2015 Fall

“Phase Transformation *in* Materials”

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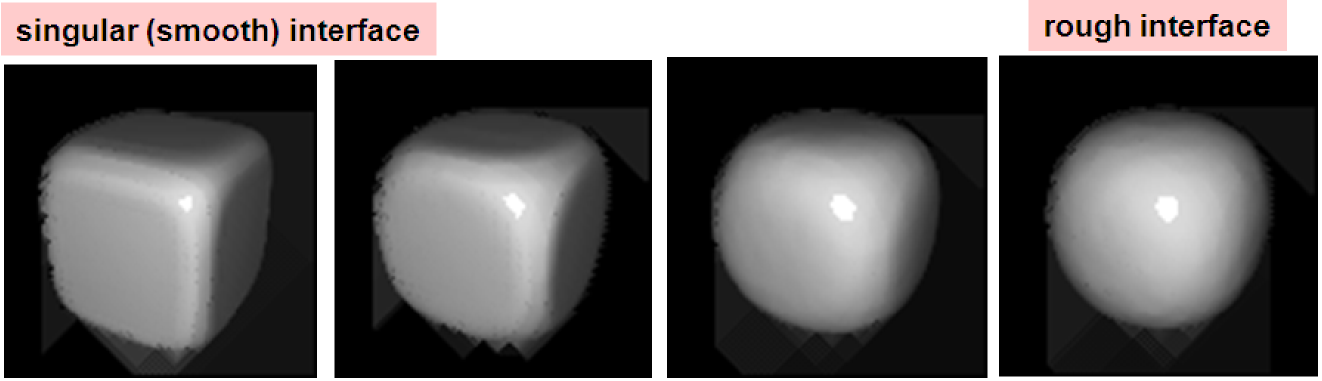
Contents for previous class

Solidification: Liquid → Solid

< Nucleation > & **< Growth >**

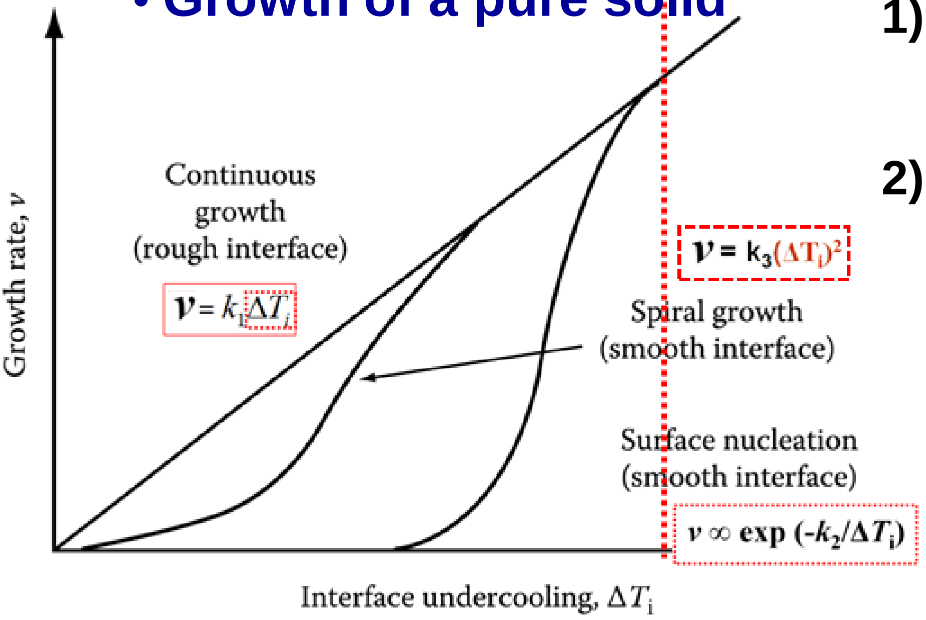
- **Equilibrium Shape and Interface Structure on an Atomic Scale**

Thermal Roughening



Heating up to the roughening transition.

- **Growth of a pure solid**



1) Continuous growth

: Atomically rough or diffuse interface

2) Lateral growth

: Atomically flat of sharply defined interface

a) Surface (2-D) nucleation b) Spiral growth

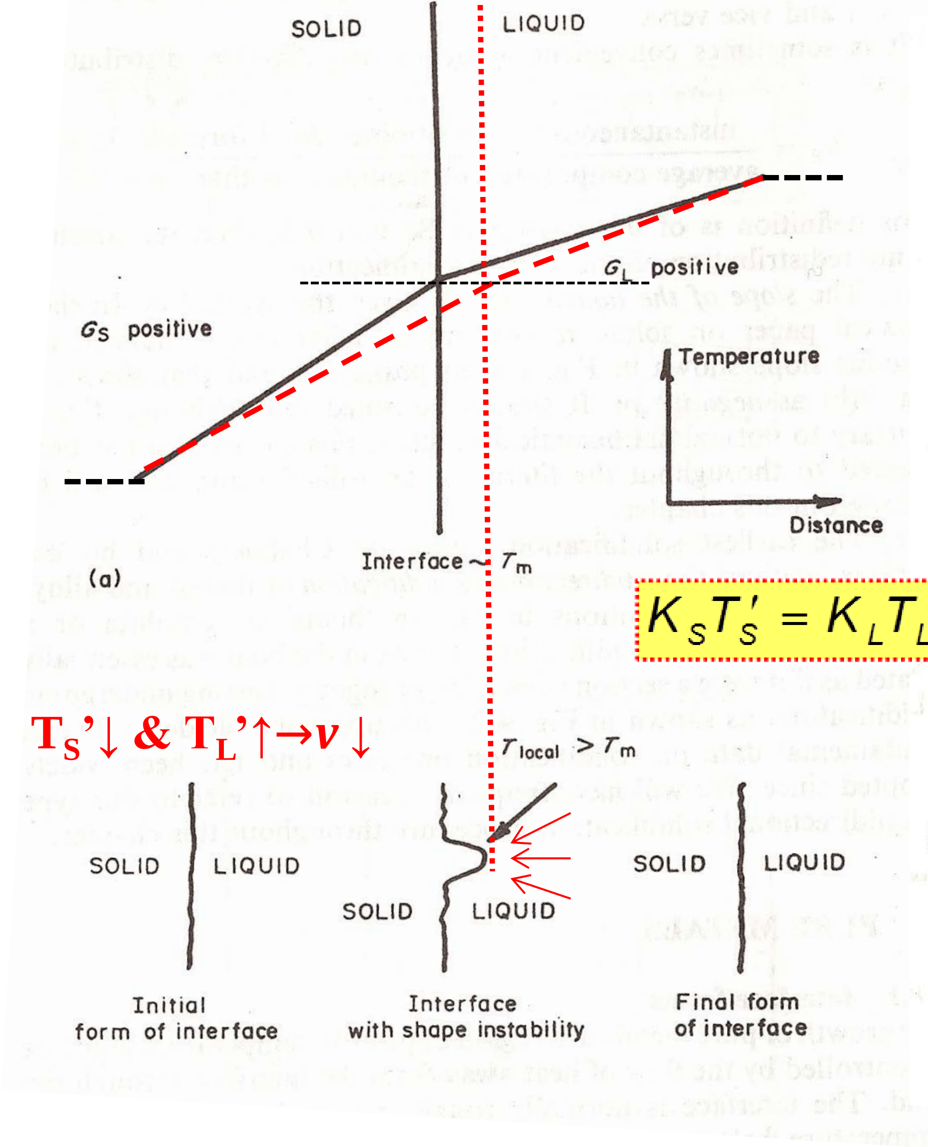
Kinetic roughening

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

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

1) Superheated liquid

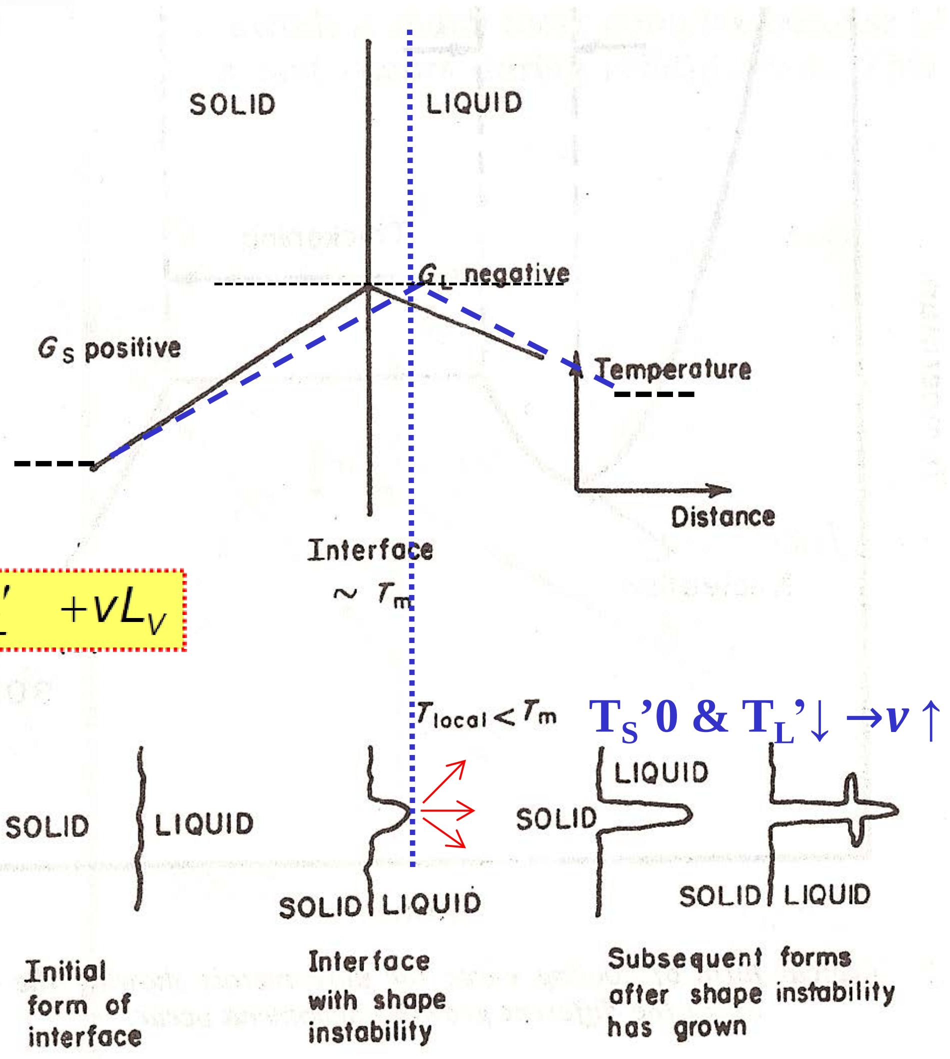
: Extraction of latent heat by conduction in the crystal



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

2) Supercooled liquid

: conduction of latent heat into the liquid



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

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

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*).

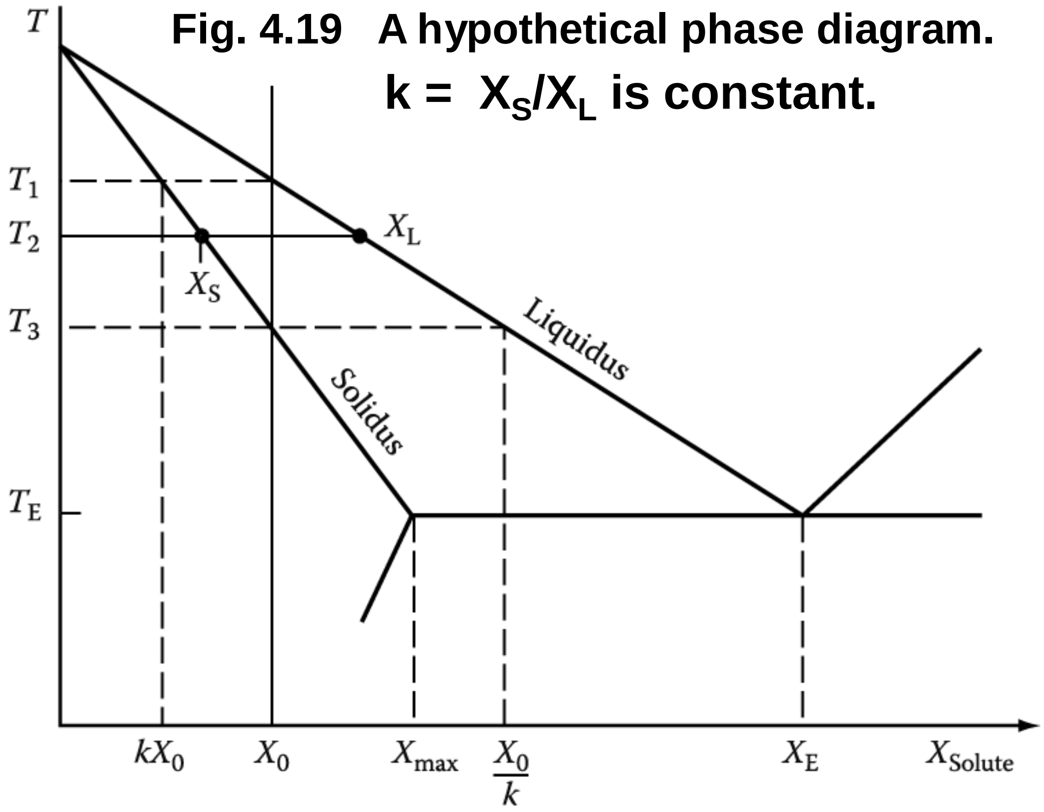
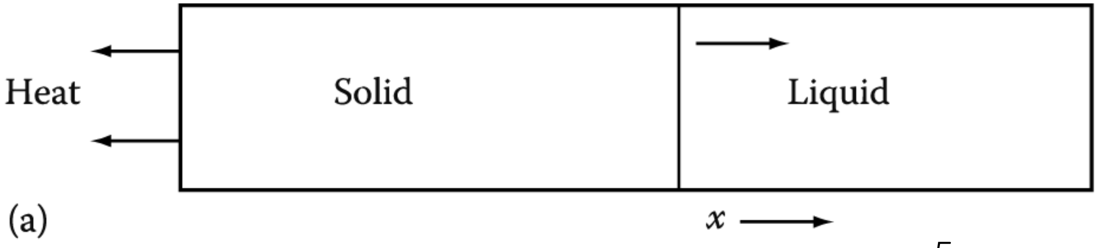


Fig. 4.19 A hypothetical phase diagram.

$k = X_S/X_L$ 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

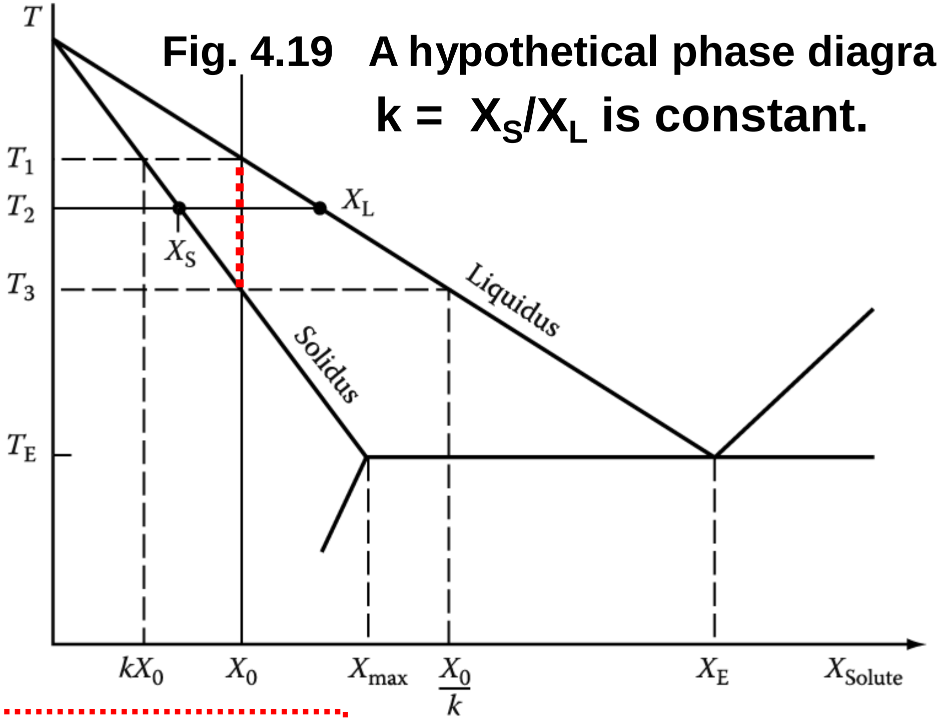


Fig. 4.19 A hypothetical phase diagram.

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

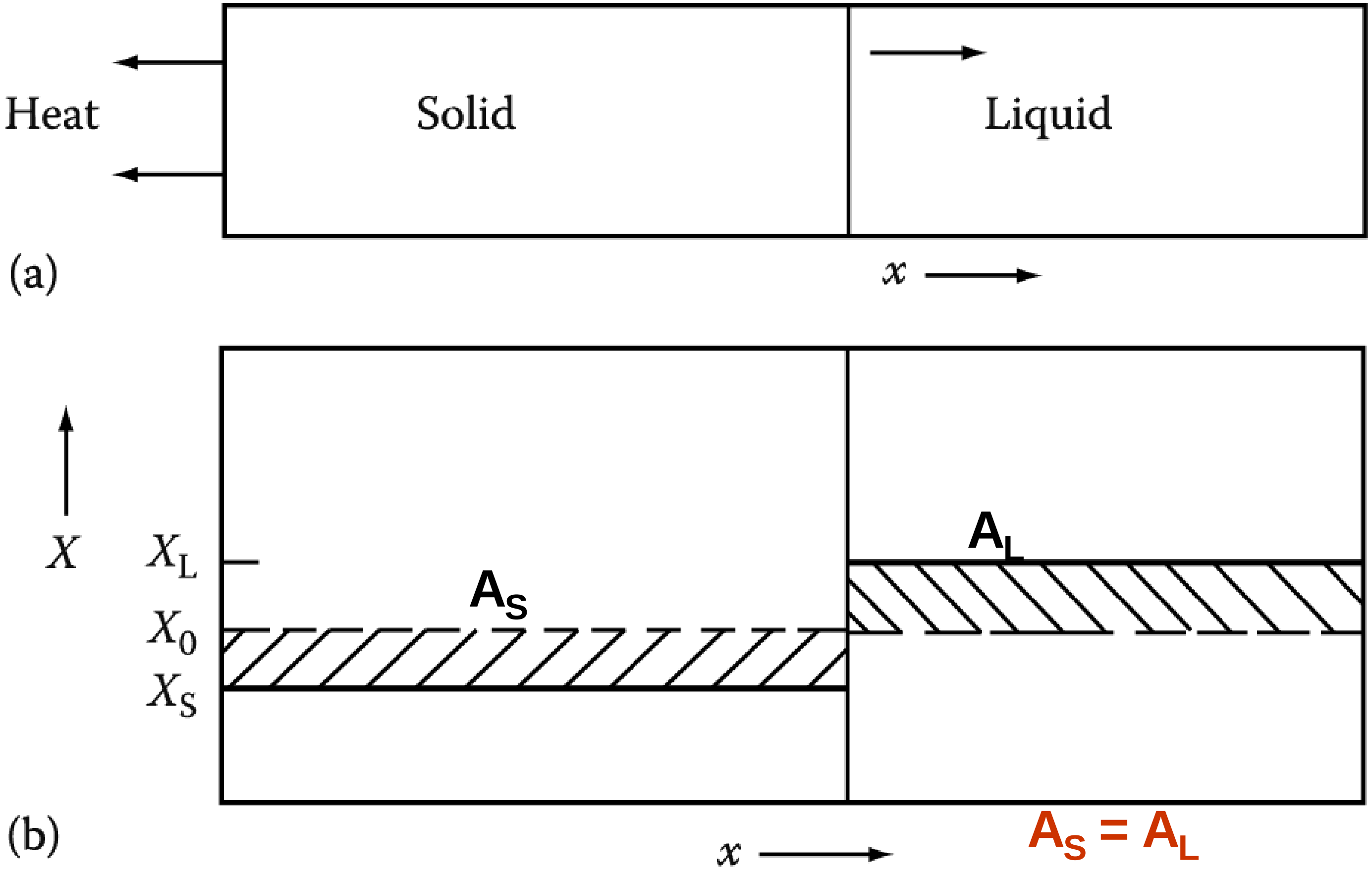
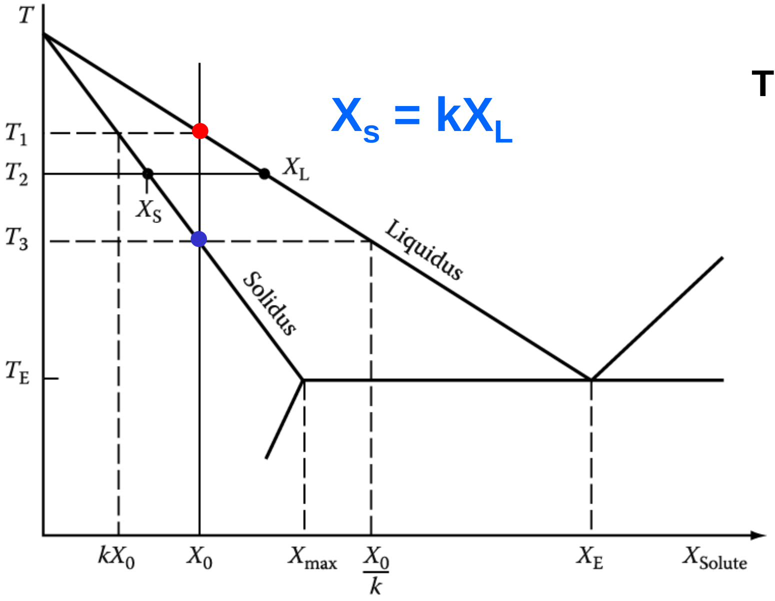


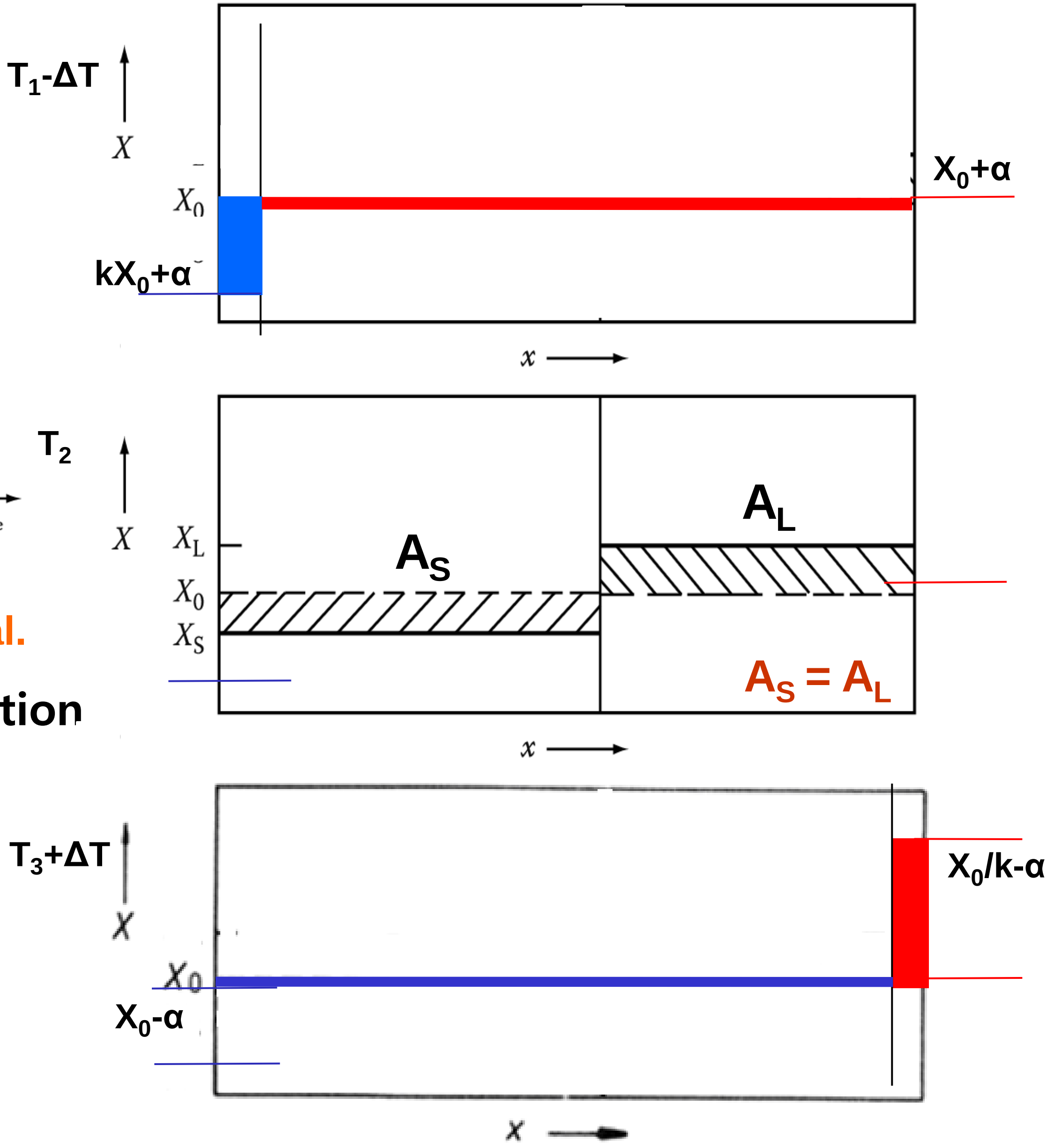
Fig. 4.20 Unidirectional solidification of alloy X_0 in Fig. 4.19. (a) A planar S/L interface and axial heat flow. (b) Corresponding composition profile at T_2 assuming complete equilibrium. Conservation of solute requires the two shaded areas to be equal. $A_S = A_L$

1) Equilibrium Solidification : perfect mixing in solid and liquid



$X_s = kX_L$

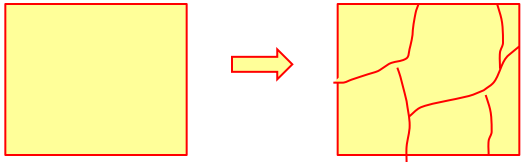
Conservation of solute requires the two shaded areas to be equal.



* Equilibrium solute concentration

$kX_0 \le X_s \le X_0$

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



Liquid

α

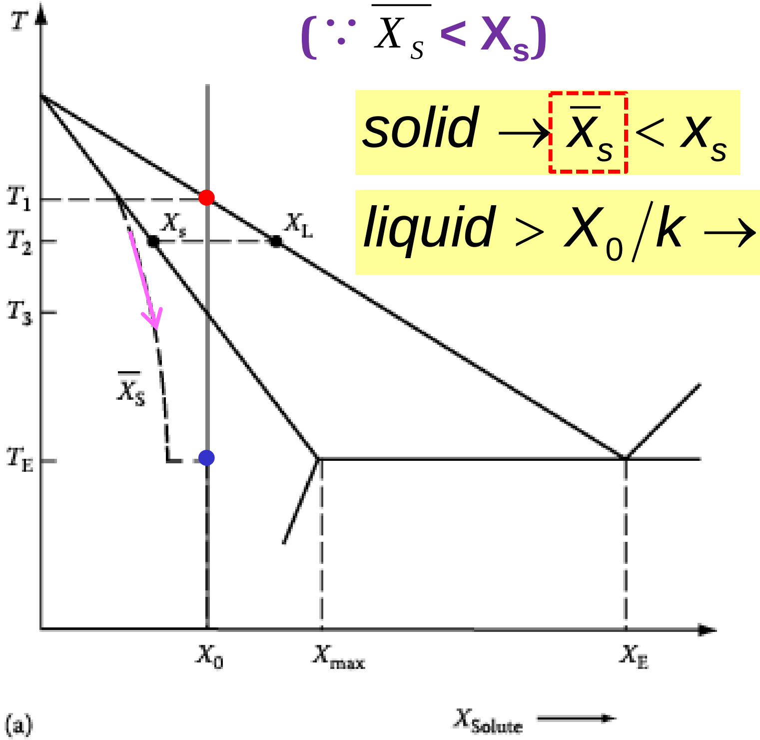
2) Non-equilibrium Solidification: No Diffusion in Solid, Perfect Mixing in Liquid

: 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

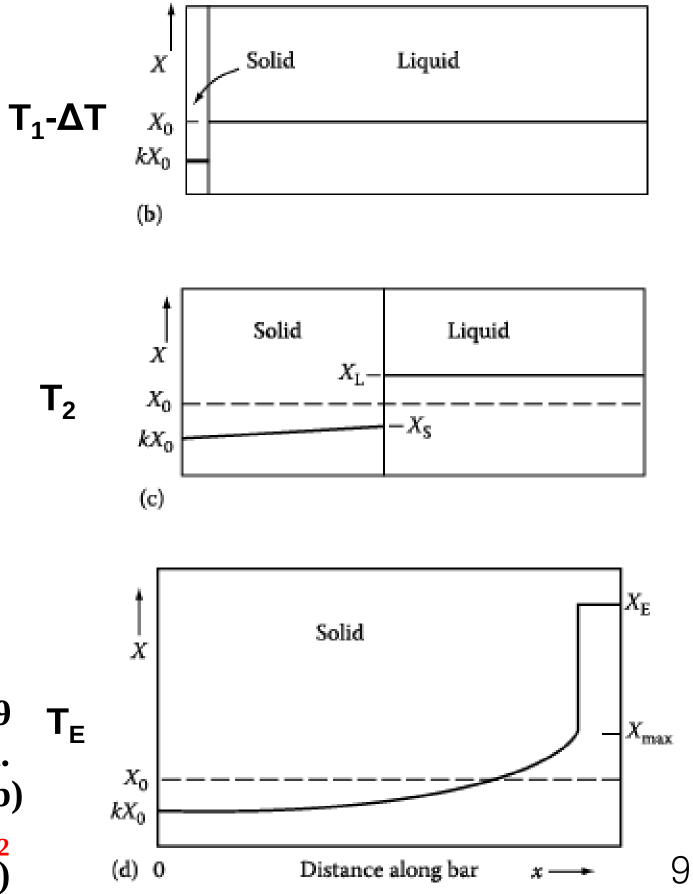
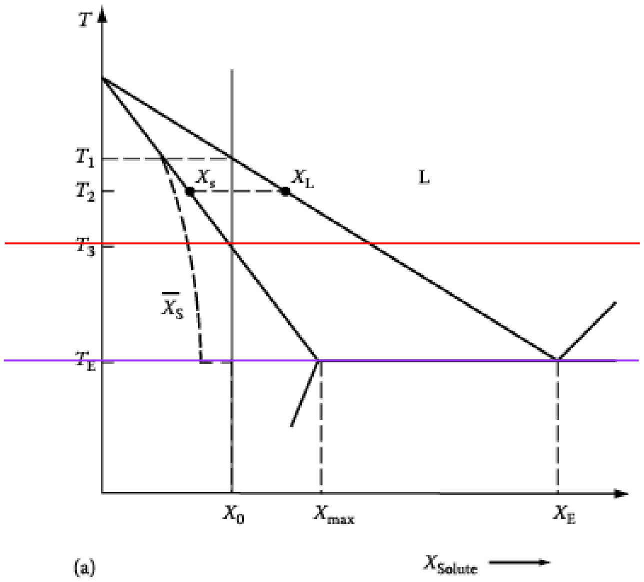


Fig. 4.21 Planar front solidification of alloy X_0 in fig. 4.19 assuming no diffusion in the solid, but complete mixing in the liquid. (a) As Fig. 4.19, but including the mean composition of the solid. (b) Composition profile just under T_1. (c) Composition profile at T_2 (compare with the profile and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

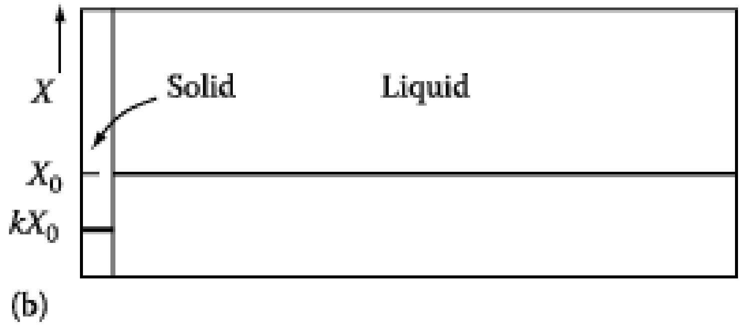
2) No Diffusion in Solid, Perfect Mixing in Liquid

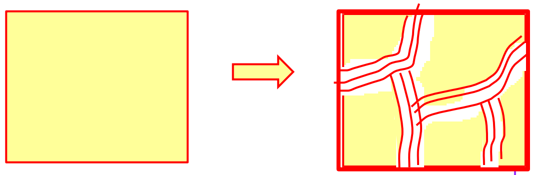
: high cooling rate, efficient stirring

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



T_1-ΔT

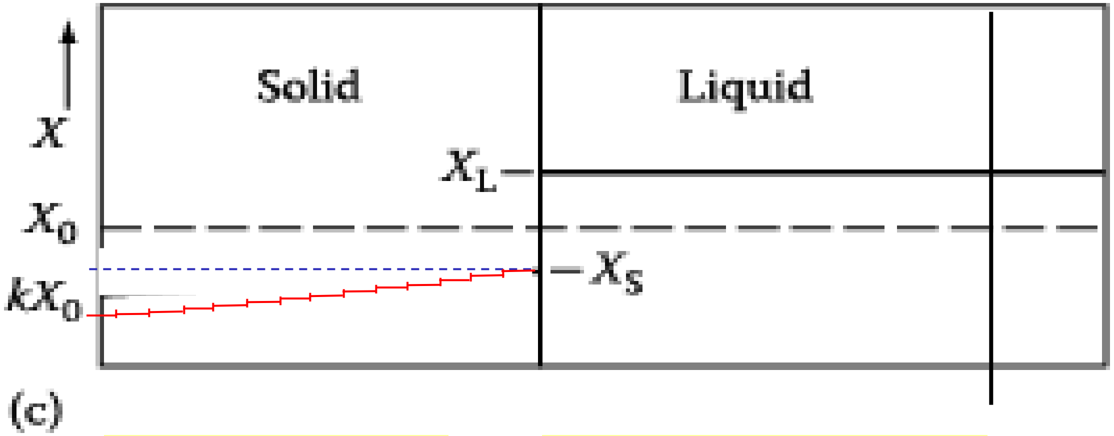


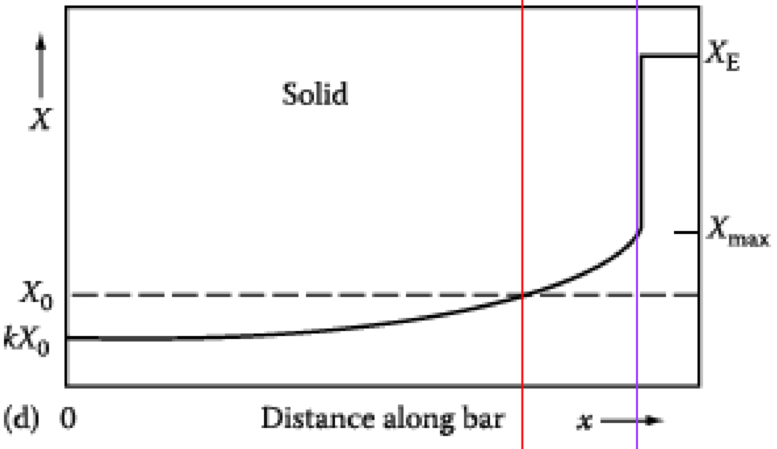


Liquid

Primary α + Eutectic

T_2





$solid \to \bar{X}_s < X_s$

$liquid > X_0/k \to X_E$

T_3

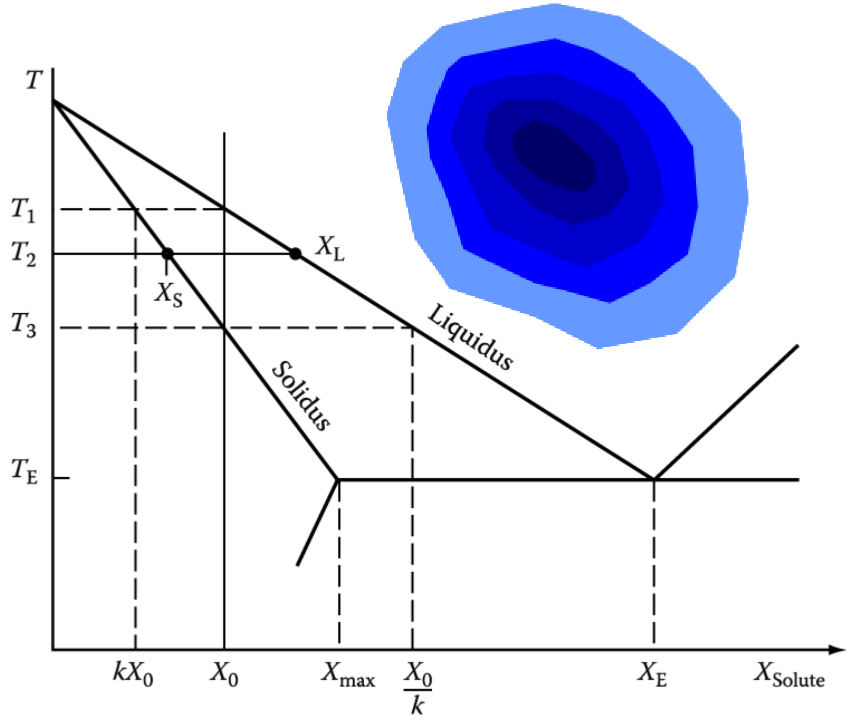
T_E

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 $f_S = 0 \rightarrow X_S, X_L$?

$X_S = kX_0$ and $X_L = X_0$

Initial conditions

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

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

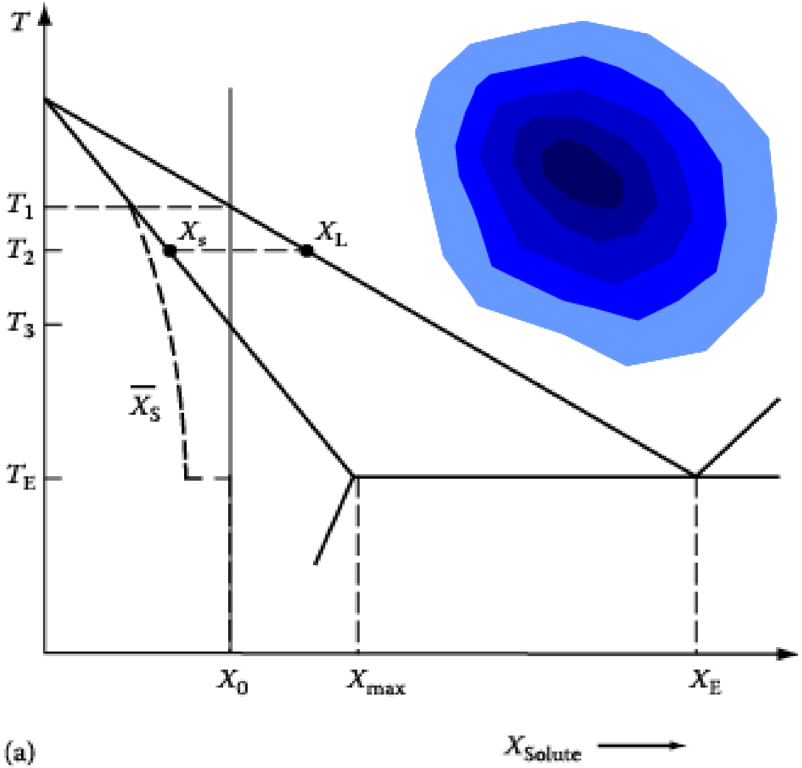
$$\ln\frac{X_L}{X_O} = (k-1)\ln(1-f_S)$$

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

$X_s = kX_L$

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

: non-equilibrium lever rule (Scheil equation)

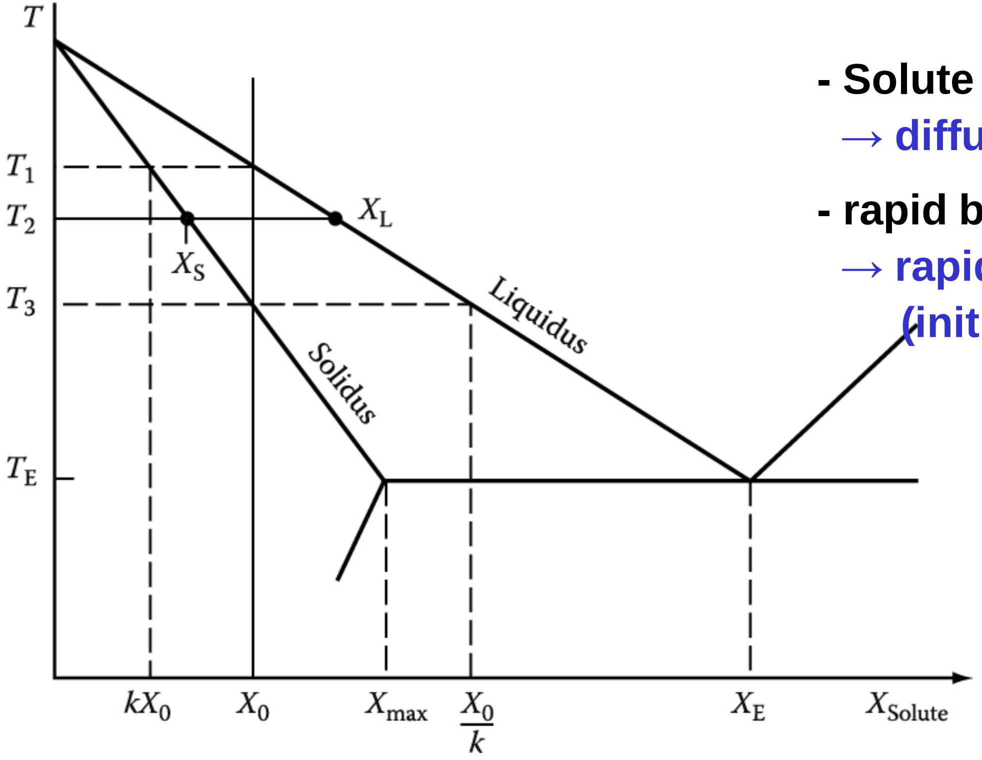


→ **quite generally applicable even for nonplanar solid/liquid interfaces provided here, the liquid composition is uniform and that the Gibbs-Thomson effect is negligible.**

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

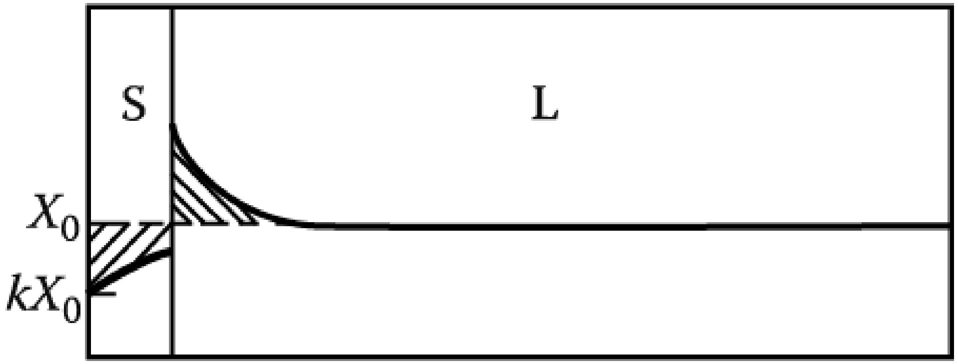
3) No Diffusion on Solid, Diffusional Mixing in the Liquid

: 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



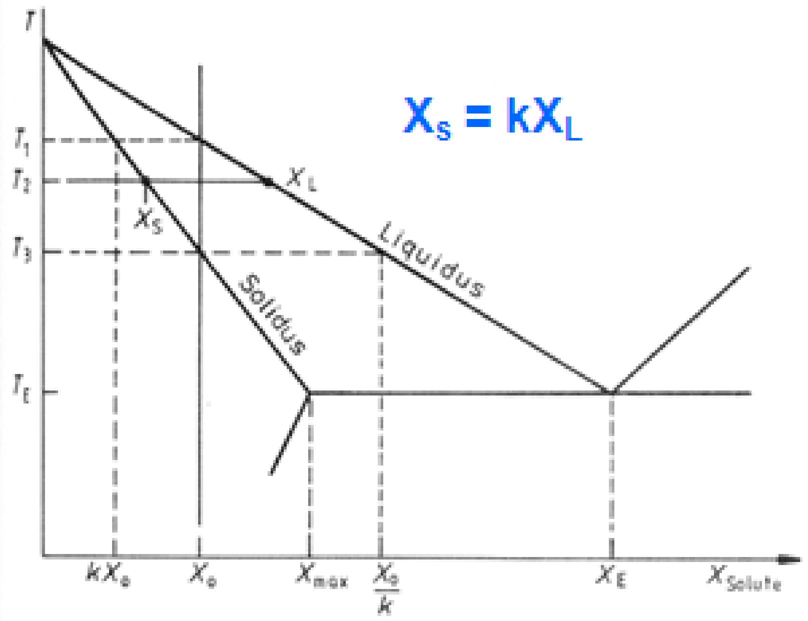
Composition profile at $T_2 < T_{S/L} < T_3$?

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

"Alloy solidification"

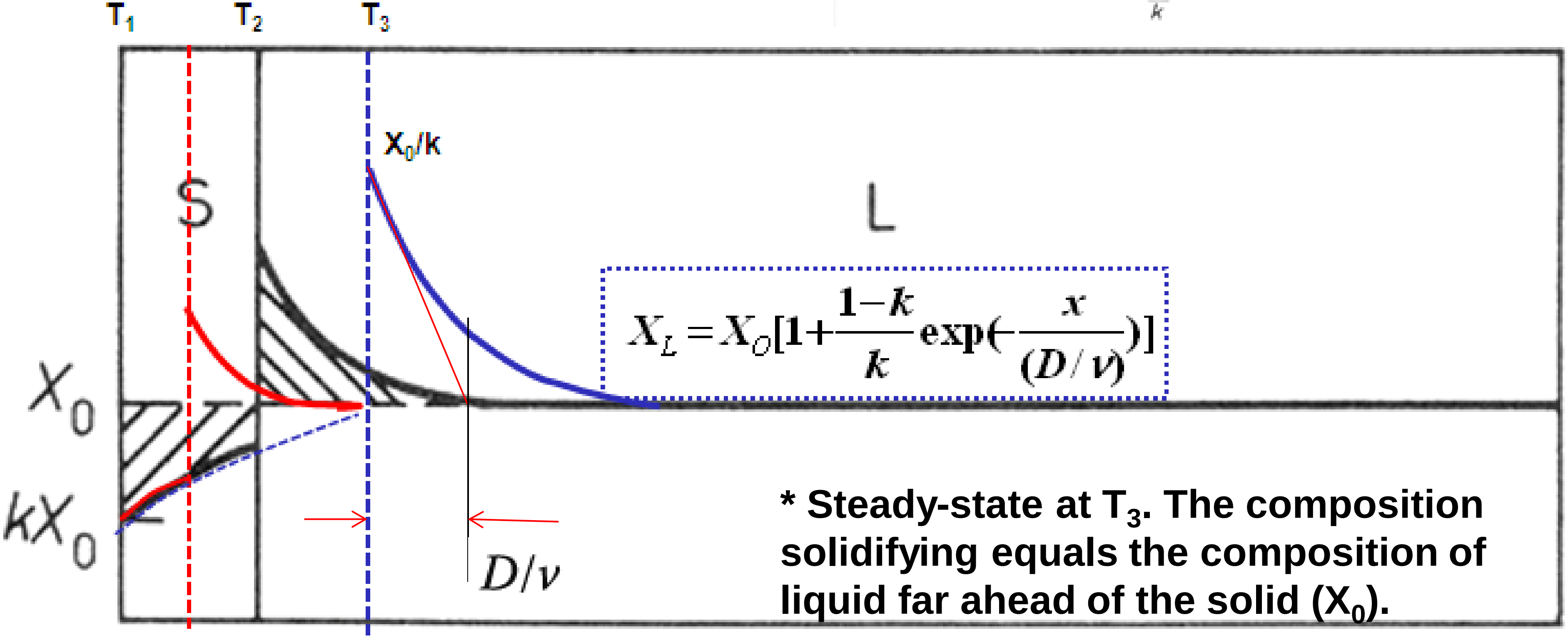
- Solidification of single-phase alloys

* No Diffusion on Solid,
Diffusional Mixing in the Liquid



$X_S = kX_L$

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

(Liquid→Solid: 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

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

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

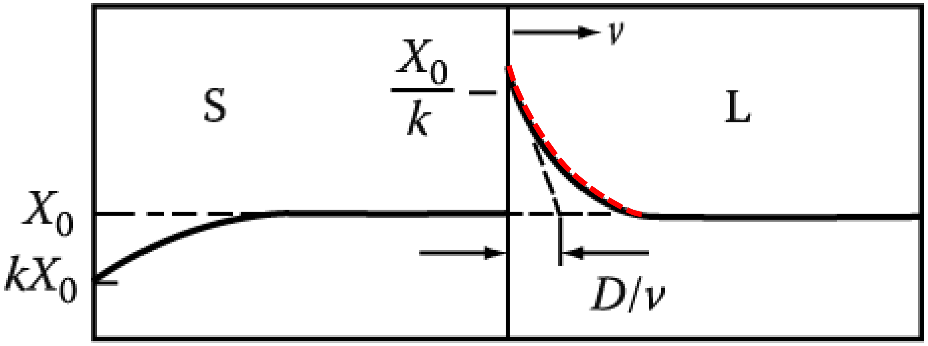
$$x = 0; X_L = X_0 / k$$

steady-state

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

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

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



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

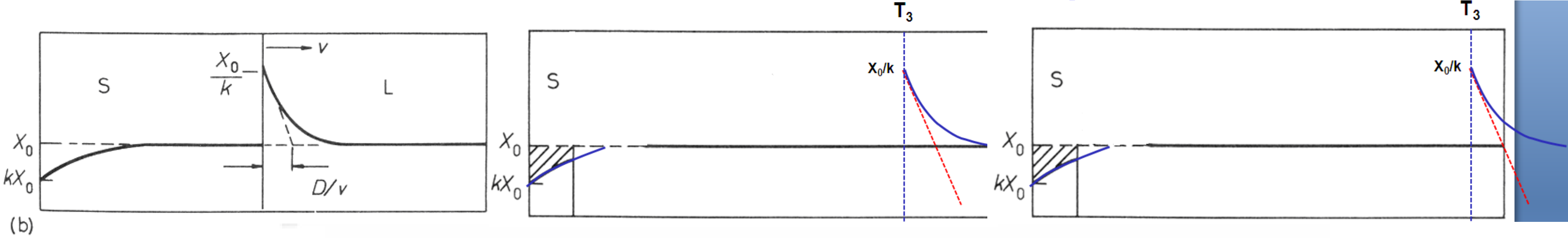
(X_L decreases exponentially from X_0/k at x=0, the interface, to X_0 at large distances from the interface. The concentration profile has a characteristic width of D/v.)

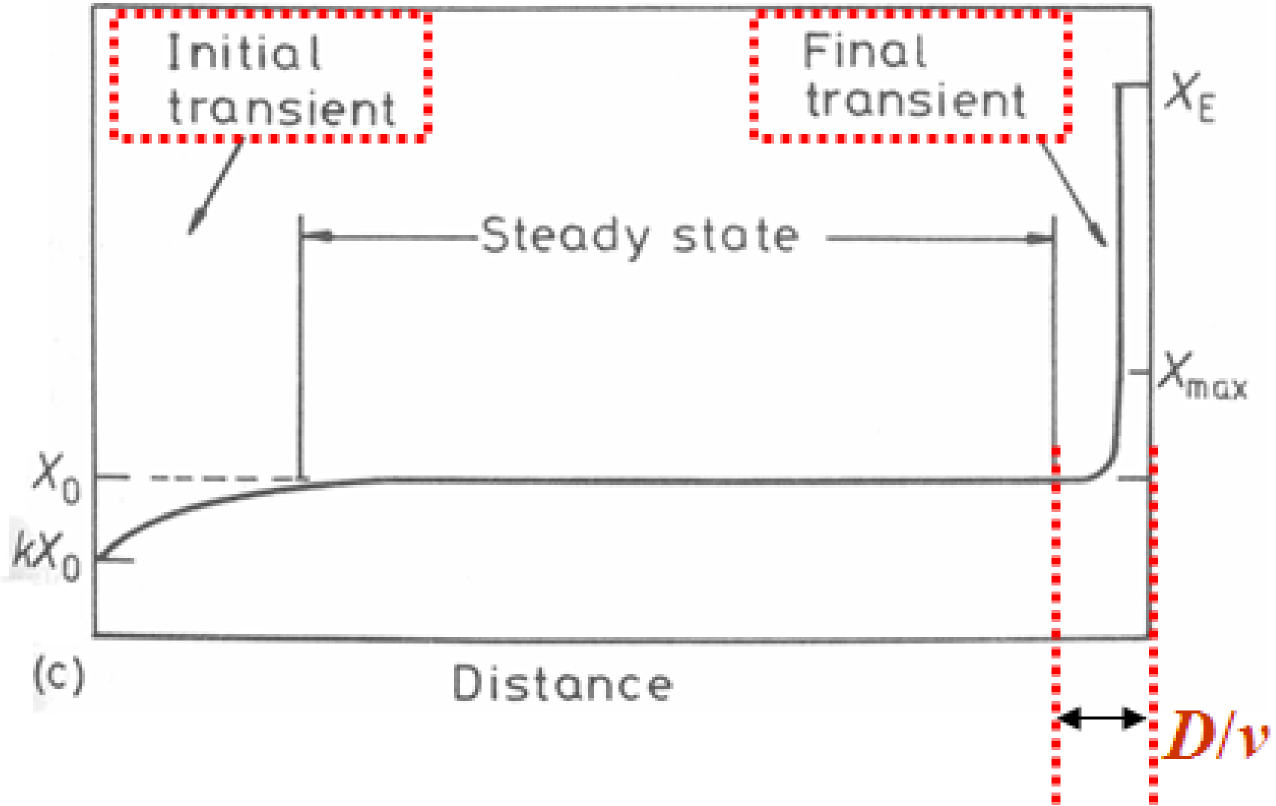
- **The concentration gradient in liquid in contact with the solid :**

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

"Alloy solidification" - Solidification of single-phase alloys

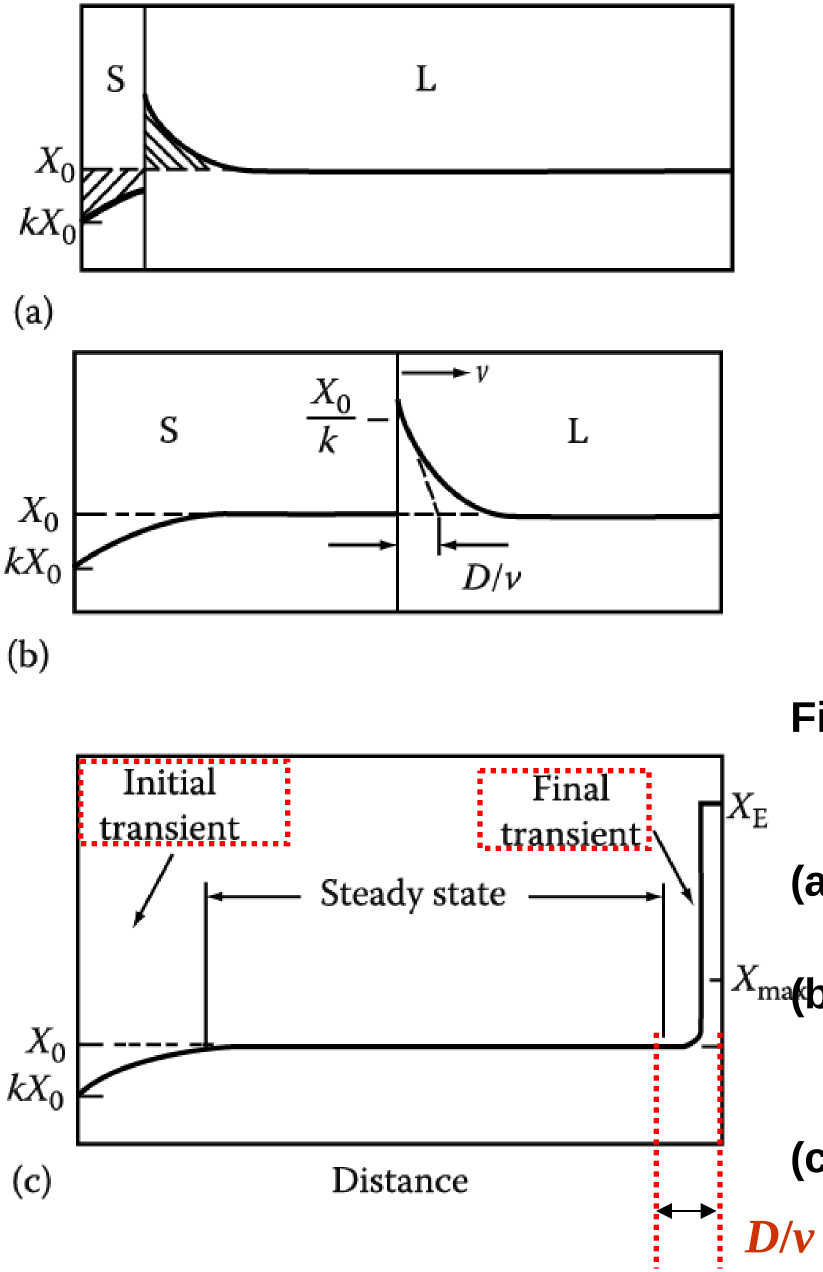
* No Diffusion on Solid, Diffusional Mixing in the Liquid





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



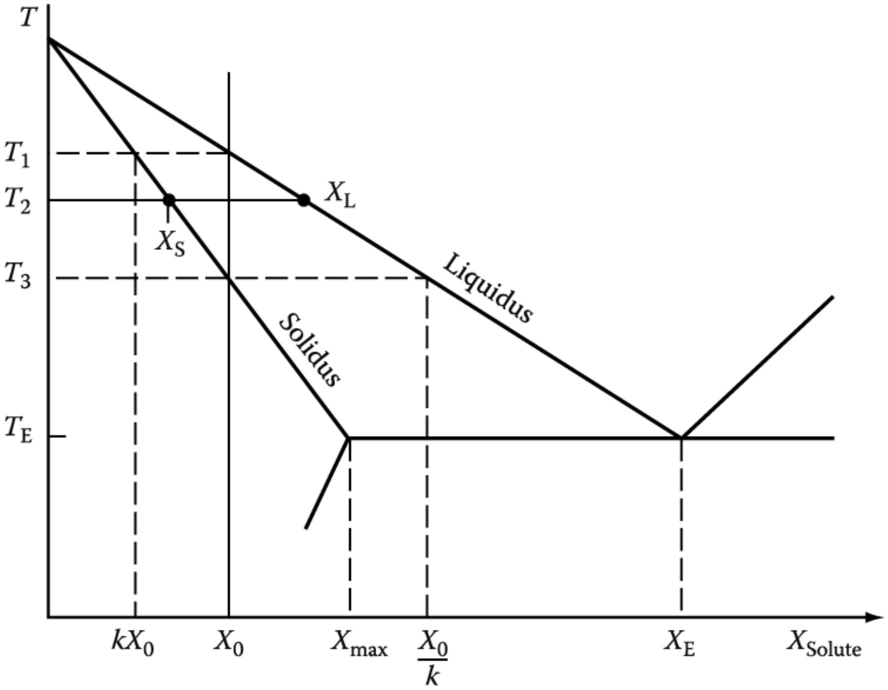


Fig. 4.22 Planar front solidification of alloy X_0 in Fig. 4.19 assuming no diffusion in solid and no stirring in the liquid.

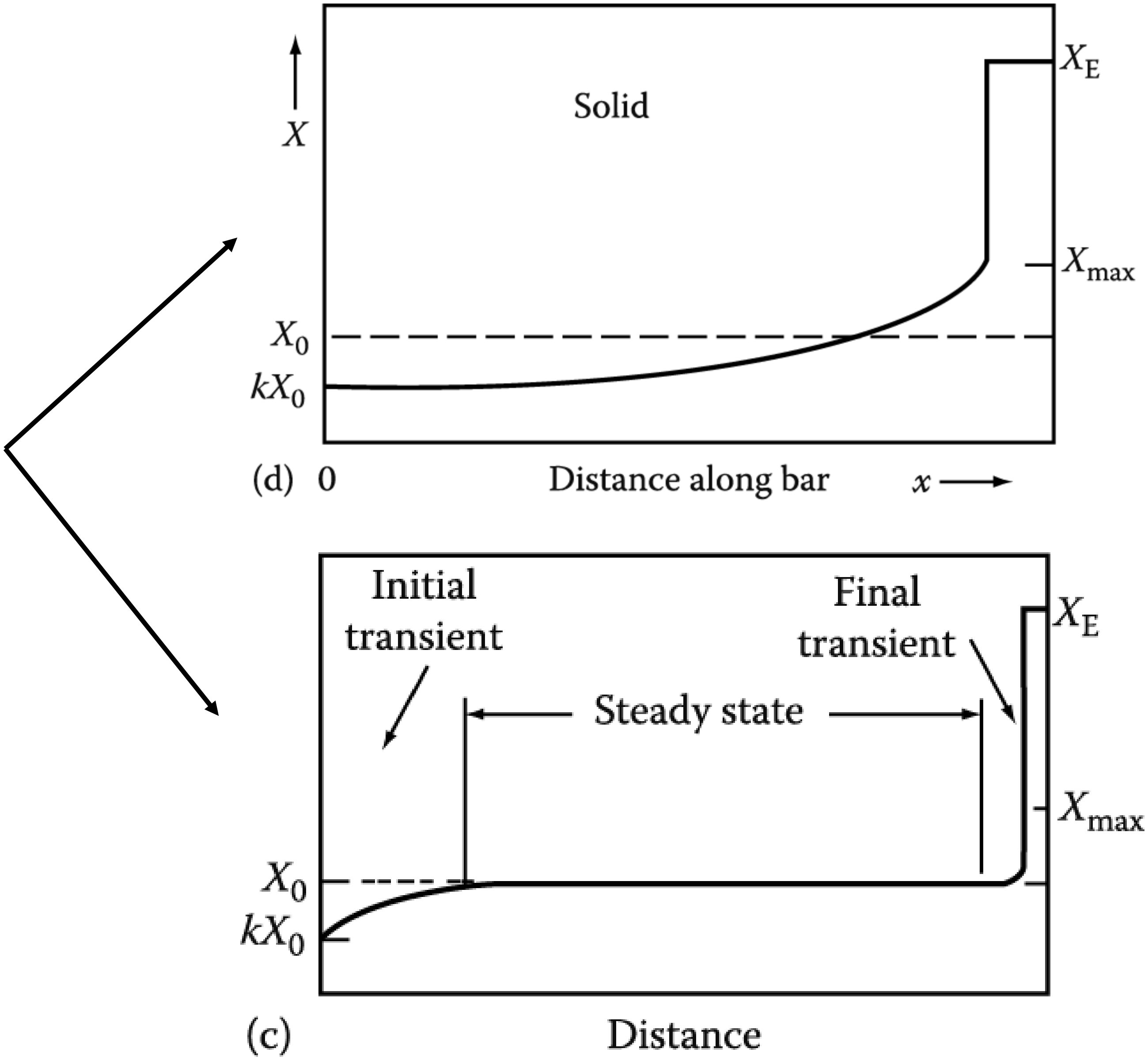
(a) Composition profile when S/L temperature is between T_2 and T_3 in Fig. 4.19.

(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



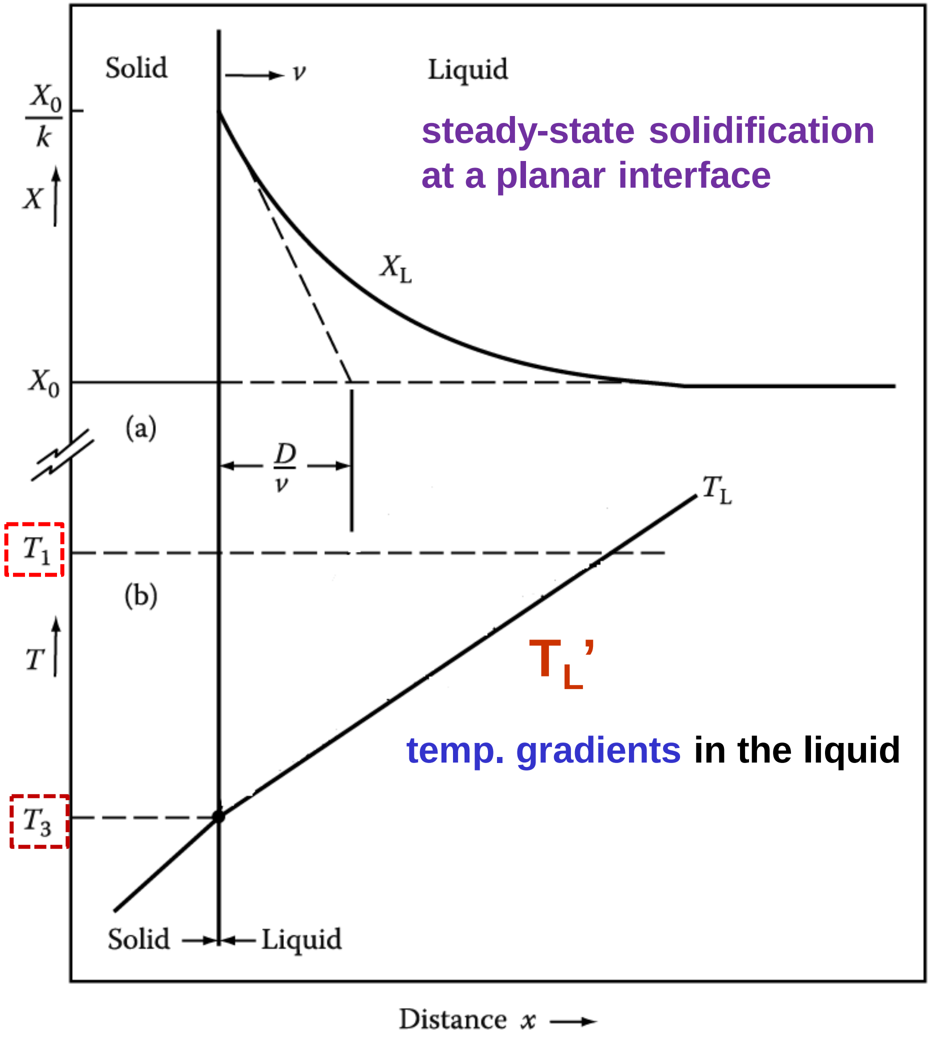
➡ **Zone Refining**

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.

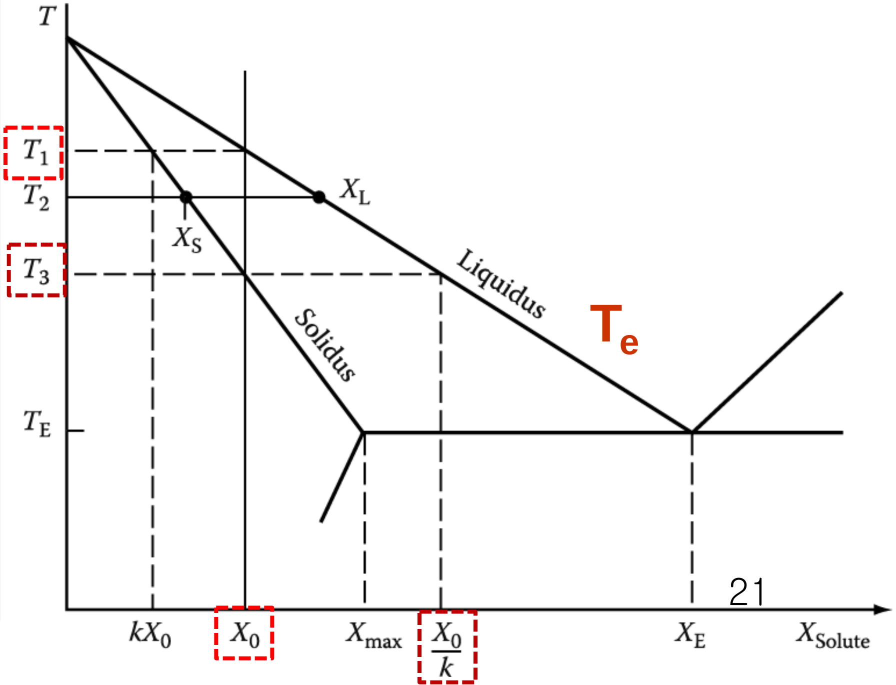


steady-state solidification at a planar interface

T_L'

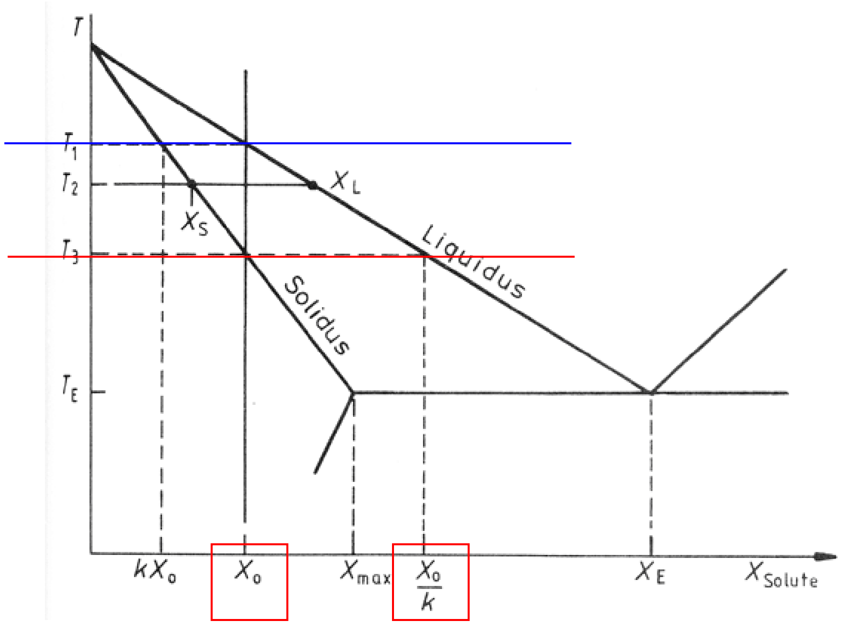
temp. gradients in the liquid

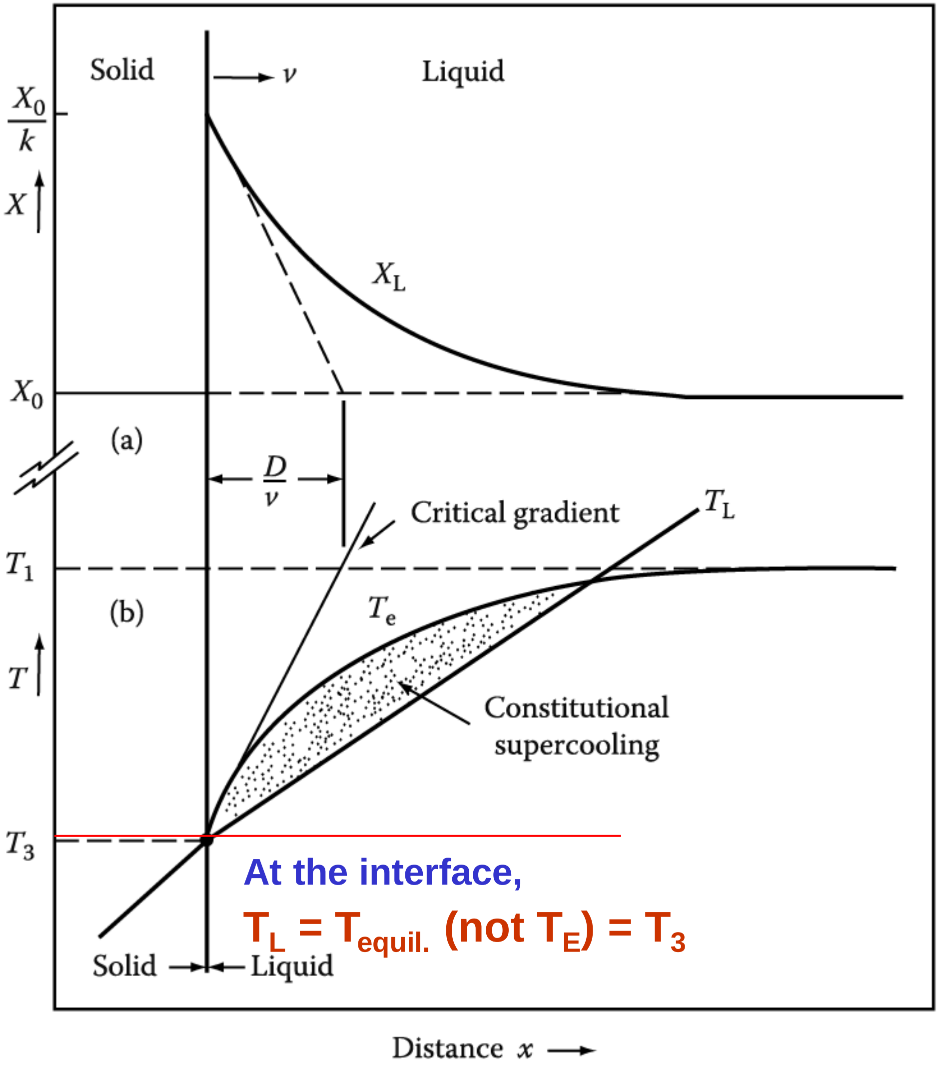
What would be T_e along the concentration profile ahead of the growth front during steady-state solidification?



* 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

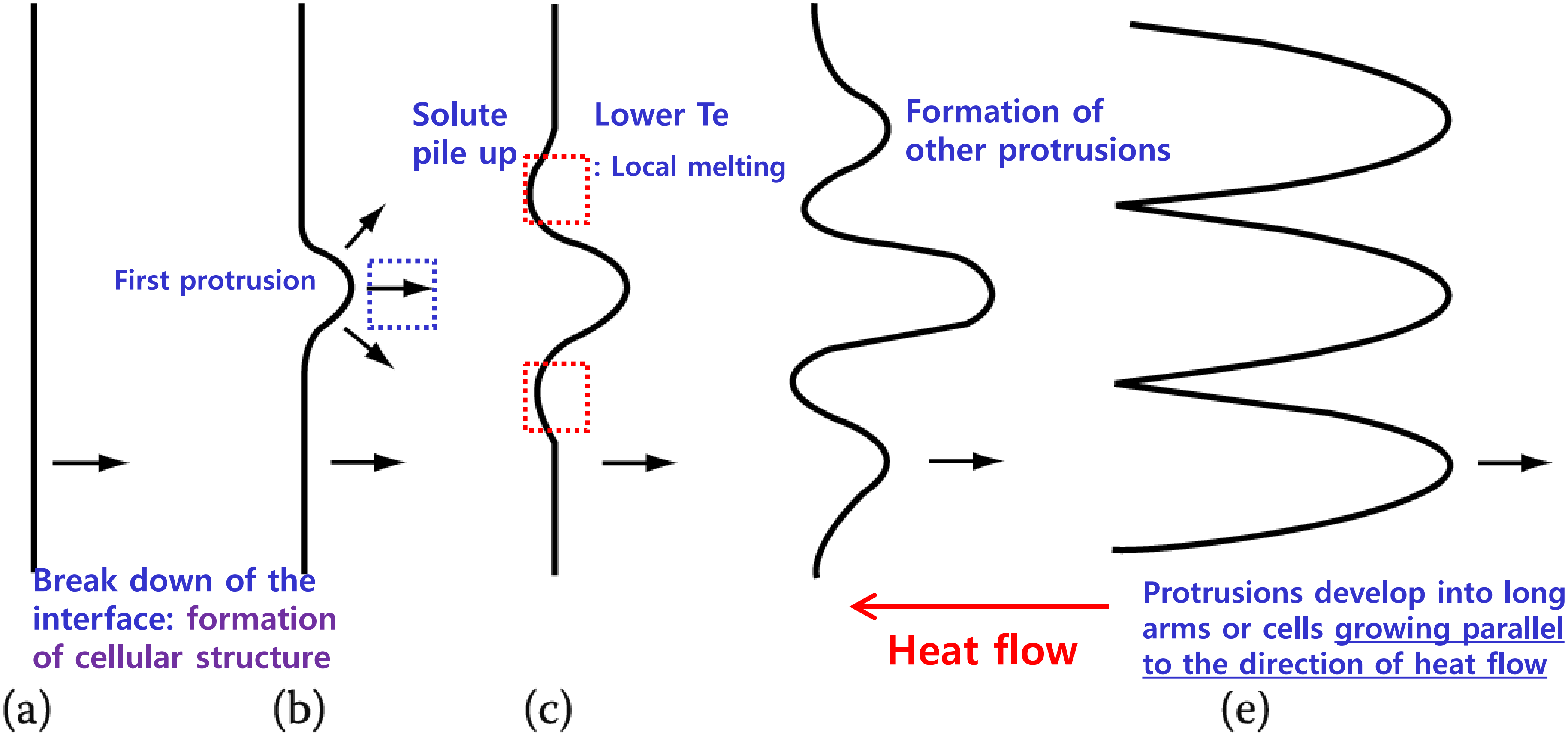
$T_L'/v < (T_1-T_3)/D$: Constitutional supercooling→ cellular/ dendritic growth

Q: Planer → Cell structure → Dendrite?

by constitutional supercooling in superheated liquid

Cellular Solidification: formation by constitutional supercooling in <u>"superheated liquid"</u>

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



Solute pile up

Lower Te : Local melting

Formation of other protrusions

First protrusion

Break down of the interface: formation of cellular structure

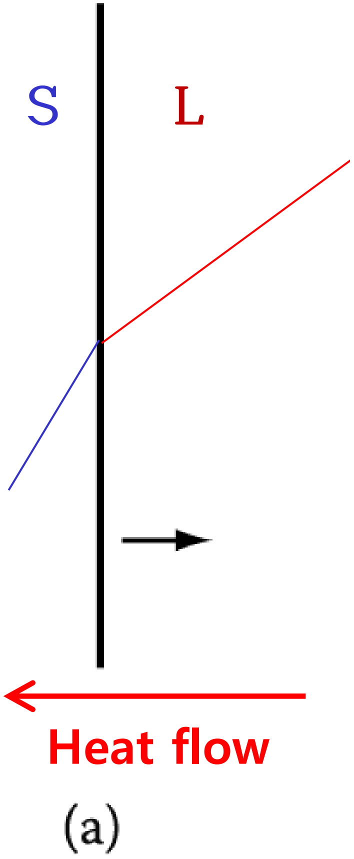
Heat flow

Protrusions develop into long arms or cells <u>growing parallel to the direction of heat flow</u>

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)



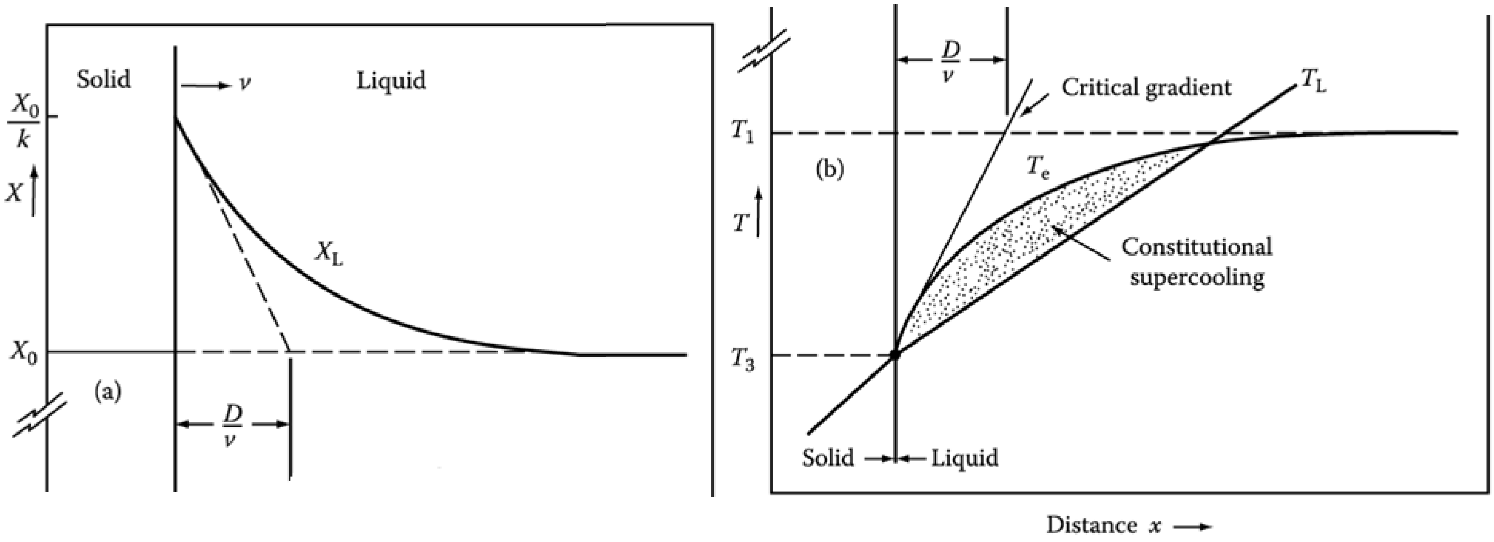
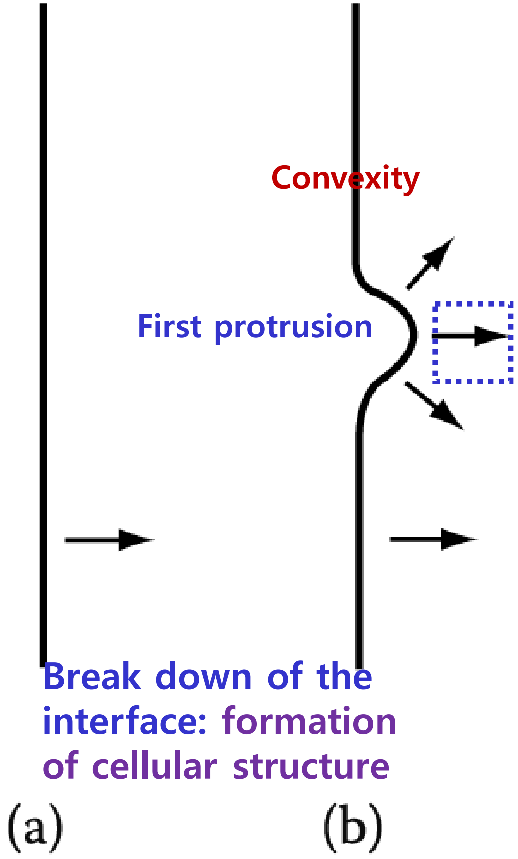


Fig. 5.30. Supercooling ahead of planar interface

<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)



Convexity

First protrusion

Break down of the interface: formation of cellular structure

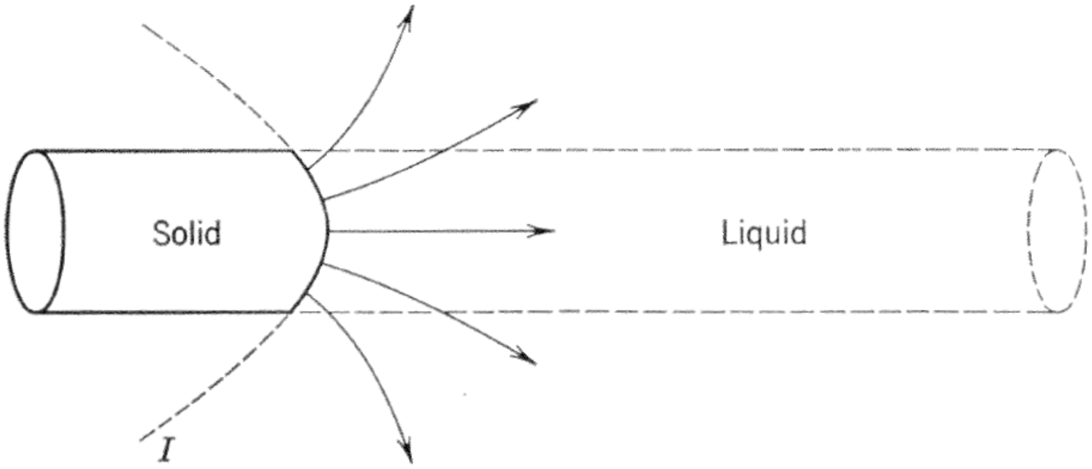
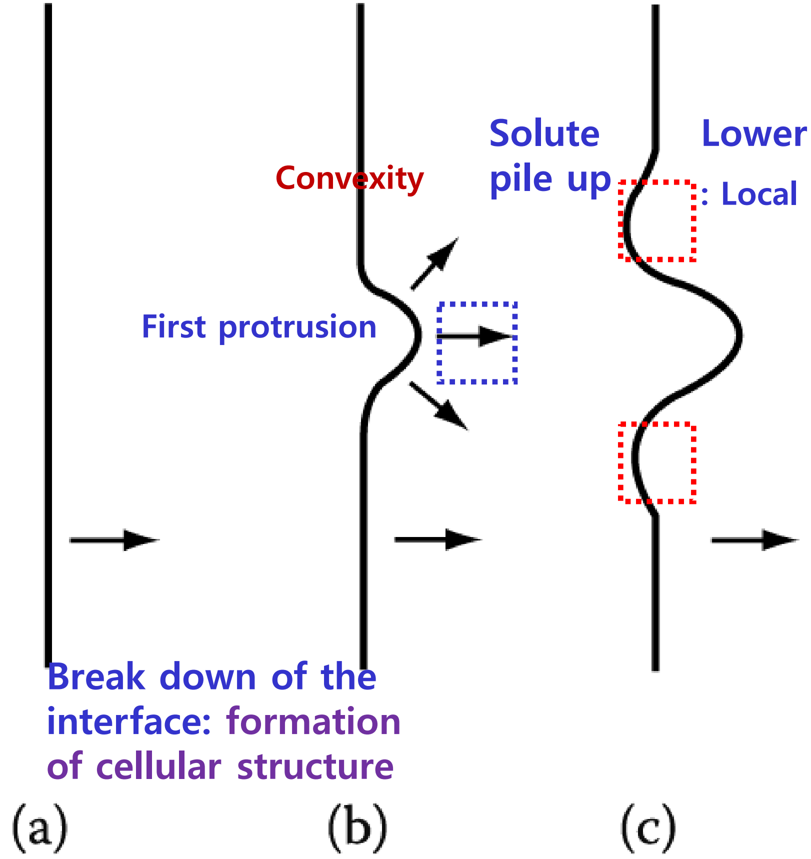


Fig. 5.14. Solute diffusion ahead of a convex interface

<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)



Convexity

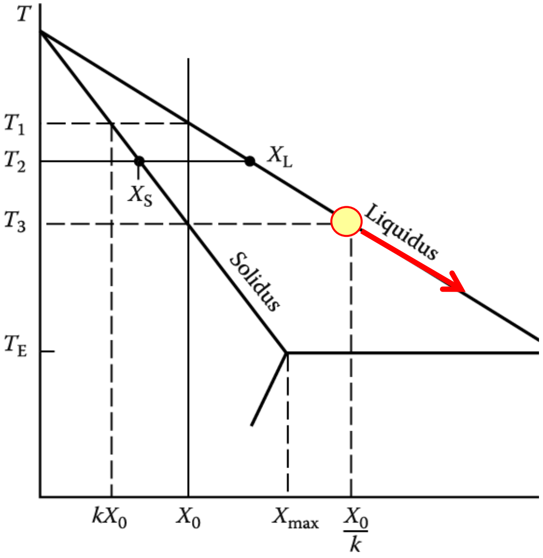
First protrusion

Solute pile up

Lower T_{equil} : Local melting

Break down of the interface: formation of cellular structure

Solute pile up→ $\mathbf{T_e}$ ↓ → $\mathbf{T_L'}$ ↑ → $\boldsymbol{v}$ ↓



Heat Balance Equation

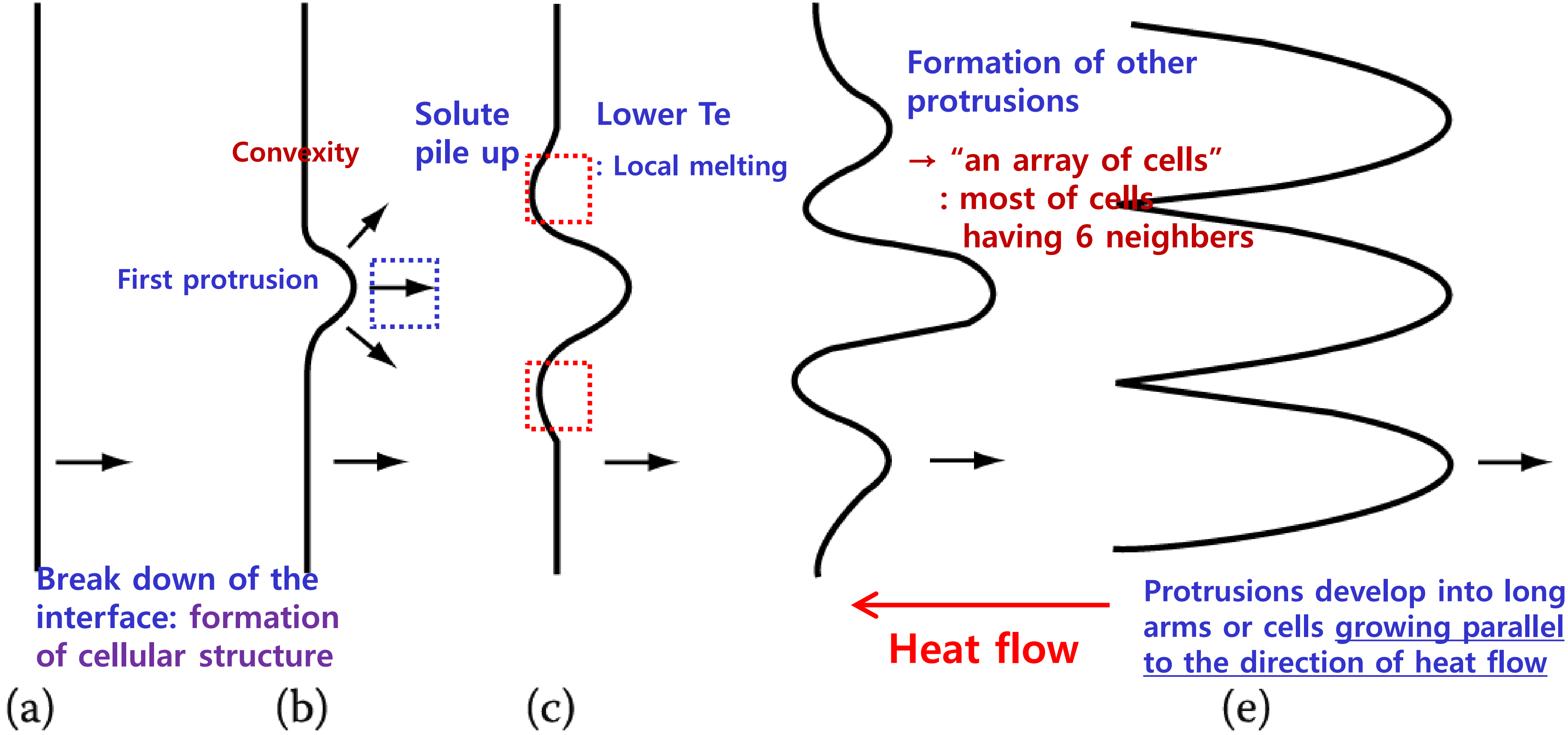
$$K_S T_S' = K_L T_L' + v L_V$$

K: thermal conductivity

<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)



Convexity

First protrusion

Solute pile up

Lower Te

: Local melting

Formation of other protrusions

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

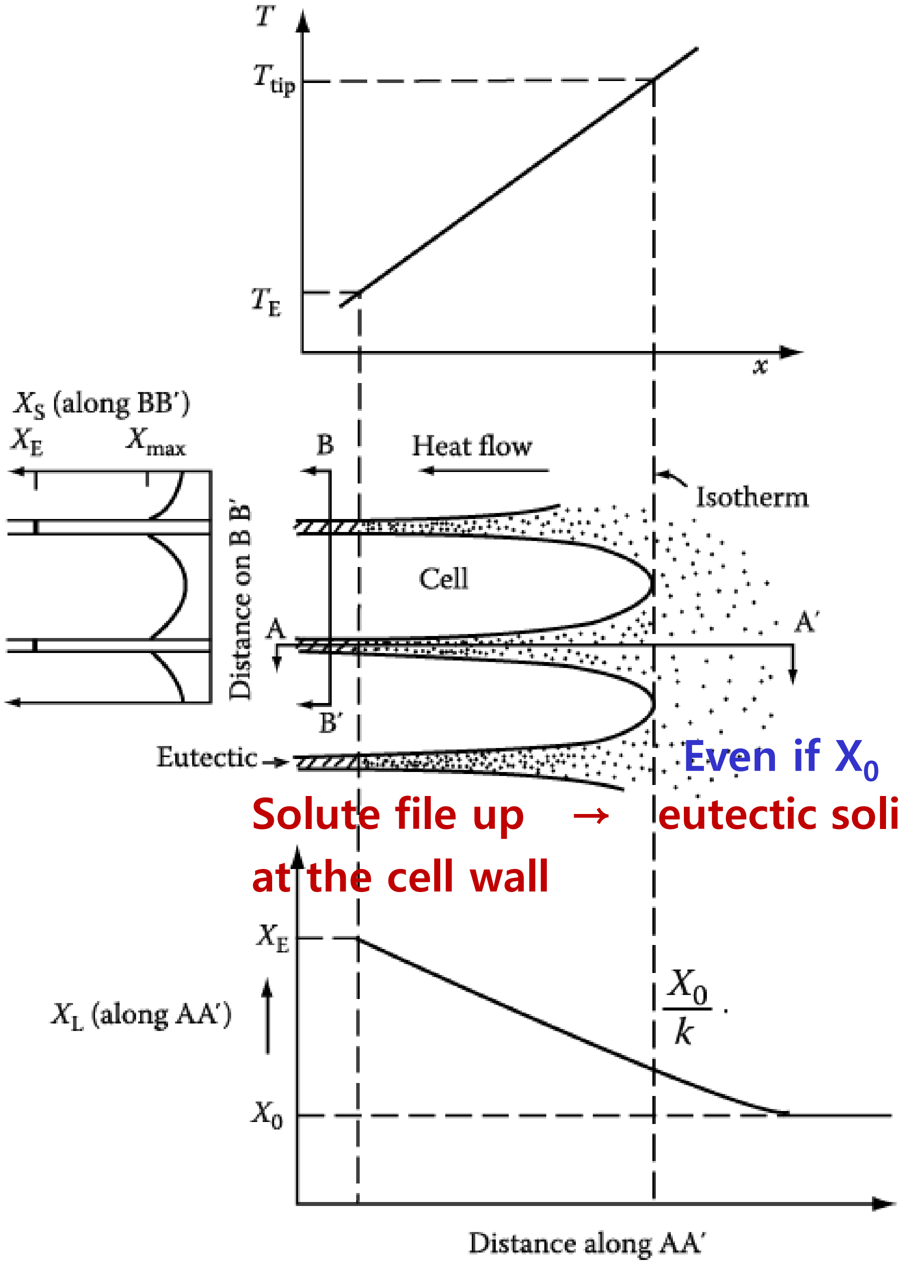
Break down of the interface: formation of cellular structure

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 2nd phases at the cell wall

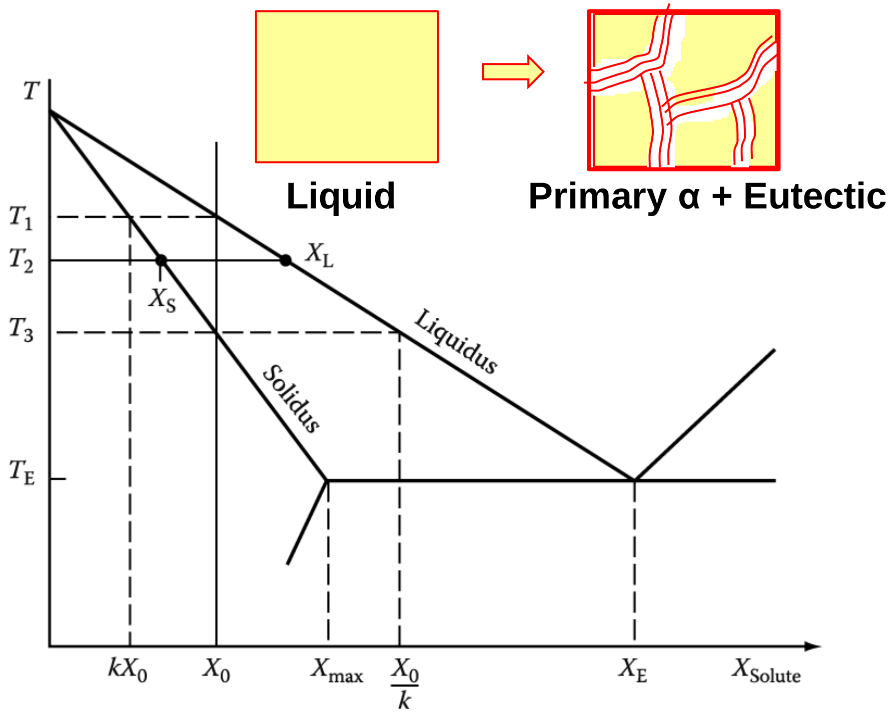
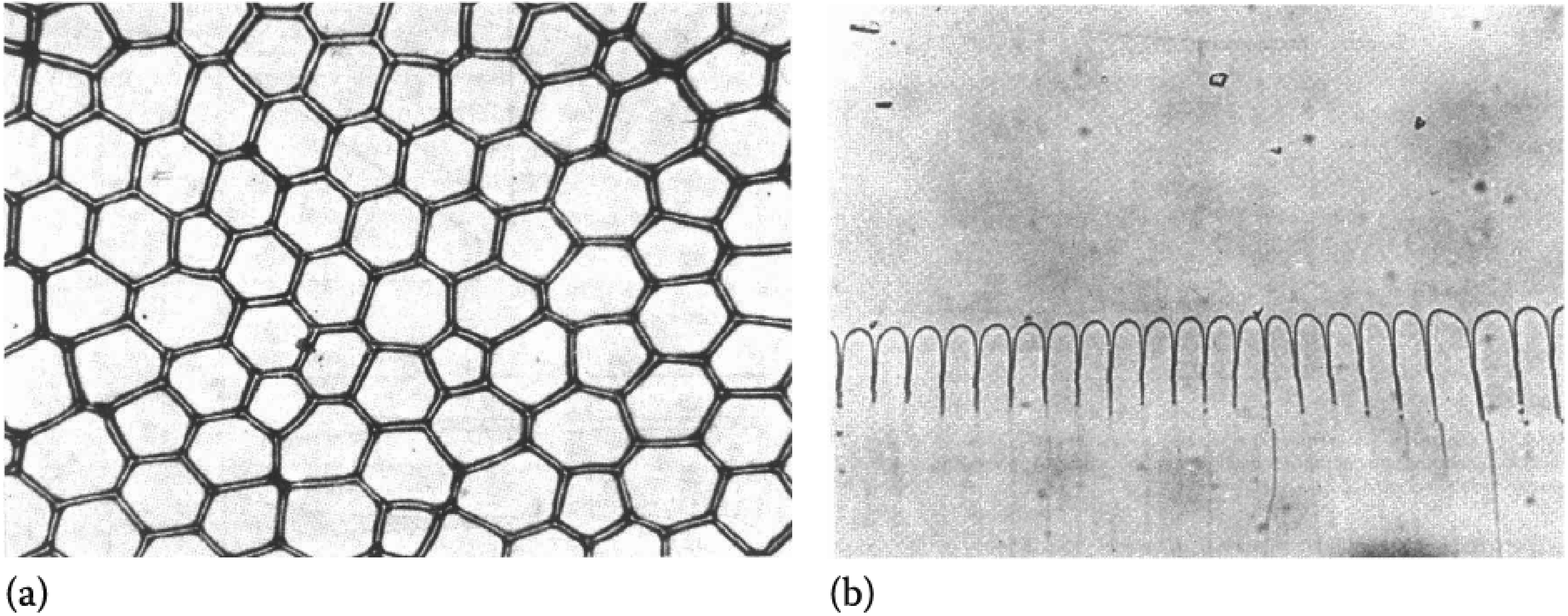


Fig. 4.25 Temperature and solute distributions associated with cellular solidification. Note that solute enrichment in the liquid between the cells, and coring in the cells with eutectic in the cell walls.



* 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)

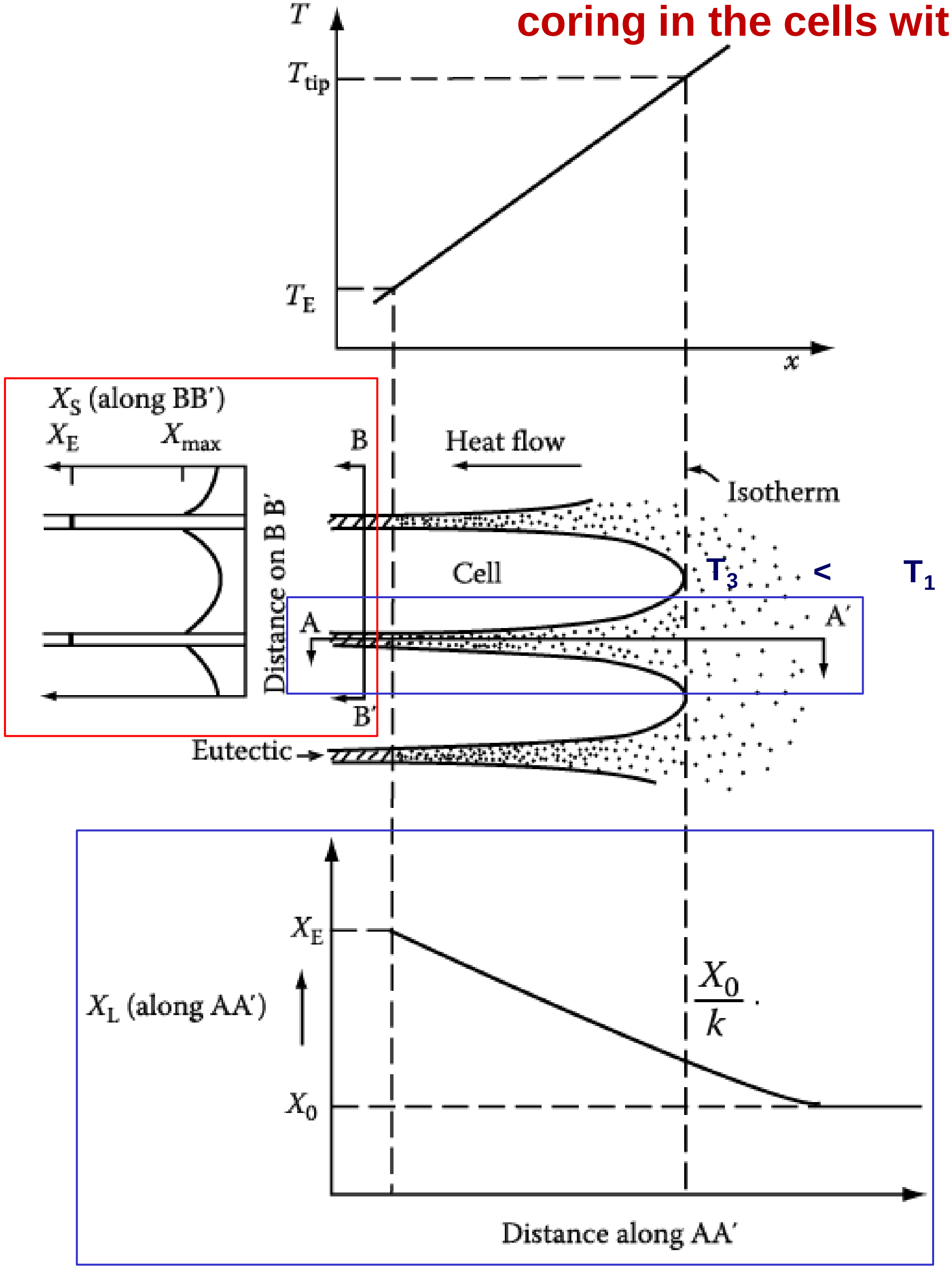
(after J.W. Rutter in Liquid Metals and Solidification, American Society for Metals, 1958, p. 243).

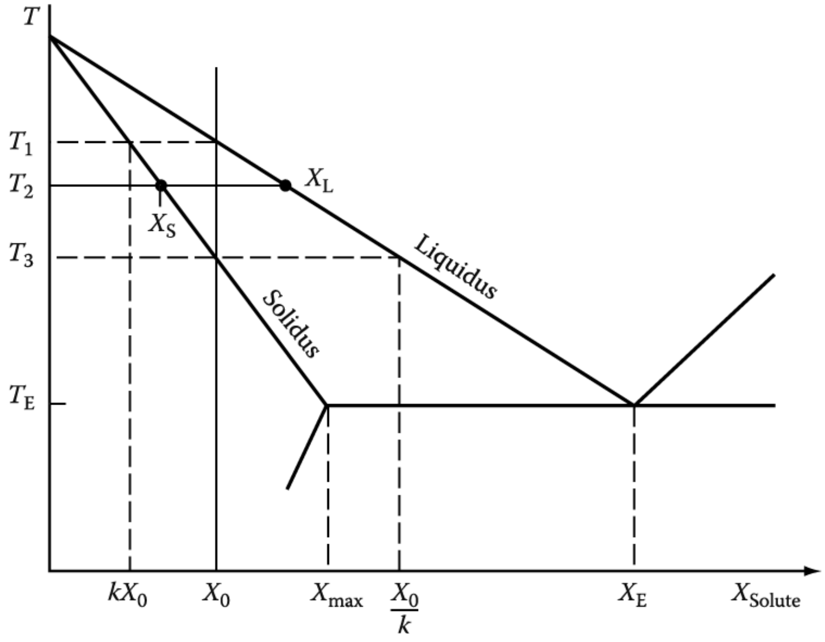
(b) Longitudinal view of cells in carbon tetrabromide (x 100)

(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.



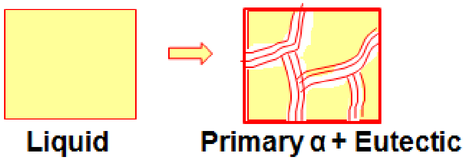


2) Tips of the cells grow into the hottest liquid and therefore contain the least solute.

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.

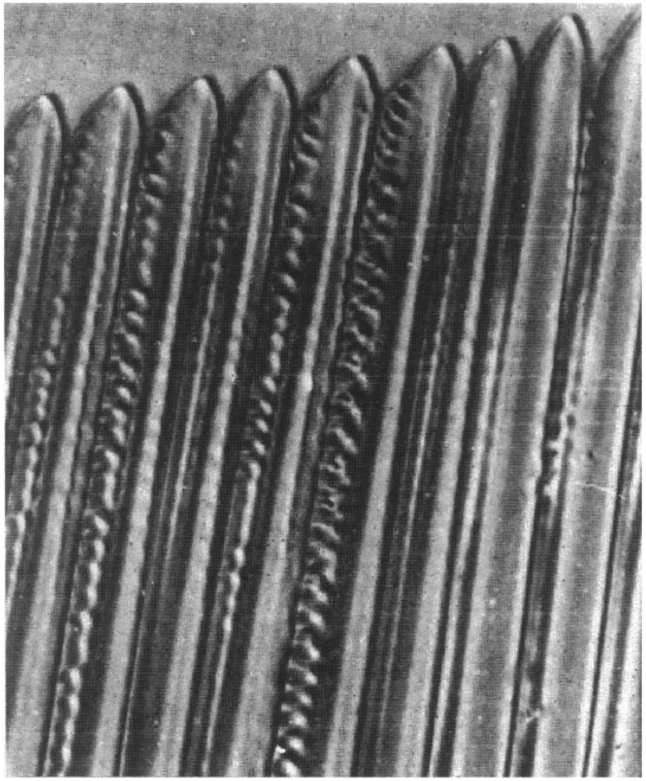


Fig. 4.27 Cellular dendrites in carbon tetrabromide.

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

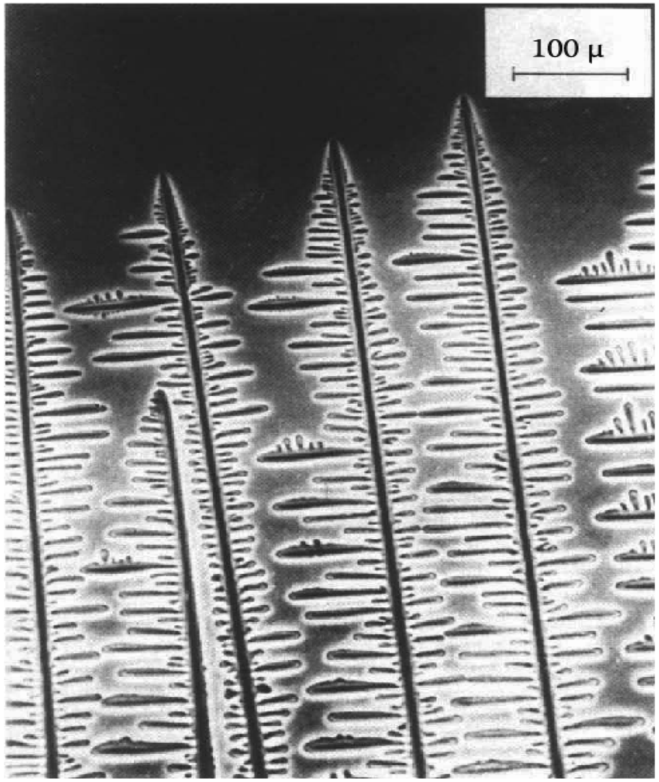


Fig. 4.28 Columnar dendrites in a transparent organic alloy.

(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)

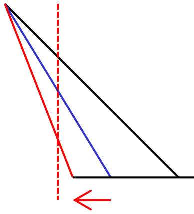
→ **Large solidification range of T_1-T_3 or high v promotes protrusions.**

⇨ **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/ 가지
들의 square array/ Dendrite
성장방향쪽으로 성장방향 변화

성장하는 crystal로 부터 발생한
잠열을 과냉각 액상쪽으로 방출함
에 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