Smooth interface, Rough interface

620℃   710℃

J.C. Heyraud, J.J. Metois, J. Crystal Growth , 84, 503 (1987)
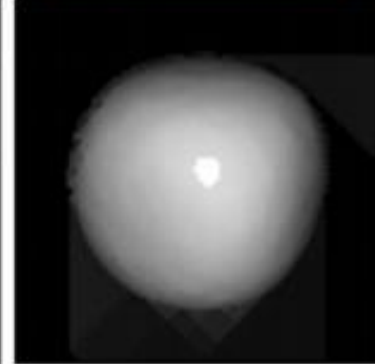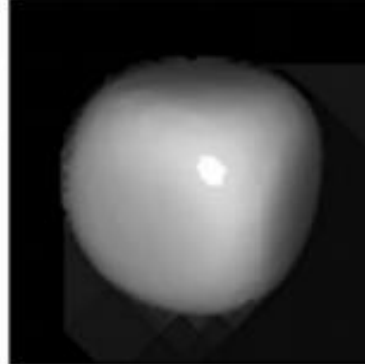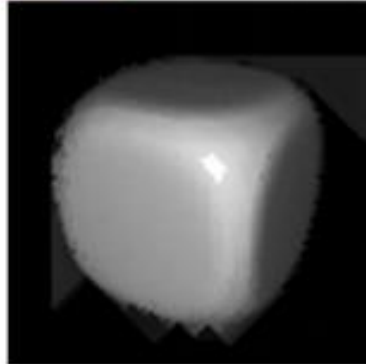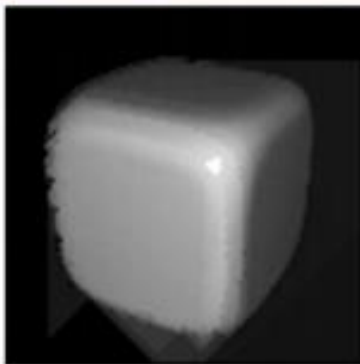

singular (smooth) interface   rough interface

Heating up to the roughening transition.

17

Two types of solid-liquid interfaces
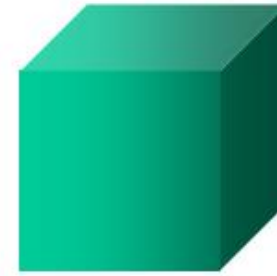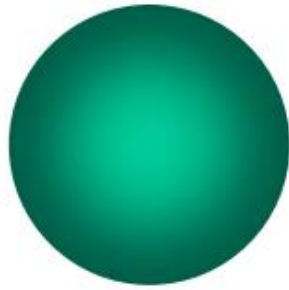
How do you like to call them?

rough interface

singular (smooth) interface

What about the dependence of surface energy on crystal directions?

isotropic γ

anisotropic γ

Do not vary with crystallographic orientation, i.e, γ-plots are spherical

Strong crystallographic effects, : solidify with low-index close-packed facets

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Rough vs. smooth interfaces
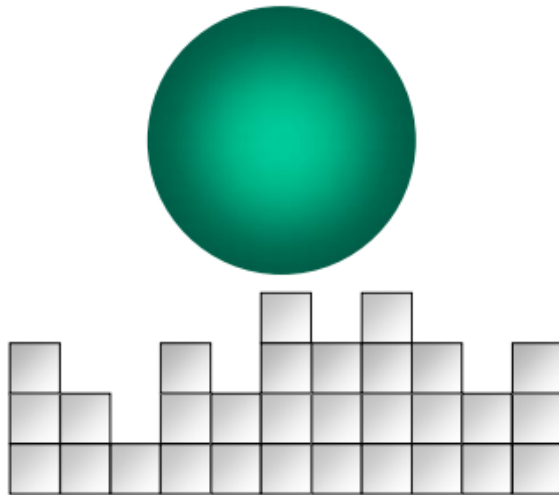
atomically-disordered

Ex) metallic systems

atomically-flat

nonmetals

Apply thermodynamics to this fact and derive more information.

Entropy-dominant	Enthalpy-dominant
weak bonding energy	strong bonding energy
stable at high T	← stable at low T

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4.2 Growth of a Pure Solid

a) Continuous growth
  : Atomically rough or diffuse interface

b) Lateral growth
  : Atomically flat of sharply defined interface
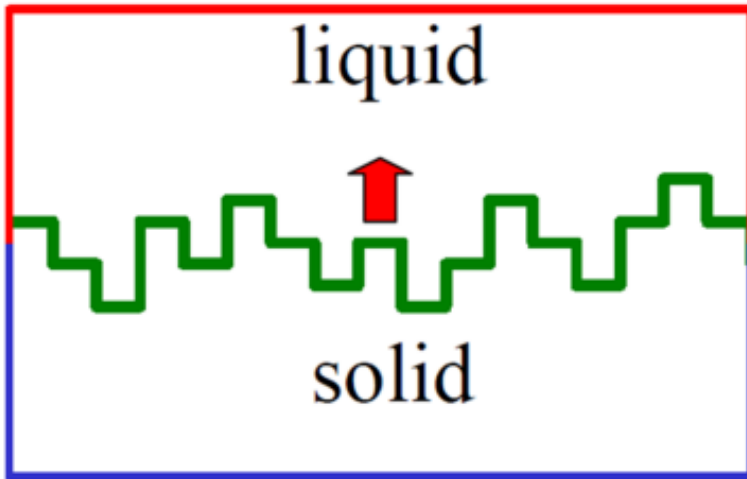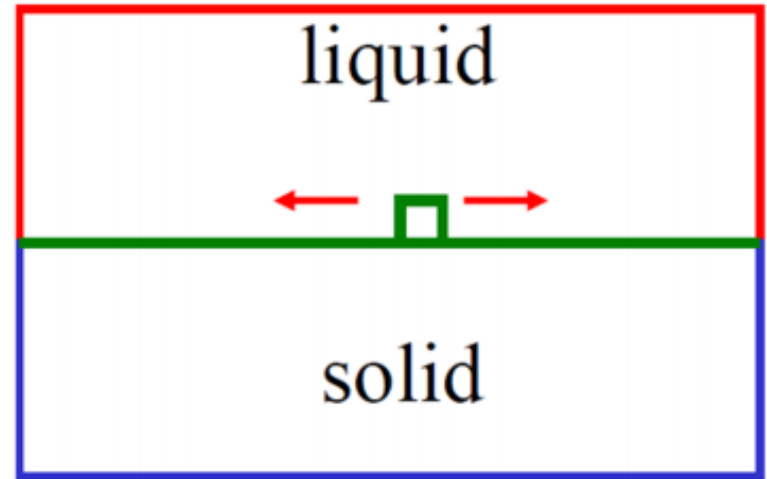
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4.2.1 Continuous Growth

❖ Solid/ liquid diffuse interface
  ≈ the migration of a random high angle grain boundary

❖ **Driving force for solidification** $\Delta G = \dfrac{L}{T_m}\Delta T_i$

(*L*: latent heat of melting, ΔT_i : undercooling of the interface)

❖ **Net rate of solidification**

$$v = k_1 \Delta T_i$$

Growth rate is usually a diffusion controlled process

  ✓ Pure metal: grow at rate controlled by heat conduction
  ✓ Alloy grow at rate controlled by solute diffusion
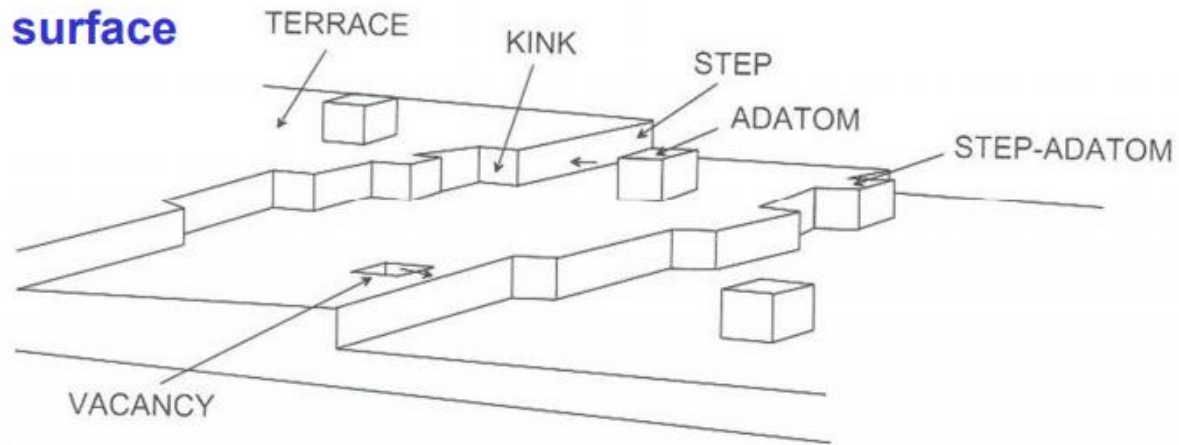
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4.2.1 Lateral Growth

❖ Metals with a high entropy of melting prefer to form atomically smooth, close packed interface.

Atomic View

Ideal Surfaces

singular   vicinal

More realistic surface

TERRACE   KINK   STEP   ADATOM   STEP-ADATOM

VACANCY
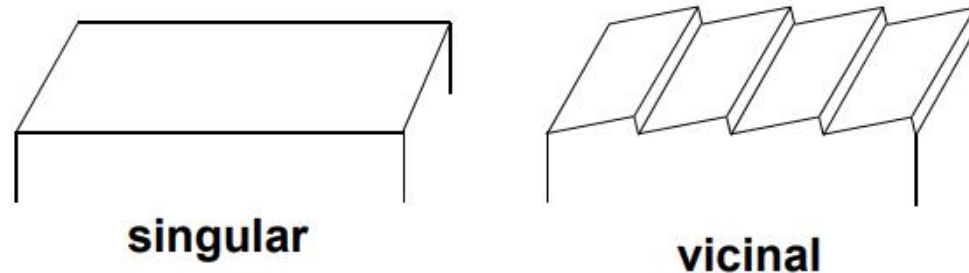
4.2.1 Lateral Growth

❖ G_{min} = Minimum interace energy, i.e. min. # of broken 'solid' bonds

❖ # of broken bonds for a single atom: flat surface – 4

ledge -2

corner – no increase

❖ **Low accommodation rate**

✓ Ledge + jog → liquid can join solid without increasing interfacial energy → lateral growth of ledge (coherent solid/ solid interface)

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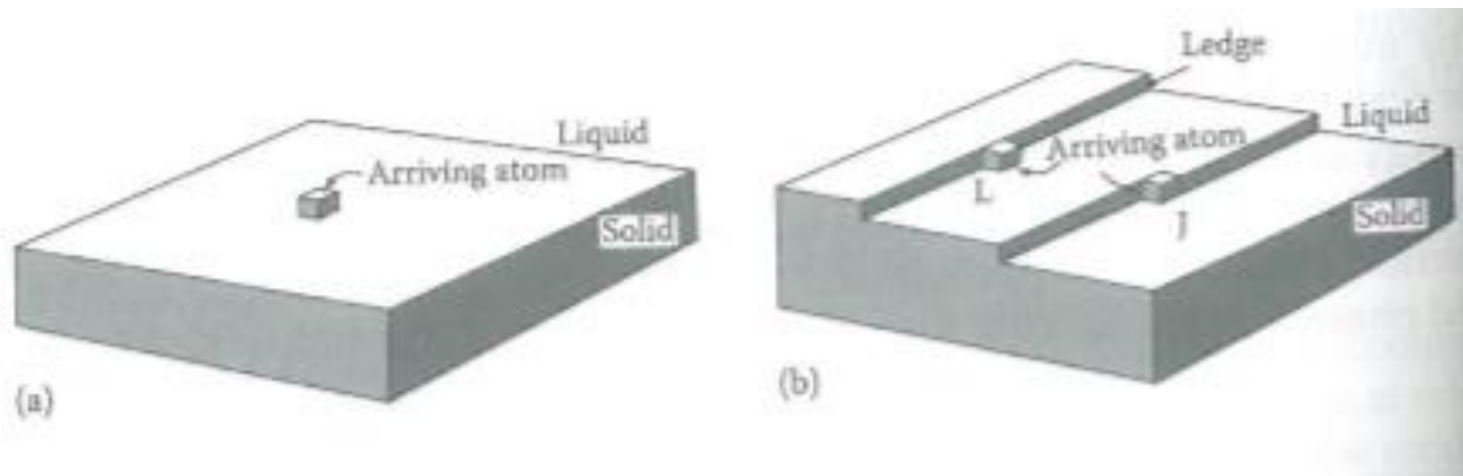
4.2 Growth of a Pure Solid

❖ **Lateral Growth**
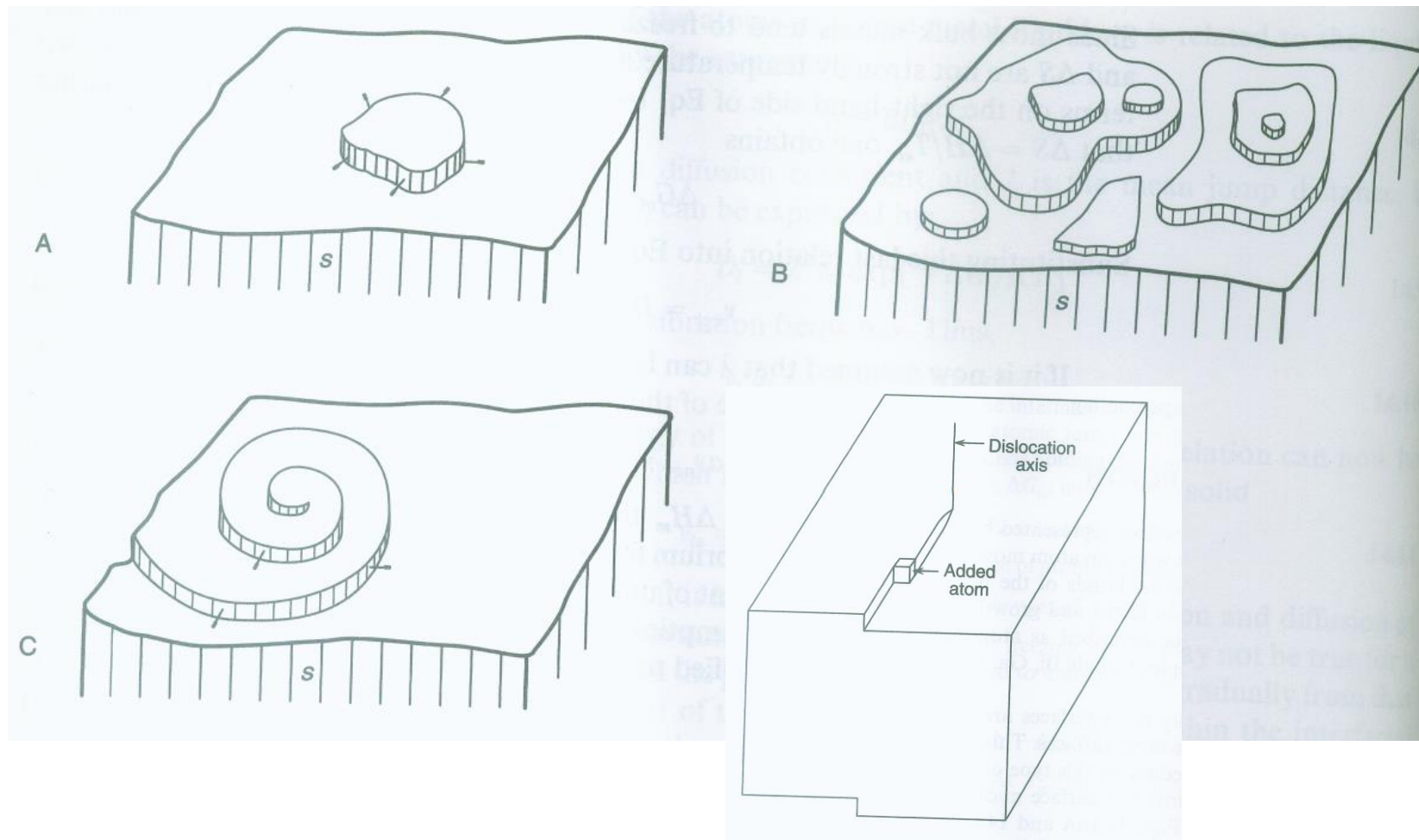
4.2 Growth of a Pure Solid

1) Surface nucleation

  ✓ If large # of atoms → form a disc-shaped layer,

  ✓ Self-stabilized and continue to grow.

  ✓ The edges of disc + contributing to E → counterbalanced by ΔG_v.

  ✓ ΔT becomes large, $r*\downarrow$.

$$\nu \propto \exp(-k^2 / \Delta T_i)$$

2) Spiral growth

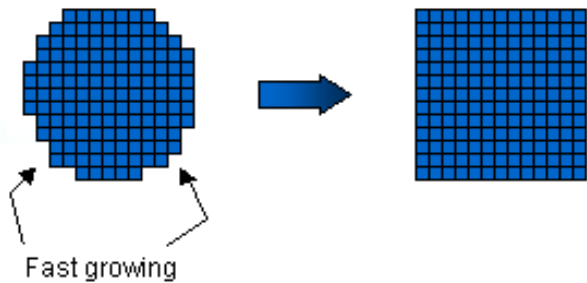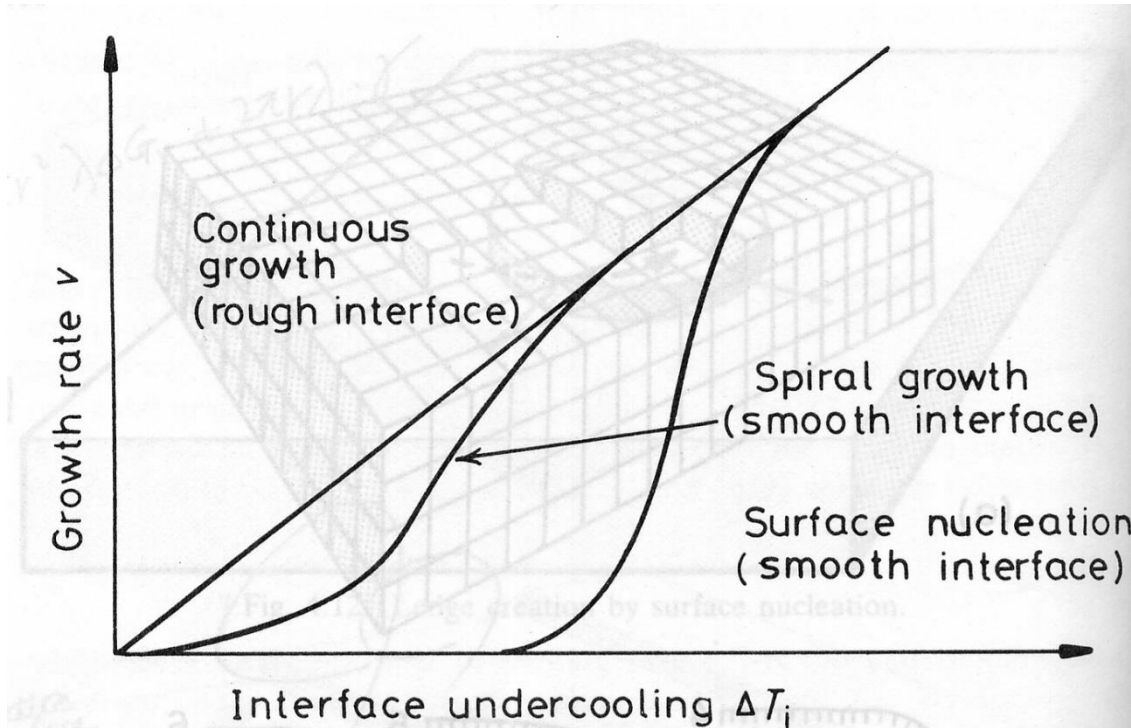 ✓ Addition of atoms to the ledge cause it to rotate around the axis of screw dislocation.

  ✓ The spiral tightens until it reaches a min radius of r^*

  ✓ v (growth rate) = $k_3 (\Delta T i)^2$
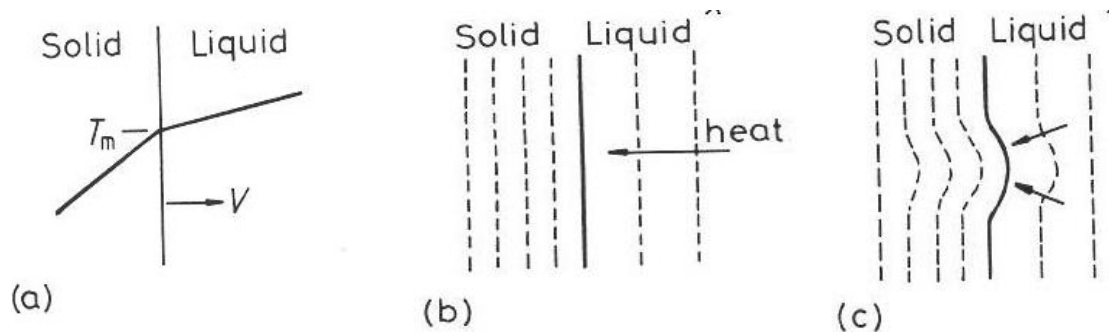
3) Growth from twin boundary

  ✓ Another permanent source of steps like spiral growth

4.2 Growth of a Pure Solid

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4.2.3 Lateral Growth of a Pure Solid

1) Superheated liquid

✓ Solid growing at v (planar)

✓ Heat from away from the interface through solid = heat inflow from liquid + L

$$K_S T_S' \;=\; K_L T_L' \;+\; v L_v$$

✓ If r is so large → Gibbs-Thompson effect can be ignored the solid/liquid interface remain at T_m (r : radius of curvature of the protrusion)

✓ dT/dx in the liquid ahead of the protrusion will increase more positively.

✓ More heat to the protrusion → melt away V ↓ to match other v in planar region

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4.2 Growth of a Pure Solid

2) Solid growing into supercooled liquid
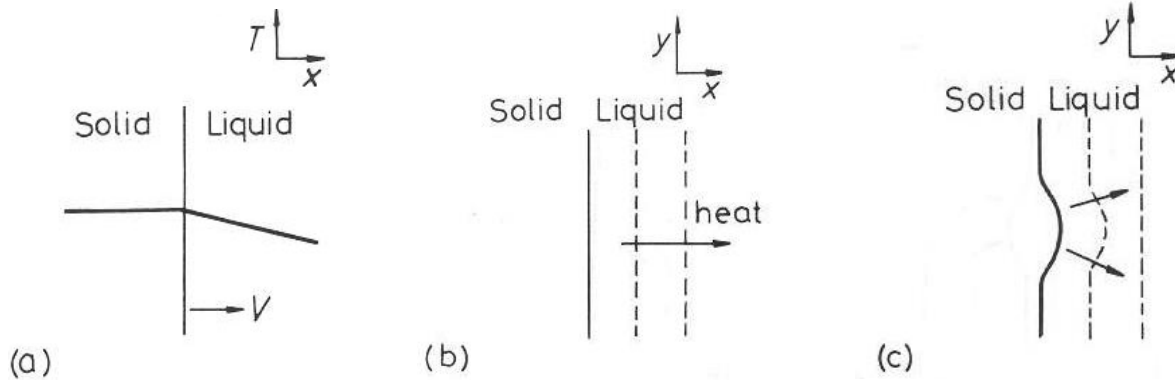
✓ Heat removed more effectively from the tip.

✓ Protrusion $\dfrac{dT_L'}{dX} < 0$ becomes more negative

✓ Heat flow from solid = the protrusion grows preferentially.

✓ Solidification begins in the bulk of the liquid.

✓ Supercooled liquid에서 solid 생성 → 잠열이 liquid로 발산

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4.2 Growth of a Pure Solid

❖ Development of Thermal Dendrite

cf. Constitutional supercooling

* shown at the beginning of solidification at the tip of dendrites
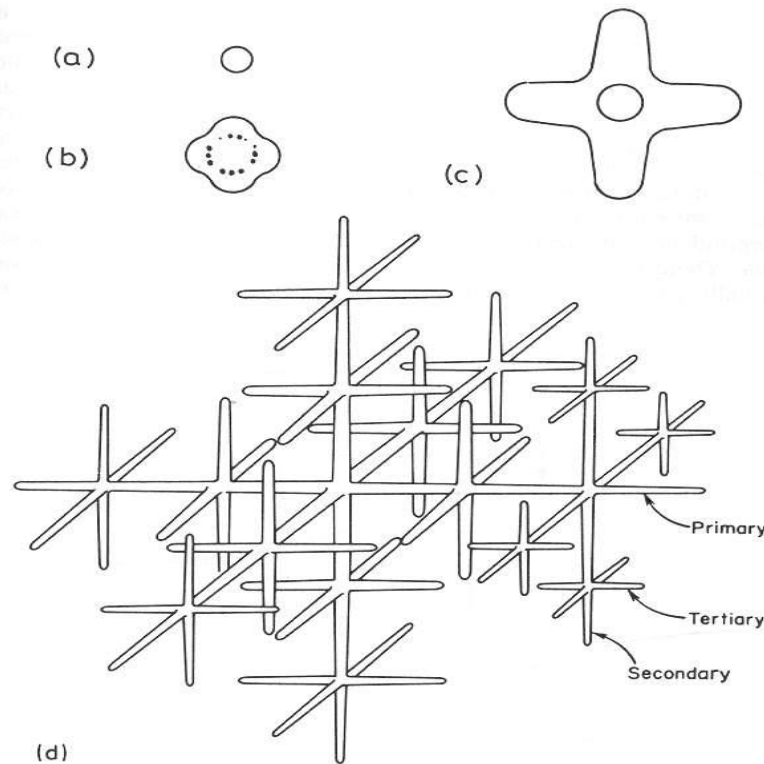
$$K_S T'_S \; = \; K_L T'_L \; + \; v L_V$$

Assume $T'_s \approx 0$

T'_L measured in the direction of v

$$\Delta T_c \; = \; Ti - T_\infty$$

4.2 Growth of a Pure Solid

$$v = \frac{-K_L T_L'}{L_V} \cong \frac{K_L}{L_V} \cdot \frac{\Delta T}{r}$$

✓ $v\uparrow$ as $r\downarrow$ due to enhanced heat conduction

$$\Delta T_r = \frac{2\gamma T_m}{L_V r} \quad \text{as a result of G-T eq.}$$

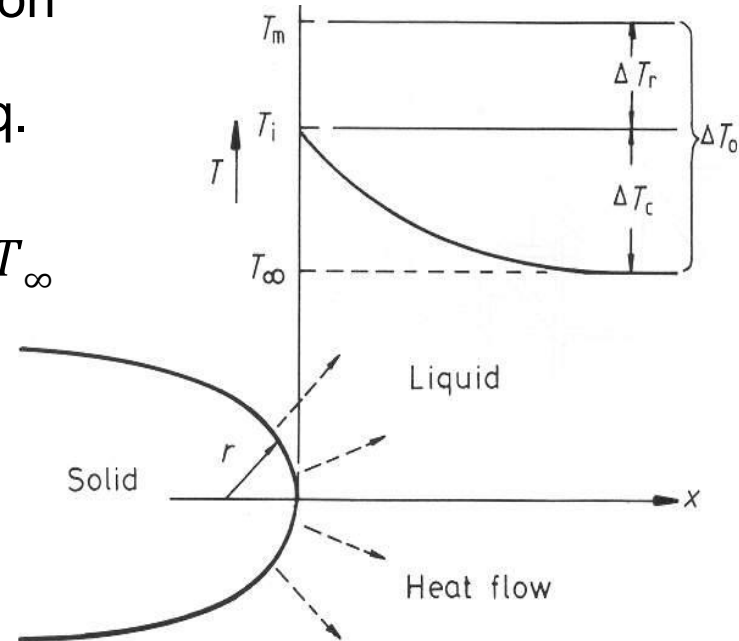Min. radius r occur when $\Delta T_r = \Delta To = Tm - T_\infty$

r_{min} = the critical nuclei radius

$$r^* = \frac{2\gamma T_m}{L_v \Delta T_o} \qquad \Delta T_r = \frac{\Delta T_o r^*}{r}$$

$$v \cong \frac{K_L}{L_V} \cdot \frac{1}{r}\left(1 - \frac{r^*}{r}\right)$$

$V \to 0$ as $r \to r^*$ and as $r \to \infty$ heat conduction slow.

$v = v_{max}$ when $r = 2r^*$

Phase Transfromation In Materials

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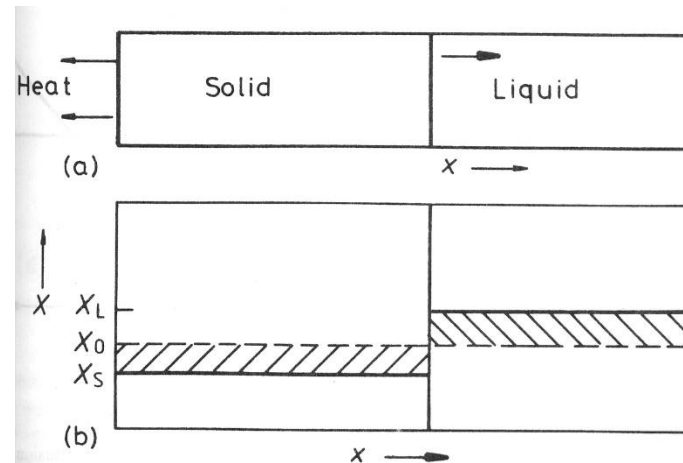
4.3 Alloy Solidification
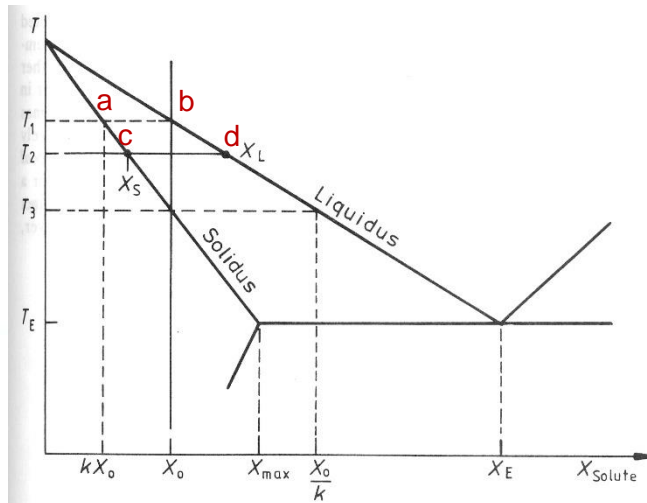
4.3.1 Solidification of single-phase alloys

$$k \text{ (partition coefficient)} = \frac{X_s}{X_L} < 1$$
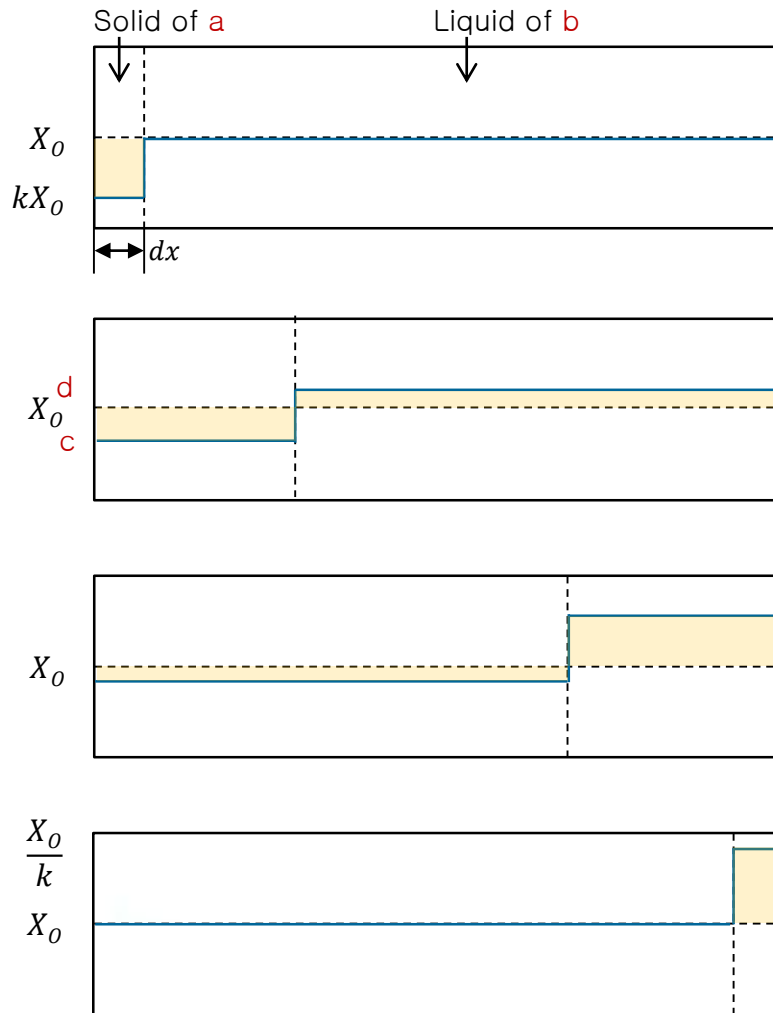
❖ Three limiting cases

1. Infinitely slow (equilibrium) solidification

   ✓ Sufficient time for diffusion in solid & liquid : kX_o, X_o

   ✓ Relative amount of solid and liquid : lever rule

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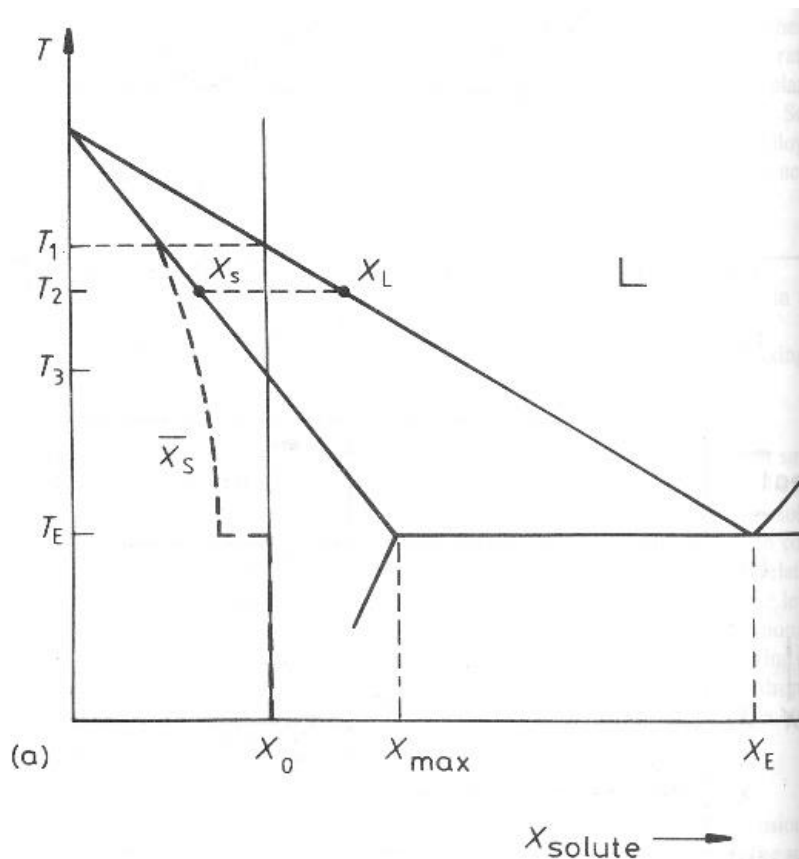Device Materials Lab.**

4.3 Alloy Solidification

- ✓ Solidification starts at T_1 (solid kX_0)

- ✓ Liquid 상의 조성 증가→ Solidification이 더 낮은 온도 ($T<T_1$)에서 생김

- ✓ Liquid와 solid의 양: lever rule

- ✓ 마지막 T_3에서 응고 종료

- ✓ 전체 bar가 X_0 조성으로 응고

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4.3 Alloy Solidification

2. No diffusion in solid, perfect mixing in liquid

(a)

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

✓ Liquid become richer than $\dfrac{X_0}{k} \rightarrow \mathrm{X_E}$

✓ Variation of X_s: solute rejected to the liquid

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4.3 Alloy Solidification

2. **No diffusion in solid, perfect mixing in liquid**

Fig. 4.21 (continued)
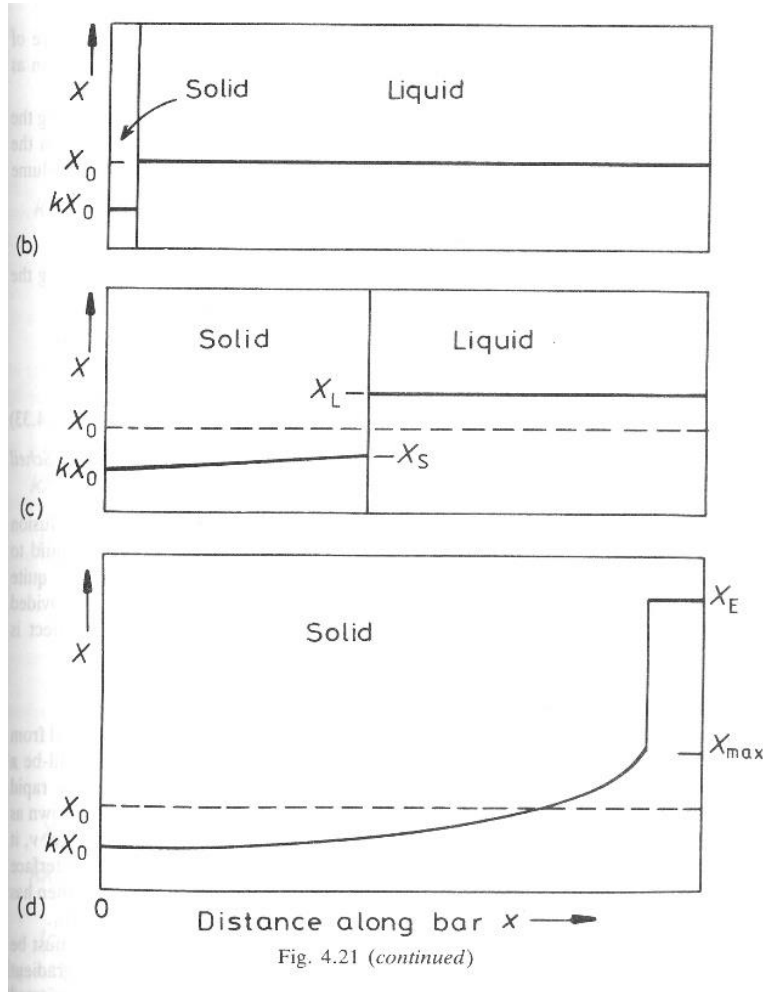
- ✓ T_1에 도달하면 응고시작
- ✓ 계면온도는 T1 이하로 감소
- ✓ Liquid/solid의 계면은 항상 "local equilibrium"
- ✓ Mean composition of solid ($\overline{X_S}$)
- ✓ 계면에서 liquid와 solid의 양 ($\overline{X_S}$와 X_L의 lever rule)
- ✓ Liquid는 $\frac{X_o}{k}$를 넘어서 X_E까지 갈 수 있다.

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4.3 Alloy Solidification

Mass balance : $(X_L - X_S)df_S = (1 - f_S)dX_L$

B.C. : $X_S = kX_O$ when $f_S = 0$

$$\int_0^{f_S} \frac{df_S}{1 - f_S} = \int_{X_)}^{X_L} \frac{dX_L}{X_L - X_S} = \int \frac{dX_L}{X_L(1 - k_O)}$$

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

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

$$\therefore \quad X_L = X_O f_L^{(k-1)} \quad \leftarrow \text{non-eq. lever rule. (Scheil eq.)}$$

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