2020 Spring

Advanced Solidification

05.20.2020

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5. Redistribution of solute during solidification

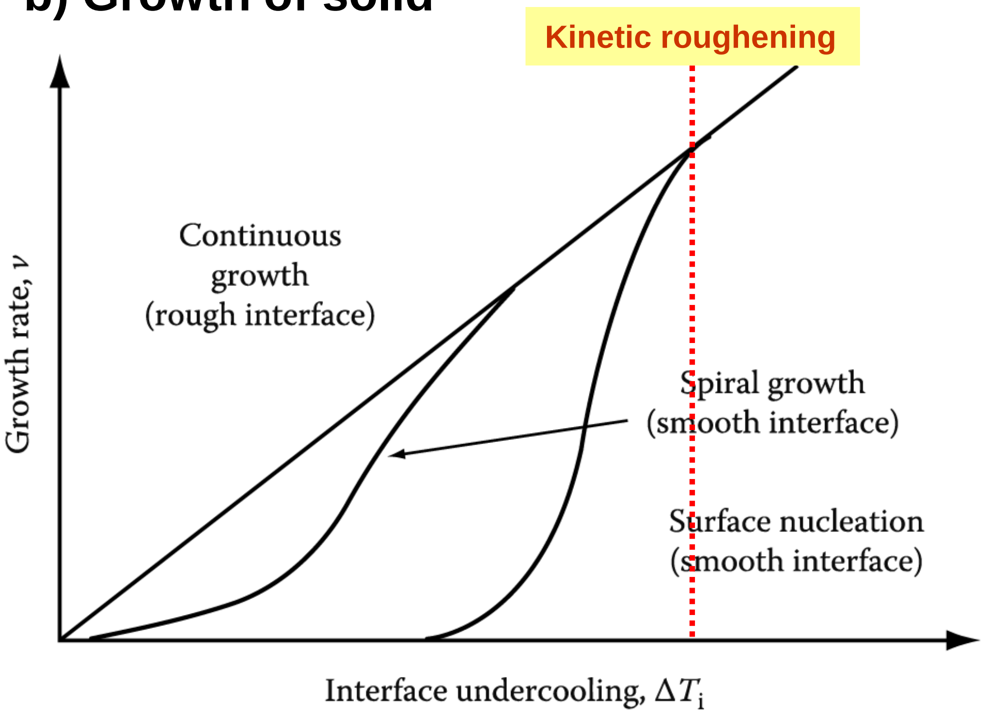
Solidification: Liquid ⟶ Solid

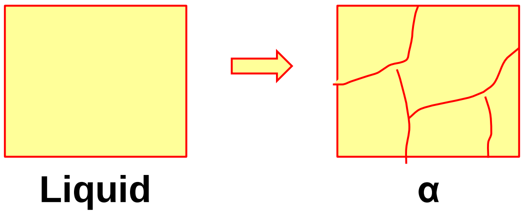
- Undercooling ΔT
- Interfacial energy
  γ_{SL} / S(θ) wetting angle

1) Pure Metals: Nucleation and Growth

a) homogeneous Nucleation or Heterogeneous Nucleation

b) Growth of solid





No compositional change during solidification

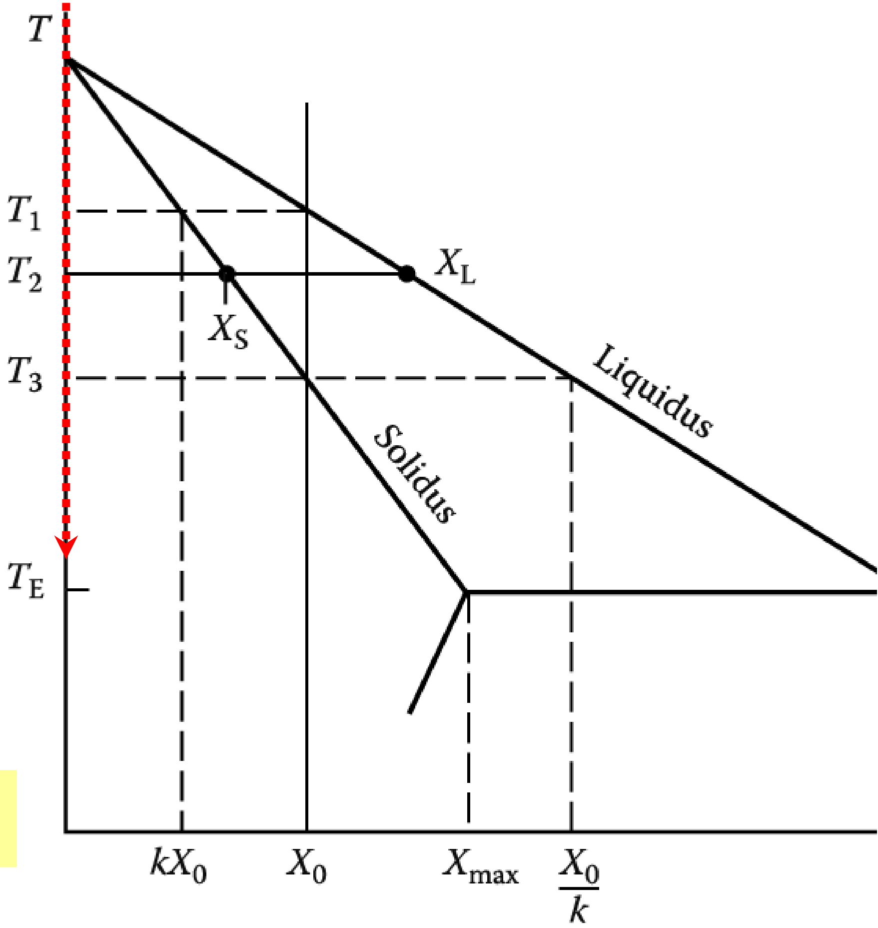


Fig. 4.19 A hypothetical phase diagram.

"Alloy solidification"

1. Solidification of single-phase alloys

- **Three limiting cases**

1) Equilibrium Solidification: perfect mixing in solid and liquid

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

3) No Diffusion in Solid, Perfect Mixing in Liquid

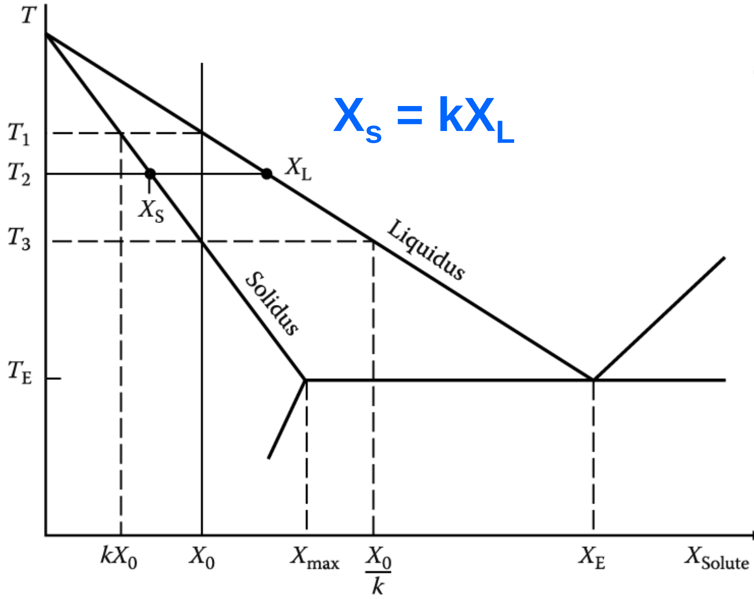
- Planar S/L interface → unidirectional solidification

- Superheated liquid

- Cellular and Dendritic Solidification

- Supercooled liquid

1) Equilibrium Solidification : perfect mixing in solid and liquid



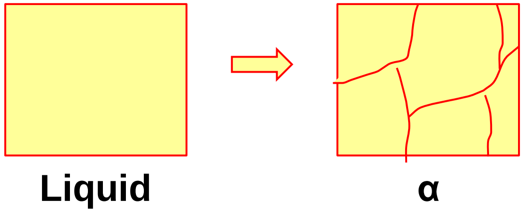
$$X_s = kX_L$$

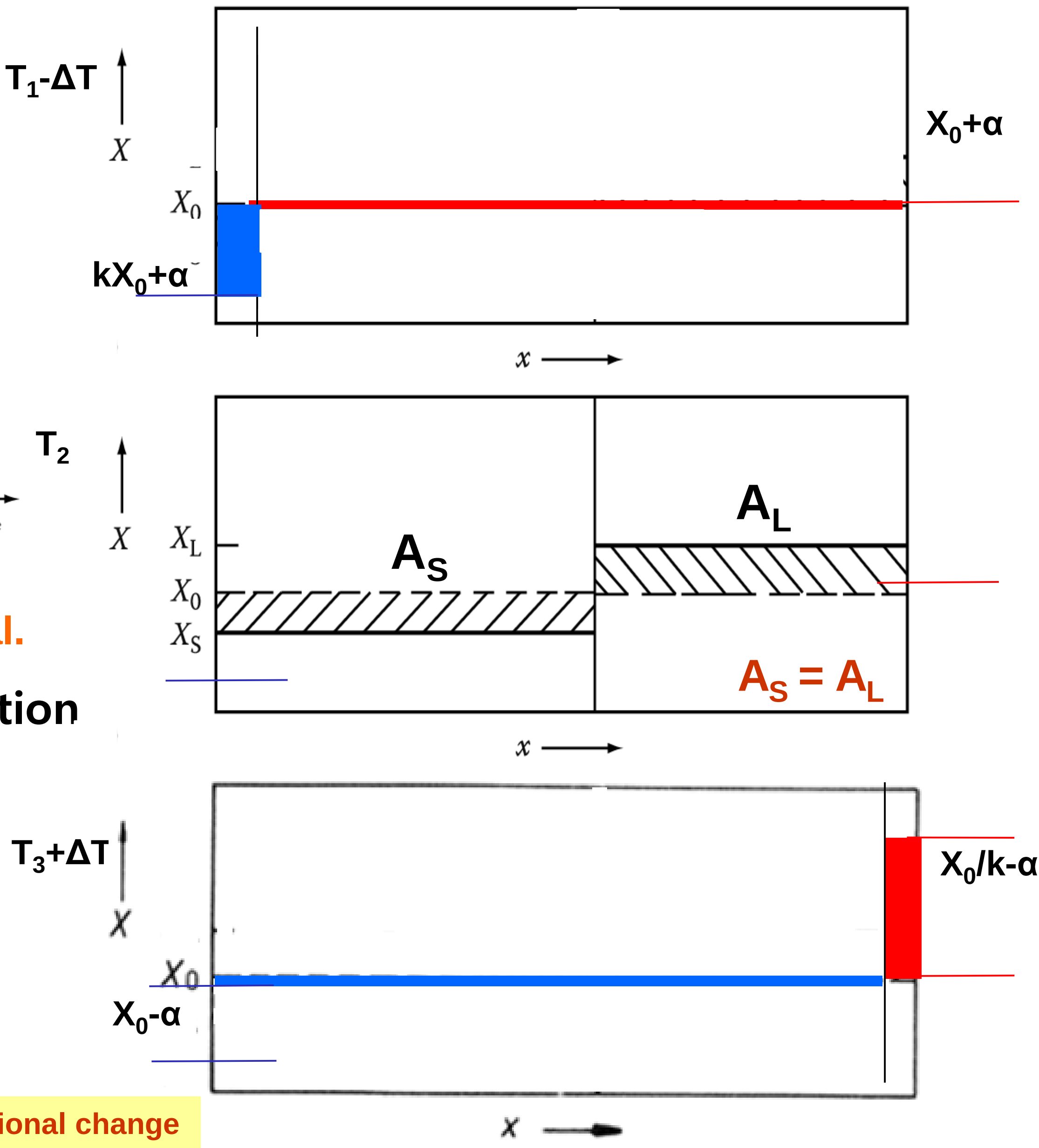
Conservation of solute requires the two shaded areas to be equal.

* **Equilibrium solute concentration**

$$kX_0 \leq X_s \leq X_0$$

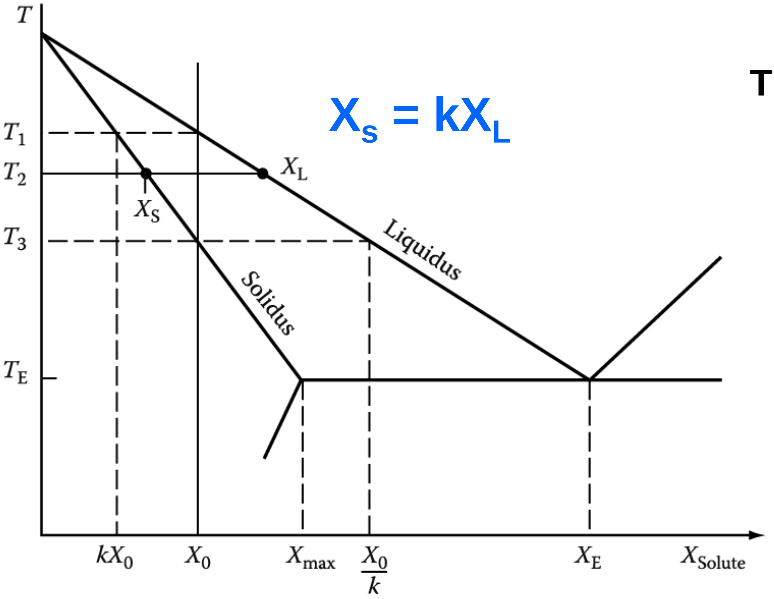
$$X_0 \leq X_L \leq X_0/k < X_E$$





Compositional change during solidification

1) Equilibrium Solidification : perfect mixing in solid and liquid



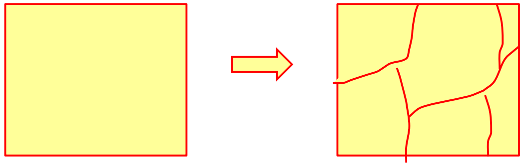
$X_s = kX_L$

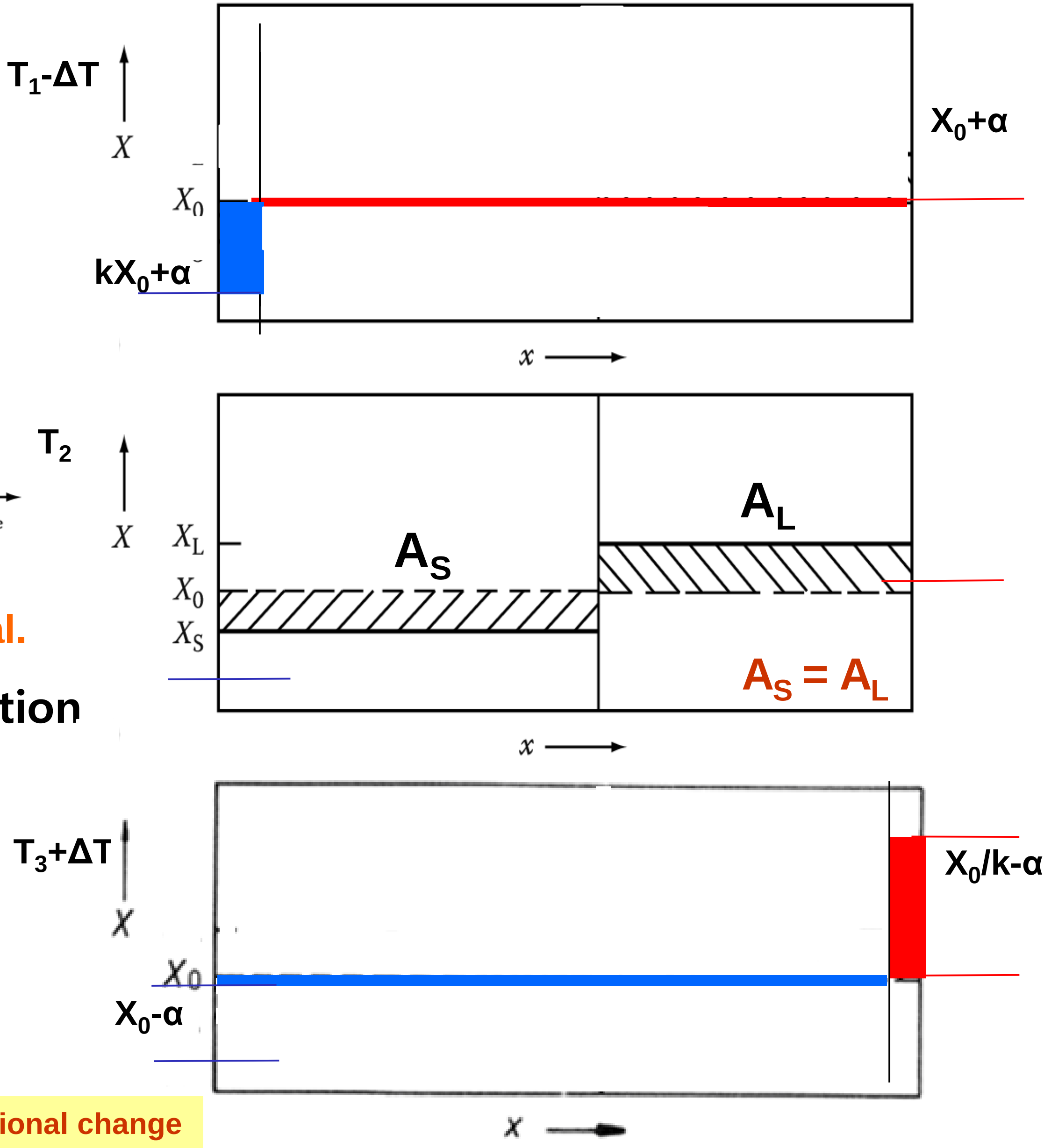
Conservation of solute requires the two shaded areas to be equal.

* **Equilibrium solute concentration**

$kX_0 \le X_s \le X_0$

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

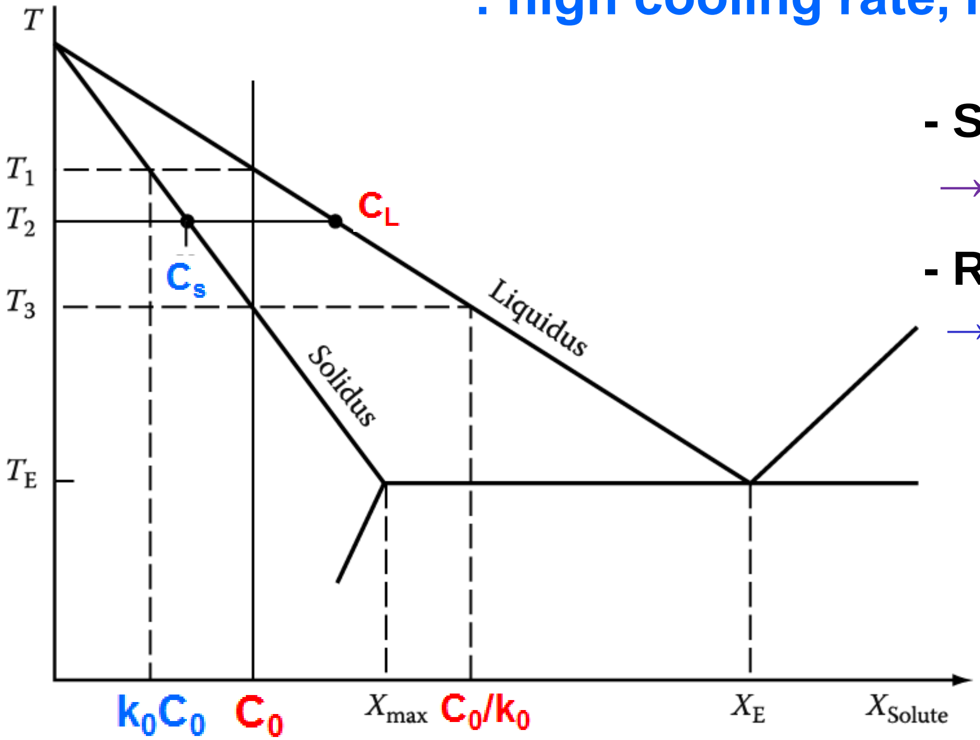




Compositional change during solidification

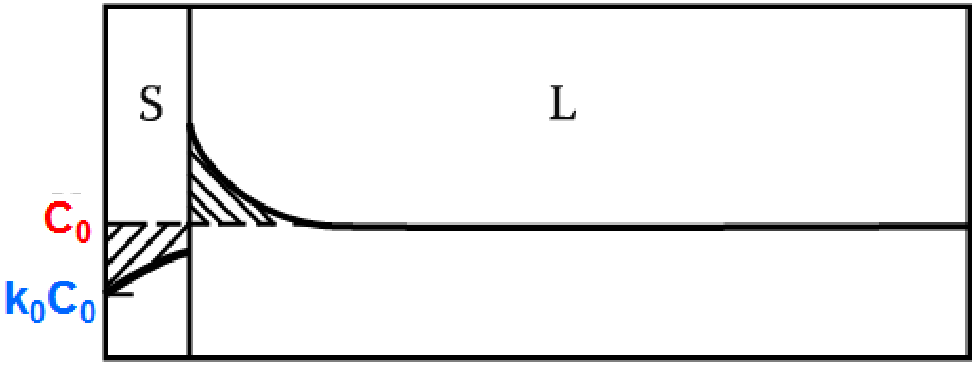
2) No Diffusion on Solid, Diffusional Mixing in the Liquid

: 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 : C_0/k_0, solid: C_0

local equil. at S/L interface



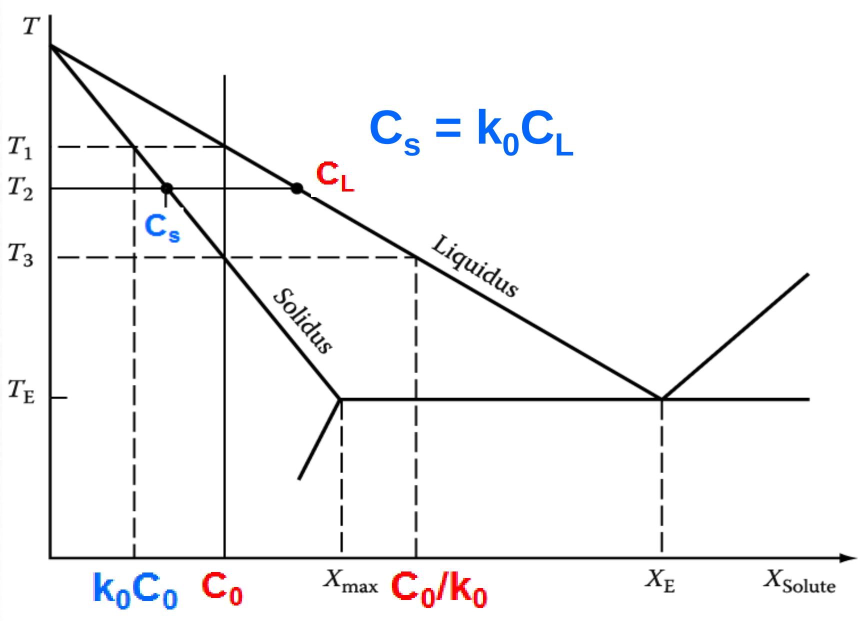
Composition profile at $T_2 < T_{S/L} < T_3$?

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

"Alloy solidification"

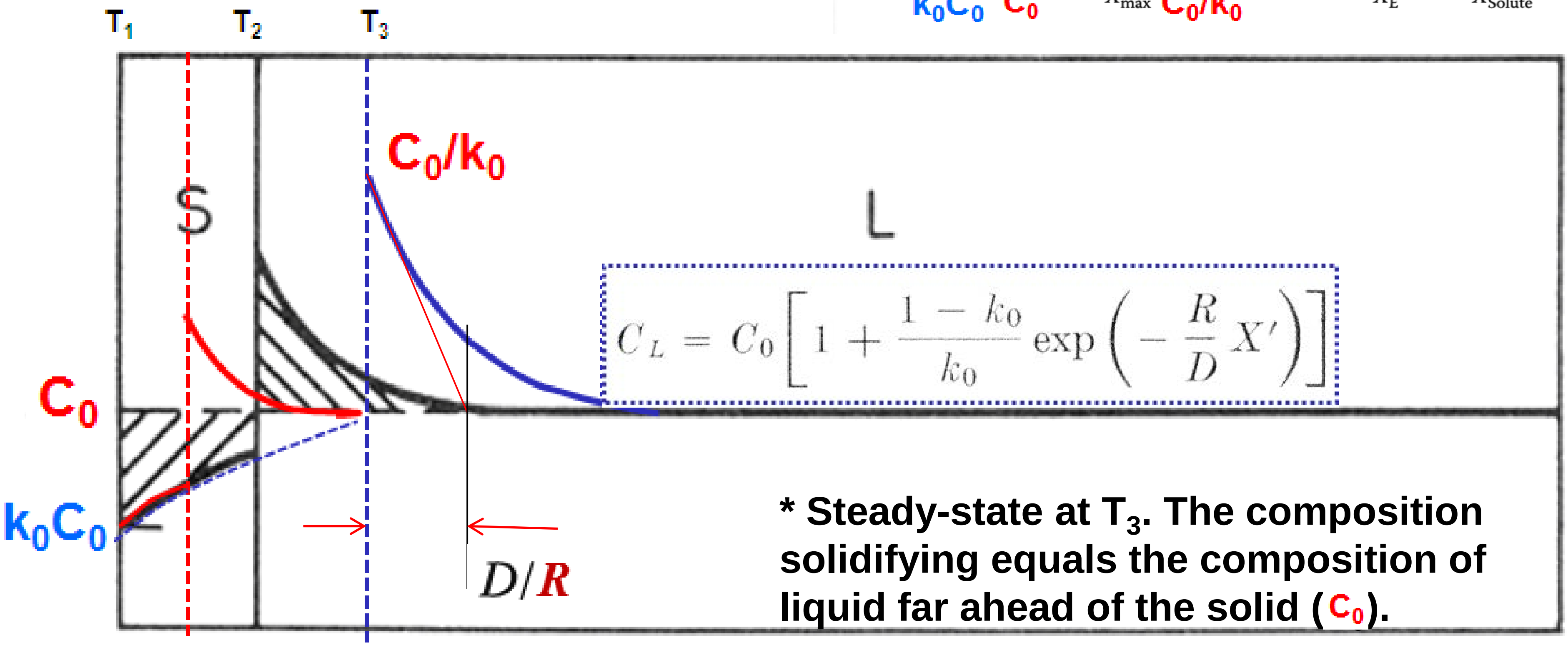
- Solidification of single-phase alloys

* No Diffusion on Solid,
Diffusional Mixing in the Liquid



$C_s = k_0C_L$

Interface temperature

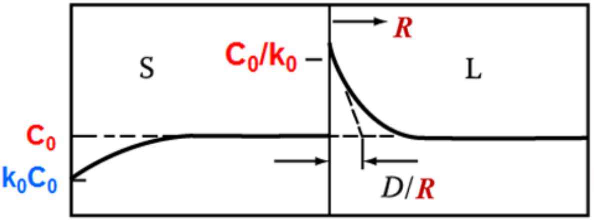


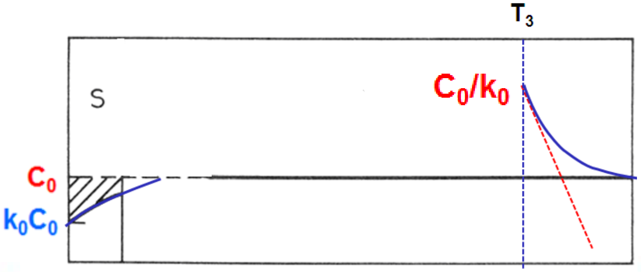
$$C_L = C_0\left[1 + \frac{1-k_0}{k_0}\exp\left(-\frac{R}{D}X'\right)\right]$$

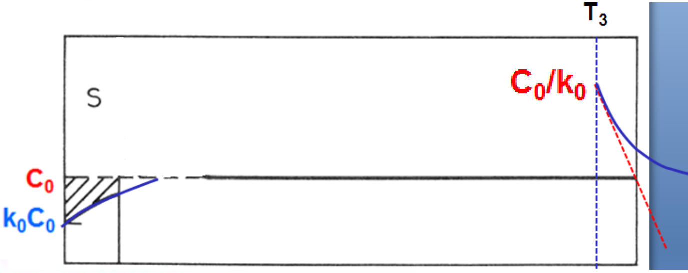
* Steady-state at T_3. The composition solidifying equals the composition of liquid far ahead of the solid (C_0).

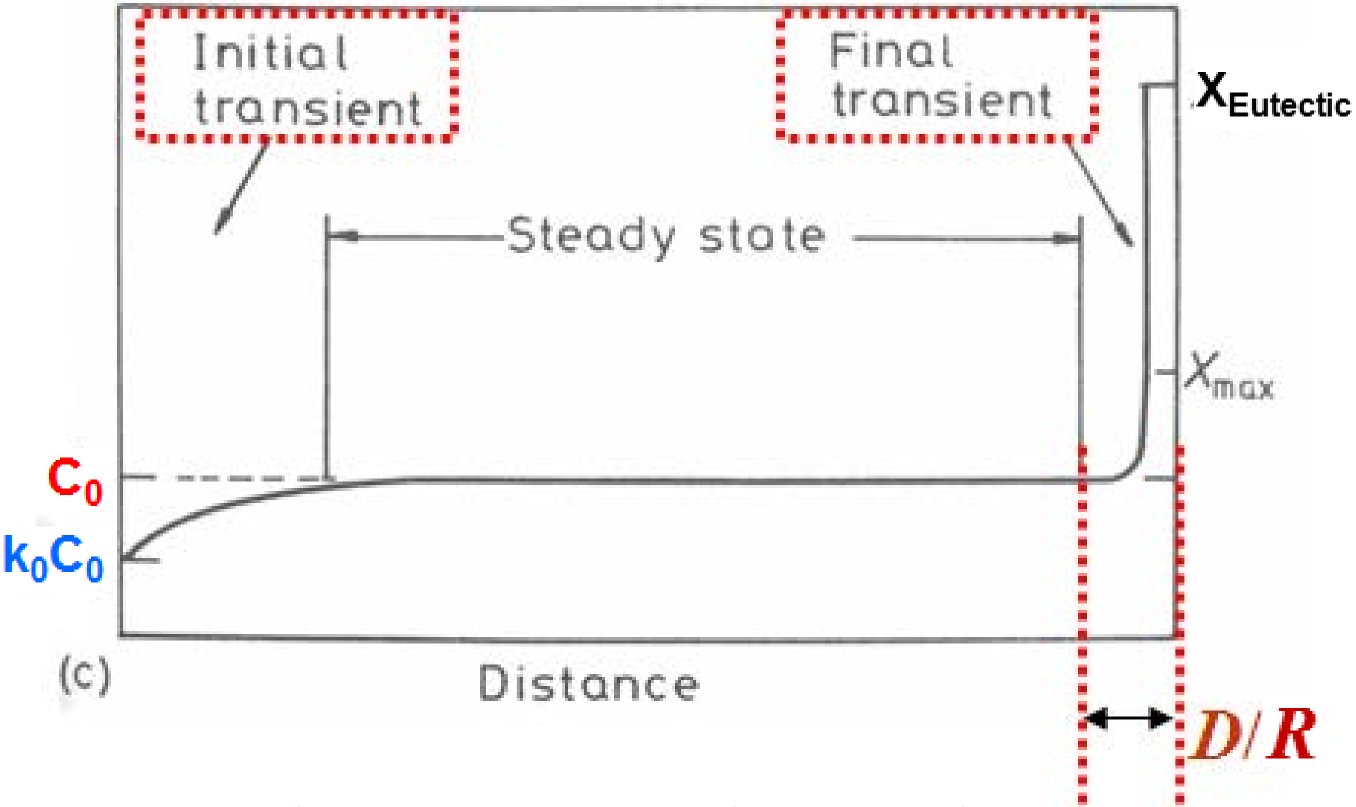
"Alloy solidification" - Solidification of single-phase alloys

* No Diffusion on Solid, Diffusional Mixing in the Liquid









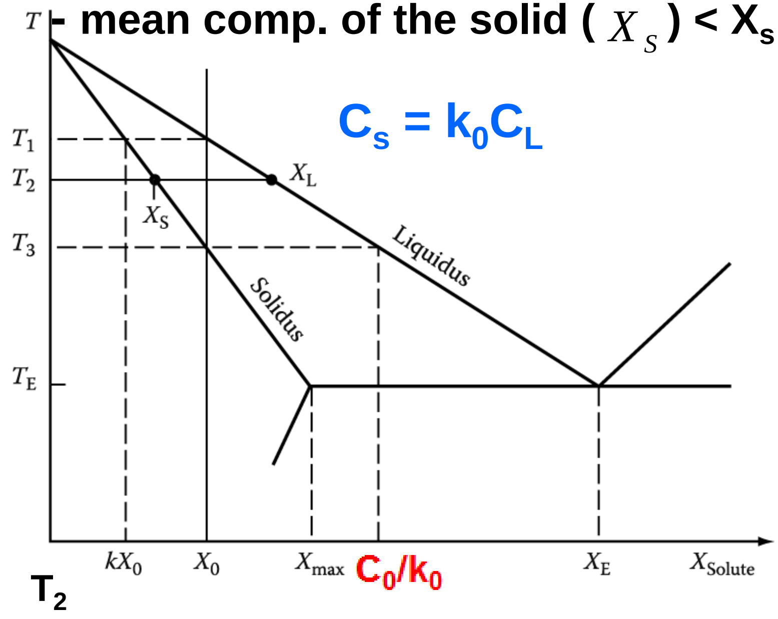
When the solid/liquid interface is within ~D/R of the end of the bar the bow-wave of solute is compressed into a very small volume and the interface composition rises rapidly leading to a final transient and eutectic formation.

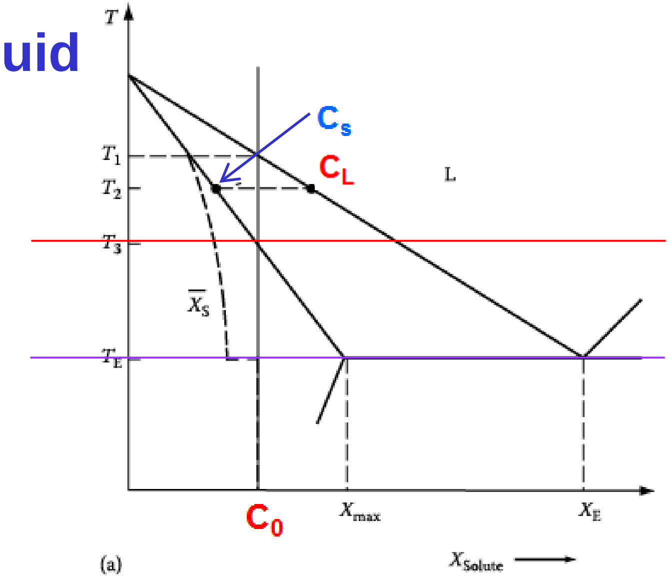
3) No Diffusion in Solid, Perfect Mixing in Liquid

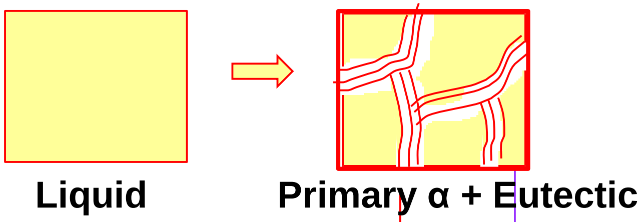
: high cooling rate, efficient stirring

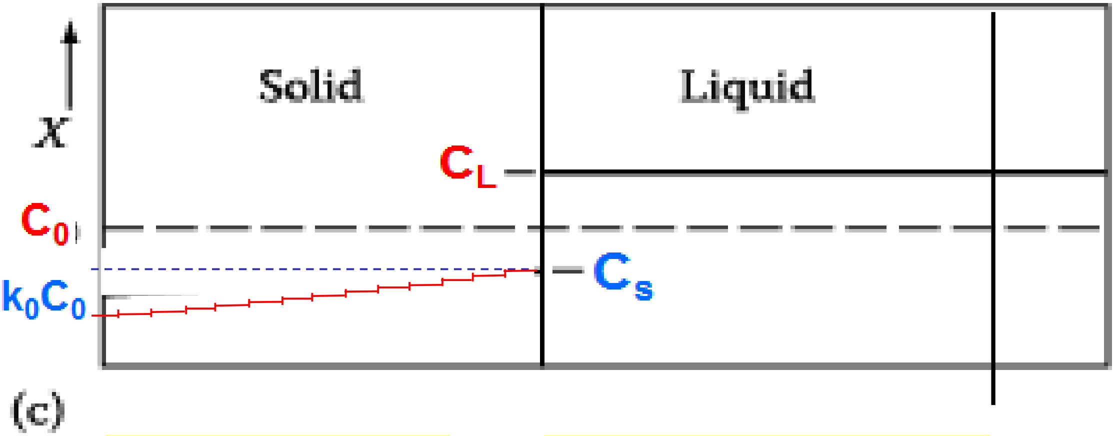
- Separate layers of solid retain their original compositions
- mean comp. of the solid ($\overline{X}_S$) < X_s

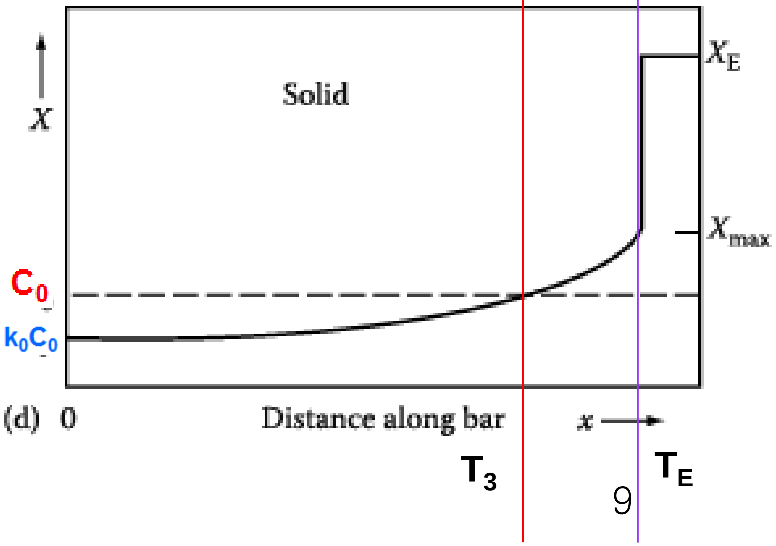
$C_s = k_0 C_L$







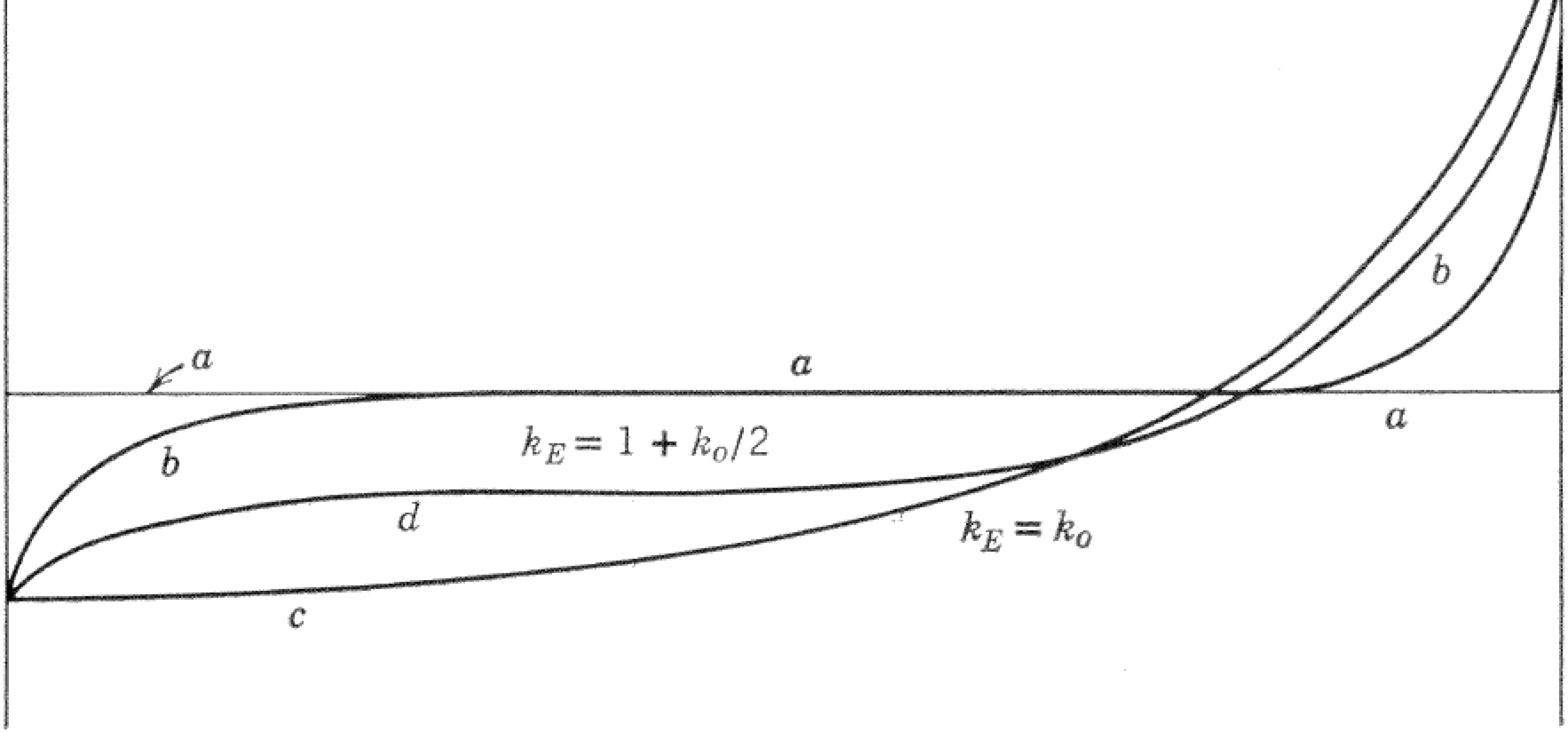




solid → $\overline{X}_s < C_s$

liquid > C_0/k_0 → X_E

Fig. 5.18. solute distribution after uniaxial solidification.
(a) Complete diffusion in solid and liquid, (b) mixing by diffusion only, (c) complete mixing in liquid ($k_E=k_0$), (d) partial mixing in liquid [$k_E = (1+k_0)/2$].



*** Comments: Solidus temperature of an alloy**

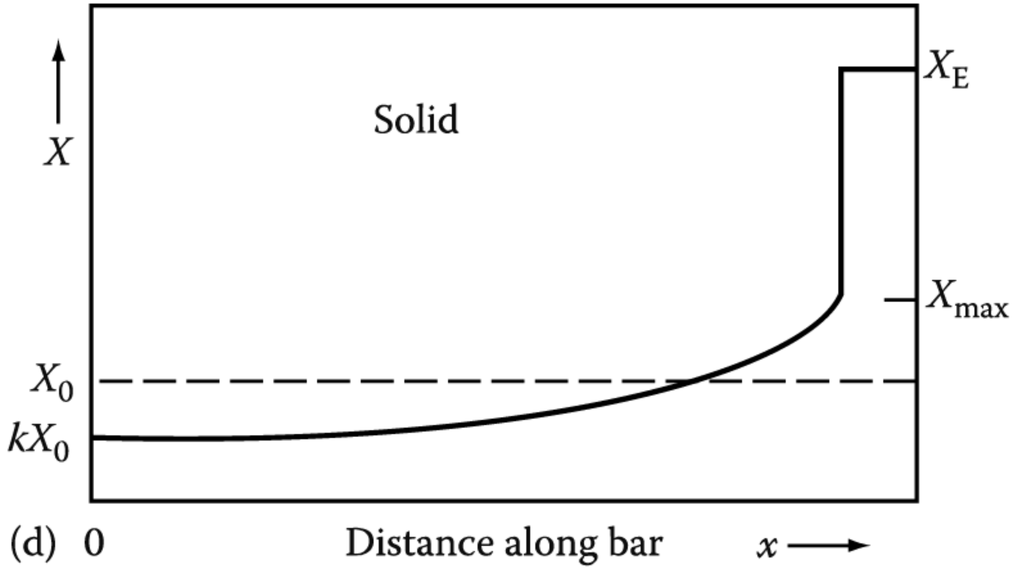
T_L: Solidification start → supercooling → T_L (recalesence)→ T_S: Solidification finish

Phase diagram → determined from cooling curve ∴T_L satisfactory, T_S large errors

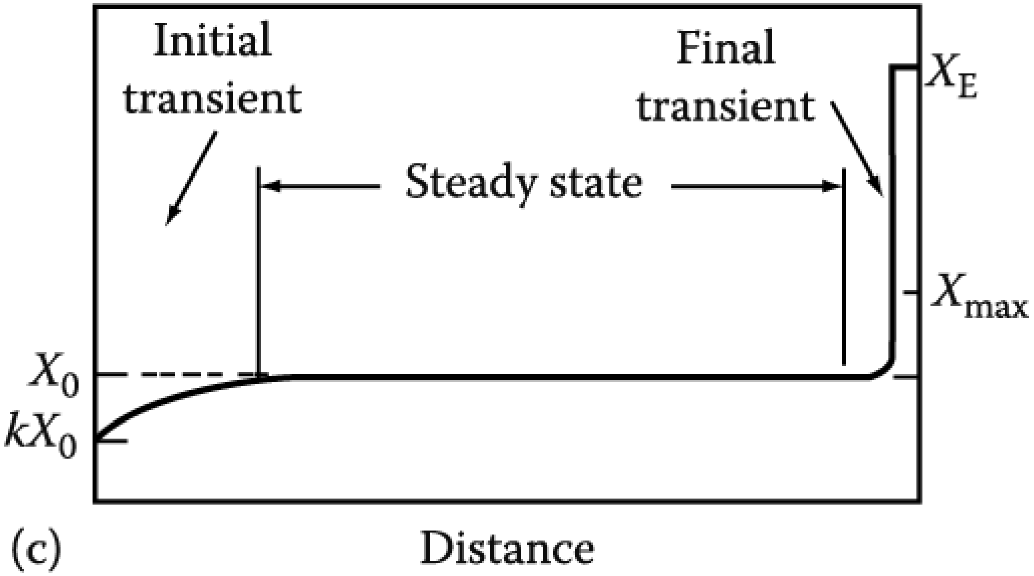
When a single-phase solid is formed, the last liquid always solidifies at a temperature below the solidus for the original liquid (of composition C_0) some times by a large amount→ Please check "Zone refining".

Concentration profiles in practice

: exhibit features between two cases



(d)



(c)

➡ **Zone Refining**

5.4 Zone Refining

: A crystal growing from a solution usually rejects either the solute or the solvent → **“Purifying Crystalline”**

(a) Distribution coefficient of any solute, k_0 ~ very small ($< 10^{-6}$)

→ Importance of R/ d/ D ↓ → Purity ↑ by multi-stage process

(b) Distribution coefficient k_0 ~close to 1,

→ Purity ↑ by multi-stage process

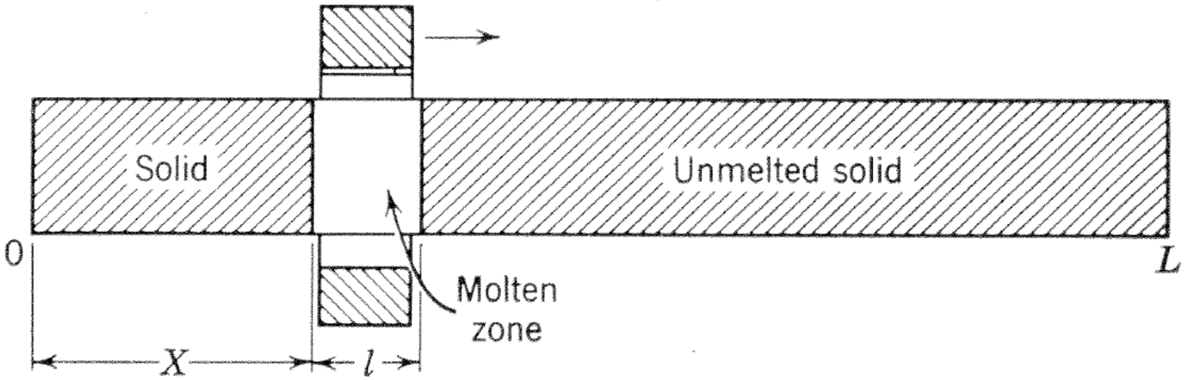
→ possible, but not practical

∵ Each successive stage would provide less material of high purity.

$$k_E = \frac{k_0}{k_0 + (1 - k_0)\exp\left(-\frac{Rd}{D}\right)}$$

Zone melting or Zone refining – W.G. Pfann Invention ~ various extension and modifications (see Pfann’s book: Zone melting, John Wiley & Sons New York, 1958)

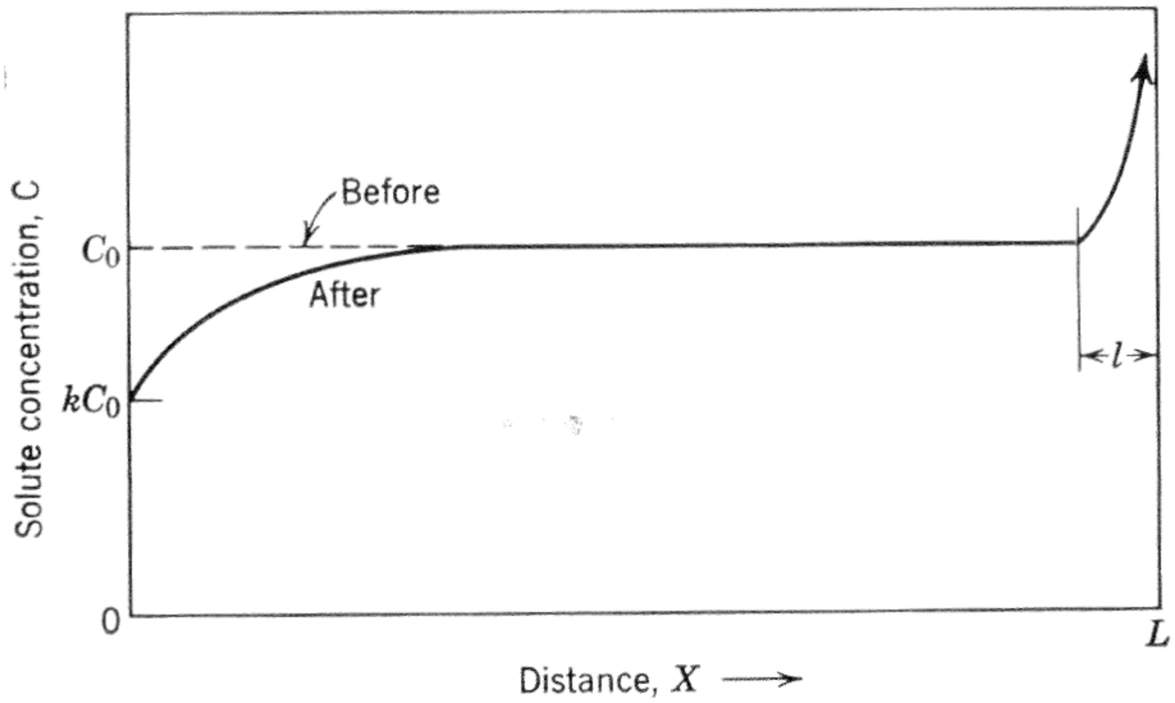
Ring heater



The form of a bar & Held in suitable container

Fig. 5.19. Zone melting, schematic. (From Ref. 9, p. 24.)

(a) Fig. 5.20. Distribution of solute after passage of one molten zone; initial concentration C_0. (From Ref.9, p. 25)



* Concentration distribution : except terminal transient region

$$\boxed{\frac{C_s}{C_0} = 1 - (1 - k_E)\exp\left(-\frac{k_E X}{l}\right)}$$

(b) Concentration gradients after multi-pass in the same direction as first: further transfer of solute from left to right

(c) Effect of k_E on purification:

low k_E (left) : small # of pass → **large decrease of** solute concentration
$k_E \sim 1$ (next page): requires a very large # to produce a comparable effect

① $k_E = 0.1$

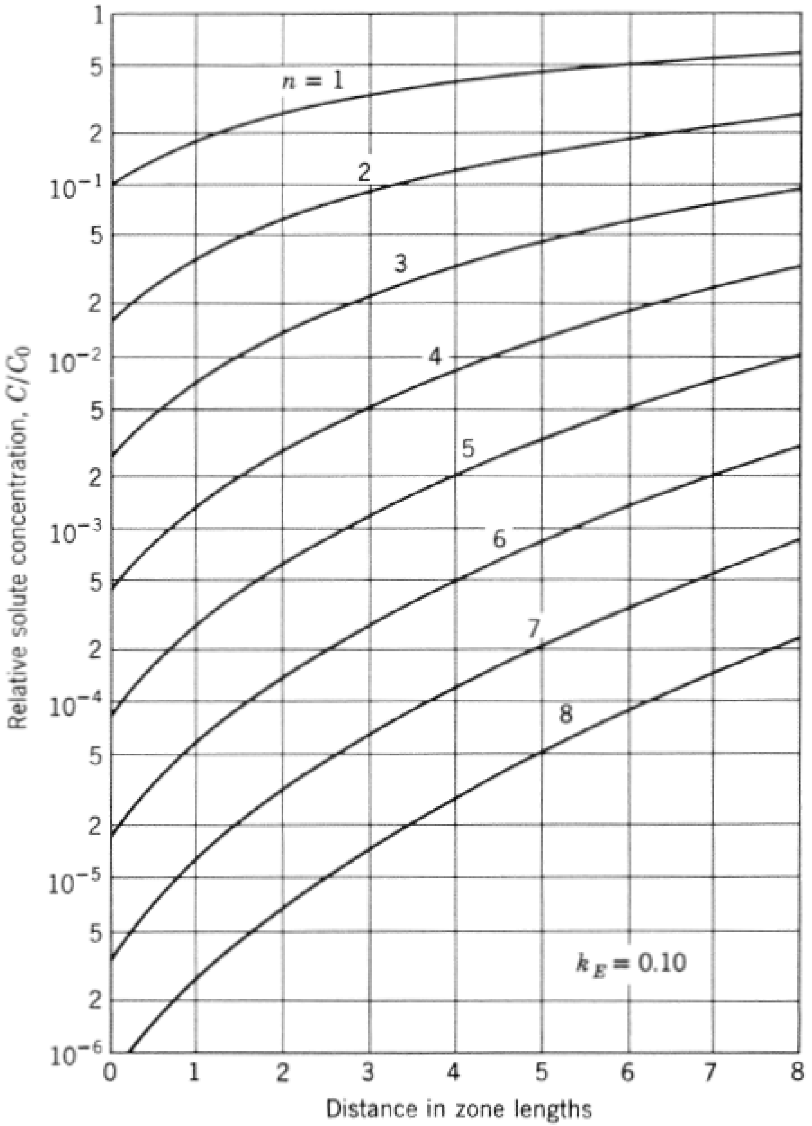


Fig. 5.22. Solute concentration after n zones for $k_E = 0.1$.

② $k_E = 0.25$

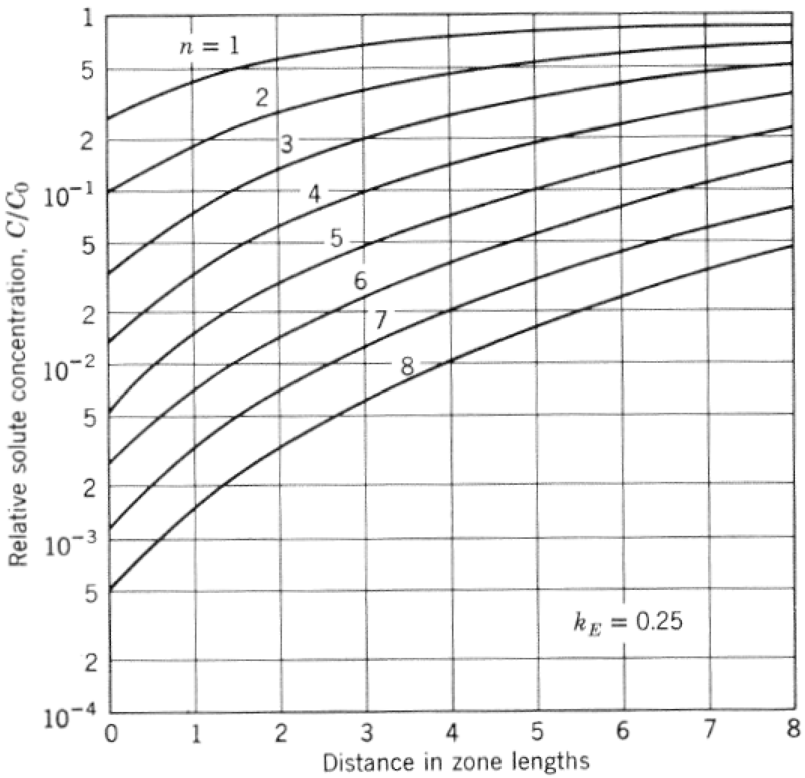


Fig. 5.21. Solute concentration against distance (in zone lengths) after passage of n zones

$$k_E = \frac{k_0}{k_0 + (1 - k_0)\exp\left(-\frac{Rd}{D}\right)}$$

(c) Effect of k_E on purification:

low k_E (left) : small # of pass → **large decrease of** solute concentration

$k_E \sim 1$: requires a very large # to produce a comparable effect

③ $k_E = 0.9524$

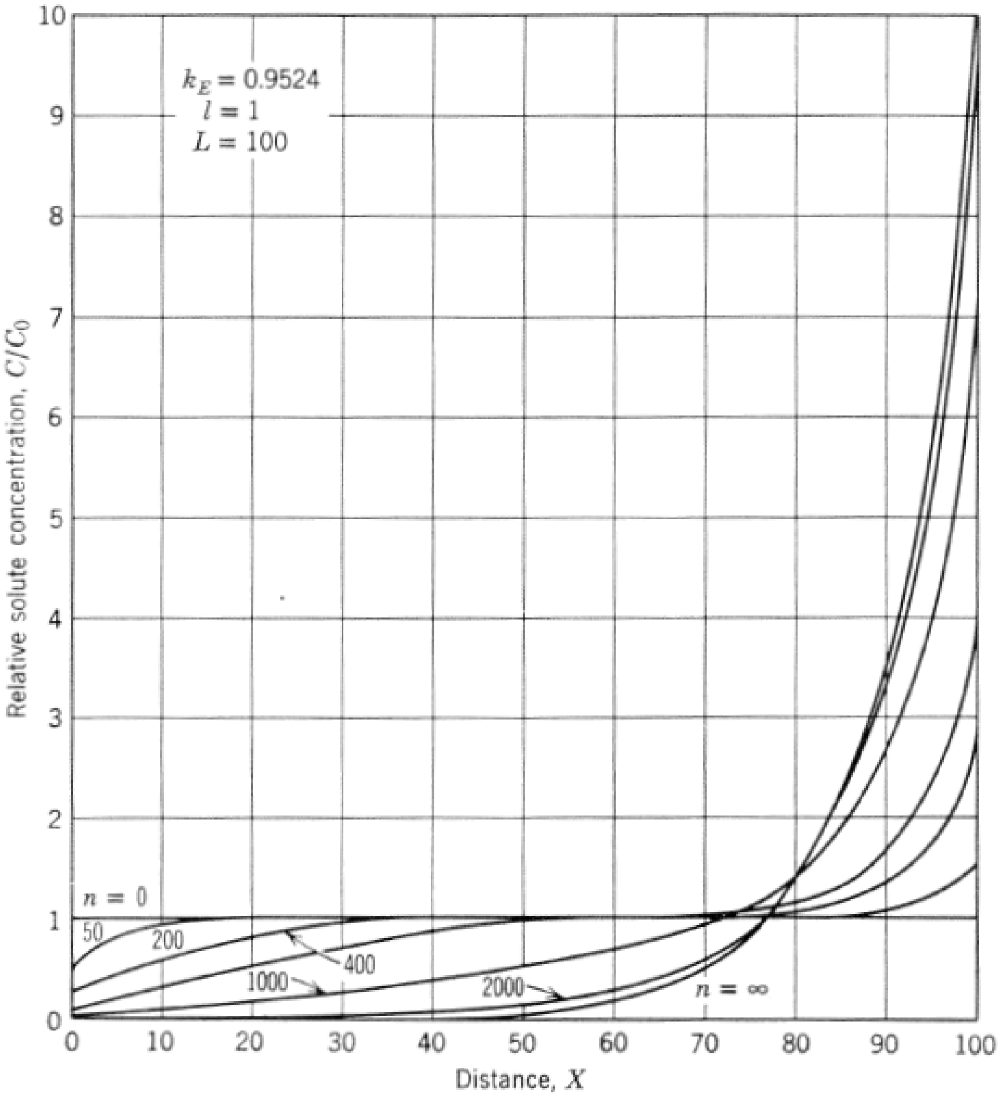
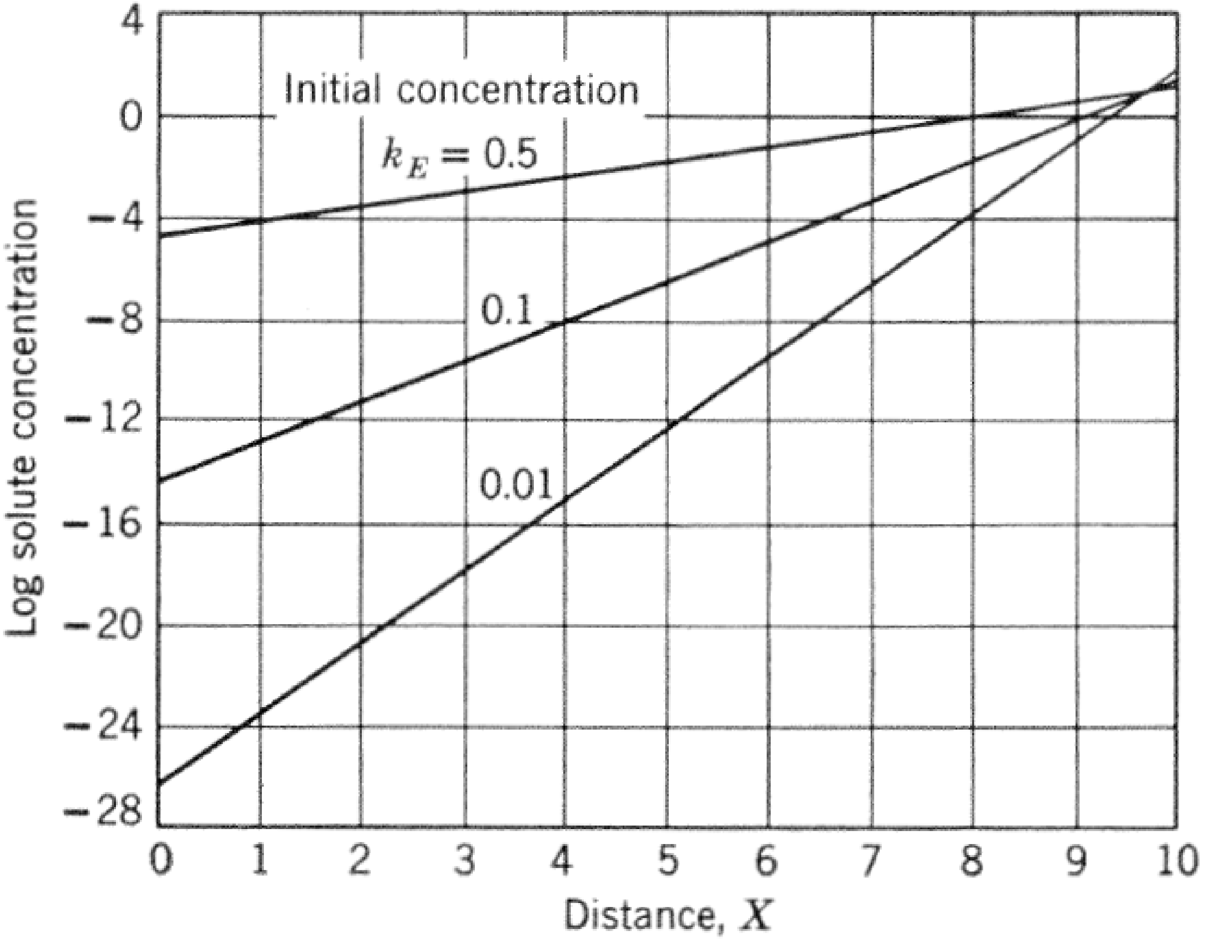


Fig. 5.23. Solute concentration for k_E = 0.95.

Figure 5.24 Limiting distribution which is approached after passage of many zones; Length of ingot is 10 zone lengths. (From Ref. 9, p. 41)



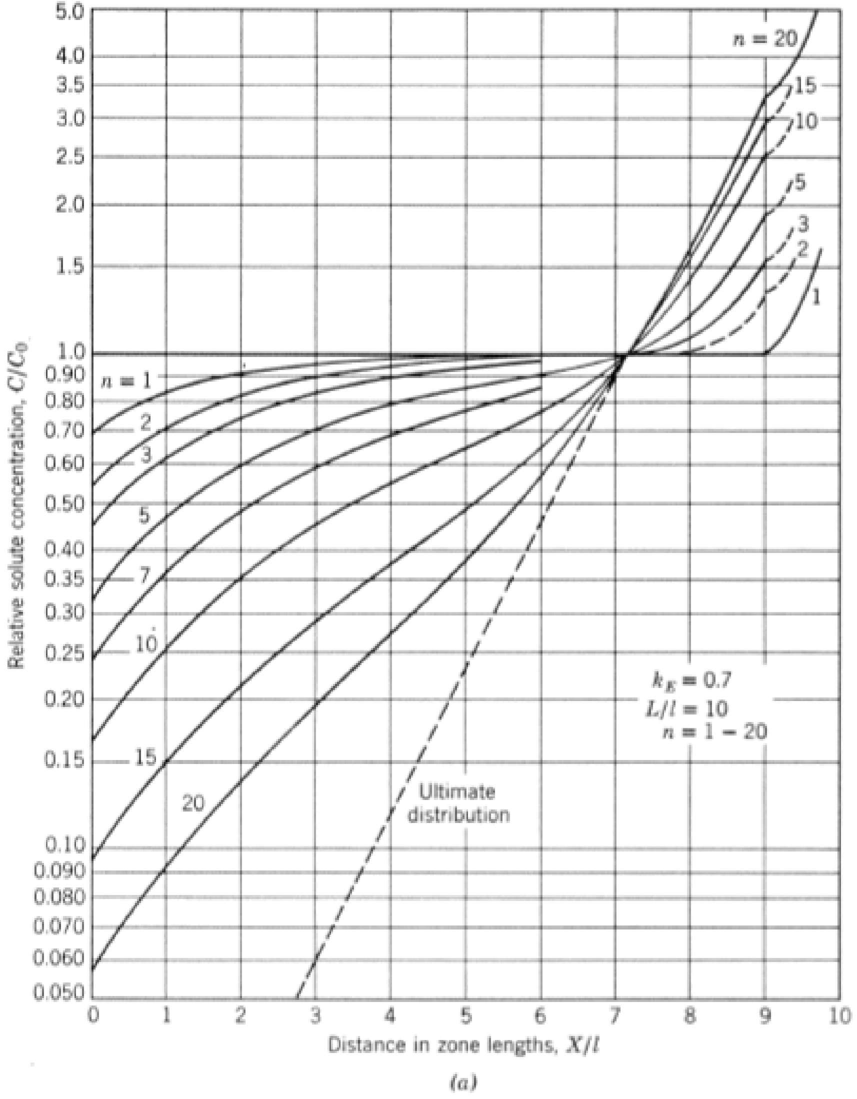
(a) How the ultimate distribution (i.e. when a steady state has been reached) varies with the value of k_E for a bar 10 zones in length.

Assumption : - Impurity to be removed have distribution coefficient less than 1.
- Solutes are rejected by growing crystals and accumulate in the terminal region.

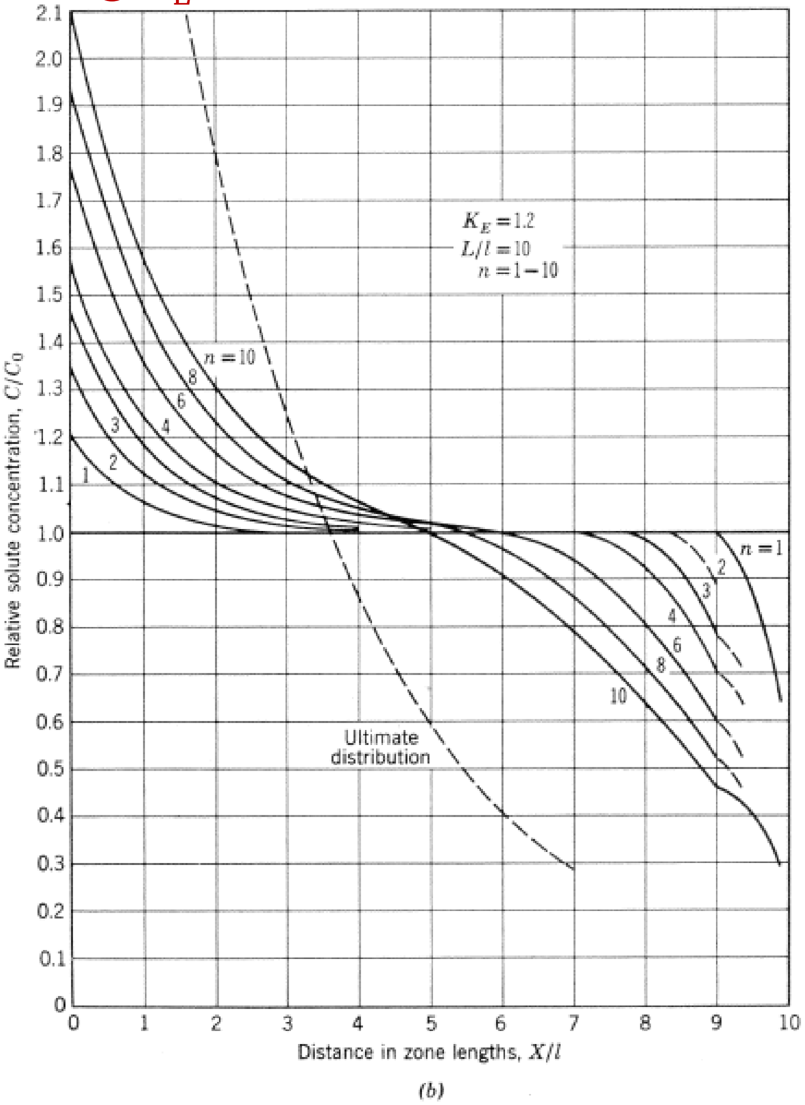
But, (b) some solute are preferentially accepted by growing crystal, and therefore, have distribution coefficients greater than 1 & accomulate in the first part to solidify

- A comparison of separation obtained with k_E =0.7 and 1.2 is shown in Fig. 5.25, where a bar ten zones in length L/l=10 is subjected to various number of passes.

① k_E = 0.7



② k_E = 1.2

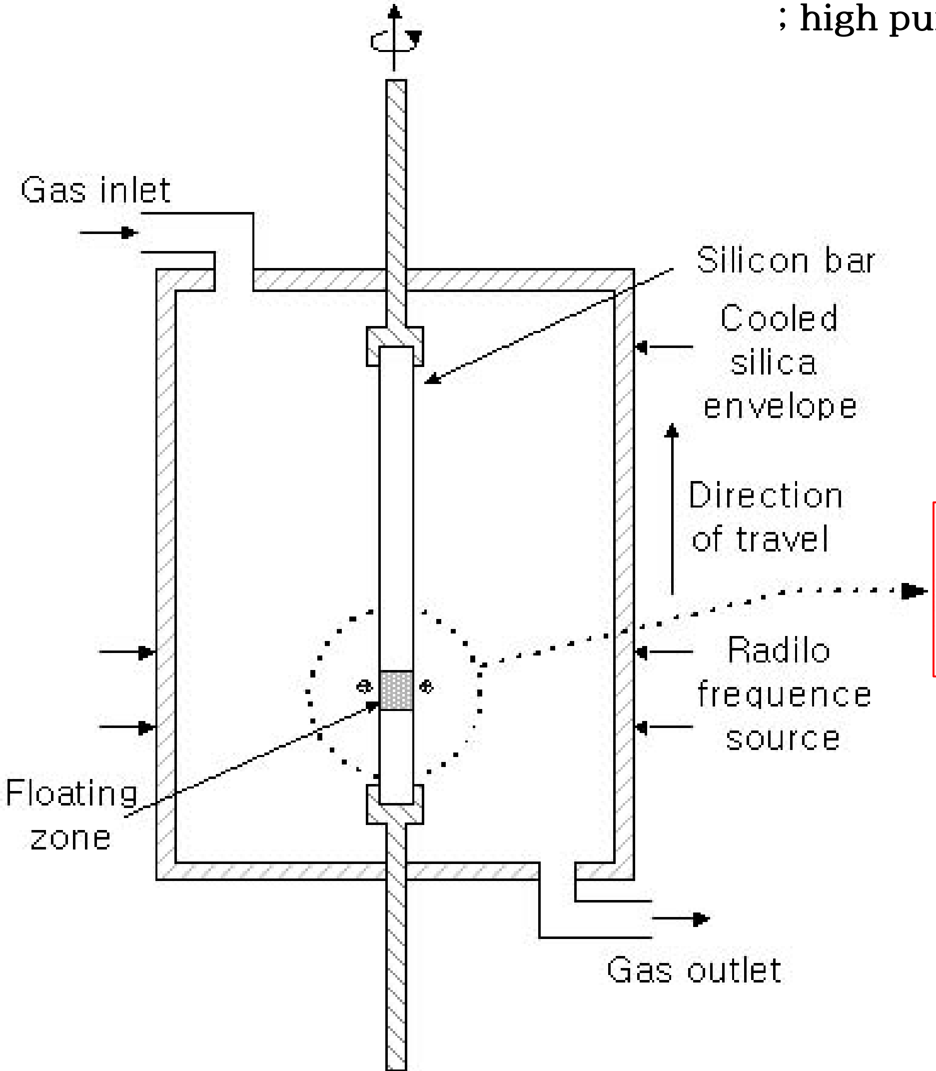


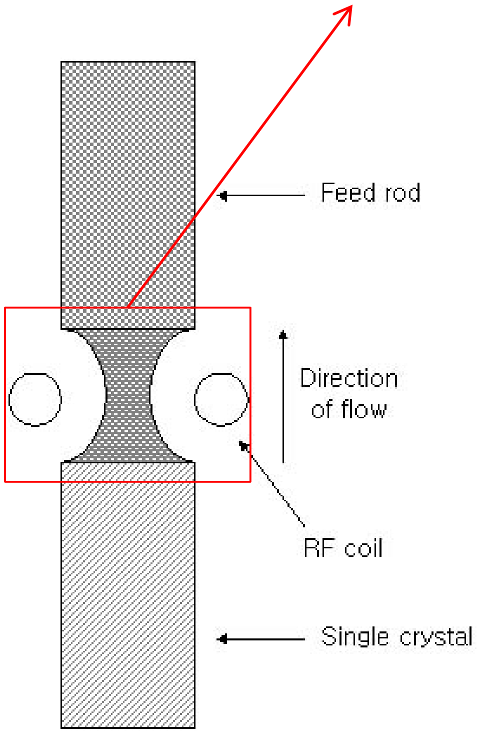
* When purifying through zone refining, metals with high reactivity and high Tm should be carefully considered for <u>contamination especially from containers.</u>→ This problem is minimized by using the various floating zone methods described below.

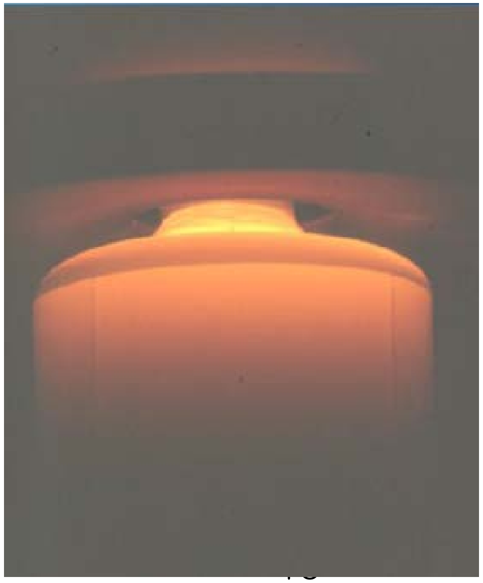
Single Crystal Growth: c) Float-zone (FZ) method

; high purity, expensive

The maintenance of the molten zone is possible by the combined force of surface tension or stress induced by surface tension and electromagnetic.





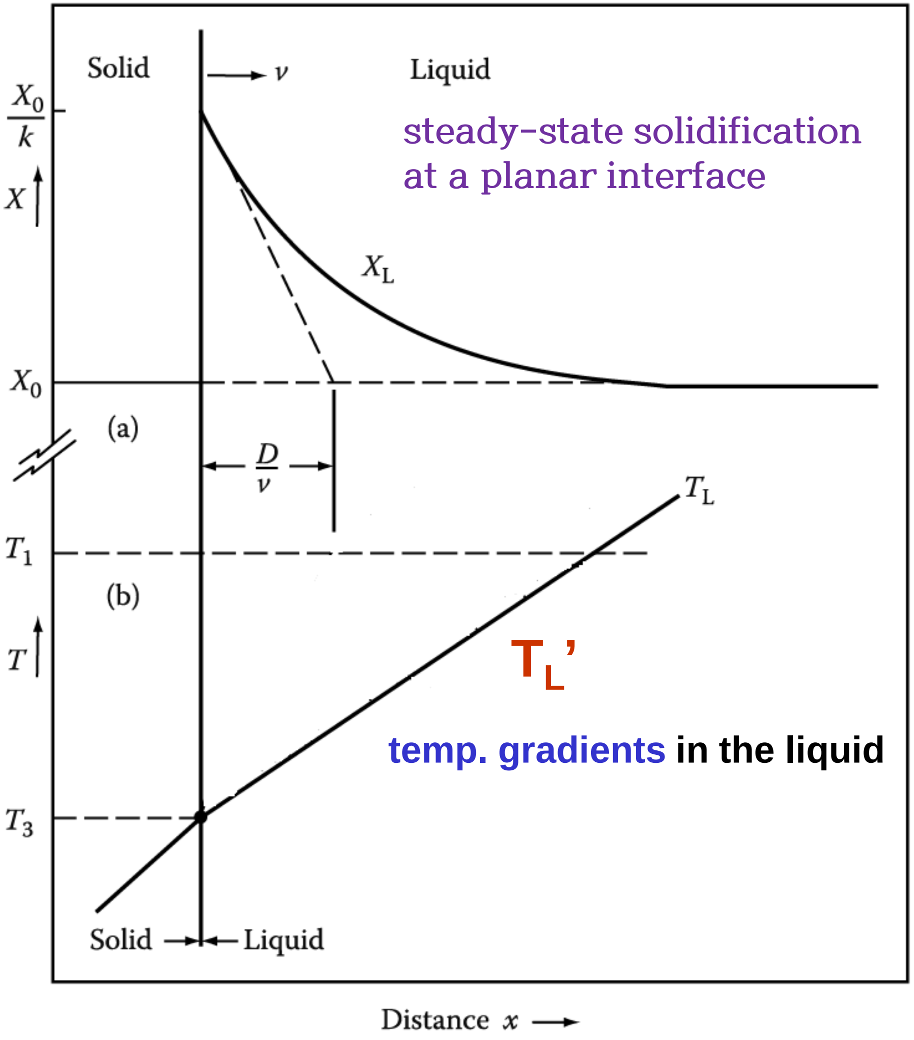


5.5 Constitutional supercooling

Page 150

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

+ complicated by the possibility of temp. gradients in the liquid.

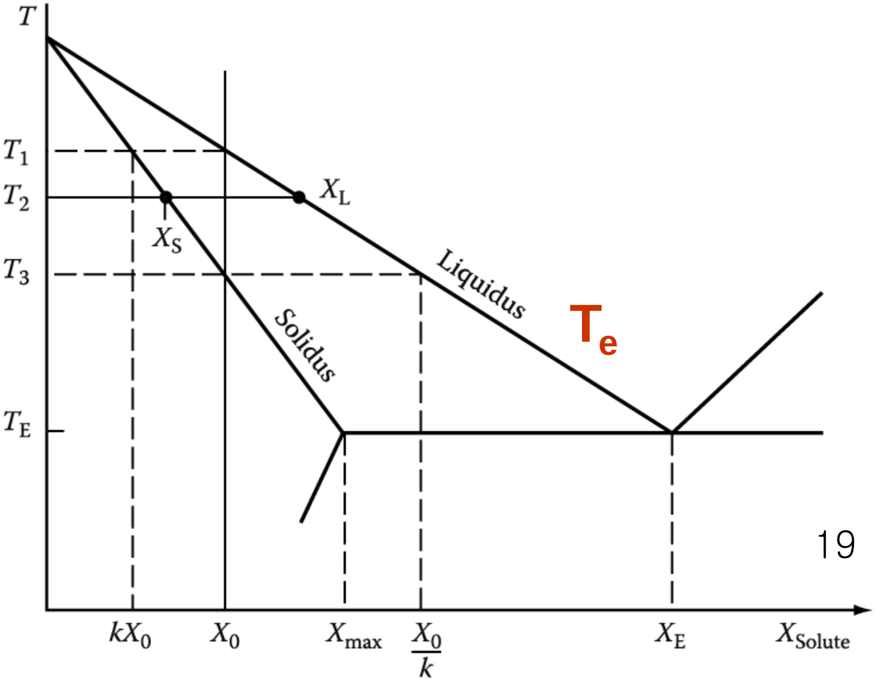


steady-state solidification at a planar interface

T_L'

temp. gradients in the liquid

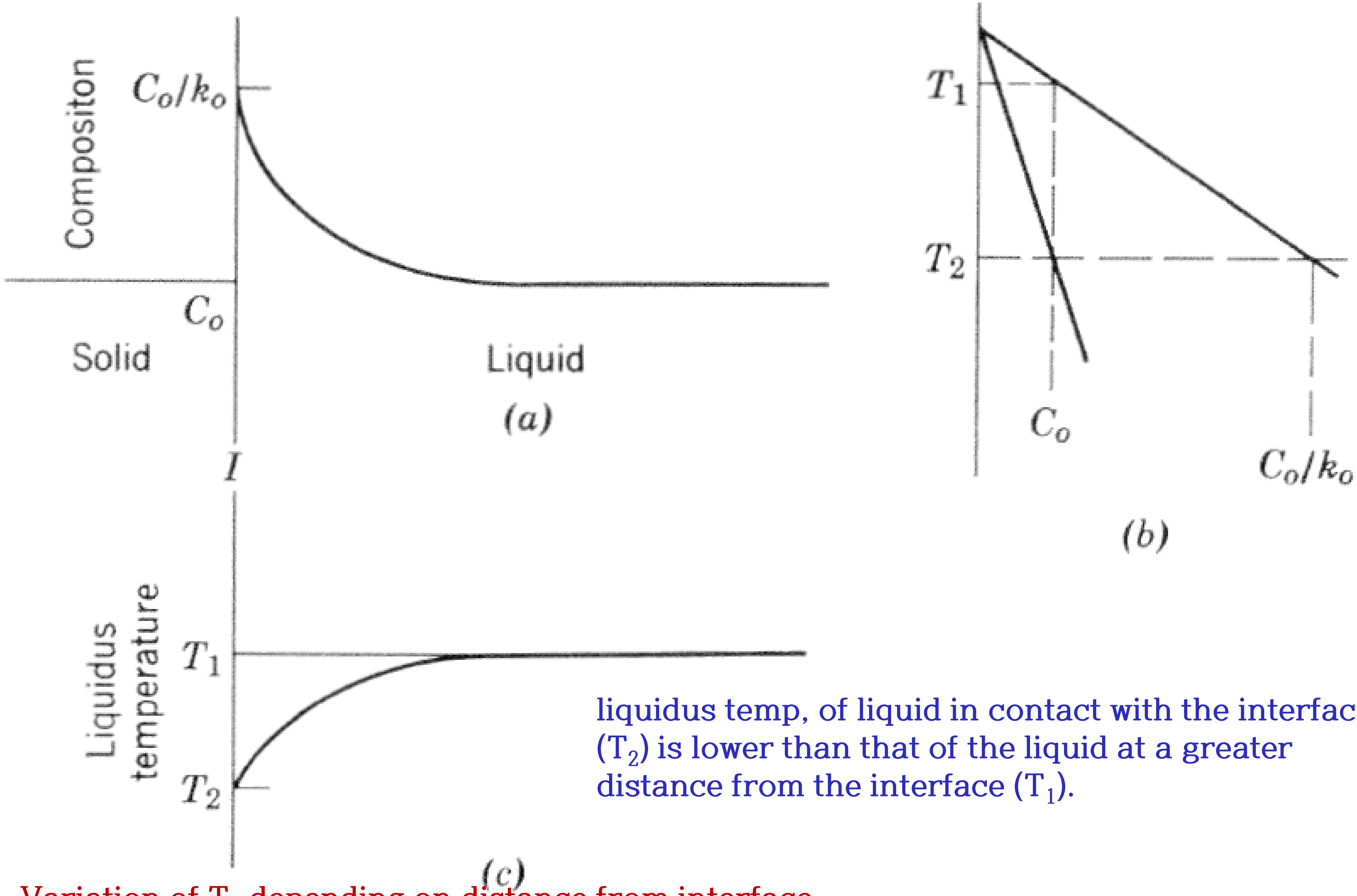
What would be “T_e“ along the concentration profile ahead of the growth front during steady-state solidification?



T_e

Assumption: Steady state condition

Typical binary alloy with $k_0=0.2$



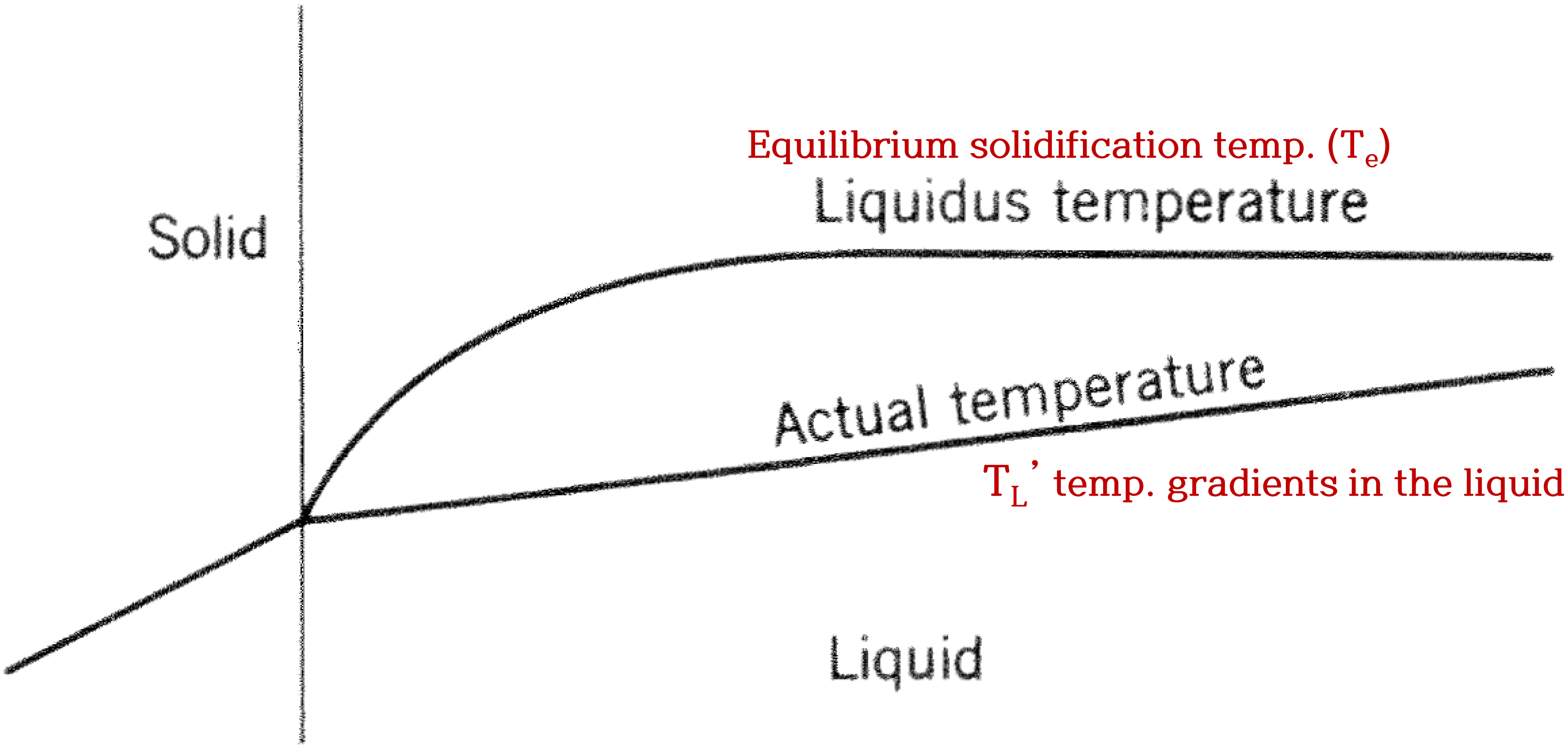
liquidus temp, of liquid in contact with the interface (T_2) is lower than that of the liquid at a greater distance from the interface (T_1).

Variation of T_e depending on distance from interface

Fig. 5.26. Variation of concentration and liquidus temperature ahead of an interface. (a) Variation of concentration, (b) relationship between concentration and liquidus temperature, (c) variation of liquidus temperature.

→ Actual temp. of liquid at interface < Temp. of bulk liquid: superheated condition

: Undercooling may occur in front of the solidification interface due to the change of the equilibrium solidification temperature (T_e) by the solute released from the solid phase.



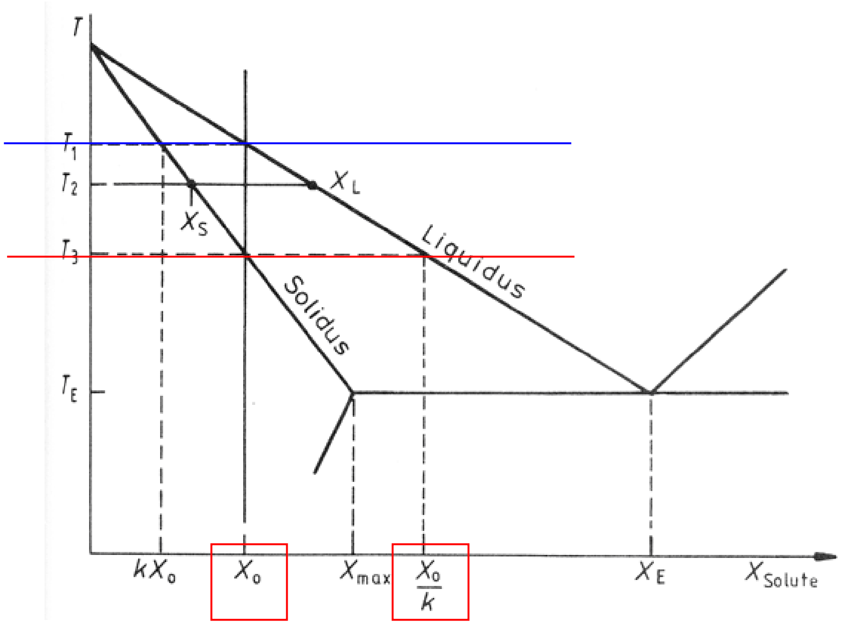
Equilibrium solidification temp. (T_e)

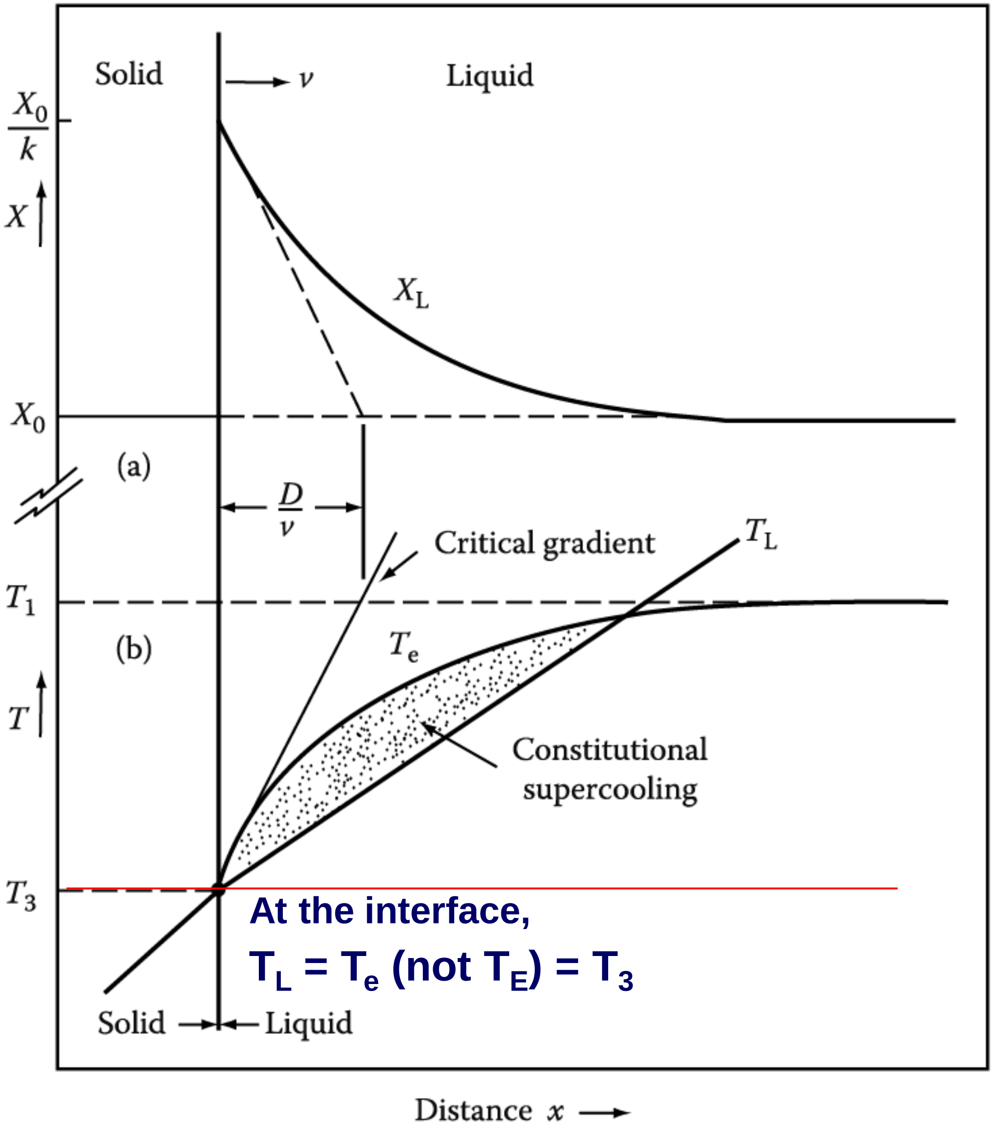
T_L' temp. gradients in the liquid

Fig. 5.27. Actual temperature of the liquid and its liquidus temperature

* Constitutional Supercooling

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





At the interface,

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

*** Actual temperature gradient in Liquid**

T_L'

*** equilibrium solidification temp. change**

T_e

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

Cellular and Dendritic Solidification

At the interface, $T_L = T_e$ (not T_E) $= T_3 \rightarrow T_{L,\ liquid} = T_1 : T' = T_1 - T_3$

- **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)

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

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

⇨ **need to well-controlled experimental conditions (temp. gradient & growth rate)**

1) **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.**

2) **Cooling rate effect : <u>Higher cooling rate</u> allow less time for lateral diffusion of the rejected solute and therefore require <u>smaller cell or dendrite arm spacings</u> to avoid constitutional supercooling.**

* Instability due to constitutional supercooling

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

1) **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.

(a) Freezing range of 90Cu-10Sn ~ very large (190 K) → the liquid ahead of the advancing interface could be constitutional supercooling by 190 K.

(b) This condition (= large undercooling) is never even approached because a very much smaller amount of supercooling is sufficient to set up an instability

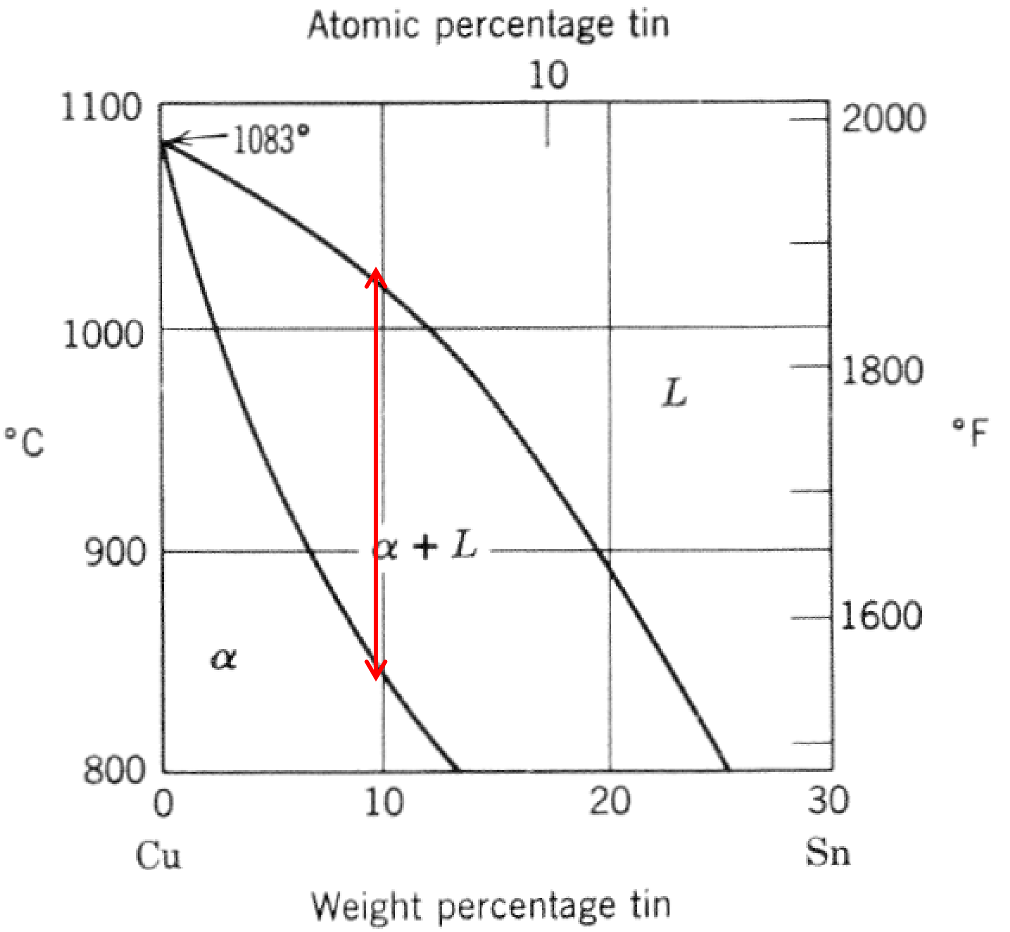


Fig. 5.28. Freezing range in copper-tin alloys

* Constitutional supercooling → Interface instability → compositional fluctuation of solid → "Periodicity of solute"

1) Axial periodicity of solute (Landau proposal)

(a) Solute content of solid varies periodically in the direction of travel of the solid-liquid interface.
→ Uniform in any plane parallel to the interface

Assumption: (a) whole of the interface advances together/ (b) Accumulation of solute, as a result of the "initial transient", increase progressively until some concentration is reached where either independent nucleation would occur in the most supercooled region, or the existing crystal would grow into that region.

(b) Landau cite evidence for periodic variation of concentration of antimony in Ge crystals grown by the Kyroplous method, but no quantitative comparison btw this theory and experiment is available. → No conclusive evidence btw Landau type of instability and periodic fluctuation in the thermal characteristics of the system

2) Transverse periodicity of solute (opposite with axial periodicity)

5.6 Cellular Substructure

: Due to instability by constitutional supercooling at superheated liquid

The instability due to constitutional supercooling can be resolved by the development of a transverse periodicity in the solidification process. → The phenomenon can be readily observed on the top (free) surface of a crystal of thin grown from the melt.

Fine regular corrugated structure ⟷ Cellular structure

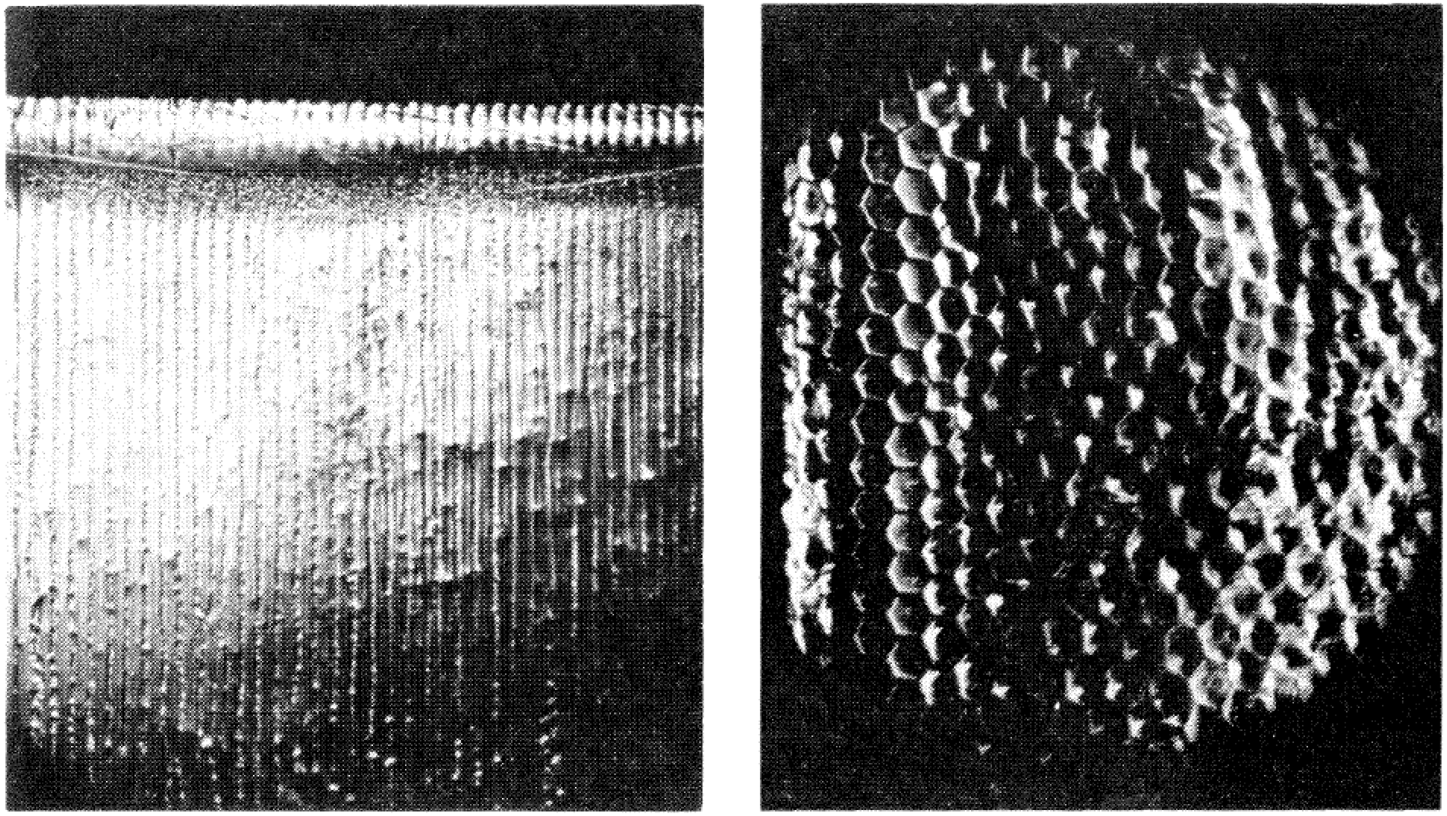


Fig. 5.29. Cellular structure (a) view of top (free) surface of tin crystal (x 75);
(b) view of decanted interfaces of tin crystal (x 75)

5.6 Cellular Substructure

: Due to instability by constitutional supercooling at superheated liquid

The instability due to constitutional supercooling can be resolved by the development of a transverse periodicity in the solidification process. → The phenomenon can be readily observed on the top (free) surface of a crystal of thin grown from the melt.

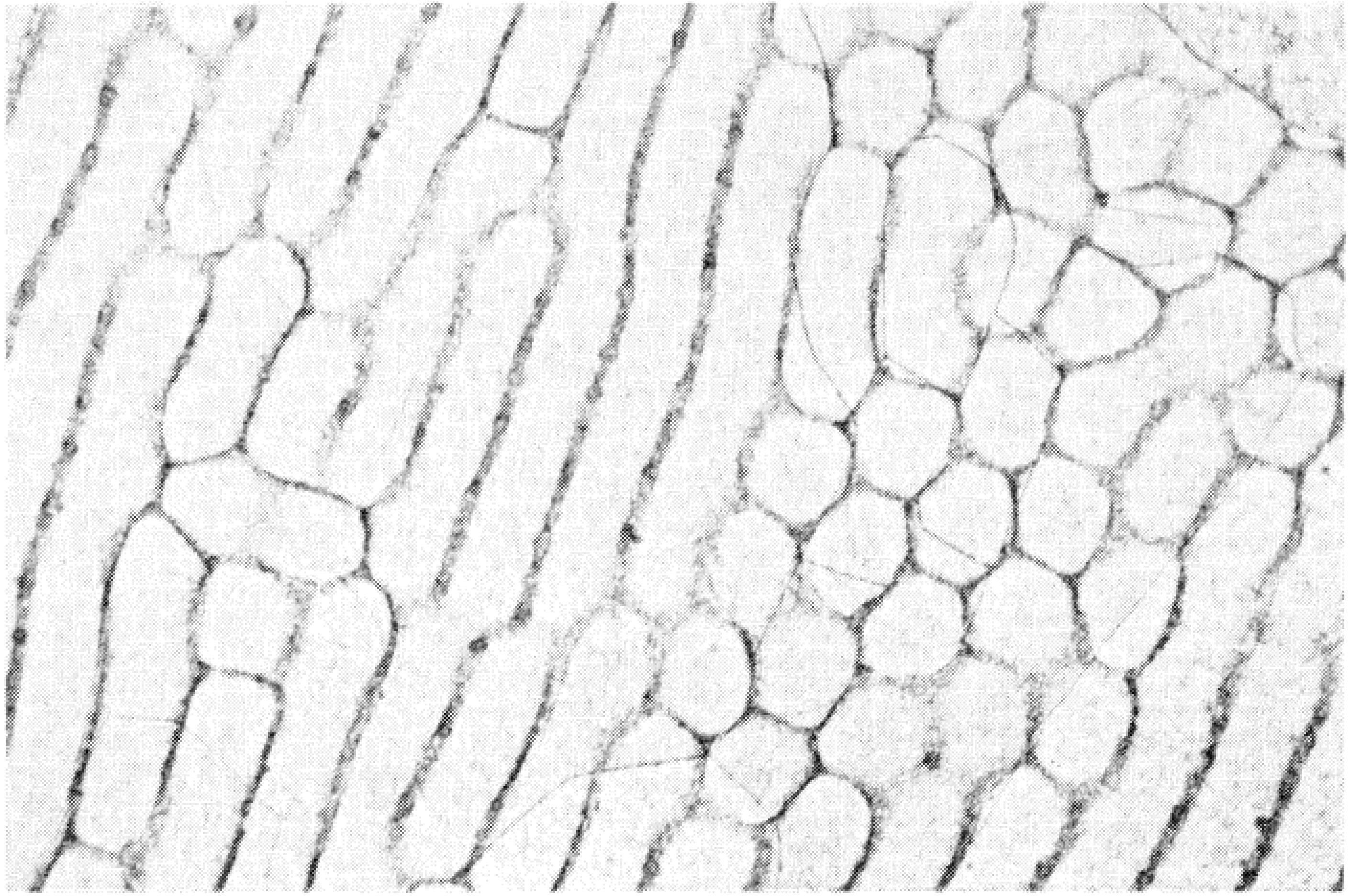


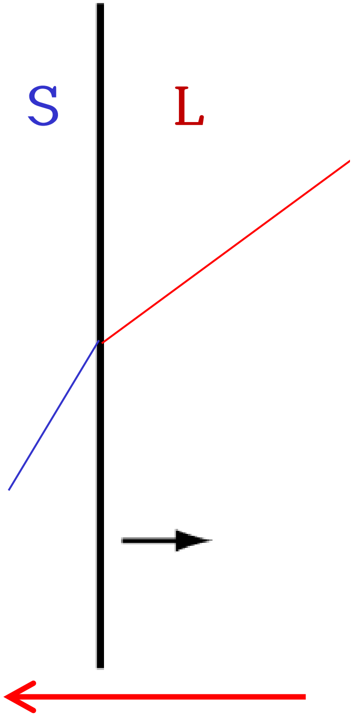
Fig. 5.29. (continue) Cellular structure (c) Less regular forms of cell

5.6 Cellular Substructure

: Due to instability by constitutional supercooling at superheated liquid

1) Origin of Cellular substructure

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



(a)

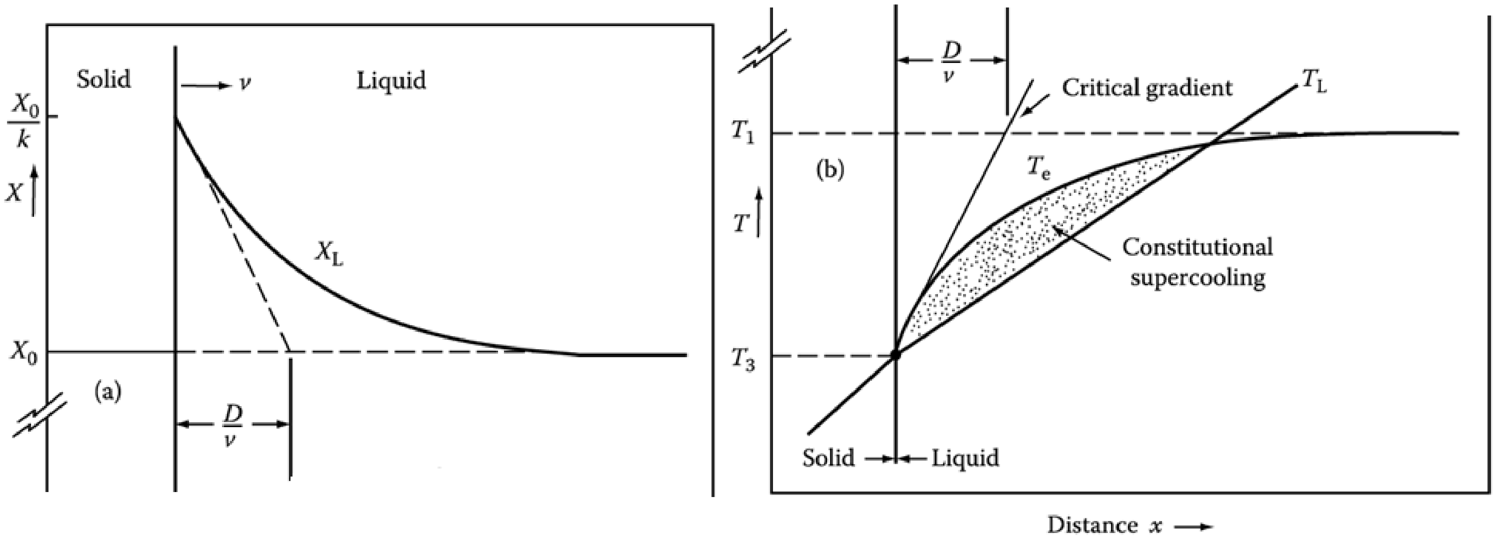


Fig. 5.30. Supercooling ahead of planar interface

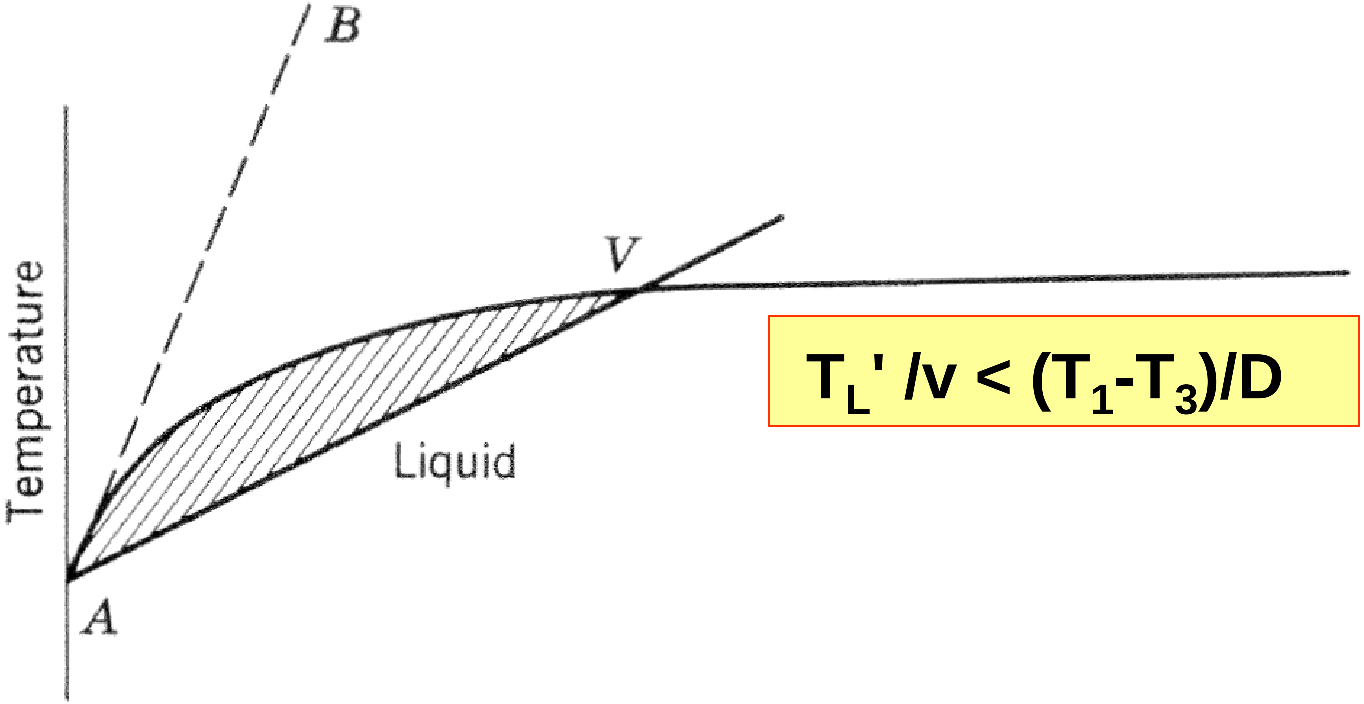
<The breakdown of an initially planar solidification front into cells>

5.6 Cellular Substructure

: Due to instability by constitutional supercooling at superheated liquid

1) Origin of Cellular substructure: discussed by solute redistribution theory

Cell formation can be suppressed by a) reducing the solute content, $(T_1-T_3)\downarrow$ / b) reducing the speed of growth, $v\downarrow$, or/ c) increasing the temperature gradient, T_L' to eliminate the region of suppercooling ($\overline{AV}$ in Fig. 5.30).



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

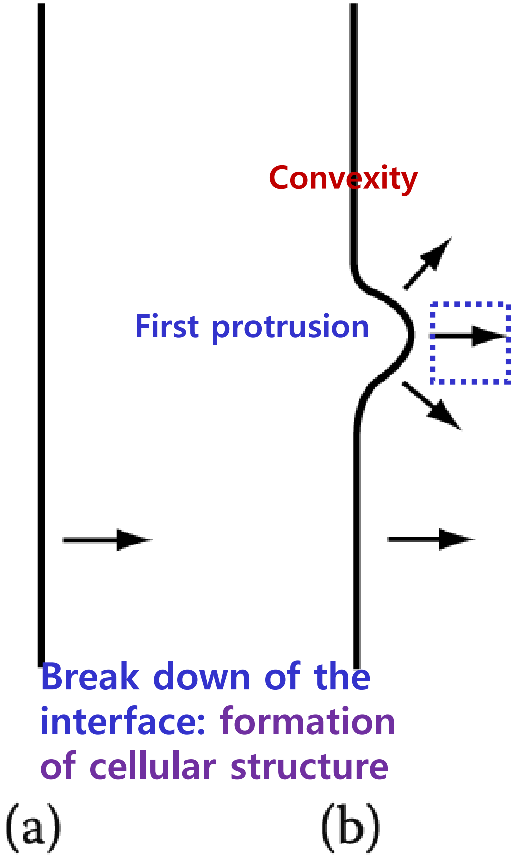
Fig. 5.30. Supercooling ahead of planar interface.

5.6 Cellular Substructure

: Due to instability by constitutional supercooling at superheated liquid

1) Origin of Cellular substructure

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



Convexity

First protrusion

Break down of the interface: formation of cellular structure

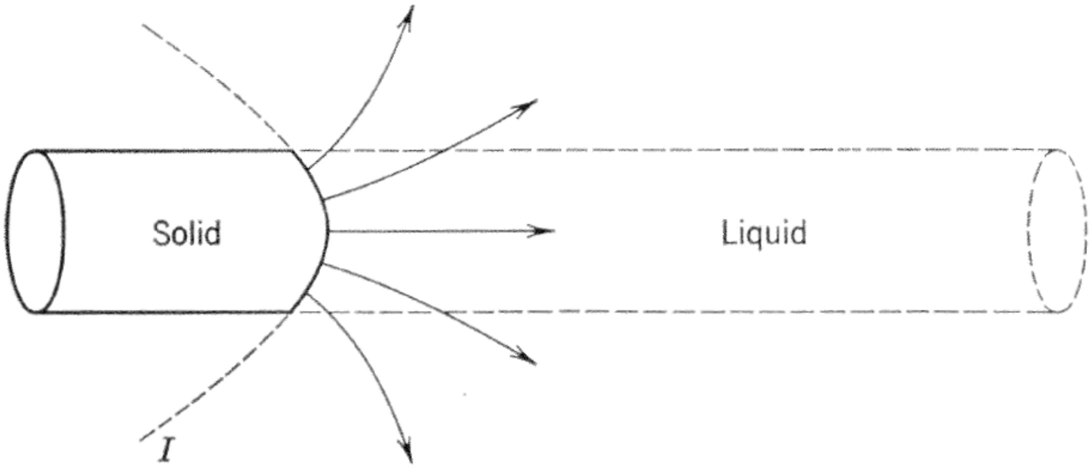


Fig. 5.14. Solute diffusion ahead of a convex interface

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

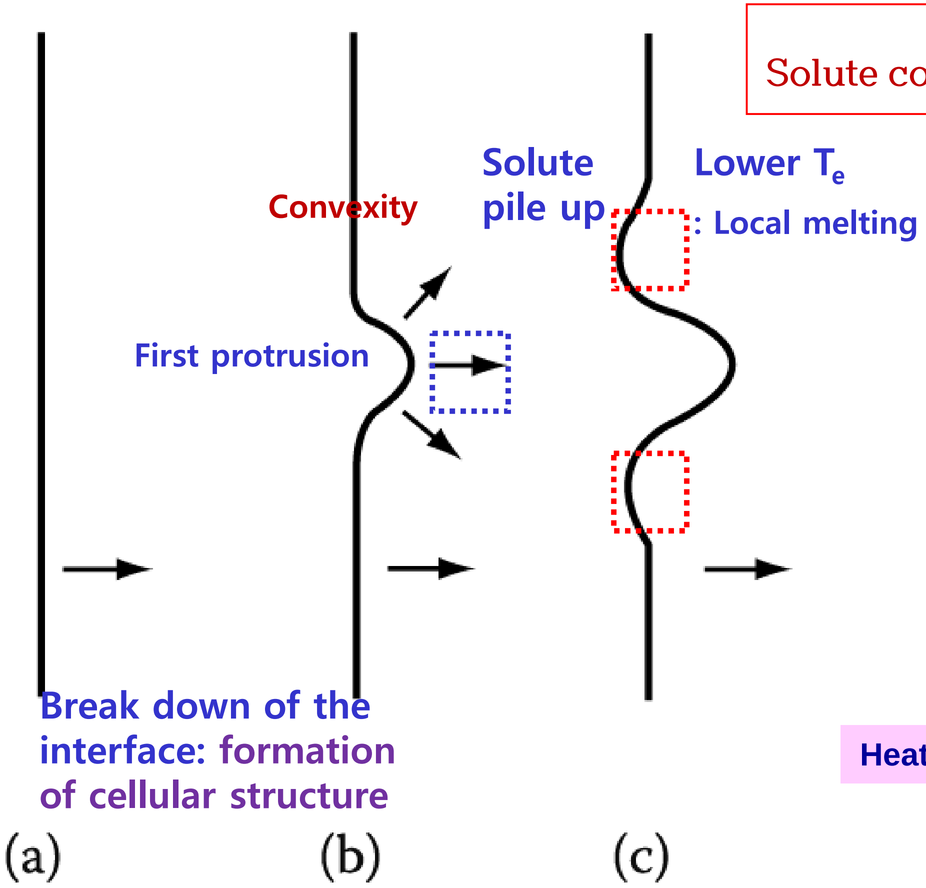
5.6 Cellular Substructure

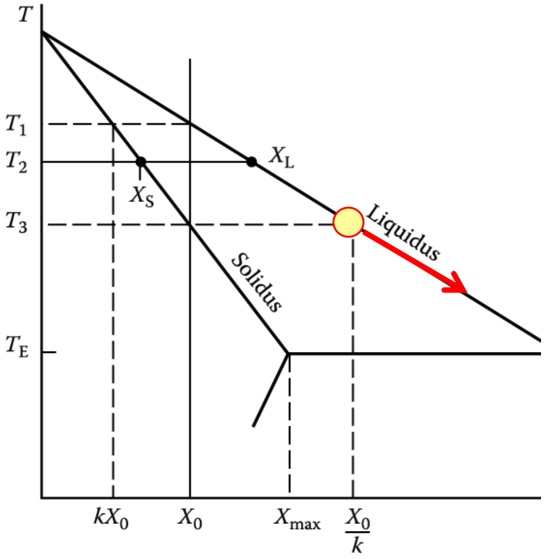
: Due to instability by constitutional supercooling at superheated liquid

1) Origin of Cellular substructure

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

Solute concentration ↑ → T_e ↓ → T_L' ↑ → v ↓





Heat Balance Equation

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

K: thermal conductivity

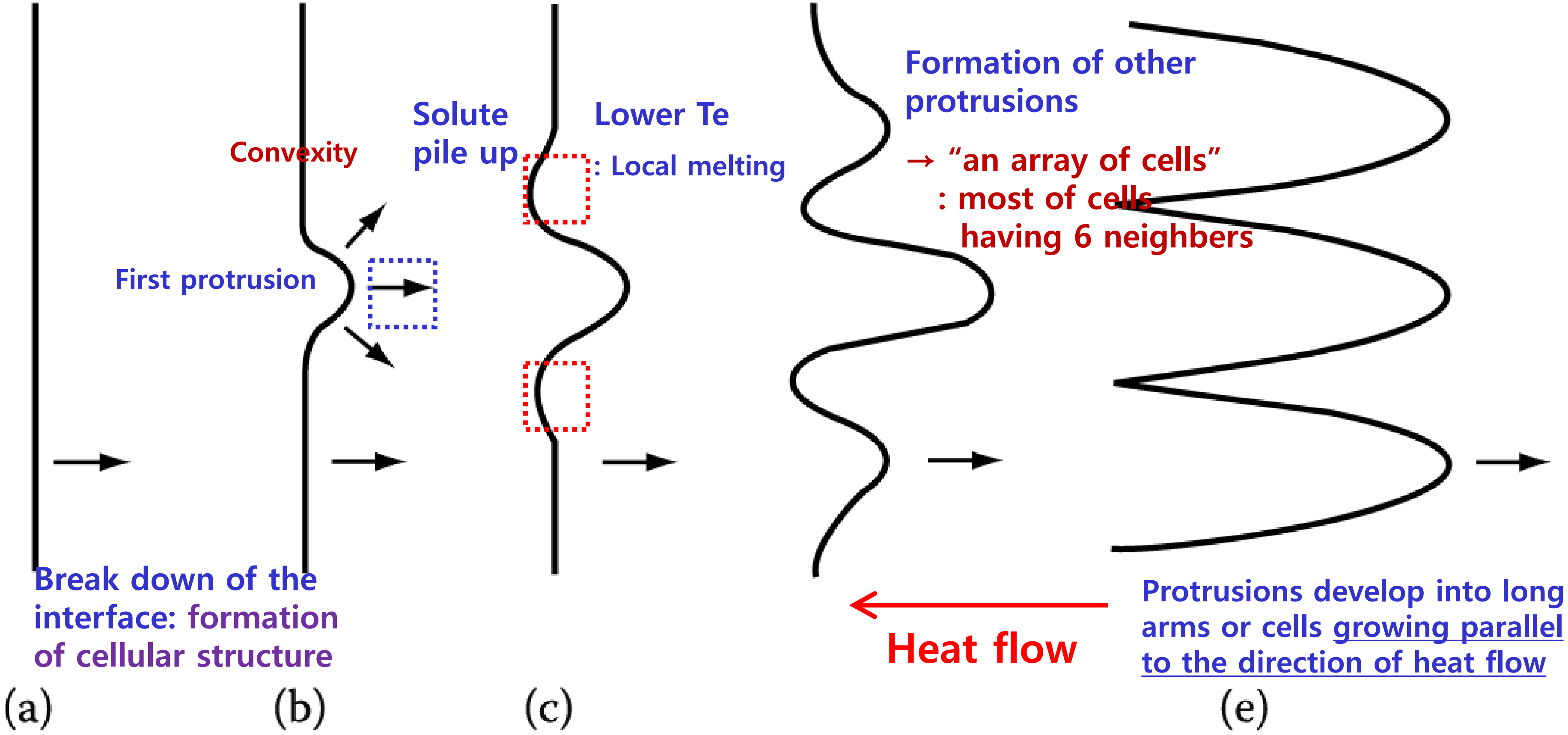
<The breakdown of an initially planar solidification front into cells>

5.6 Cellular Substructure

: Due to instability by constitutional supercooling at superheated liquid

1) Origin of Cellular substructure

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



Convexity

First protrusion

Solute pile up

Lower Te : Local melting

Formation of other protrusions

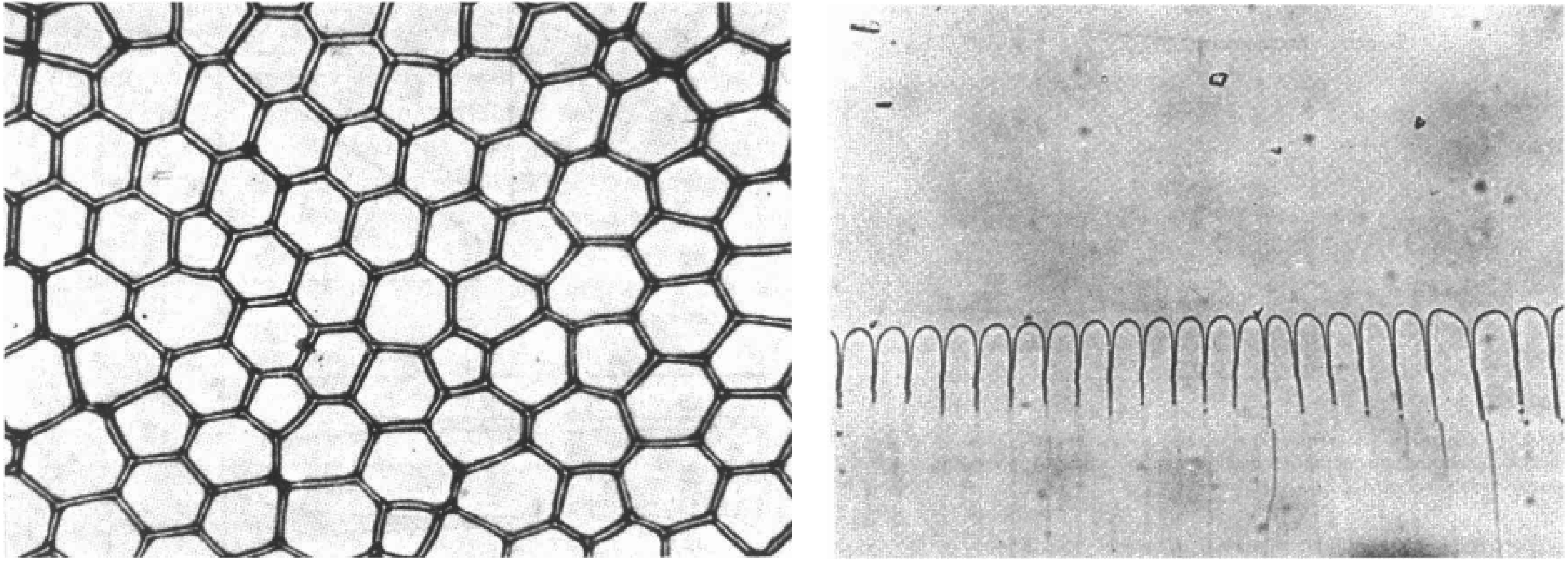
→ "an array of cells"
: most of cells having 6 neighbors

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>



* Cellular microstructures

Note that each cell has virtually the same orientation as its neighbors and <u>together they form a single grain</u>.

(a) A decanted interface of a cellularly solidified Pb-Sn alloy (x 120)

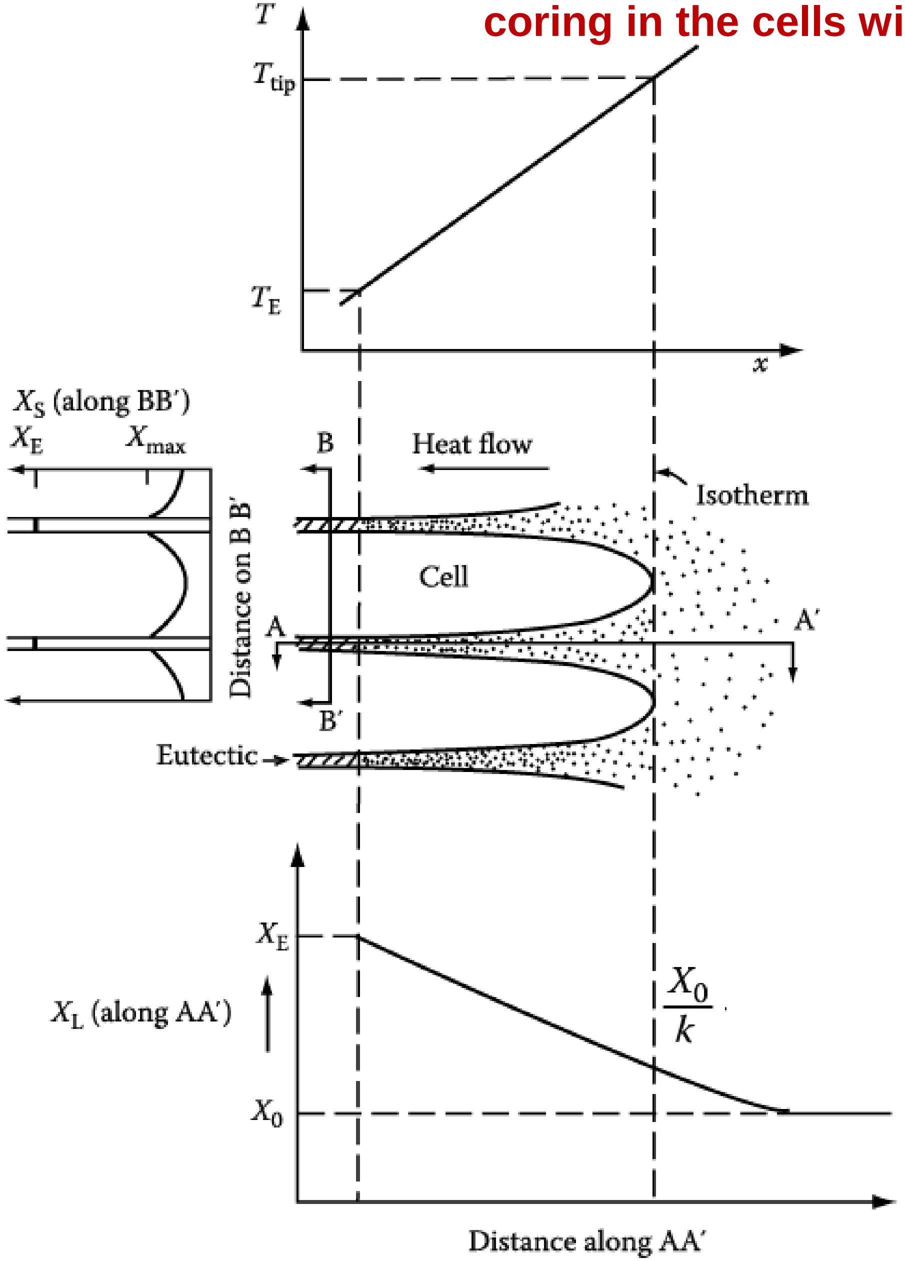
(after J.W. Rutter in Liquid Metals and Solidification, American Society for Metals, 1958, p. 243).

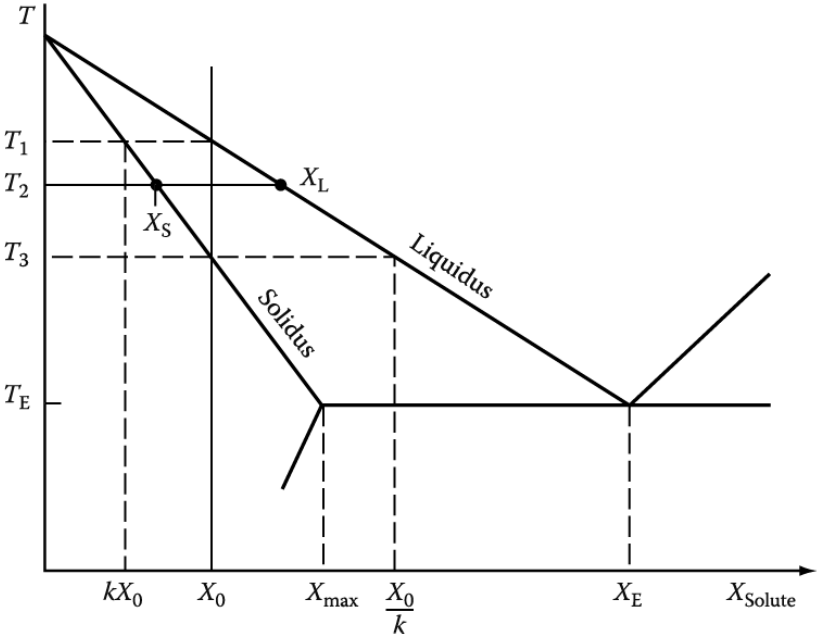
(b) Longitudinal view of cells in carbon tetrabromide (x 100)

(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

Solidification of Pure Metal : Thermal gradient dominant

⇕

Solidification of single phase alloy: Solute redistribution dominant

a) Constitutional Supercooling (C.S.)

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

Cellular growth:
Thin zone formation by C.S. at the sol. Interface
Dome type tip / (surrounding) hexagonal array

Cellular dendritic growth:
T↓ → Increase of C.S. zone
Pyramid shape of cell tip /
Square array of branches /
Growth direction change toward Dendrite growth direction

Free dendritic growth:
formed by releasing the latent heat from the growing crystal toward the supercooled liquid
Dendrite growth direction/
Branched rod-type dendrite

→ "Nucleation of new crystal in liquid"

Temperature above the interface at which growth occurs

b) Segregation

: normal segregation, grain boundary segregation, cellular segregation, dendritic segregation, inversegregation, coring and intercrystalline segregation, gravity segregation

5.6 Cellular Substructure

: Due to instability by constitutional supercooling at superheated liquid

2) Quantitative studies of cell formation

* Critical temp gradient where no constitutional supercooling occurs

Assumption: Steady state distribution of solute

If m = slope of liquidus line, dT_E/dC_L & T_0: Equip. temp. for the pure metal

$$\boxed{T_E = T_0 - mC_L}$$

(Equip. temp. for the alloy)

a) Equilibrium temperature of alloy at distance X in front of interface

R Growth rate

$$T_E = T_0 - mC_0\left[1 + \frac{1-k_0}{k_0}\exp\left(-\frac{R}{D}X\right)\right]$$

D diffusivity

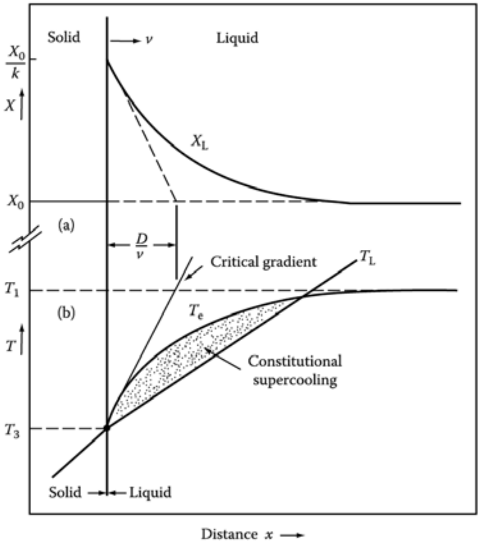
b) Actual temperature of alloy at distance X in front of interface

$$T = \boxed{T_0 - m\frac{C_0}{k_0}} + \boxed{G}X$$

Interface temperature

(Ignoring the supercooling required to provide the kinetic driving force)

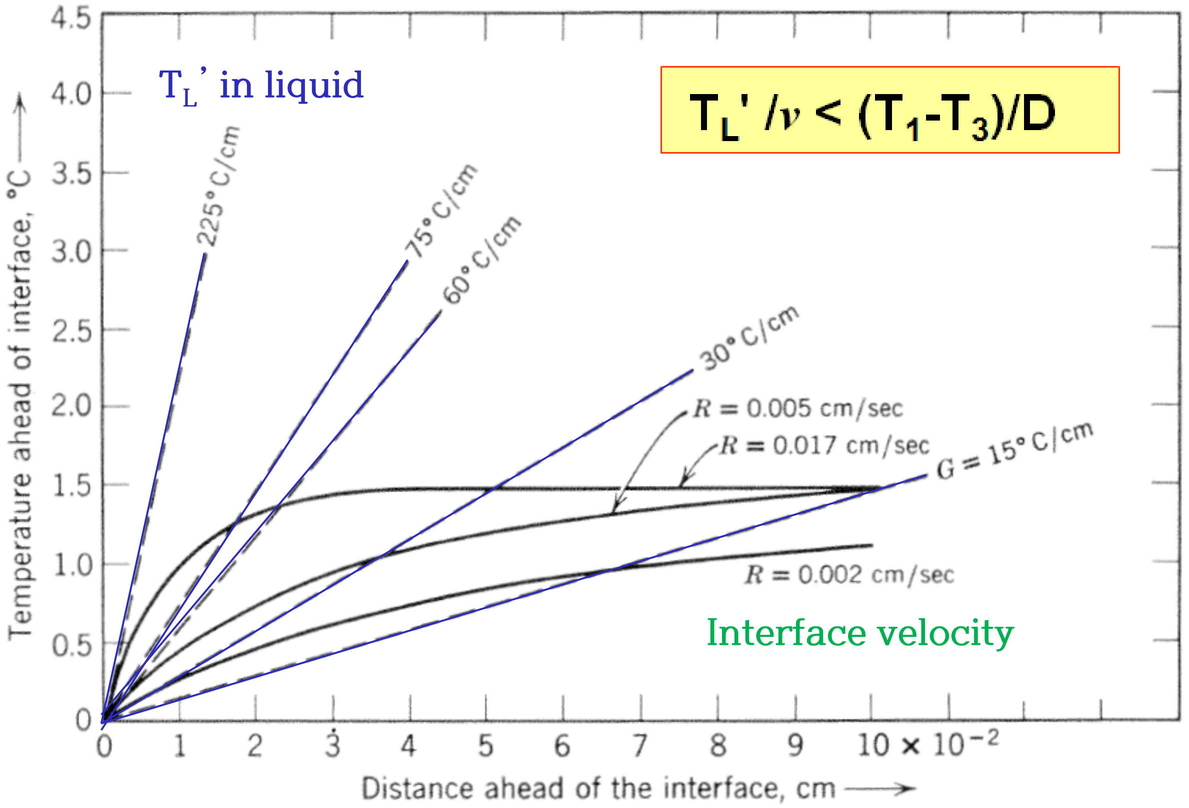
Temp gradient in the liquid in degrees per centimeter, T_L'



2) Quantitative studies of cell formation

Fig. 5.32. distribution of temperature and liquid temperature ahead of an advancing planar interface, for selected values of R and G. (From Ref. 3, p. 434.)

Interface velocity T_L' in liquid



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

⇨ **“Length of the supercooled zone” is given by the value of X (distance) at $T=T_E$.**

$$1-\exp\left(\frac{R}{D}X\right)=\frac{G}{mC_0(1-k_0)/k_0}X$$

2) Quantitative studies of cell formation

⇨ **The critical ratio of temperature gradient (G) to growth rate (R) is that at which the length of the supercooled zone is zero, or the slopes at the origin of the "liquidus temperature" lines are equal.**

$$\boxed{\frac{G}{R} = \frac{mC_0}{D} \cdot \frac{1-k_0}{k_0}}$$

G/R ∝ solute concentration (C_0)

or G/RC_0 = constant

⇨ **These experiments confirm the cell formation is a result of the instability produce by constitutional supercooling.**

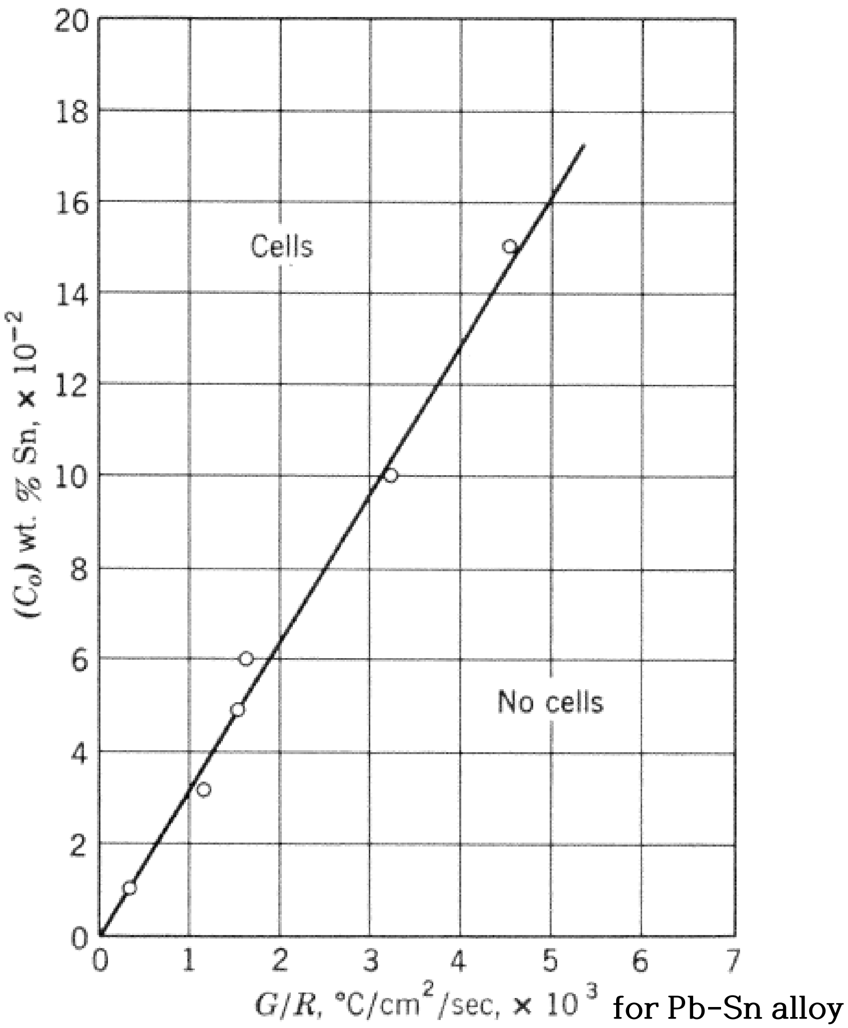


Fig. 5.33. Conditions for cellular solidification

2) Quantitative studies of cell formation

*** Since C.S. cannot exist until an enriched (or depleted) boundary layer has been formed, it follows that cells should not form immediately when solidification begins, even if uniform values of G and R are immediately established.**

⇨ **There "must" be an "incubation distance" for the formation of cells.**

$$Z = \frac{D}{k_0 R} \ln\left[1 - \frac{GD}{C_0 R m (1 - k_0)/k_0}\right]$$

: typical experimental case ~ order of one millimeter

*** Rutter : Suggesting a method to find the purity of a metal as a critical condition of cell formation ① Assumption: single solute with k_0 (equil. Distribution coefficient)/ Using directly measured G and R values → C_0 composition calculation**

$$C_0 = \frac{k_0}{1 - k_0} \cdot \frac{D}{m} \cdot \frac{G}{R}$$

: for experimentally convenient values of G and R, C_0 can be determined when it is btw $6\text{x}10^{-4}$ ~ $2\text{x}10^{-1}$ wt.%.

② If there is more than one solute→still possible to obtain information about purity; but the information is restricted to an assessment of the combined effect of solutes.

Assumption : solution ~ so dilute = no interaction between solutes

$$\frac{G}{R} = \Sigma\{C_0{}^1 \cdot [(1 - k_0{}^1)/k_0{}^1] \cdot (m^1/D)\}$$