2017 Fall

"Phase Transformation *in* Materials"

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Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for today's class

Solidification: Liquid → Solid

* **Nucleation in Pure Metals**

- **Homogeneous Nucleation**

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

r* & ΔG* ↓ as ΔT ↑

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

- **Heterogeneous Nucleation**

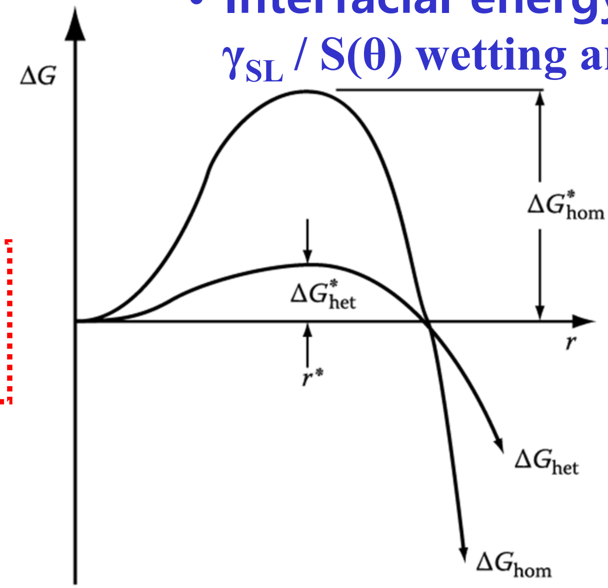
$$\Delta G^*_{het} = S(\theta)\Delta G^*_{hom}$$

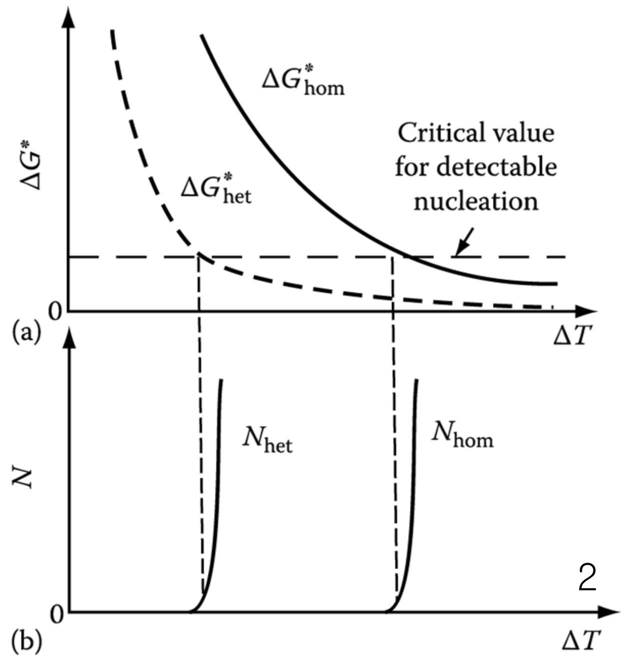
$$\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)$$

- **Nucleation of melting**

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

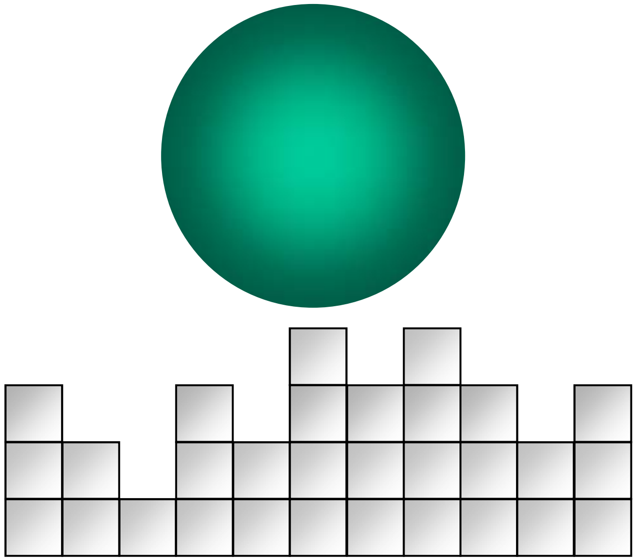
- **Undercooling ΔT**
- **Interfacial energy**
  γ_{SL} / S(θ) wetting angle





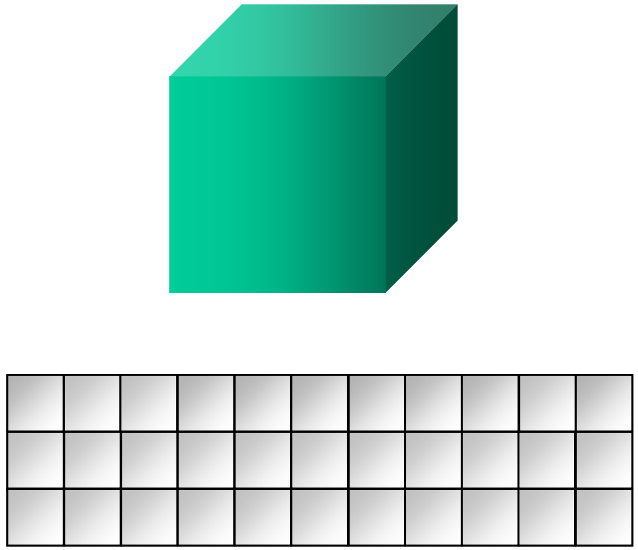
* Growth

Equilibrium Shape and Interface Structure on an Atomic Scale



atomically-disordered

Ex) metallic systems



atomically-flat

nonmetals

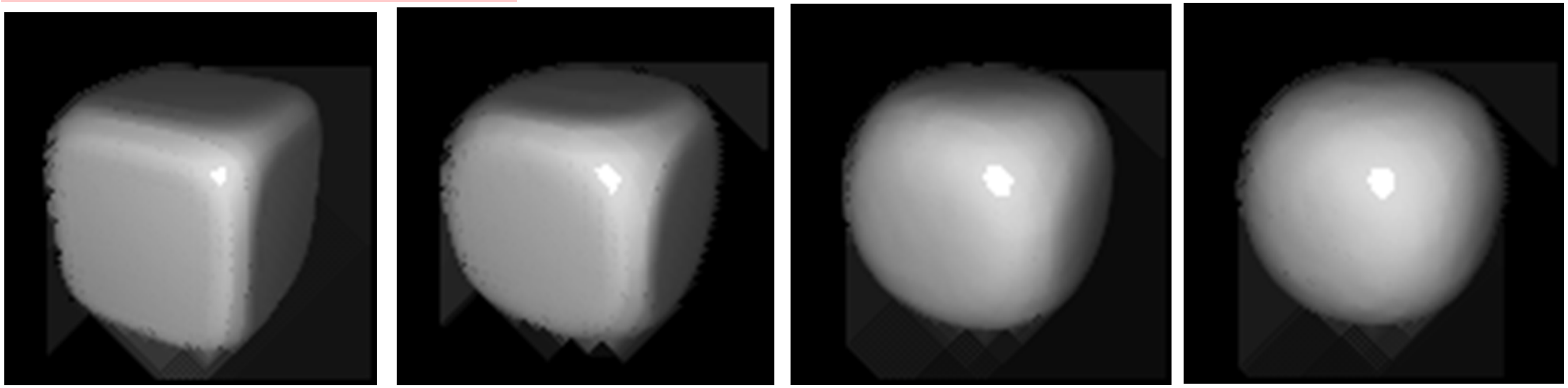
Apply thermodynamics to this fact and derive more information.

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

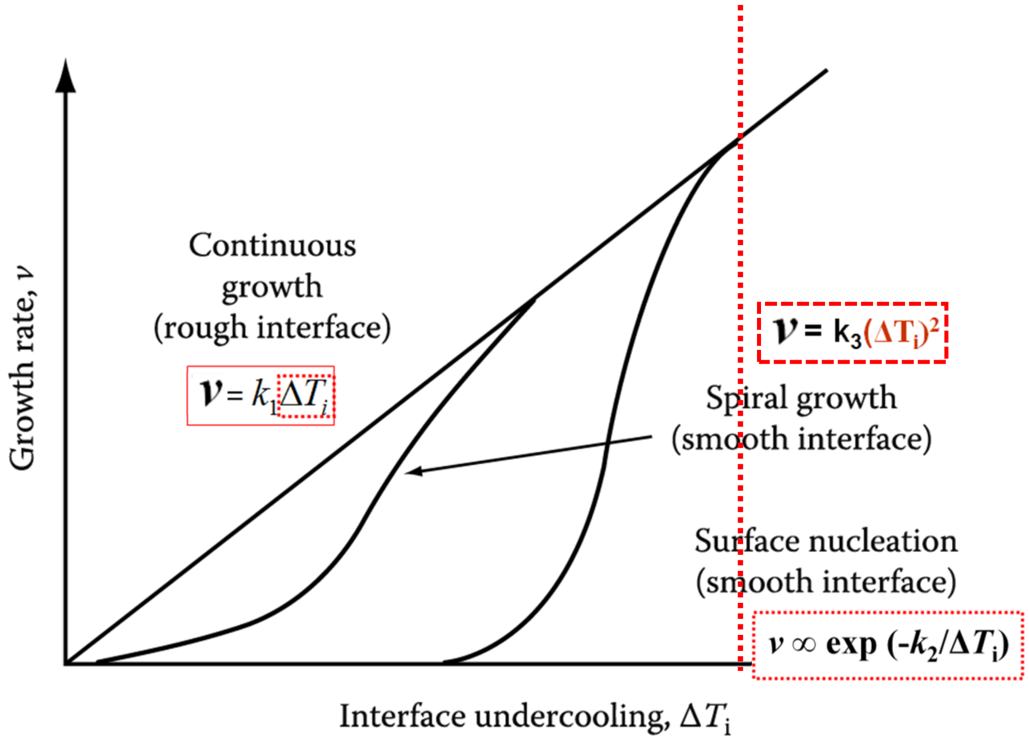
Smooth interface - Growth by Screw Dislocation
Growth by 2-D Nucleation

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

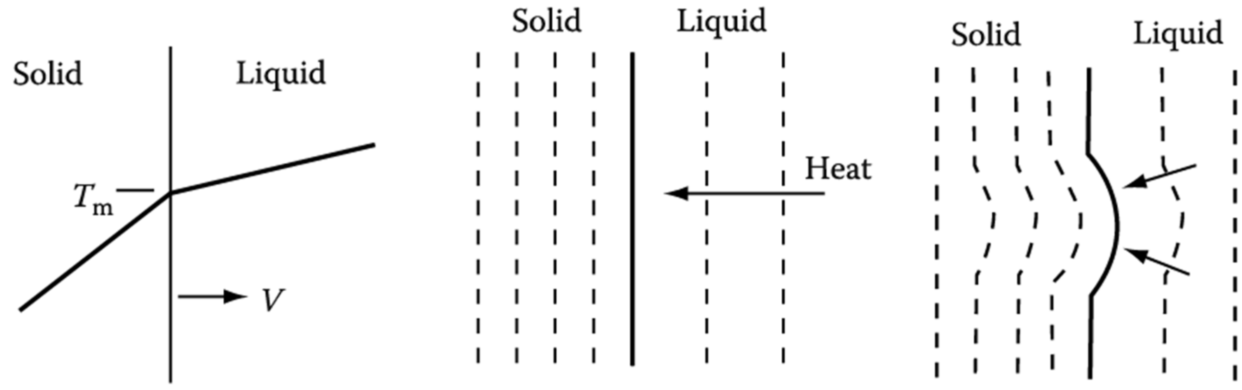


4.2.3 Heat Flow and Interface Stability - Planar interface

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. $T_L{}'\uparrow$ & $T_S{}'\downarrow$

More heat to the protrusion → melt away

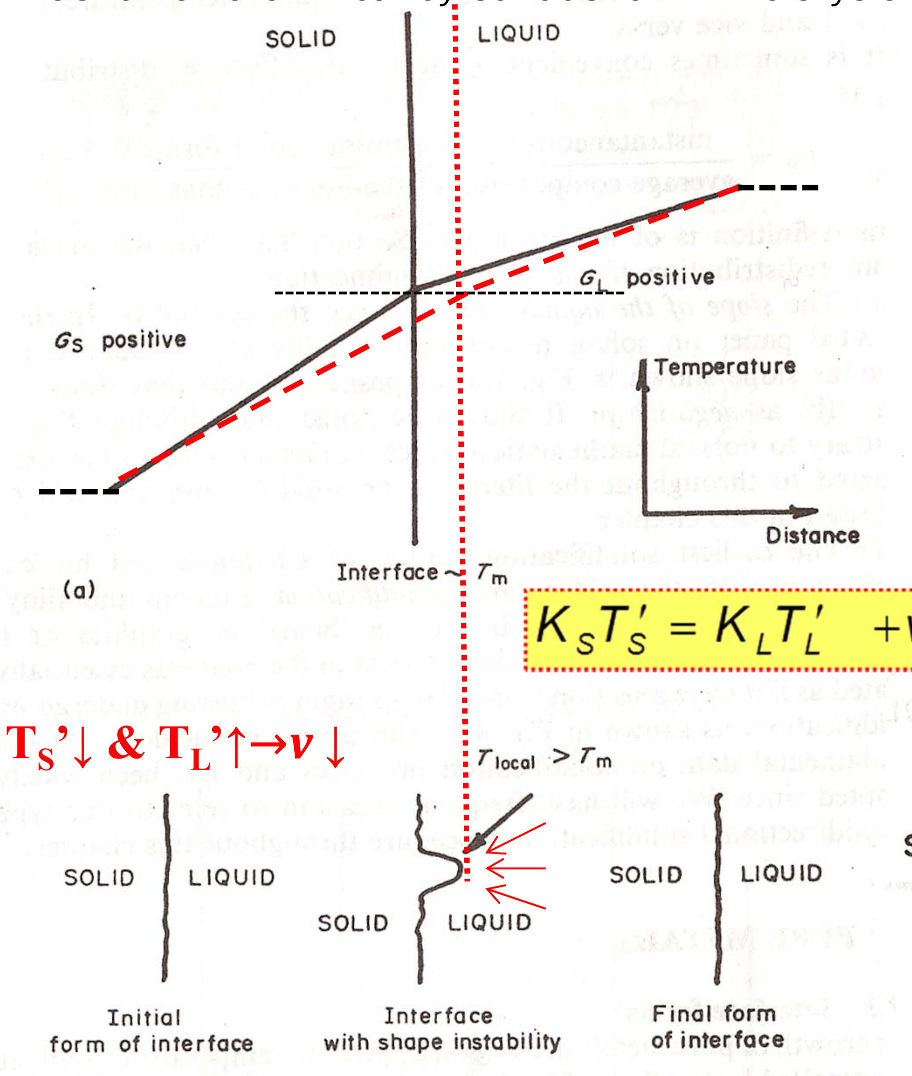
v of protrusion ↓ to match other v in planar region

mould walls

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

1) Superheated liquid

: Extraction of latent heat by conduction in the crystal

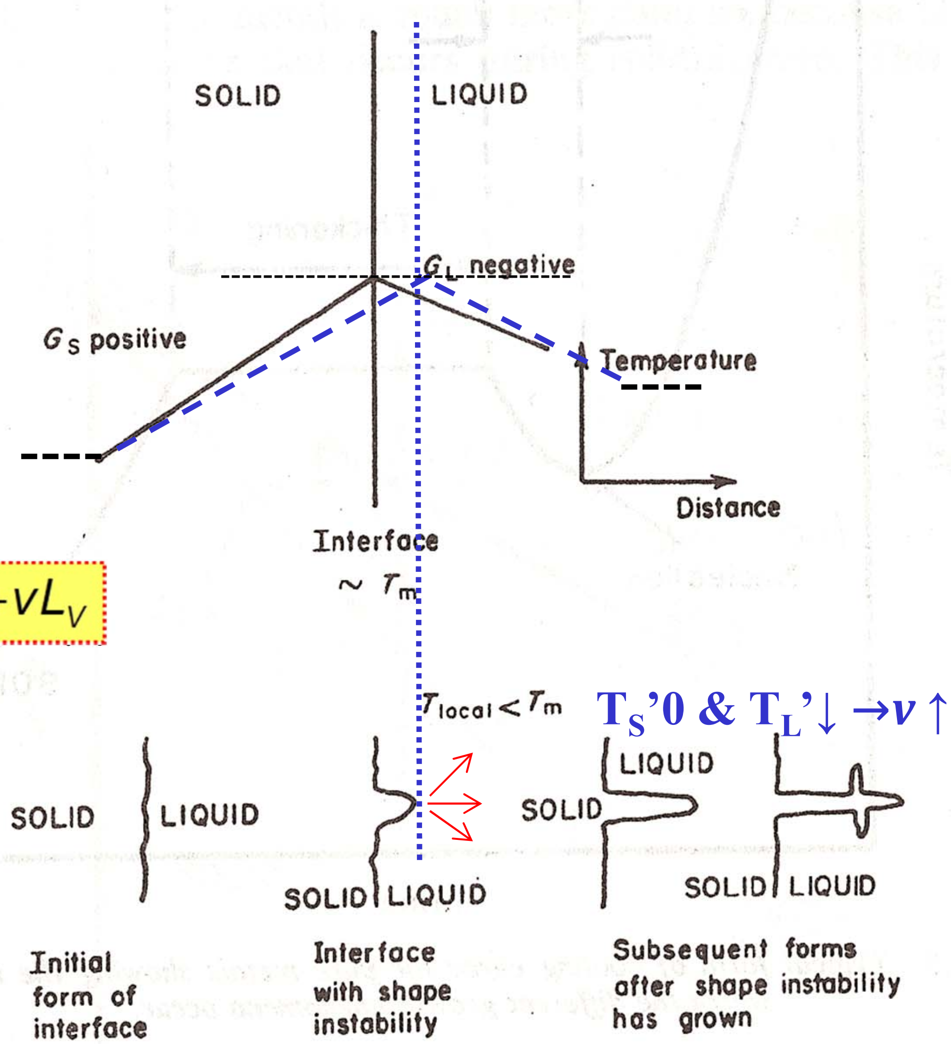


$T_S{}'\downarrow$ & $T_L{}'\uparrow \rightarrow v\downarrow$

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

2) Supercooled liquid

: conduction of latent heat into the liquid



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

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**

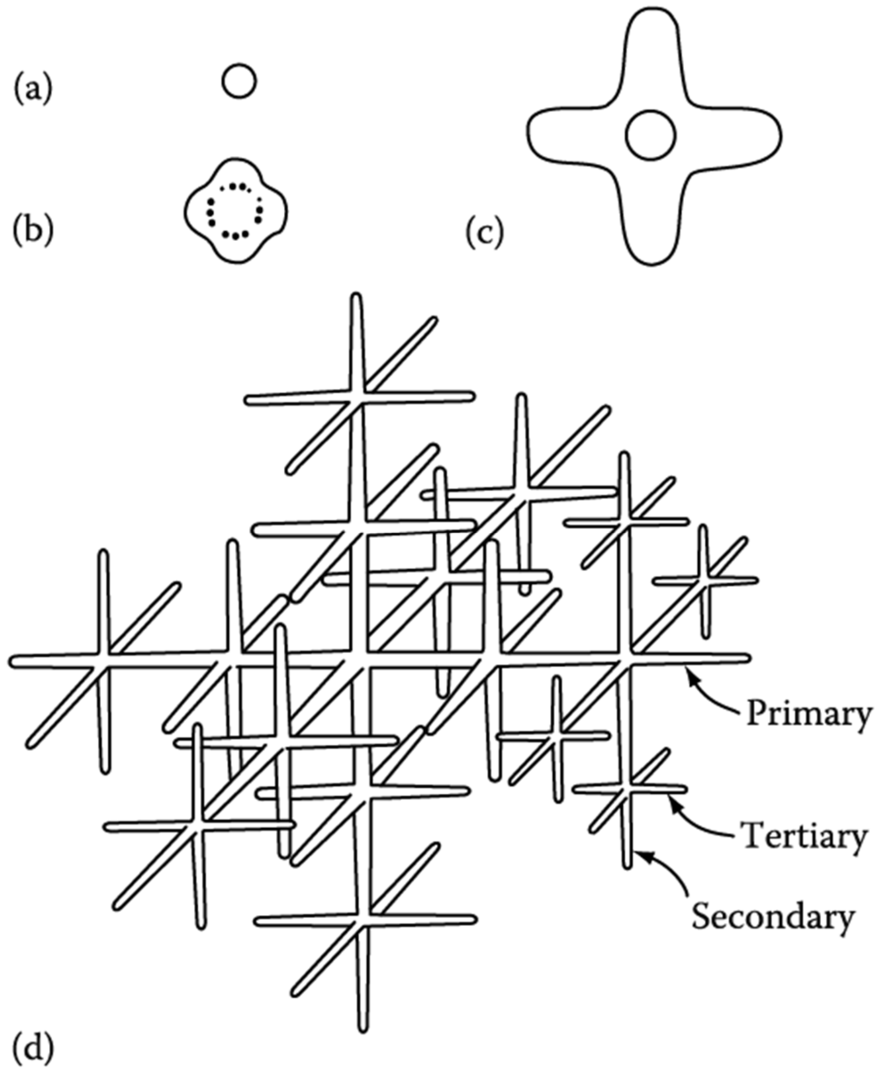


Fig. 4.17 The development of thermal dendrites: (a) a spherical nucleus; (b) the interface becomes unstable; (c) primary arms develop in crystallographic directions (<100> in cubic crystals); (d) secondary and tertiary arms develop

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

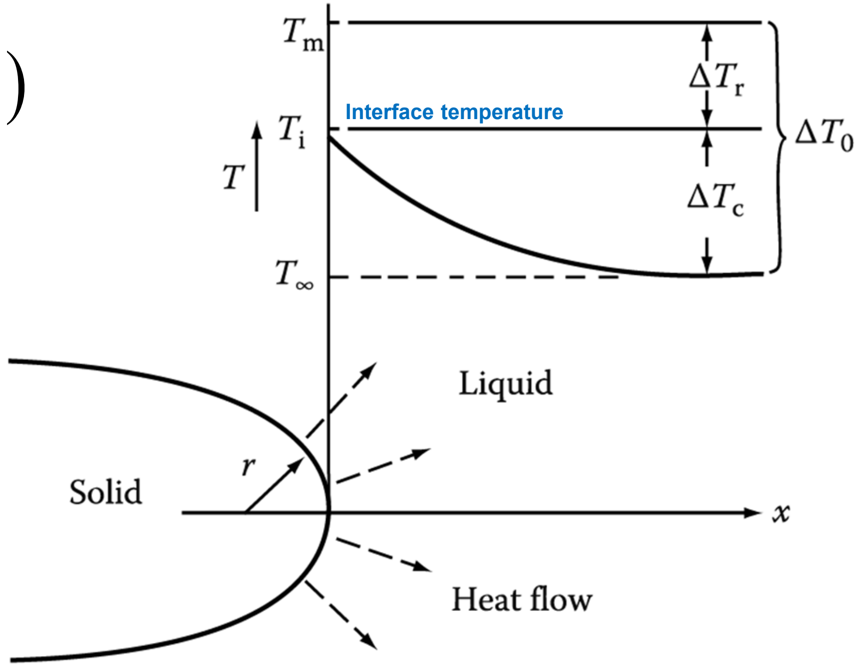
From $K_S T_S' = K_L T_L' + v L_V$

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

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

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

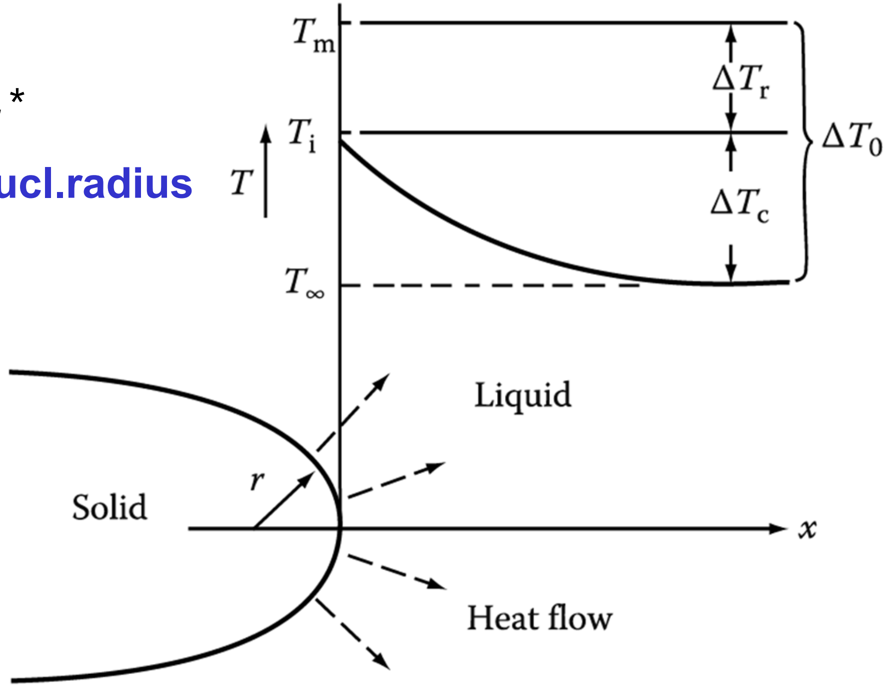
Minimum possible radius (r)?

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

The crit.nucl.radius

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

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



Express ΔT_r by r, r^* and ΔT_o.

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

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

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

Maximum velocity?

$$\rightarrow \; r = 2r^*$$

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

Q: Alloy solidification?

1. Solidification of single-phase alloys

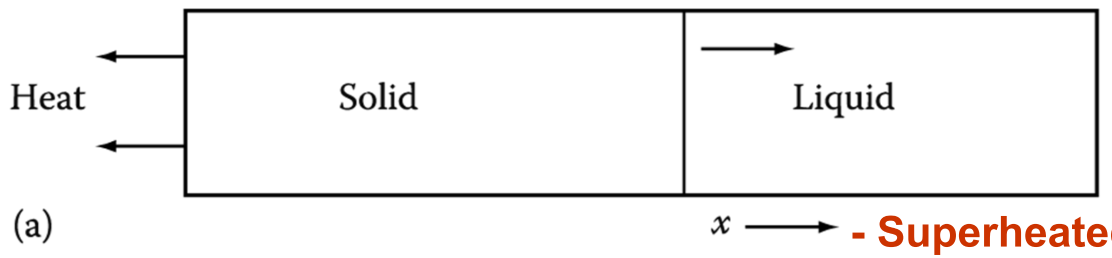
- **Three limiting cases**

  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

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

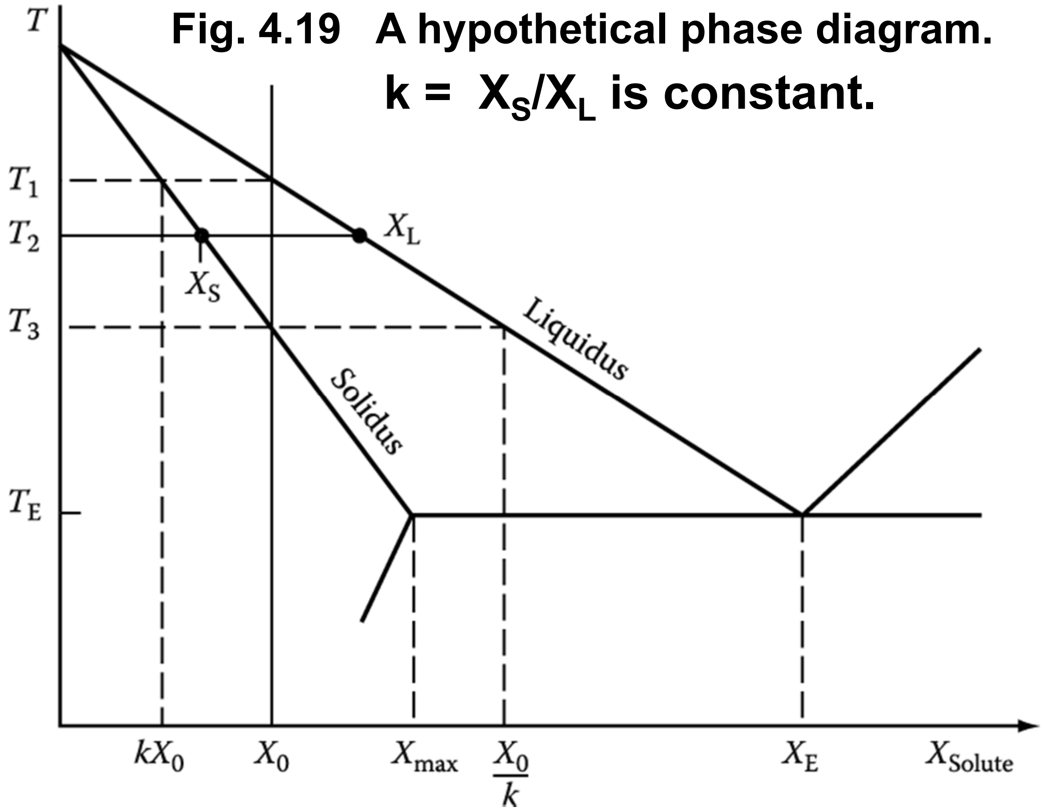
k : partition coefficient

X : mole fraction of solute

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

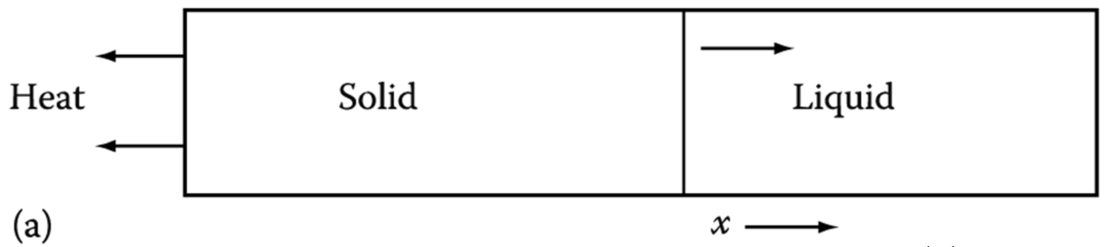
Fig. 4.19 A hypothetical phase diagram.

$k = X_S/X_L$ is constant.



Planar S/L interface

→ unidirectional solidification



1. Solidification of single-phase alloys

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

1) Equilibrium Solidification

(perfect mixing in solid & liquid)

→ low cooling rate

: infinitely slow solidification

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

partition coefficient

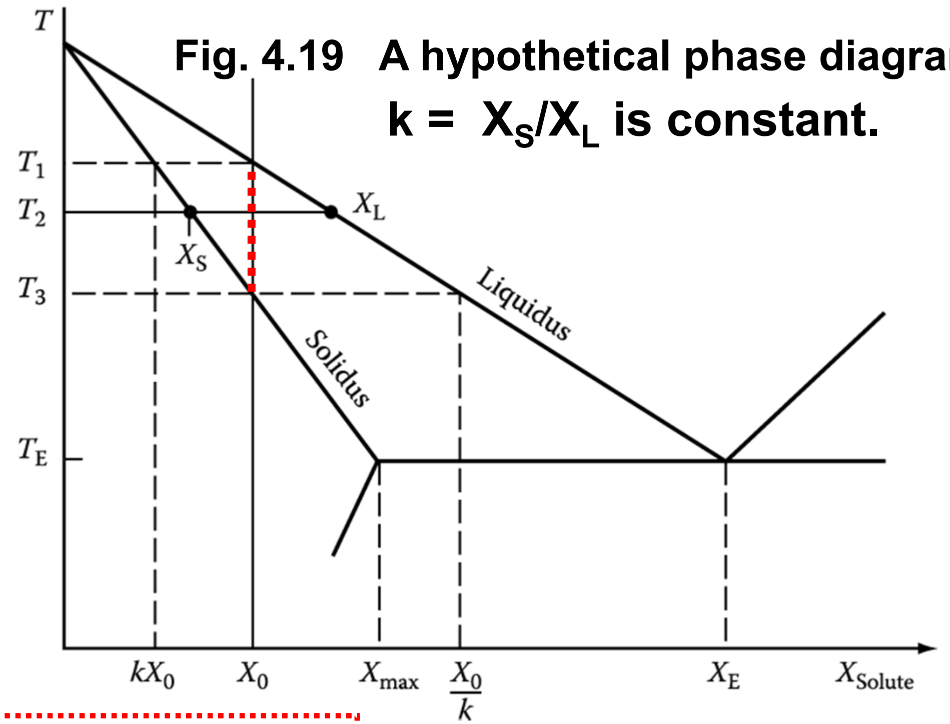


Fig. 4.19 A hypothetical phase diagram.

k = X_S/X_L is constant.

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

Composition vs x at T_2

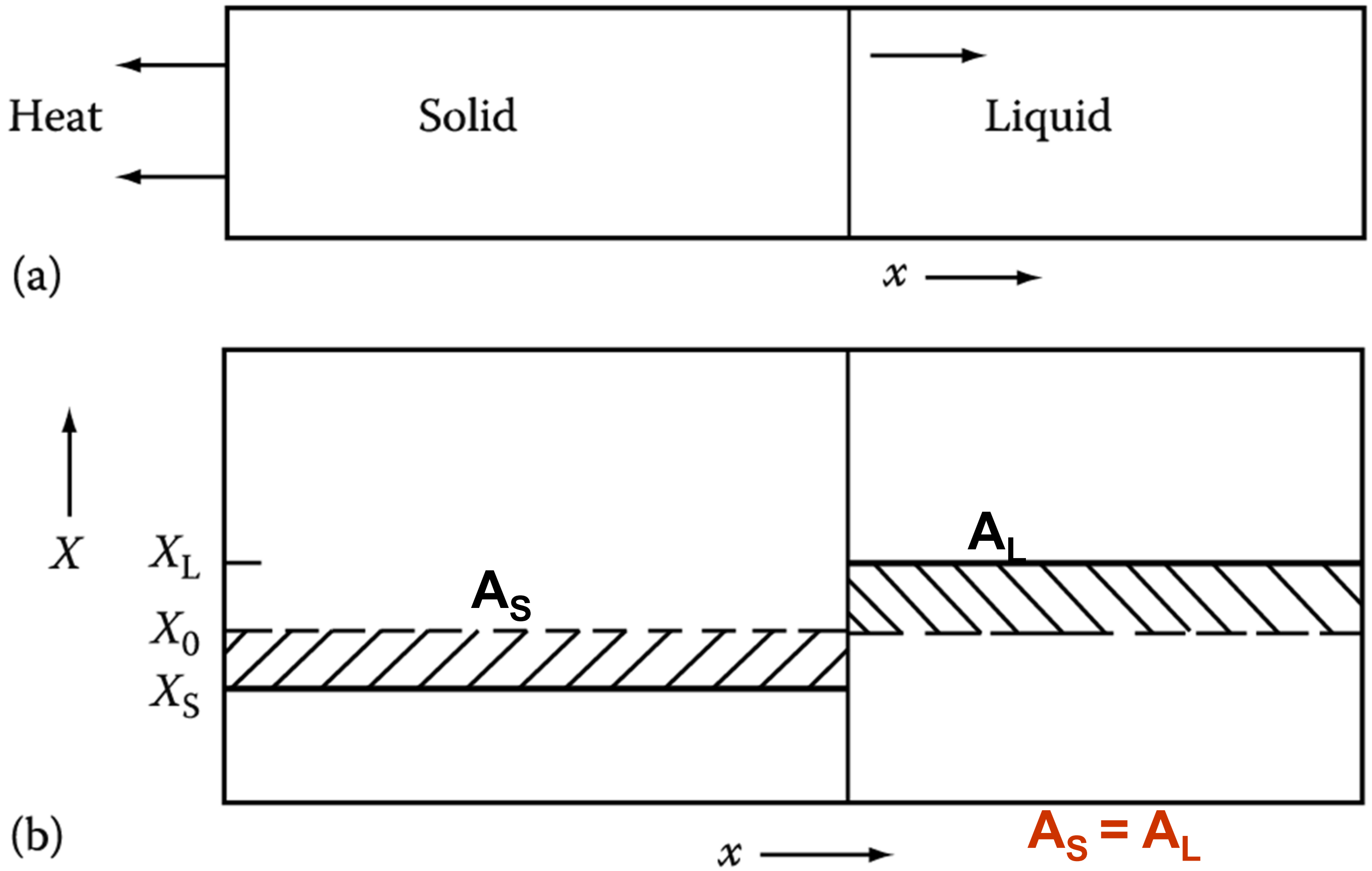
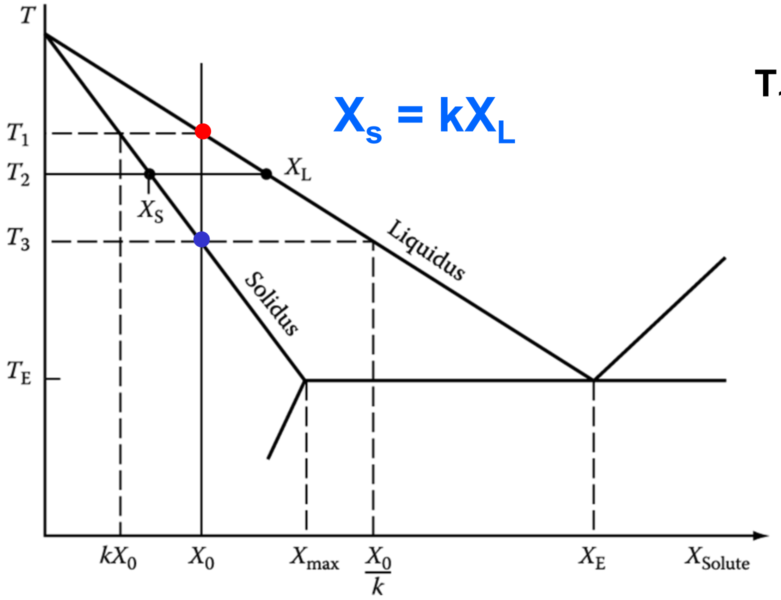
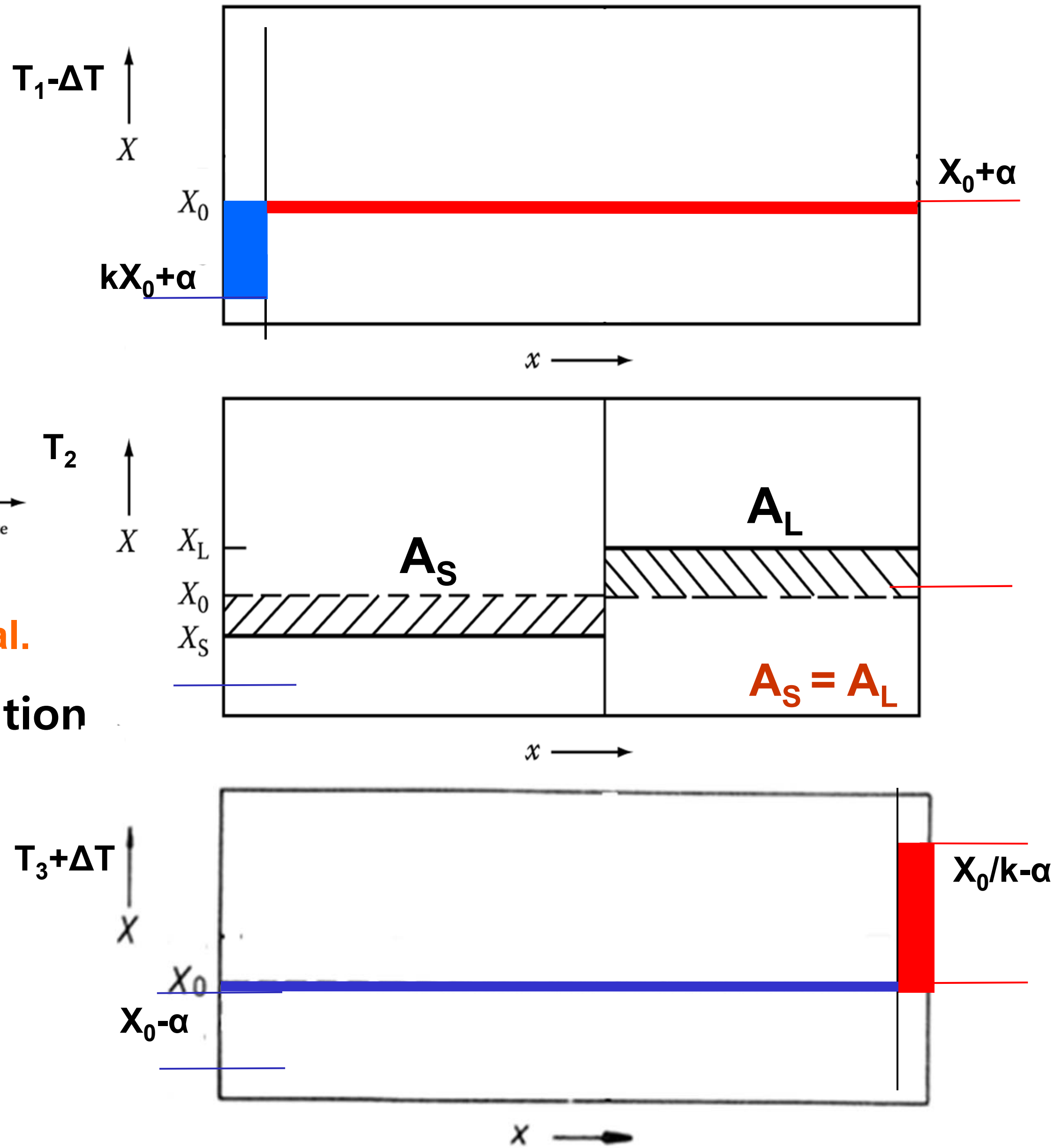


Fig. 4.20 Unidirectional solidification of alloy X_0 in Fig. 4.19. (a) A planar S/L interface and axial heat flow. (b) Corresponding composition profile at T_2 assuming complete equilibrium. Conservation of solute requires the two shaded areas to be equal. $A_S = A_L$

1) Equilibrium Solidification : perfect mixing in solid and liquid



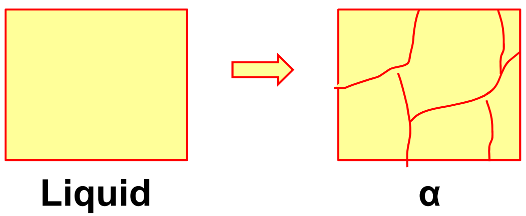
Conservation of solute requires the two shaded areas to be equal.



* Equilibrium solute concentration

$kX_0 \leq X_s \leq X_0$

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



2) 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

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

$solid \rightarrow \overline{X}_S < X_S$

$liquid > X_0/k \rightarrow X_E$

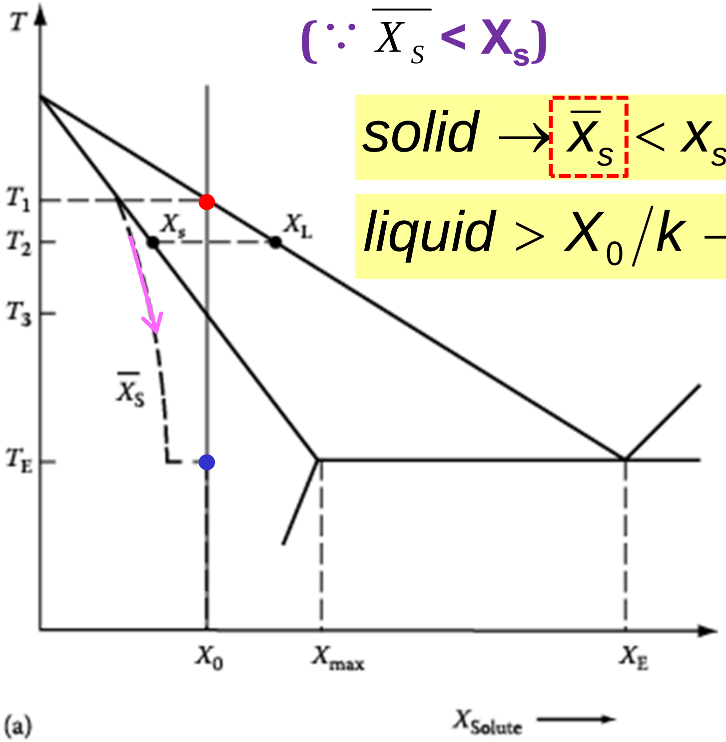


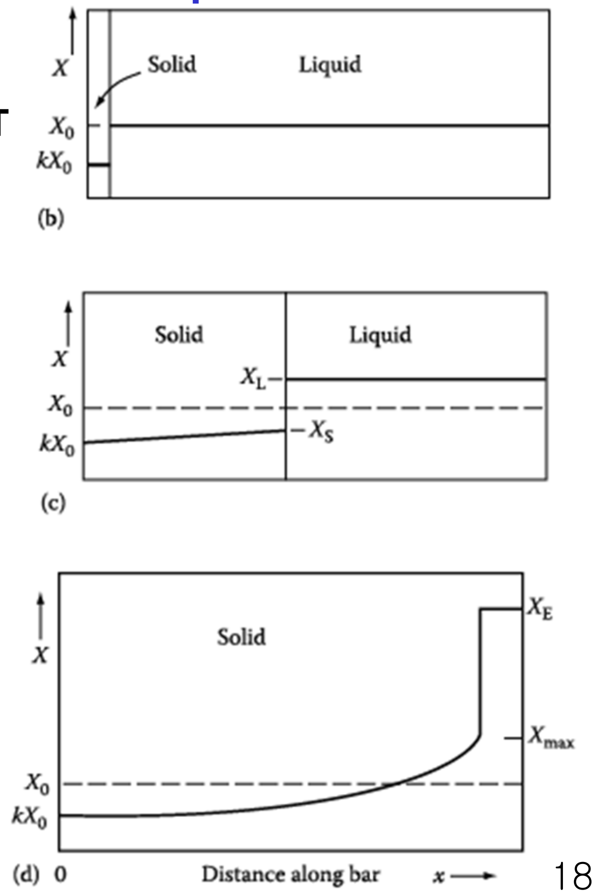
Fig. 4.21 Planar front solidification of alloy X_0 in fig. 4.19 assuming no diffusion in the solid, but complete mixing in the liquid. (a) As Fig. 4.19, but including the mean composition of the solid. (b) Composition profile just under T_1. (c) Composition profile at T_2 (compare with the profile and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

local equil. at S/L interface

T_1-ΔT

T_2

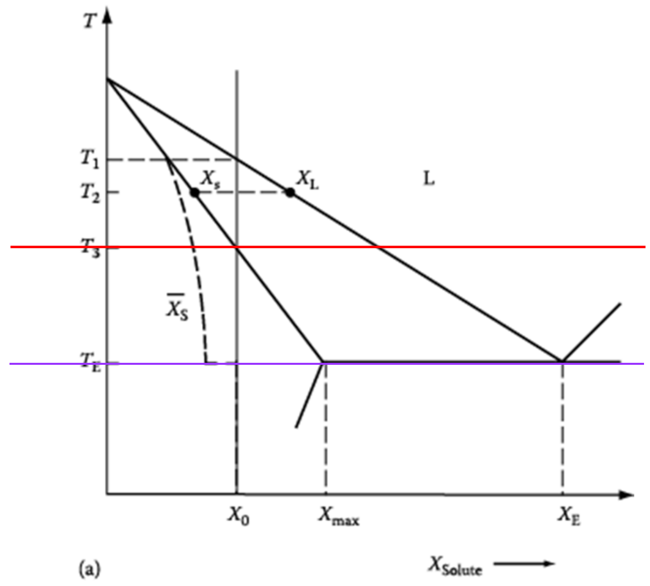
T_E

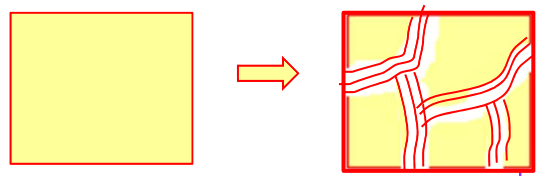


2) No Diffusion in Solid, Perfect Mixing in Liquid

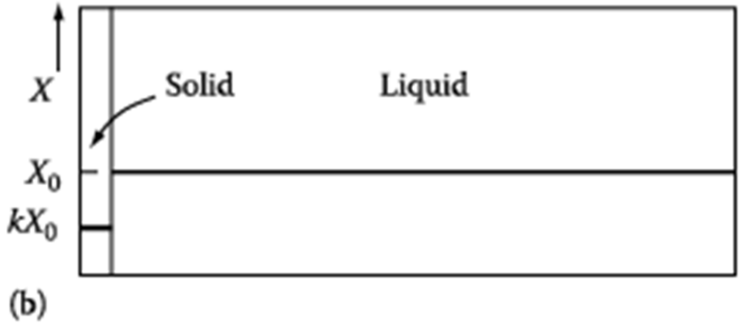
: high cooling rate, efficient stirring

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

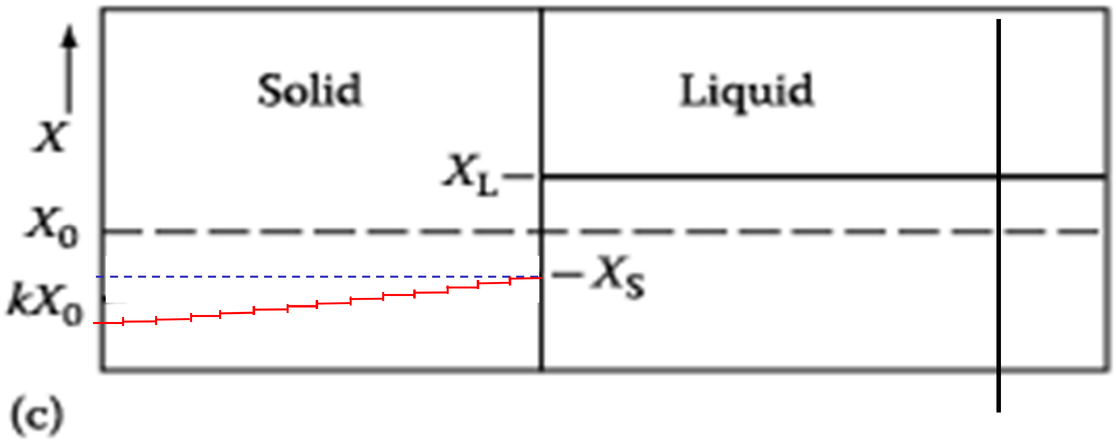


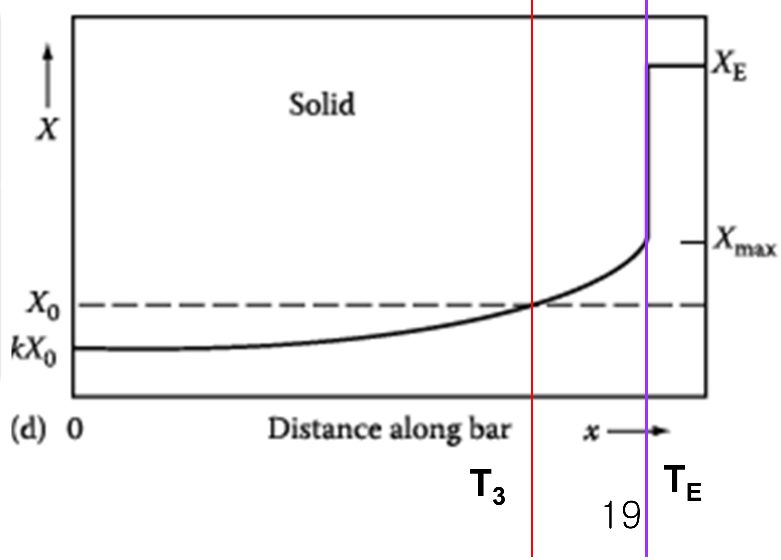


T_1-ΔT



T_2





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

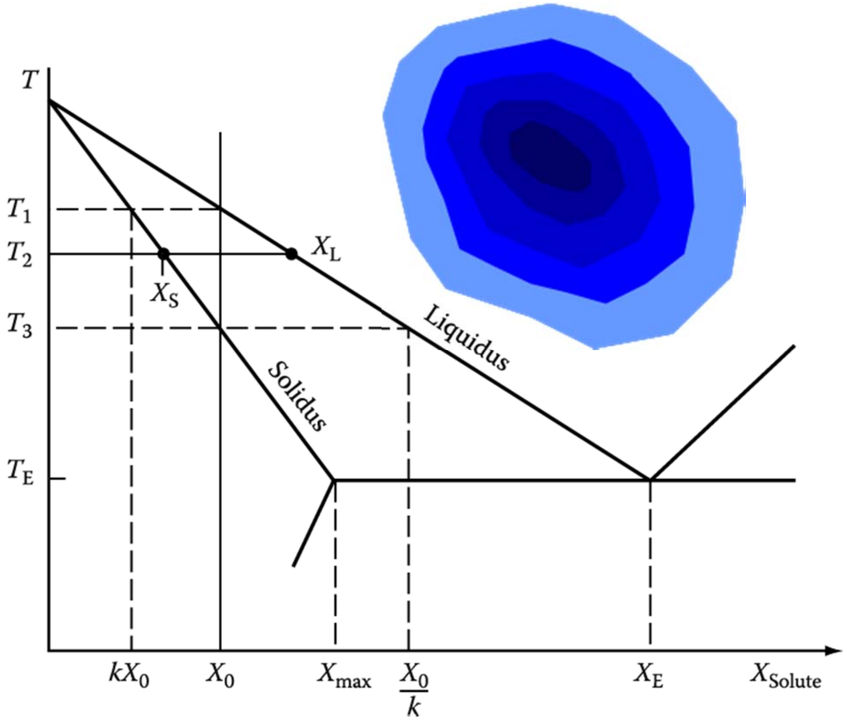
$liquid > X_0/k \rightarrow X_E$

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 $f_S = 0 \rightarrow X_S, X_L$?

$X_S = kX_0$ and $X_L = X_0$

Initial conditions

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

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

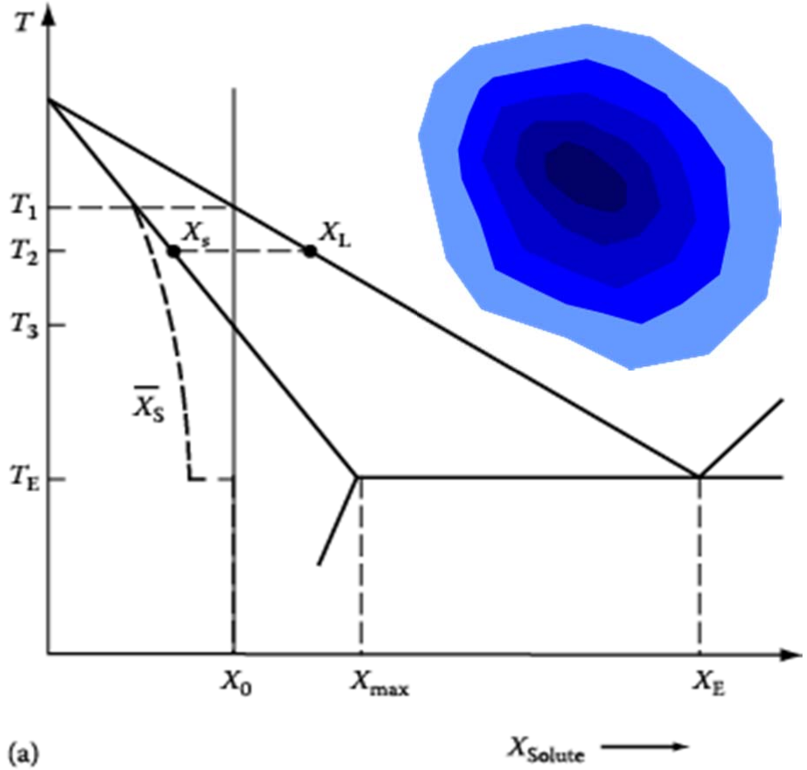
$$\ln\frac{X_L}{X_O} = (k-1)\ln(1-f_S)$$

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

$X_s = kX_L$

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

: non-equilibrium lever rule (Scheil equation)

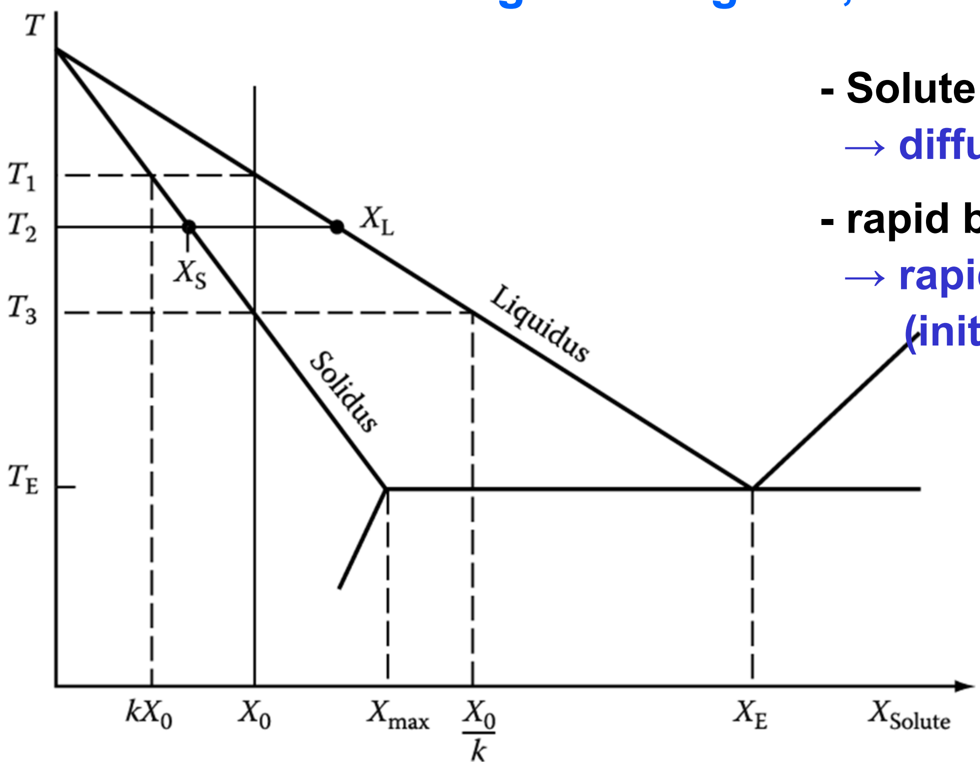


→ quite generally applicable even for nonplanar solid/liquid interfaces provided here, the liquid composition is uniform and that the Gibbs-Thomson effect is negligible.

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

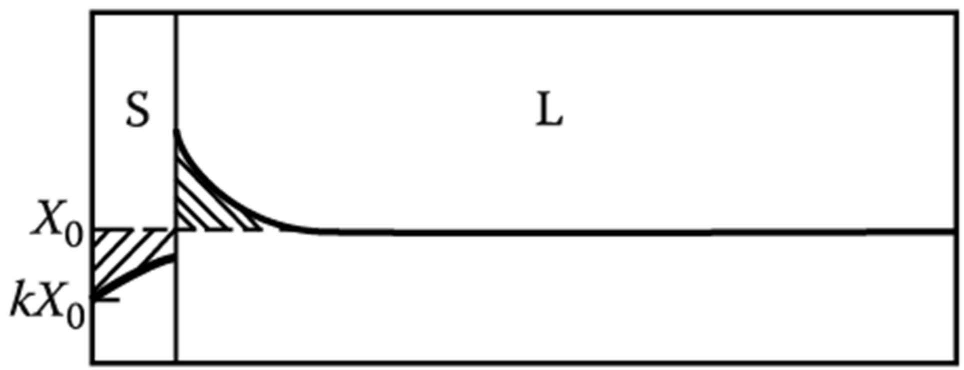
3) No Diffusion on Solid, Diffusional Mixing in the Liquid

: 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



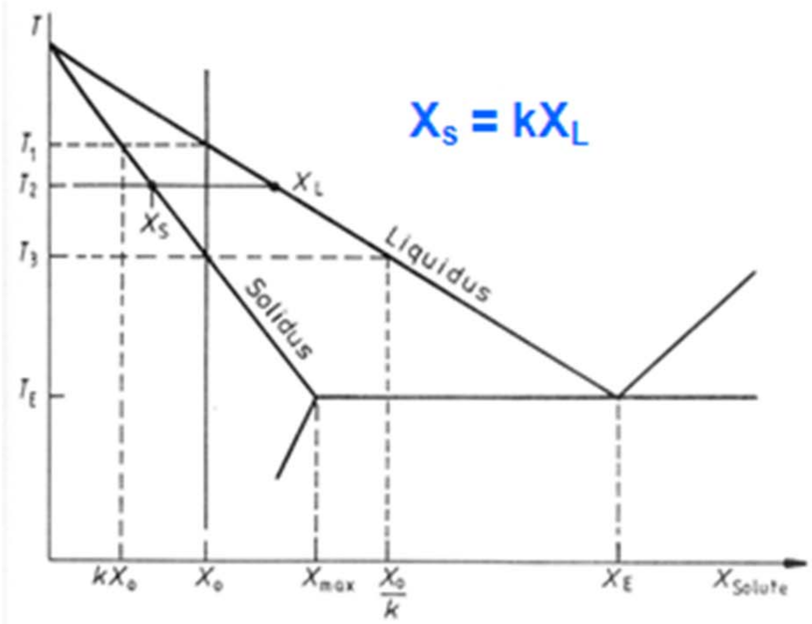
Composition profile at $T_2 < T_{S/L} < T_3$?

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

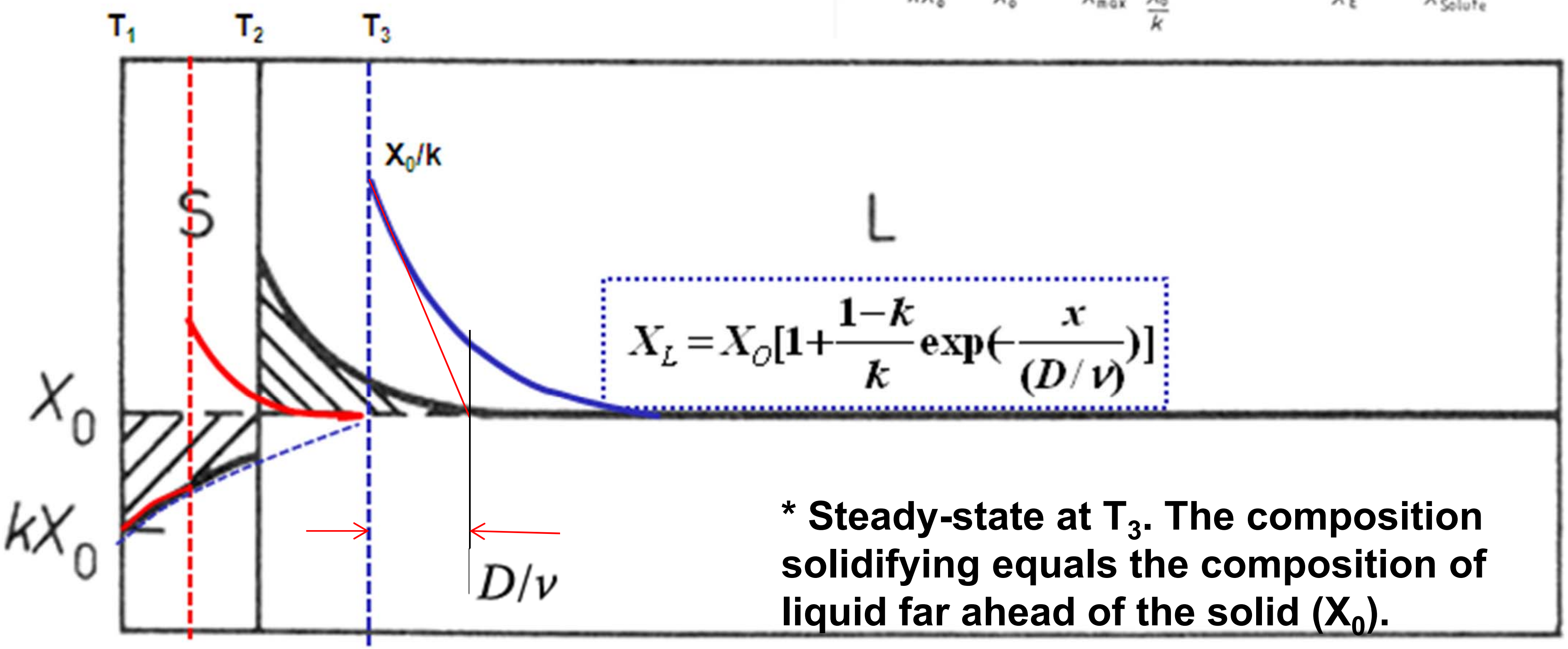
“Alloy solidification”

- Solidification of single-phase alloys

* No Diffusion on Solid, Diffusional Mixing in the Liquid



Interface temperature



* 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.

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

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

(Solidification rate of alloy: excess solute control)

⬍

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

(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

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

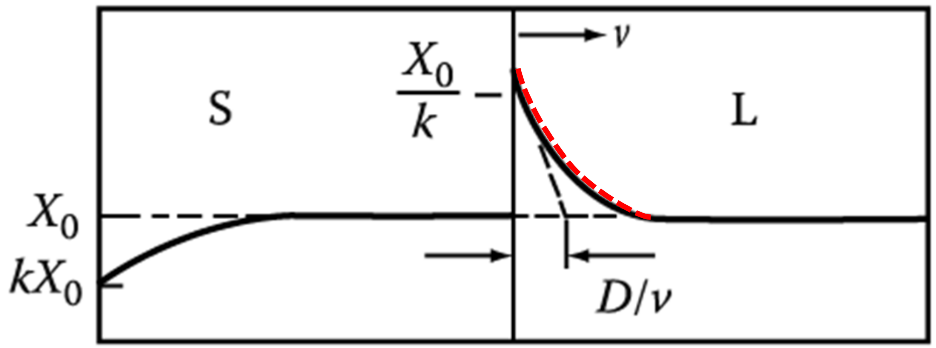
$$\ln(X_L - X_0) = -\frac{v}{D}x + c$$

$$x = 0;\ X_L = X_0 / k$$ steady-state

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

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

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



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

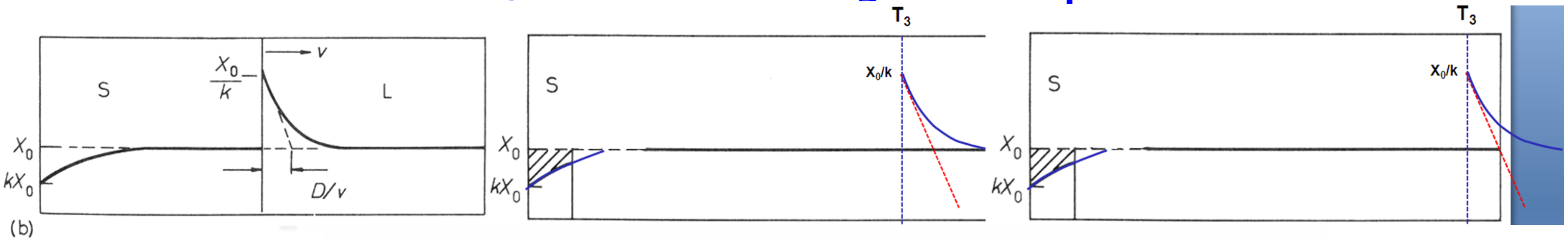
(X$_L$ decreases exponentially from X$_0$/k at x=0, the interface, to X$_0$ at large distances from the interface. The concentration profile has a characteristic width of D/v.)

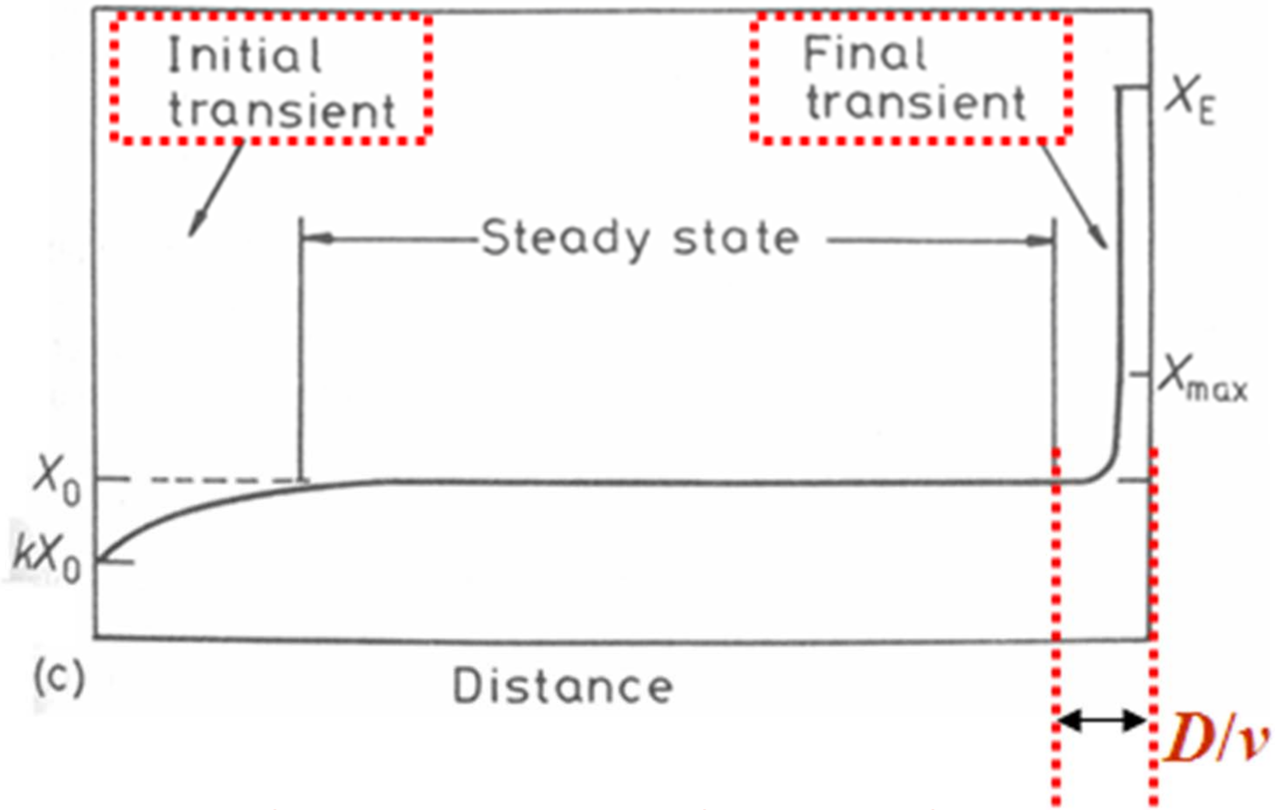
- The concentration gradient in liquid in contact with the solid :

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

"Alloy solidification" - Solidification of single-phase alloys

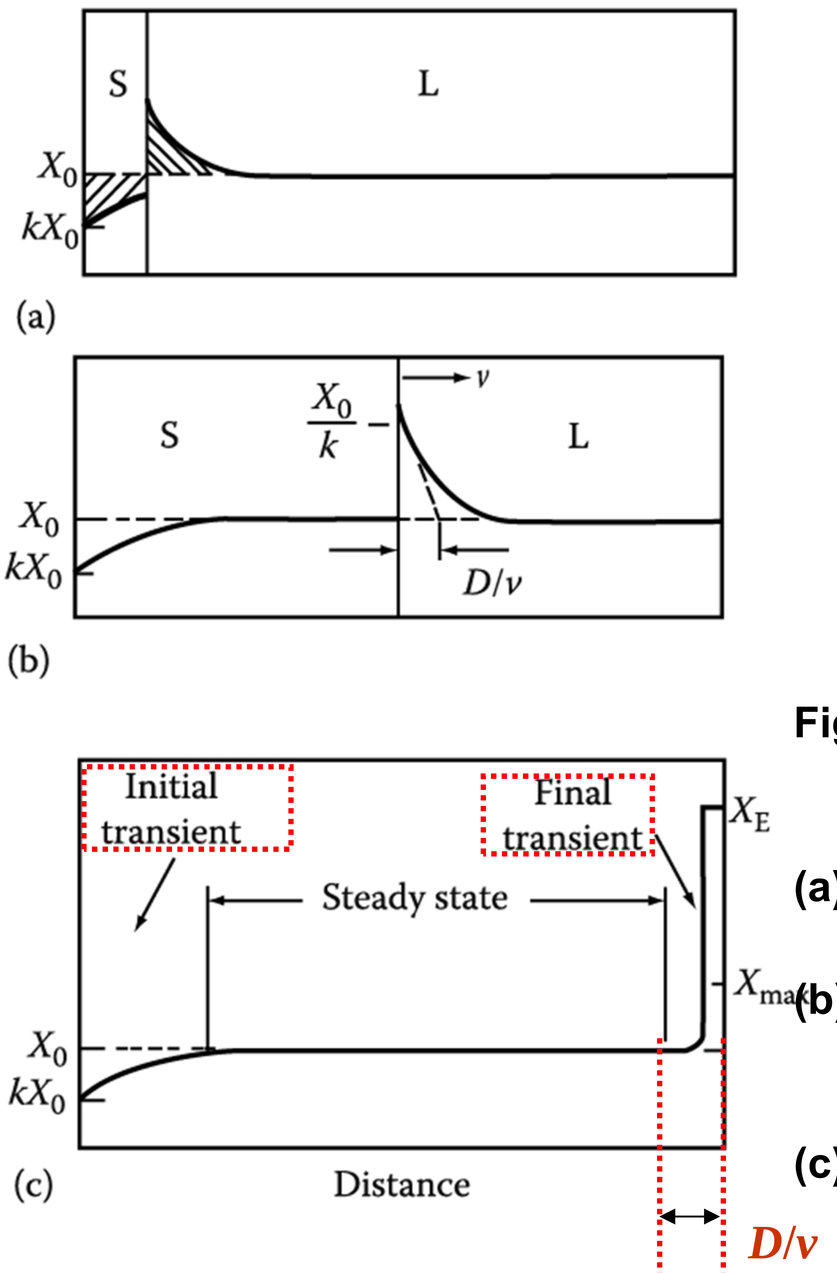
* No Diffusion on Solid, Diffusional Mixing in the Liquid





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



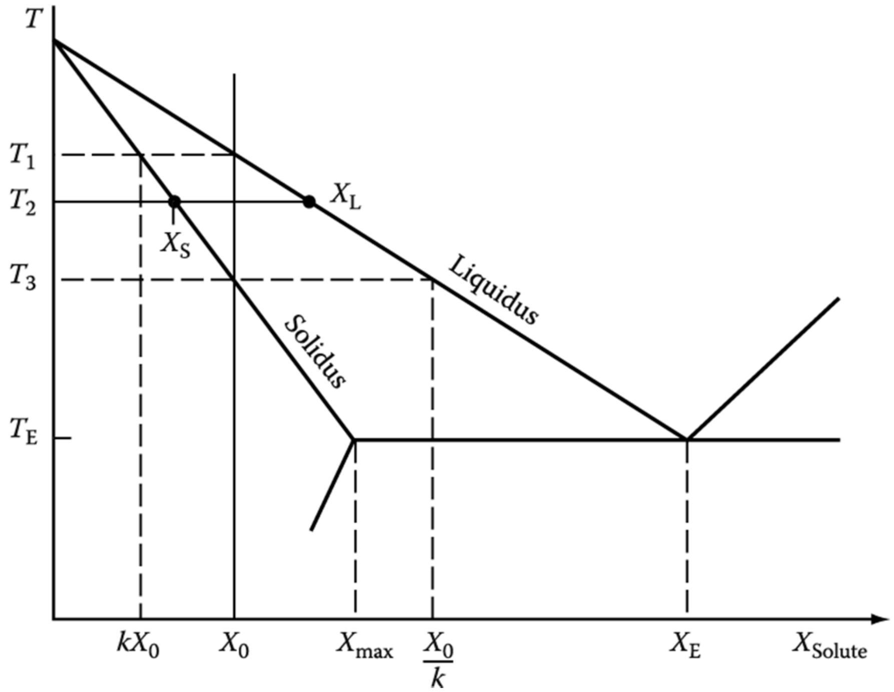


Fig. 4.22 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in solid and no stirring in the liquid.

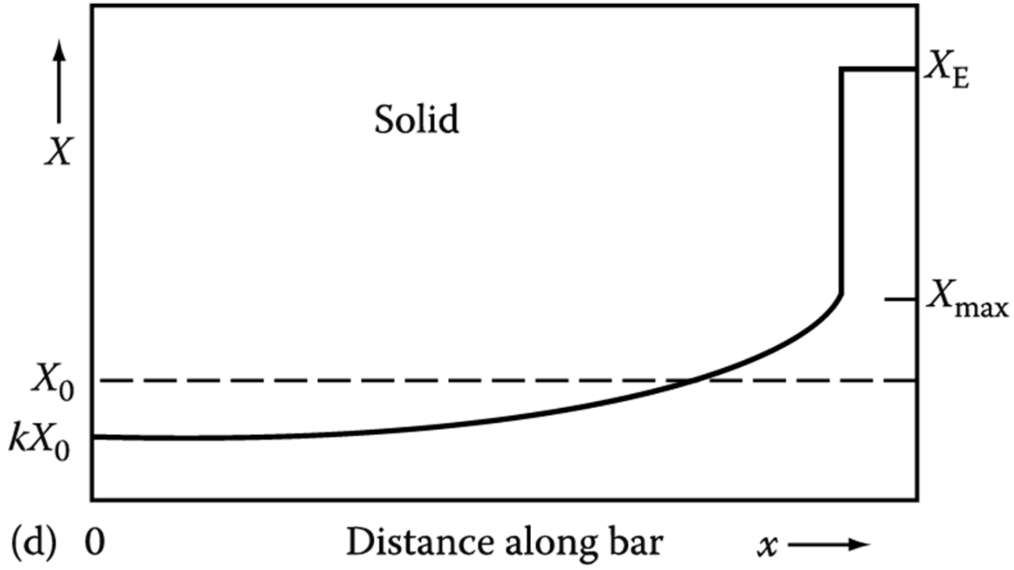
(a) Composition profile when S/L temperature is between T_2 and T_3 in Fig. 4.19.

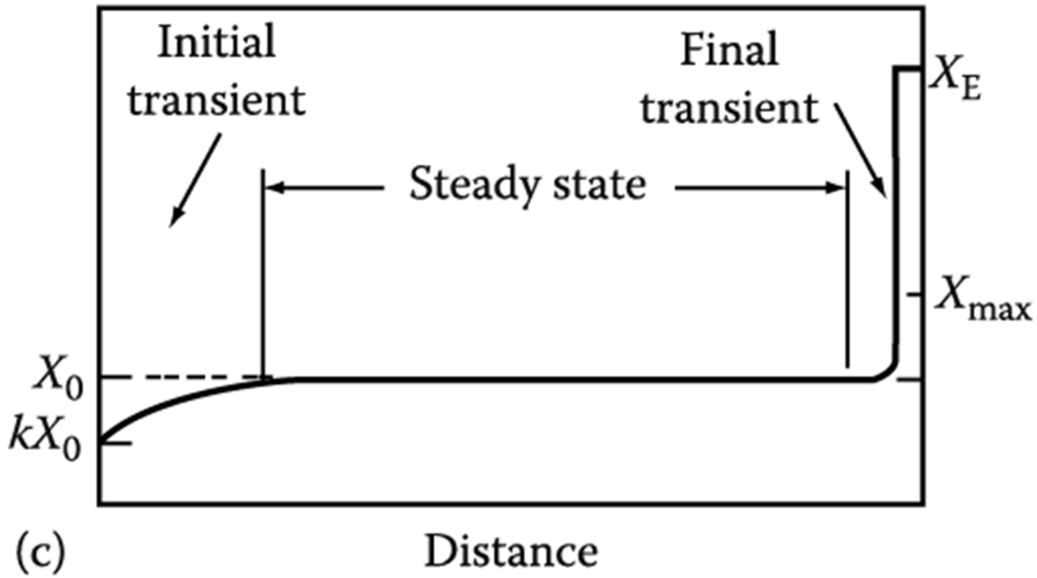
(b) Steady-state at T_3. The composition solidifying equals the composition of liquid far ahead of the solid (X_0).

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

Concentration profiles in practice

: exhibit features between two cases





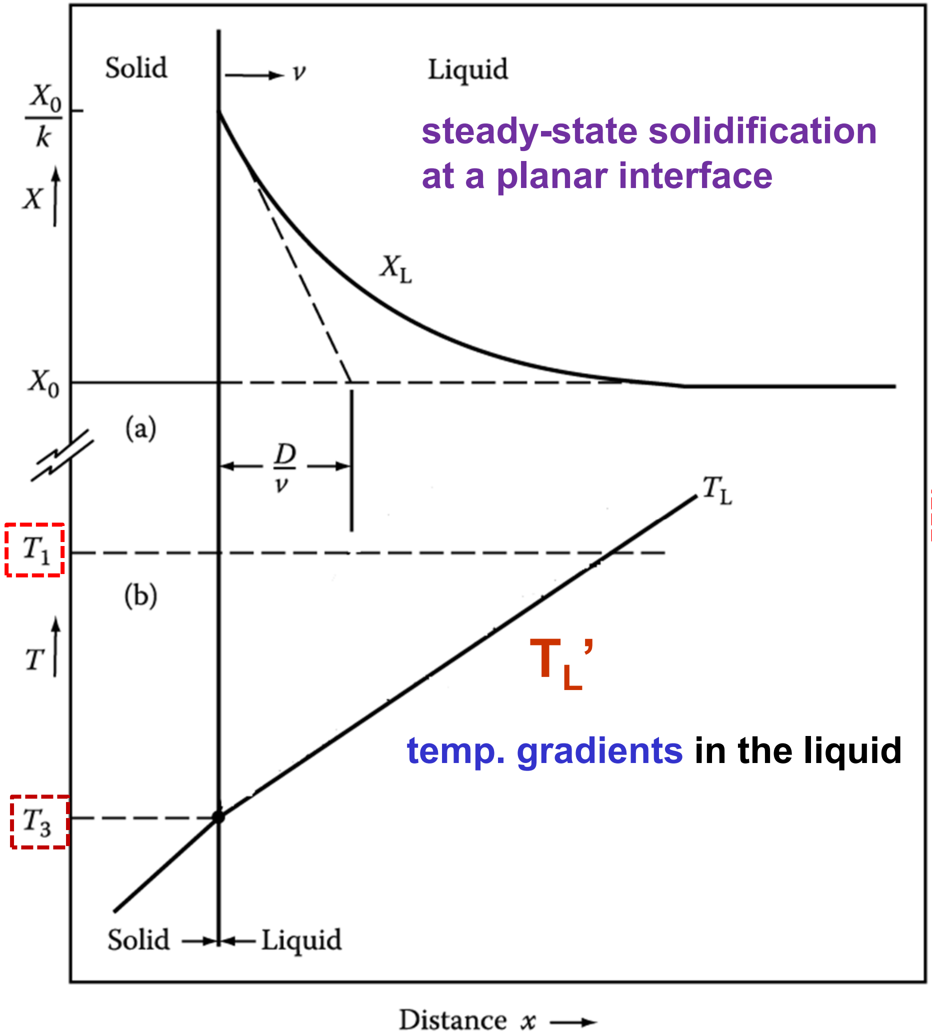
➡ **Zone Refining**

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

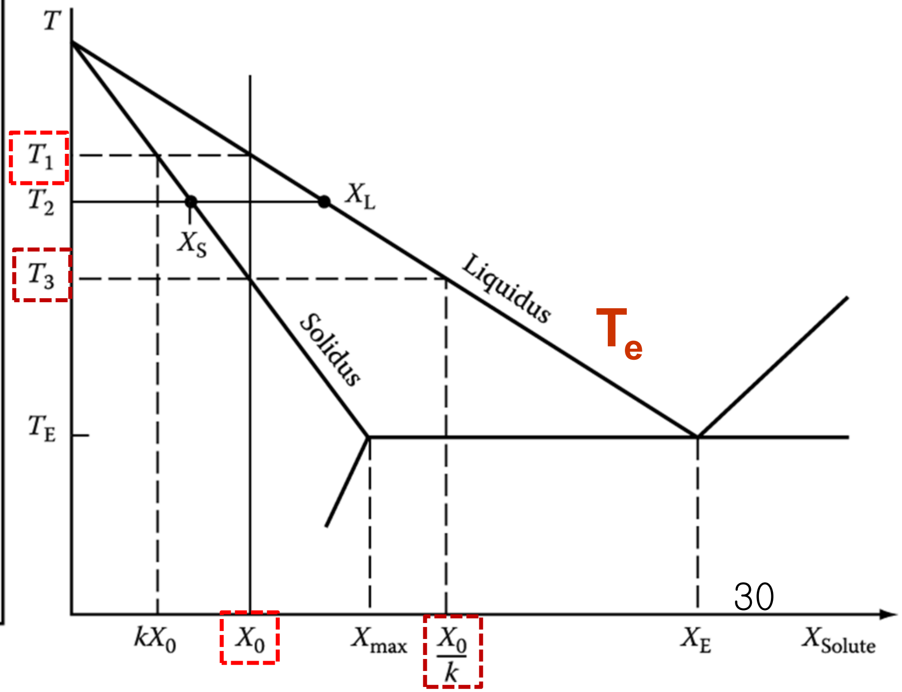
2. Cellular and Dendritic Solidification

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.

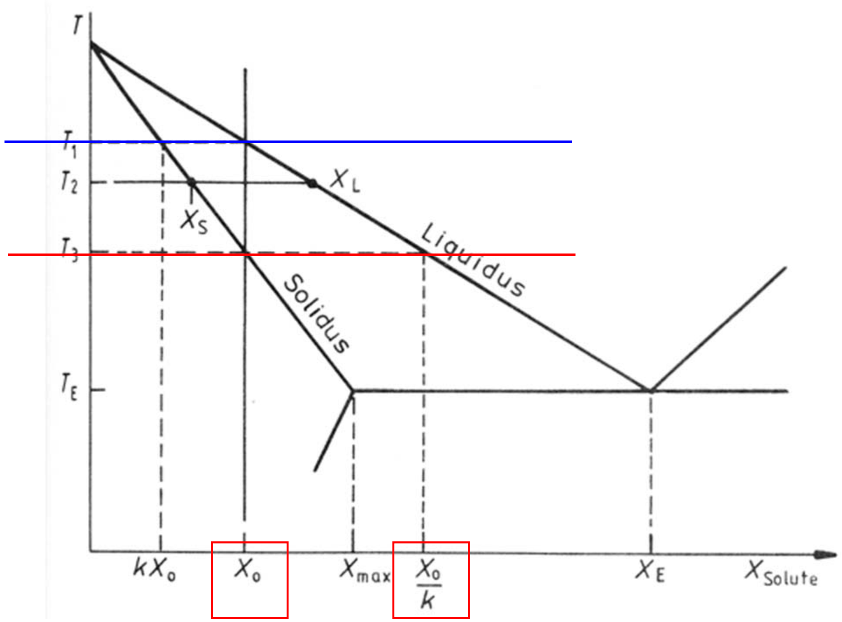


What would be T_e along the concentration profile ahead of the growth front during steady-state solidification?



* Constitutional Supercooling

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

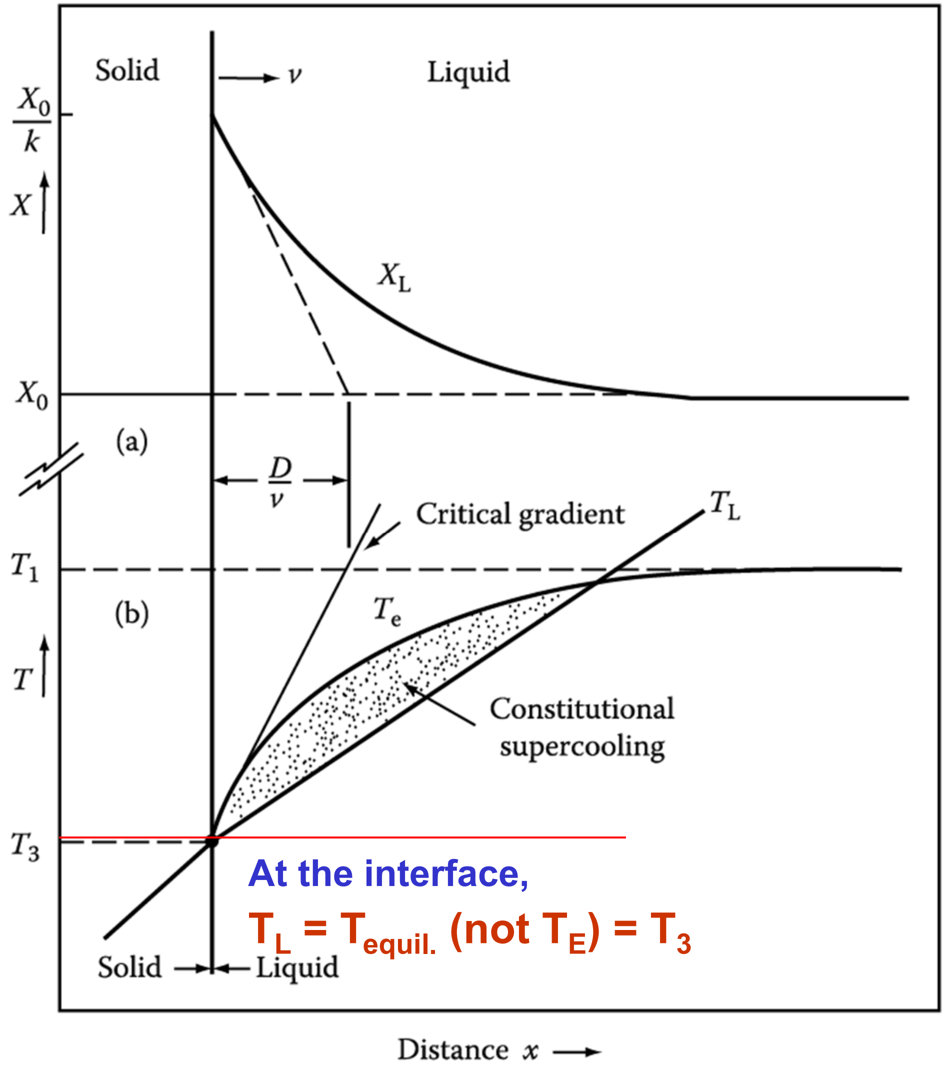


*** Actual temperature gradient in Liquid**

T_L'

*** equilibrium solidification temp. change**

$T_{equil.}$



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

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

Solidification of Pure Metal : Thermal gradient dominant

⇕

Solidification of single phase alloy: Solute redistribution dominant

a) Constitutional supercooling

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

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