Diffusion and Kinetics

Lecture: **Solidification and Growth Kinetics**

Nikolai V. Priezjev

Textbook: Phase transformations in metals and alloys (Third Edition), By: Porter, Easterling, and Sherif (CRC Press, 2009).

Solidification and Growth Kinetics

- Nucleation in Pure Metals

  1) Homogeneous Nucleation, 2) Nucleation Rate, 3) Heterogeneous Nucleation

- Growth of a Pure Solid

  1) Growth mechanisms: Continuous and Lateral

- Alloy Solidification
- Solidification of Ignots and Casting
- Rate of a phase transformation

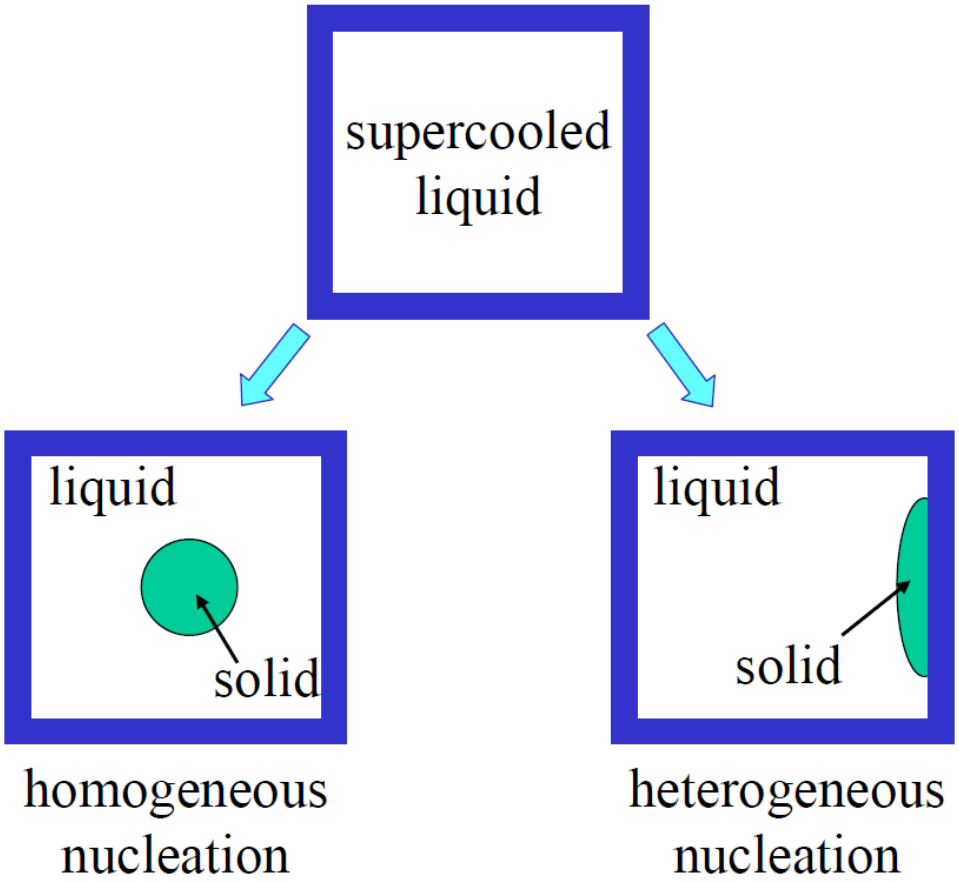
Reading: Chapter 4 of Porter, Easterling, Sherif

Nucleation

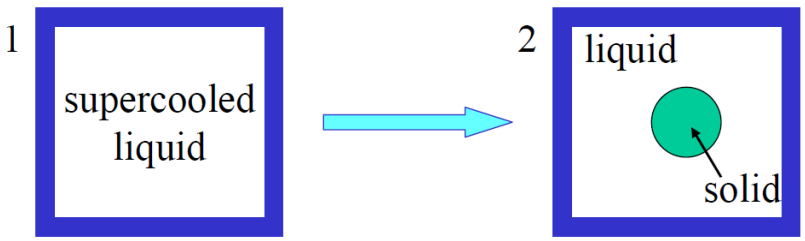
Heterogeneous – the new phase appears on the walls of the container, at impurity particles, etc.

Homogeneous – solid nuclei spontaneously appear within the undercooled phase.

Let's consider solidification of a liquid phase undercooled below the melting temperature as a simple example of a phase transformation.



Homogeneous nucleation



Is the transition from undercooled liquid to a solid spherical particle in the liquid a spontaneous one?

That is, does the Gibbs free energy decreases?

The formation of a solid nucleus leads to a Gibbs free energy change of $\Delta G = G_2 - G_1 = \underbrace{-V_S (G_v^L - G_v^S)}_{\text{negative below } T_m} + \underbrace{A^{SL}\gamma^{SL}}_{\text{always positive}}$

V_S – volume of the solid sphere

A^{SL} – solid/liquid interfacial area

γ^{SL} – solid/liquid interfacial energy

$\Delta G_v = G_v^L - G_v^S$ is the difference between free energies per unit volume of solid and liquid

at $T < T_m$, $G_v^S < G_v^L$ – solid is the equilibrium phase

Reminder: Driving force for solidification (ΔG_v)

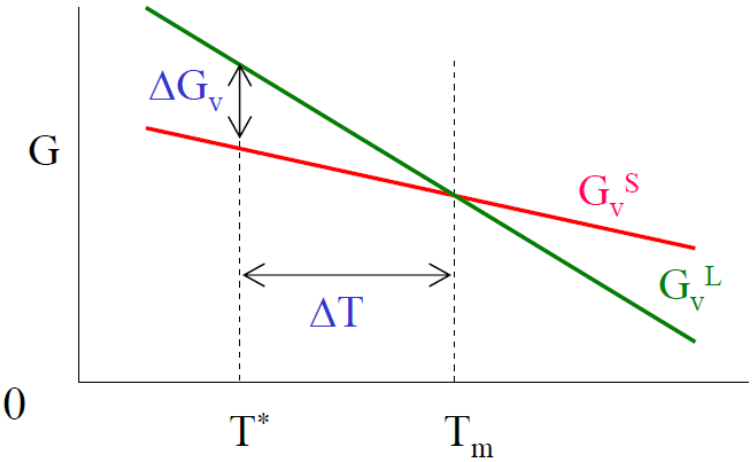
When a liquid is cooled below the melting temperature, there is a driving force for solidification, $\Delta G_v = G_v^L - G_v^S$

At temperature T^*

$$G_v^L = H_v^L - T^* S_v^L$$

$$G_v^S = H_v^S - T^* S_v^S$$

$$\Delta G_v = \Delta H_v - T^* \Delta S_v$$



At temperature T_m

$$\Delta G_v = \Delta H_v^m - T_m \Delta S_v^m = 0$$

$$\Delta S_v^m = \frac{\Delta H_v^m}{T_m}$$

For small undercooling ΔT we can assume that ΔH_v and ΔS_v are independent of temperature (neglect the difference in C_p between liquid and solid)

$$\Delta G_v \approx \Delta H_v^m - T^* \frac{\Delta H_v^m}{T_m} = \frac{\Delta H_v^m \Delta T}{T_m}$$

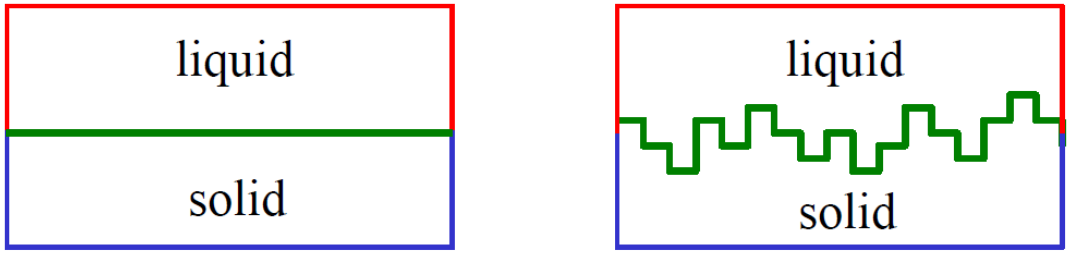
At any temperature below T_m there is a driving force for solidification. The liquid solidify at $T < T_m$. If energy is added/removed *quickly*, the system can be significantly undercooled or (supercooled).

$$\Delta G_v = \frac{\Delta H_m \Delta T}{T_m}$$

As we will see, the contribution of interfacial energy (γ^{SL}) results in a kinetic barrier for the phase transformation.

Origin of the interfacial energy (γ_{SL})

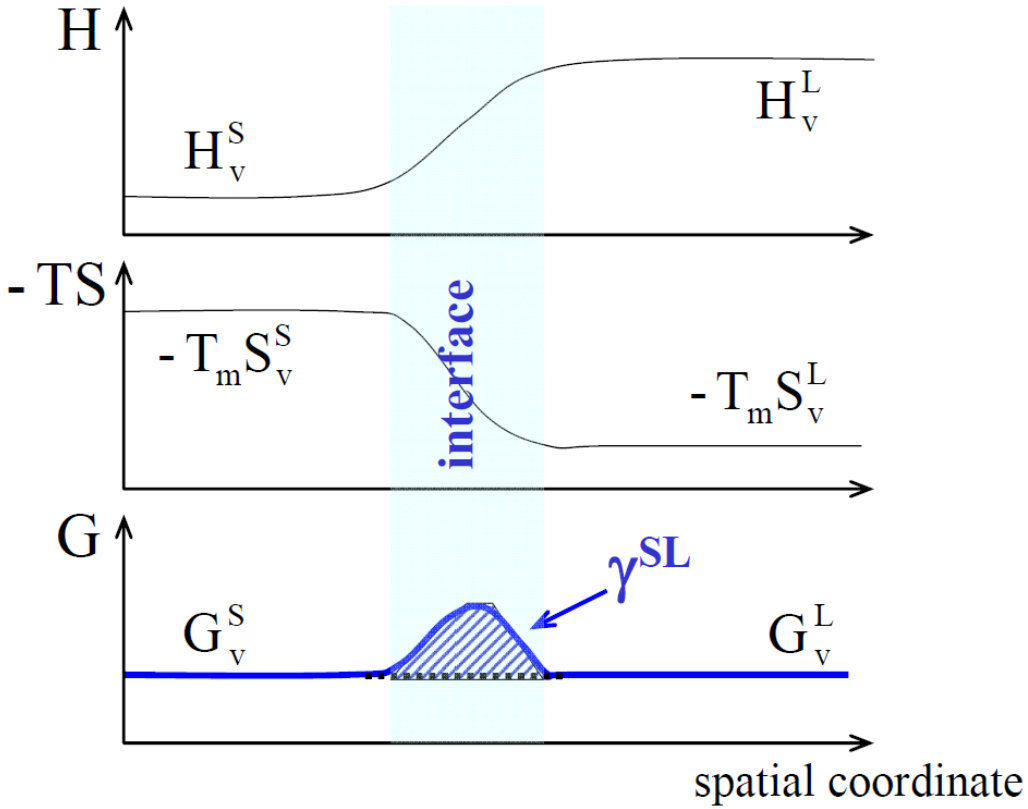
Consider a solid-liquid interface. Depending on the type of material and crystallographic orientation of the interface, the interface can be atomically flat (smooth, faceted) or rough (diffuse).



free energies of liquid and solid per unit volume:

$$G_v^L = H_v^L - TS_v^L$$

$$G_v^S = H_v^S - TS_v^S$$



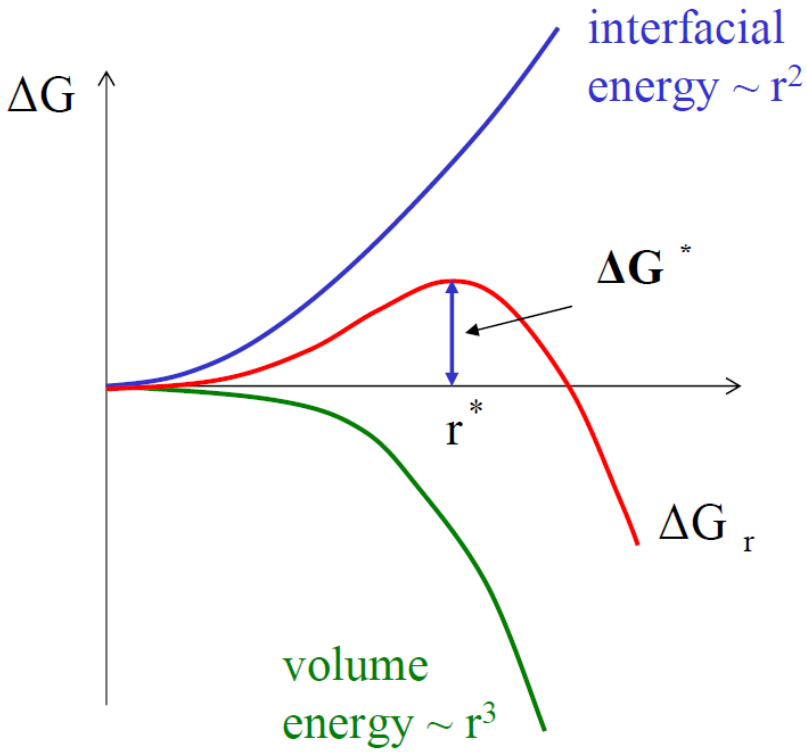
Homogeneous nucleation

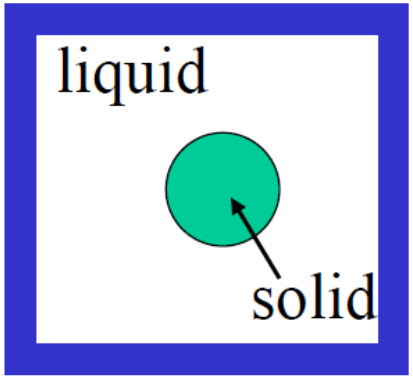
$$\Delta G = G_2 - G_1 = -V_S \Delta G_v + A^{SL}\gamma^{SL}$$

For a spherical nucleus with radius r: $\mathbf{V_S = \frac{4}{3}\pi r^3}$

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma^{SL}$$

$$\mathbf{A^{SL} = 4\pi r^2}$$





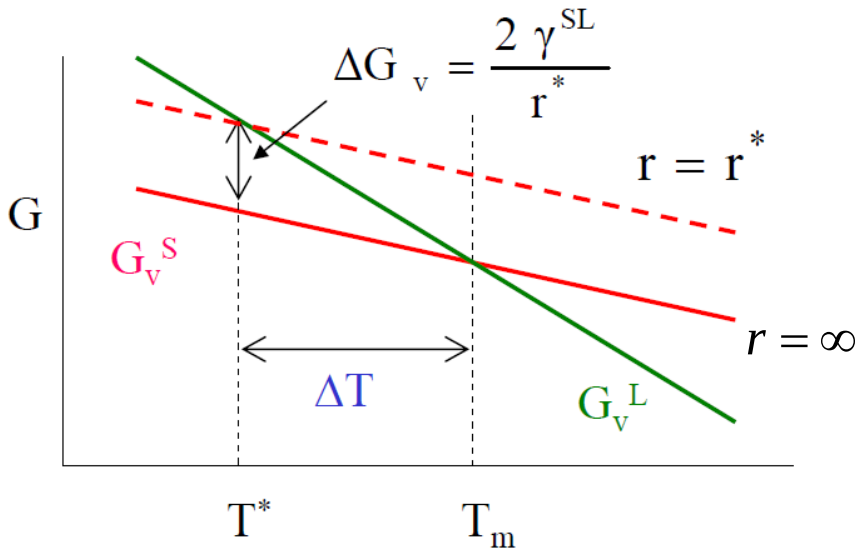
For nucleus with a radius r > r*, the Gibbs free energy will decrease if the nucleus grows. **r* is the critical nucleus size, ΔG^* is the nucleation barrier.**

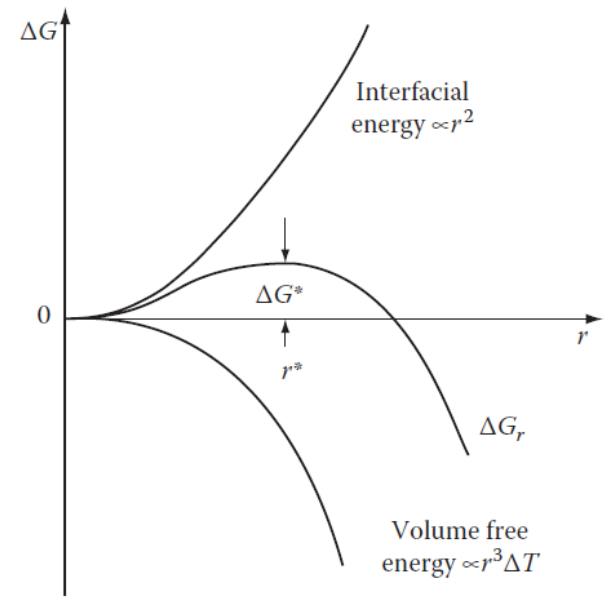
Homogeneous nucleation

At $r = r^*$ $$\frac{d\Delta G}{dr} = -4\pi r^2 \Delta G_v + 8\pi r \gamma^{SL} = 0$$

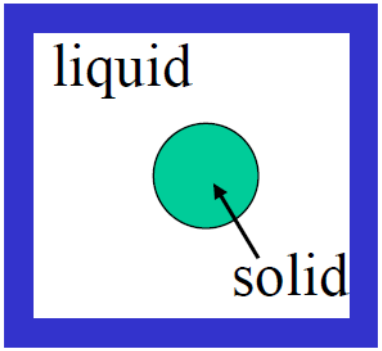
$$r^* = \frac{2\gamma^{SL}}{\Delta G_v} \qquad \Delta G^* = \frac{16\pi\left(\gamma^{SL}\right)^3}{3\left(\Delta G_v\right)^2}$$

Gibbs-Thomson effect





Temperature of ***unstable*** equilibrium of a solid cluster of radius r* with undercooled liquid.



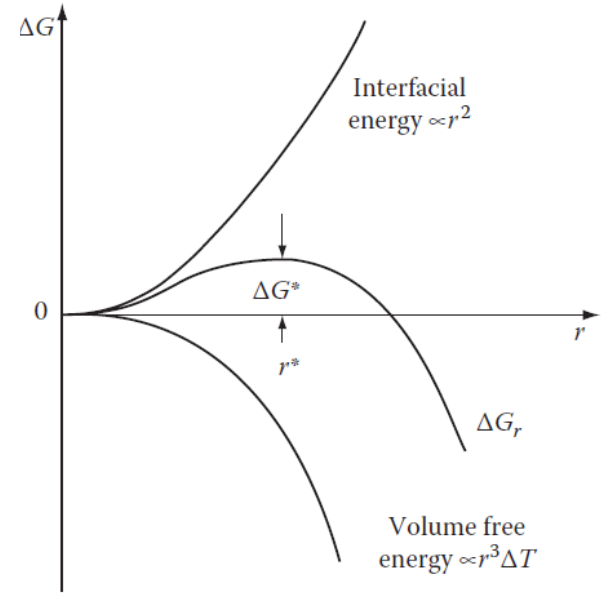
Homogeneous nucleation

$$r^* = \frac{2\gamma^{SL}}{\Delta G_v} \qquad \Delta G^* = \frac{16\pi\left(\gamma^{SL}\right)^3}{3\left(\Delta G_v\right)^2}$$

The difference between the Gibbs free energy of liquid and solid (also called "driving force" for the phase transformation) is proportional to the undercooling below the melting temperature, $\Delta T = T_m - T$:

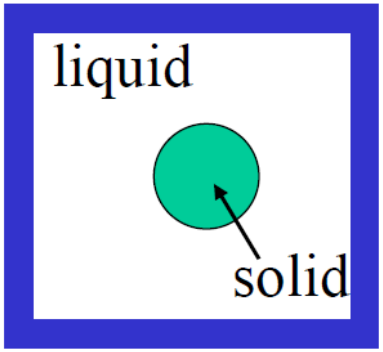
$$\Delta G_v = \frac{\Delta H_m \Delta T}{T_m}$$

where H_m is the latent heat of melting (or fusion)



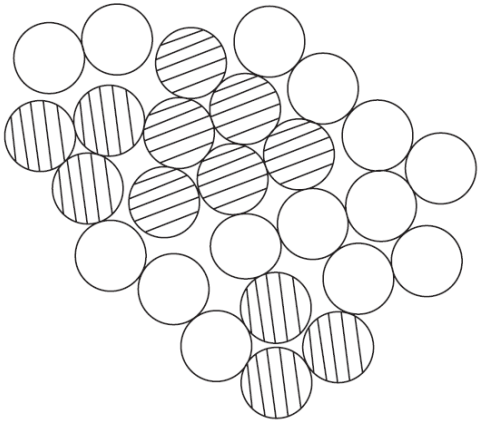
Therefore: $$r^* = \left(\frac{2\gamma^{SL} T_m}{\Delta H_m}\right)\frac{1}{\Delta T}$$

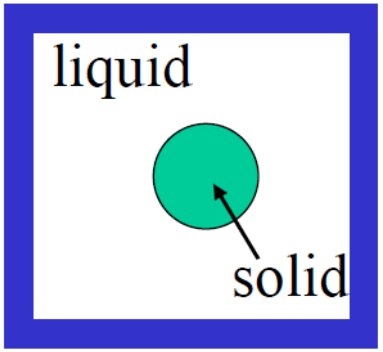
$$\Delta G^* = \left(\frac{16\pi\left(\gamma^{SL}\right)^3 T_m^2}{3\left(\Delta H_m\right)^2}\right)\frac{1}{\left(\Delta T\right)^2}$$



Both r* and G* decrease with increasing undercooling

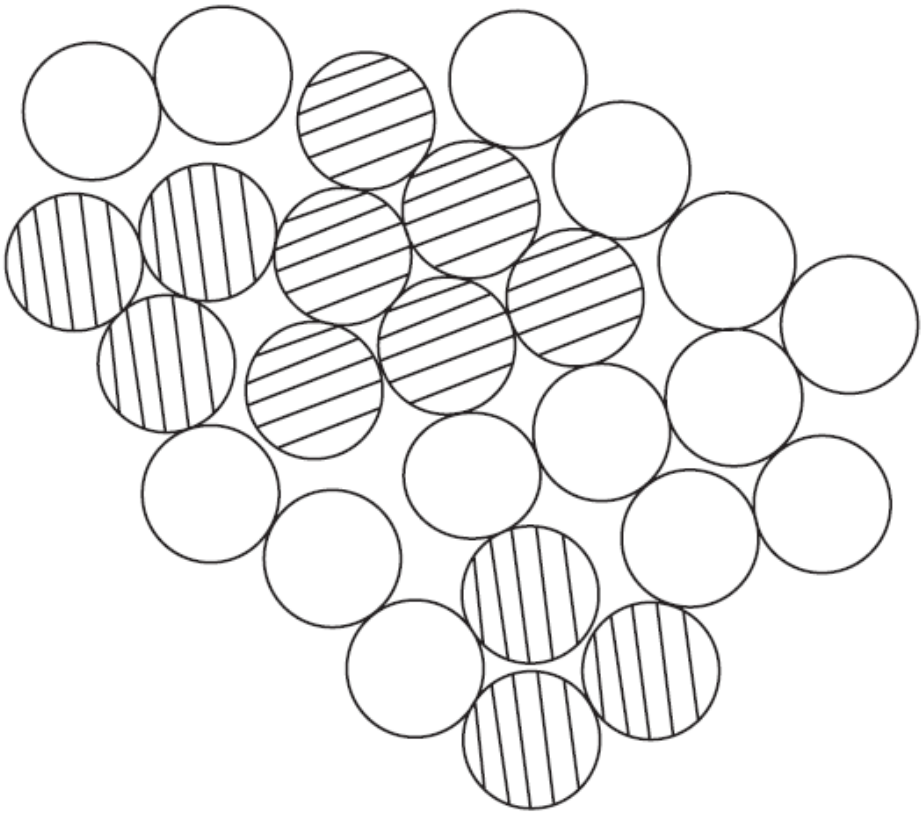
Homogeneous nucleation





https://www.slideshare.net/NikolaiPriezjev

Homogeneous nucleation



A two-dimensional representation of an instantaneous picture of the liquid structure. Many close packed crystal-like clusters (shaded) are present.

A number of spherical clusters of radius r is given by

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

$$n_0 = \text{number of atoms in the system}$$

$$\text{when } T > T_m \text{ valid for all r}$$

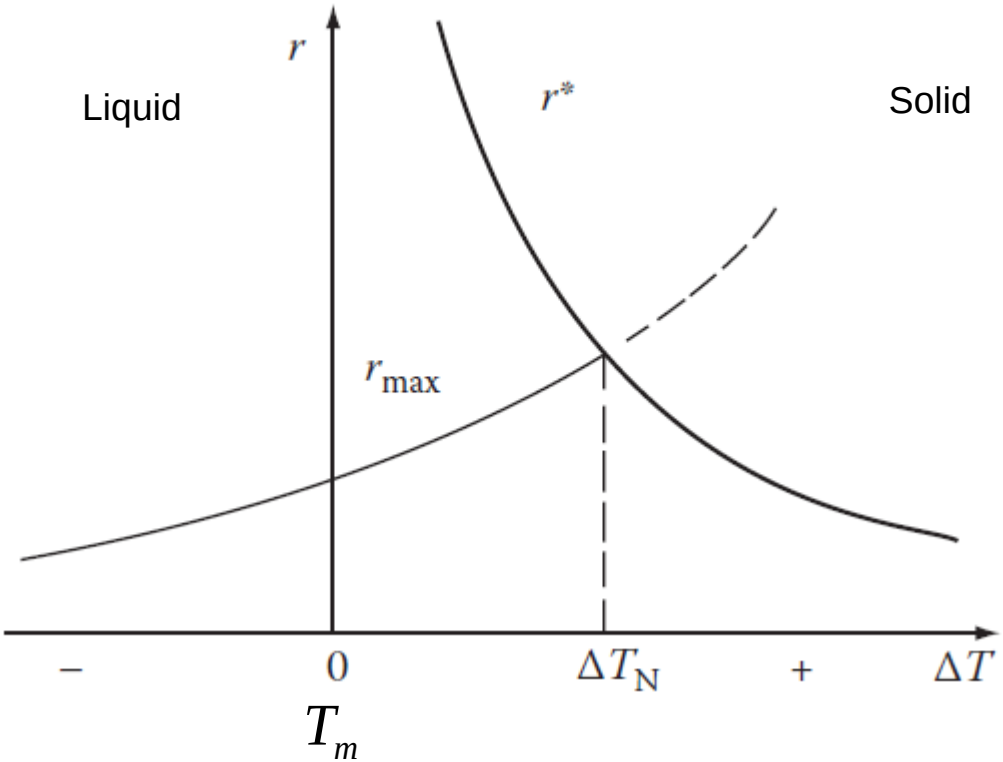
$$\text{when } T < T_m \text{ valid for r} < \text{r}^*$$

$$\text{when } T < T_m \text{ clusters r} > \text{r}^* \text{ are stable nuclei}$$

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$

<u>Example</u>: 1mm^3 copper at T_m (~10^{20} atoms):
~10^{14} clusters of 0.3nm radius (~10 atoms)
~10 clusters with radius 0.6nm (~60 atoms)

Homogeneous nucleation



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

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

A number of spherical clusters of radius r is given by

$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

$$n_0 = \text{number of atoms in the system}$$

$$\text{when } T > T_m \text{ valid for all r}$$

$$\text{when } T < T_m \text{ valid for r} < \text{r}^*$$

$$\text{when } T < T_m \text{ clusters r} > \text{r}^* \text{ are stable nuclei}$$

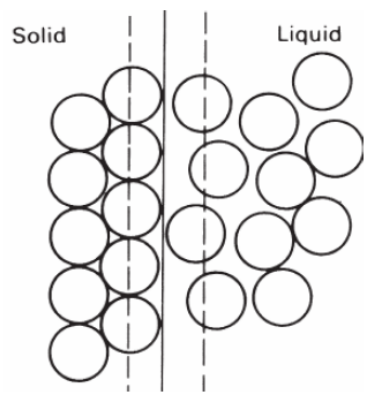
$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$

Homogeneous nucleation

There is an energy barrier of ΔG^* for formation of a solid nucleus of critical size r^*. The probability of energy fluctuation of size ΔG^* is given by the Arrhenius equation and the rate of homogeneous nucleation is

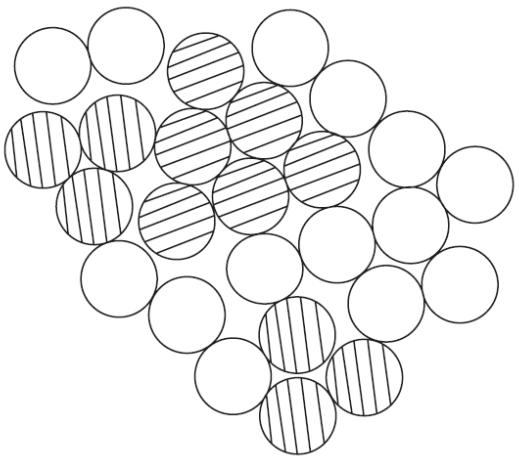
$$\dot{N} \sim \nu_d \exp\left(-\frac{\Delta G^*}{kT}\right) \quad \text{nuclei per m}^3 \text{ per s}$$

where ν_d is the frequency with which atoms from liquid attach to the solid nucleus. The rearrangement of atoms needed for joining the solid nucleus typically follows the same temperature dependence as the diffusion coefficient:



$$\nu_d \sim \exp\left(-\frac{Q_d}{kT}\right)$$

Therefore: $$\dot{N} \sim \exp\left(-\frac{Q_d}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$



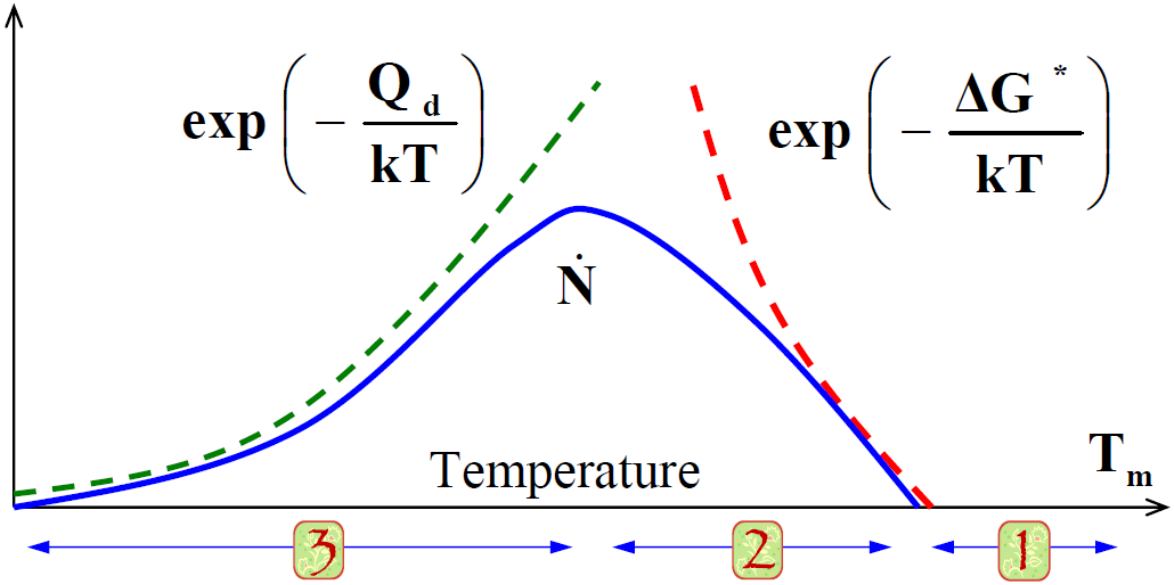
$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

$$r^* = \left(\frac{2\gamma^{SL} T_m}{\Delta H_m}\right)\frac{1}{\Delta T}$$

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

Rate of homogeneous nucleation

$$\dot{N} \sim \exp\left(-\frac{Q_d}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$



1 $\Delta G^* > Q_d \Rightarrow \exp(-\Delta G^*/kT) << \exp(-Q_d/kT)$

ΔG^* is too high - nucleation is suppressed

2 $\Delta G^* \leq Q_d \Rightarrow \exp(-\Delta G^*/kT) > \exp(-Q_d/kT)$

$\Delta G^* \sim 1/\Delta T^2$ – decreases with T – sharp rise of homogeneous nucleation (diffusion is still active)

3 $\exp(-Q_d/kT)$ – too small – low atomic mobility suppresses the nucleation rate

$$r^* = \left(\frac{2\gamma^{SL} T_m}{\Delta H_m}\right)\frac{1}{\Delta T}$$

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

Rate of homogeneous nucleation

In many phase transformations, it is difficult to achieve the level of undercooling that would suppress nucleation due to the drop in the atomic mobility (regime 3 in the previous slide). The nucleation typically happens in regime 2 and is defined by the probability of energy fluctuation sufficient to overcome the activation barrier ΔG^*_r:

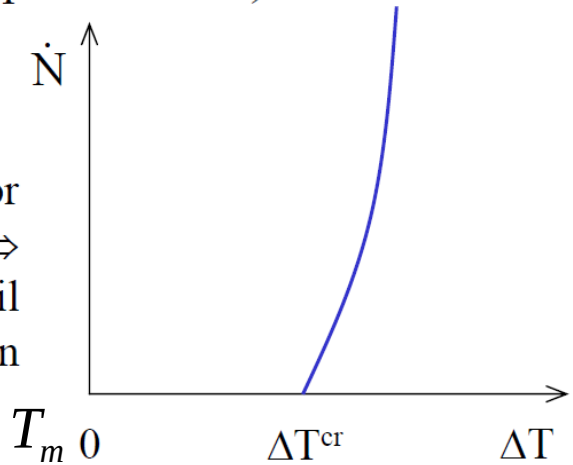
$$\dot{N} \sim \exp\left(-\frac{\Delta G^*}{kT}\right)$$

Using $$\Delta G^*_r = \left(\frac{16\pi\left(\gamma^{SL}\right)^3 T_m^2}{3\left(\Delta H_v^m\right)^2}\right)\frac{1}{(\Delta T)^2}$$

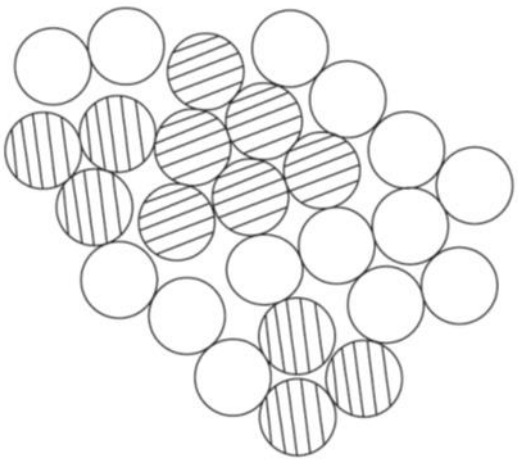
$$\boxed{\dot{N} = I_0 \exp\left(-\frac{A}{(\Delta T)^2}\right)}$$

very strong temperature dependence!

where A has a relatively weak dependence on temperature (as compared to ΔT^2)

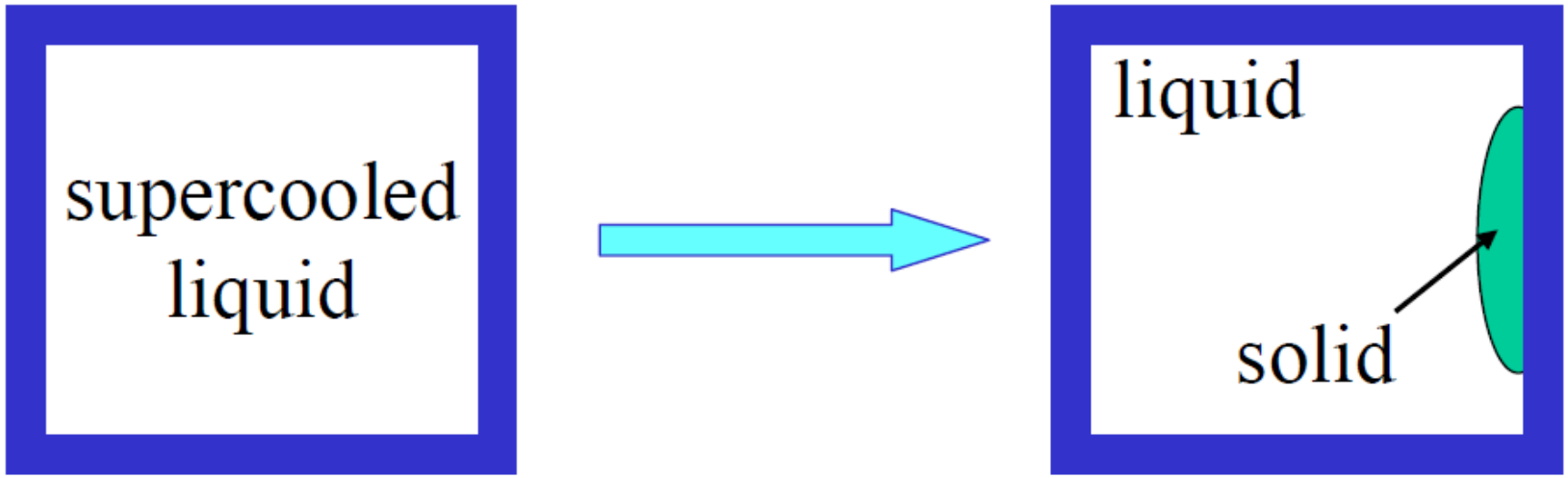


There is critical undercooling for homogeneous nucleation ΔT^{cr} $\Rightarrow$ there are virtually no nuclei until ΔT^{cr} is reached, and there is an "explosive" nucleation at ΔT^{cr}.



$$A = \frac{16\pi\gamma_{SL}^3 T_m^2}{3H_m^2 kT}$$

Heterogeneous nucleation

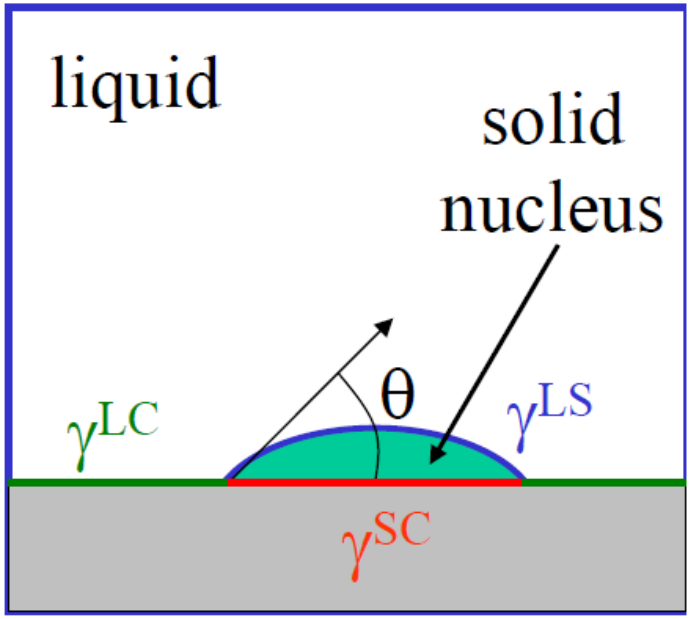


the new phase appears on the walls of the container, at impurity particles, grain boundaries, etc.

https://www.slideshare.net/NikolaiPriezjev

Heterogeneous nucleation

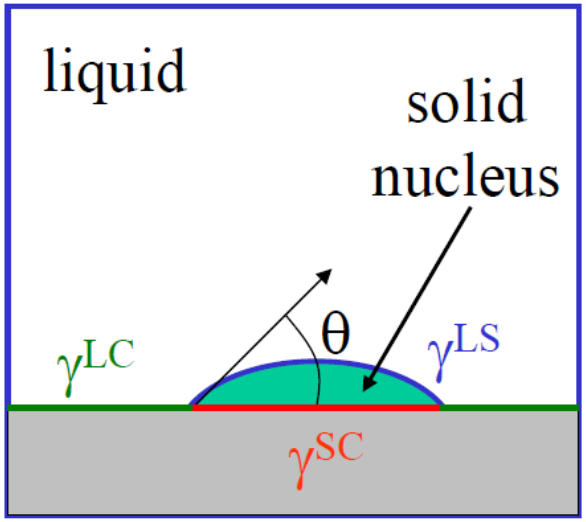
Let's consider a simple example of heterogeneous nucleation of a nucleus of the shape of a spherical cap on a wall of a container. Three interfacial energies:



γ^{LC} – liquid container interface,
γ^{LS} – liquid-solid interface,
γ^{SC} – solid-container interface.

Balancing the interfacial tensions in the plane of the container wall gives $\gamma^{LC} = \gamma^{SC} + \gamma^{LS} \cos(\theta)$ and the wetting angle θ is defined by $\cos(\theta) = (\gamma^{LC} - \gamma^{SC}) / \gamma^{LS}$

Heterogeneous nucleation



The formation of the nucleus leads to a Gibbs free energy change of $\Delta G_r^{het} = -V_S \Delta G_v + A^{SL}\gamma^{SL} + A^{SC}\gamma^{SC} - A^{SC}\gamma^{LC}$

$V_S = \pi r^3 (2 + \cos(\theta)) (1 - \cos(\theta))^2/3$

$A^{SL} = 2\pi r^2 (1 - \cos(\theta))$ and $A^{SC} = \pi r^2 \sin^2(\theta)$

One can show that

$$\Delta G_r^{het} = \left\{ -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma^{SL} \right\} S(\theta) = \Delta G_r^{hom} S(\theta)$$

$$S(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2/4$$

Shape factor

Heterogeneous nucleation

$$\Delta G_r^{het} = \left\{ -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma^{SL} \right\} S(\theta) = \Delta G_r^{hom} S(\theta)$$

where $S(\theta) = (2+\cos\theta)(1-\cos\theta)^2/4 \le 1$

At $r = r^*$ $\quad \dfrac{d\Delta G_r}{dr} = \left(-4\pi r^2 \Delta G_v + 8\pi r \gamma^{SL}\right) S(\theta) = 0$

$$r^* = \frac{2\gamma^{SL}}{\Delta G_v}$$

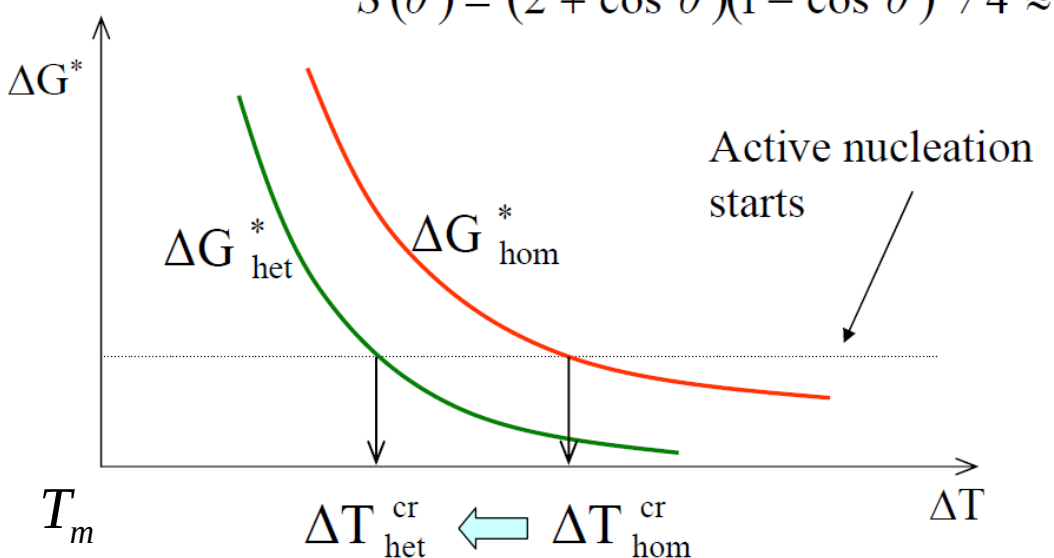
- same as for homogeneous nucleation

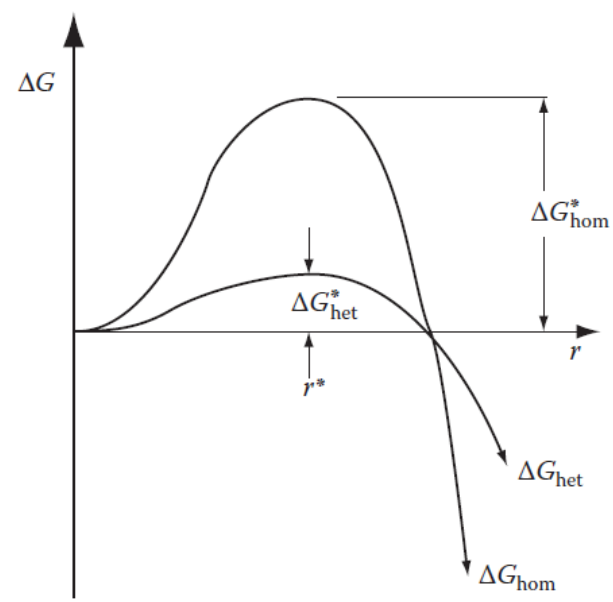
Gibbs-Thomson effect

$$\Delta G_{het}^* = S(\theta)\frac{16\pi\left(\gamma^{SL}\right)^3}{3\left(\Delta G_v\right)^2} = S(\theta)\Delta G_{hom}^*$$

$S(\theta)$ can be small $\Rightarrow$ *if* $\theta = 10^\circ$

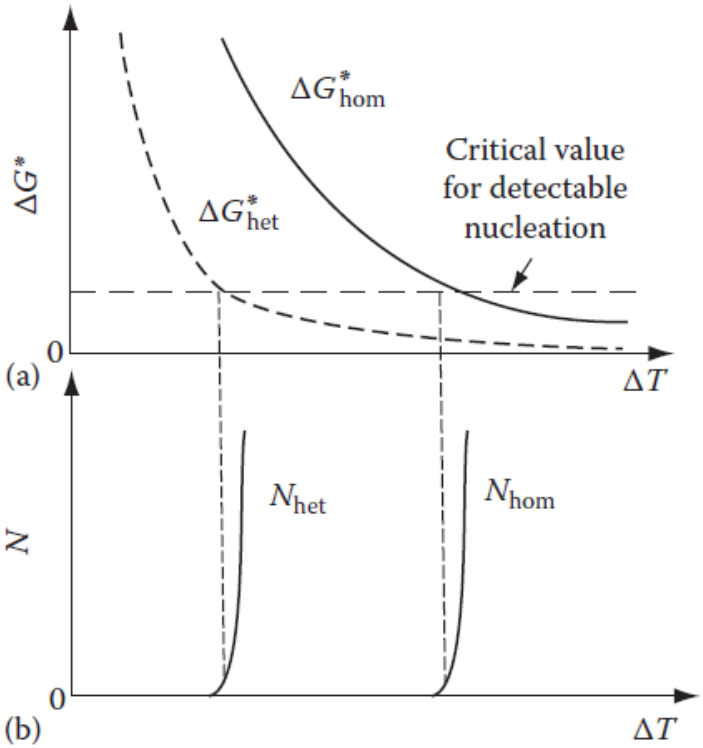
$$S(\theta) = (2+\cos\theta)(1-\cos\theta)^2/4 \approx 10^{-4}$$





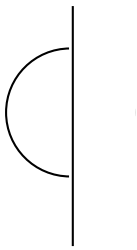
$\theta = 90^{\circ}, S = 0.5$

Heterogeneous nucleation



T_m

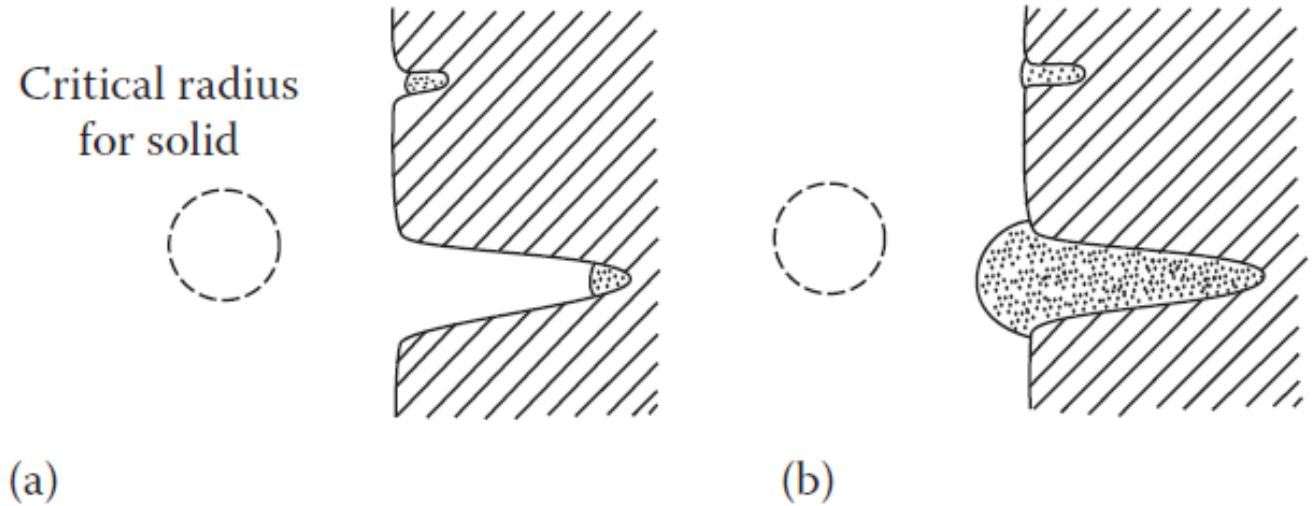
Heterogeneous nucleation



$\theta = 90^{O}$

$V^{*} = \text{large}$

$r^{*} = \text{small}$



Heterogeneous nucleation in mould-wall cracks, (a) The critical nuclei, (b) The upper nucleus cannot grow out of the crack while the lower one can.

$$\Delta G^{*} = \frac{1}{2} V^{*} \Delta G_{v}$$

$$r^{*} = \left(\frac{2\gamma_{SL} T_{m}}{H_{m}} \right) \frac{1}{\Delta T}$$

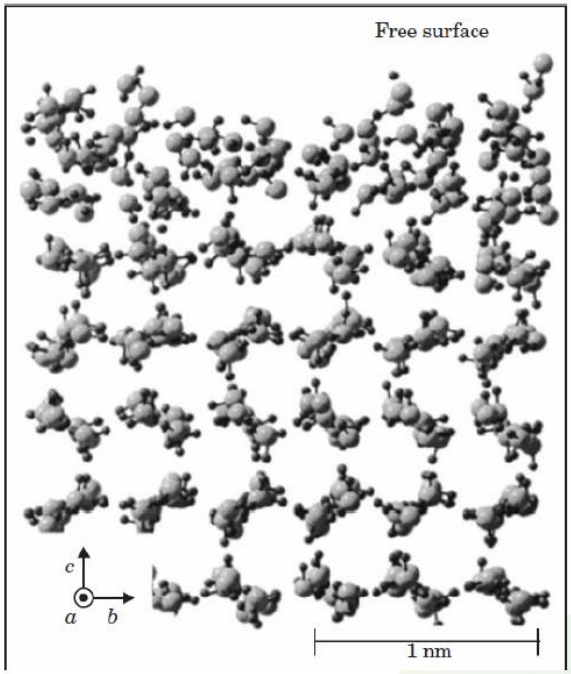
*V** = volume of the critical nucleus (sphere or cap)

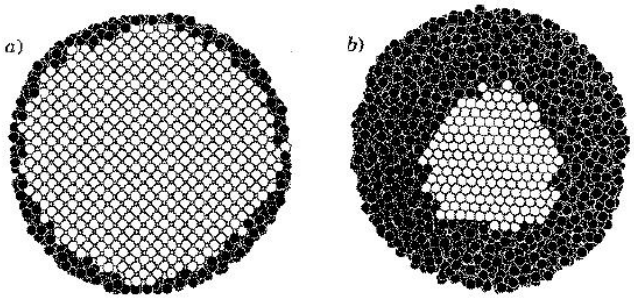
Pre-melting

For solid/liquid/vapor interfaces, often

$$\gamma^{\text{Solid-Vapor}} > \gamma^{\text{Solid-Liquid}} + \gamma^{\text{Liquid-Vapor}}$$

in this case, no superheating is needed for nucleation of liquid and surface melting can take place below $T_m \Rightarrow$ pre-melting





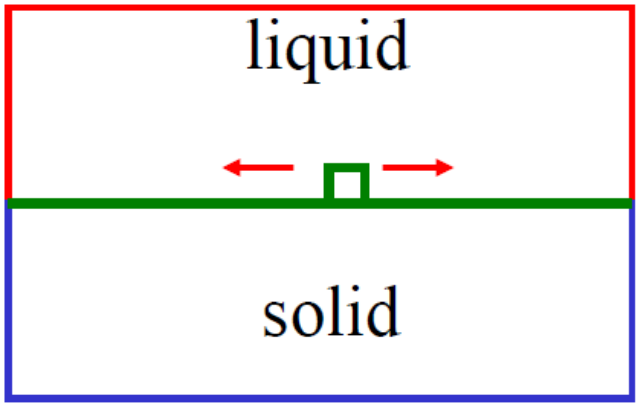
cross-section of an atomic cluster close to T_m
(*simulations by J. Sethna, Cornell University*)

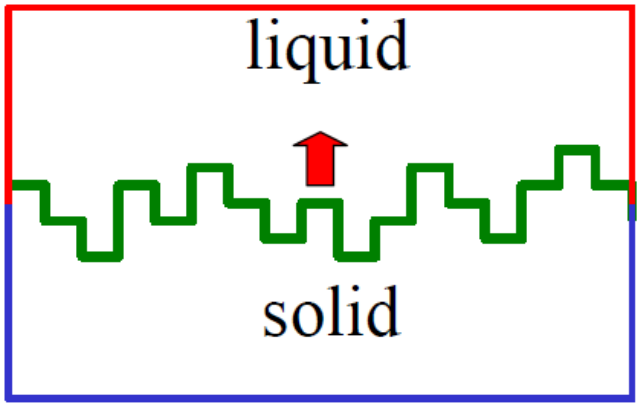
Why ice is slippery?
Physics Today,
Dec. 2005, pp. 50-55

Figure 1. An ice skater exerts pressures on the order of a few hundred atmospheres on the ice surface, enough to reduce the melting temperature by only a few degrees. Premelting—the development of a liquid-like surface layer at temperatures below freezing—and frictional heating of the ice as skaters move around must account for ice's slipperiness at the wide variety of subzero temperatures found in nature. (*Ice Skating*, by Hy Sandham, 1885, courtesy of the Library of Congress.)

Growth mechanisms

The next step after the nucleation is growth. Atomically rough (diffuse) interfaces migrate by continuous growth, whereas atomically flat interfaces migrate by ledge formation and lateral growth.





Growth rate: $v = k_1 \Delta T_i$

The rate of the continuous growth (typical for metals) is typically controlled by heat transfer to the interfacial region for pure materials and by solute diffusion for alloys.

Growth mechanisms

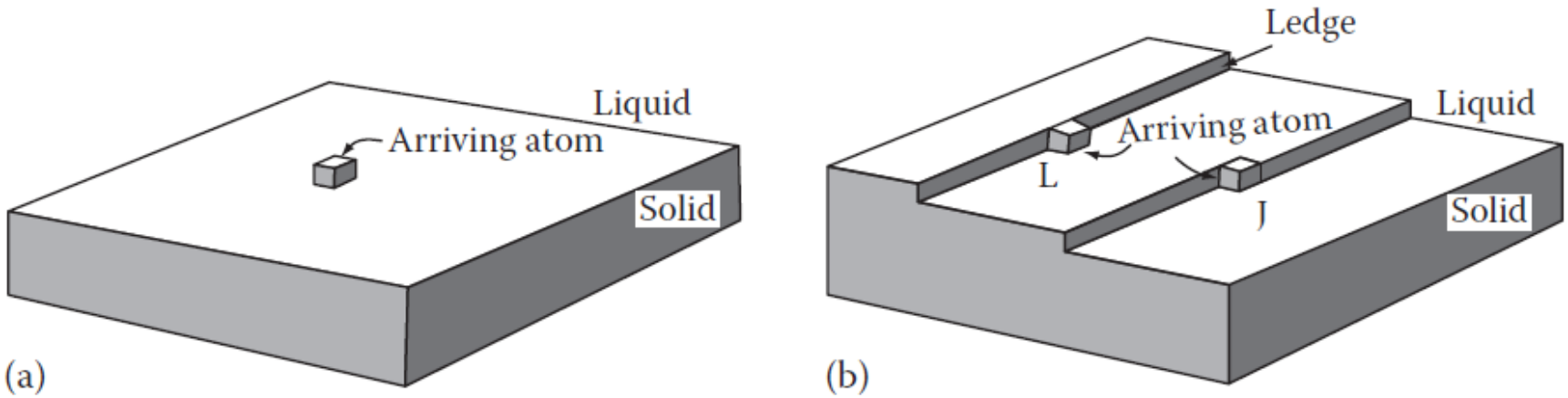
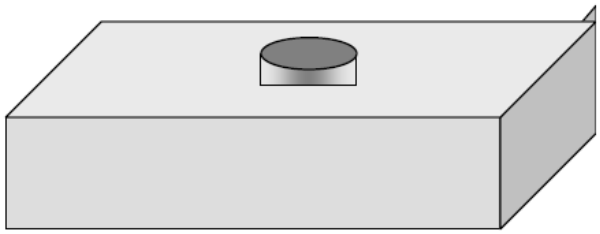


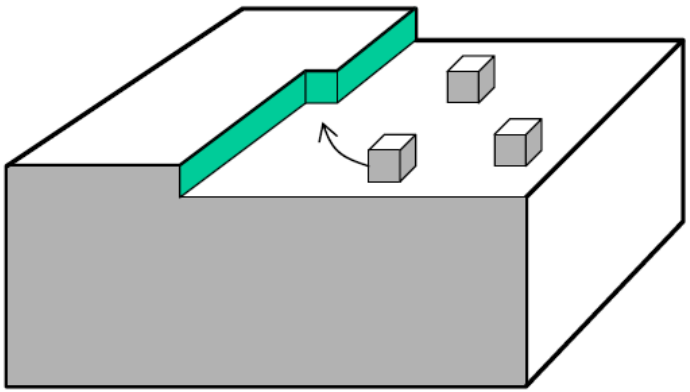
Figure 4.11
Atomically smooth solid/liquid interfaces with atoms represented by cubes. (a) Addition of a single atom onto a flat interface increases the number of 'broken bonds' by four. (b) Addition to a ledge (L) only increases the number of broken bonds by two, whereas at a jog in a ledge (J) there is no increase.

Growth in the case of atomically flat interfaces can proceed from existing interfacial steps (e.g. due to the screw dislocations or twin boundaries) or by surface nucleation and lateral growth of 2D islands.

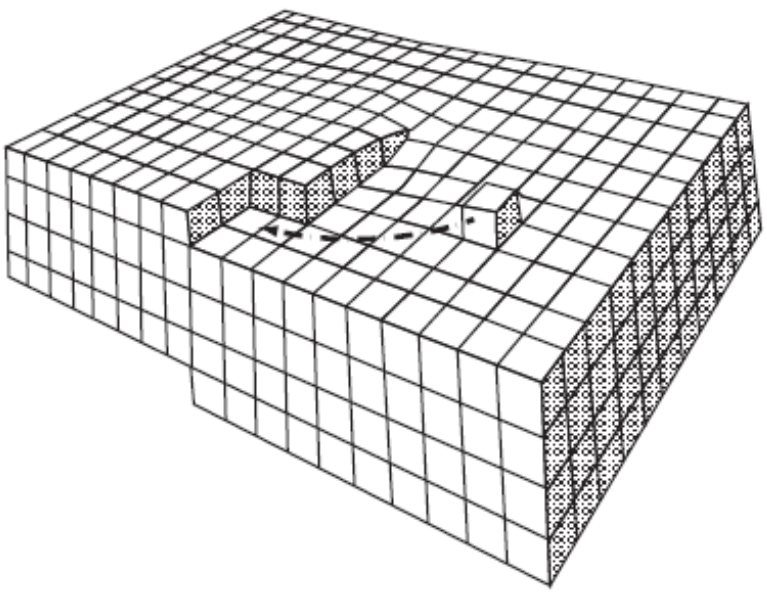
Growth rate: $v \propto \exp(-k_2 / \Delta T_i)^2$



Growth mechanisms

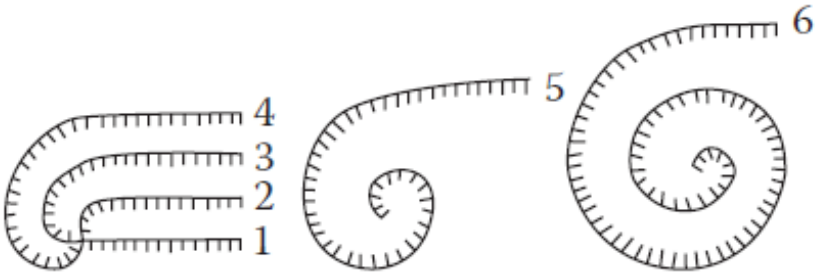


Smooth solid-liquid interfaces typically advance by the lateral growth of ledges. Ledges can result from surface nucleation or from dislocations that is intersecting the interface.



(a)

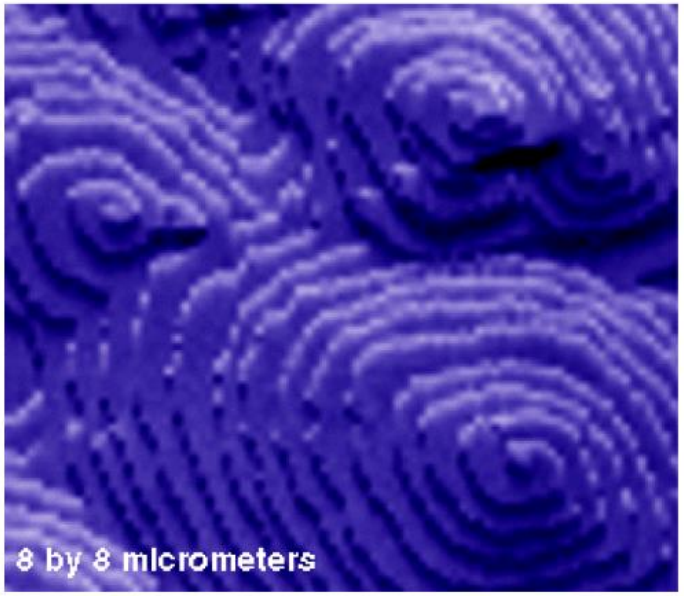
Growth rate: $v = k_3(\Delta T_i)^2$

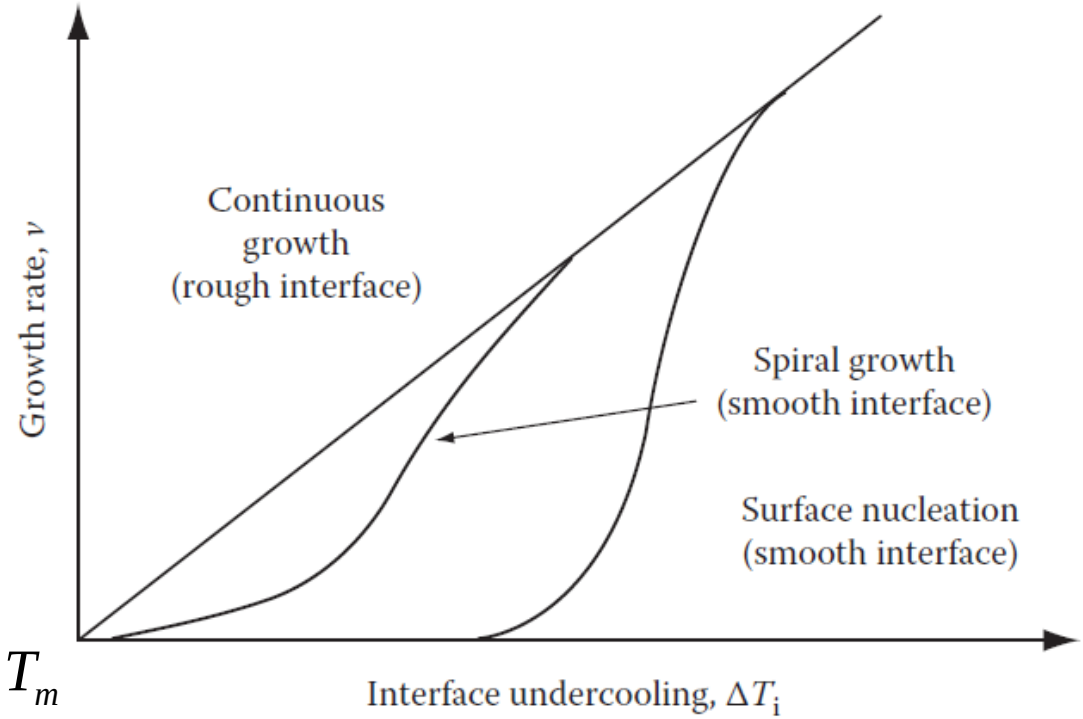


(b)

Growth mechanisms

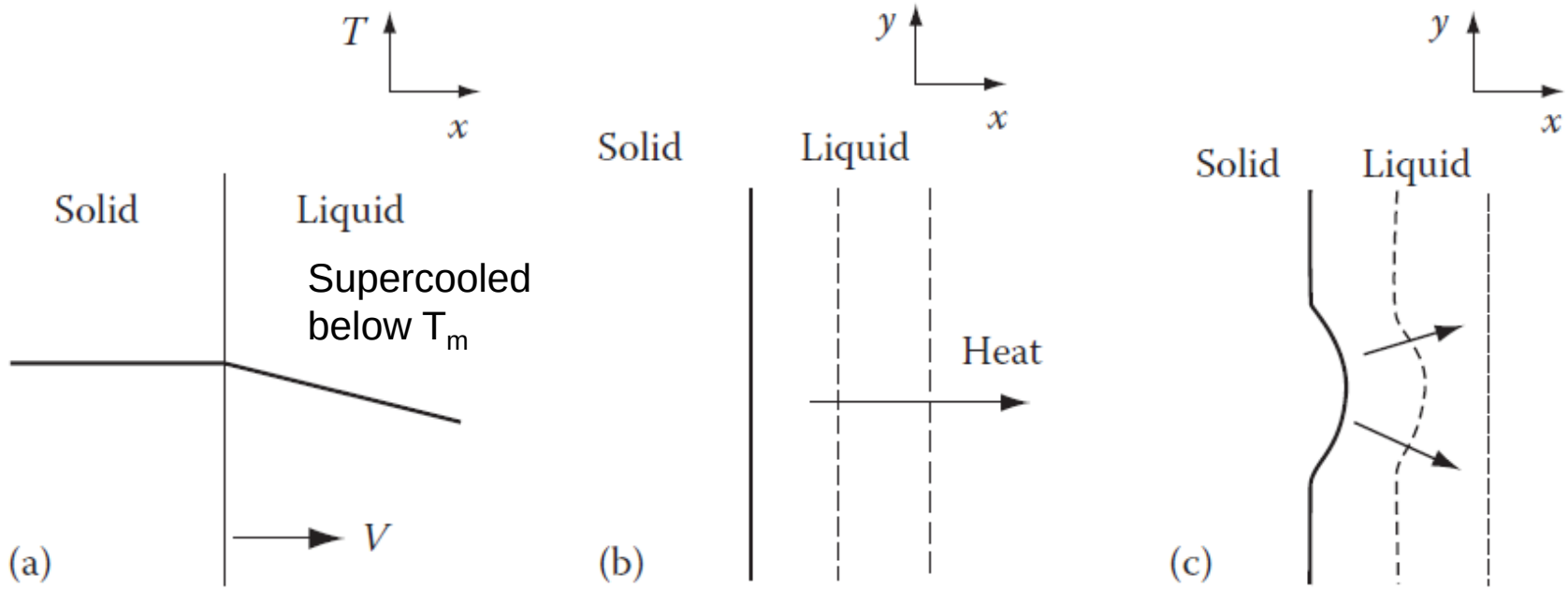
Spiral growth on dislocations AFM images of growing crystal of KDP (potassium dihydrogen phosphate) by De Yoreo and Land, LLNL and Malkin and Kuznetsov, University of California





The influence of interface undercooling (ΔT_i) on growth rate for atomically rough and smooth interfaces.

4.2.3 Heat Flow and Interface Instability (pure Metals)



(a) Temperature distribution for solidification when heat is extracted through the liquid,
(b) for a planar S/L interface, and (c) for a protrusion.

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

Thermal conductivity

Temperature gradient

Rate of growth of the solid

Latent heat of fusion per unit volume

4.2.3 Heat Flow and Interface Instability

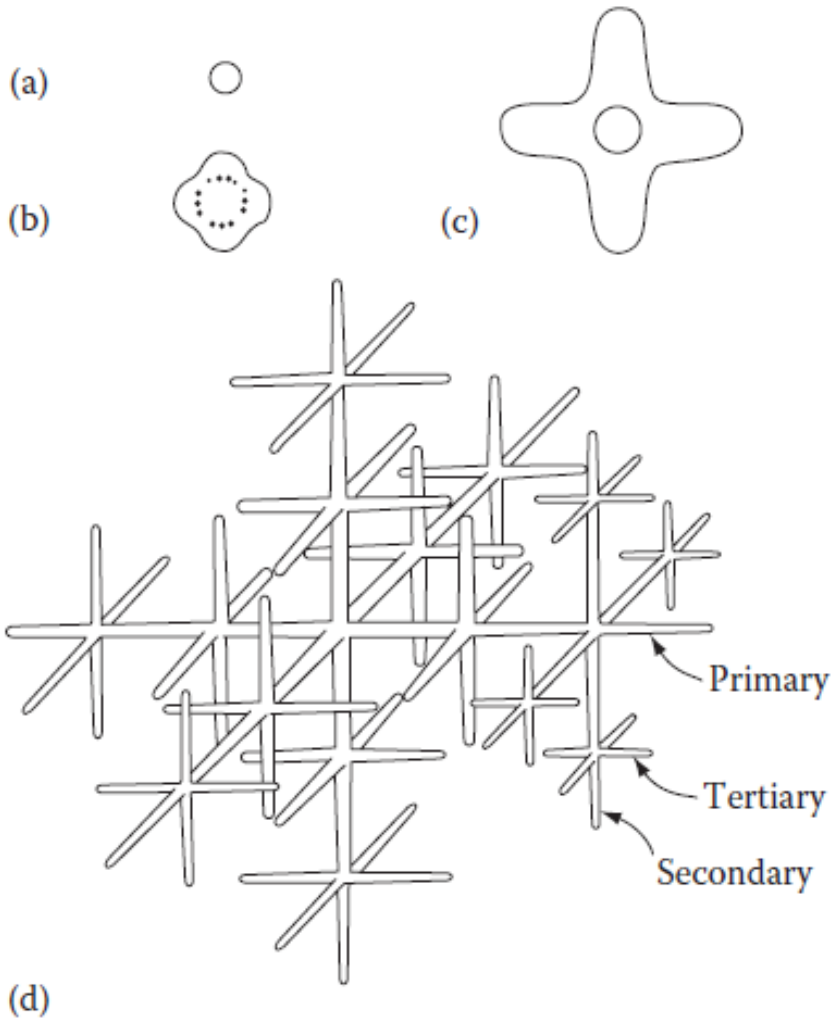
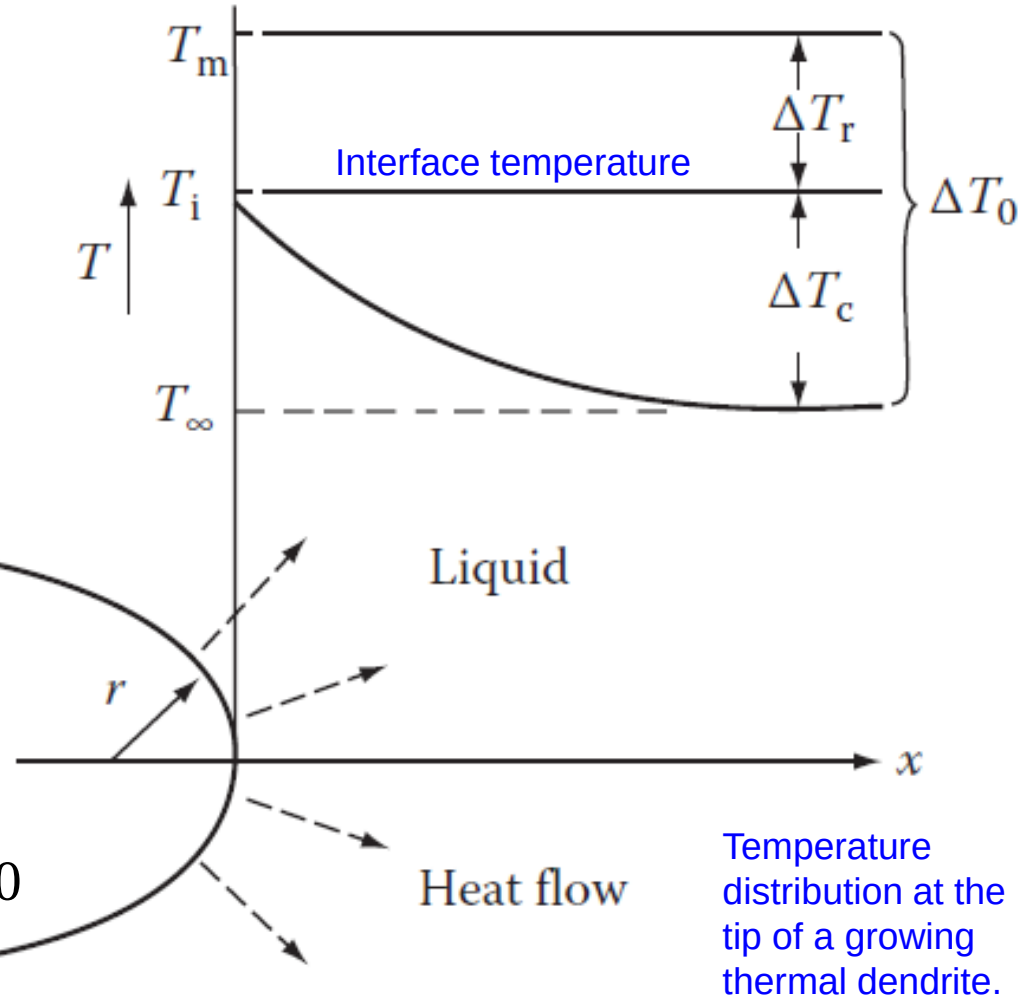


Figure 4.17
The development of thermal dendrites: (a) a spherical nucleus; (b) the interface becomes unstable; (c) primary arms develop in crystallographic directions (⟨100⟩ in cubic crystals); (d) secondary and tertiary arms develop (after R.E. Reed-Hill, *Physical Metallurgy Principles*, 2nd. edn., Van Nostrand,

4.2.3 Heat Flow and Interface Instability

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

$$v = \frac{-K_L T_L'}{L_v} \approx \frac{K_L}{L_v} \cdot \frac{\Delta T_c}{r}$$



Isothermal solid $T_S' = 0$

Temperature distribution at the tip of a growing thermal dendrite.

Gibbs-Thomson effect:

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

Driving force for solidification

$$\Delta T_r = \frac{2\gamma T_m}{L_v r} = \frac{\Delta T_0 r^*}{r}$$

$$r^* = \frac{2\gamma T_m}{L_v \Delta T_0}$$

Minimum possible critical nucleus radius

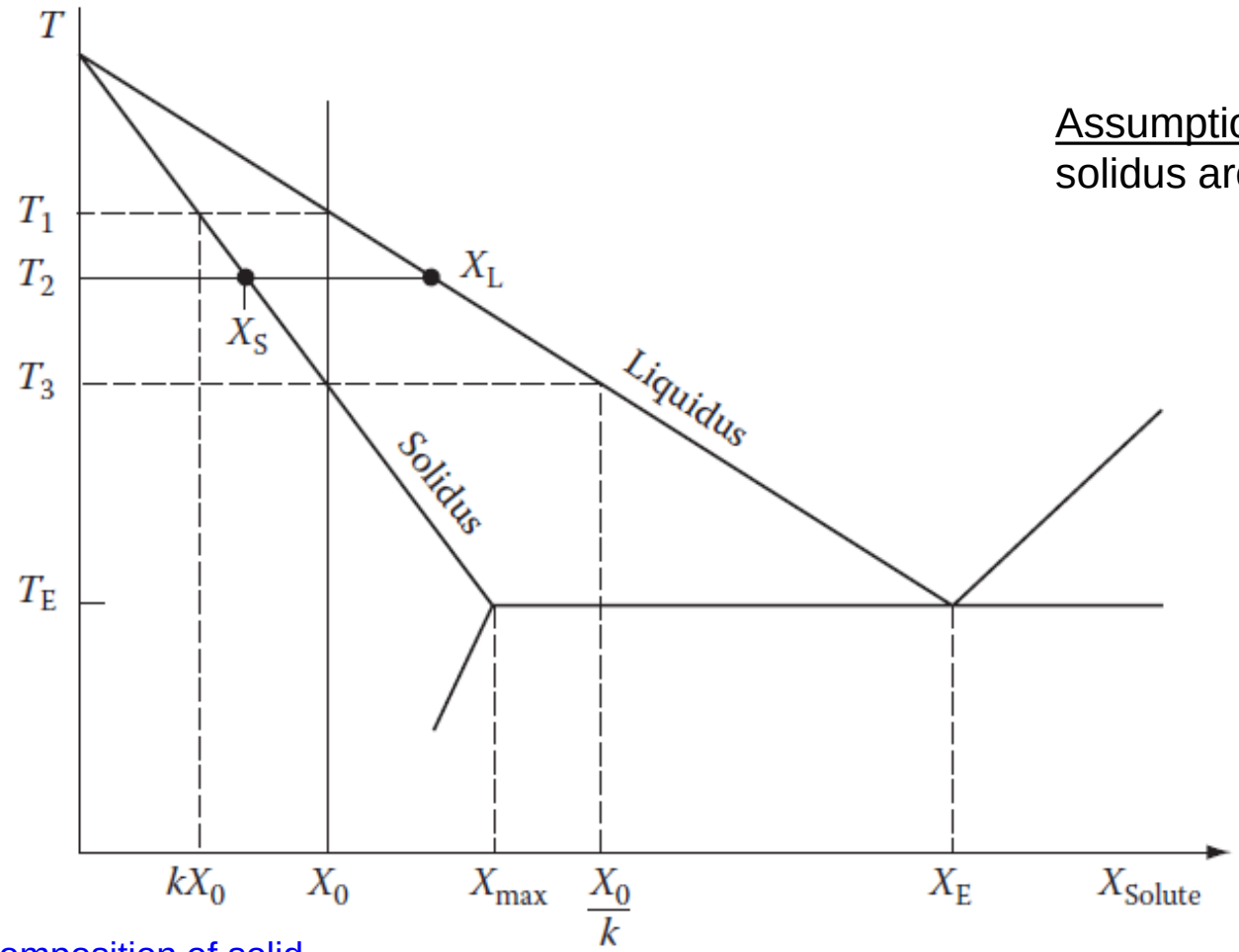
$$v \approx \frac{K_L}{L_v} \cdot \frac{\Delta T_0}{r}\left(1 - \frac{r^*}{r}\right)$$

$v \approx 0,\ r \to r^*$ Gibbs-Thomson effect

$v \approx 0,\ r \to \infty$ Slow heat conduction

$v = \max,\ r = 2r^*$ Maximum velocity

4.3 Binary Alloy Solidification



Assumption: liquidus and solidus are straight lines

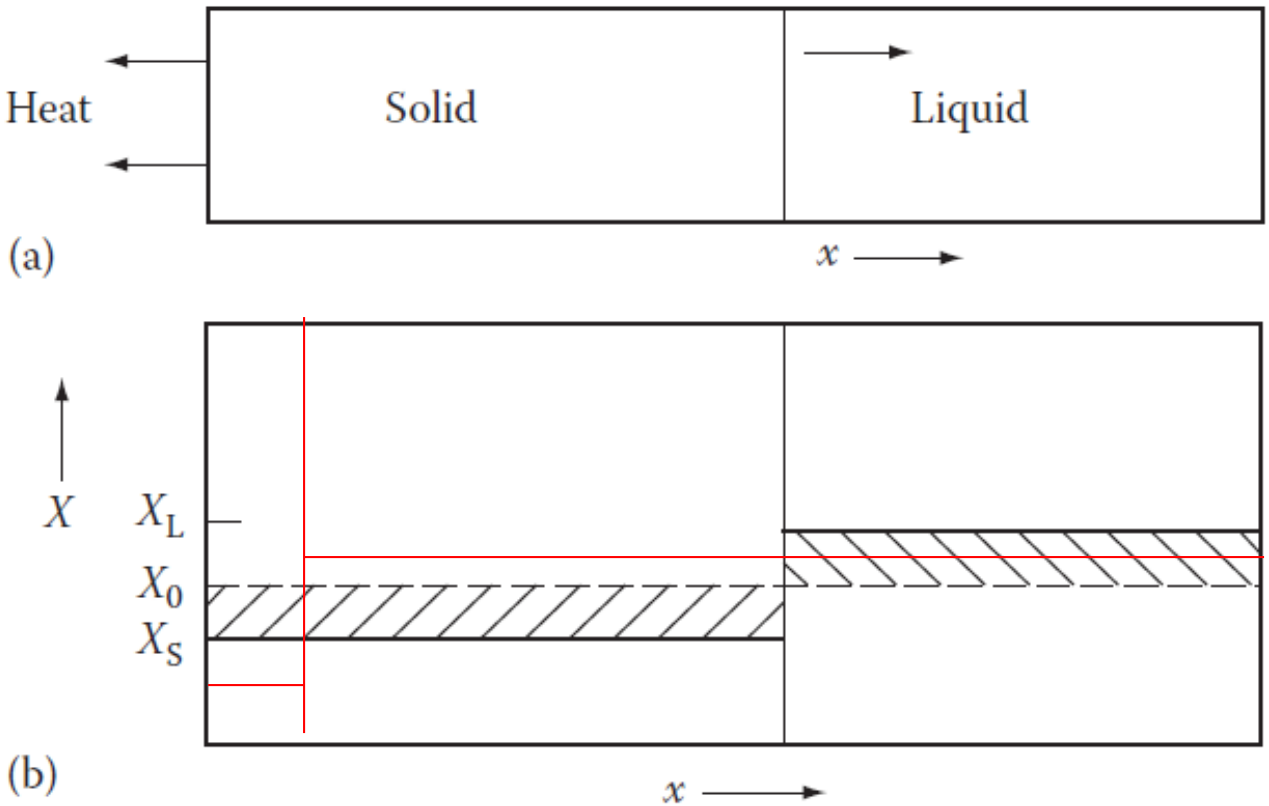
composition of solid

composition of liquid

A hypothetical phase diagram, partition coefficient $k = X_S/X_L$ is constant (independent of T)

X_S = mole fraction of solute in the solid
X_L = mole fraction of solute in the liquid at equilibrium

4.3 Binary Alloy Solidification

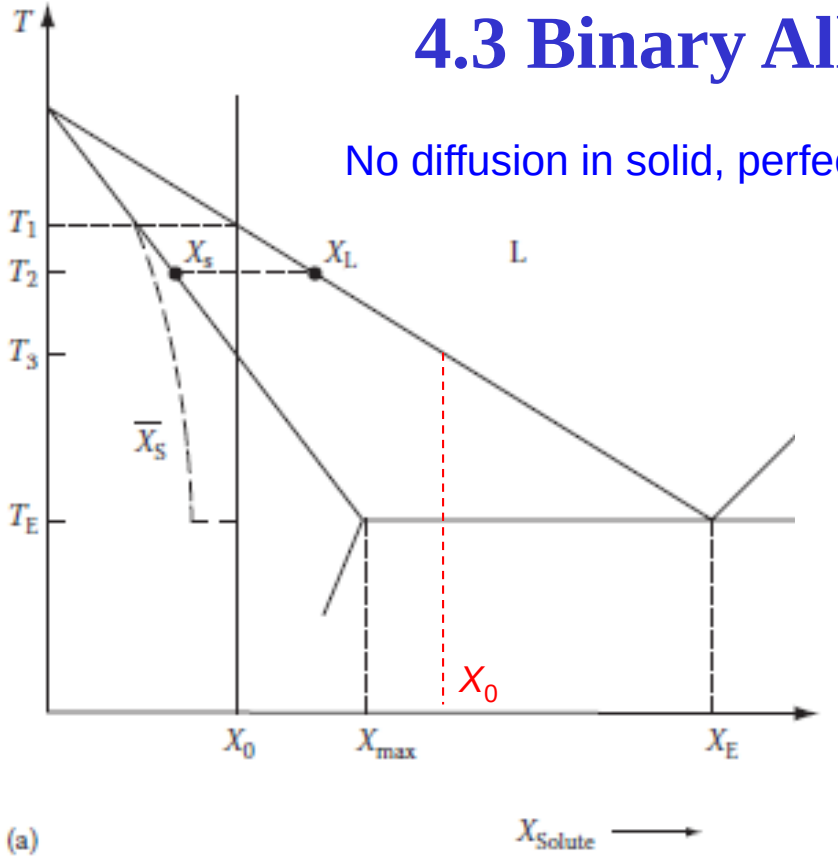


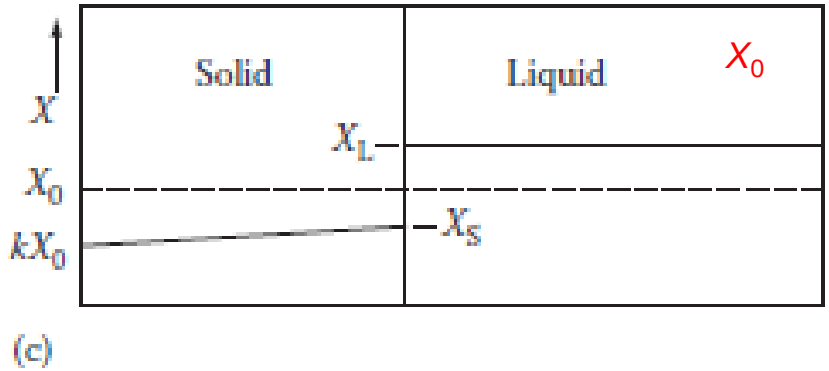
Unidirectional solidification of alloy at X_0. (a) A planar S/L interface and axial heat flow. (b) Corresponding composition profile at T_2 assuming complete equilibrium. Conservation of solute requires the two shaded areas to be equal. *Infinitely slow solidification*.

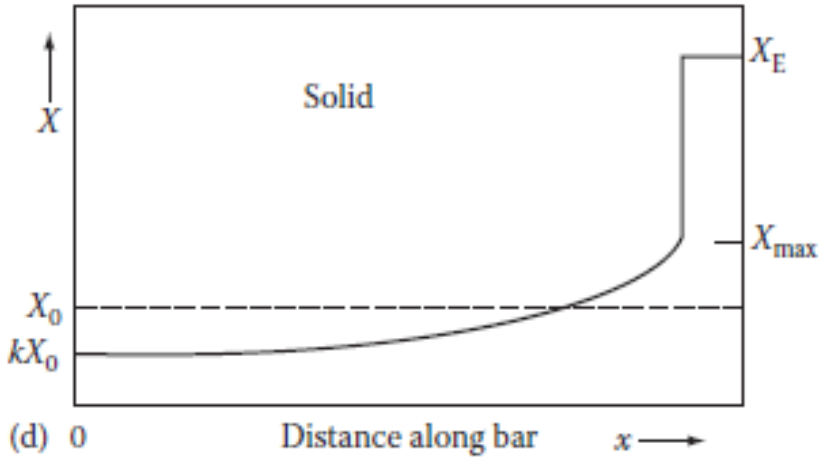
4.3 Binary Alloy Solidification

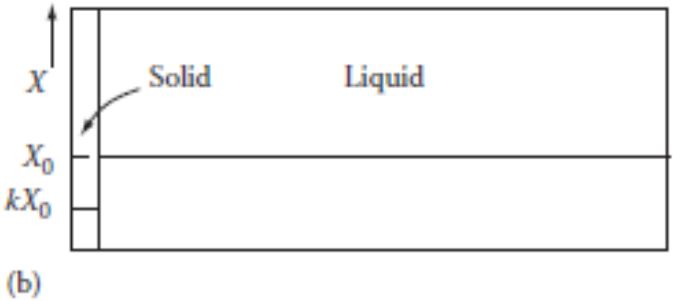
No diffusion in solid, perfect mixing (stirring) in liquid

Liquid richer in solute



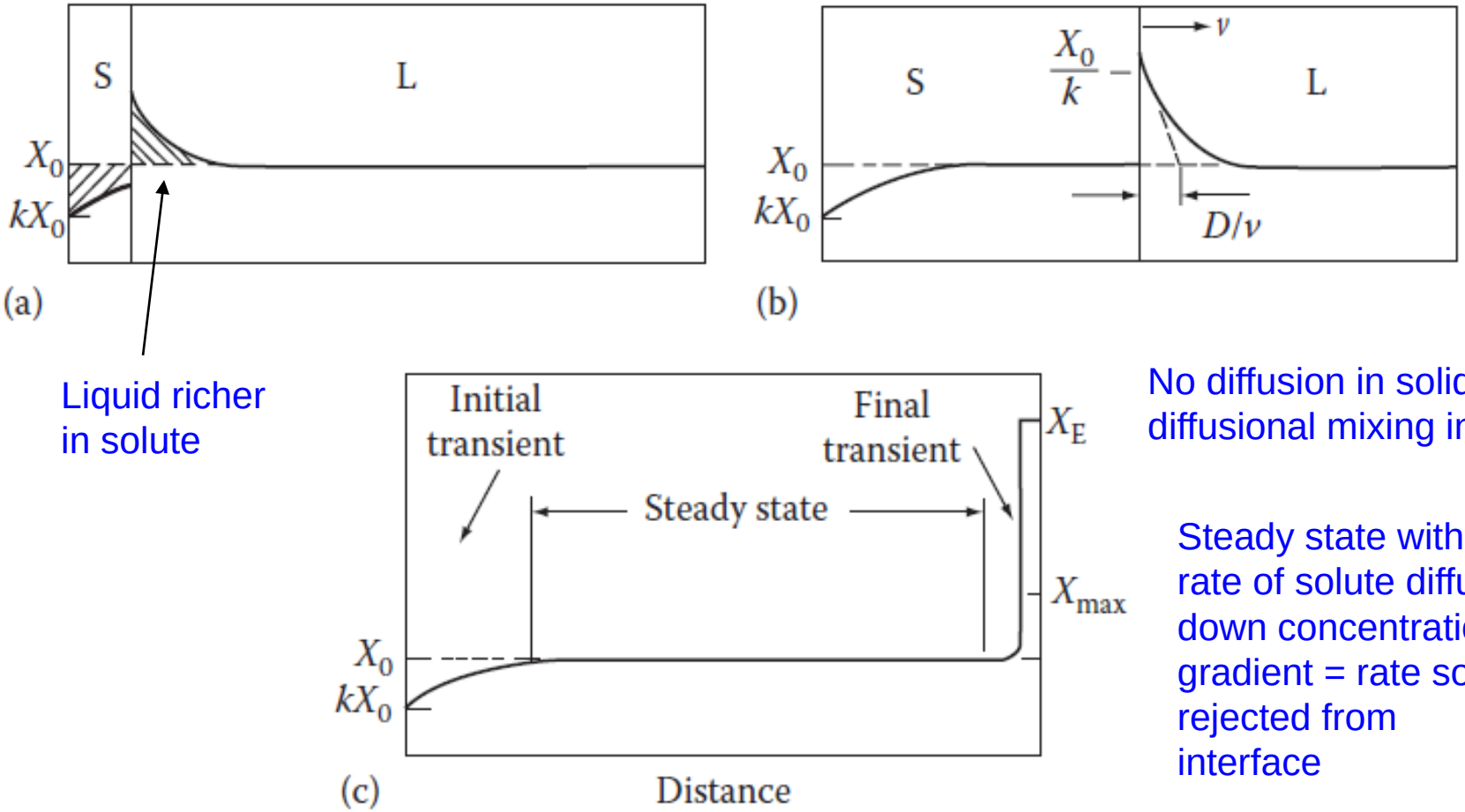






Planar front solidification of alloy X_0 assuming no diffusion in the solid, but complete mixing in the liquid. (a) As before, but including the mean composition of the solid (dashed curve). (b) Composition profile just under T_1. (c) Composition profile at T_2. (d) Composition profile at the eutectic temperature and below.

4.3 Binary Alloy Solidification



Liquid richer in solute

No diffusion in solid, diffusional mixing in liquid

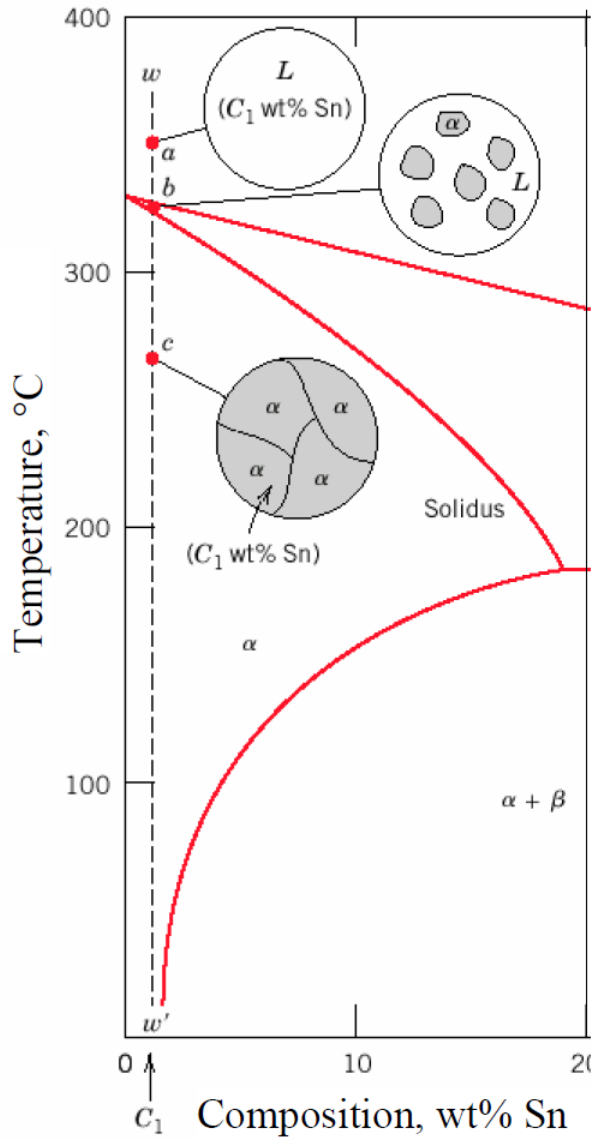
Steady state with v: rate of solute diffusion down concentration gradient = rate solute rejected from interface

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

Figure 4.22
Planar front solidification of alloy X_0 in Fig. 4,19 assuming no diffusion in the solid and no stirring in the liquid. (a) Composition profile when S/L interface temperature is between T_2 and T_3 in Fig. 4.19. (b) Steady-state solidification at T_3. The composition solidifying equals the composition of the liquid far ahead of the solid (X_0). (c) Composition profile at T_E and below, showing the final transient.

Development of microstructure in eutectic alloys (I)

Several different types of microstructure can be formed in slow cooling an different compositions. Let's consider cooling of liquid lead – tin system as an example.

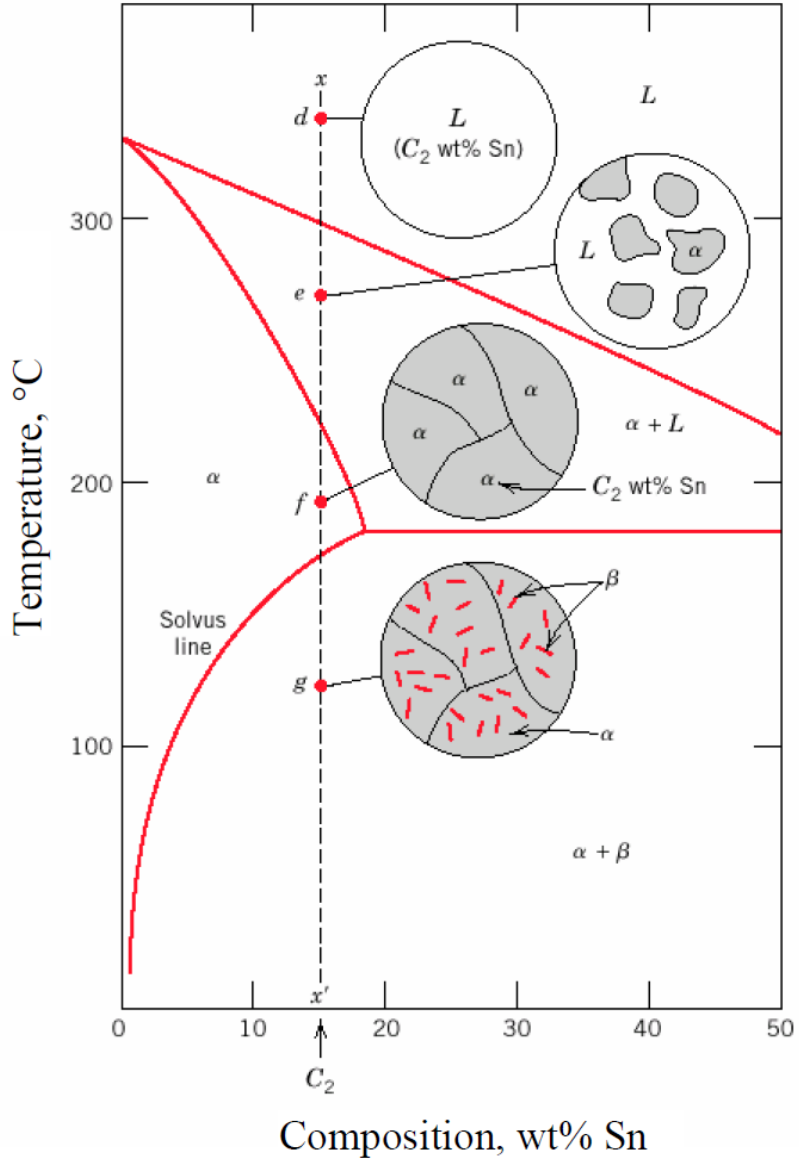


In the case of lead-rich alloy (0-2 wt. % of tin) solidification proceeds in the same manner as for isomorphous alloys (e.g. Cu-Ni) that we discussed earlier.

$$L \rightarrow \alpha + L \rightarrow \alpha$$

Development of microstructure in eutectic alloys (II)

At compositions between the room temperature solubility limit and the maximum solid solubility at the eutectic temperature, β phase nucleates as the α solid solubility is exceeded upon crossing the solvus line.



L

⇓

$\alpha + L$

⇓

α

⇓

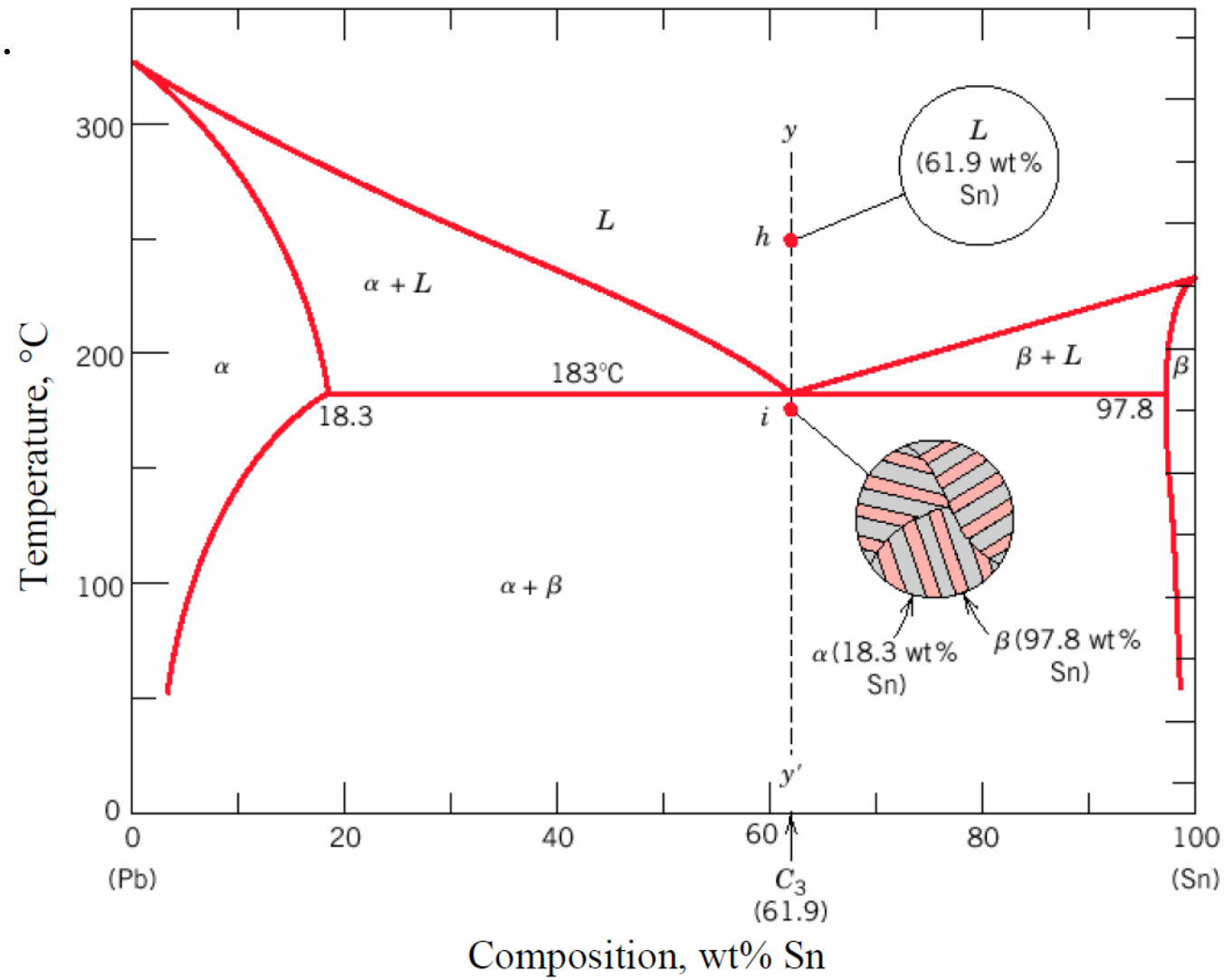
$\alpha + \beta$

Development of microstructure in eutectic alloys (III)

Solidification at the eutectic composition

No changes above the eutectic temperature T_E. At T_E all the liquid transforms to α and β phases (*eutectic reaction*).

$$L \rightarrow \alpha + \beta$$

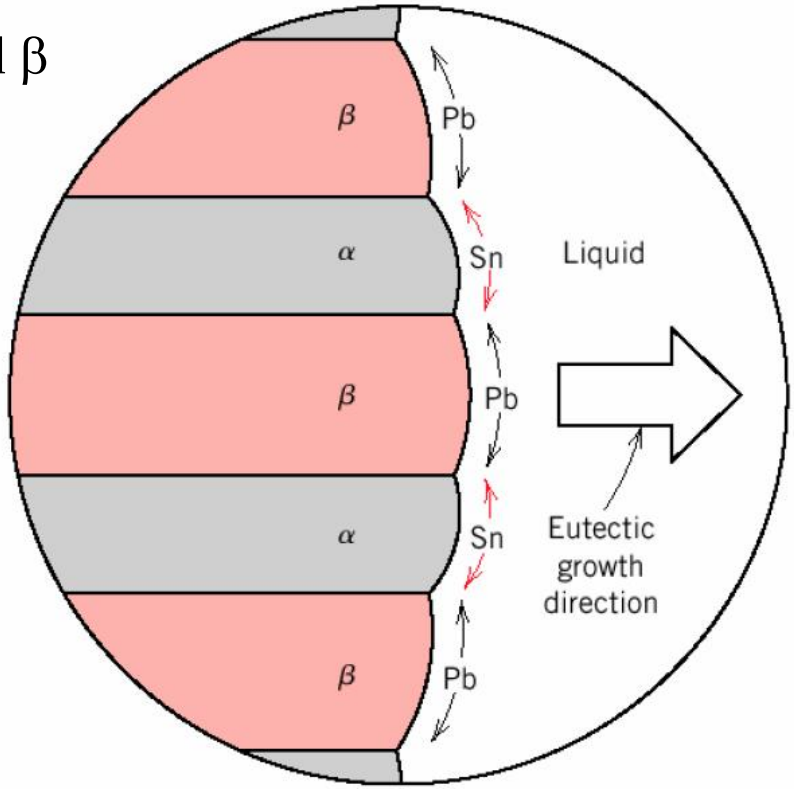


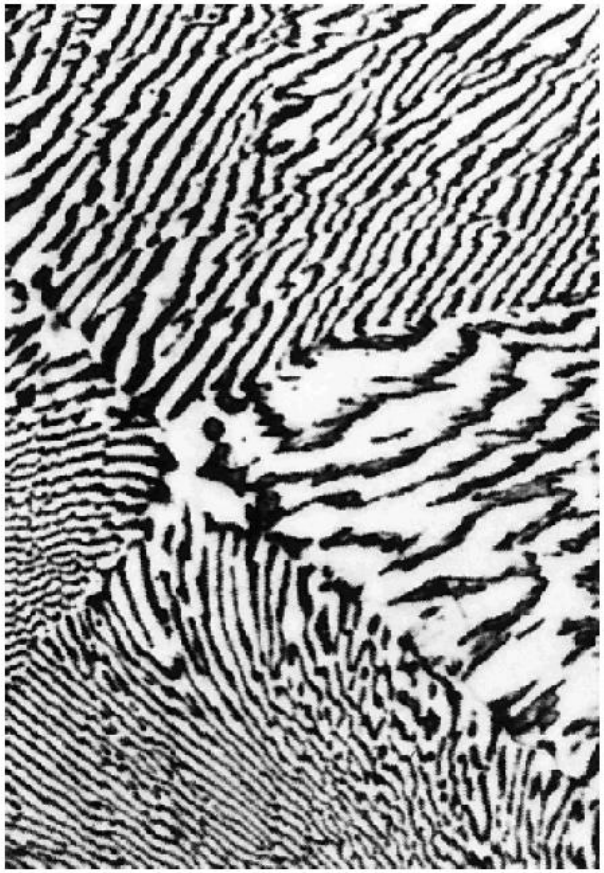
Development of microstructure in eutectic alloys (IV)

Solidification at the eutectic composition

Compositions of α and β phases are very different → eutectic reaction involves redistribution of Pb and Sn atoms by atomic diffusion.

This simultaneous formation of α and β phases result in a layered (lamellar) microstructure that is called **eutectic structure**.



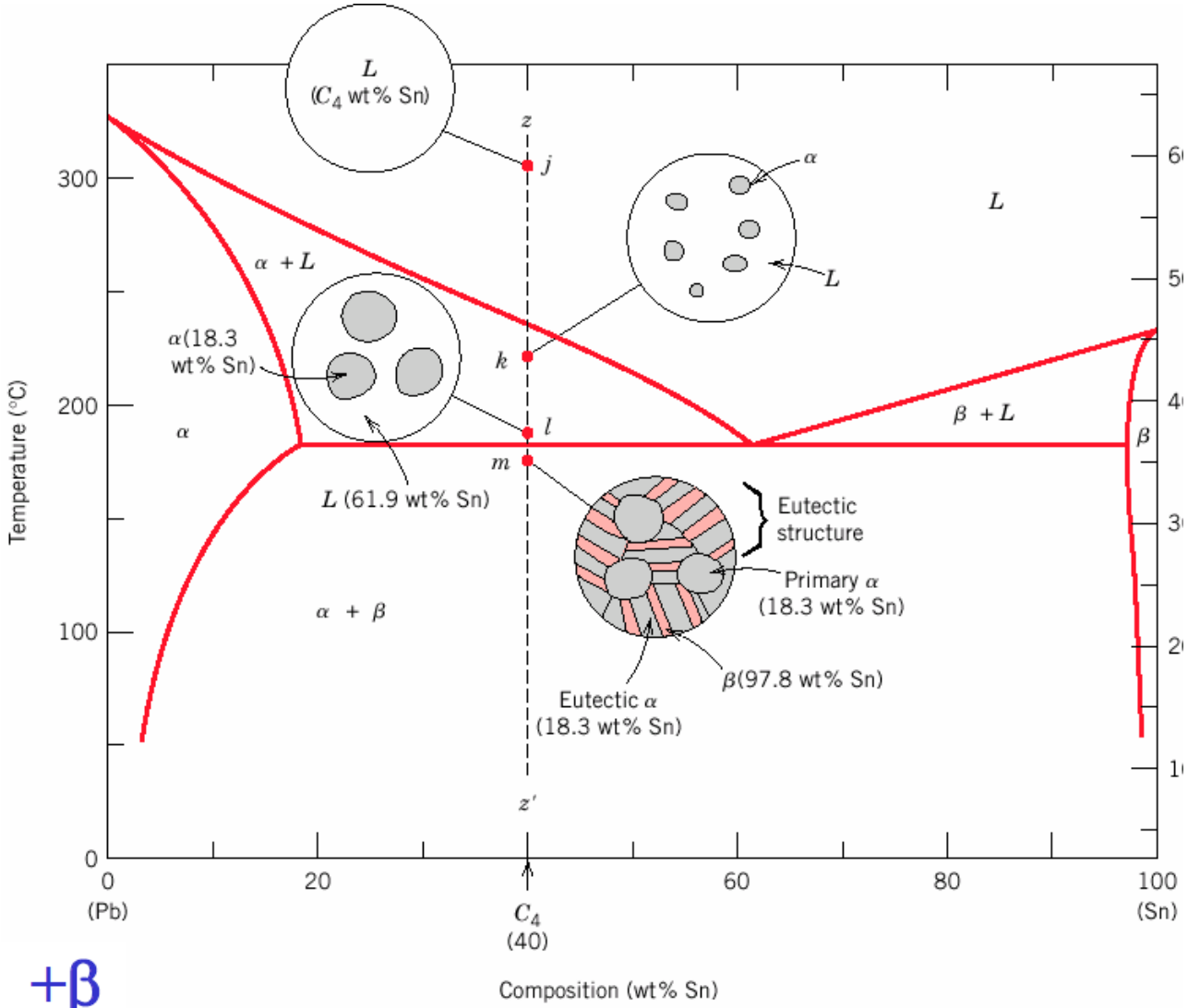


Formation of the eutectic structure in the lead-tin system. In the micrograph, the dark layers are lead-reach α phase, the light layers are the tin-reach β phase.

Development of microstructure in eutectic alloys (V)

Compositions other than eutectic but within the range of the eutectic isotherm

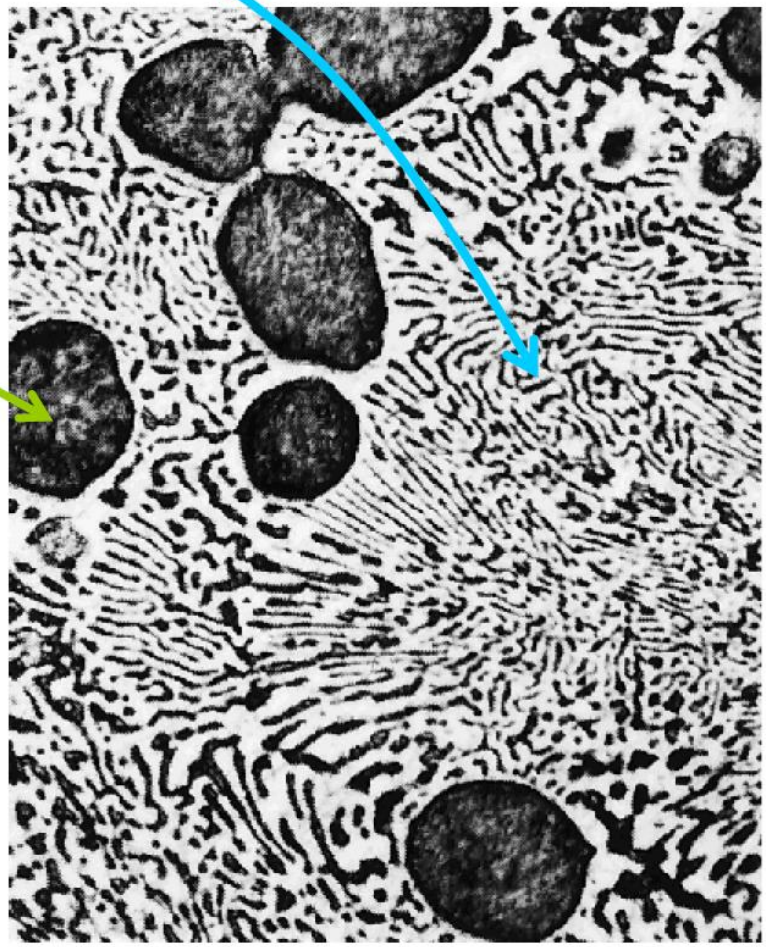
Primary α phase is formed in the α + L region, and the eutectic structure that includes layers of α and β phases (called **eutectic α** and **eutectic β** phases) is formed upon crossing the eutectic isotherm.



$L \rightarrow \alpha + L \rightarrow \alpha + \beta$

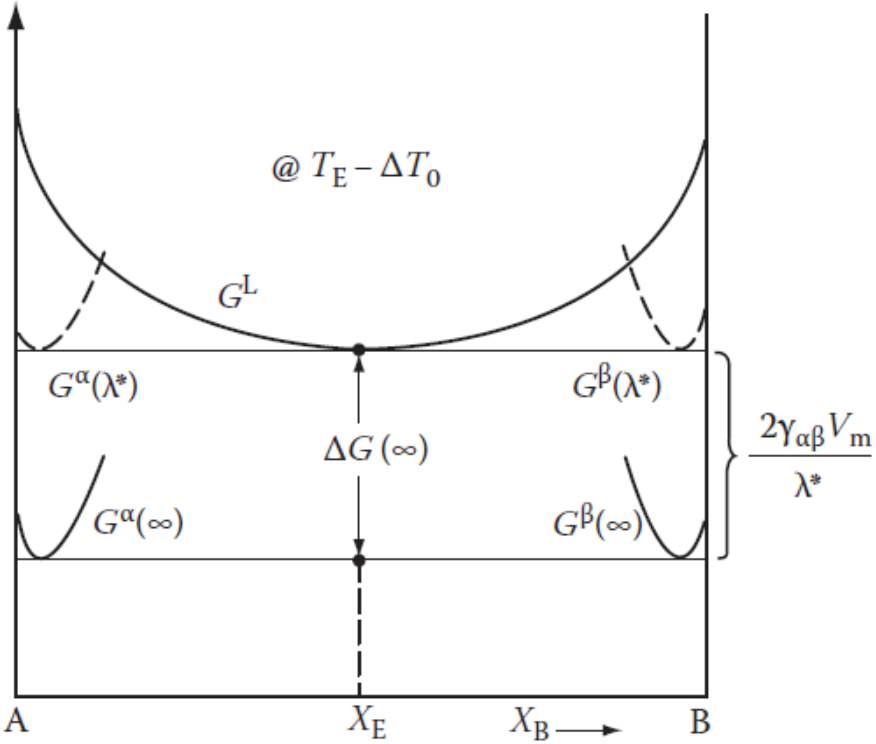
Development of microstructure in eutectic alloys (VI)

Microconstituent – element of the microstructure having a distinctive structure. In the case described in the previous page, microstructure consists of two microconstituents, primary α phase and the eutectic structure.

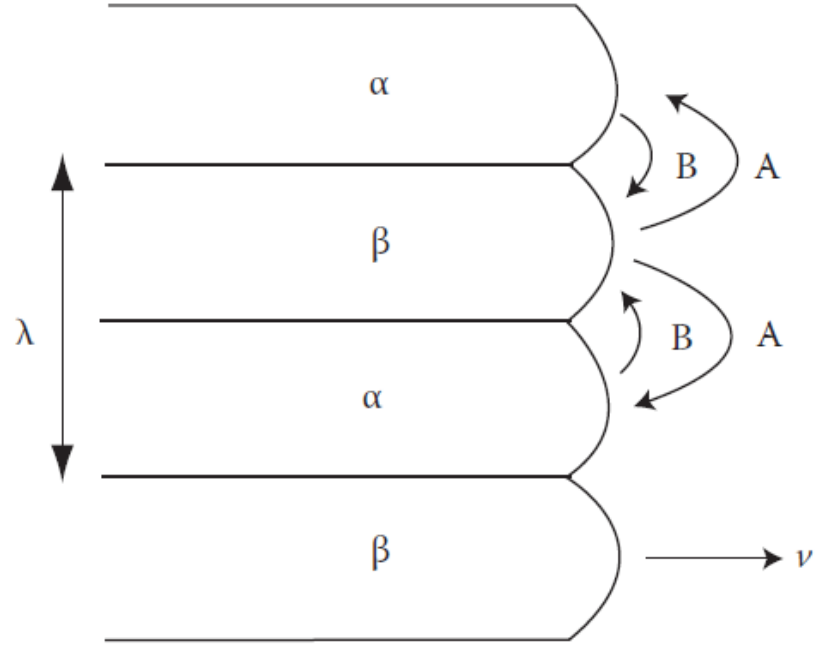


Although the eutectic structure consists of two phases, it is a microconstituent with distinct lamellar structure and fixed ratio of the two phases.

4.3 Growth of Lamellar Eutectics



Molar free energy diagram at a temperature ΔT_0 below the eutectic temperature, for the case $\lambda = \lambda^*$.



Interdiffusion in the liquid ahead of a eutectic front.

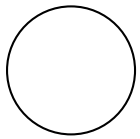
$$\Delta G(\lambda) = -\Delta G(\lambda = \infty) + \frac{2\gamma_{\alpha\beta} V_m}{\lambda}$$

=0

$$\Delta G(\lambda = \infty) = \frac{\Delta H \cdot \Delta T_0}{T_E}$$

$$\lambda^* = \frac{2\gamma_{\alpha\beta} V_m T_E}{\Delta H \cdot \Delta T_0}$$

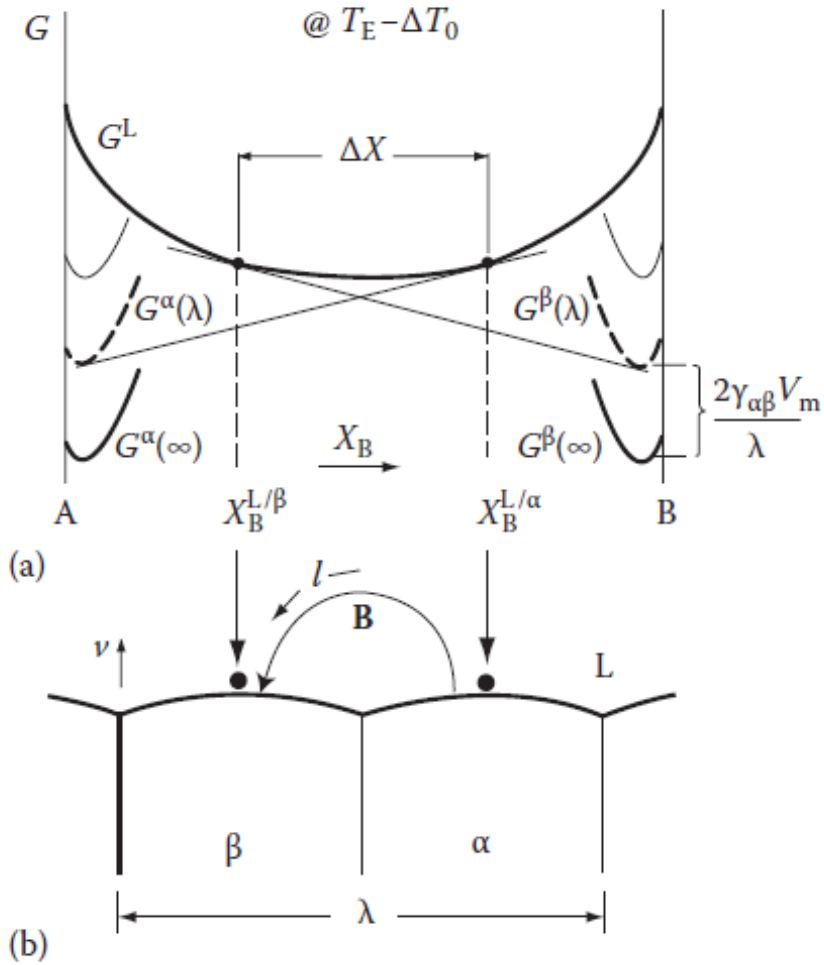
<u>Gibbs-Thomson effect</u>:

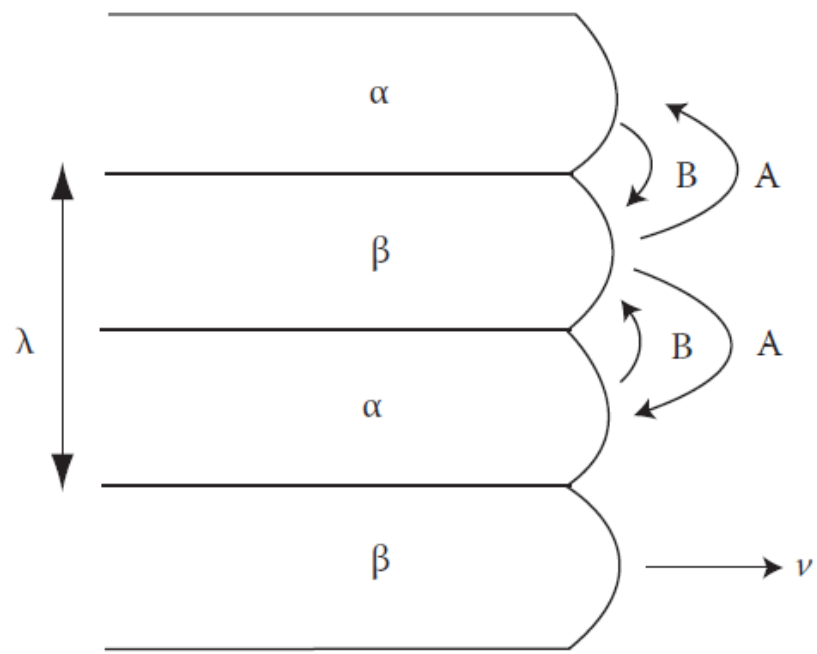


$$\Delta G_\gamma = \frac{2\gamma}{r} = \frac{\Delta H \, \Delta T}{T_m}$$

Driving force for solidification

4.3 Growth of Lamellar Eutectics





Interdiffusion in the liquid ahead of a eutectic front.

$$v = k_1 D \frac{\Delta X}{\lambda} \qquad \Delta X = \Delta X_0 \left(1 - \frac{\lambda^*}{\lambda}\right)$$

$$\Delta X_0 \propto \Delta T_0$$

$$\boxed{v = k_2 D \, \Delta T_0 \frac{1}{\lambda}\left(1 - \frac{\lambda^*}{\lambda}\right)}$$

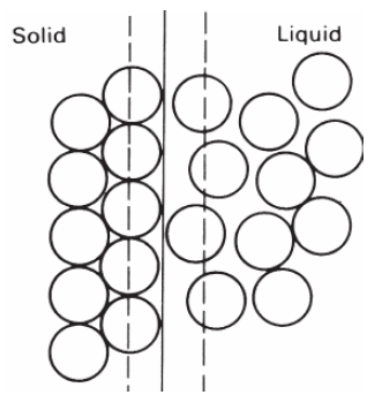
(a) Molar free energy diagram at (T_E - ΔT_0) for the case $\lambda^* < \lambda < \infty$, showing the composition difference available to drive diffusion through the liquid (ΔX).
(b) Model used to calculate the growth rate.

Homogeneous nucleation

There is an energy barrier of ΔG^* for formation of a solid nucleus of critical size r^*. The probability of energy fluctuation of size ΔG^* is given by the Arrhenius equation and the rate of homogeneous nucleation is

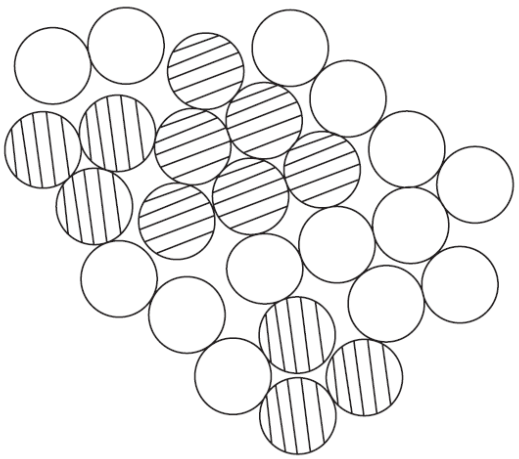
$$\dot{N} \sim \nu_d \exp\left(-\frac{\Delta G^*}{kT}\right) \quad \text{nuclei per m}^3 \text{ per s}$$

where ν_d is the frequency with which atoms from liquid attach to the solid nucleus. The rearrangement of atoms needed for joining the solid nucleus typically follows the same temperature dependence as the diffusion coefficient:



$$\nu_d \sim \exp\left(-\frac{Q_d}{kT}\right)$$

Therefore: $$\dot{N} \sim \exp\left(-\frac{Q_d}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$



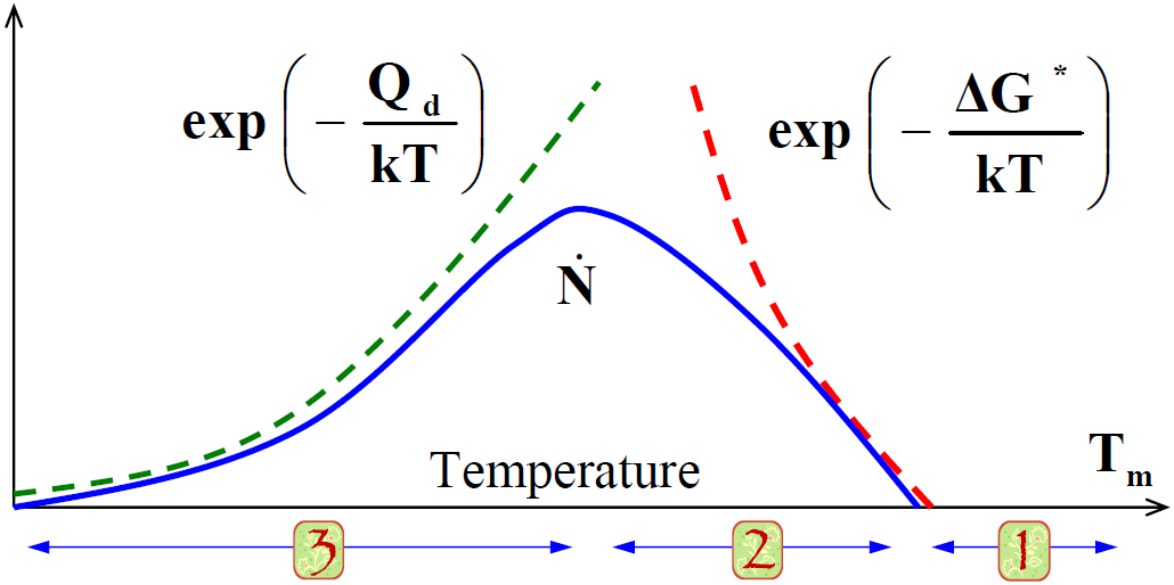
$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

$$r^* = \left(\frac{2\gamma^{SL} T_m}{\Delta H_m}\right)\frac{1}{\Delta T}$$

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

Rate of homogeneous nucleation

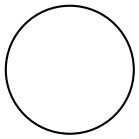
$$\dot{N} \sim \exp\left(-\frac{Q_d}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$



Gibbs-Thomson effect:

$$\Delta G_\gamma = \frac{2\gamma}{r} = \frac{\Delta H\ \Delta T}{T_m}$$

Driving force for solidification



1 $\Delta G^* > Q_d \Rightarrow \exp(-\Delta G^*/kT) << \exp(-Q_d/kT)$

ΔG^* is too high - nucleation is suppressed

2 $\Delta G^* \leq Q_d \Rightarrow \exp(-\Delta G^*/kT) > \exp(-Q_d/kT)$

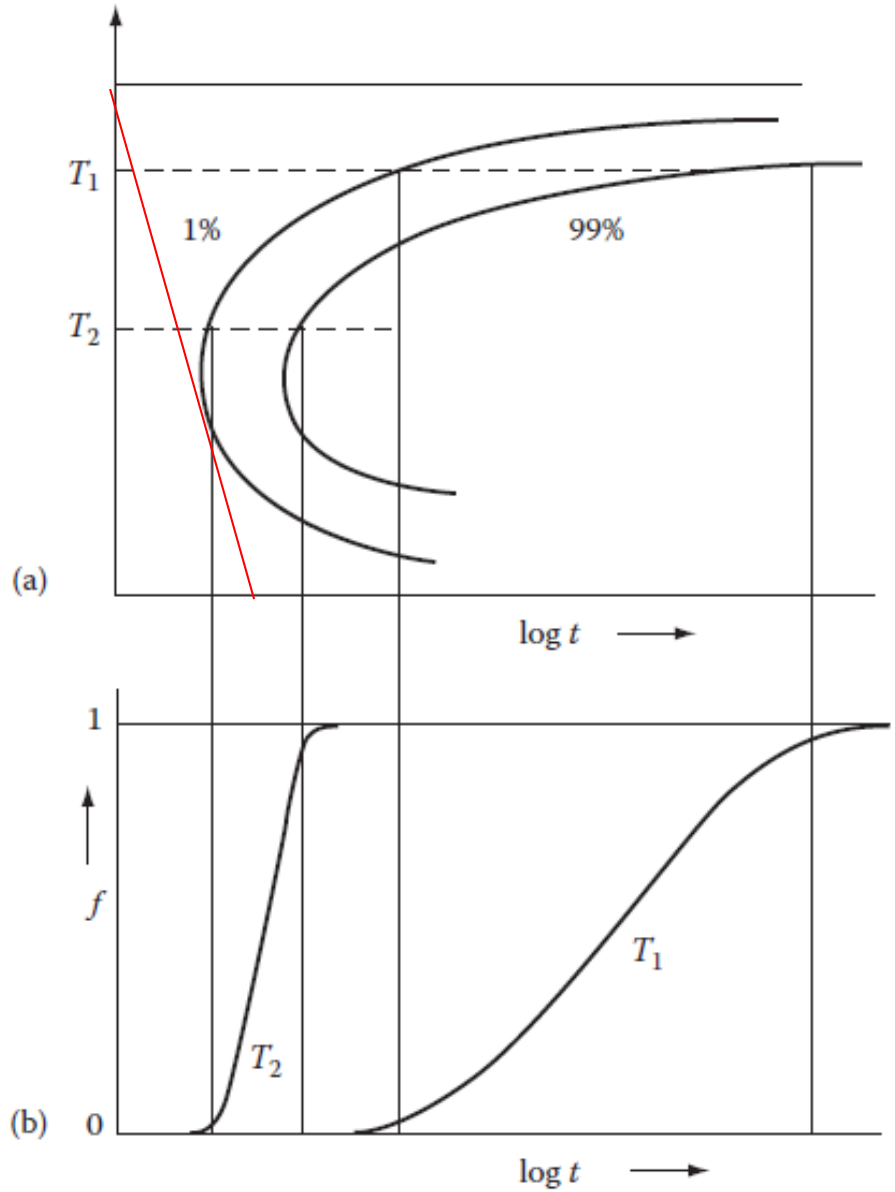
$\Delta G^* \sim 1/\Delta T^2$ – decreases with T – sharp rise of homogeneous nucleation (diffusion is still active)

3 $\exp(-Q_d/kT)$ – too small – low atomic mobility suppresses the nucleation rate

$$r^* = \left(\frac{2\,\gamma^{SL}\,T_m}{\Delta H_m}\right)\frac{1}{\Delta T}$$

$$\Delta G^* = \left(\frac{16\,\pi\,(\gamma^{SL})^3\,T_m^2}{3\,(\Delta H_m)^2}\right)\frac{1}{(\Delta T)^2}$$

5. TTT (Time Temperature Transformation) Diagrams

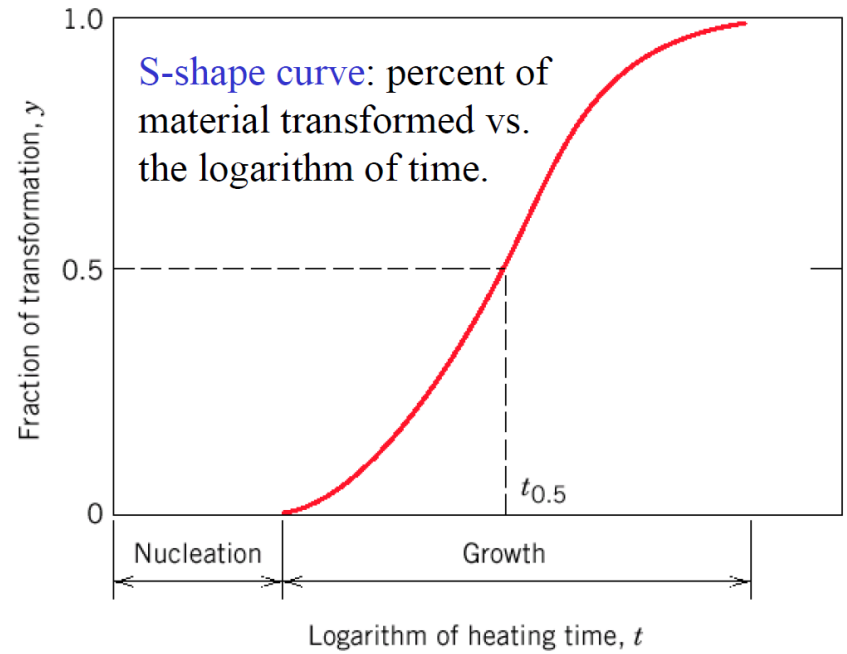


Most phase transformations involve change in composition ⇒ redistribution of atoms via diffusion is required.

The process of phase transformation involves:

- **Nucleation** of of the new phase - formation of stable small particles (nuclei) of the new phase. Nuclei are often formed at grain boundaries and other defects.
- **Growth** of new phase at the expense of the original phase.

$$y = 1 - \exp(-kt^n) \quad \textbf{Avrami Equation}$$



The percentage transformation versus time for different transformation temperatures.