2021 Fall

“Phase Transformation *in* Materials”

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Contents for previous class

Solidification: Liquid ⟶ Solid

- Nucleation in Pure Metals
- Homogeneous Nucleation

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

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$

r* & ΔG* ↓ as ΔT ↑

$$N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\} \sim \frac{1}{\Delta T^2}$$

- Heterogeneous Nucleation

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

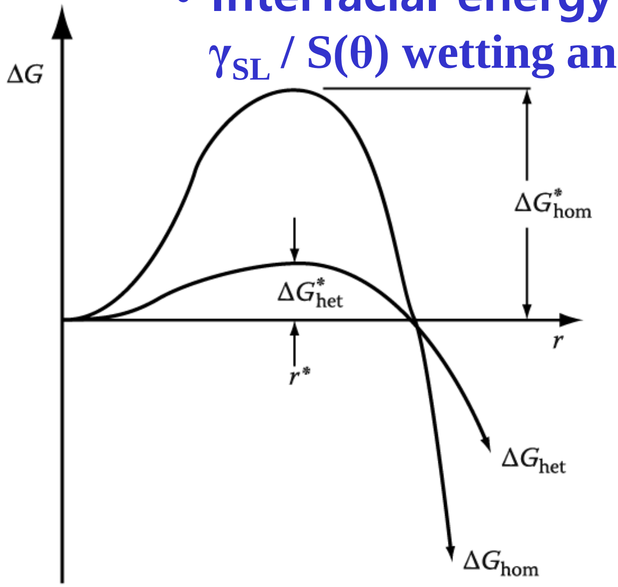
$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

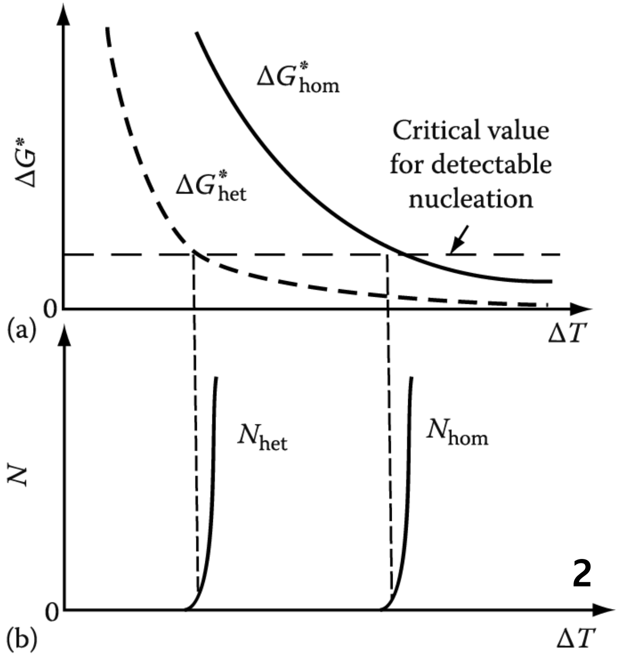
- Nucleation of melting

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$ **(commonly)**

- Undercooling ΔT
- Interfacial energy

  γ_{SL} / S(θ) wetting angle





Contents for previous class

Solidification: Liquid → Solid

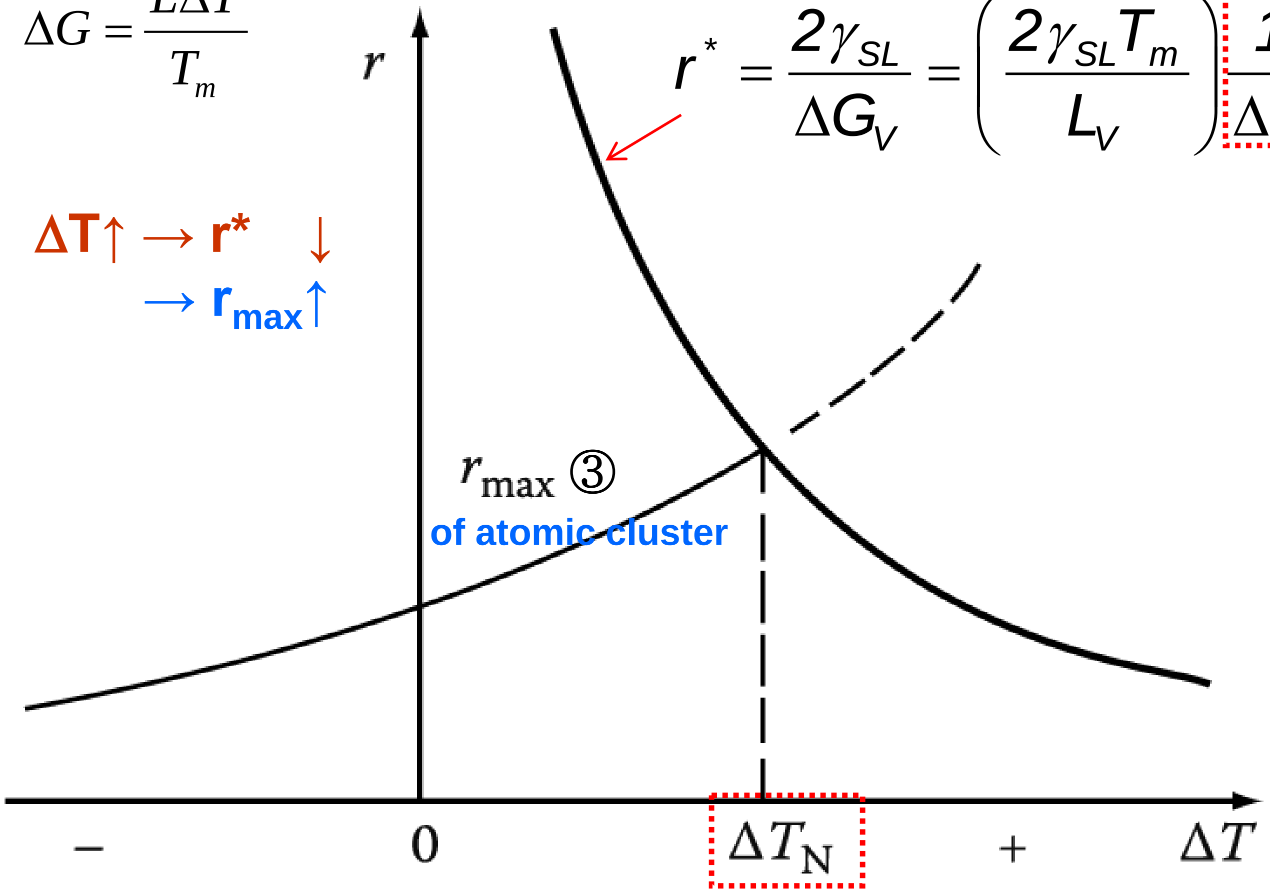
The creation of a critical nucleus ~ thermally activated process

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

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

$\Delta T\uparrow \rightarrow r^* \downarrow$

$\rightarrow r_{max}\uparrow$



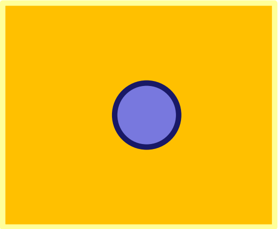
ΔT_N is **the critical undercooling** for homogeneous nucleation.

Fig. 4.5 The variation of r* and r_{max} with undercooling ΔT

The number of clusters with r^* at $\Delta T < \Delta T_N$ is negligible.

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

Liquid T_m Undercooled Liquid Solid

No superheating required!

- Interfacial energy ⇨ No ΔT_N

$$\boxed{\gamma_{SL}+\gamma_{LV}<\gamma_{SV}}$$

Melting: Liquid ← Solid

Solidification: Liquid → Solid

< Nucleation >
&
< Growth >

- Nucleation in Pure Metals

- Equilibrium Shape and Interface Structure on an Atomic Scale

- Growth of a pure solid

1) Continuous growth
: Atomically rough or diffuse interface

2) Lateral growth
: Atomically flat of sharply defined interface

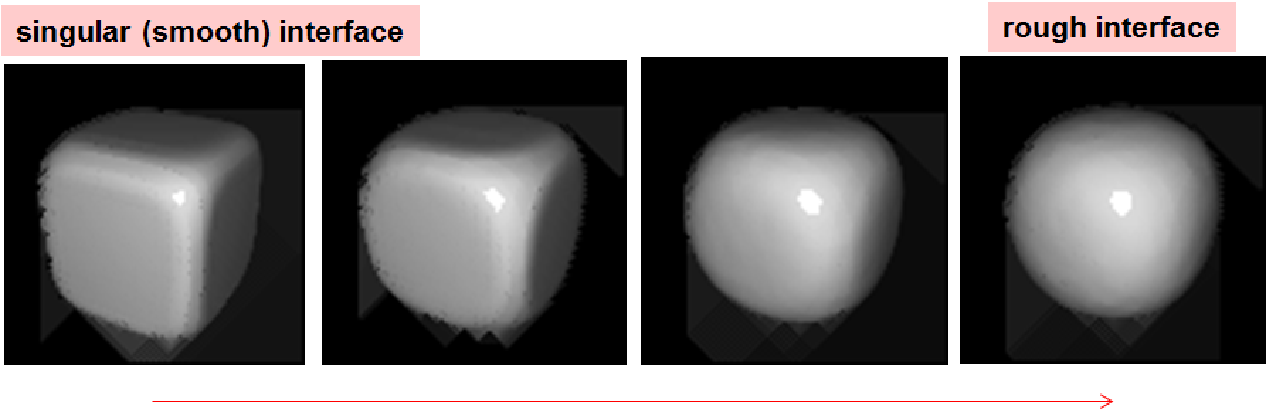
- Heat Flow and Interface Stability

4.3 Alloy solidification

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

Q: Rough interface vs Singular interface?

Thermal Roughening



Heating up to the roughening transition.

Equilibrium Shape and Interface Structure on an Atomic Scale

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

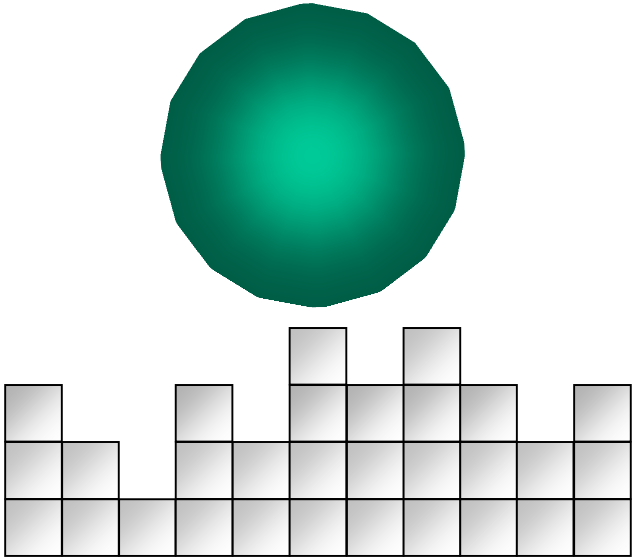
Water Drops ↔ Natural Minerals

Topaz (황옥)

Stibnite (휘안광)

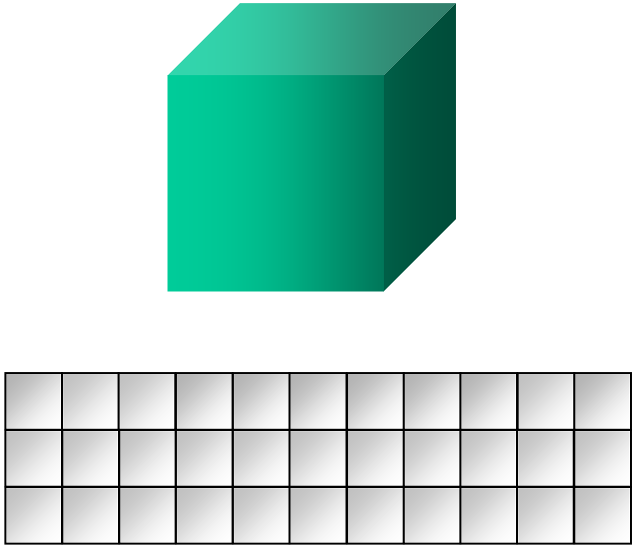
How differ the structure of the surface on an atomic scale?

Equilibrium Shape and Interface Structure on an Atomic Scale



atomically-disordered

Ex) metallic systems



atomically-flat

nonmetals

Apply thermodynamics to this fact and derive more information.

stable at high T ← **stable at low T**

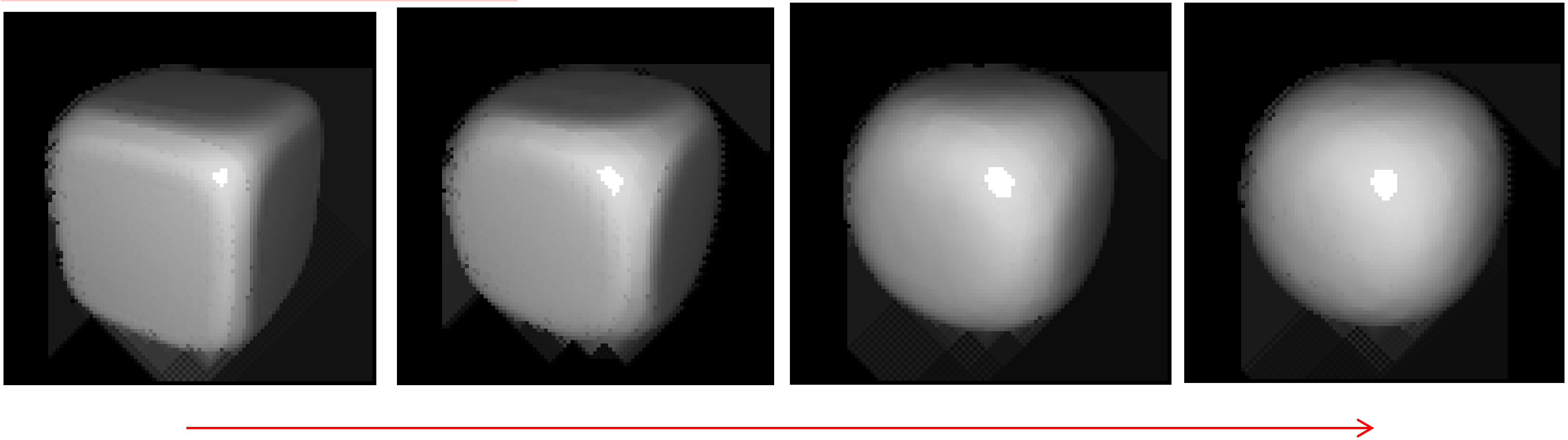
Entropy-dominant

Enthalpy-dominant

weak bonding energy

strong bonding energy

Thermal Roughening



singular (smooth) interface

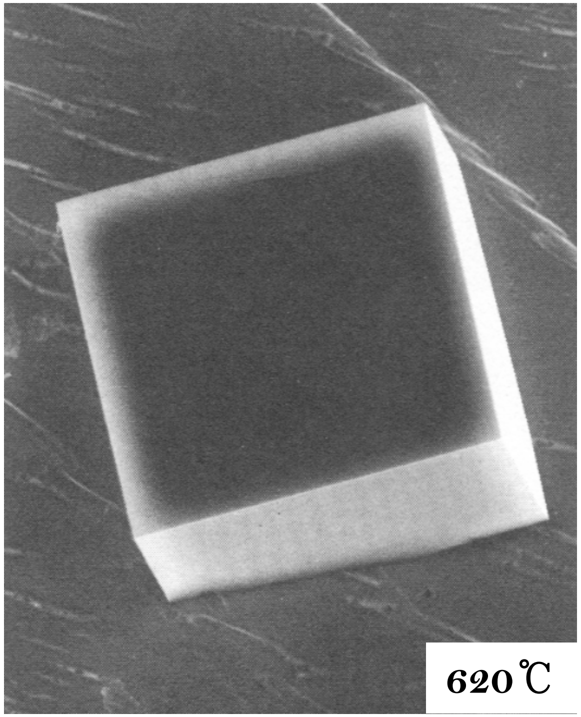
rough interface

Enthalpy-dominant

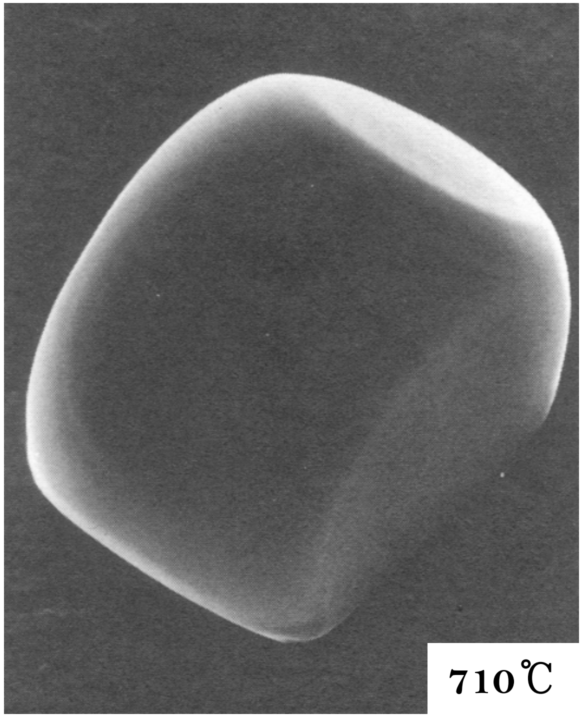
Entropy-dominant

Heating up to the roughening transition.

✓ Equilibrium shape of NaCl crystal



Thermal Roughening



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

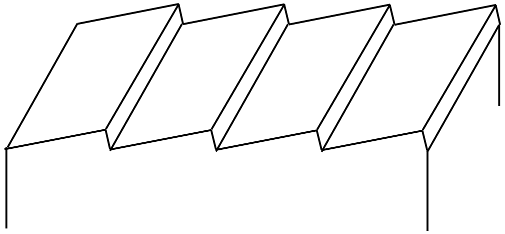
Compare the kinetic barrier for atomic attachment.

Which has a low growth barrier?

Atomic View

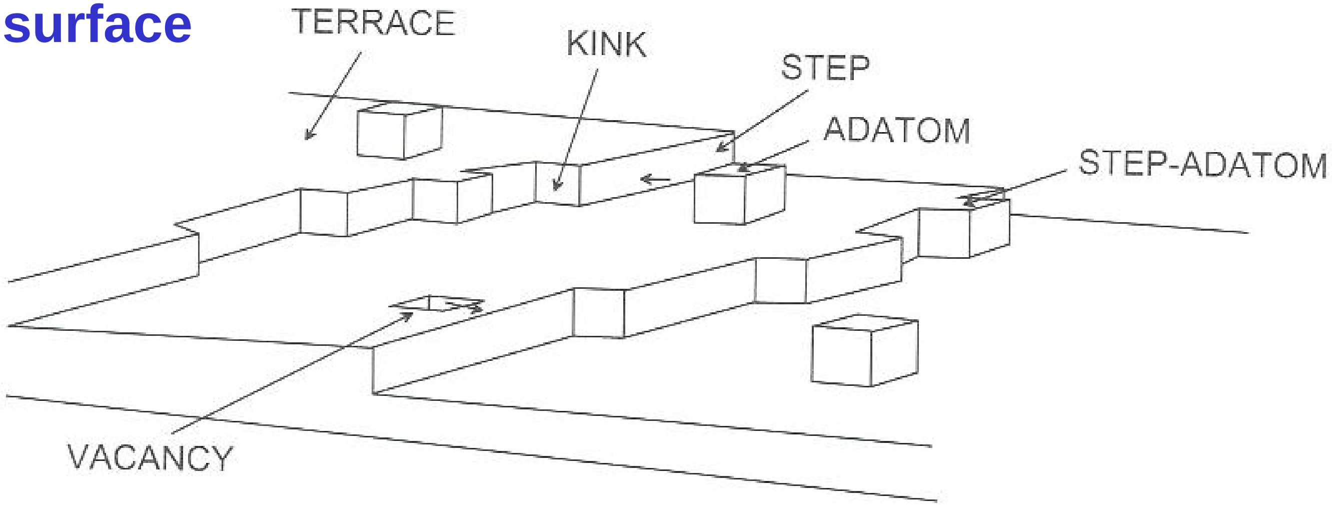
Ideal Surfaces

singular



vicinal

More realistic surface



- **Realistic surfaces of crystals typically look like this at low temperature**
- → **At sufficiently high temperature, the structure becomes atomically rough**

(Thermal Roughening)

Q: What kinds of Growth in a pure solid exist?

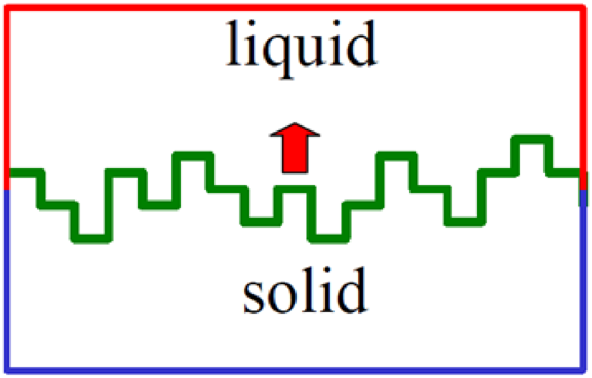
Two types of solid-liquid interface

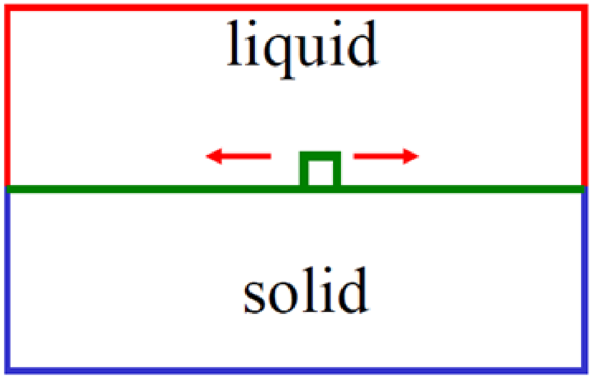
a) Continuous growth

: Atomically rough or diffuse interface

b) Lateral growth

: Atomically flat of sharply defined interface





4.2. Growth of a pure solid

: The next step after the nucleation is growth.

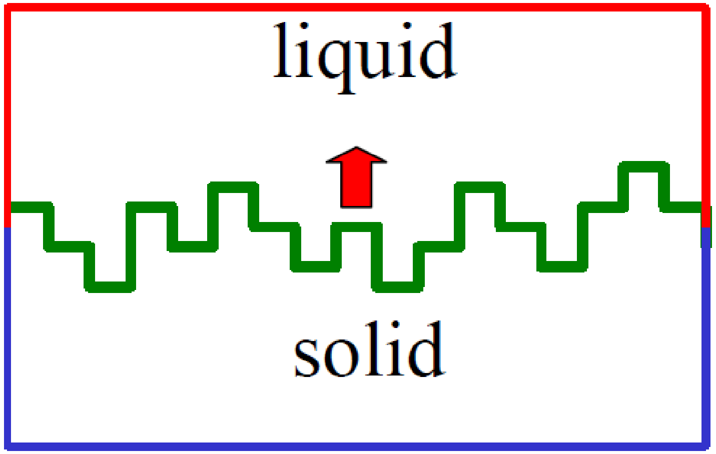
Two types of solid-liquid interface

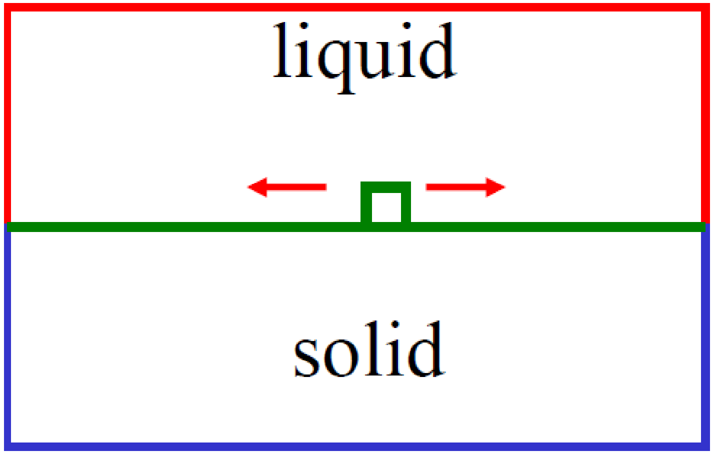
a) Continuous growth

: Atomically rough or diffuse interface

b) Lateral growth

: Atomically flat of sharply defined interface





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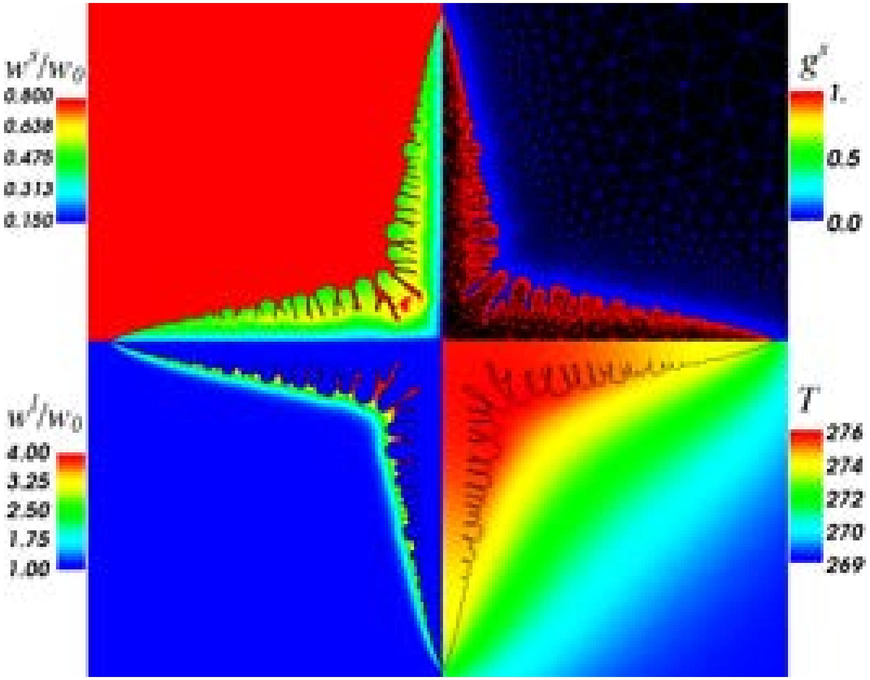
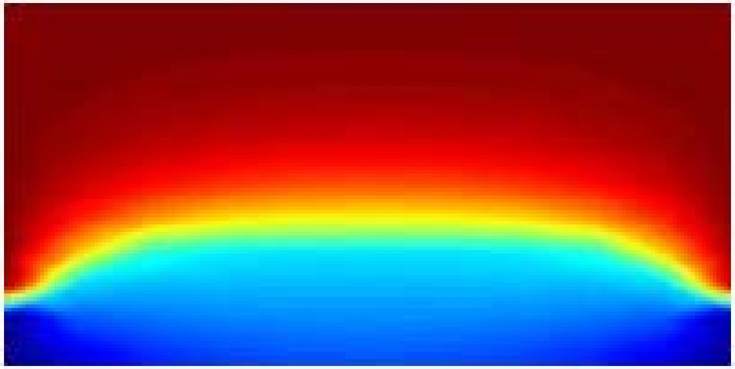
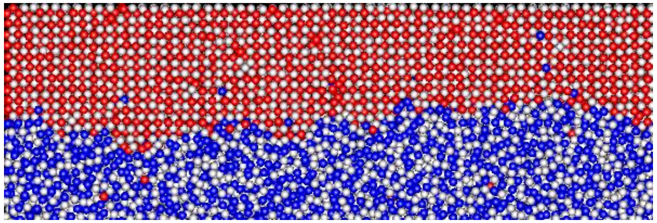




a) Continuous growth

The **migration of a rough solid/liquid interface** can be treated in a similar way to the migration of **a random high angle grain boundary.**

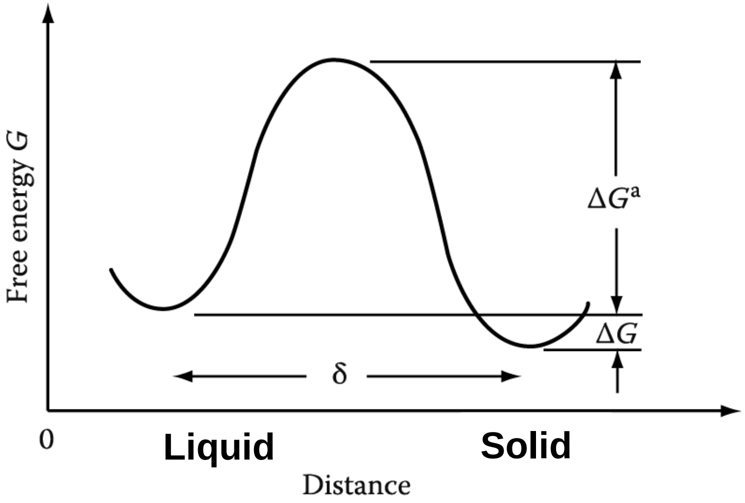


- Driving force for solidification

$$\boxed{\Delta G = \frac{L}{T_m}\boxed{\Delta T_i}}$$

L: latent heat of melting

ΔT_i : undercooling of the interface



- Net rate of solidification

$$\boxed{v = k_1\boxed{\Delta T_i}}$$

k_1: properties of boundary mobility

Reference (eq. 3.21) $v = M \cdot \Delta G / V_m$

The rate of the continuous growth (typical for metals) is usually a "diffusion controlled process".

- **Pure metal grow at a rate controlled by heat transfer to the interfacial region.**
- **Alloy grow at a rate controlled by solute diffusion.**

b) Lateral growth

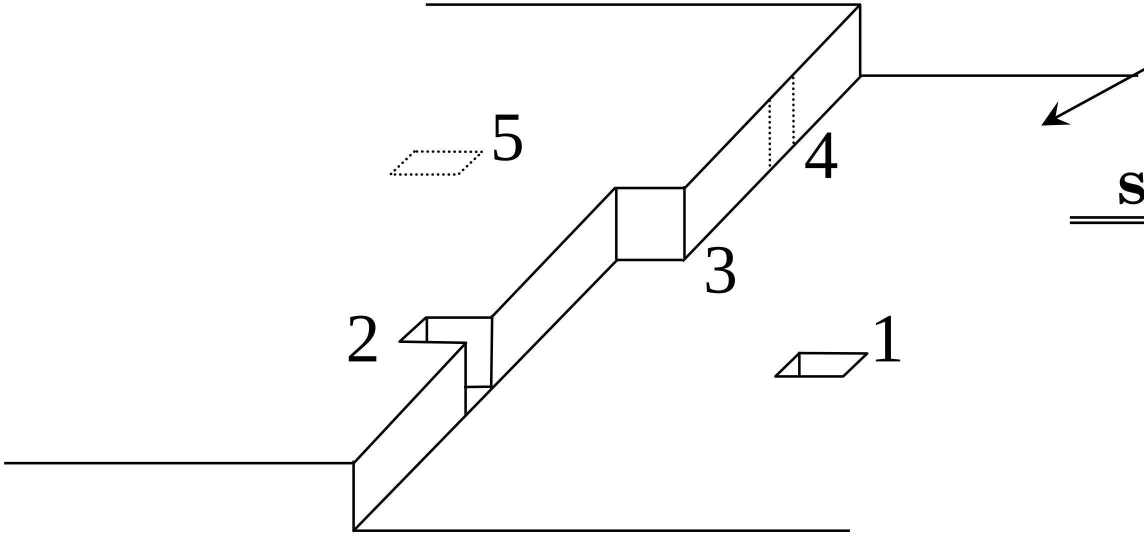
- **Materials with a high entropy of melting (~high T_m) prefer to form atomically smooth, closed-packed interfaces.**
- **For this type of interface the minimum free energy also corresponds to the minimum internal energy, i.e. a minimum number of broken 'solid' bonds.**

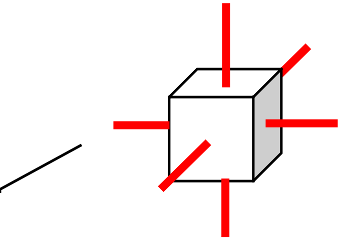
Two ways in which ledges and jogs (kinks) can be provided.

① Surface (2-D) nucleation **② Spiral growth**

Condition for Atomic Attachment

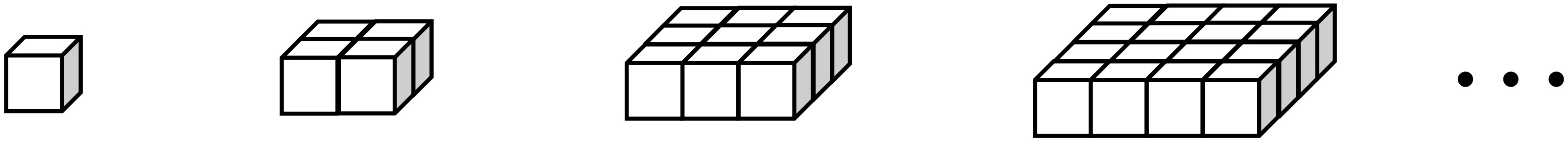
Suppose the building unit (atom) has 6 bonds to be saturated





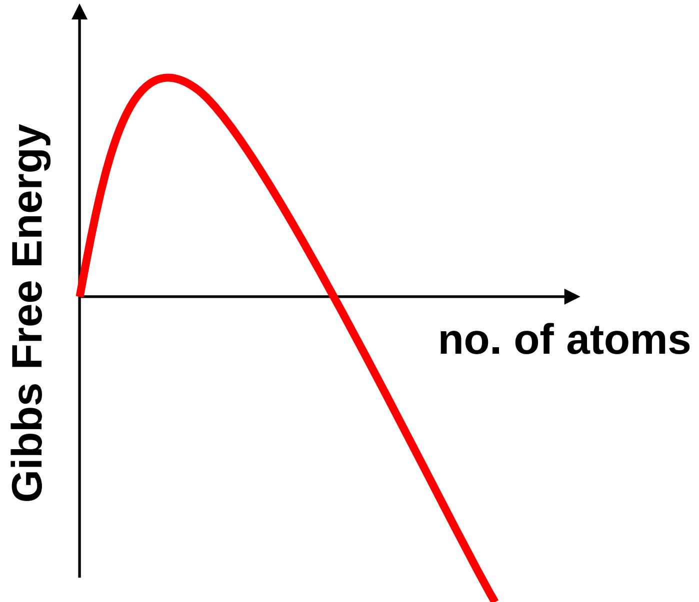
site	$\Delta E / atom$		
1	-4ϕ	*stable*	
2	-2ϕ	*stable*	
3	0ϕ	*stable*	: *kink*
4	$+2\phi$	*unstable*	
5	$+4\phi$	*unstable*	

How many unsaturated bonds are there if they are epitaxial to the underneath atomic layer?



$+4\phi / atom$	$+8\phi / 4\ atoms$	$+12\phi / 9\ atoms$	$+16\phi / 16\ atoms$
$\Delta f = -kT\ln(P/P_e)$	$4\Delta f$	$9\Delta f$	$16\Delta f$
$+4\phi / atom$	$+2\phi / atom$	$+\frac{4}{3}\phi / atom$	$+1\phi / atom$
ΔE/atom	ΔE/atom	ΔE/atom	ΔE/atom

Draw the plot showing how the free energy varies with the number of atoms in the presence of supersaturation (driving force) for growth.



→ 2-Dimensional Nucleation ①

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

→ self-stabilized and continue to grow.

- **Δ*T* becomes large, r* ↓.**

- $\boxed{v \infty \exp(-k_2/\Delta T_i)}$

② Spiral growth: Growth by Screw Dislocation

Crystals grown with a low supersaturation were always found to have a 'growth spirals' on the growing surfaces.

- **addition of atoms to the ledge cause it to rotate around the axis of screw dislocation**
- **If atoms add at an equal rate to all points along the step, the angular velocity of the step will be initially greatest nearest to the dislocation core.**
- **the spiral tightens until it reaches a minimum radius of r***
- $v = k_3(\Delta T_i)^2$

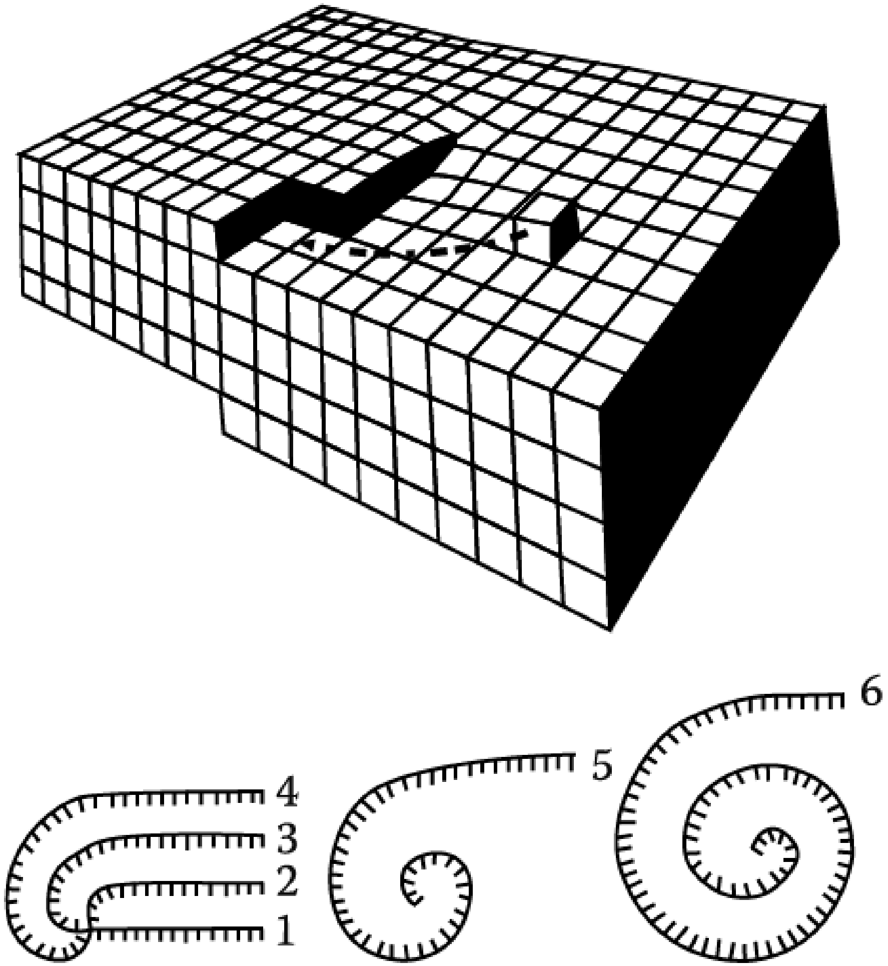
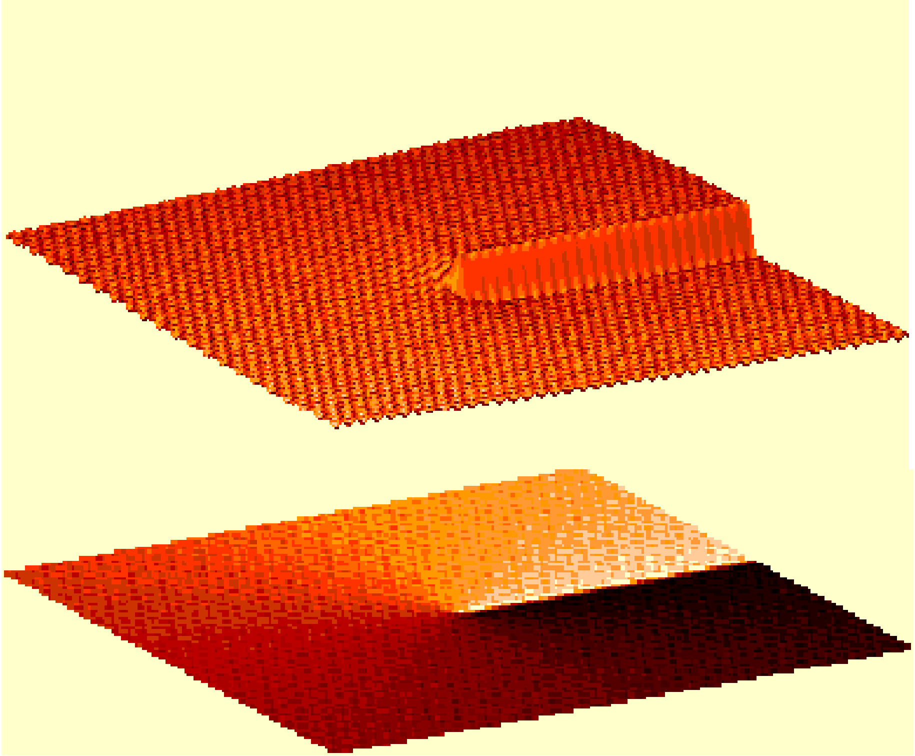


Fig. 4. 13 Spiral growth. (a) A screw dislocation terminating in the solid/liquid interface showing the associated ledge. Addition of atoms at the ledge causes it to rotate with an angular velocity decreasing away from the dislocation core so that a growth spiral develops as shown in (b).

Growth by Screw Dislocation



Burton, Cabrera and Frank (BCF, 1948) elaborated the spiral growth mechanism, assuming steps are atomically disordered…

Their interpretation successfully explained the growth velocity of crystals as long as the assumption is valid…

③ Growth from twin boundary → "feather crystal" under small ΔT

- **another permanent source of steps like spiral growth**

  → not monoatomic height ledge but macro ledge

Kinetic Roughening

Rough interface - Ideal Growth → diffusion-controlled → dendritic growth

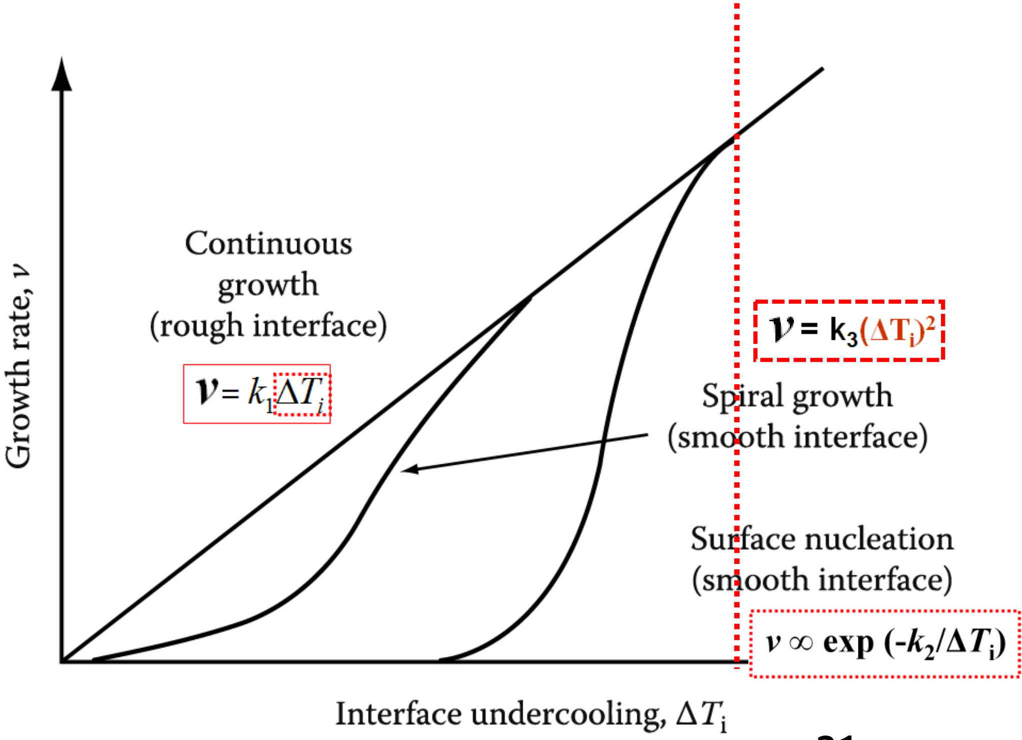
Smooth interface - Growth by Screw Dislocation
Growth by 2-D Nucleation

Small ΔT → "feather" type of growth ⟷ Large ΔT → cellular/dendritic growth

The growth rate of the singular interface cannot be higher than ideal growth rate.

When the growth rate of the singular Interface is high enough, it follows the ideal growth rate like a rough interface.

→ kinetic roughening



Q: Heat Flow and Interface Stability

1) Superheated liquid

: Extraction of latent heat by conduction in the crystal

2) Supercooled liquid

: conduction of latent heat into the liquid

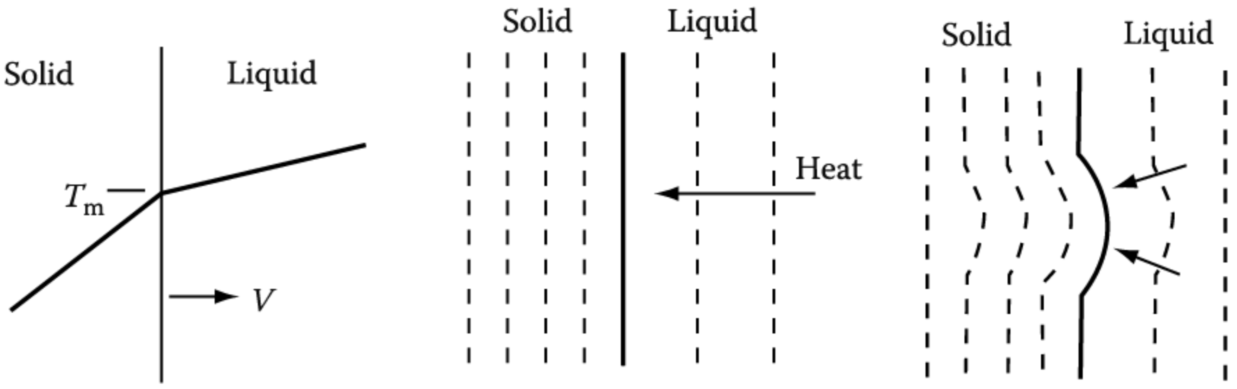
→ Development of Thermal Dendrite

4.2.3 Heat Flow and Interface Stability - Planar interface

1) Superheated liquid

Consider the solidification front with heat flow from L to S.

solid growing at *v* (planar)



(a) (b) (c)

Heat flow away from the interface through the solid $K_S T'$

$K_L T_L'$ **- Heat flow from the liquid**

vL_V **- Latent heat generated at the interface**

Heat Balance Equation

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

K: thermal conductivity

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. **T_L'↑ & T_S'↓**

More heat to the protrusion → melt away

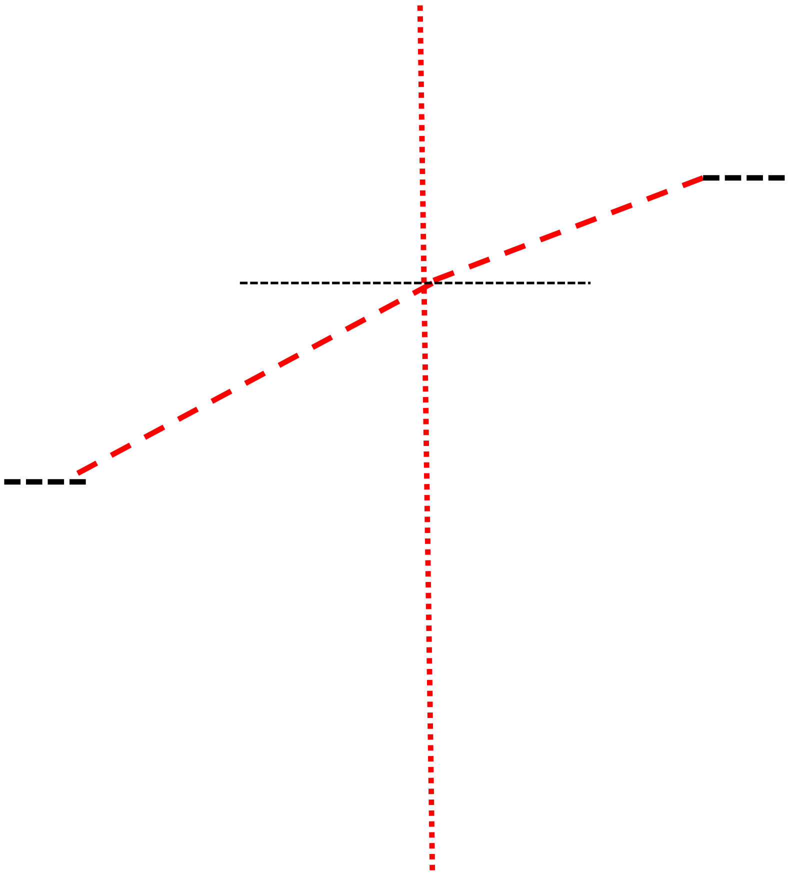
***v* of protrusion ↓ to match other *v* in planar region**

mould walls

“Removal of latent heat” → Heat Flow and Interface Stability

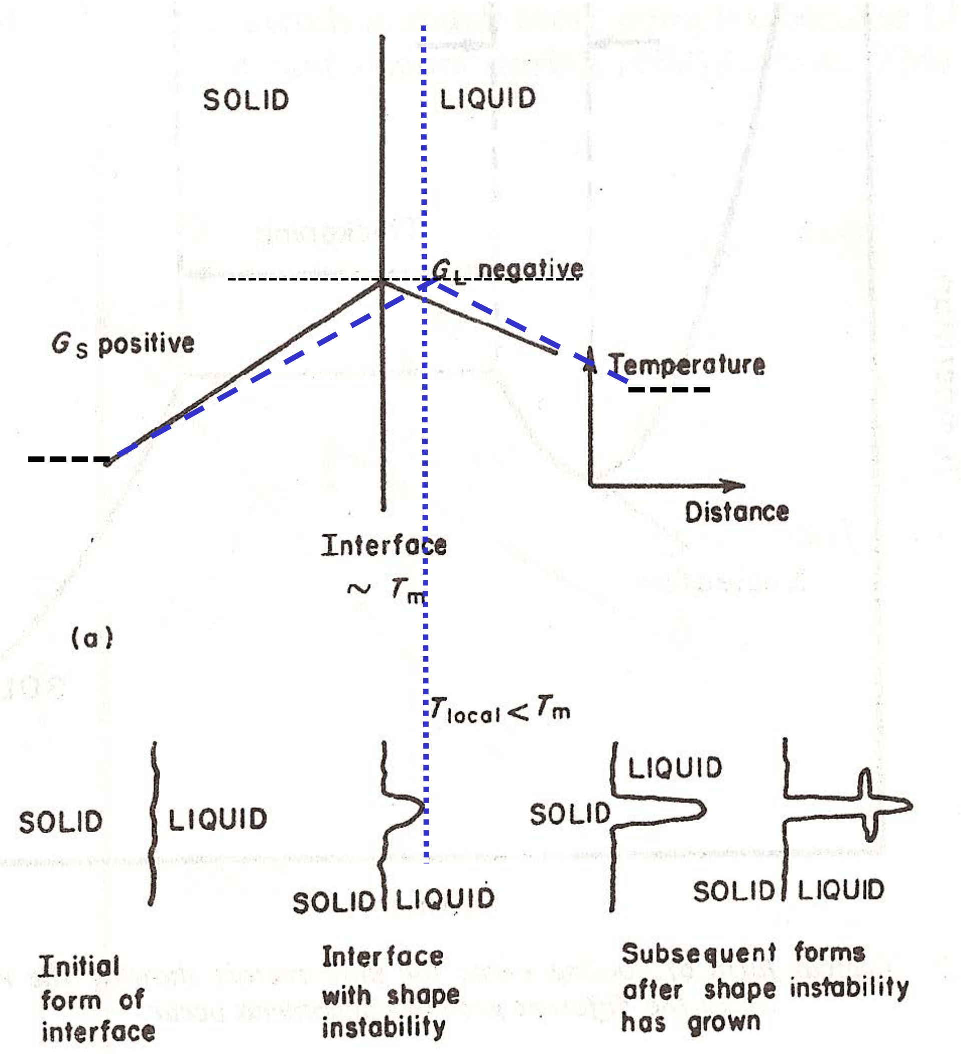
1) Superheated liquid

: Extraction of latent heat by conduction in the crystal



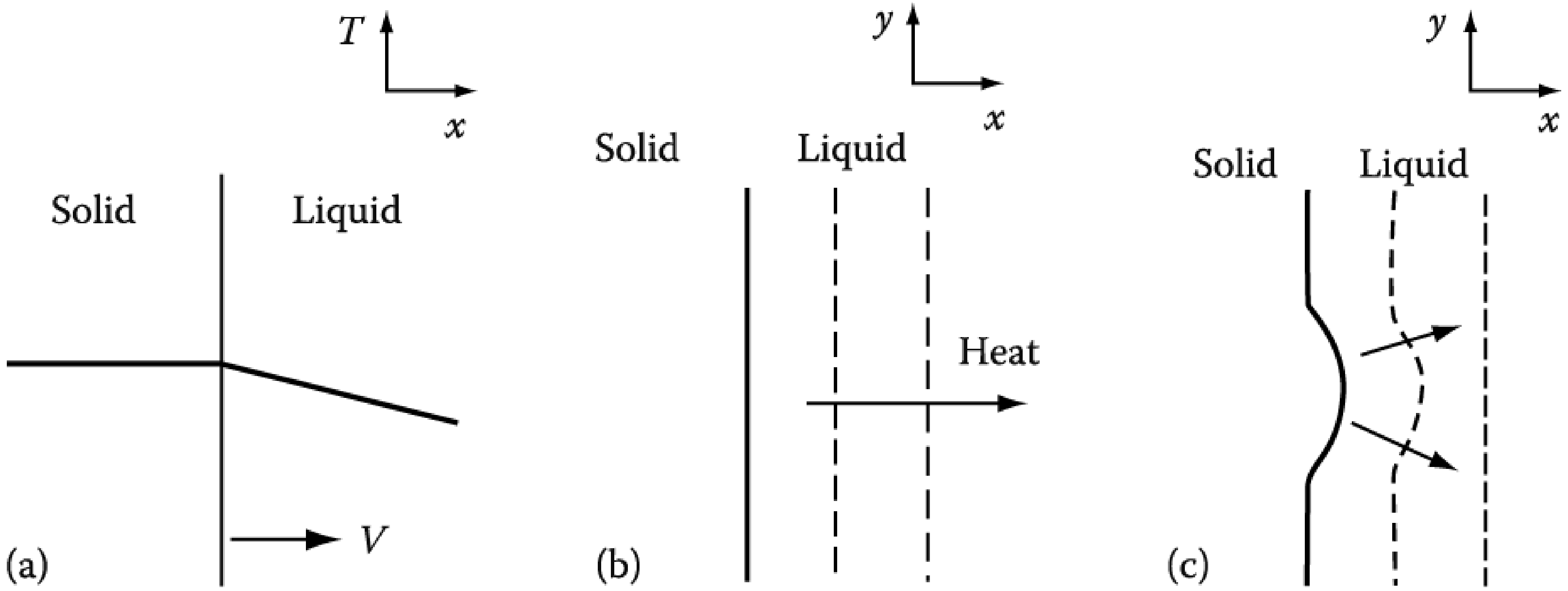
2) Supercooled liquid

: conduction of latent heat into the liquid



Heat Flow and Interface Stability - Planar interface

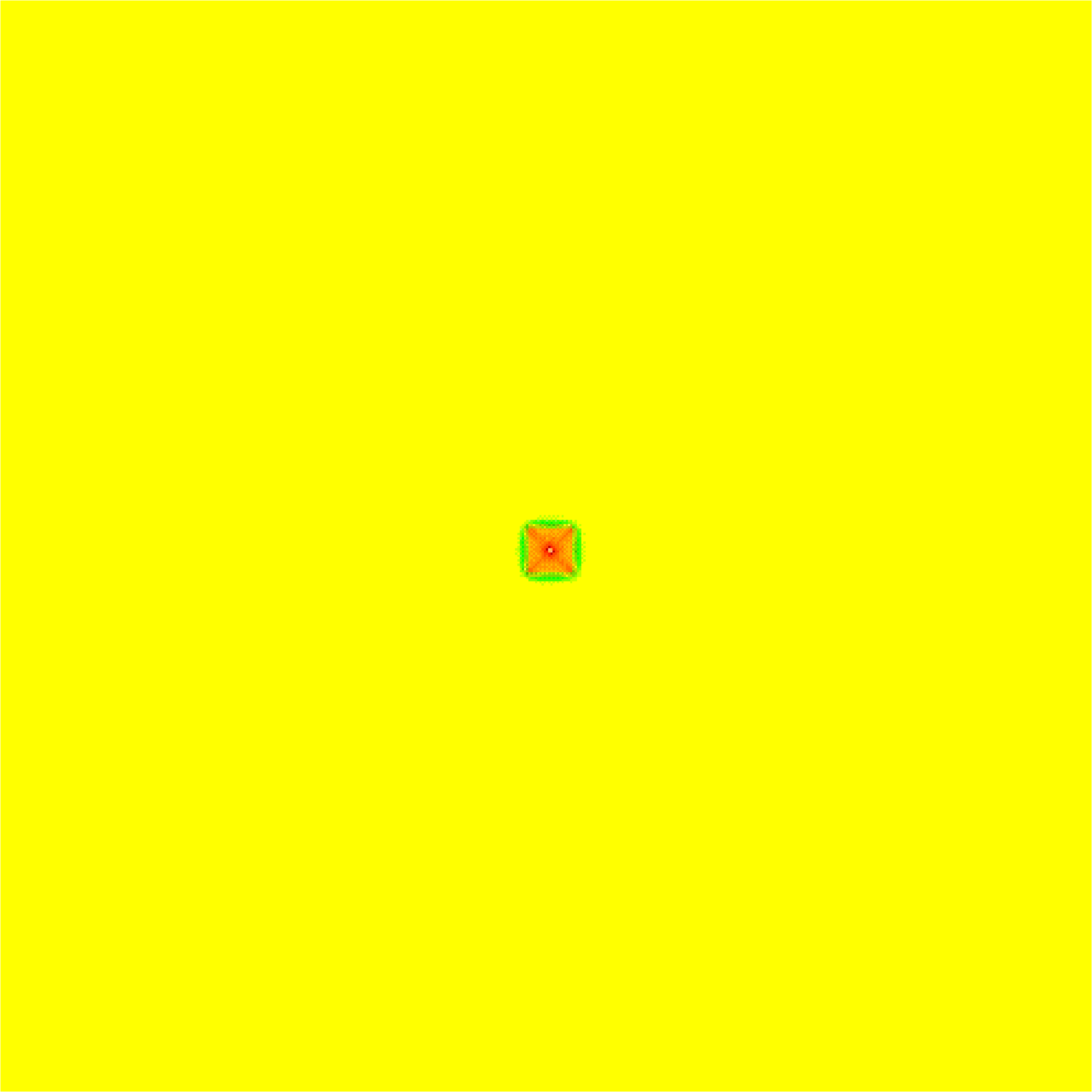
2) Solid growing into supercooled liquid



- **protrusion** $\frac{dT_L'}{dX} < 0$ **becomes more negative**

- **heat flow from solid = the protrusion grows preferentially.**

Solidification: Liquid ⟶ Solid



4 Fold Symmetric Dendrite Array

Development of Thermal Dendrite

cf) constitutional supercooling

When does heat flow into liquid?

→ **Liquid should be supercooled below T_m.**

→ **Nucleation at impurity particles in the bulk of the liquid**

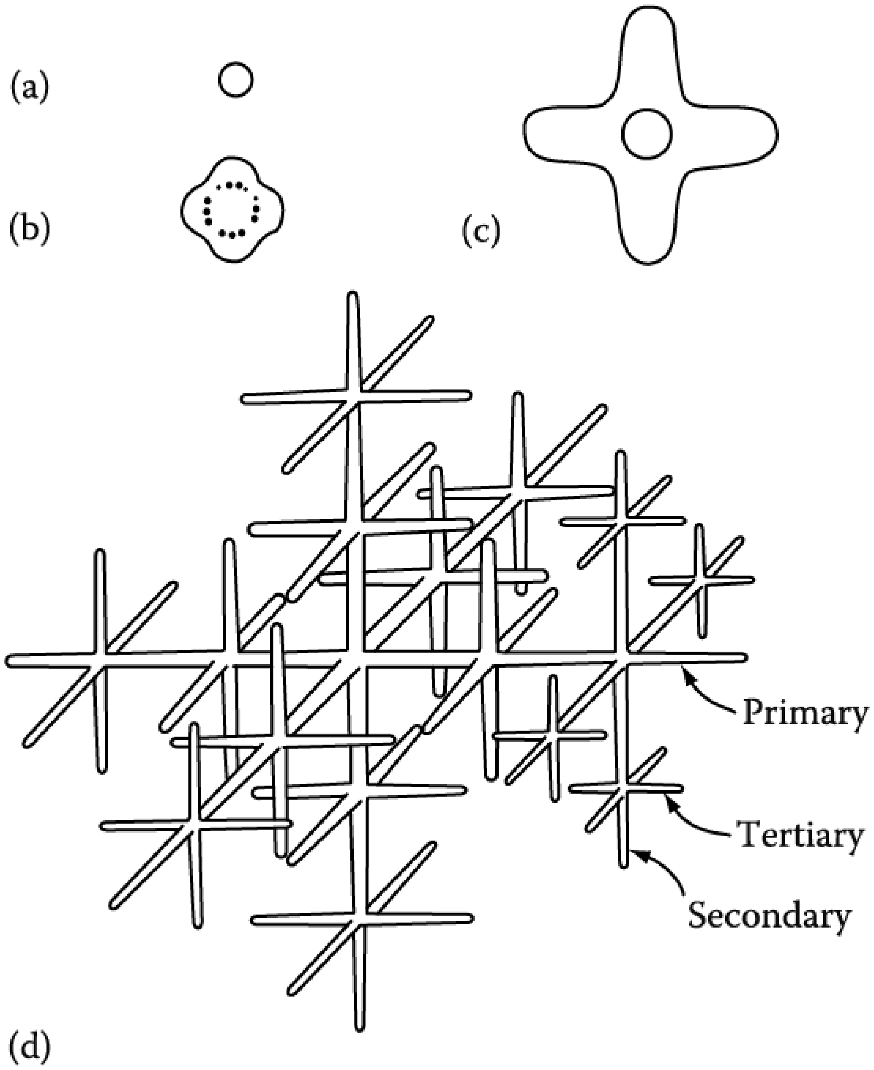


Fig. 4.17 The development of thermal dendrites: (a) a spherical nucleus; (b) the interface becomes unstable; (c) primary arms develop in crystallographic directions (<100> in cubic crystals); (d) secondary and tertiary arms develop

Q: How to calculate the growth rate (v) in the tip of a growing dendrite?

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 $\left(T'_S = 0\right)$

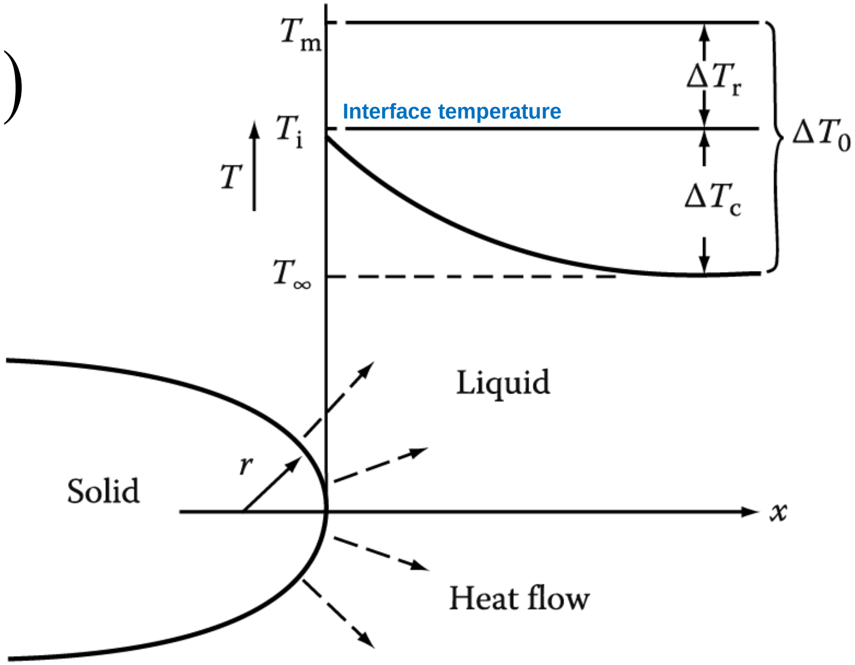
From $K_S T'_S = K_L T'_L + v L_V$

$$\text{If } \; T'_S = 0, \quad v = \frac{-K_L T'_L}{L_V}$$

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

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

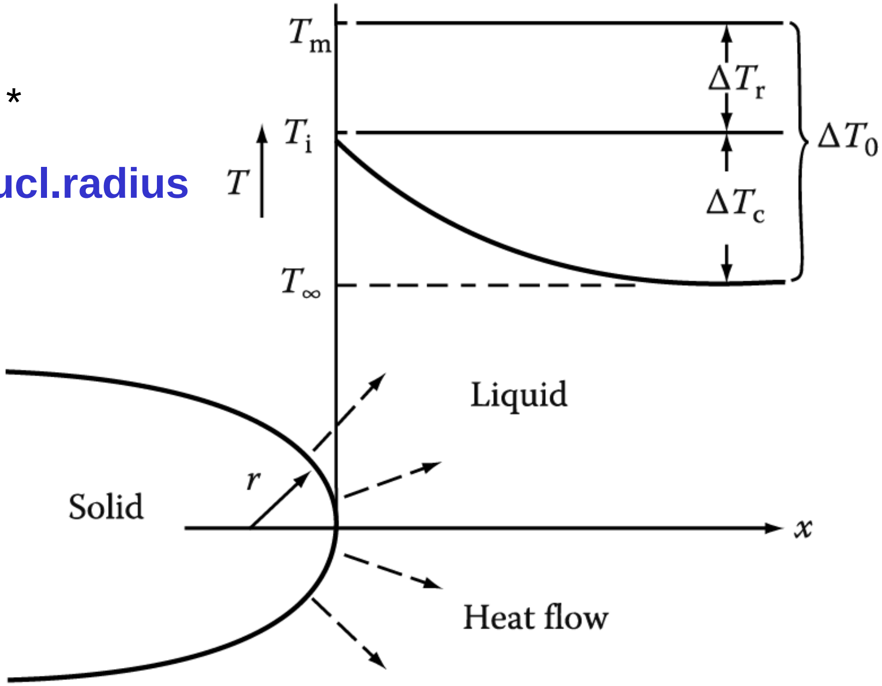
Minimum possible radius (r)?

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

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

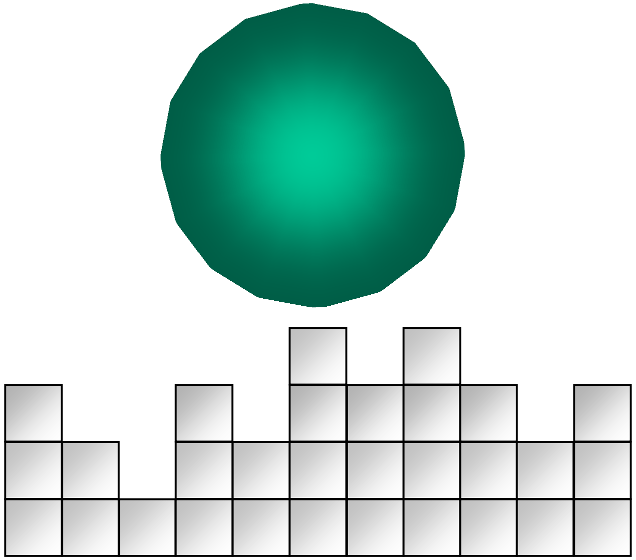
as $r \rightarrow \infty$ due to slower heat condution

Maximum velocity?

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

* Growth

Equilibrium Shape and Interface Structure on an Atomic Scale



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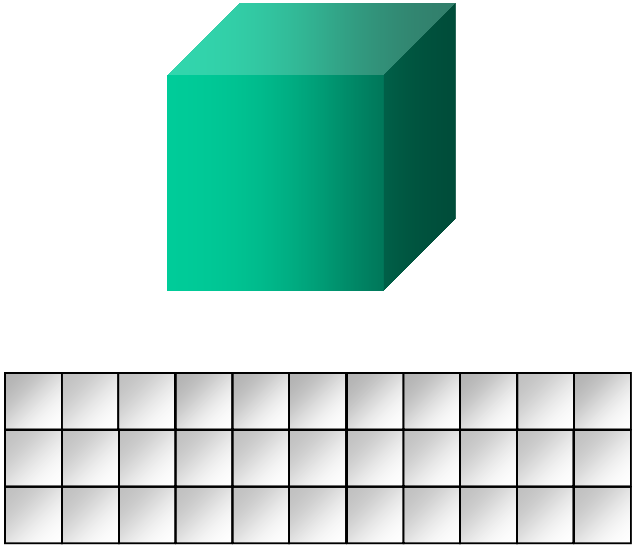

atomically-flat

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Enthalpy-dominant

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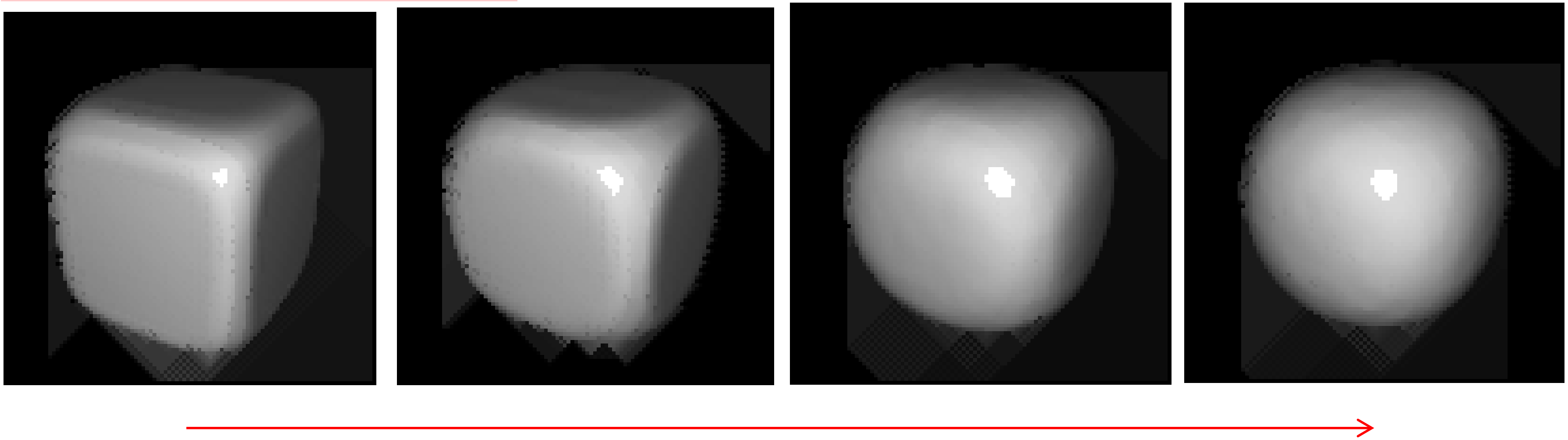
Thermal Roughening

singular (smooth) interface

rough interface



Enthalpy-dominant

Entropy-dominant

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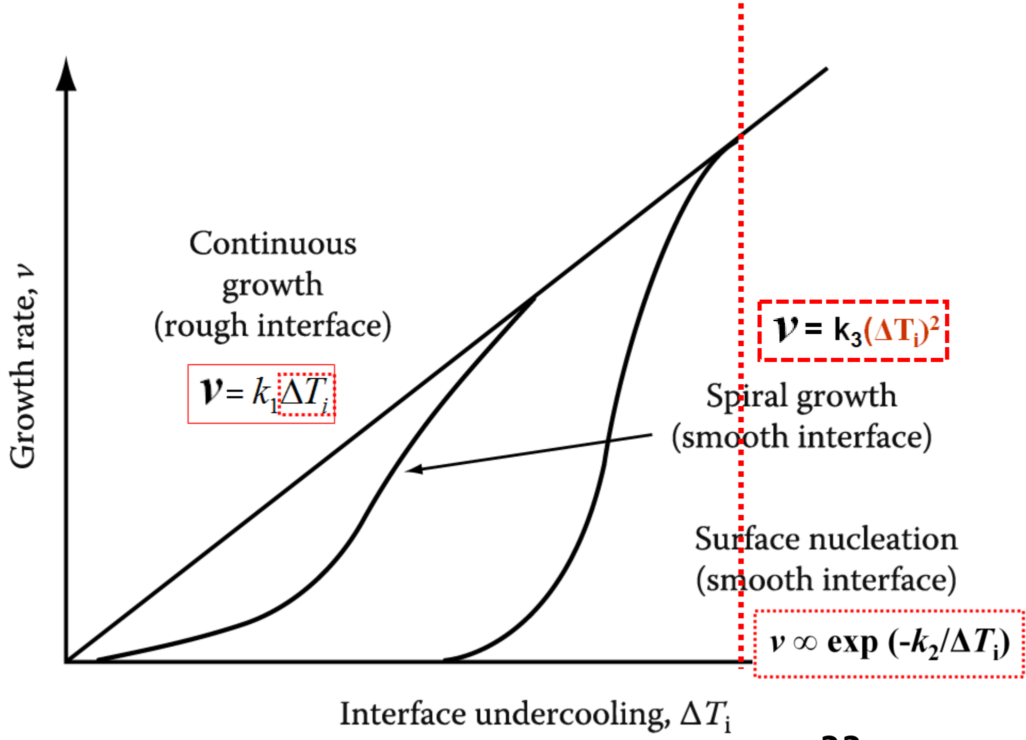
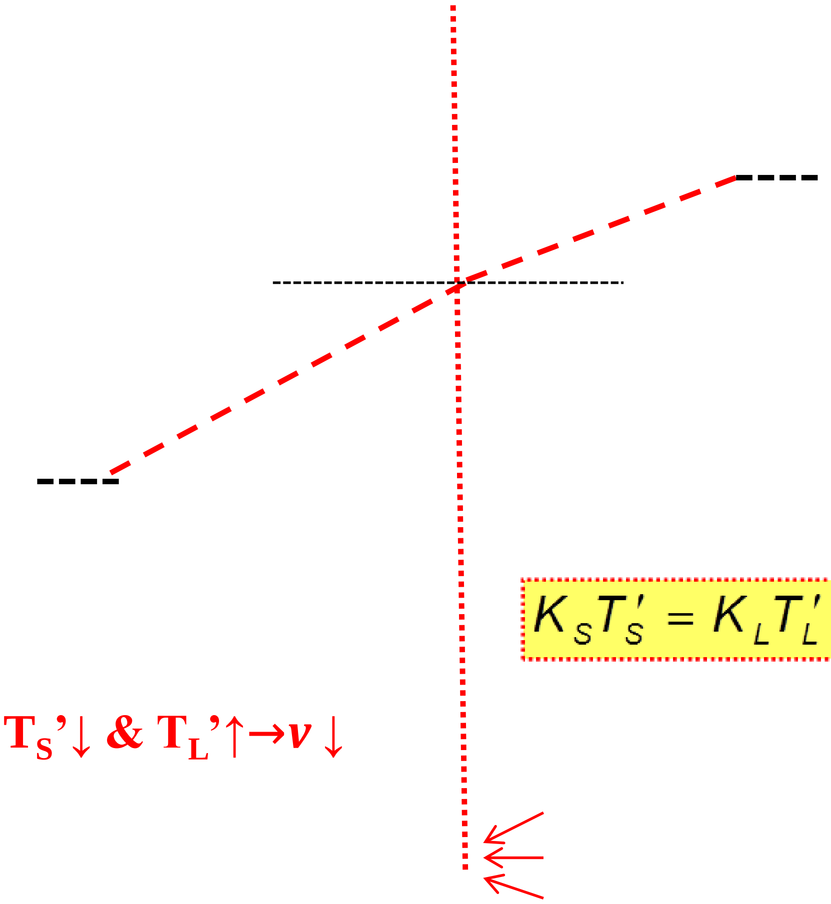


“Removal of latent heat” → Heat Flow and Interface Stability

1) Superheated liquid

: Extraction of latent heat by conduction in the crystal

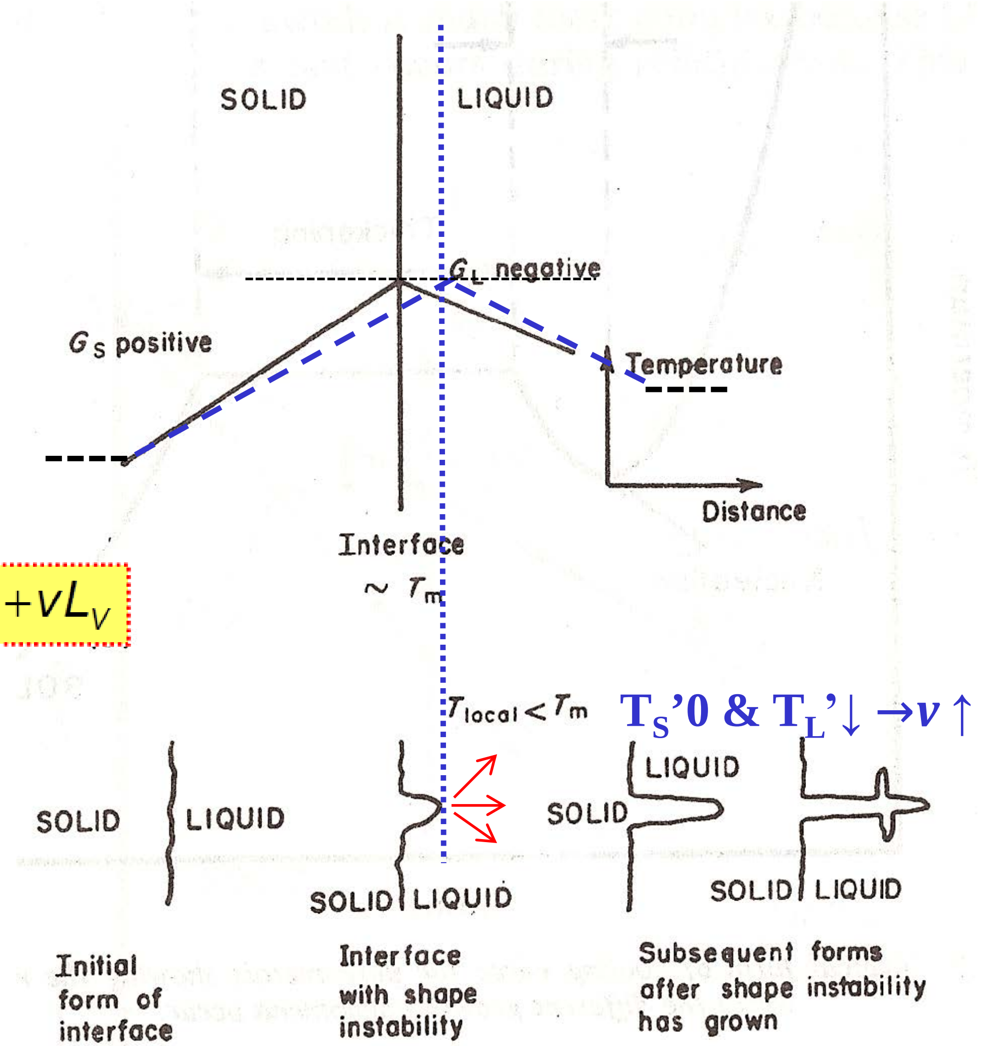


$$K_S T'_S = K_L T'_L \quad + vL_V$$

$T_S'\downarrow$ & $T_L'\uparrow \rightarrow v\downarrow$

2) Supercooled liquid

: conduction of latent heat into the liquid



$T_S'0$ & $T_L'\downarrow \rightarrow v\uparrow$

Development of Thermal Dendrite

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

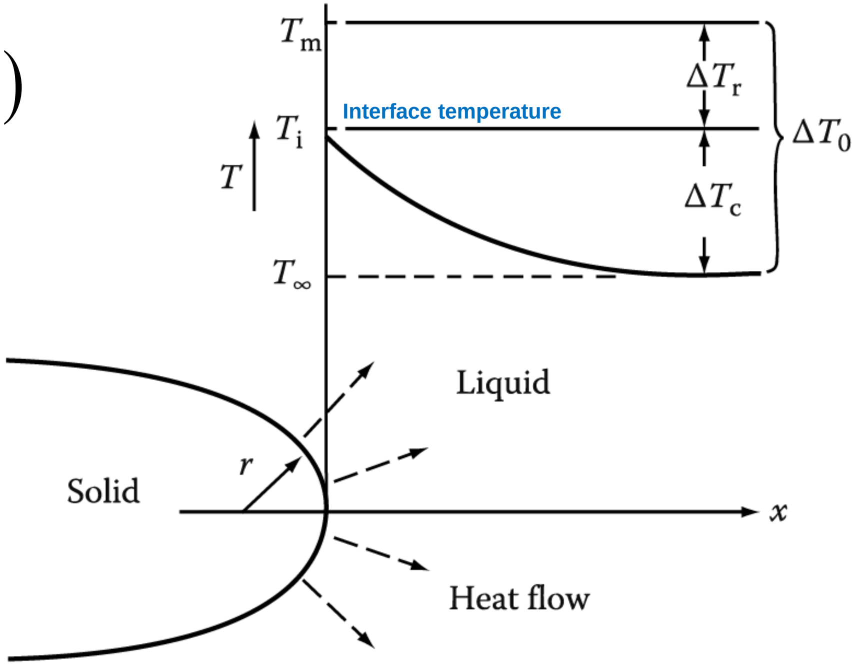
From $K_S T_S' = K_L T_L' + v L_V$

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

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

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

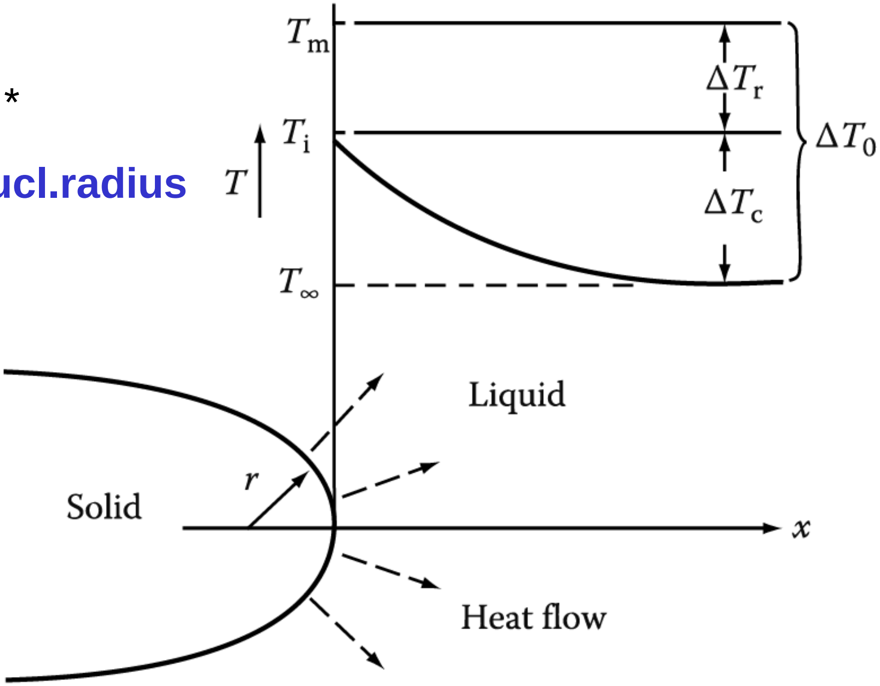
Minimum possible radius (r)?

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

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?

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

2021 Fall

"Phase Transformation *in* Materials"

17th lecture

Eun Soo Park

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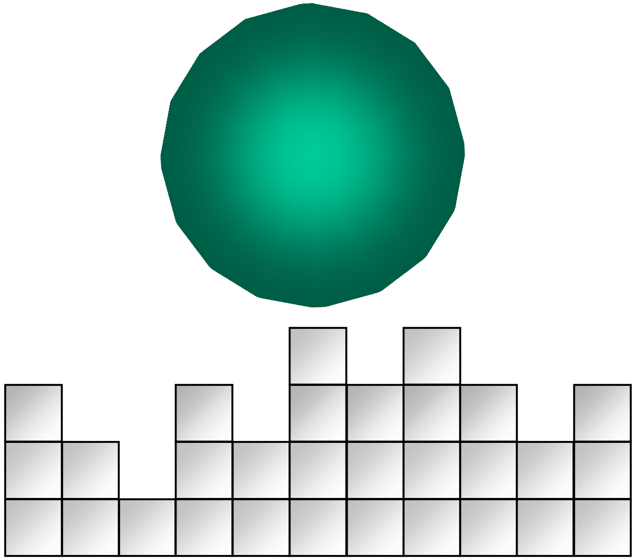
Email: espark@snu.ac.kr
Office hours: by an appointment

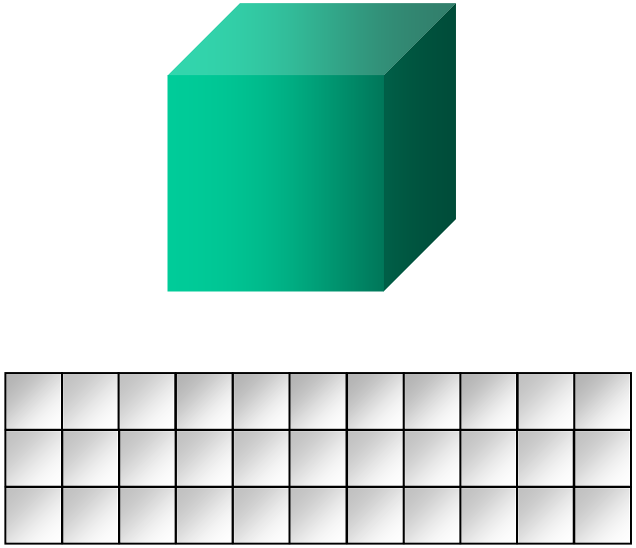
* Growth

Equilibrium Shape and Interface Structure on an Atomic Scale



atomically-disordered

Ex) metallic systems



atomically-flat

nonmetals

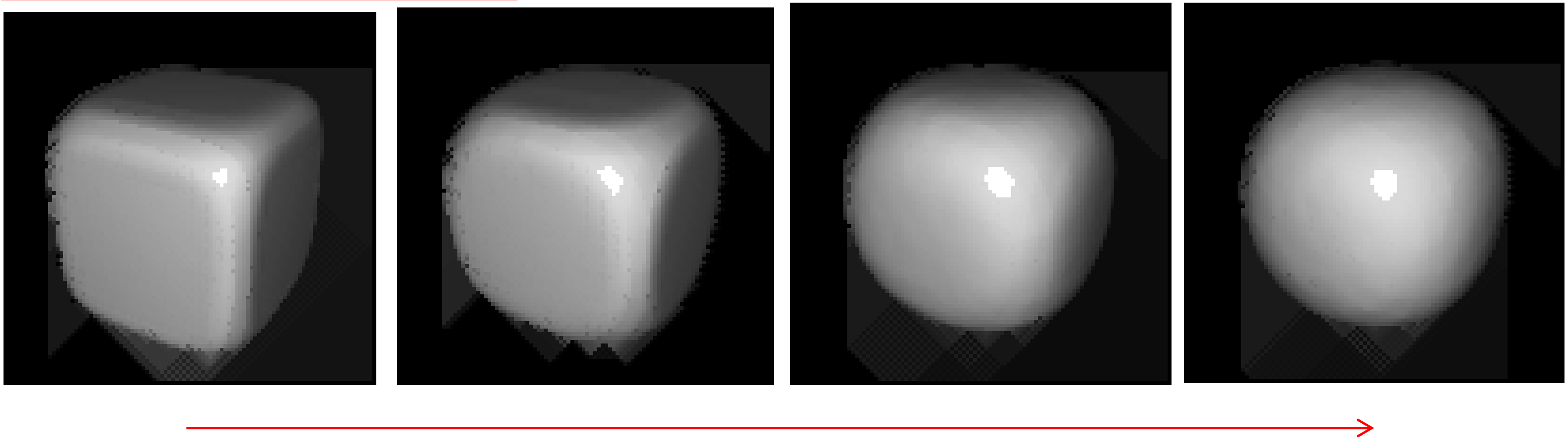
Apply thermodynamics to this fact and derive more information.

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

Thermal Roughening

singular (smooth) interface

rough interface



Enthalpy-dominant

Entropy-dominant

Heating up to the roughening transition.

Kinetic Roughening

Rough interface - Ideal Growth → diffusion-controlled → dendritic growth

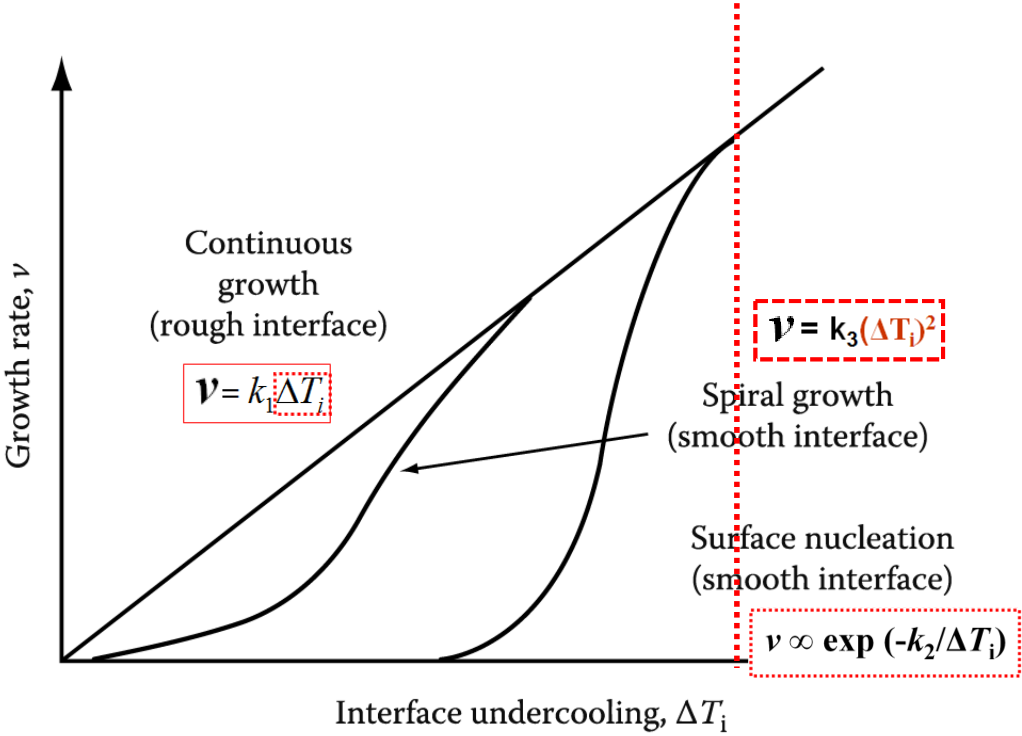
Smooth interface - Growth by Screw Dislocation
Growth by 2-D Nucleation

Small ΔT → "feather" type of growth ↔ Large ΔT → cellular/dendritic growth

The growth rate of the singular interface cannot be higher than ideal growth rate.

When the growth rate of the singular Interface is high enough, it follows the ideal growth rate like a rough interface.

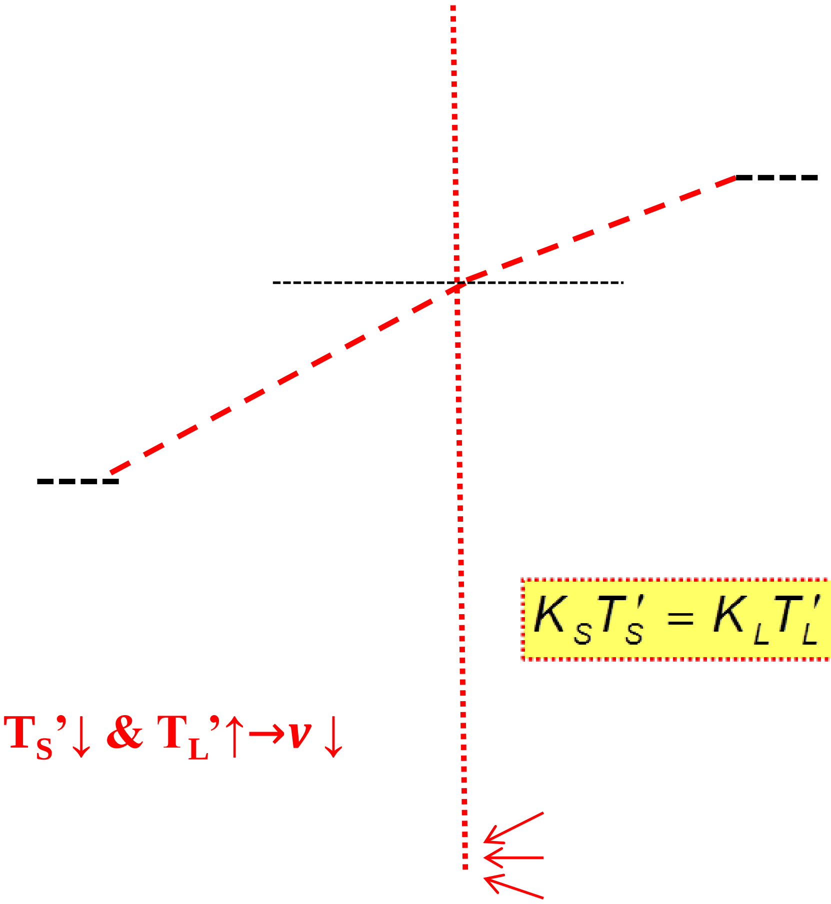
→ kinetic roughening



"Removal of latent heat" → Heat Flow and Interface Stability

1) Superheated liquid

: Extraction of latent heat by conduction in the crystal



$T_S'\downarrow$ & $T_L'\uparrow \rightarrow v\downarrow$

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2) Supercooled liquid

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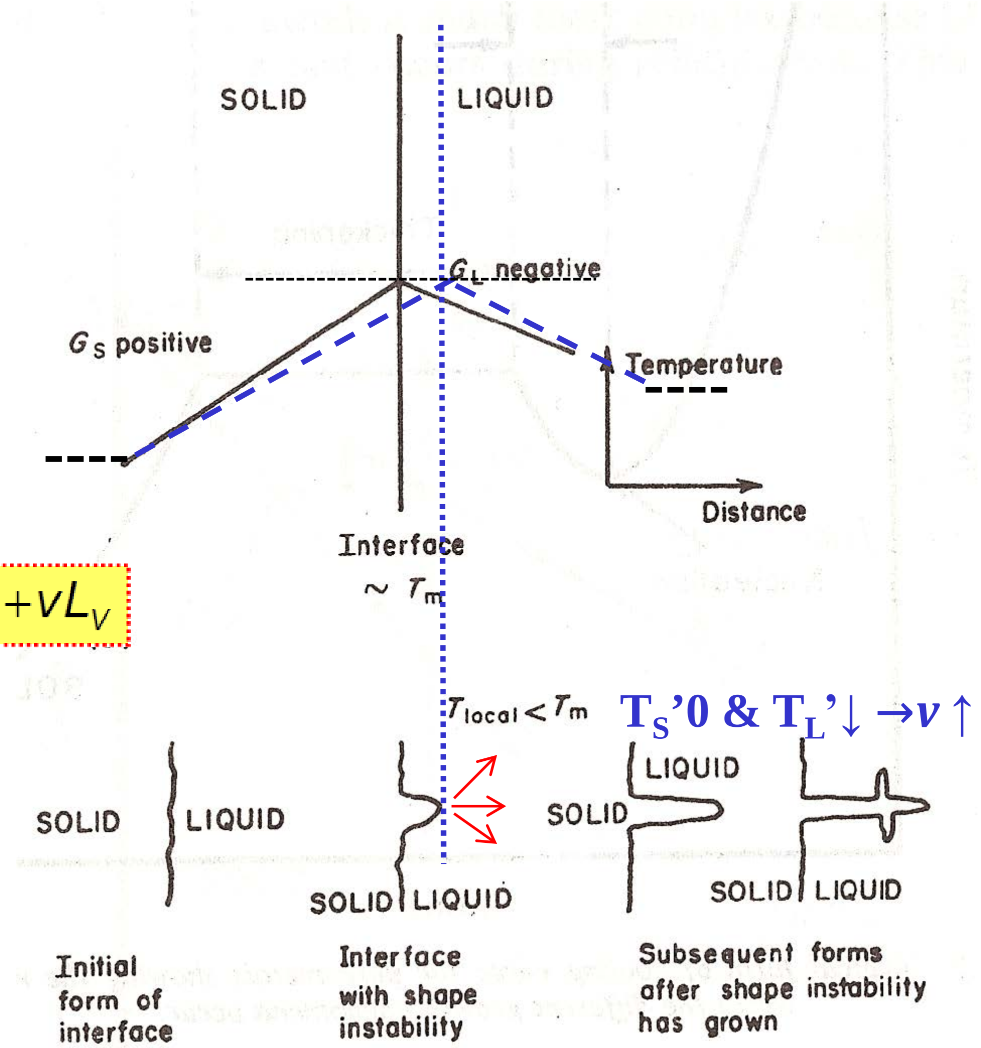

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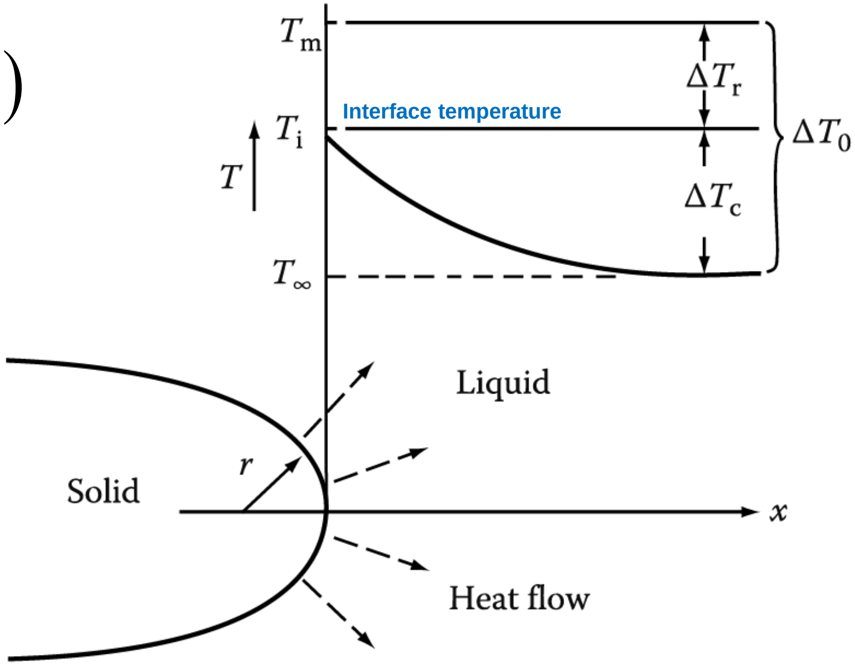

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$$r_{min} : \Delta T_r \to \Delta T_0 = T_m - T_\infty \to r^*$$

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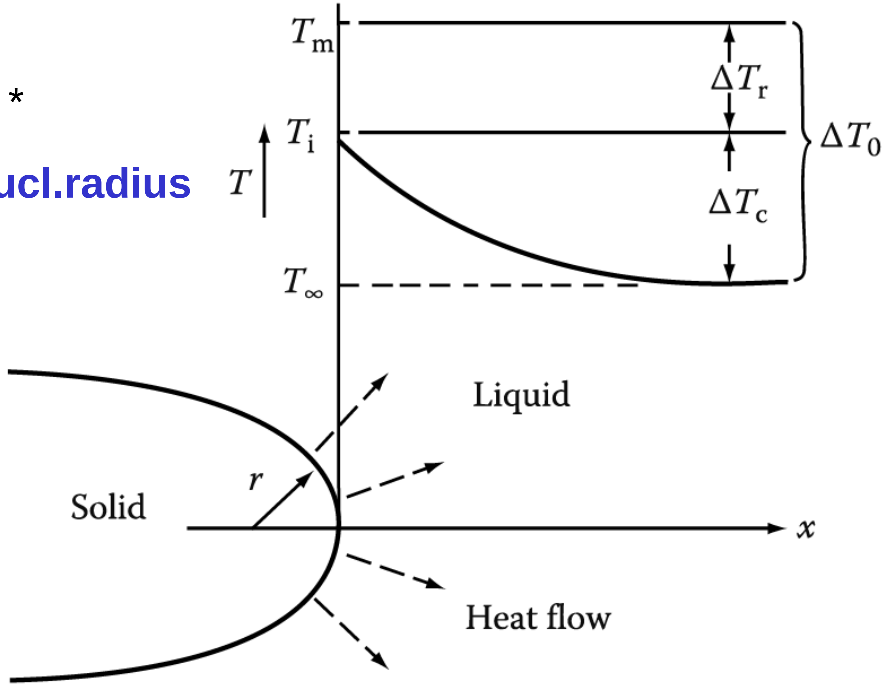

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$$\boxed{v \cong \frac{K_L}{L_V}\cdot\frac{\Delta T_c}{r} = \frac{K_L}{L_V}\cdot\frac{\left(\Delta T_0 - \Delta T_r\right)}{r} = \frac{K_L}{L_V}\cdot\frac{\Delta T_0}{r}\left(1-\frac{r^*}{r}\right)}$$

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

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

Maximum velocity?

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

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

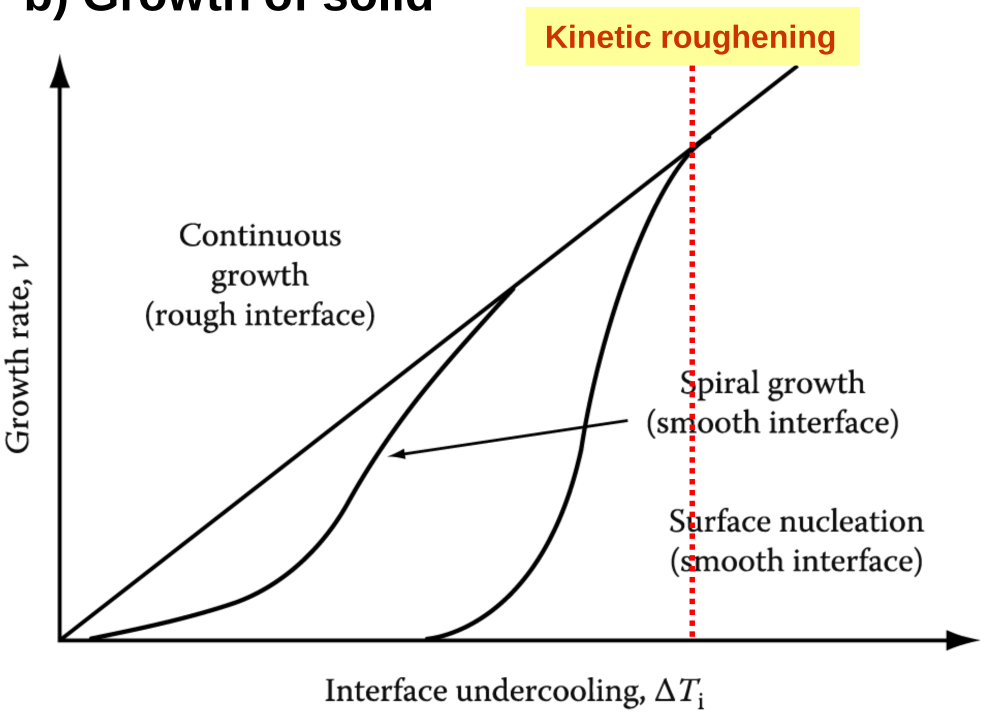
Solidification: Liquid → Solid

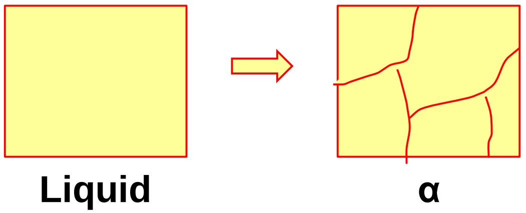
1) Pure Metals: Nucleation and Growth

a) homogeneous Nucleation or Heterogeneous Nucleation

- Undercooling ΔT
- Interfacial energy
  γ_{SL} / S(θ) wetting angle

b) Growth of solid





No compositional change during solidification

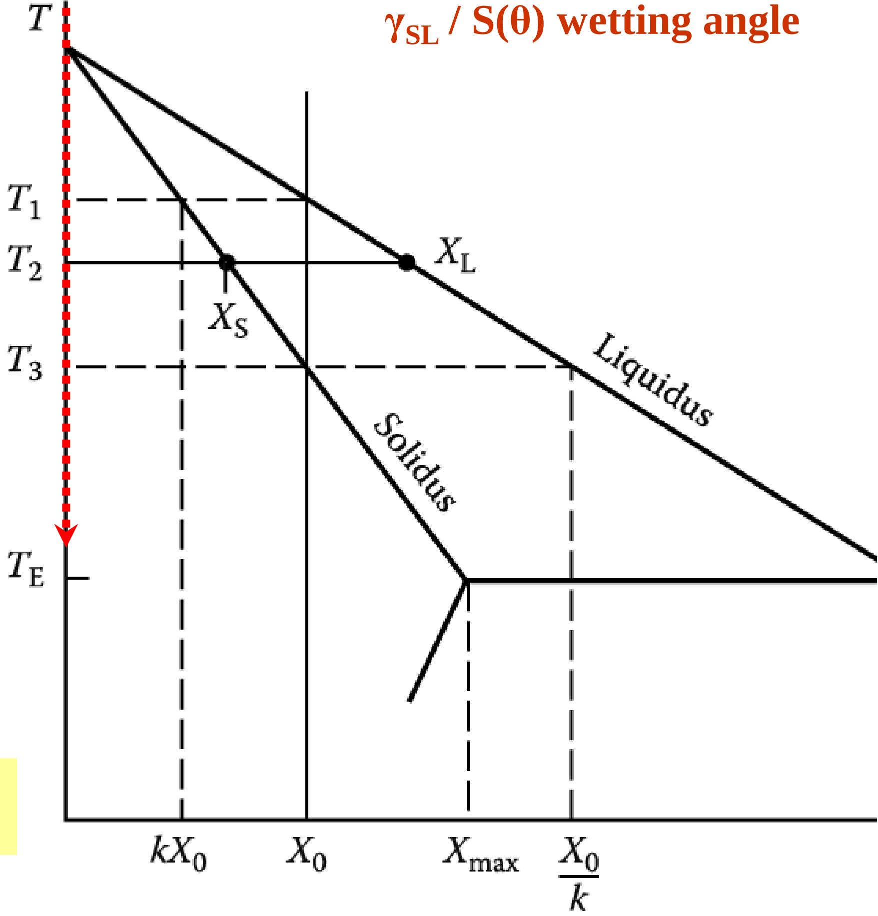


Fig. 4.19 A hypothetical phase diagram.

Q: Alloy solidification?

1. Solidification of single-phase alloys

- **Three limiting cases**

  1) Equilibrium Solidification: perfect mixing in solid and liquid

  2) No Diffusion in Solid, Perfect Mixing in Liquid

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

- Planar S/L interface → unidirectional solidification

- Superheated liquid

- Cellular and Dendritic Solidification

- Constitutional supercooling

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 const. (independent of *T*).

Planar S/L interface
→ unidirectional solidification

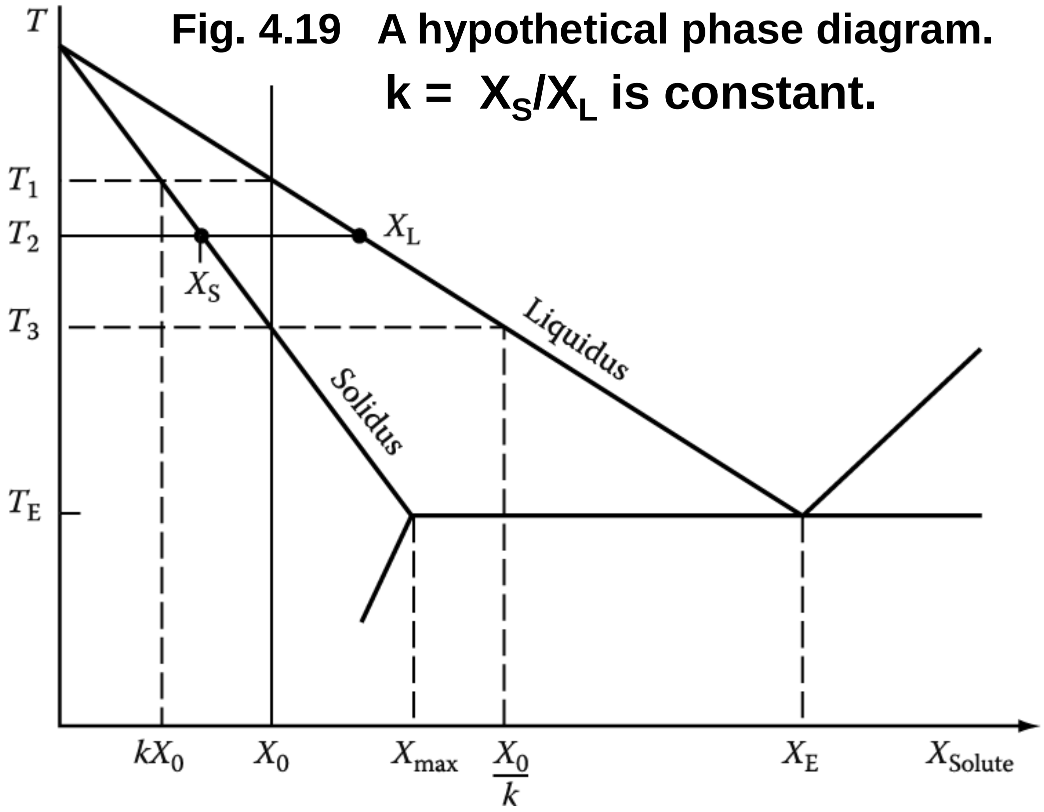
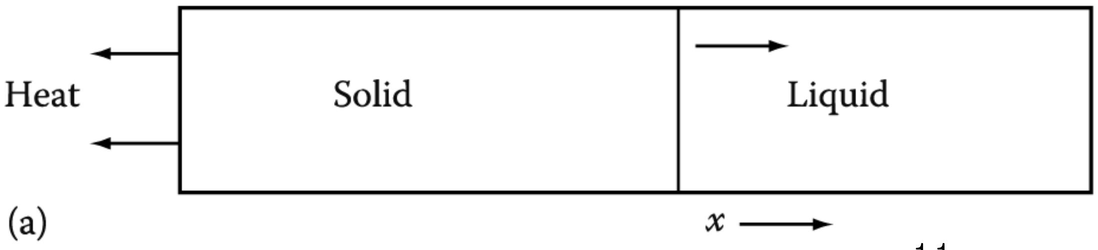


Fig. 4.19 A hypothetical phase diagram.
k = X_S/X_L is constant.



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

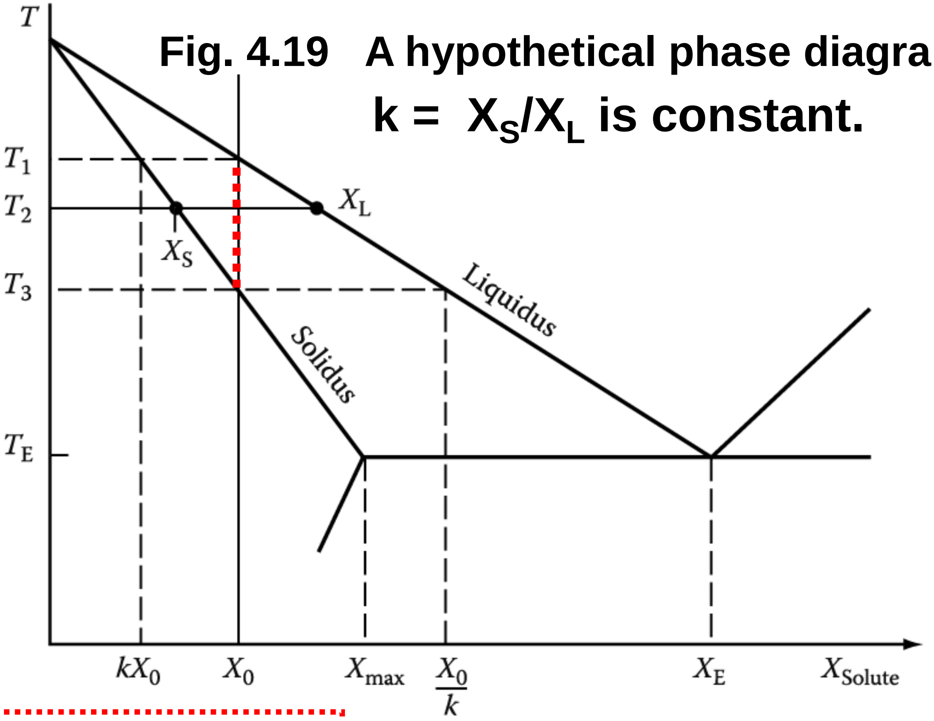
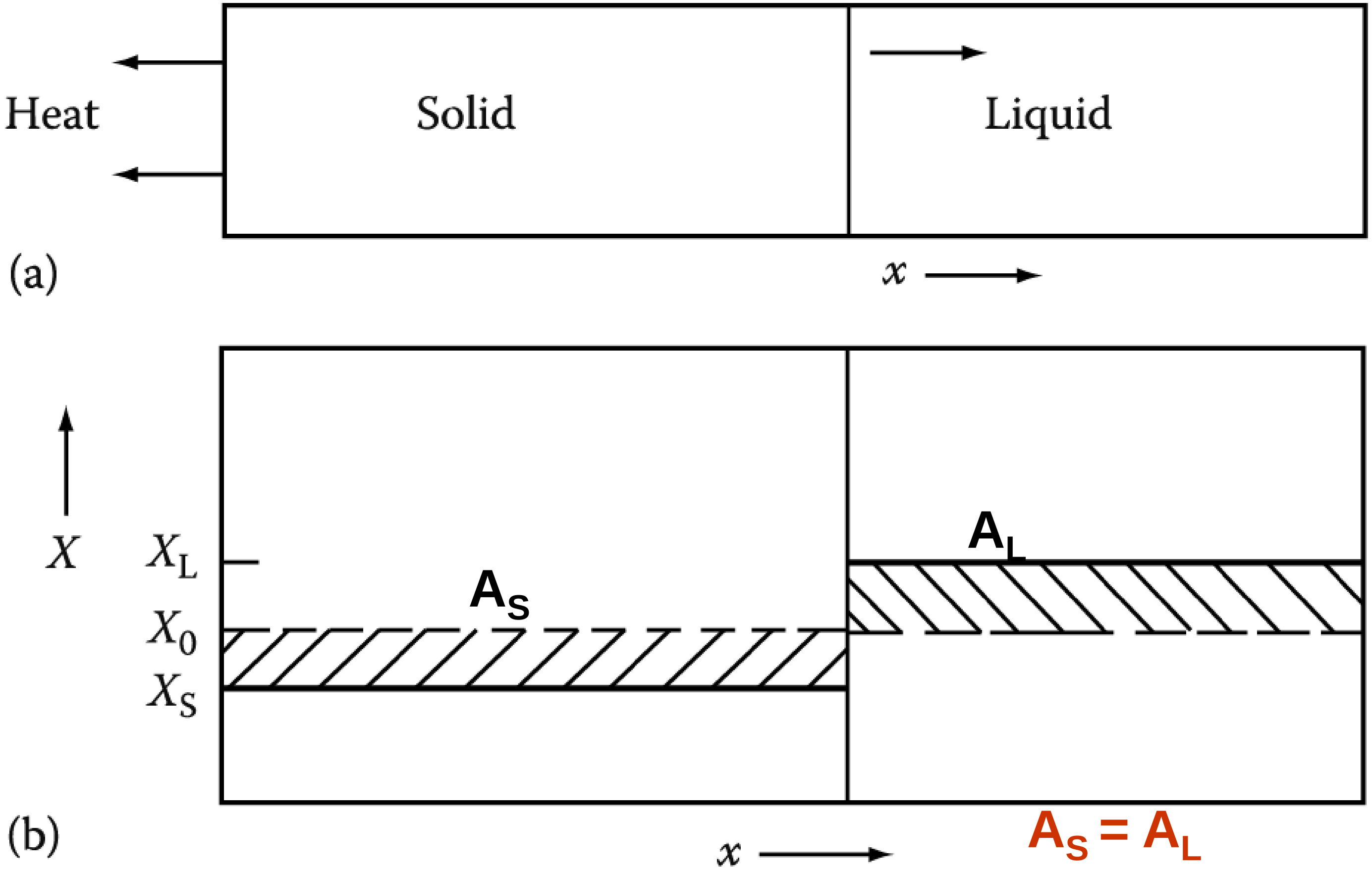


Fig. 4.19 A hypothetical phase diagram.

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).**

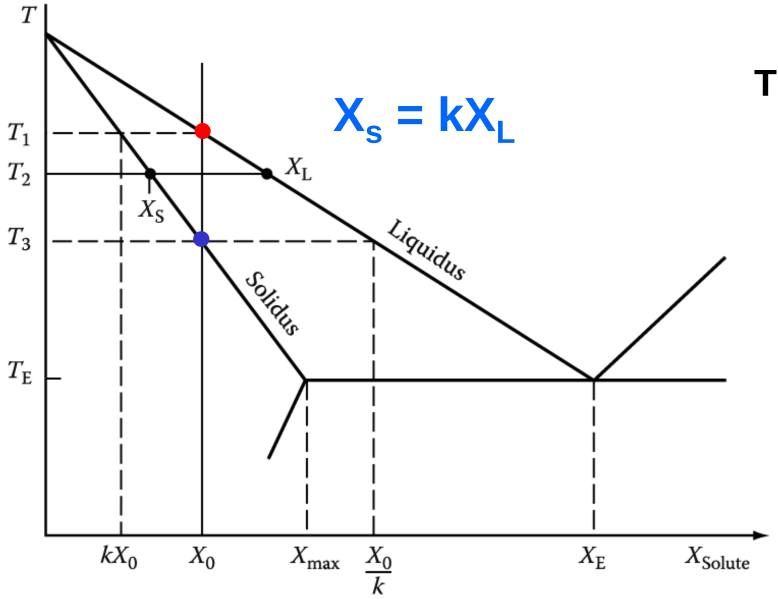
Composition vs x at T_2



$A_S = A_L$

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.** $A_S = A_L$

1) Equilibrium Solidification : perfect mixing in solid and liquid



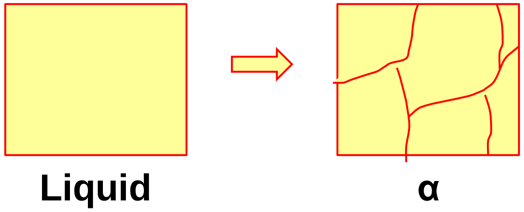
$X_S = kX_L$

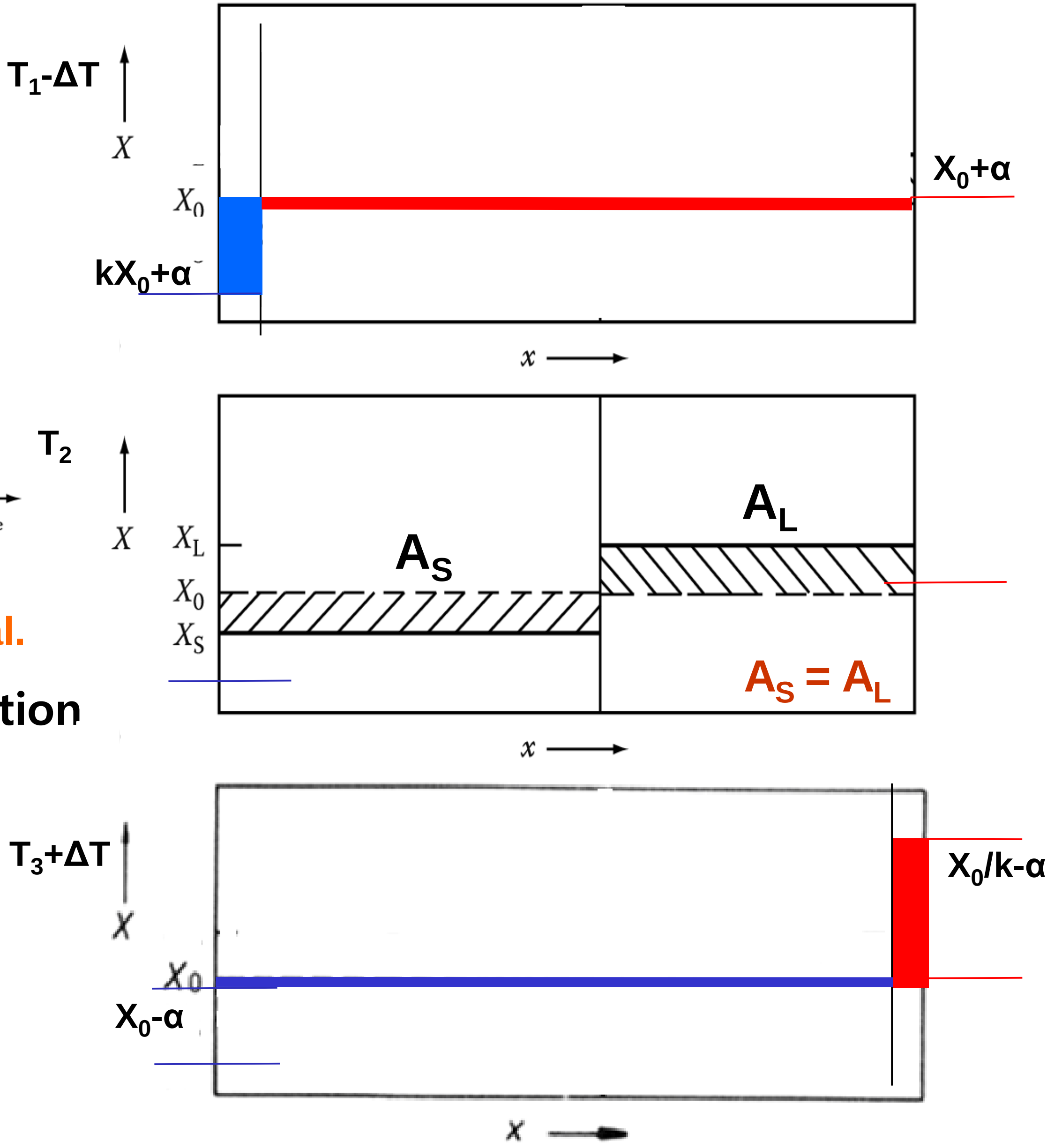
Conservation of solute requires the two shaded areas to be equal.

* **Equilibrium solute concentration**

$kX_0 \le X_S \le X_0$

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





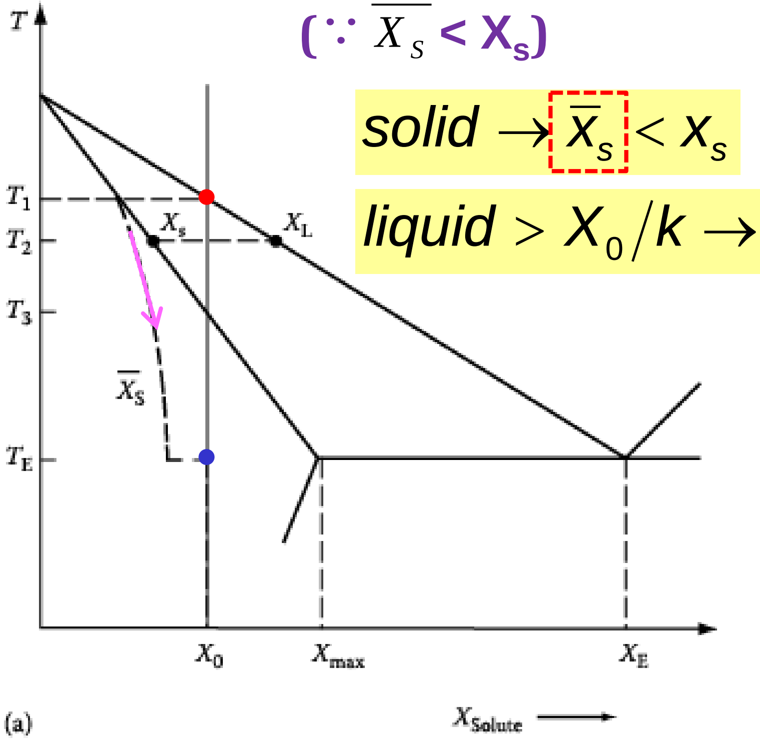
2) Non-equilibrium Solidification: No Diffusion in Solid, Perfect Mixing in Liquid

: 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 $X_0/K \rightarrow X_E$ at the last part of solidification.
- Variation of X_s: solute rejected to the liquid → solute increase in the liquid

($\because \overline{X}_S < X_s$)



$$solid \rightarrow \boxed{\overline{X}_s} < X_s$$

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

local equil. at S/L interface

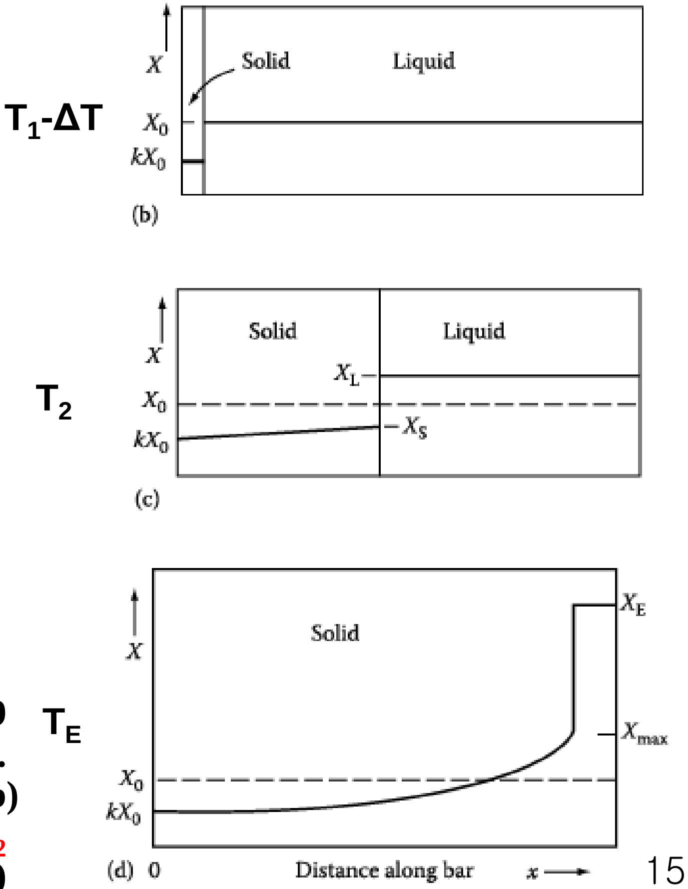
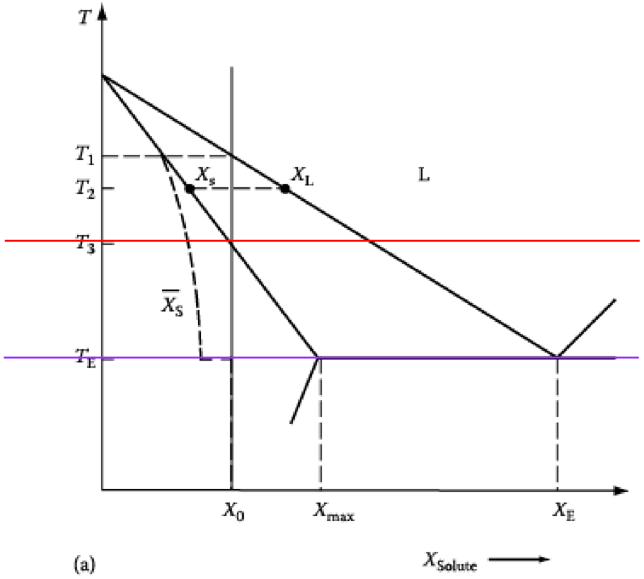


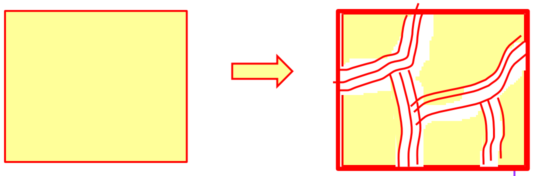
Fig. 4.21 Planar front solidification of alloy X_0 in fig. 4.19 assuming no diffusion in the solid, but complete mixing in the liquid. (a) As Fig. 4.19, but including the mean composition of the solid. (b) Composition profile just under T_1. (c) Composition profile at T_2 (compare with the profile and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

2) No Diffusion in Solid, Perfect Mixing in Liquid

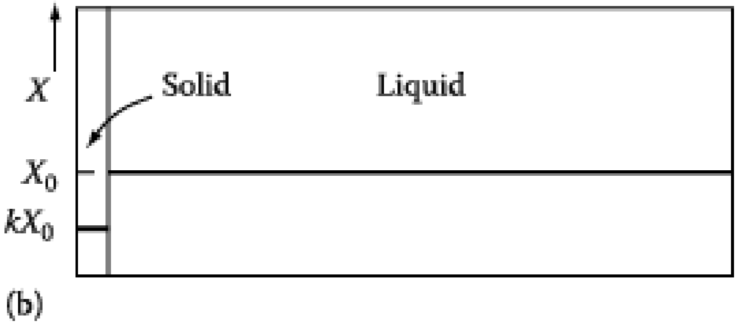
: high cooling rate, efficient stirring

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

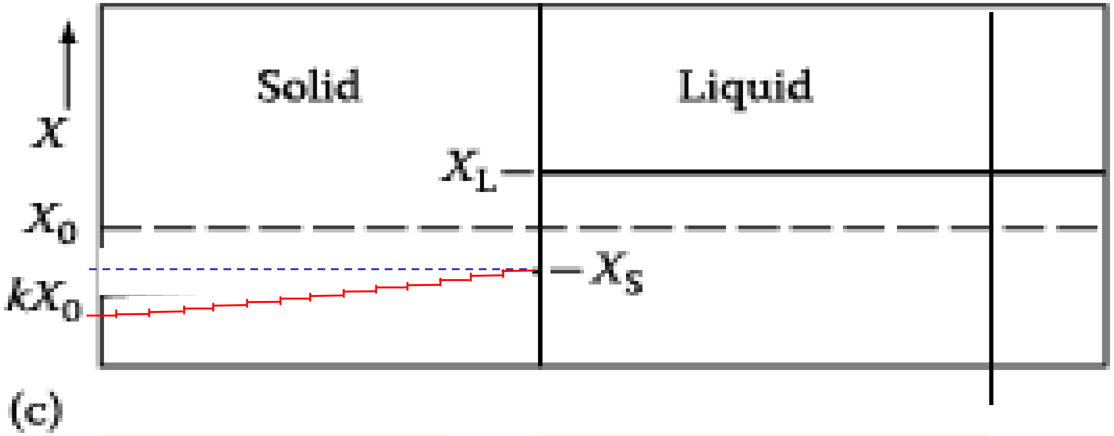


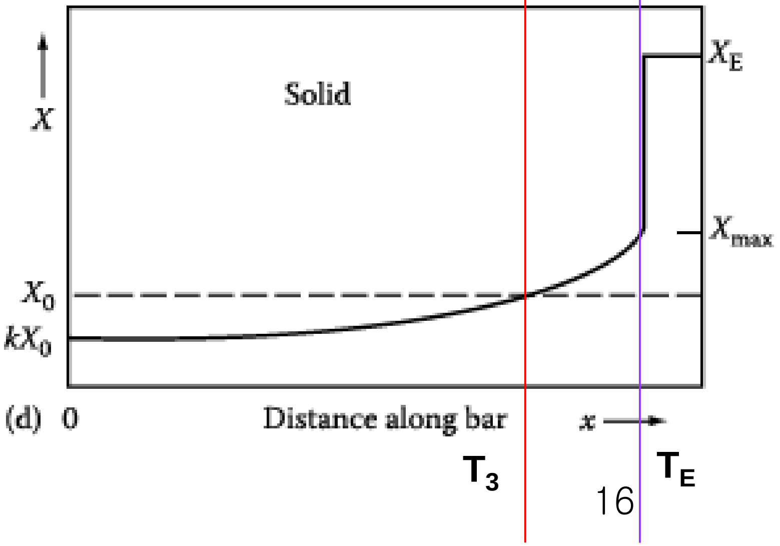


T$_1$-ΔT



T$_2$

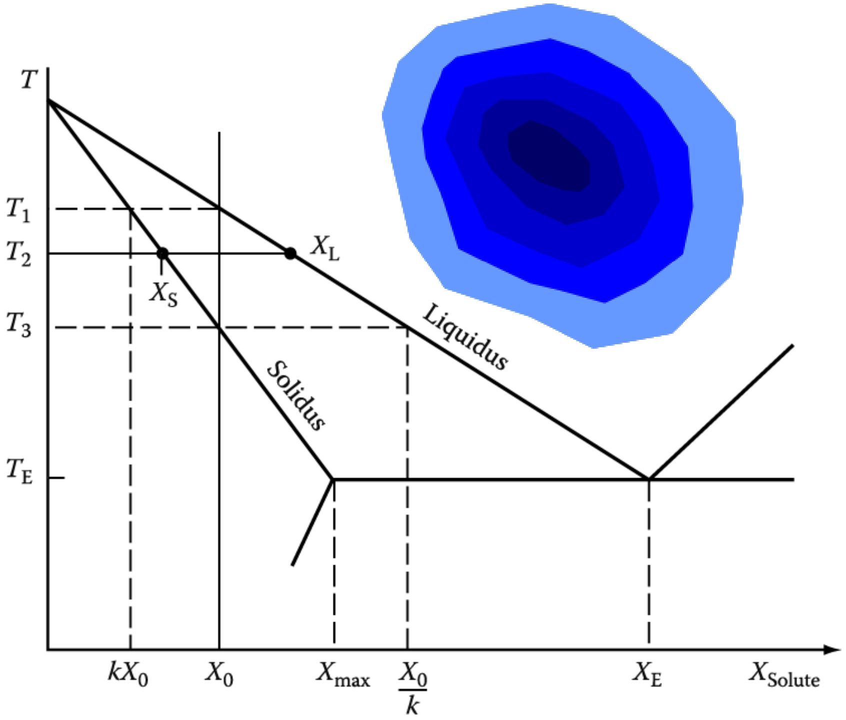




$solid \to \bar{x}_s < x_s$

$liquid > X_0/k \to X_E$

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



When cooled by ΔT 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

The variation of X_S along the solidified bar

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 $X_L = X_0$**

Initial conditions

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

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

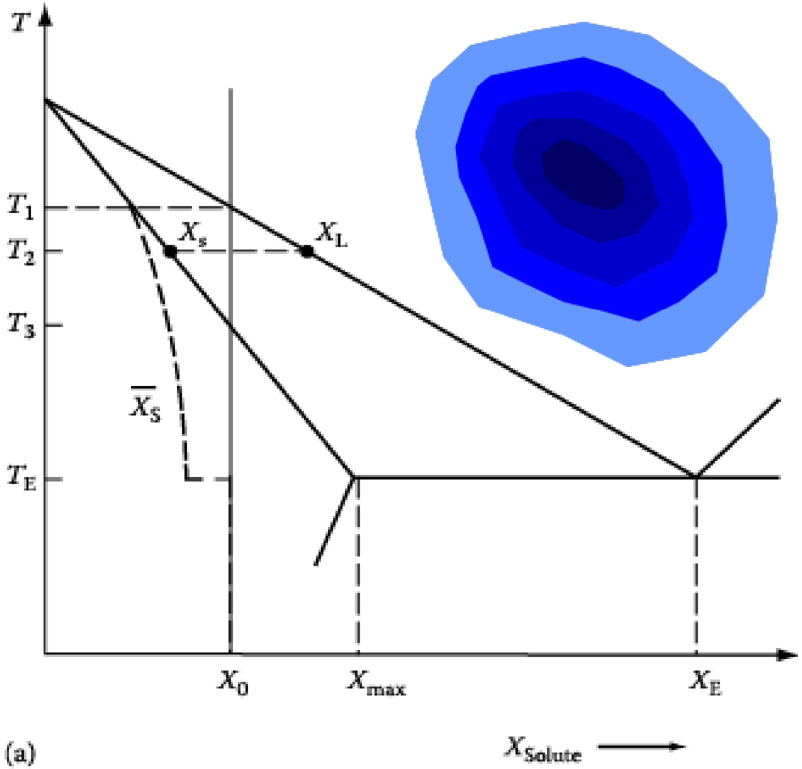
$$\ln\frac{X_L}{X_O} = (k-1)\ln(1-f_S)$$

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

$X_s = kX_L$

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

: non-equilibrium lever rule (Scheil equation)

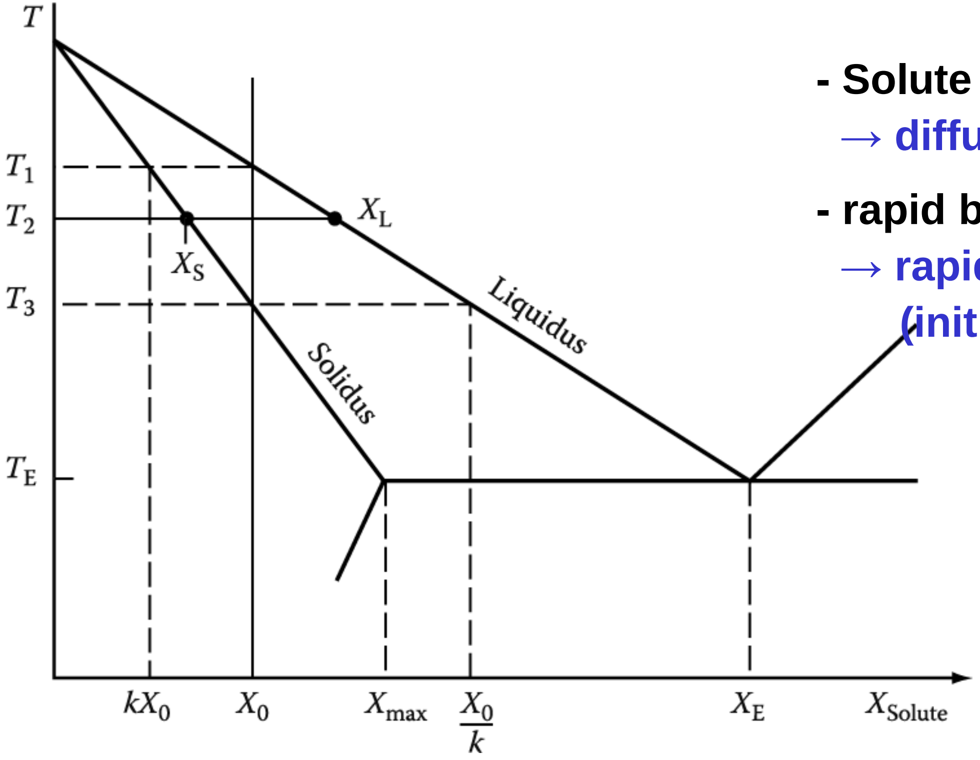


→ **quite generally applicable even for nonplanar solid/liquid interfaces provided here, the liquid composition is uniform and that the Gibbs-Thomson effect is negligible.**

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

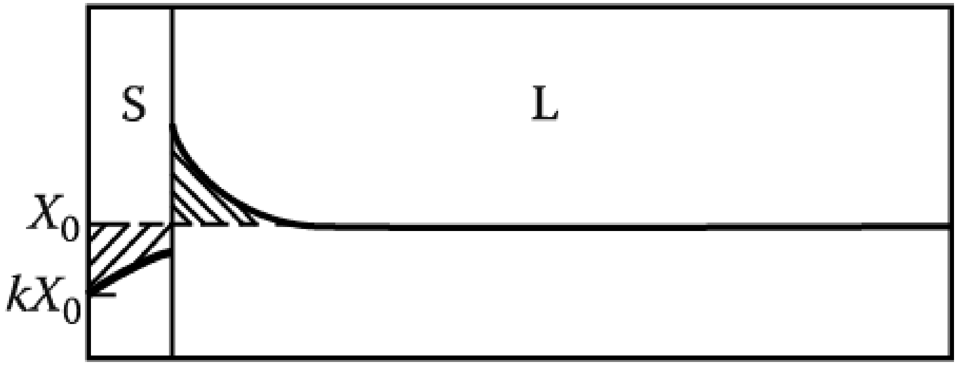
3) No Diffusion on Solid, Diffusional Mixing in the Liquid

: high cooling rate, no stirring→ diffusion



- **Solute rejected from solid**
  → diffuse into liquid with limitation
- **rapid build up solute in front 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



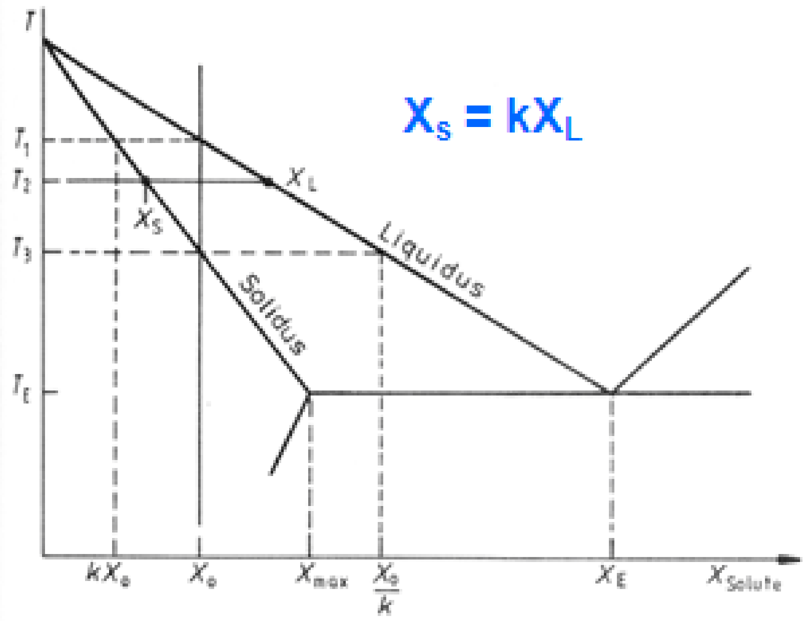
Composition profile at $T_2 < T_{S/L} < T_3$?

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

"Alloy solidification"

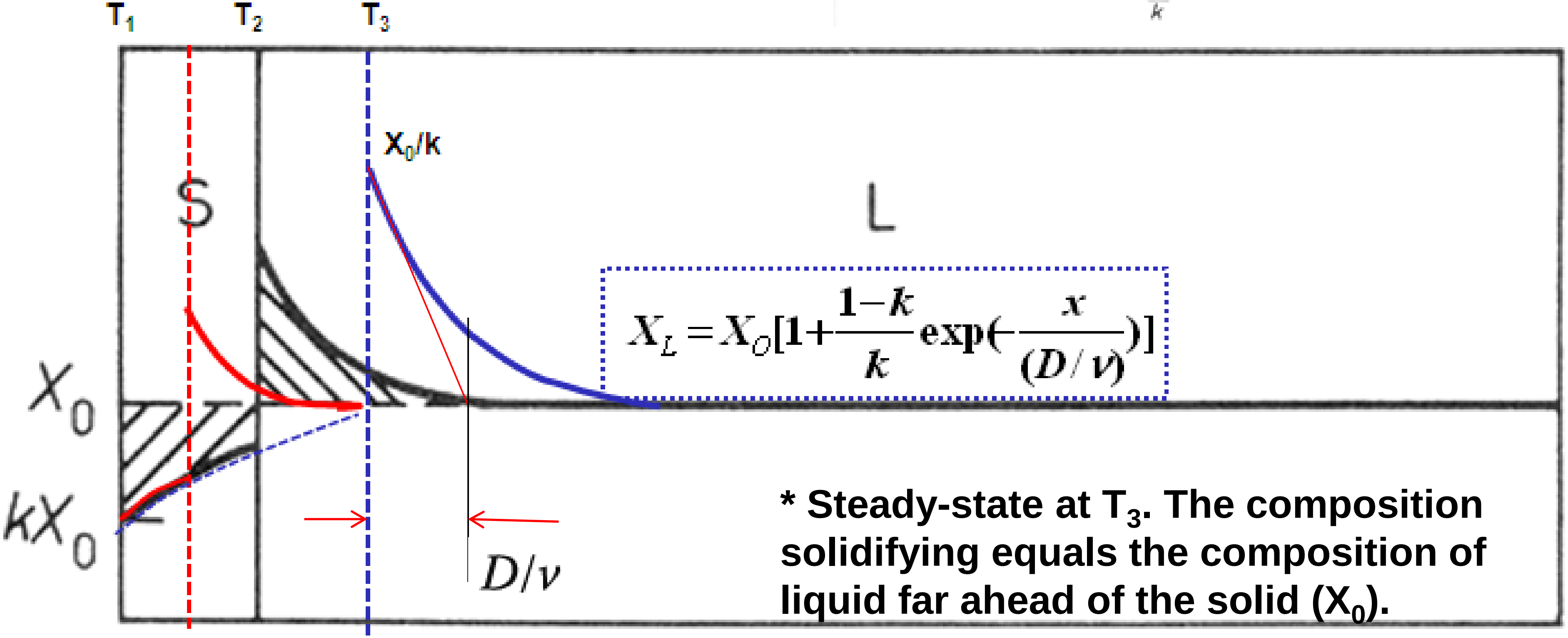
- Solidification of single-phase alloys

* No Diffusion on Solid,
Diffusional Mixing in the Liquid



$X_S = kX_L$

Interface temperature



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

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

No Diffusion on Solid, Diffusional Mixing in the Liquid

During steady-state growth,

(Interface →liquid: Diffusion rate)

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

(Solid→Interface: solute rejecting rate)

Set up the equation.

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

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

(Solidification rate of alloy: excess solute control)

$$\Updownarrow$$

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

(Solidification rate of pure metal: latent heat control, 10^4 times faster than that of alloy)

Solve this equation.

$$X_S = X_0 \quad for \quad all \quad x \geq 0$$

steady-state

$$\frac{dX_L}{X_L - X_0} = -\frac{v}{D}dx$$

$$\ln(X_L - X_0) = -\frac{v}{D}x + c$$

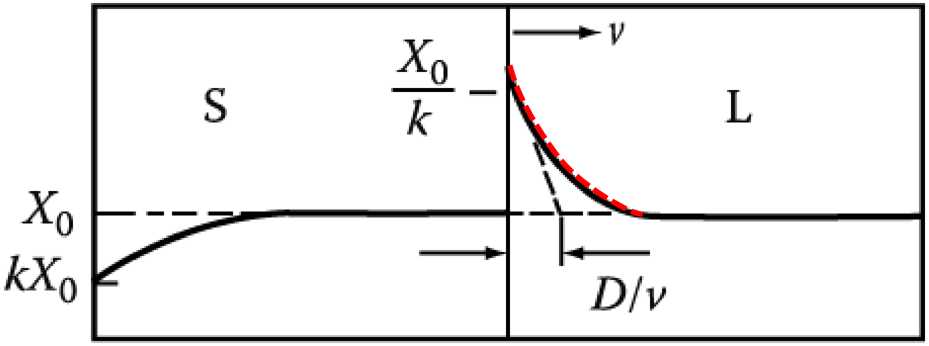
$$x = 0; X_L = X_0 / k$$

steady-state

$$c = \ln\left(\frac{X_0}{k} - X_0\right)$$

$$\ln \frac{X_L - X_0}{X_0(\frac{1}{k} - 1)} = -\frac{v}{D}x$$

$$X_L - X_0 = X_0(\frac{1-k}{k})e^{-\frac{vx}{D}}$$



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

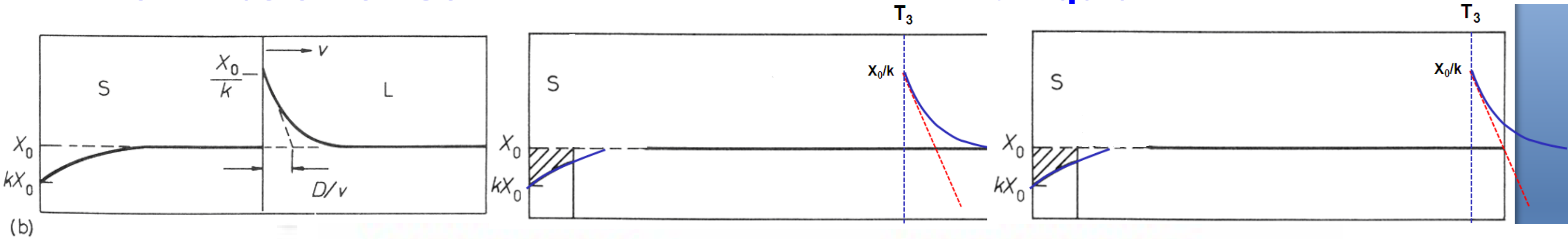
(X_L decreases exponentially from X_0/k at x=0, the interface, to X_0 at large distances from the interface. The concentration profile has a characteristic width of D/v.)

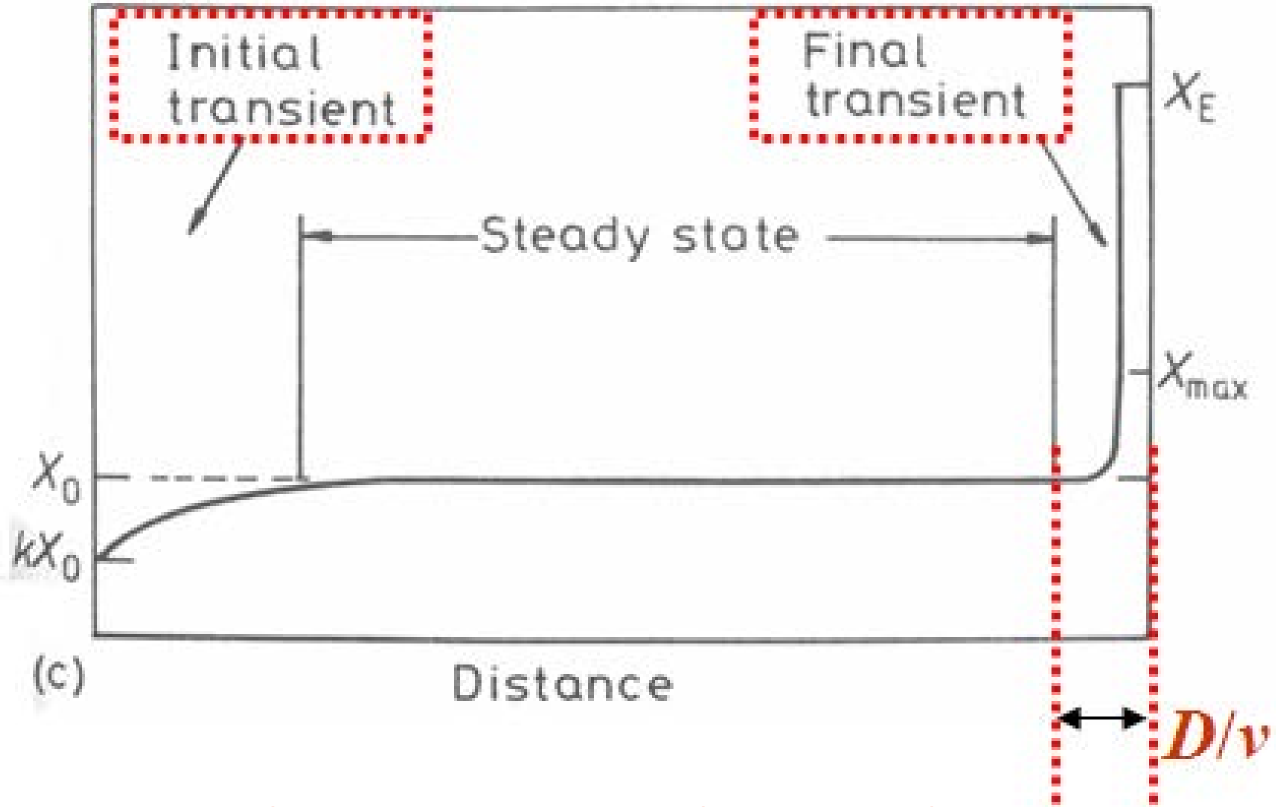
- The concentration gradient in liquid in contact with the solid :

$$J = -DX'_L = v(X_L - X_S) \qquad X'_L = -\frac{X_L - X_S}{D/v}$$

"Alloy solidification" - Solidification of single-phase alloys

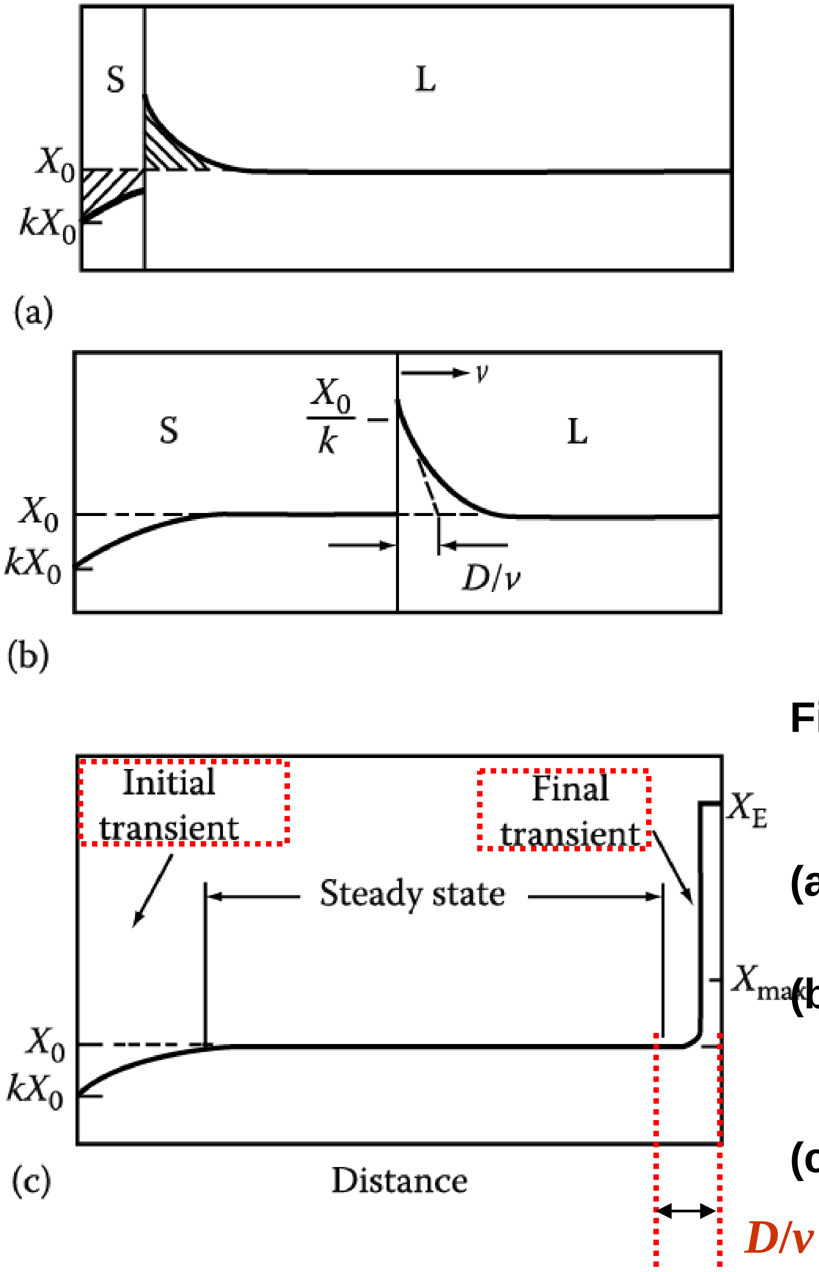
* No Diffusion on Solid, Diffusional Mixing in the Liquid





When the solid/liquid interface is within ~D/v of the end of the bar the bow-wave of solute is compressed into a very small volume and the interface composition rises rapidly leading to a final transient and eutectic formation.

No Diffusion on Solid, Diffusional Mixing in the Liquid



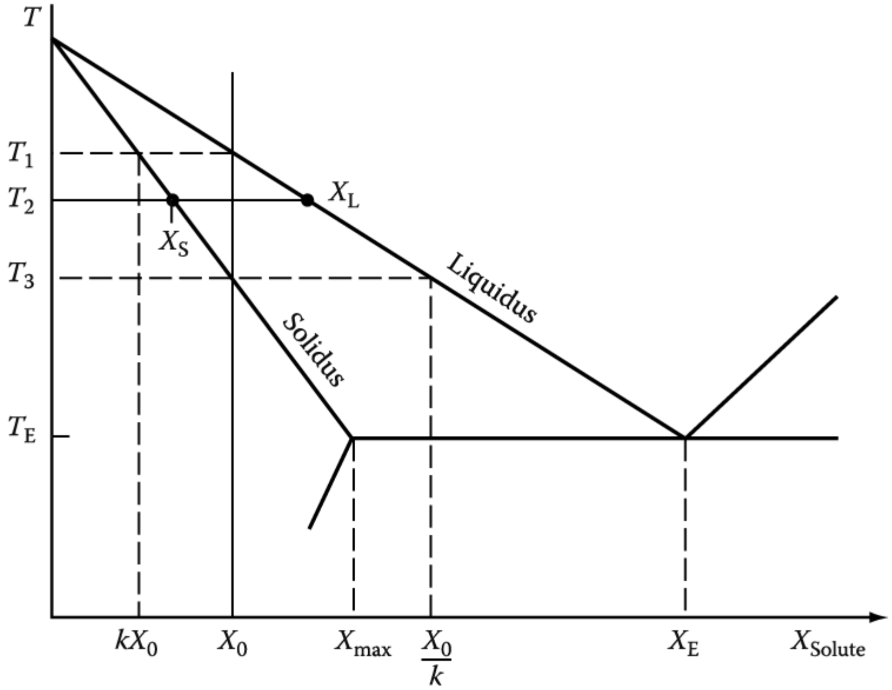


Fig. 4.22 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in solid and no stirring in the liquid.

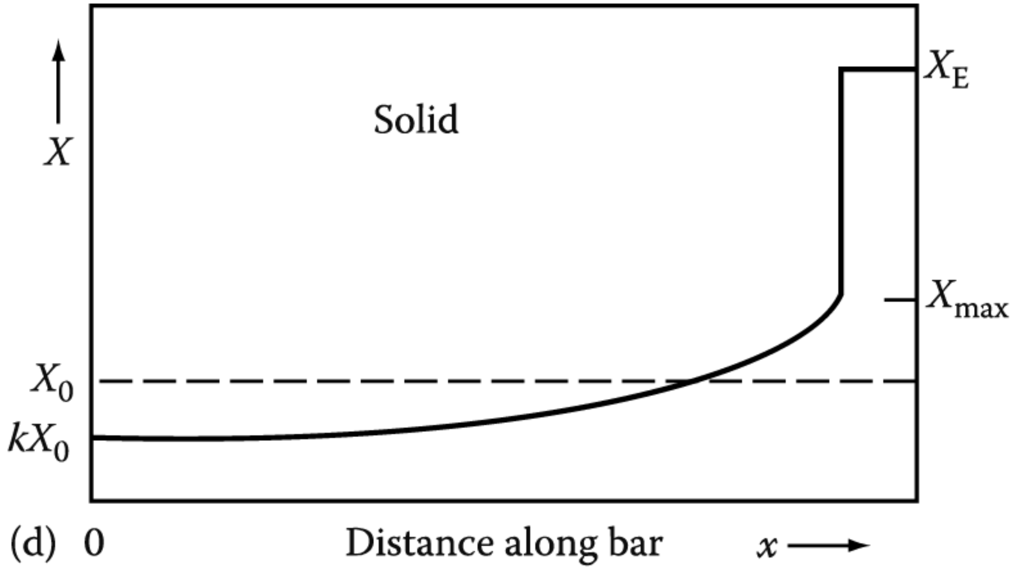
(a) Composition profile when S/L temperature is between T_2 and T_3 in Fig. 4.19.

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

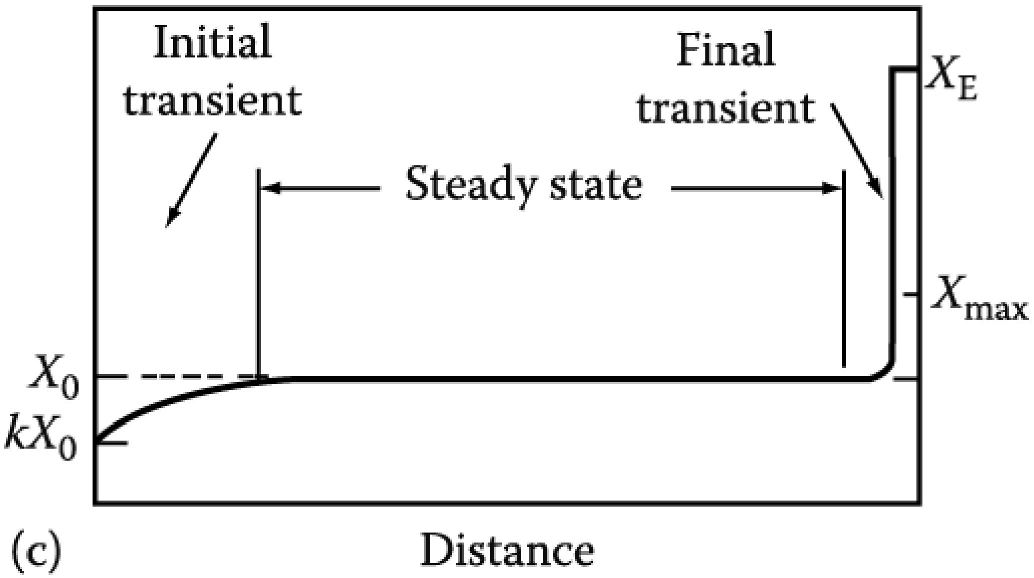
(c) Composition profile at T_E and below, showing the final transient.

Concentration profiles in practice

: exhibit features between two cases



(d)



(c)

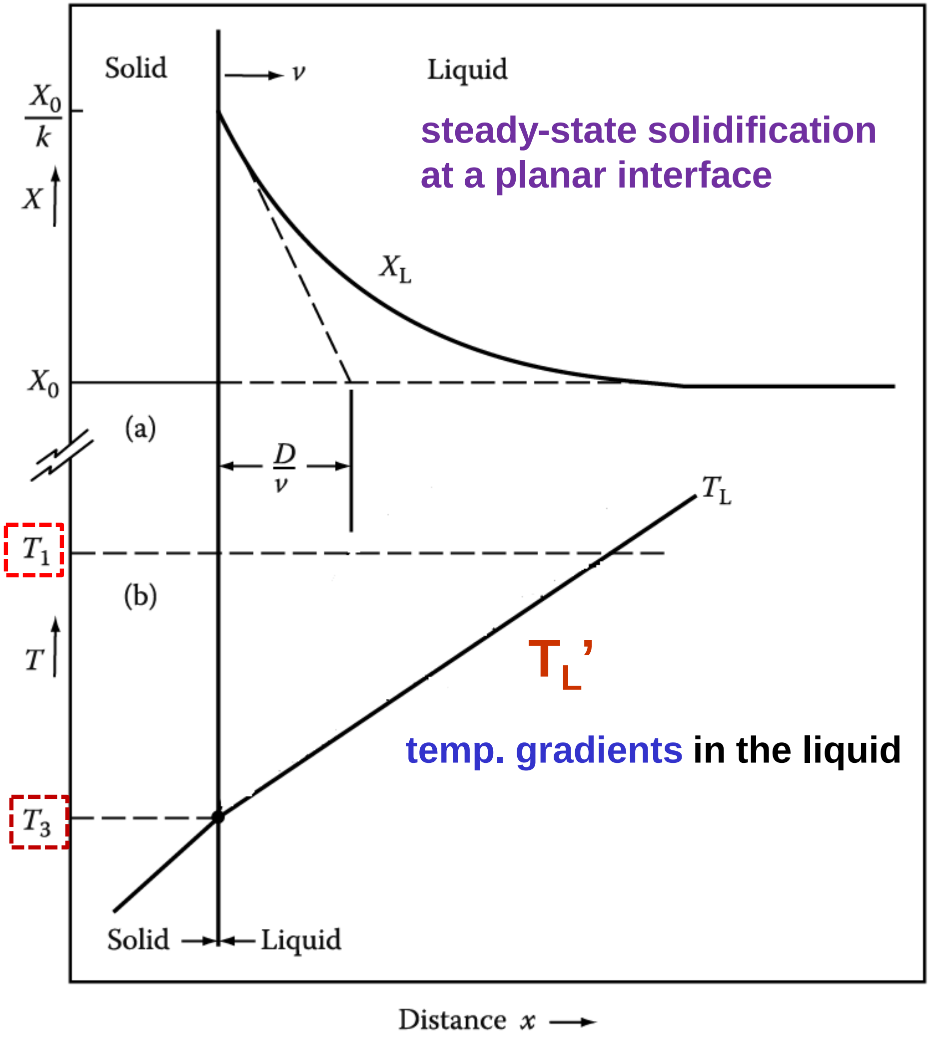
➡ **Zone Refining**

Q: Cellular and Dendritic Solidification by “constitutional supercooling” in alloy

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.

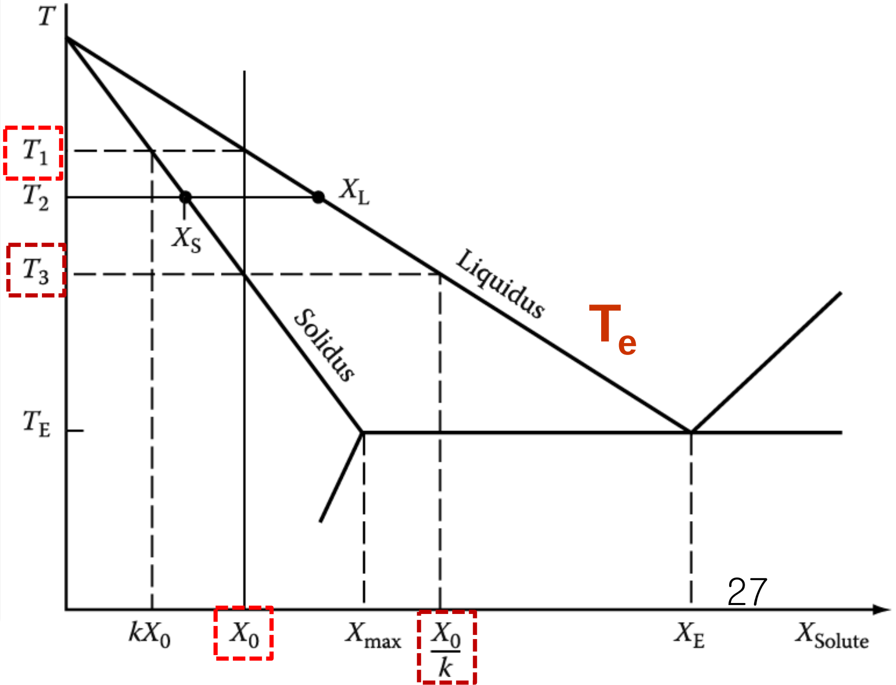


steady-state solidification at a planar interface

T_L'

temp. gradients in the liquid

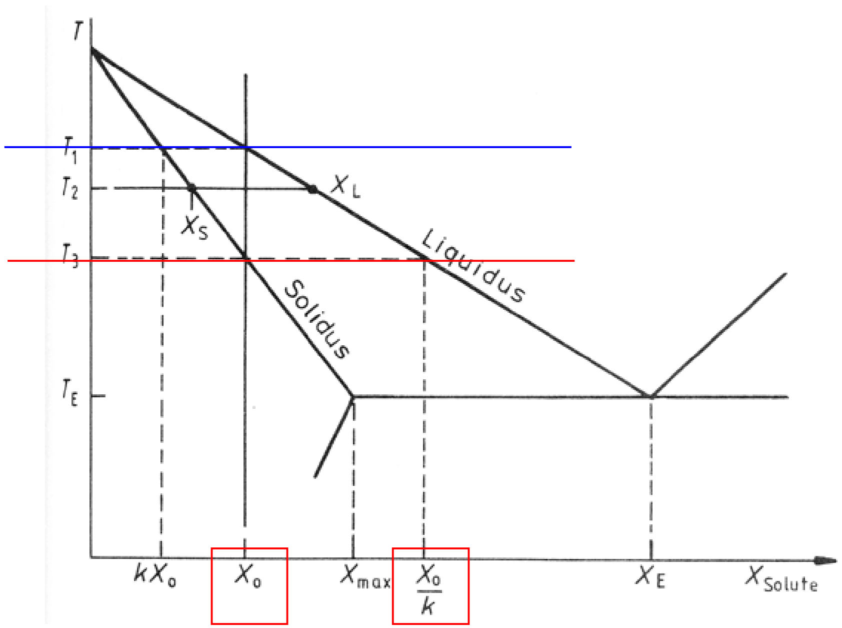
What would be T_e along the concentration profile ahead of the growth front during steady-state solidification?

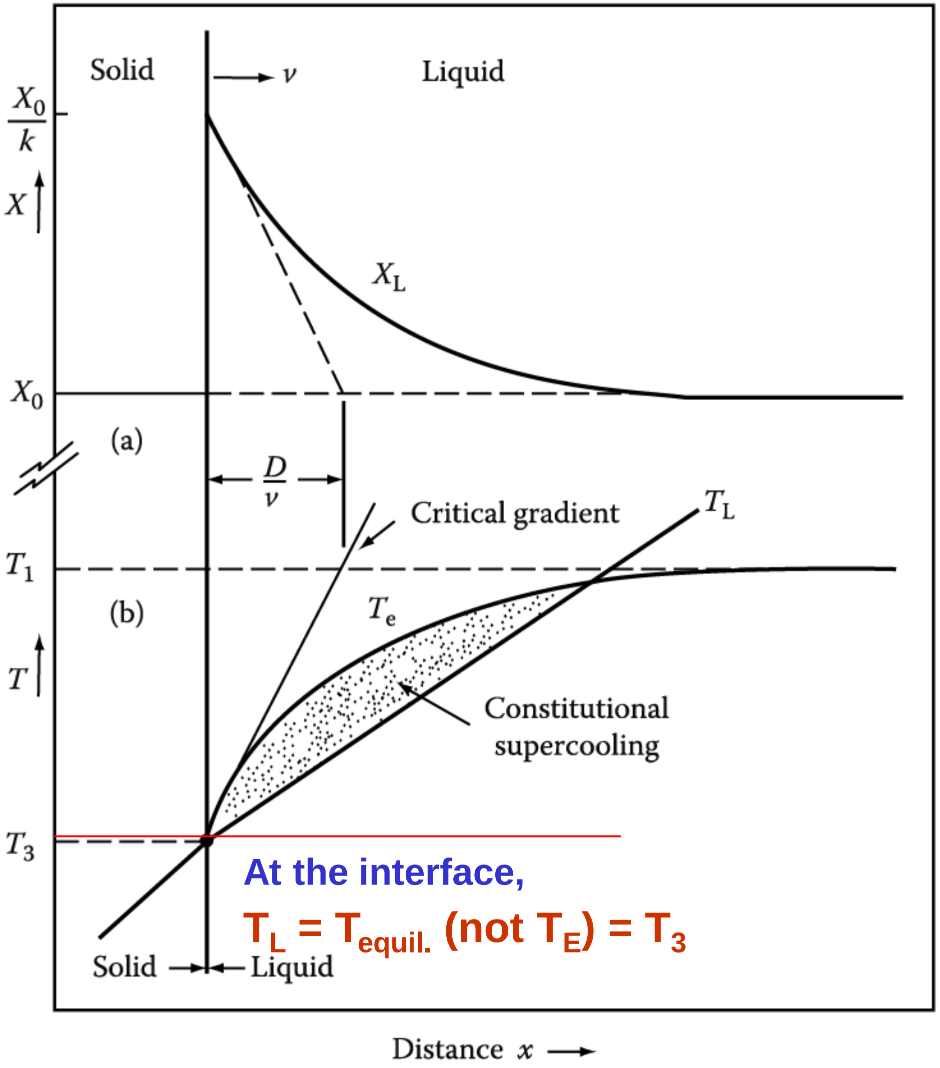


T_e

* Constitutional Supercooling

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





At the interface,

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

* Actual temperature gradient in Liquid

T_L'

* equilibrium solidification temp. change

$T_{equil.}$

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

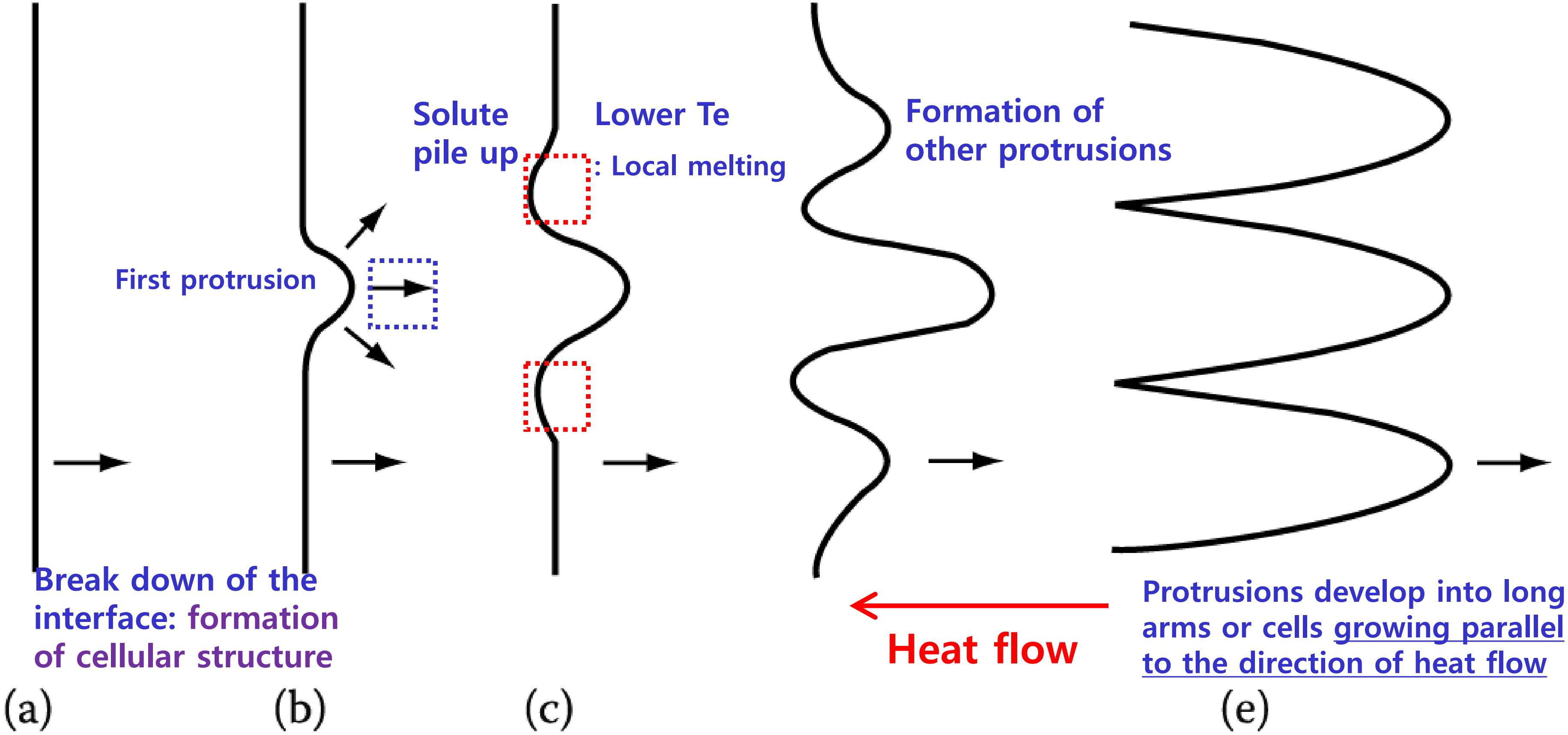
$T_L'/v < (T_1-T_3)/D$: Constitutional supercooling → **cellular/ dendritic growth**

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)



First protrusion

Solute pile up

Lower Te : Local melting

Formation of other protrusions

Break down of the interface: formation of cellular structure

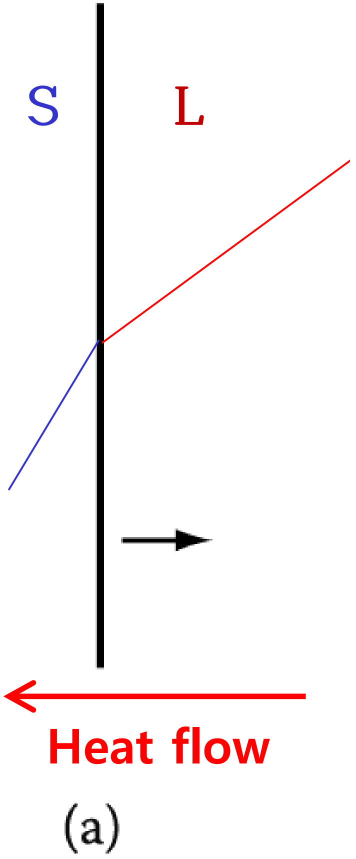
Heat flow

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

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)



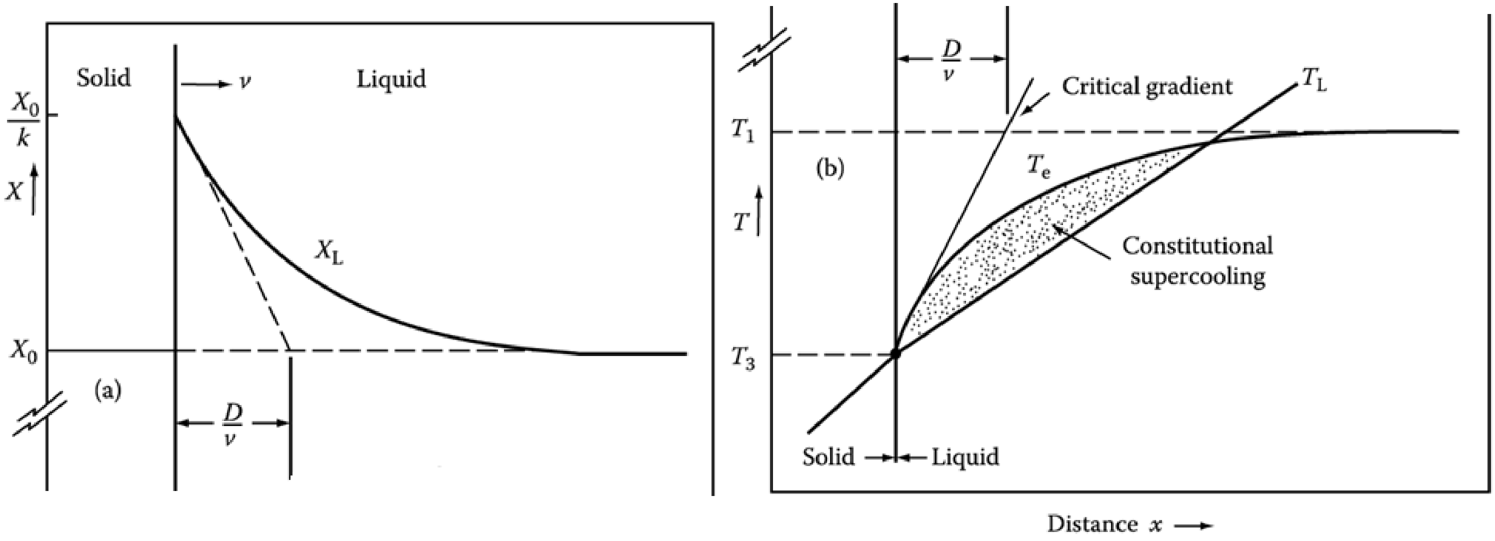
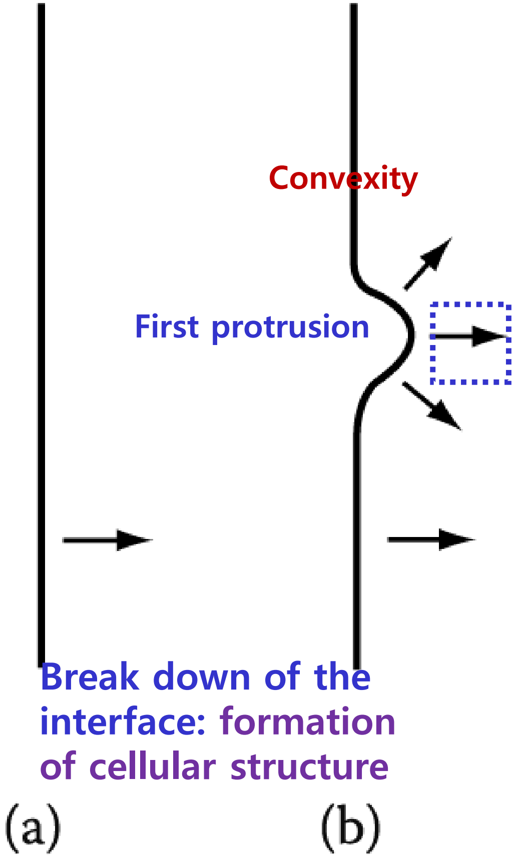


Fig. 5.30. Supercooling ahead of planar interface

<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

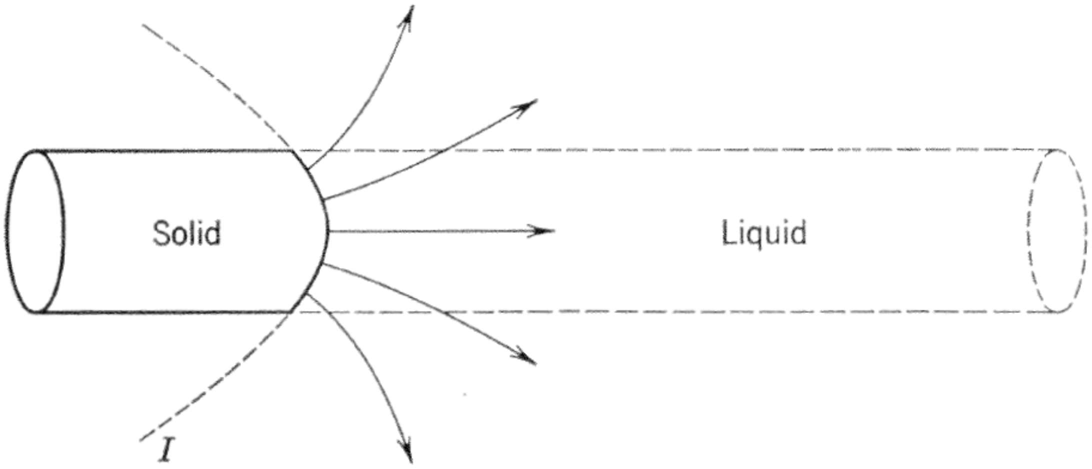
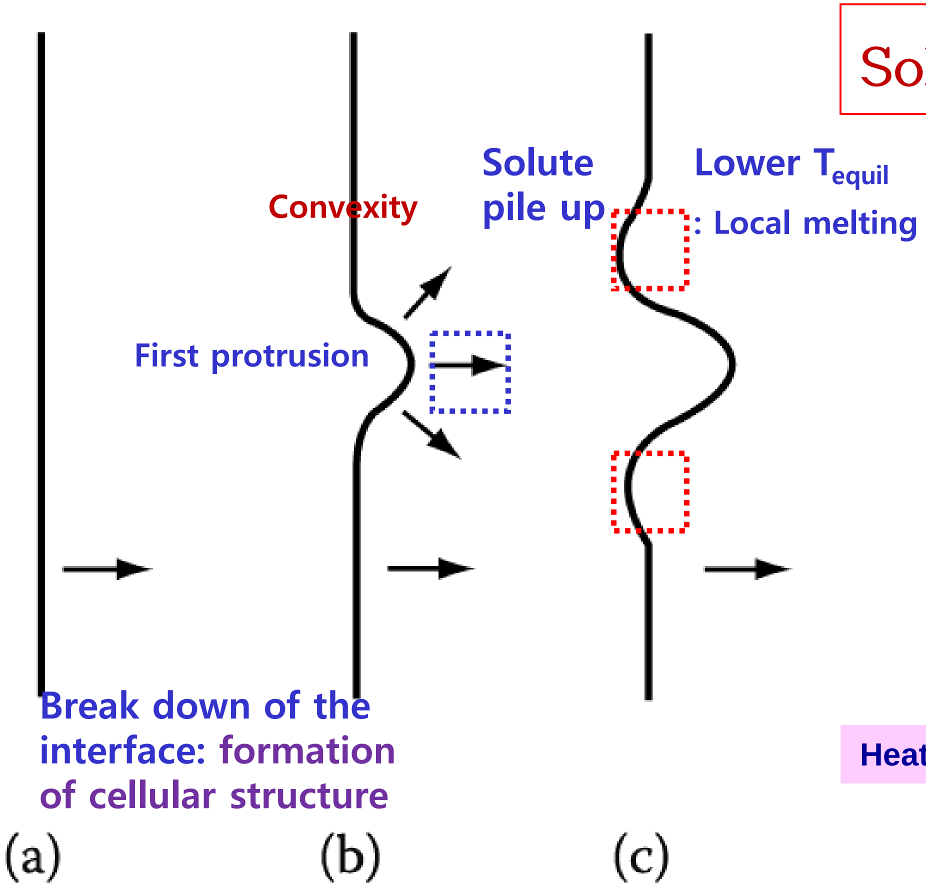


Fig. 5.14. Solute diffusion ahead of a convex interface

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

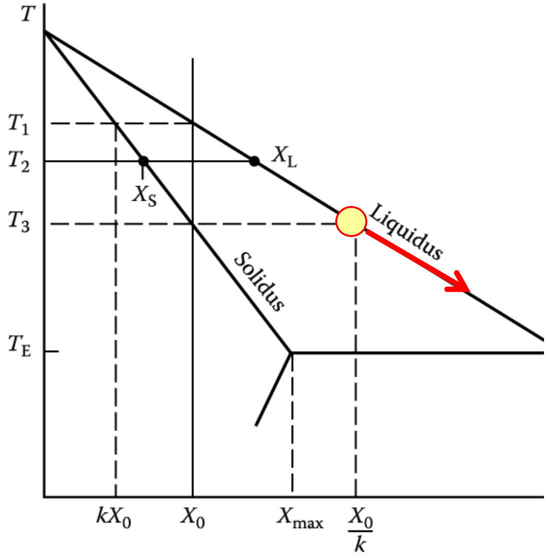
Cellular Solidification: formation by constitutional supercooling in "superheated liquid"

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



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

Solute pile up→ T_e ↓ → T_L' ↑ → v ↓



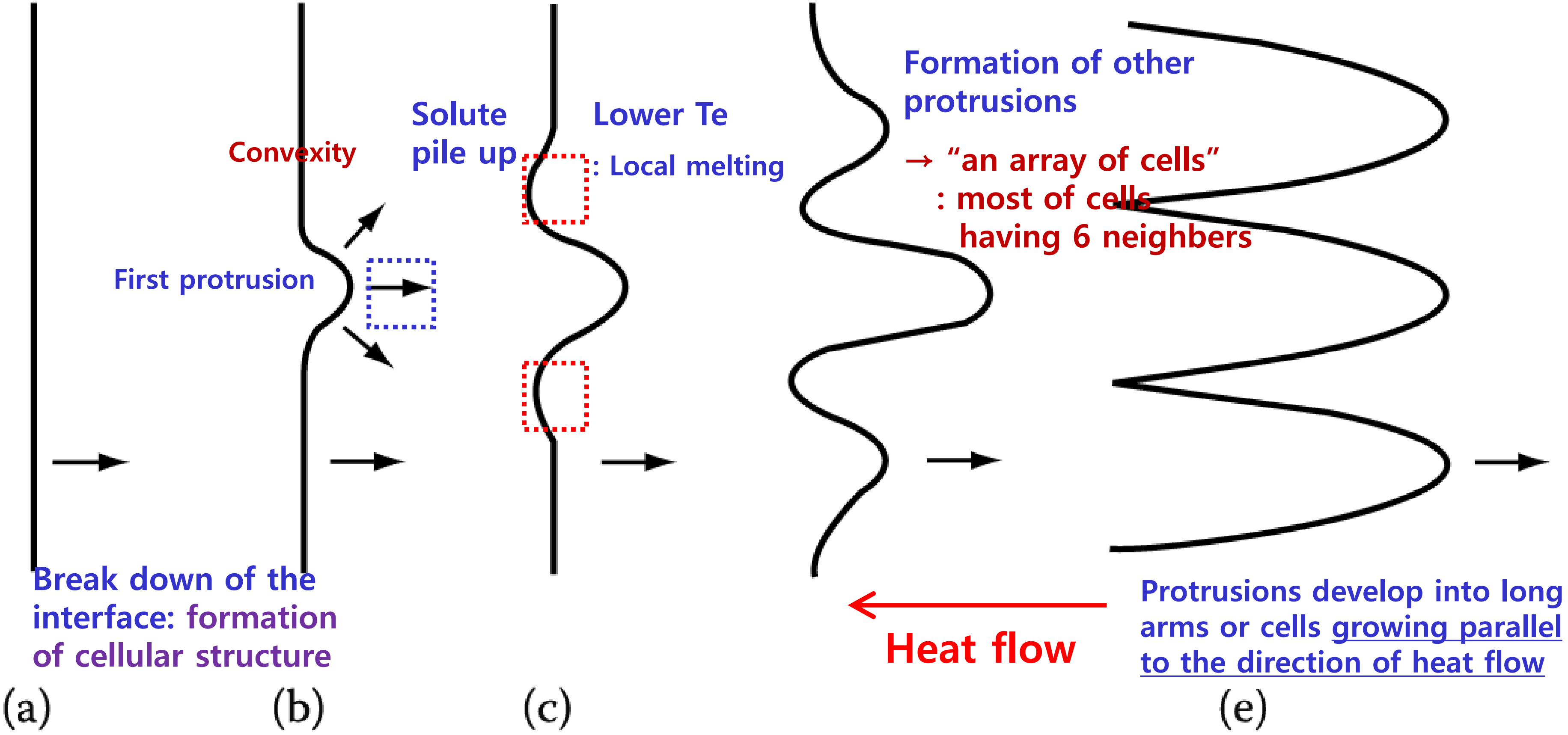
Heat Balance Equation

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

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

Solute pile up

Lower Te

: Local melting

First protrusion

Formation of other protrusions

→ "an array of cells"
: most of cells
having 6 neighbors

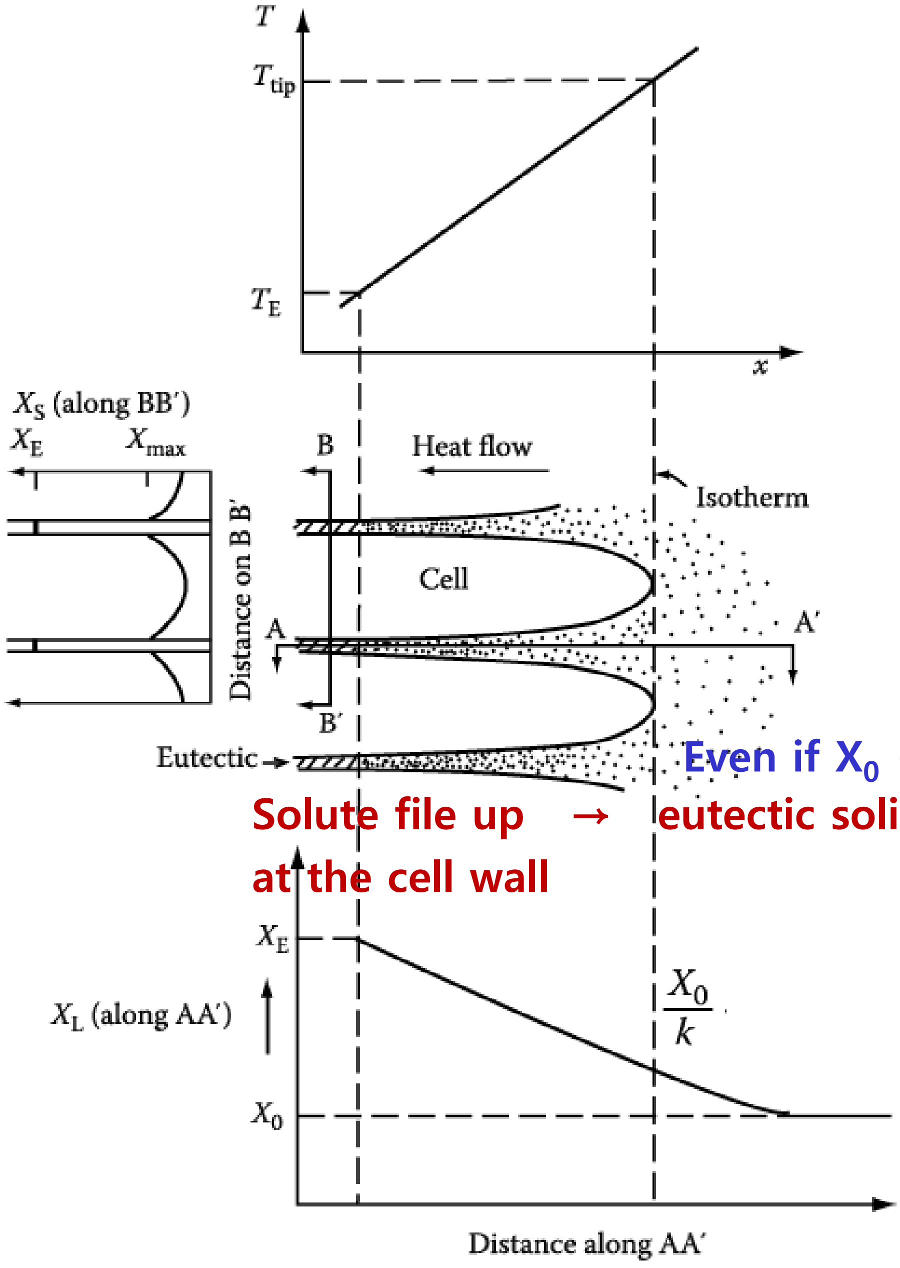
Break down of the interface: formation of cellular structure

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 2^{nd} phases at the cell wall

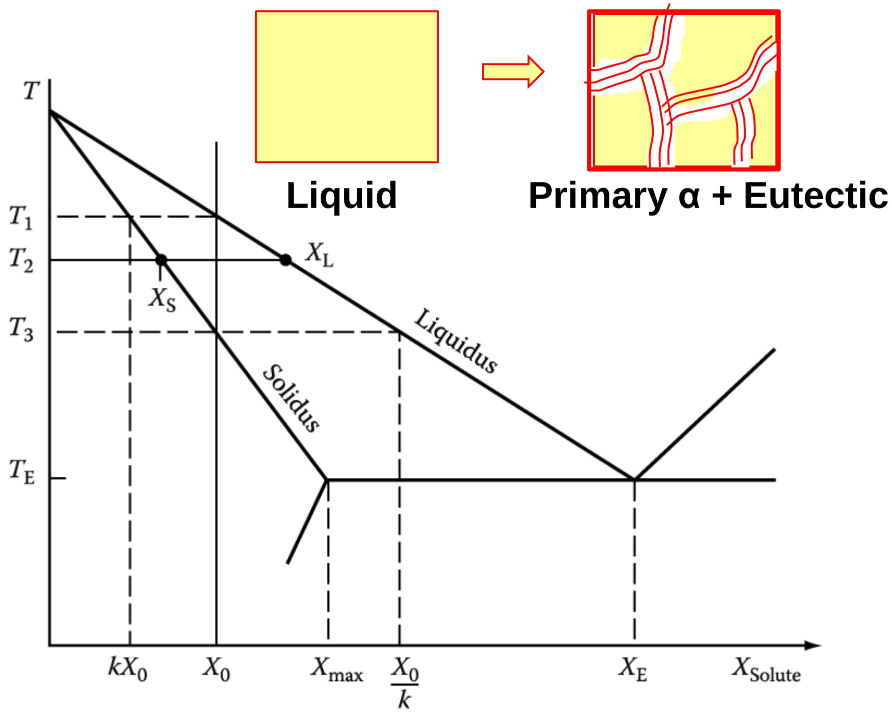
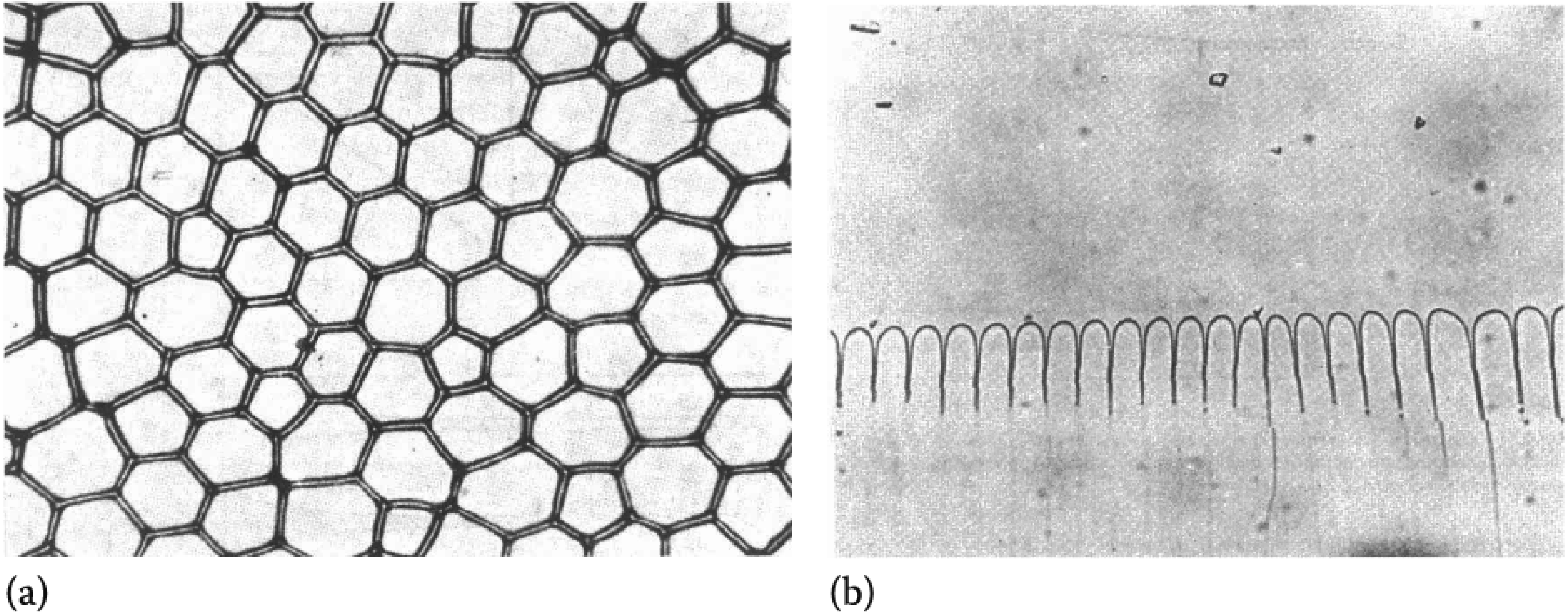


Fig. 4.25 **Temperature and solute distributions associated with cellular solidification. Note that solute enrichment in the liquid between the cells, and coring in the cells with eutectic in the cell walls.**



* 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)

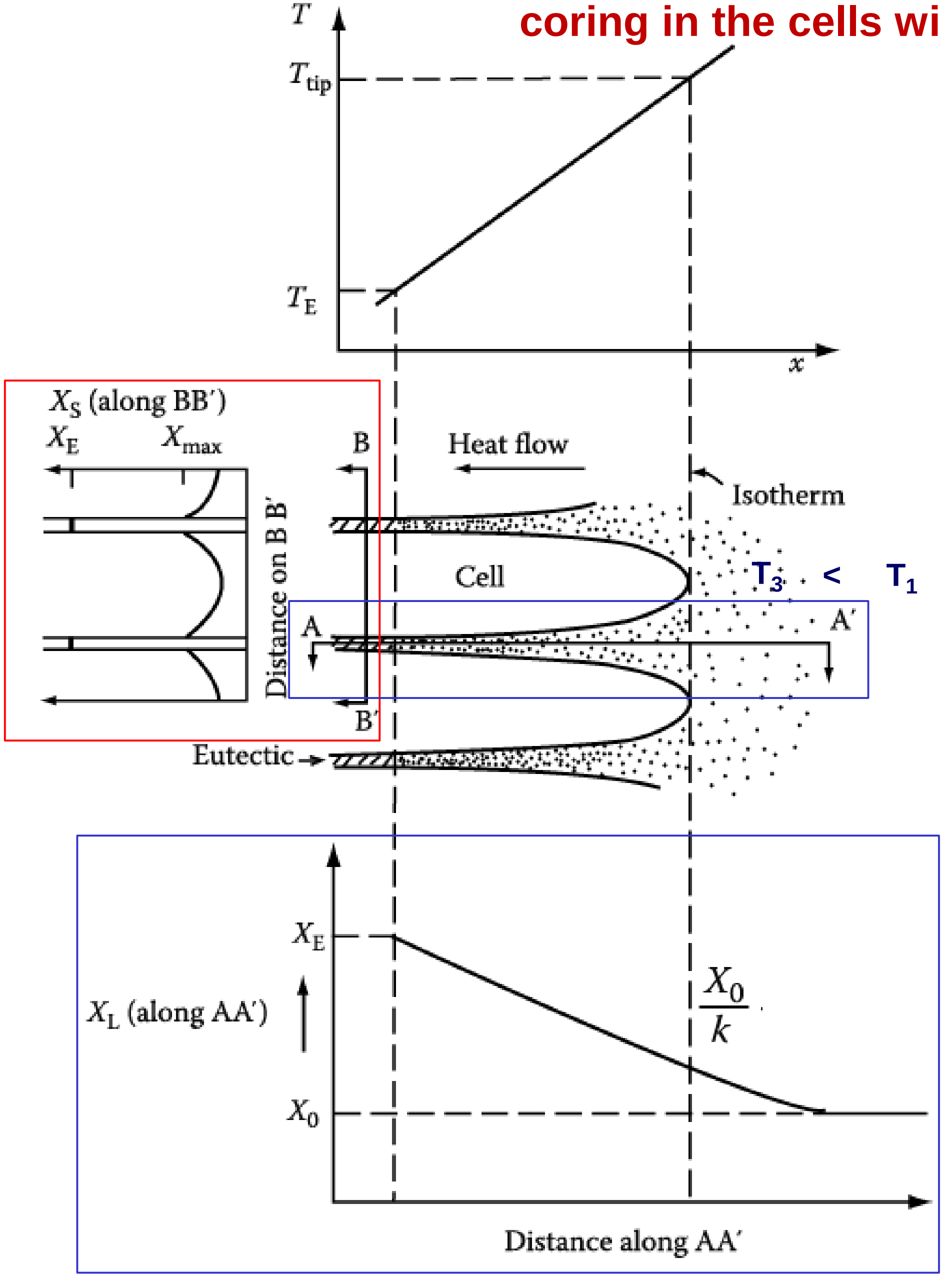
(after J.W. Rutter in Liquid Metals and Solidification, American Society for Metals, 1958, p. 243).

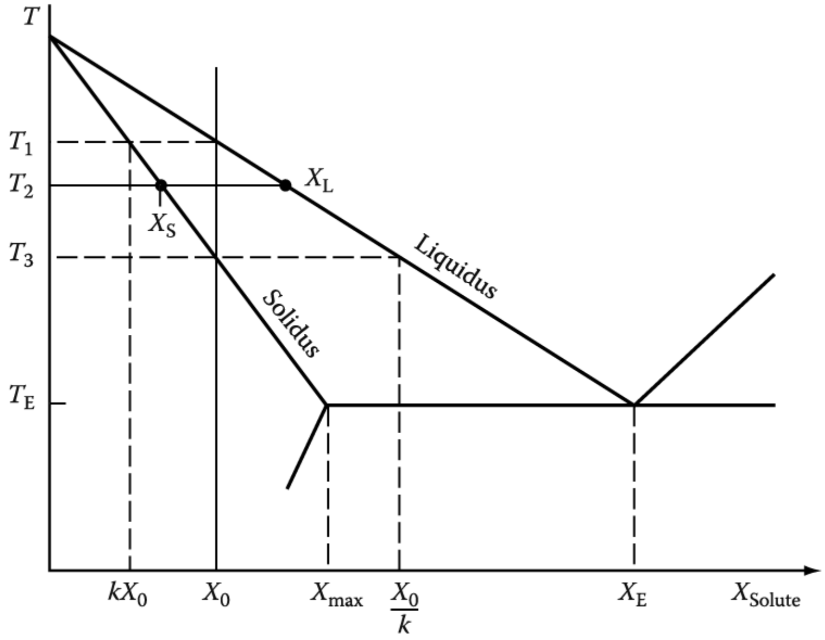
(b) Longitudinal view of cells in carbon tetrabromide (x 100)

(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**.



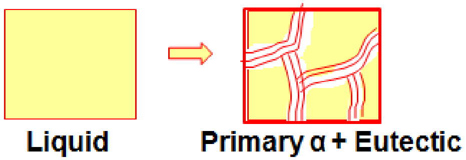


2) **Tips of the cells grow into the hottest liquid and therefore contain the least solute.**

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.

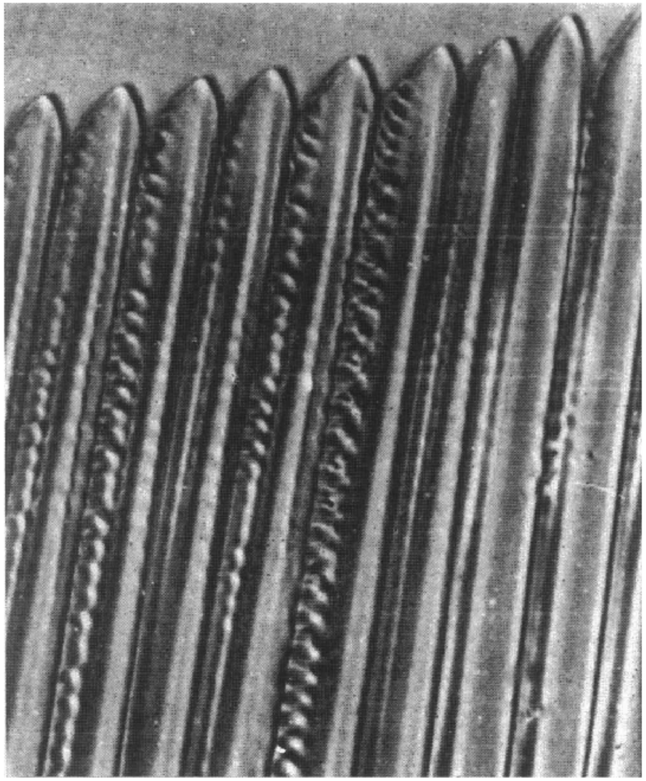


Fig. 4.27 Cellular dendrites in carbon tetrabromide.

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

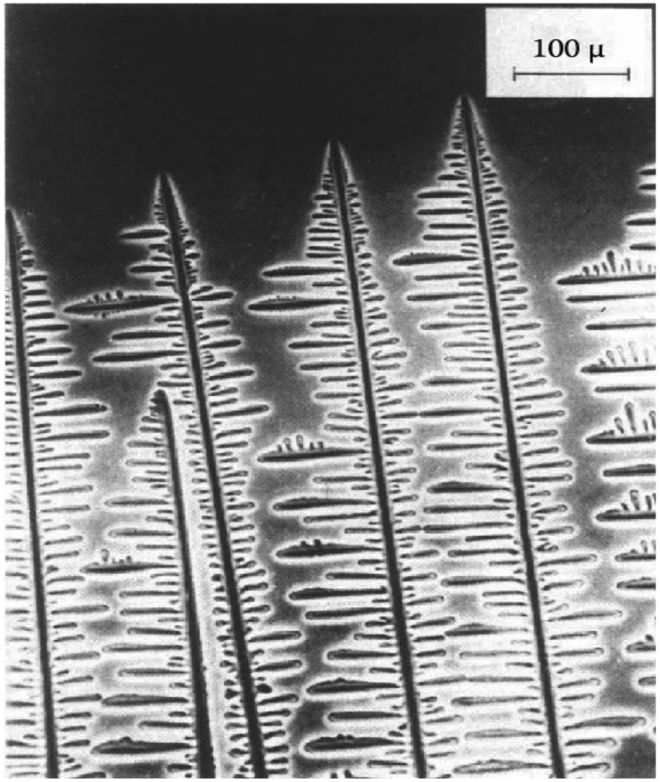


Fig. 4.28 Columnar dendrites in a transparent organic alloy.

(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

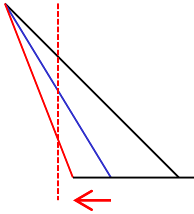
$T_L'/v > (T_1-T_3)/D$ (T_1-T_3 : Equilibrium freezing range of alloy)

⟶ 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/ 가지들의 square array/ Dendrite 성장방향쪽으로 성장방향 변화

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