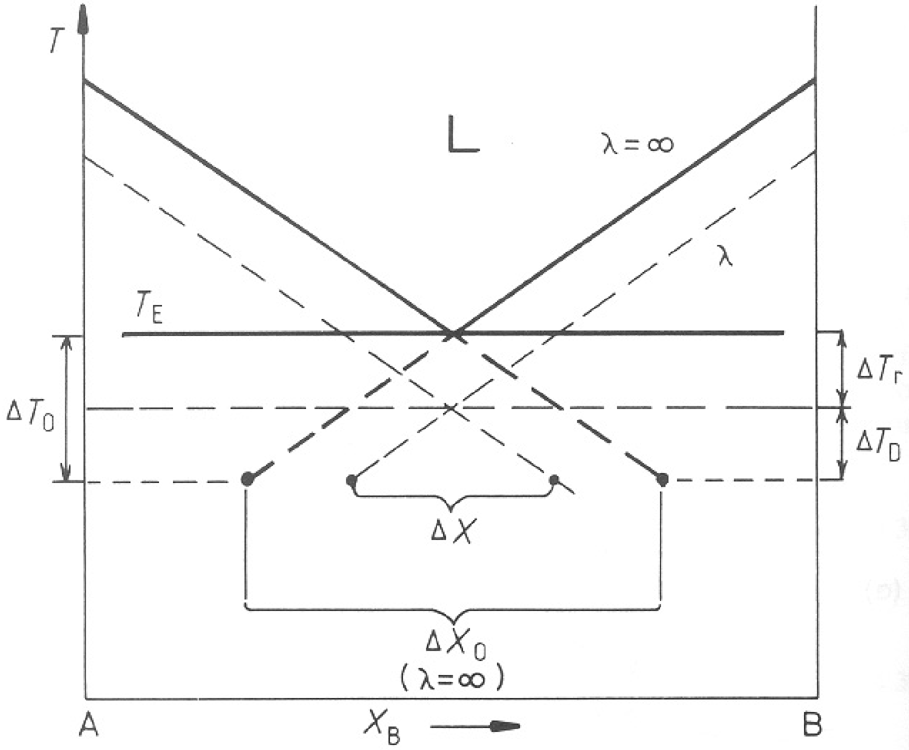
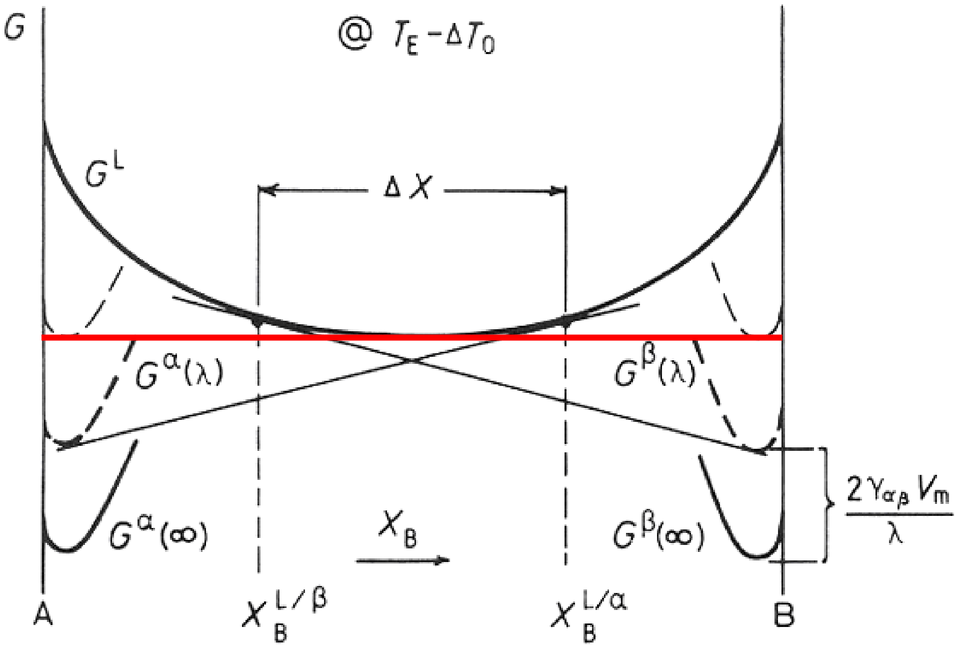


Fig. 4.34 Eutectic phase diagram showing the relationship between ΔX and ΔX_0 (exaggerated for clarity)



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

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,

$$v_0\lambda_0^2 = k_3$$

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

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

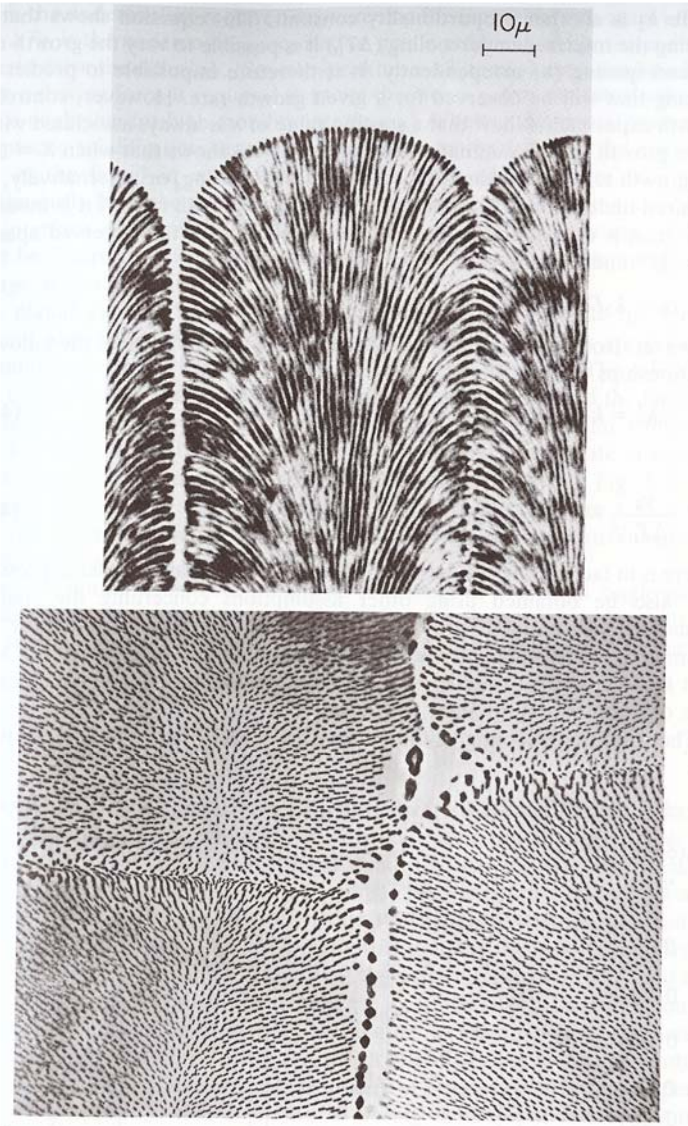
계면 곡률효과 극복 과냉도

확산위해 충분한 조성차주기 위한 과냉

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

$\Delta T_0 = 0$ 계면 등은 항상 등온

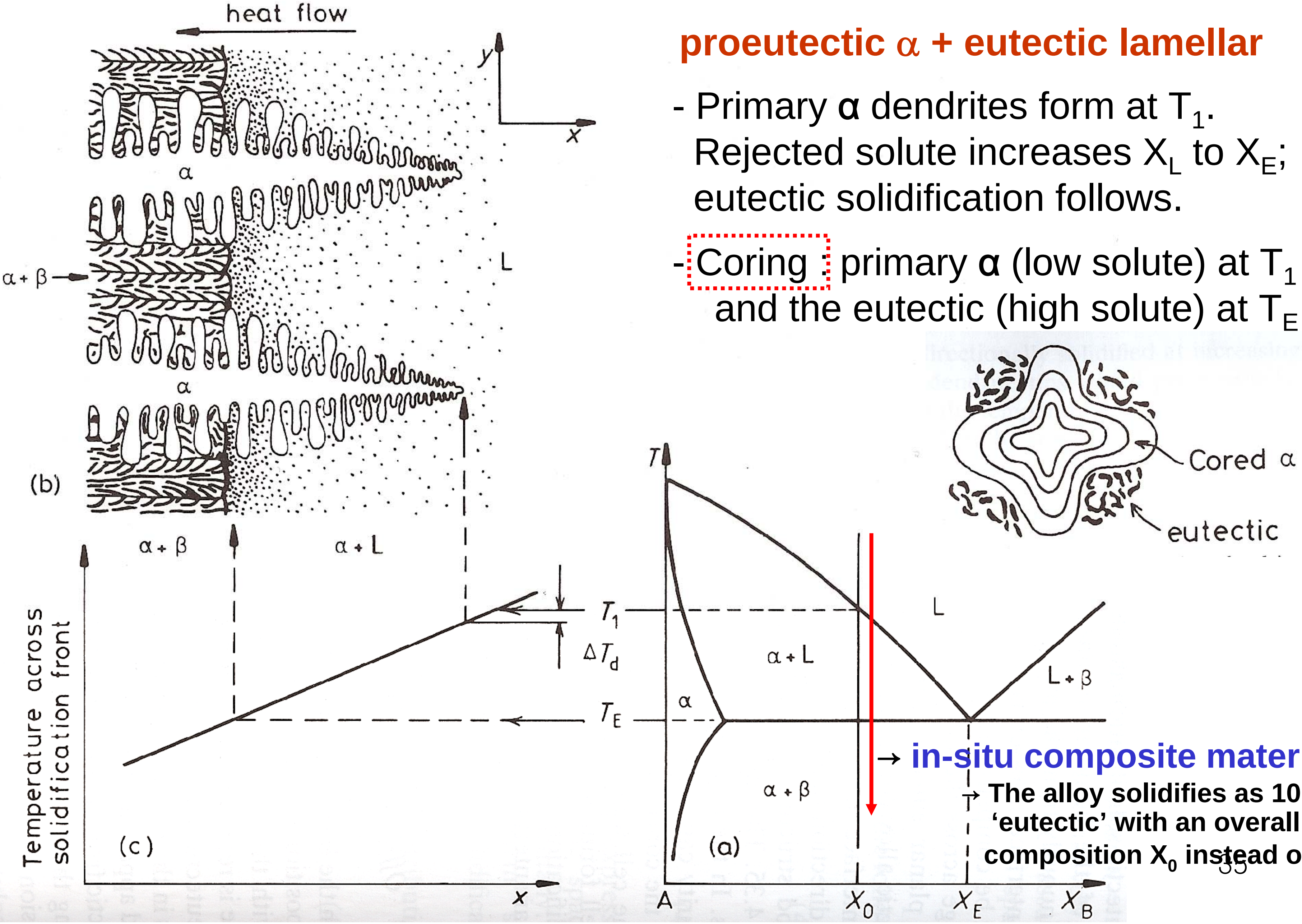
ΔT_r 로 극복해야 함 → 계면의 곡률을 따라 변화



4.3.3 Off-eutectic Solidification

proeutectic α + eutectic lamellar

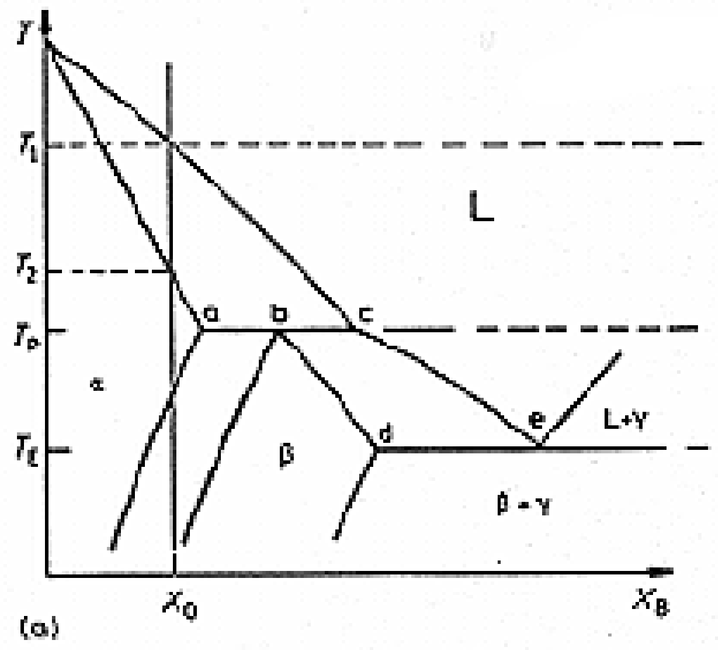
- Primary **α** dendrites form at T_1. Rejected solute increases X_L to X_E; eutectic solidification follows.
- Coring : primary **α** (low solute) at T_1 and the eutectic (high solute) at T_E.

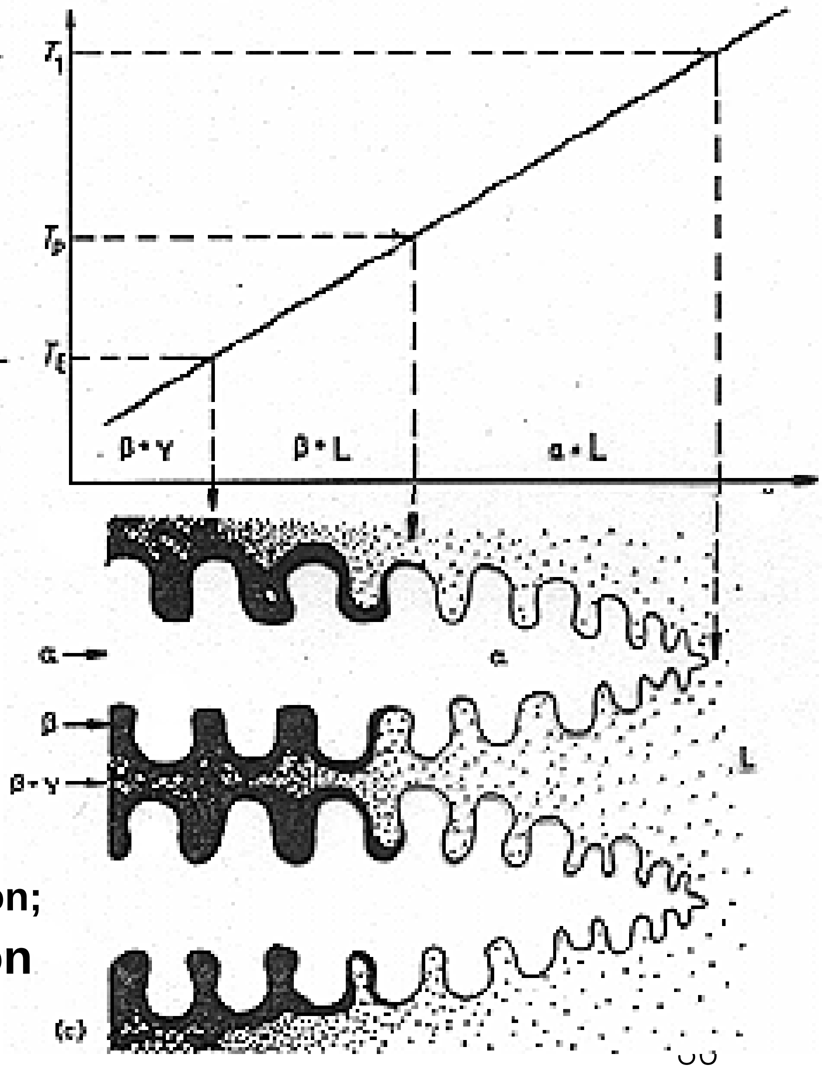


→ **in-situ composite materials**

→ **The alloy solidifies as 100% 'eutectic' with an overall composition X_0 instead of X_E.**

4.3.4 Peritectic Solidification





- L + α → β , difficult to complete.

- α dendrites first form at T_1;
  Liquid reaches the composition 'c';
  β forms as the result of the peritectic reaction;
  α coring is isolated from further reaction
  finally β + γ eutectic forms.