2017 Fall

"Calculation and Applications Phase Equilibria"

Principles *of* Solidification

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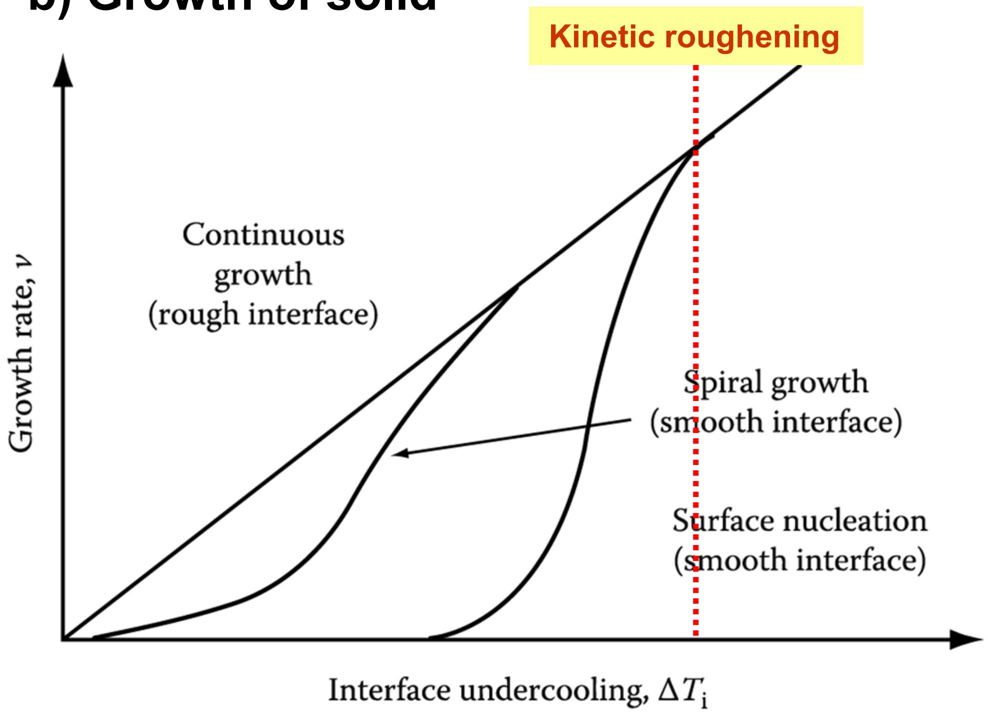
Solidification: Liquid ⟶ Solid

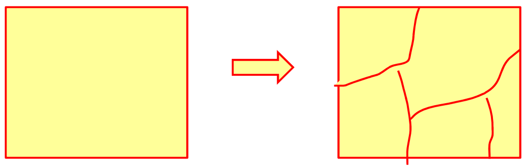
1) Pure Metals: Nucleation and Growth (thermally activated process)

a) homogeneous Nucleation or Heterogeneous Nucleation

- Undercooling ΔT
- Interfacial energy
  γ_{SL} / $S(\theta)$ wetting angle

b) Growth of solid





No compositional change during solidification

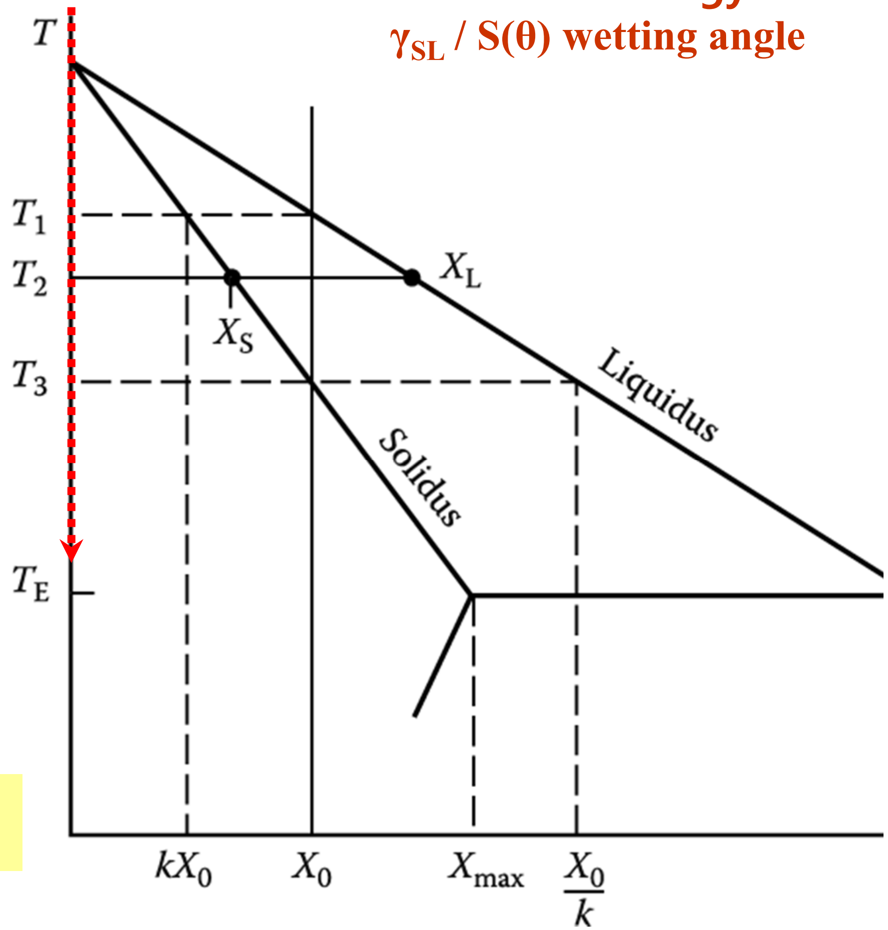


Fig. 4.19 A hypothetical phase diagram.

Chapter 5. Redistribution of solute during solidification

"Alloy solidification"

1. Solidification of single-phase alloys

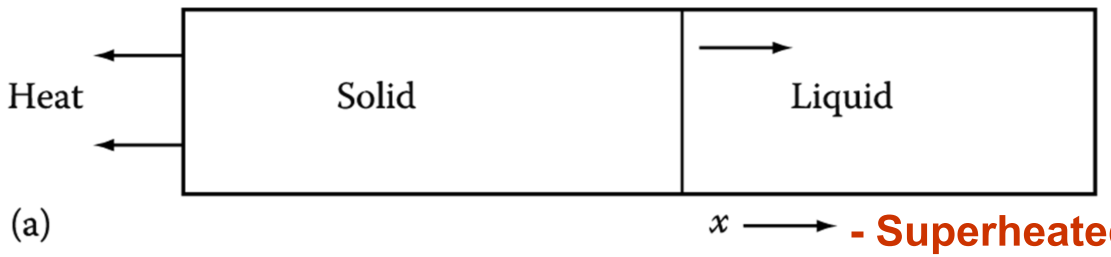
- **Three limiting cases**

  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

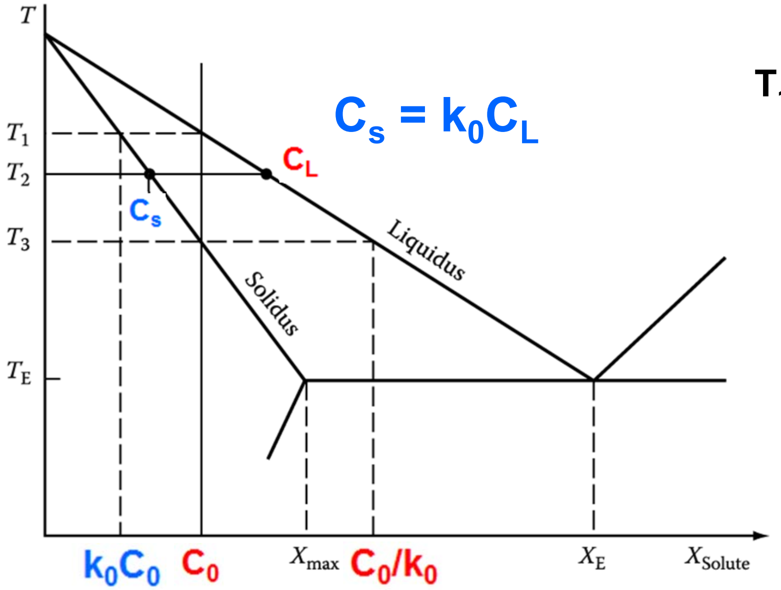


- Superheated liquid

- Cellular and Dendritic Solidification

- Constitutional Supercooling

1) Equilibrium Solidification : perfect mixing in solid and liquid

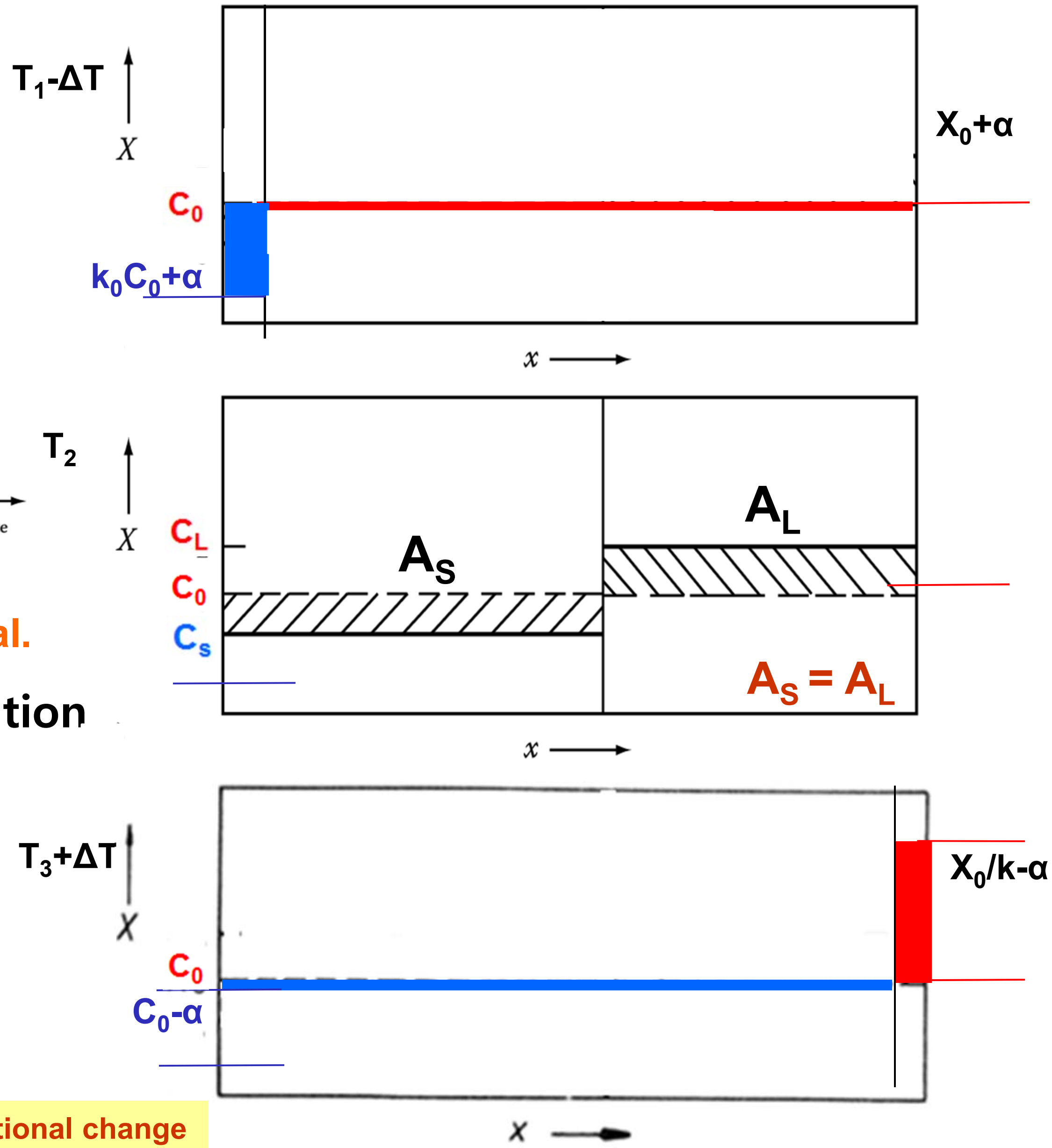


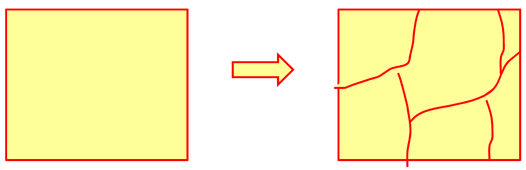
Conservation of solute requires the two shaded areas to be equal.

* Equilibrium solute concentration

$k_0C_0 \leq C_s \leq C_0$

$C_0 \leq C_L \leq C_0/k_0 < X_{Eutectic}$



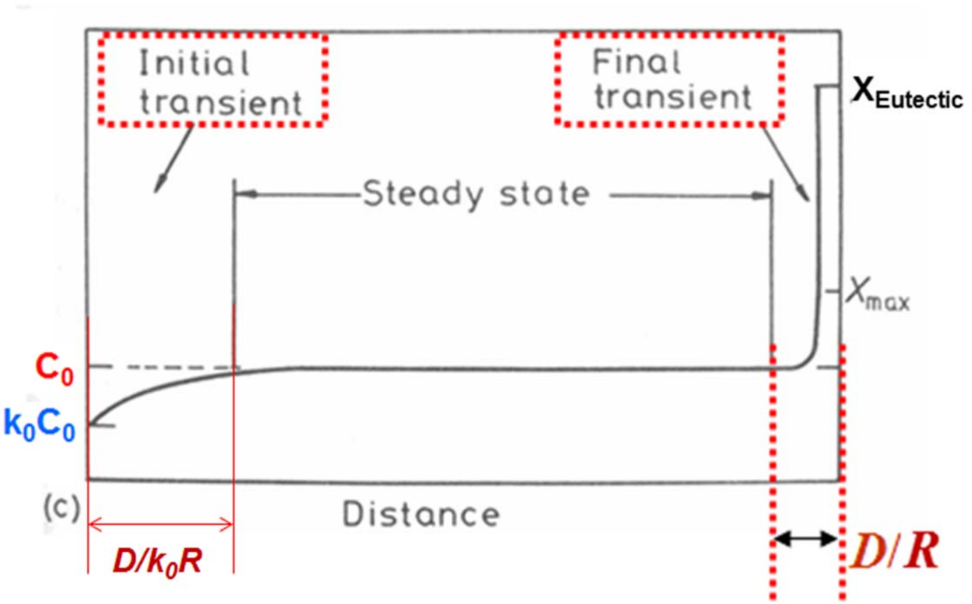


Liquid α

Compositional change during solidification

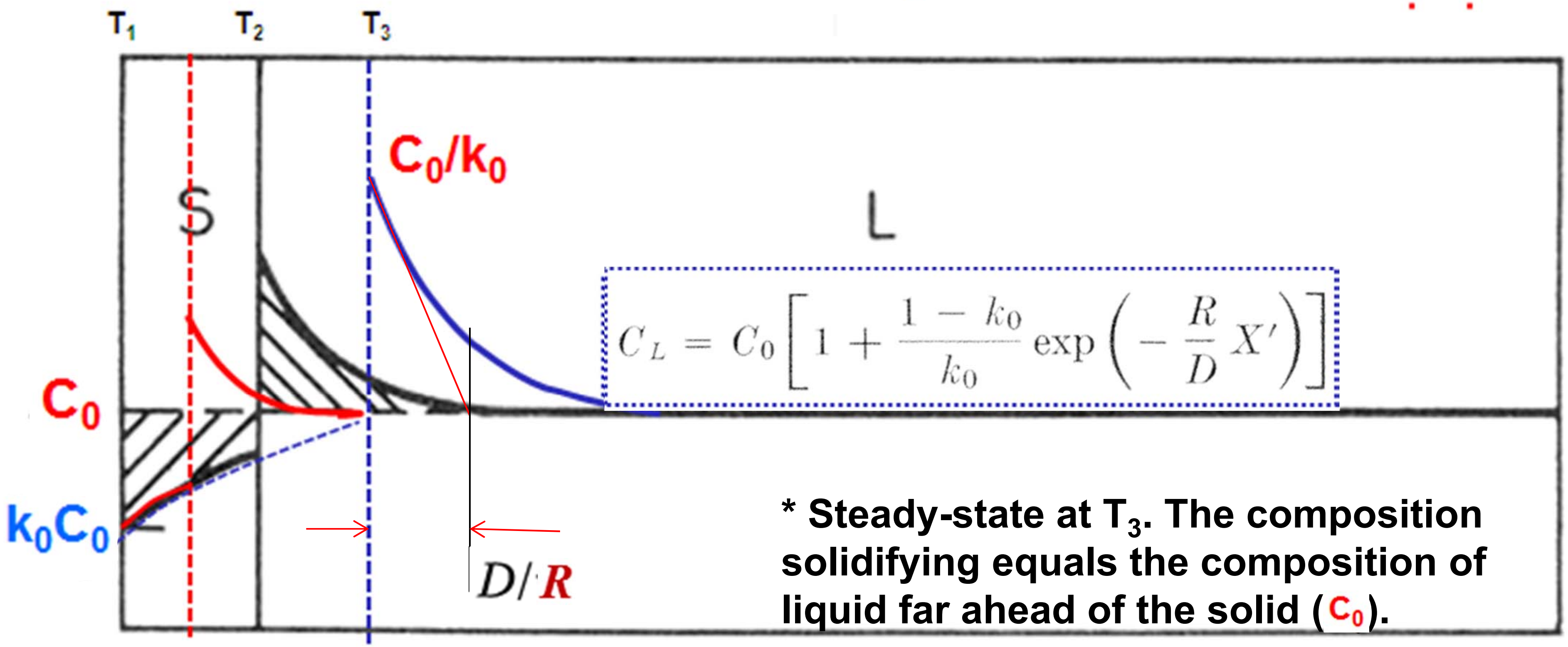
"Alloy solidification"

- Solidification of single-phase alloys



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

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).**

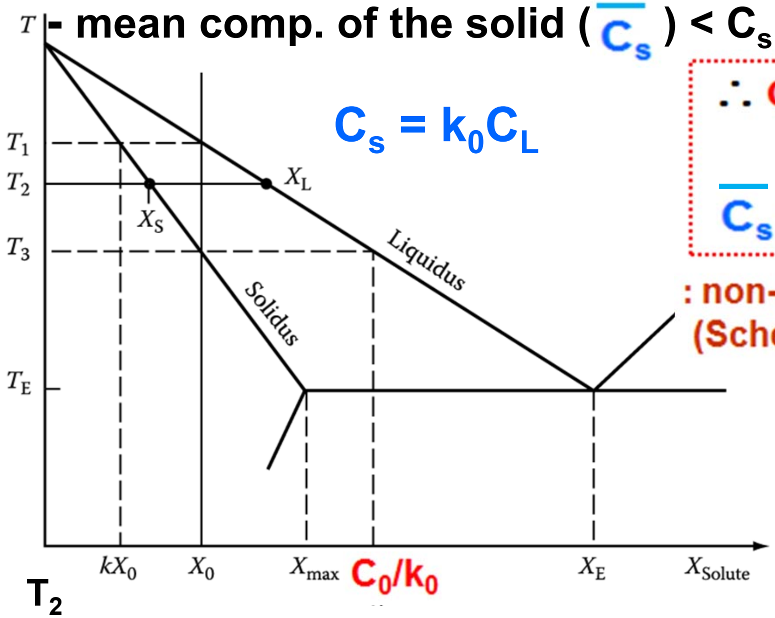
3) No Diffusion in Solid, Perfect Mixing in Liquid

: high cooling rate, efficient stirring

- Separate layers of solid retain their original compositions

- mean comp. of the solid ($\overline{C_s}$) < C_s

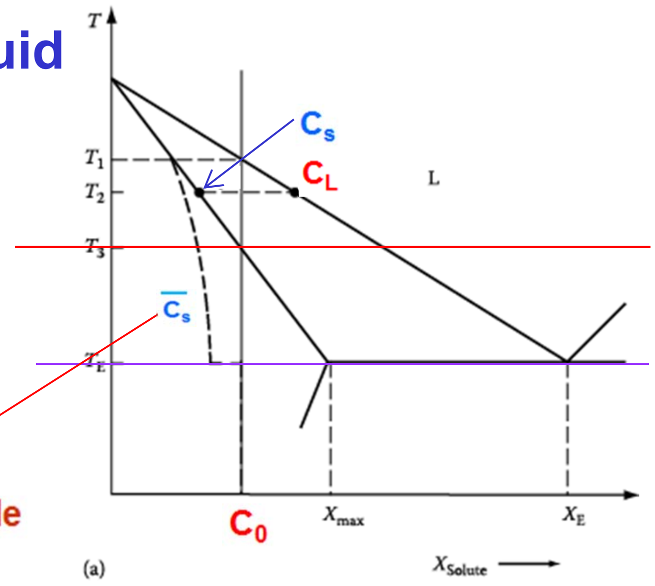
$C_s = k_0 C_L$

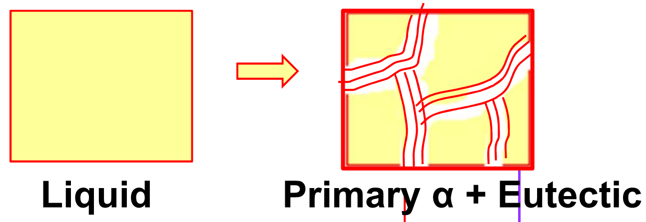


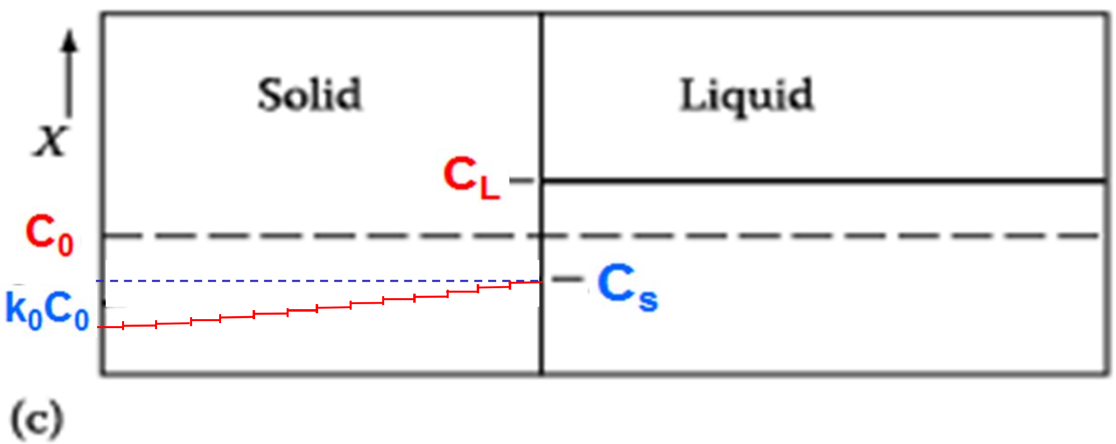
$$\therefore C_L = C_0 f_L^{(k-1)}$$

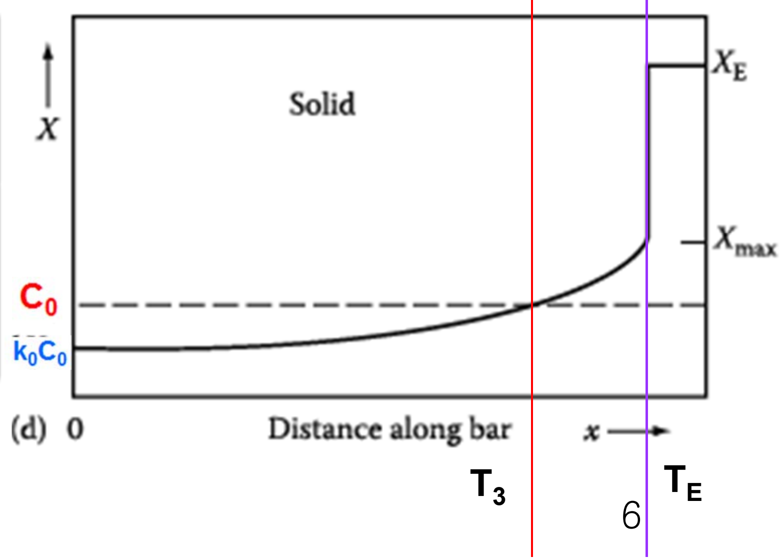
$$\overline{C_s} = k C_0 (1 - f_S)^{(k-1)}$$

: non-equilibrium lever rule (Scheil equation)





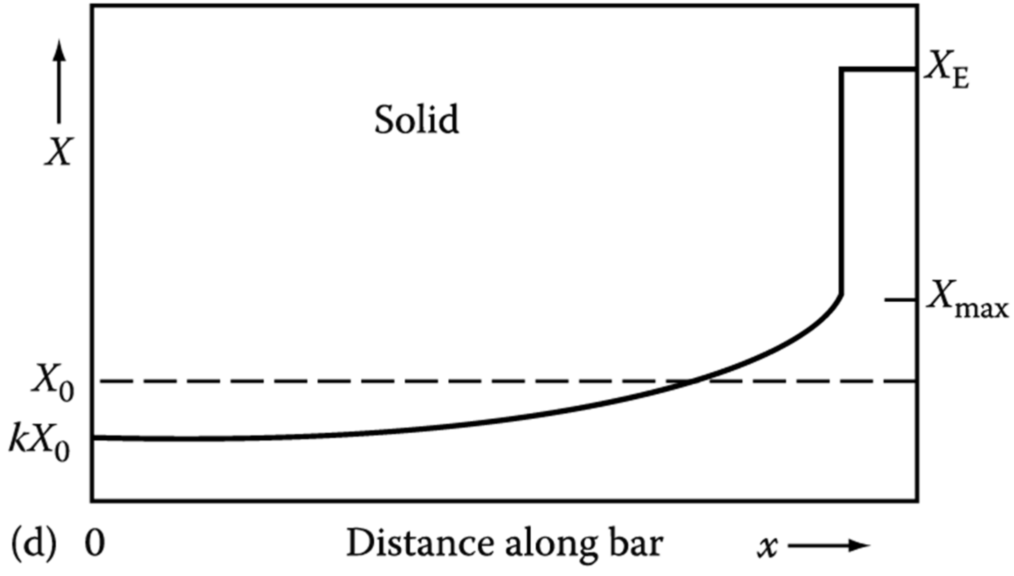


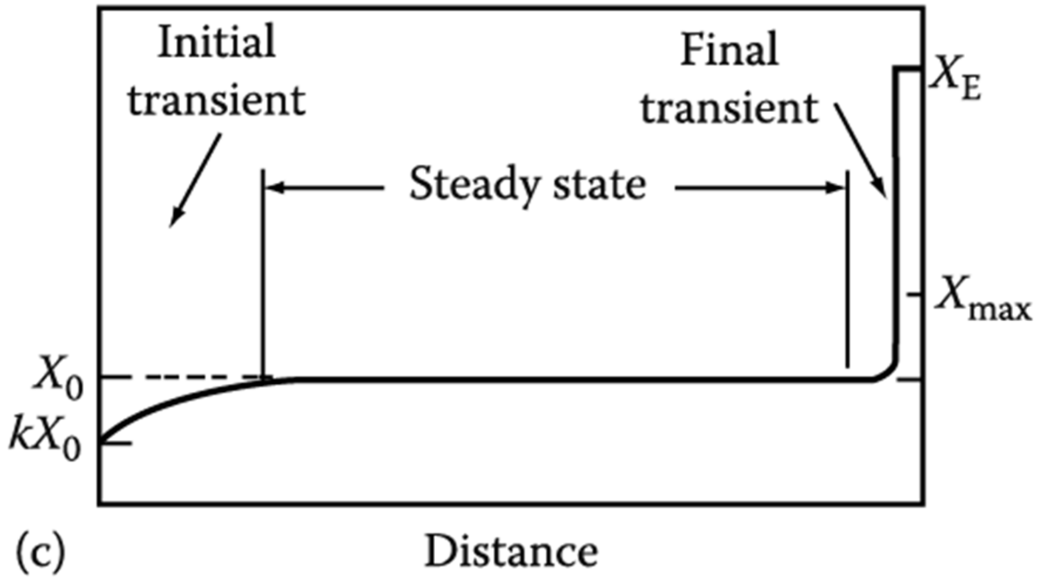


$solid \rightarrow \bar{X}_s < C_s$ $\quad$ $liquid > C_0/k_0 \rightarrow X_E$

Concentration profiles in practice

: exhibit features between two cases





➡ **Zone Refining**

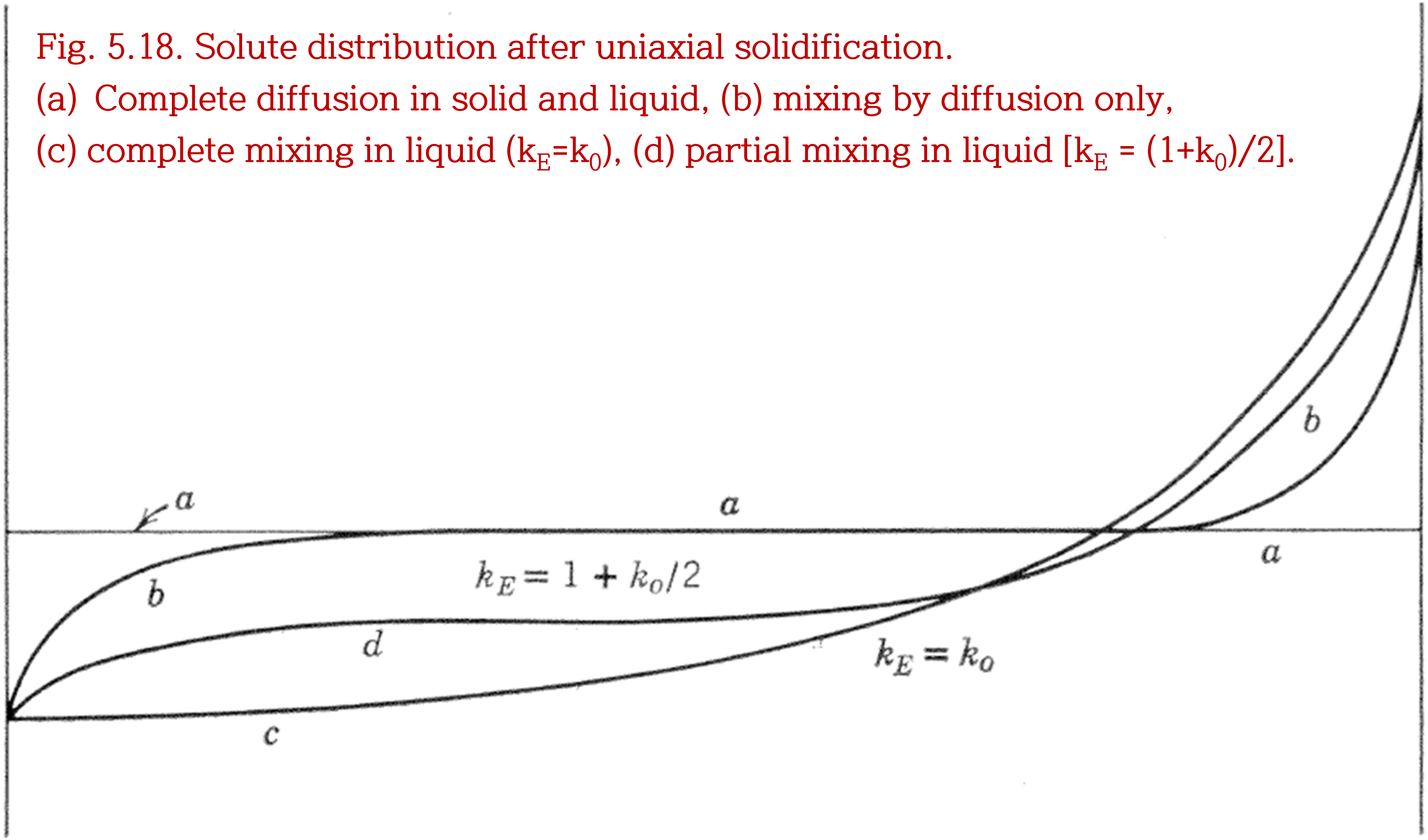


Fig. 5.18. Solute distribution after uniaxial solidification.
(a) Complete diffusion in solid and liquid, (b) mixing by diffusion only,
(c) complete mixing in liquid (k_E=k_0), (d) partial mixing in liquid [k_E = $(1+k_0)/2$].

* Comments: Solidus temperature of an alloy

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

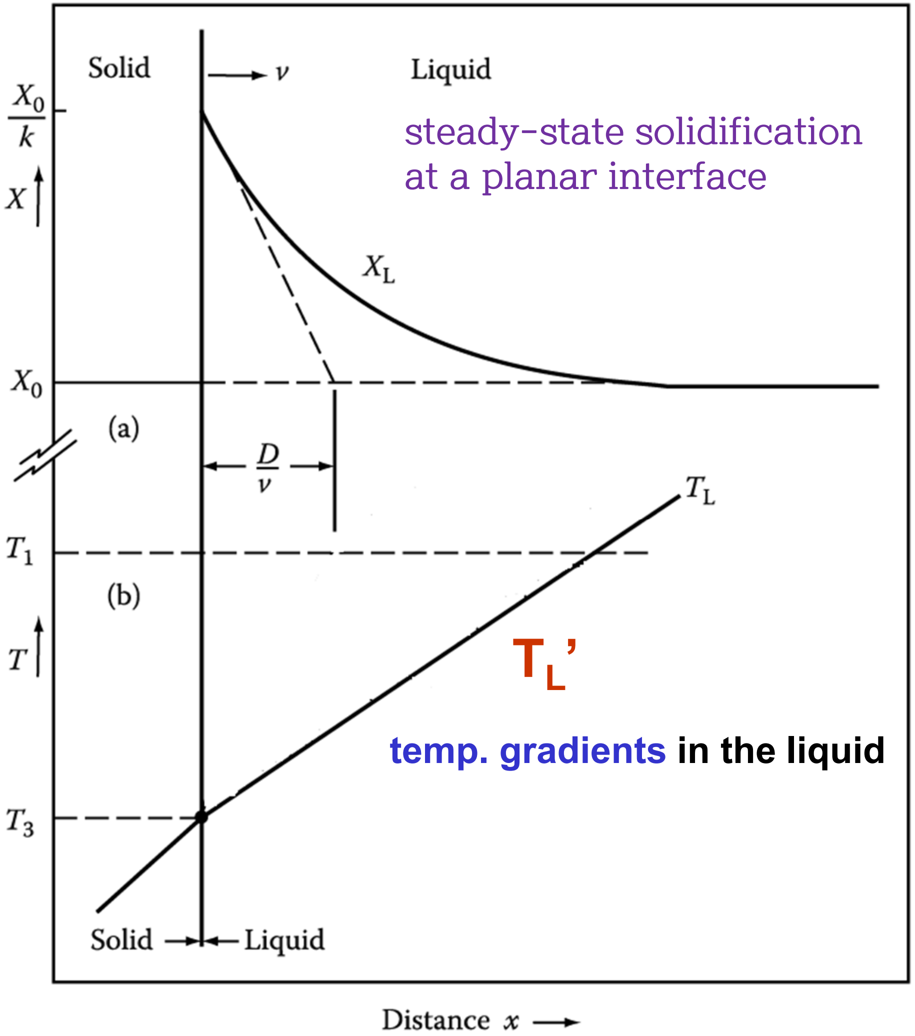
Phase diagram → determined from cooling curve ∴ T_L satisfactory, T_S large errors

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".

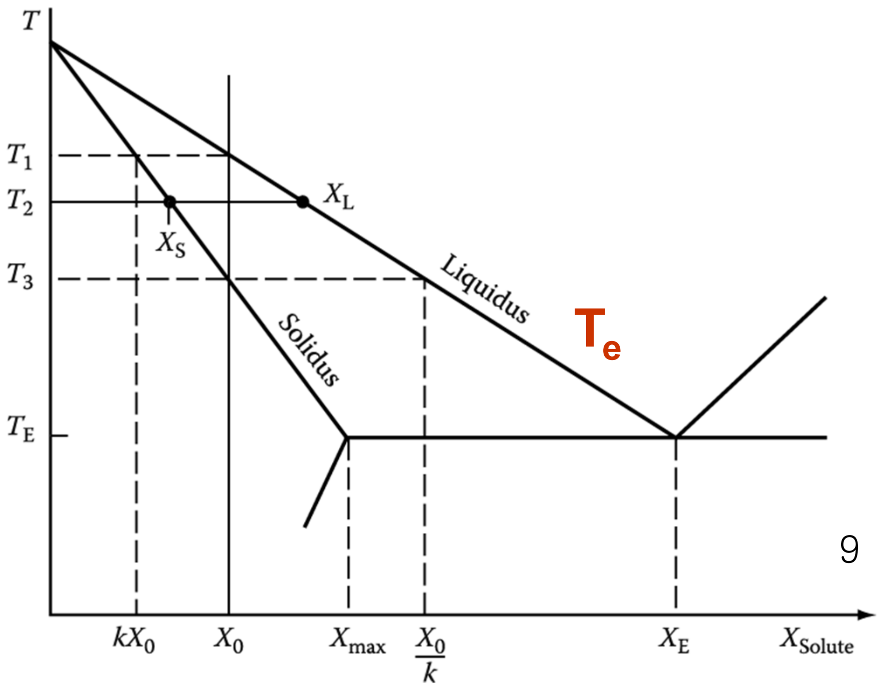
5.5 Constitutional supercooling

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.

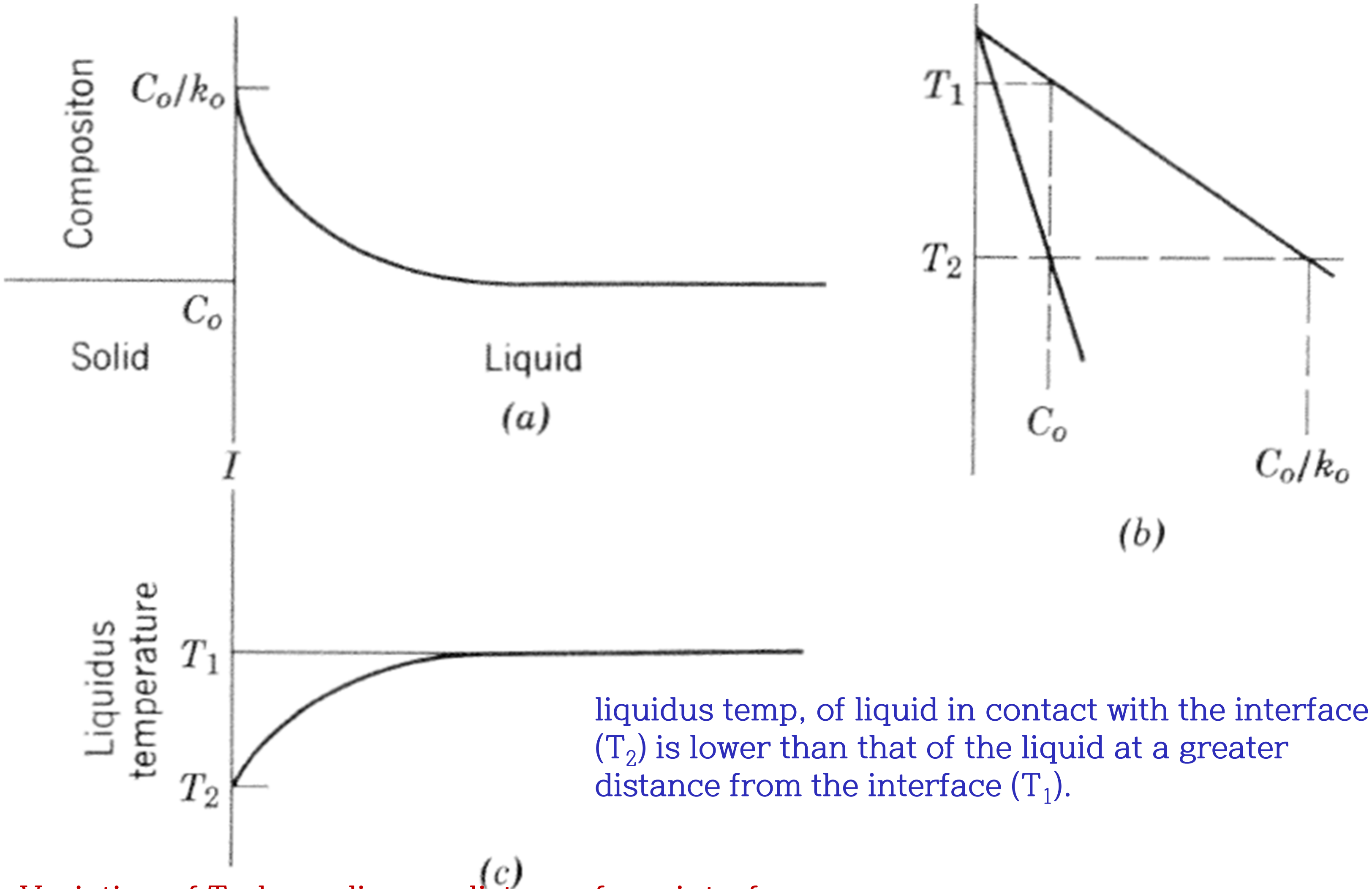


What would be "T_e" along the concentration profile ahead of the growth front during steady-state solidification?



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.

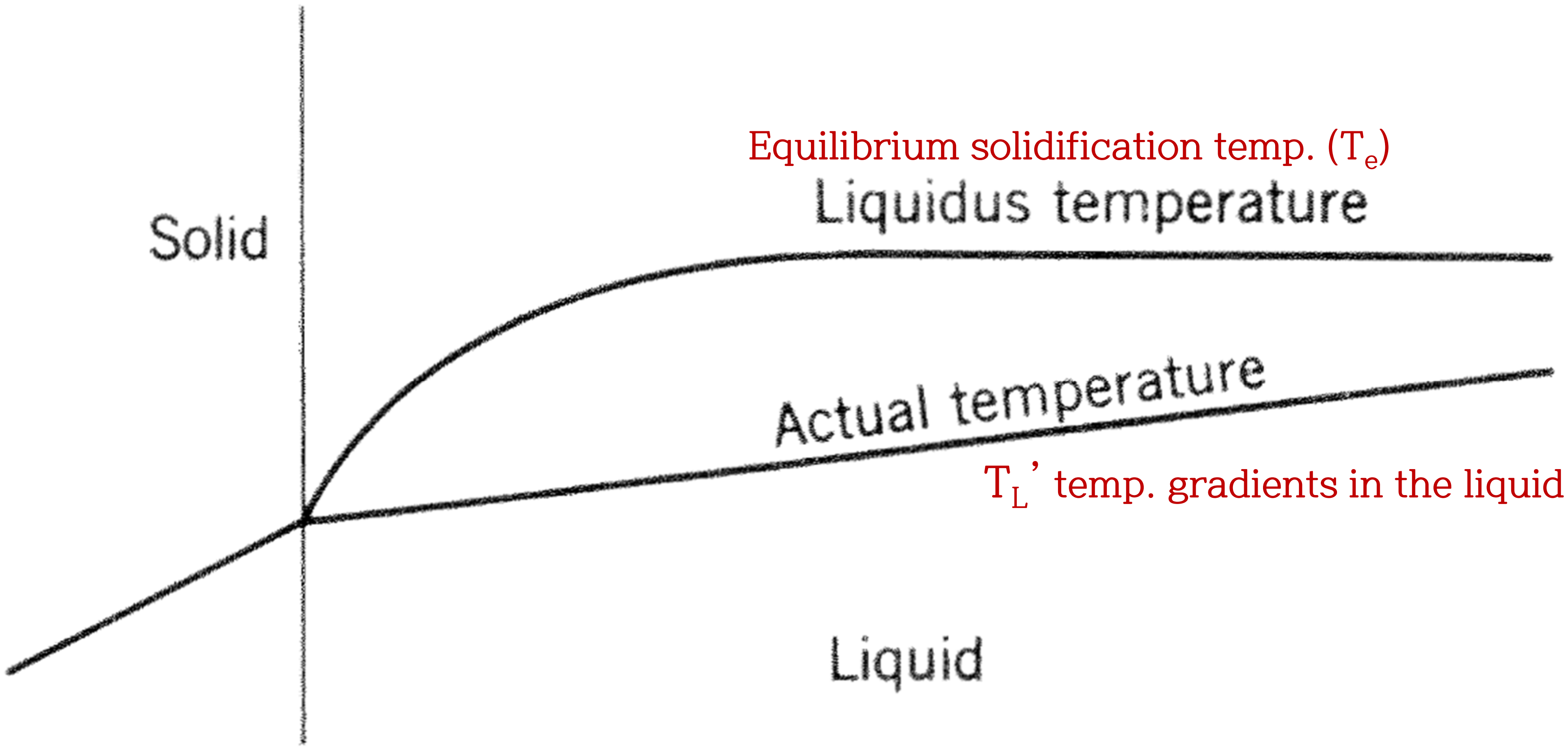
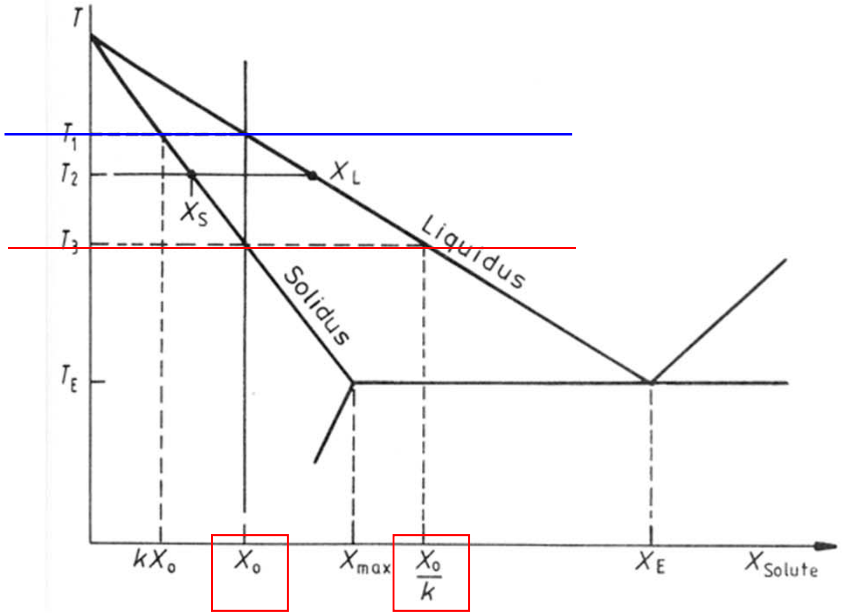


Fig. 5.27. Actual temperature of the liquid and its liquidus temperature

* Constitutional Supercooling

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

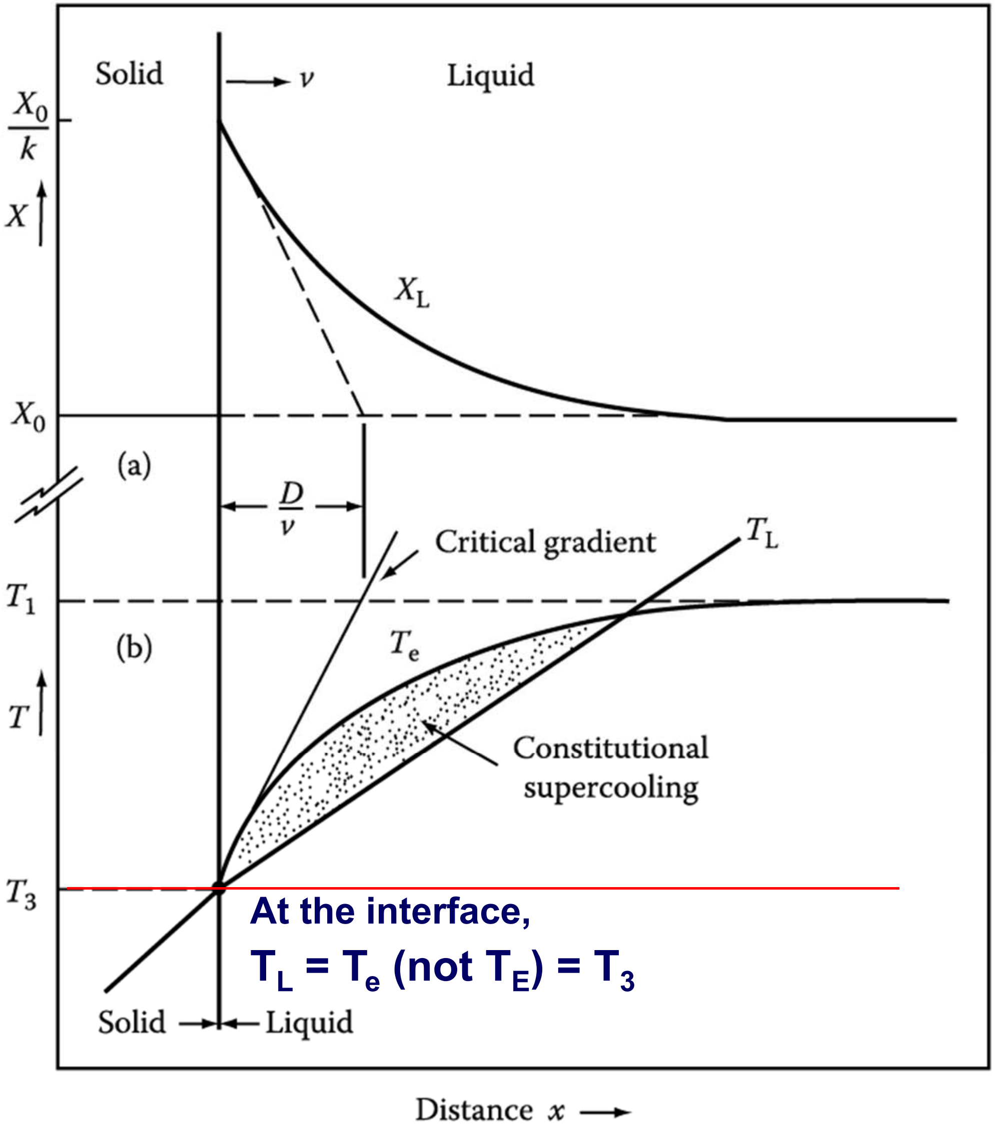


* Actual temperature gradient in Liquid

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)

→ 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:** $T_L'/v < (T_1-T_3)/D$

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 : 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.

* 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

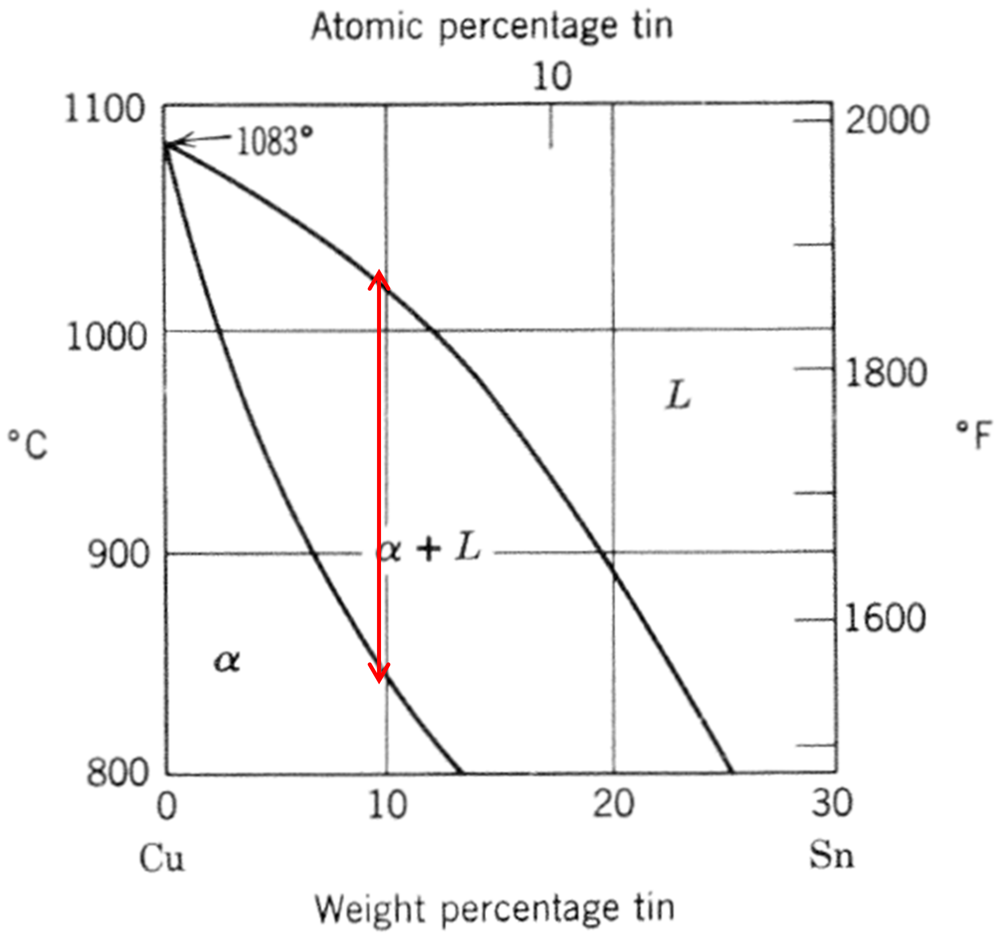


Fig. 5.28. Freezing range in copper-tin alloys

* **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

<u>The instability due to constitutional supercooling</u> 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.

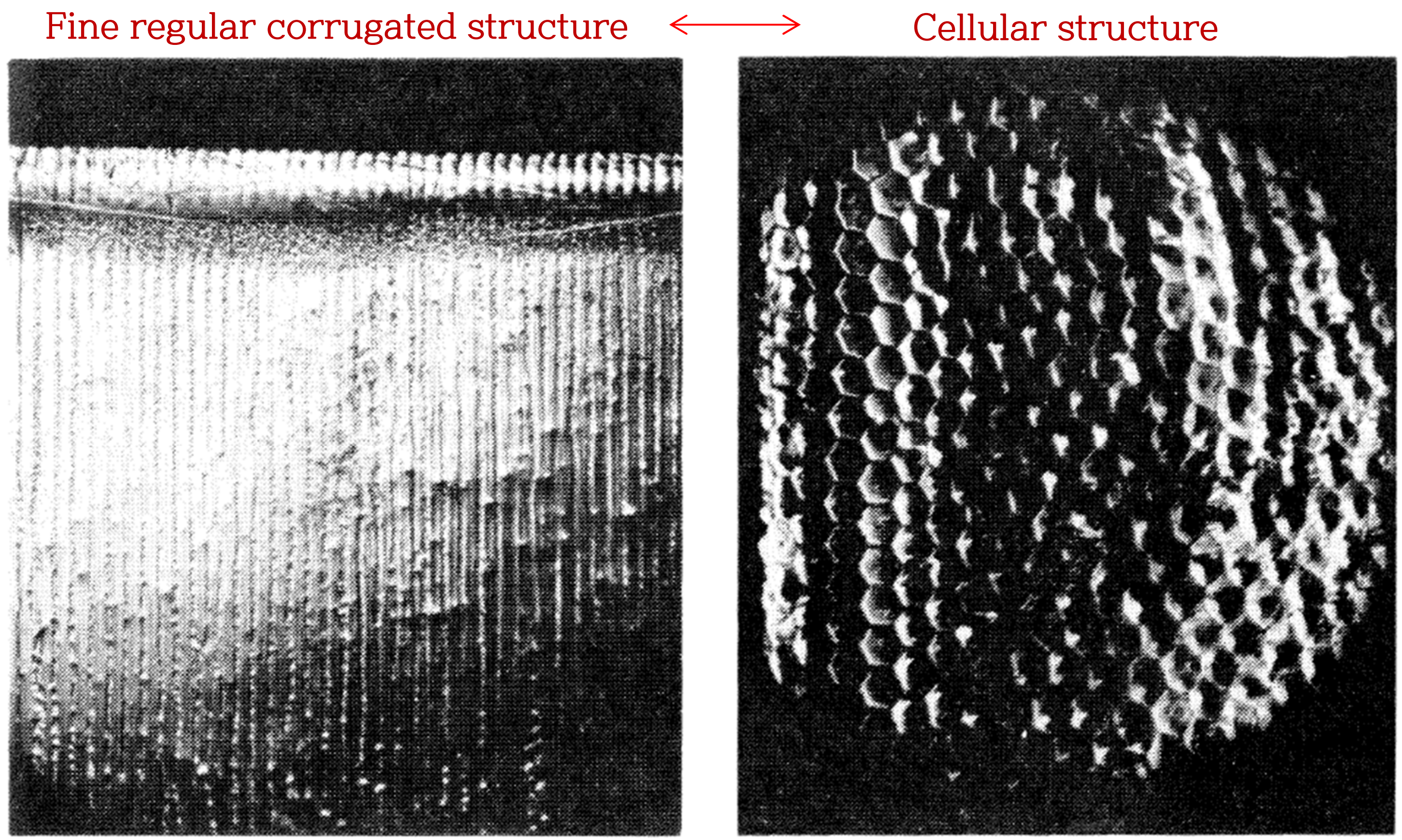


Fig. 5.29. Cellular structure (a) view of top (free) surface of tin crystal (x 75); (b) view of decanted interfaces of tin crystal (x 75)

5.6 Cellular Substructure

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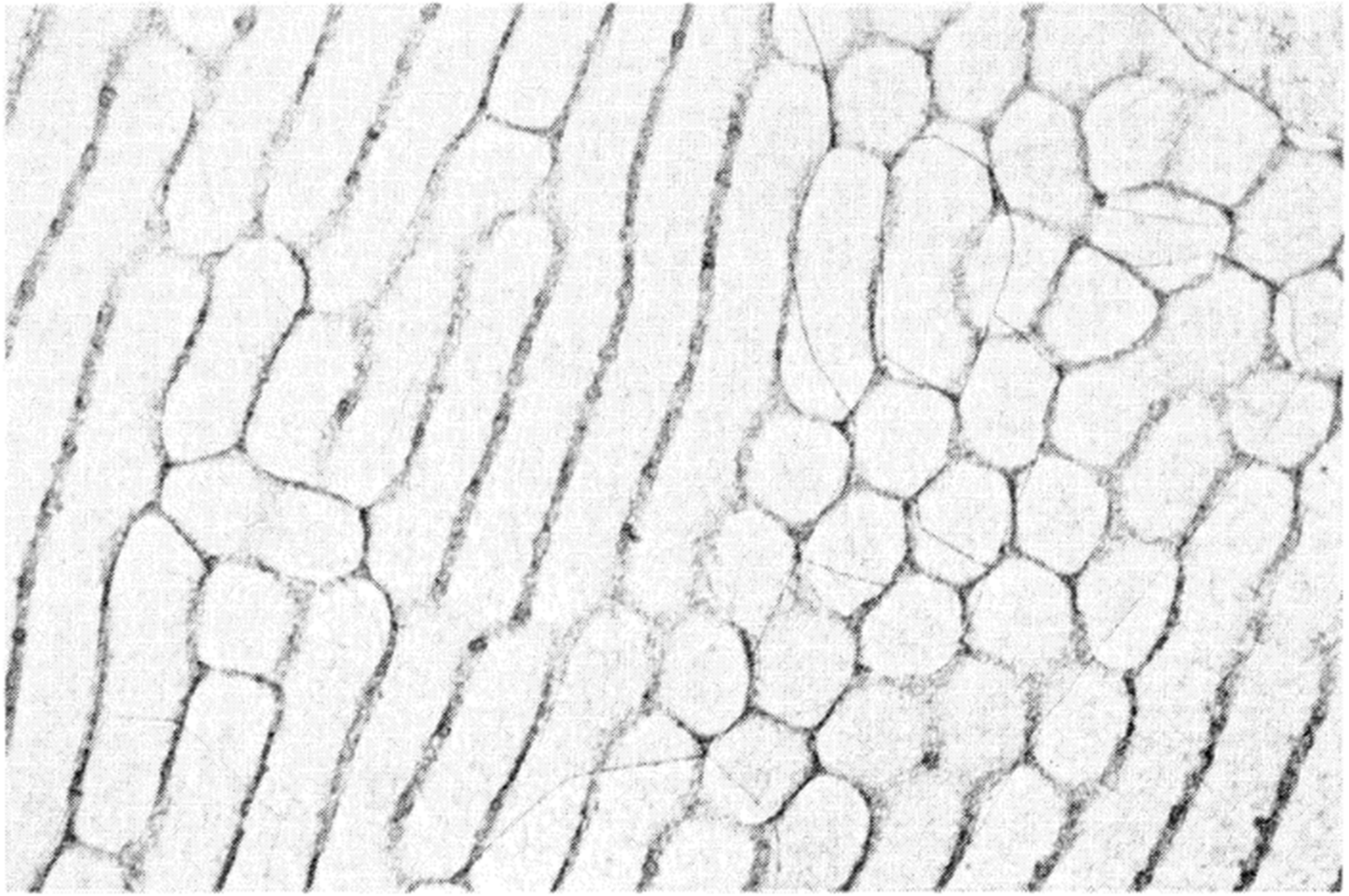


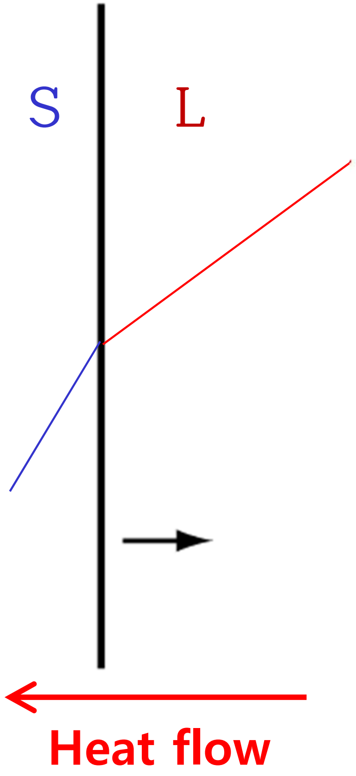
Fig. 5.29. (continue) Cellular structure (c) Less regular forms of cell

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)

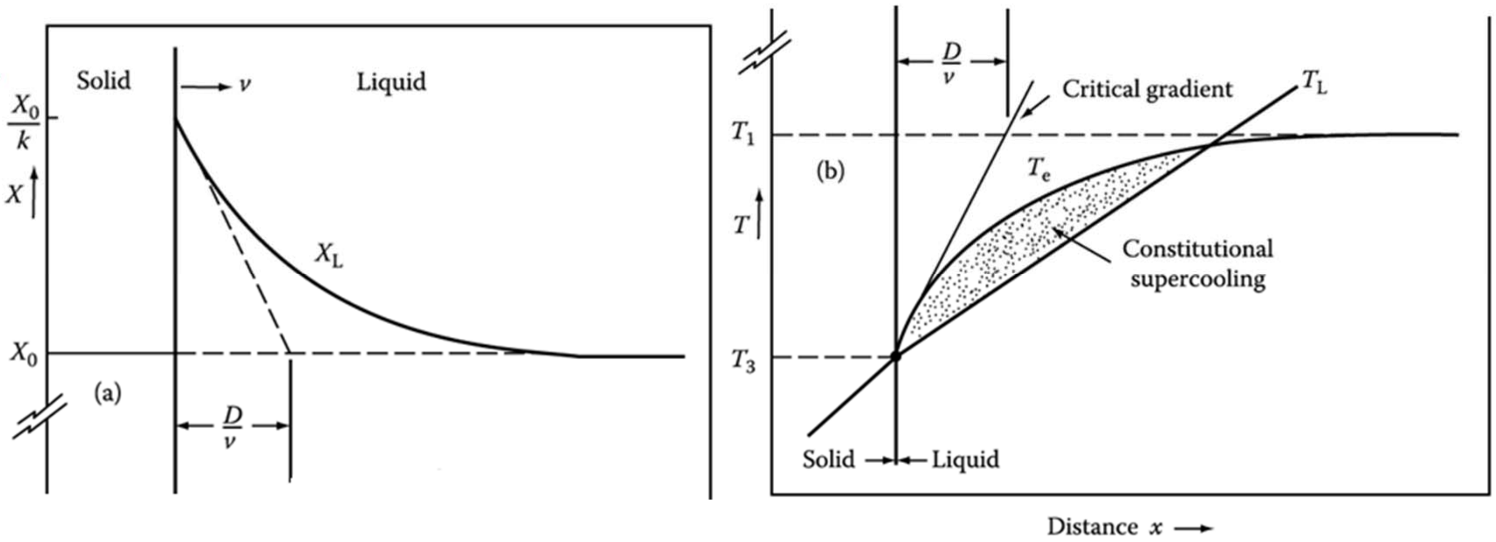


Fig. 5.30. Supercooling ahead of planar interface

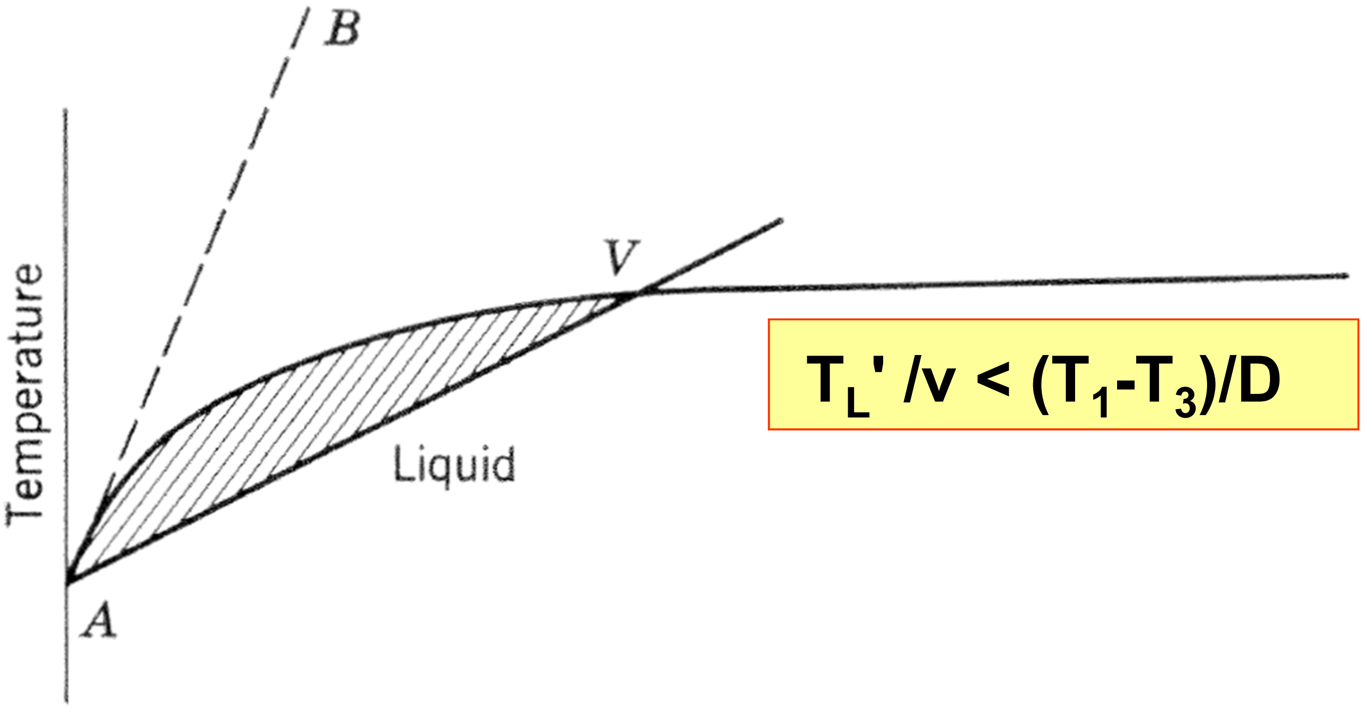
<The breakdown of an initially planar solidification front into cells>

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.

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1) Origin of Cellular substructure

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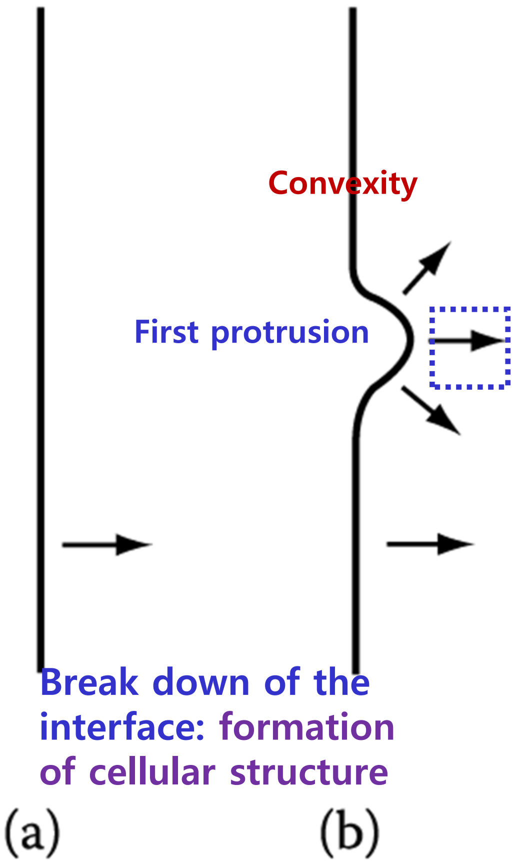


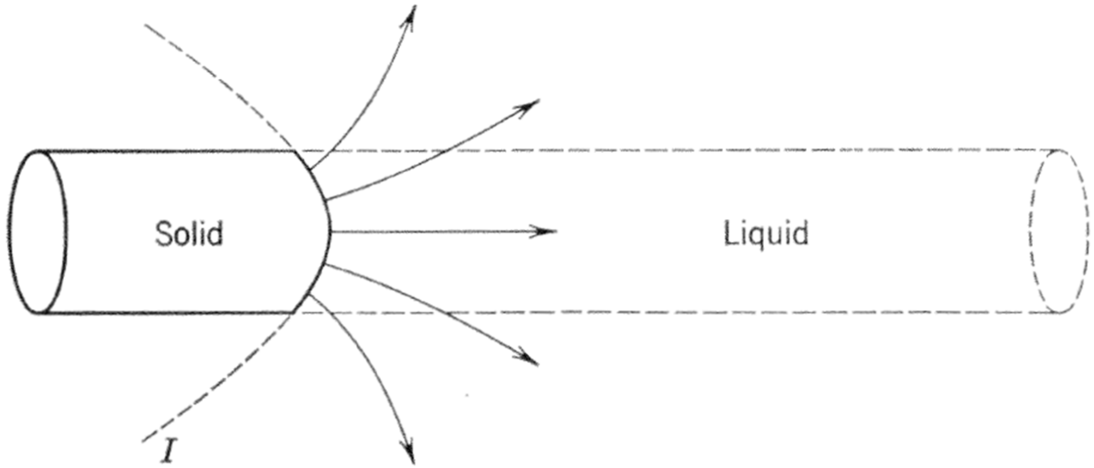


Fig. 5.14. Solute diffusion ahead of a convex interface

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

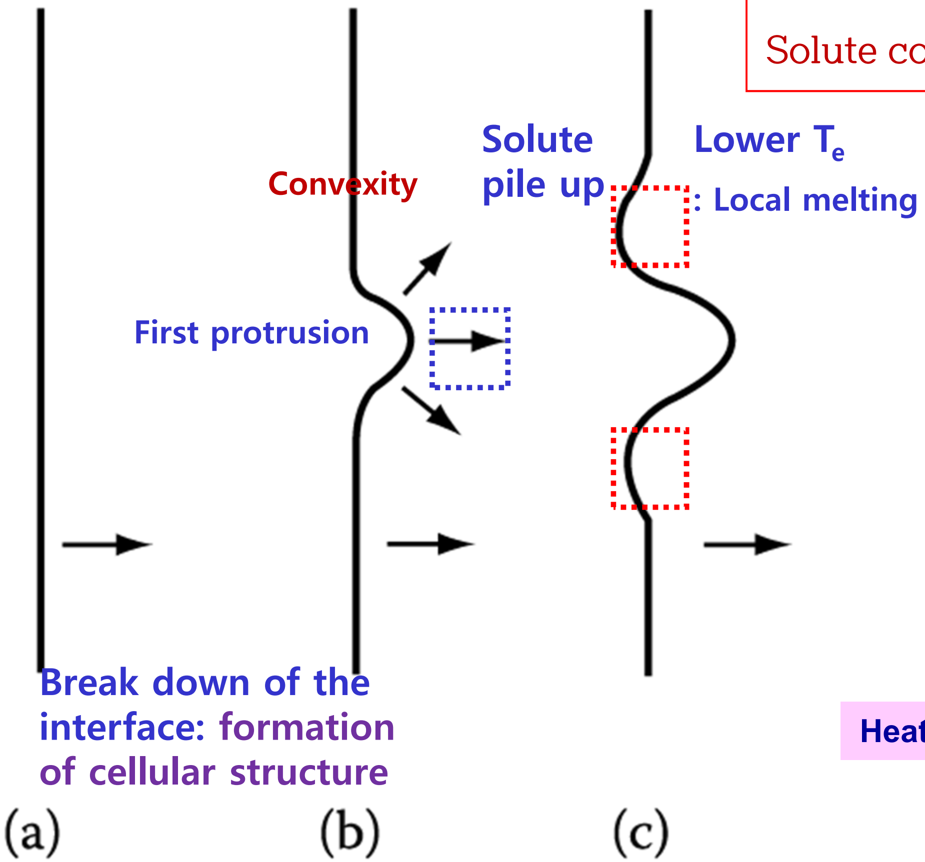
5.6 Cellular Substructure

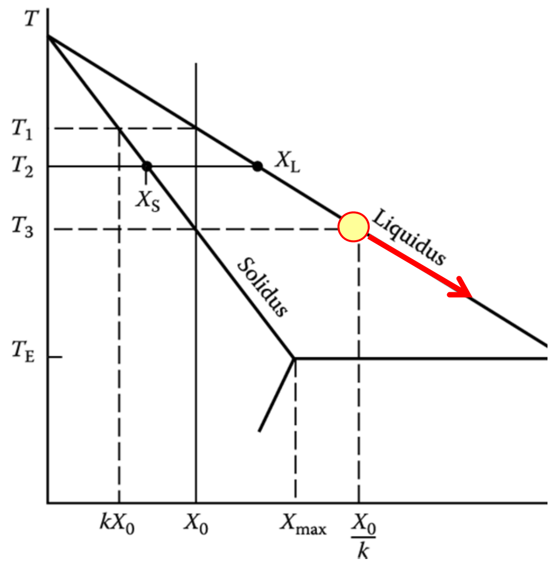
: Due to instability by constitutional supercooling at superheated liquid

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

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

K: thermal conductivity

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

5.6 Cellular Substructure

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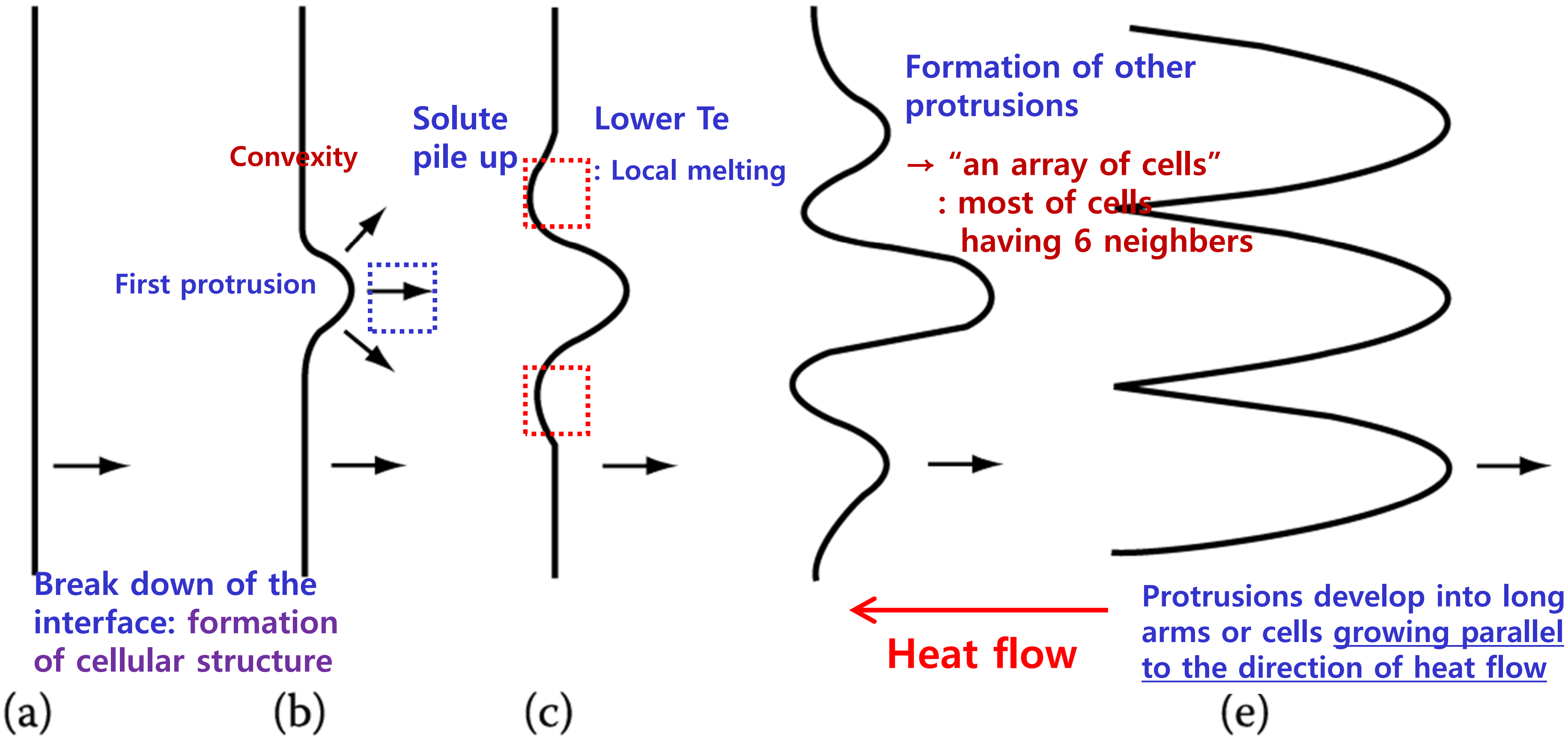
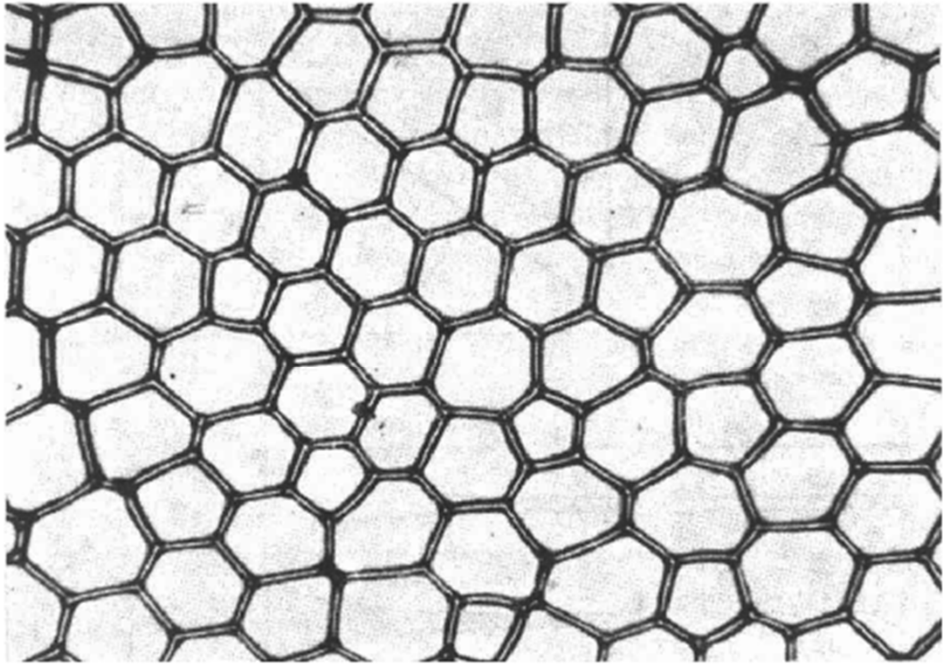
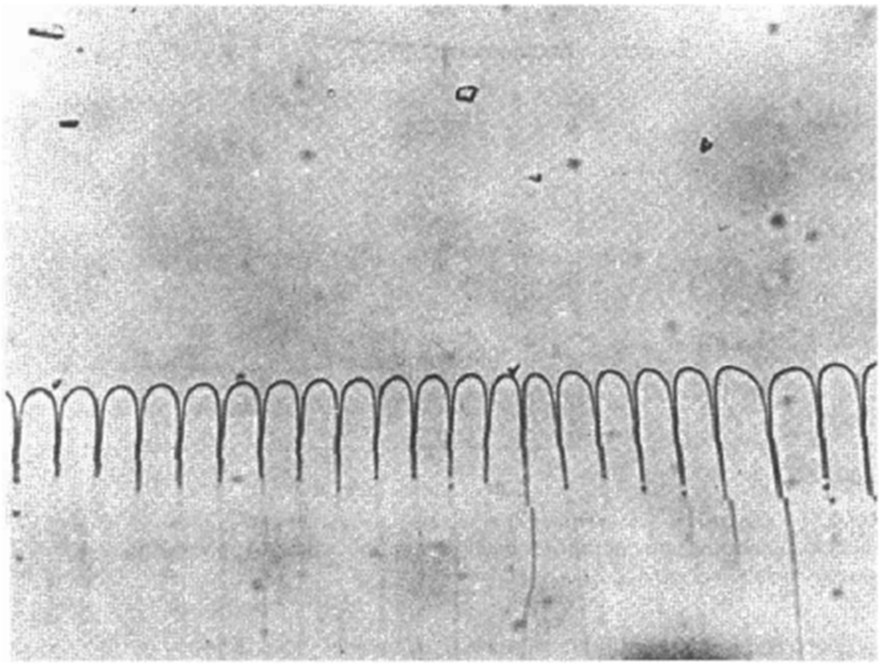
If temperature gradient ahead of an initially planar interface is gradually reduced below the critical value, (constitutional supercooling at interface, (a))



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



(a)



(b)

* 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)

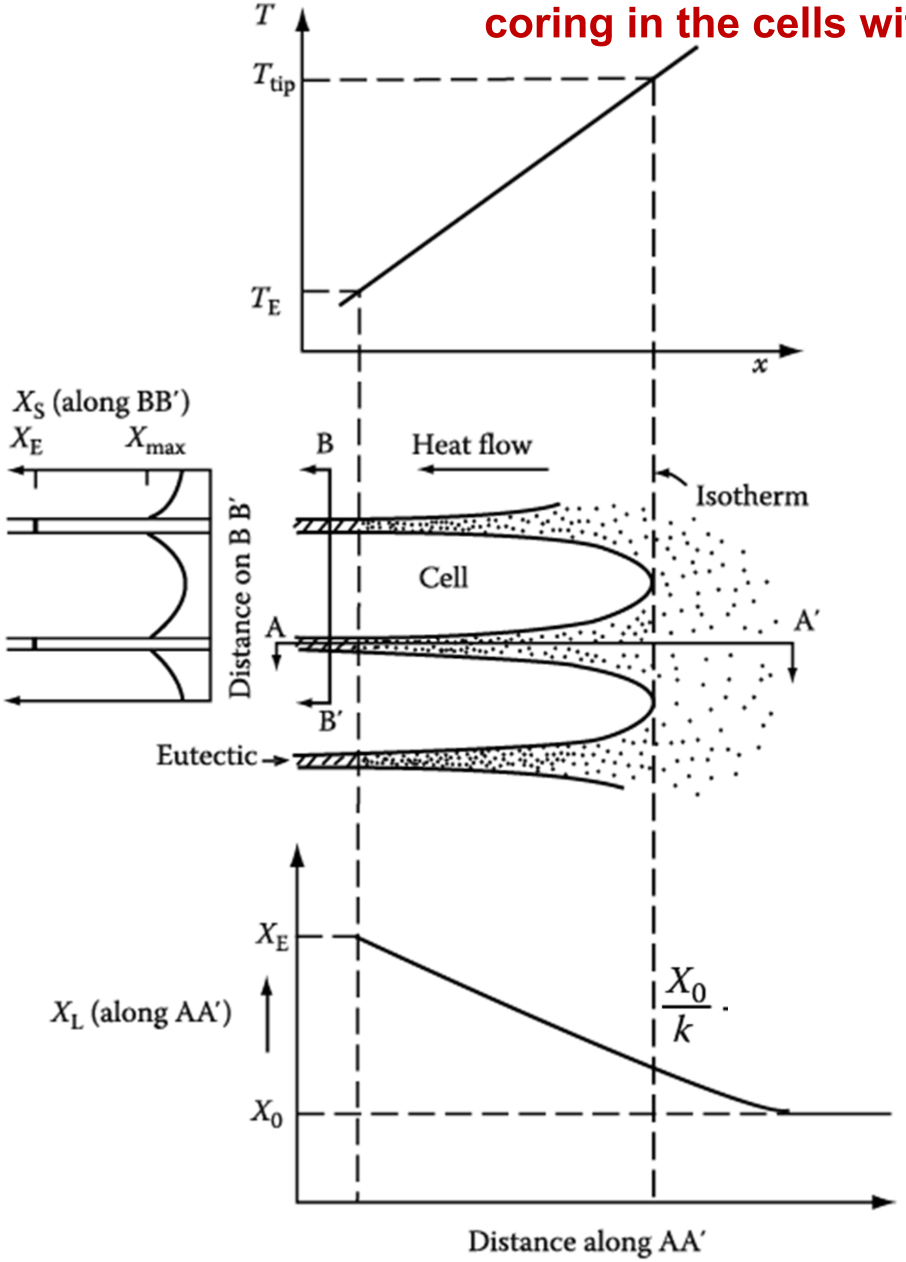
(after J.W. Rutter in Liquid Metals and Solidification, American Society for Metals, 1958, p. 243).

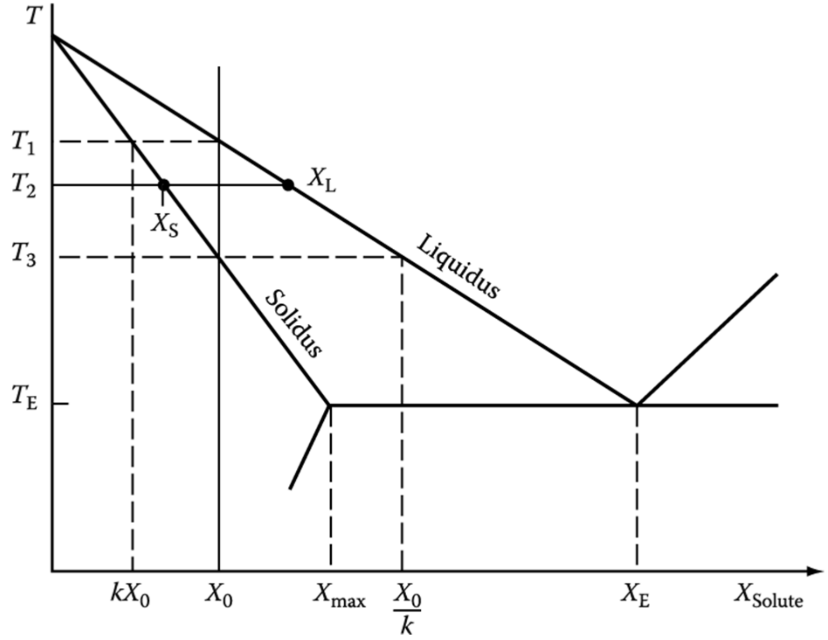
(b) Longitudinal view of cells in carbon tetrabromide (x 100)

(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