

2017 Spring

“Calculation and Applications Phase Equilibria”

Principles *of* Solidification

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Contents for previous and today's class

* **Two-Phase Equilibrium** * **Origin of Defects**

→ **Binary phase diagrams**

* **Chapter 2 Solidification as an Atomistic Process**

→ **Chapter 3 Nucleation**

- **Metastability of Supercooled Liquids**
- **Equilibrium conditions for a curved interface**
- **Calculation of critical radius**
- **The process of Nucleation**

Binary phase diagrams

1) Simple Phase Diagrams

Both are ideal soln. → At T change, curvature and width change of G curve by S

2) Systems with miscibility gap

$$\Delta H_{mix}^L = 0 \quad \Delta H_{mix}^S > 0$$

At T change, curvature and width change of G curve by S + shape change of curve by H

4) Simple Eutectic Systems

$$\Delta H_{mix}^L = 0 \quad \Delta H_{mix}^S \gg 0$$

→ miscibility gap extends to the melting temperature.

3) Ordered Alloys

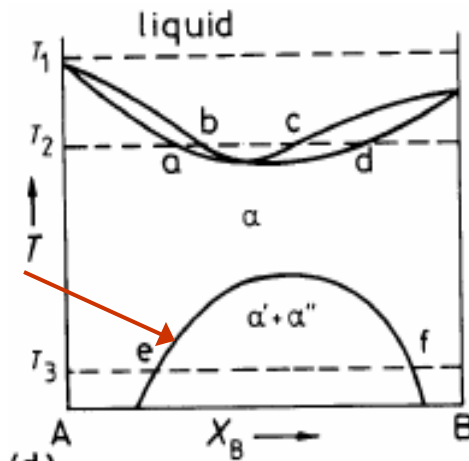
$$\Delta H_{mix}^L = 0 \quad \Delta H_{mix}^S < 0$$

$\Delta H_{mix} < 0$ → A atoms and B atoms like each other. → Ordered alloy at low T

$\Delta H_{mix} \ll 0$ → The ordered state can extend to the melting temperature.

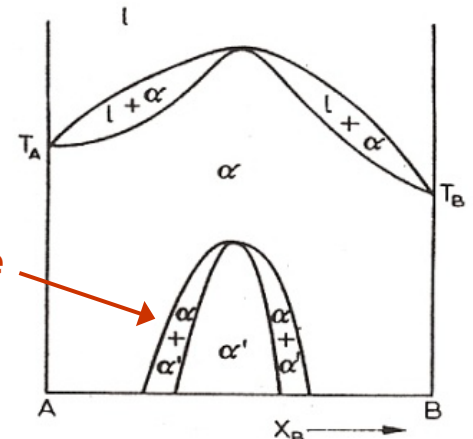
$$\Delta H_{mix}^\alpha > \Delta H_{mix}^l > 0$$

miscibility gap



$$\Delta H_{mix}^\alpha < \Delta H_{mix}^l < 0$$

Ordered phase



Microstructure is the collection of defects in the materials.

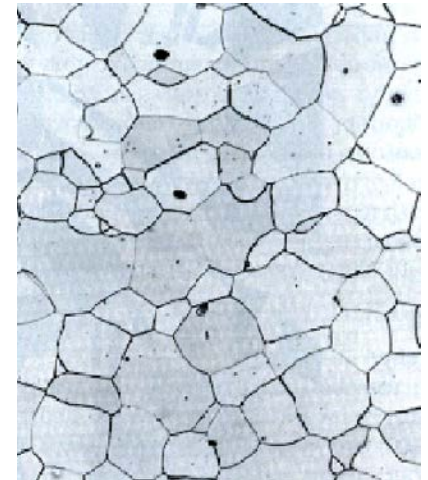
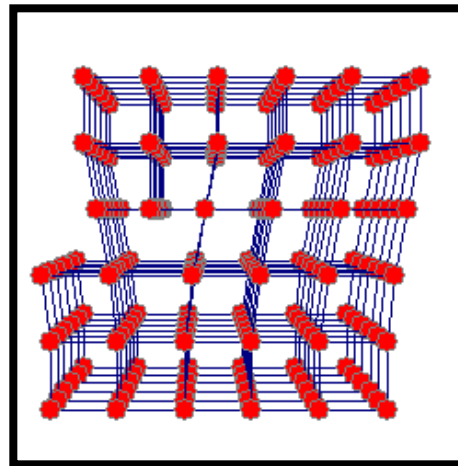
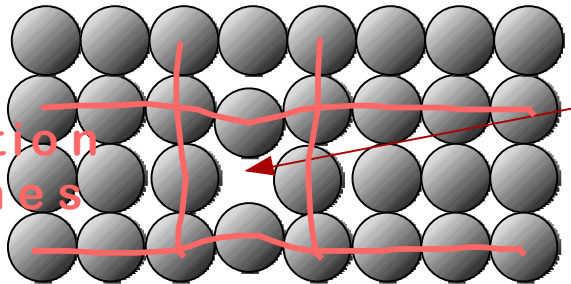
□ **Imperfection** in Metallic Materials ;

Point defect : Vacancies, interstitials, Impurities

Line defect : Dislocations, Cellular and lineage substructure

Plane defect : Grain Boundaries, Free Surfaces

Bulk defect : Voids, Cracks



Heterogeneous Nucleation

Heterogeneous nucleation must occur on some substrate:

grain boundaries

triple junctions

dislocations

(existing) second phase particles

Consider a grain boundary: why is it effective?

Answer: by forming on a grain boundary, an embryo can offset its “cost” in interfacial energy by **eliminating some grain boundary area.**

c) Quenched-in Vacancies

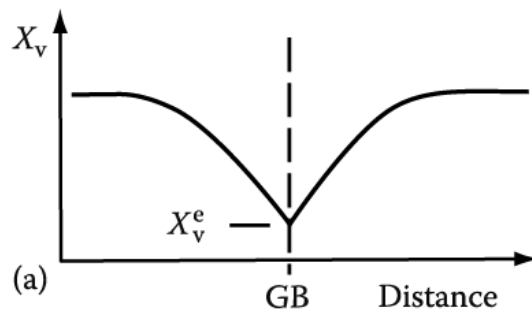
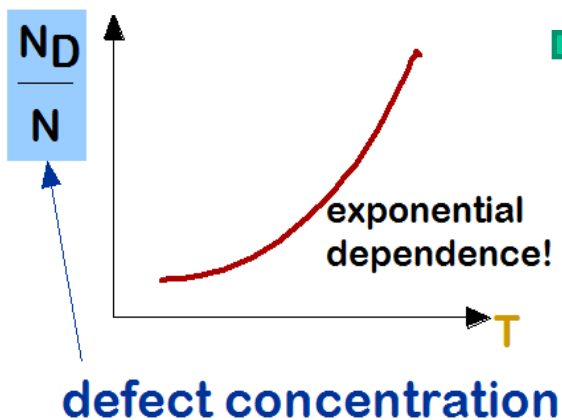
In the vicinity of grain boundaries on subsequent aging,

Precipitate-Free Zone(PFZ) due to Vacancy Diffusion during quenching

Solute concentration within the zone ~ largely unchanged, but no precipitate at GB
 \therefore a critical vacancy supersaturation must be exceeded for nucleation to occur.

$$X_v^e = \exp \frac{-\Delta G_v}{RT}$$

$T \uparrow \rightarrow X_v^e \uparrow$



Similar PFZs can also form at inclusions and dislocations.

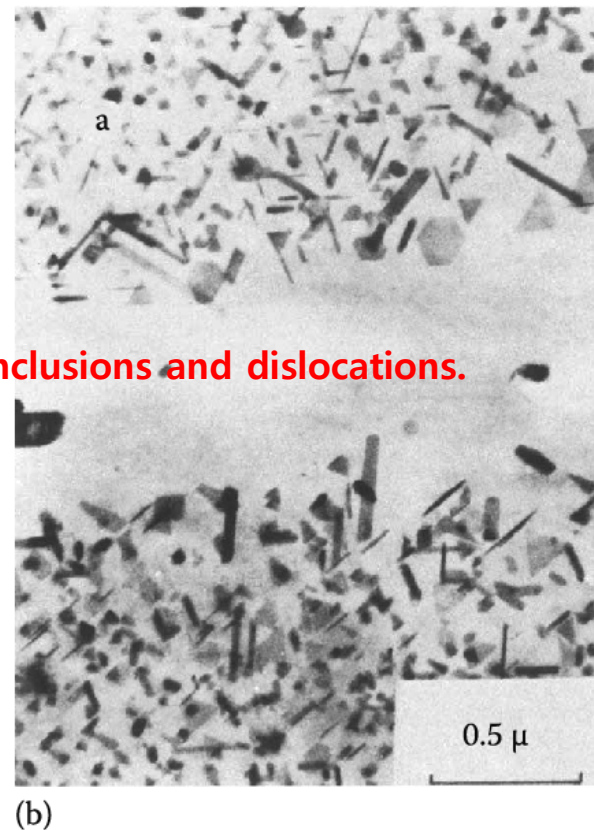
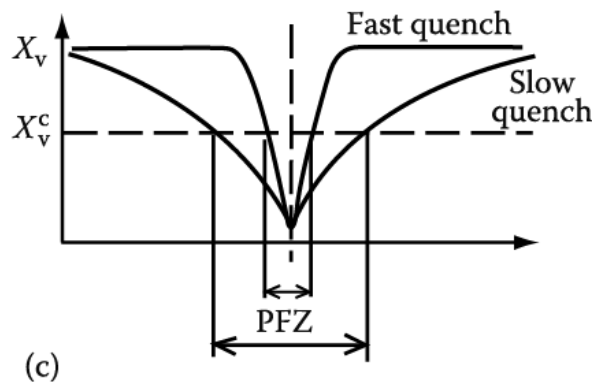


Fig. 5.35 A PFZ due to vacancy diffusion to a grain boundary during quenching.
 (a) Vacancy concentration profile. (b) A PFZ in an Al-Ge alloy (x 20,000)
 (c) Dependence of PFZ width on critical vacancy concentration X_v^c and rate of quenching.

Liquid ↔ Solid transformation at T_m

Chapter 1: Equilibrium consideration (Thermodynamics)

Chapter 2: Atomic mechanism (Kinetics)

Chapter 3. Nucleation

3.1. Metastability of Supercooled Liquid

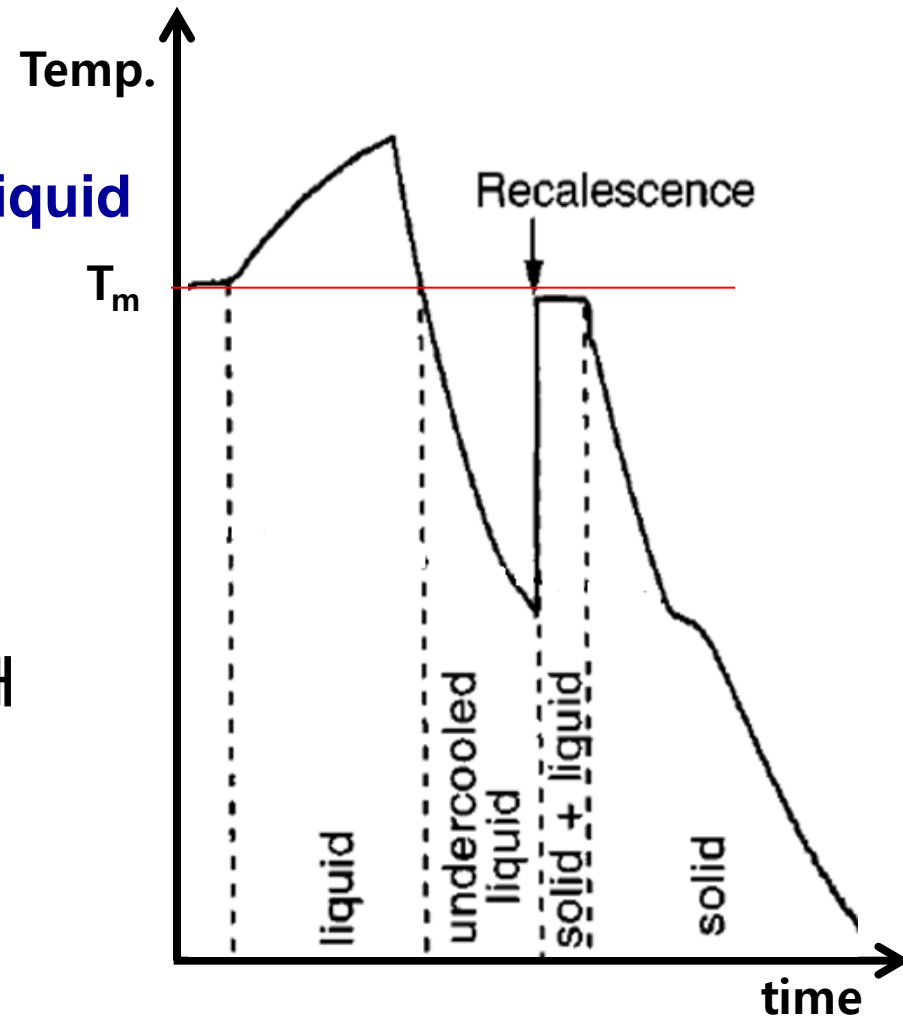
Solidification:

Liquid → **Solid**

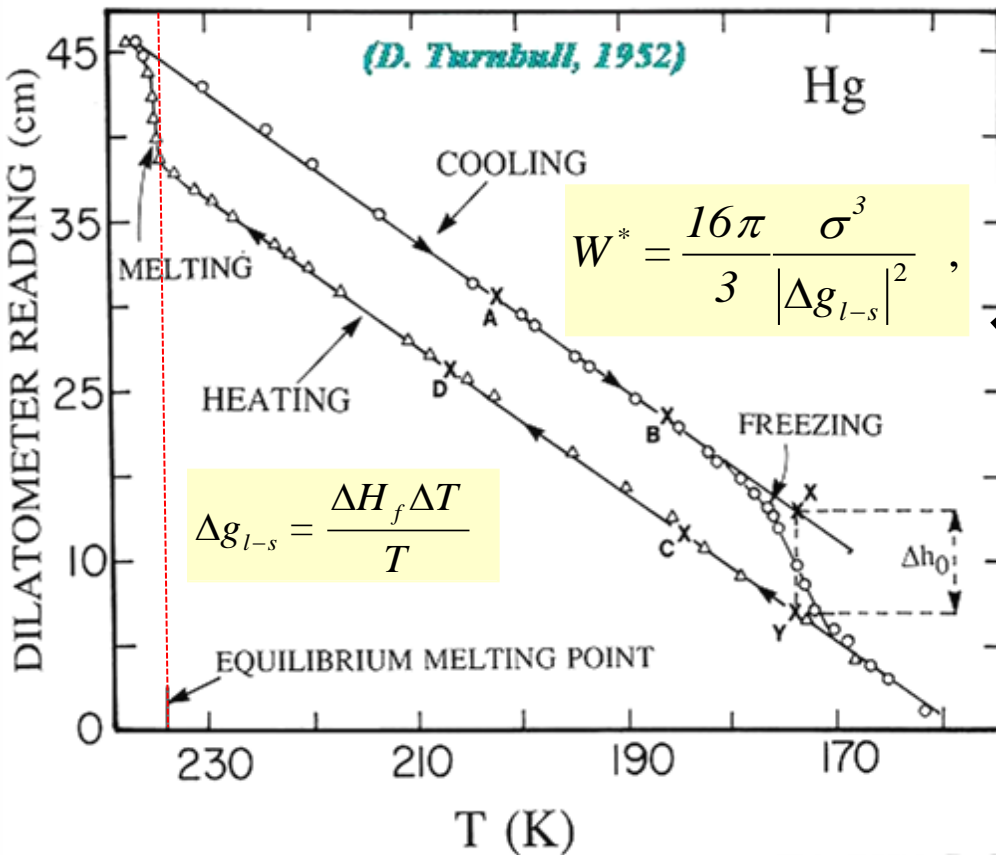


Metastable supercooled liquid의 존재

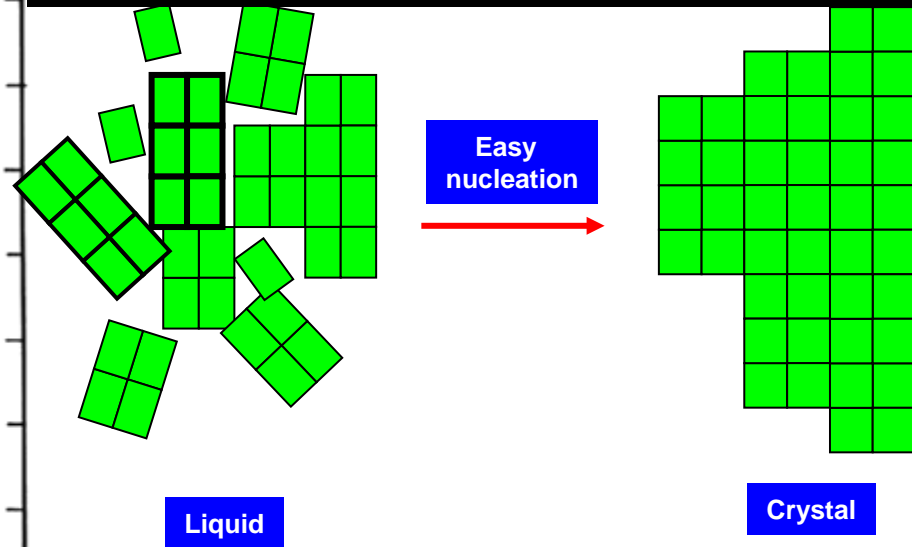
Why?



Turnbull's Insight for Supercooling



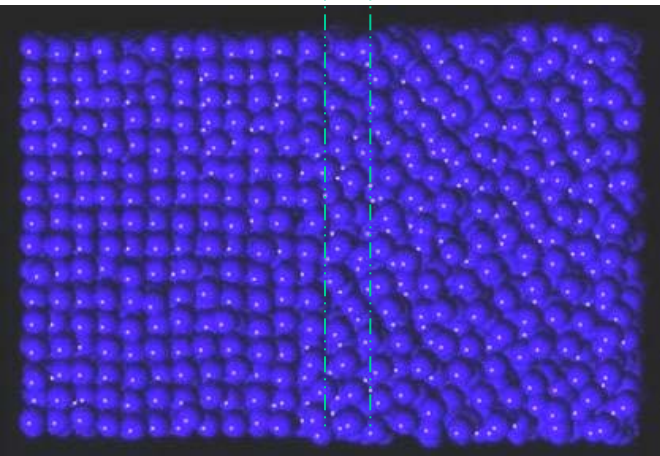
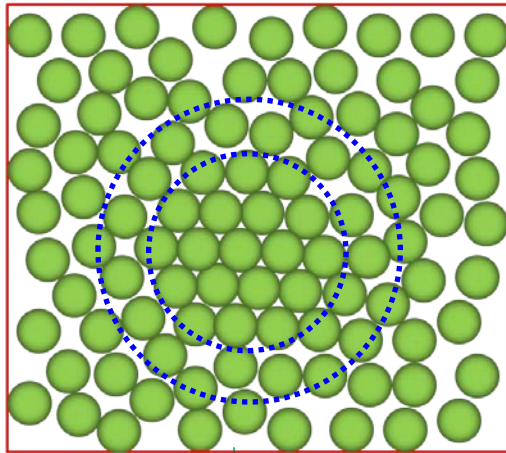
Microcrystalline structure for liquid metals
 –Same short range order with crystals!



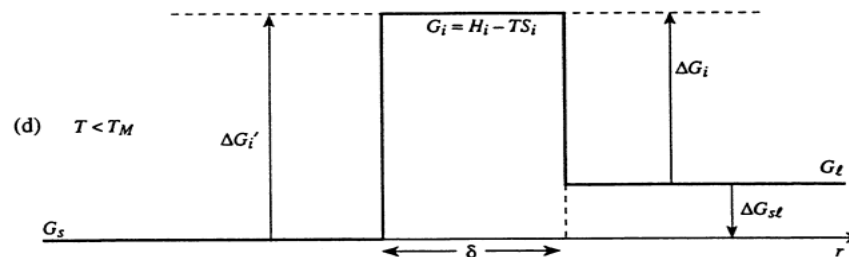
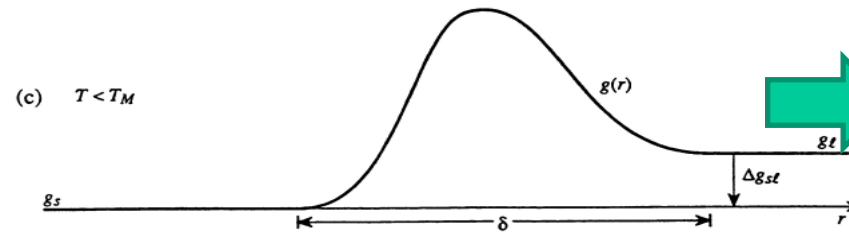
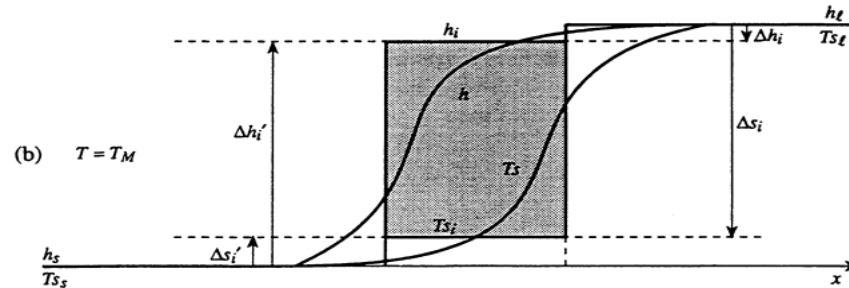
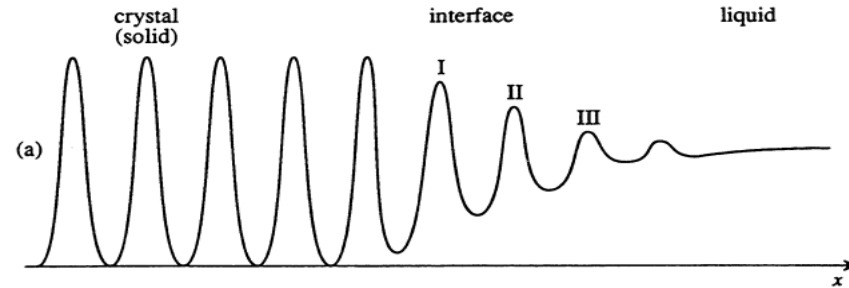
- ◆ How does the liquid metals resist on the crystallization?
- ◆ What is the origin of high nucleation barrier against the crystallization?
- What is the structure of interface between liquids and crystals?
- ◆ What is the local order of liquid metals?

Turnbull's solid-liquid interface

Turnbull's insight : Liquid orders substantially near a crystal surface due to entropy decreasing caused by the crystal-melt interfacial tension



Solid state physics v47, 1 (1994)



Supercooling

3.2. Equilibrium condition for a curved interface

Stability of curved interface

1) Atomic consideration

a) Equilibrium: Geometrical factors $G_F = G_M$ (planer interface)

→ If it is curved, “escape angle” changes with curvature.

① $S \rightarrow L$: if Solid is convex structure $\rightarrow G_M \uparrow$, concave structure $\rightarrow G_M \downarrow$
 $\Delta G_M \propto$ curvature of the surface $\propto 1/r$

→ if “Spherical” crystal containing n atoms $\propto n^{1/3}$

② $L \rightarrow S$: reverse direction of ($S \rightarrow L$) case

$\therefore G_M^n$ for $S \rightarrow L$ transition

for atoms at the surface of a spherical crystal containing n atoms

$$G_M^n = (1 + \alpha/n^{1/3}) G_M, \quad G_F^n = (1 - \alpha/n^{1/3}) G_F$$

Convex surface = less firmly bound = fewer nearest neighbors in the crystal

→ easier escape than that of flat surface

b) Average energy for escape

$$L^n = (1 - \beta/n^{1/3}) L_1$$

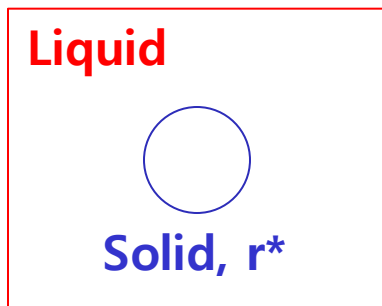
→ β is calculated from the number of neighbors
(ex. FCC structure: $\beta = 1.33$)

If the rate for the melting process $\uparrow \rightarrow r \downarrow$ &
the rate for the freezing process $\downarrow \rightarrow T_E \downarrow$.

$\therefore T_{E, \text{small crystal}} < T_{E, \text{large crystal}}$

Thus, at any temperature below T_E , there is a radius of curvature
at which the rates of melting and of freezing are equal.

= critical radius r^*



a) if $T_E + \Delta T (+)$, $R_M > R_F \rightarrow r \downarrow$

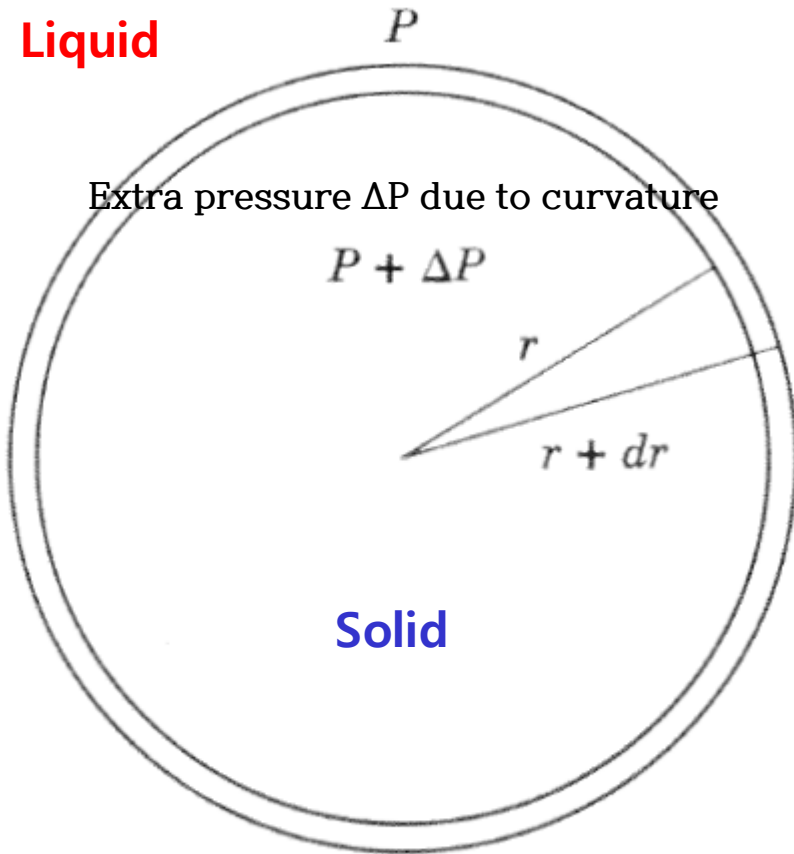
$\rightarrow T_E \rightarrow T_E' \downarrow \rightarrow \Delta T (+) \uparrow \rightarrow R_M \gg R_F$

b) if $T_E + \Delta T (-)$, $R_M < R_F \rightarrow r \uparrow$

$\rightarrow T_E \rightarrow T_E' \uparrow \rightarrow \Delta T (-) \uparrow \rightarrow R_M \ll R_F$

2) Thermodynamic treatment of equilibrium across a curved interface

Liquid



$$r \rightarrow r + dr, P \rightarrow P + \Delta P$$

The work done is equal to the increase in free energy of the interface; Thus,

$$P dr \times 4\pi r^2 = [4\pi(r + dr)^2 - 4\pi r^2]\sigma$$

whence

$$P = \frac{2\sigma}{r}$$

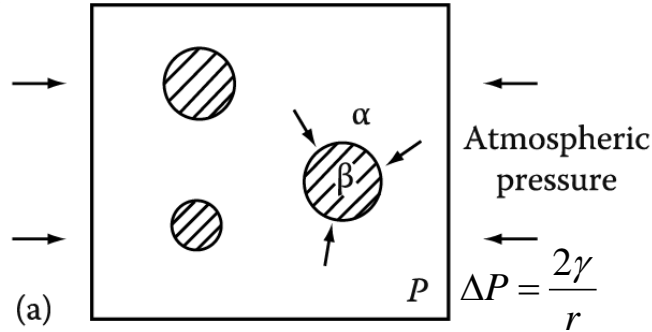
Fig. 3.1. Pressure due to surface tension.

The G curves so far have been based on the molar Gs of infinitely large amounts of material of a perfect single crystal. Surfaces, GBs and interphase interfaces have been ignored.

1.6 Influence of Interfaces on Equilibrium

$$\Delta G = \Delta P \cdot V \Rightarrow \Delta G = \frac{2\gamma V_m}{r}$$

Extra pressure ΔP due to curvature of the α/β



The concept of a pressure difference is very useful for spherical liquid particles, but it is less convenient in solids (often nonspherical shape).

$$dG = \Delta G_\gamma dn = \gamma dA \quad \Delta G_\gamma = \gamma dA/dn$$

Since $n=4\pi r^3/3V_m$ and $A = 4\pi r^2$ $\Delta G = \frac{2\gamma V_m}{r}$

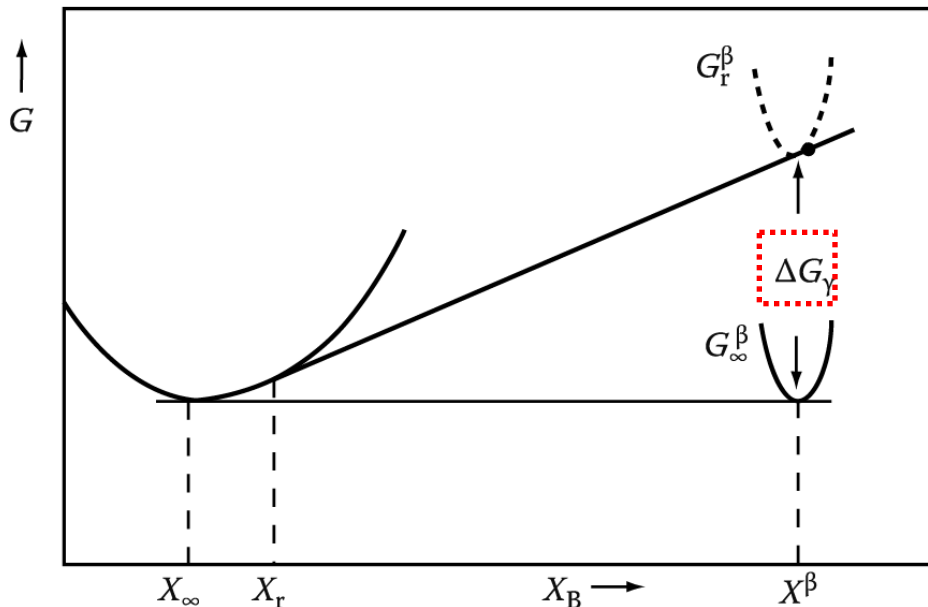


Fig. 1.38 The effect of interfacial E on the solubility of small particle

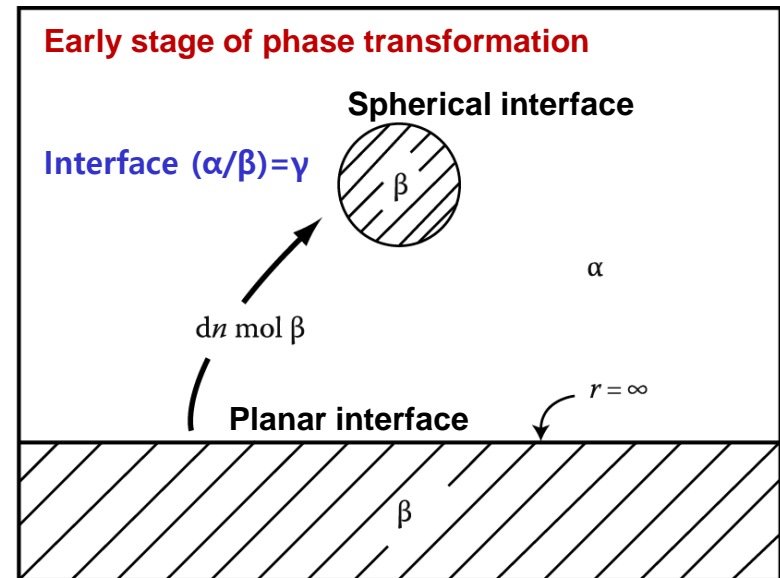
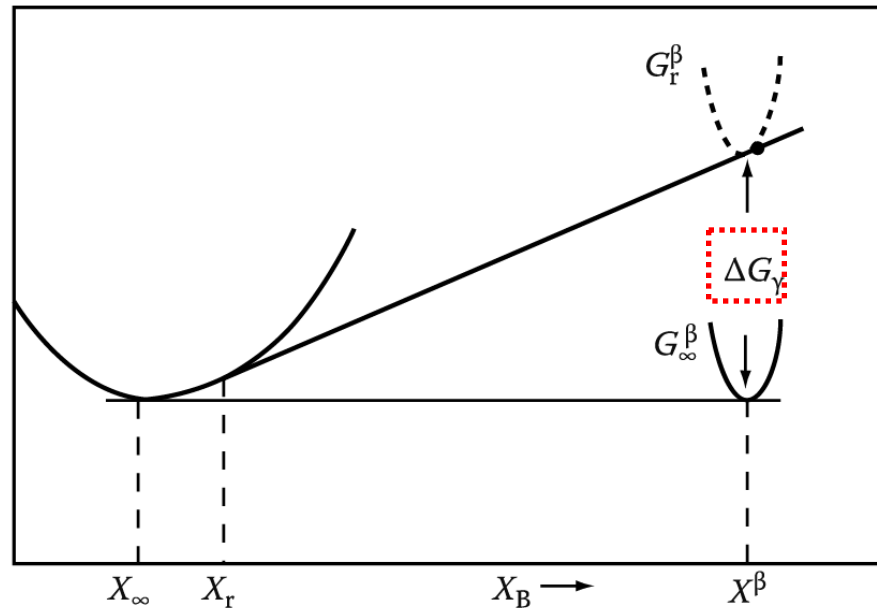


Fig. 1.39 Transfer of dn mol of β from large to a small particle.

Gibbs-Thomson effect (capillarity effect):

Free energy increase due to interfacial energy

Quite large solubility differences can arise for particles in the range $r=1-100$ nm. However, for particles visible in the light microscope ($r>1\mu\text{m}$) capillarity effects are very small.



(b)

Fig. 1.38 The effect of interfacial energy on the solubility of small particles.

$$X_B^e = A \exp\left\{-\frac{Q}{RT}\right\}$$

$$X_B^e = \exp\left(-\frac{\Delta G_B + \Omega}{RT}\right)$$

$$X_B^{r=\infty} = \exp\left(-\frac{\Delta G_B + \Omega}{RT}\right)$$

$$X_B^{r=r} = \exp\left(-\frac{\Delta G_B + \Omega - 2\gamma V_m / r}{RT}\right)$$

$$= X_B^{r=\infty} \exp\left(\frac{2\gamma V_m}{RT r}\right)$$

For small values of the exponent,

$$\frac{X_B^{r=r}}{X_B^{r=\infty}} = \exp\left(\frac{2\gamma V_m}{RT r}\right) \approx 1 + \frac{2\gamma V_m}{RT r}$$

Ex) $\gamma = 200 \text{ mJ/m}^2$, $V_m = 10^{-5} \text{ m}^3$, $T = 500 \text{ K}$

$$\frac{X_r}{X_\infty} = 1 + \frac{1}{r(\text{nm})}$$

For $r = 10$ nm, solubility $\sim 10\%$ increase

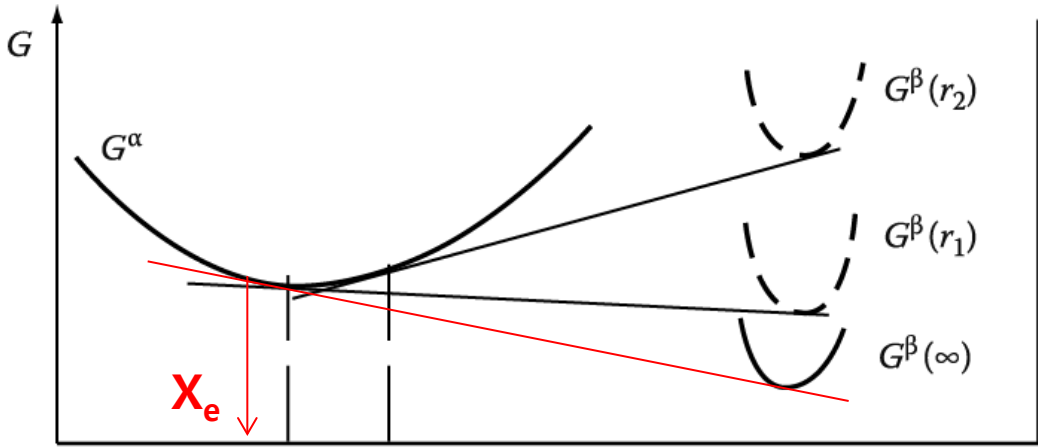
Microstructure of a two phase alloy is always unstable if the total interfacial free E is not a minimum. →

5.5.6. Particle Coarsening

(smaller total interfacial area → loss of strength or disappearance of GB pinning effect → particular concern in the design of materials for high temp. applications)

Two Adjacent Spherical Precipitates with Different Diameters

(Gibbs-Thomson effect: radius of curvature ↓ → X_B ↑) Assumption: volume diffusion is the rate controlling factor



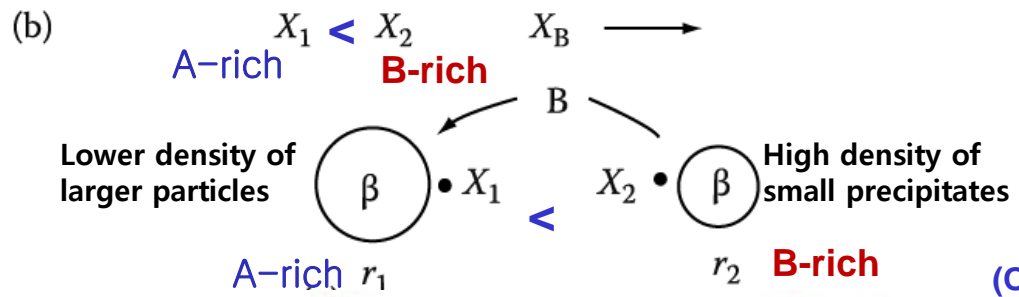
$$(\bar{r})^3 - r_0^3 = kt$$

Average radius

where $k \propto D\gamma X_e$

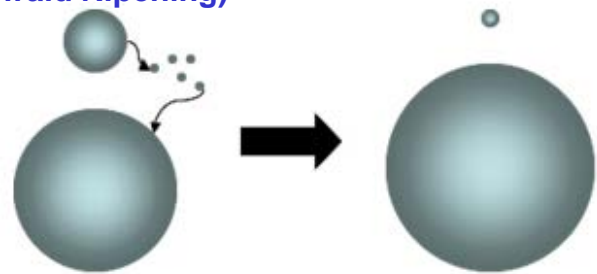
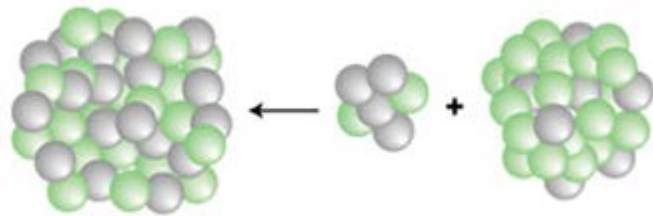
(X_e : Equil. solubility of very large particles)

Coarsening rate $\frac{d\bar{r}}{dt} \propto \frac{k}{\bar{r}^2}$



D and $X_e \sim \exp(-Q/RT)$
 \bar{r} rapidly increase with increasing temp. ⇒ CR ↑

(Ostwald Ripening)



: Concentration gradient in matrix → diffusion → small particle_shrink/ large particle_grow

3.3 Calculation of critical radius

1) Assumption: no work is done in compressing the solid (two phases were at the same pressure), $T_E \rightarrow T_E - \Delta T$, $\Delta G_p (2\sigma/r^*) = \Delta P$

$$G^L = H^L - TS^L$$

$$G^S = H^S - TS^S$$

$$\Delta G_p = \Delta H - T \Delta S$$

$$L : \Delta H = H^L - H^S$$

(Latent heat)

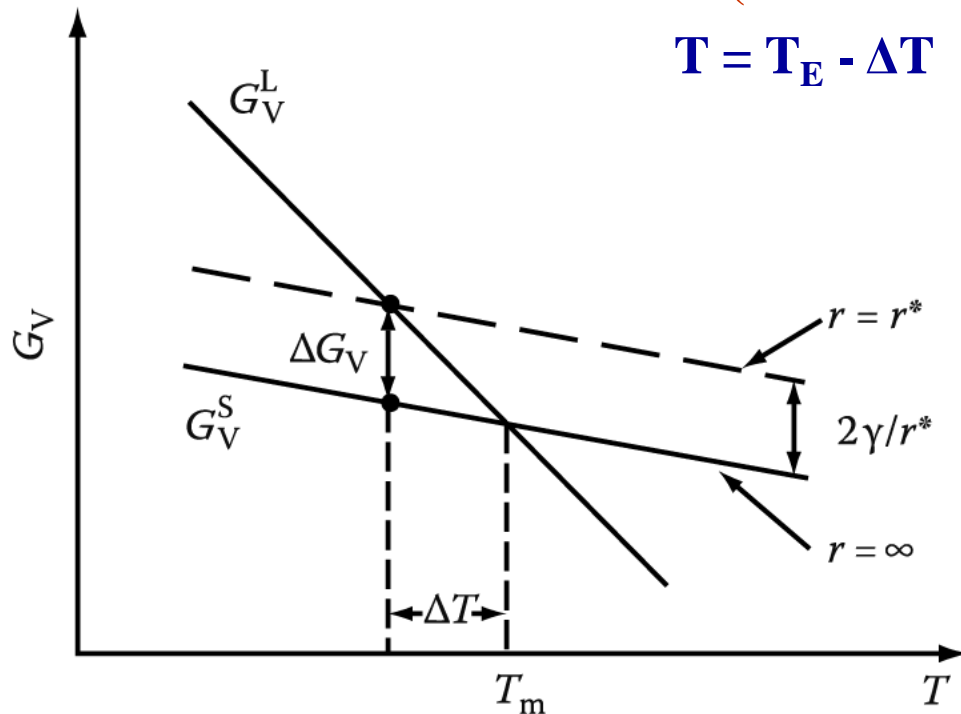
$$T = T_E - \Delta T$$

$$\Delta G_p = 0 = \Delta H - T_E \Delta S$$

$$\Delta S = \Delta H / T_E = L / T_E$$

$$\Delta G_p = L - T(L/T_E) \approx (L\Delta T) / T_m$$

$$\Delta G_V = \Delta G_P = \frac{L\Delta T}{T_E}$$



For incompressible solid,

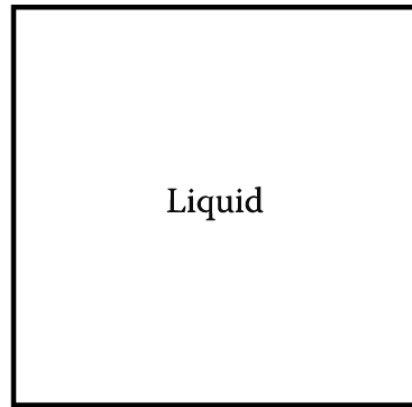
$$\frac{L\Delta T}{T_E} = \frac{2\sigma}{r^*}, \quad \text{or} \quad r^* = \frac{2\sigma T_E}{L\Delta T}$$

$\Delta H, \Delta S$: independent of temperature

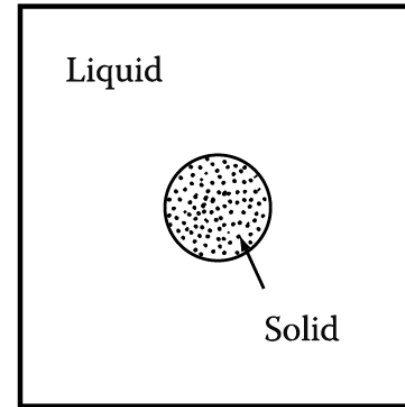
→ if the nucleation status is not incompressible, $\Delta G_p = \Delta P$

(ex. Nucleation of gas or vapor in liquid)

2) Calculation of critical radius II



(a) G_1



(b) $G_2 = G_1 + \Delta G$

$$G_1 = (V_S + V_L)G_V^L$$

$$G_2 = V_S G_V^S + V_L G_V^L + A_{SL} \gamma_{SL}$$

G_V^S, G_V^L : free energies per unit volume

$$\Delta G = G_2 - G_1 = -V_S (G_V^L - G_V^S) + A_{SL} \gamma_{SL}$$

for spherical nuclei (isotropic) of radius : r

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

2) Calculation of critical radius II

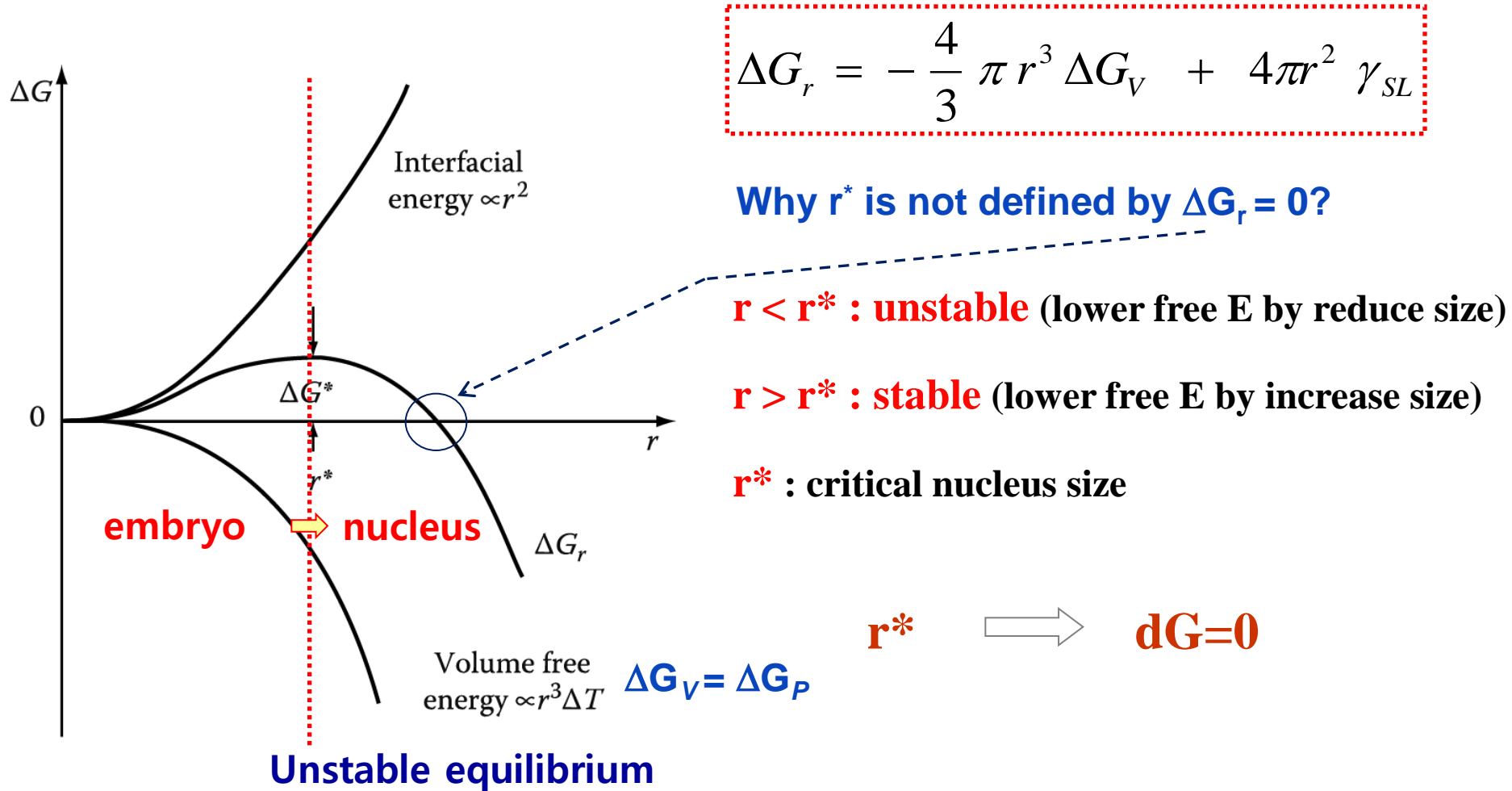


Fig. 4. 2 The free energy change associated with homogeneous nucleation of a sphere of radius r .

Gibbs-Thompson Equation

ΔG of a spherical particle of radius, r

$$\Delta G_{r(s)} = 4\pi r^2 \gamma$$

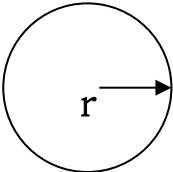
ΔG of a supersaturated solute in liquid in equilibrium with a particle of radius, r

$$\Delta G_{r(l)} = \frac{4\pi r^3}{3} \times \Delta G_V$$

Equil. condition for open system

→ $\Delta\mu$ should be the same.

$$\Delta\mu = 8\pi r \gamma = 4\pi r^2 \Delta G_V$$



$$\frac{2\gamma V_m}{r} \text{ /mole or } \frac{2\gamma}{r} \text{ / per unit volume}$$

$$\Delta G_V = 2\gamma_{SL} / r^*$$

r^* : in (unstable) equilibrium with surrounding liquid

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

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

$$\Delta G_V = \frac{L\Delta T}{T_m}$$

- Critical condition of Nucleation → Depends on the curvature of the crystal surface
- To calculate r^* under a given ΔT : $\sigma = \gamma_{SL}$ (Sol.-Liq. Interfacial E) measurement required

$$r^* = \frac{2\sigma T_E}{L\Delta T}$$

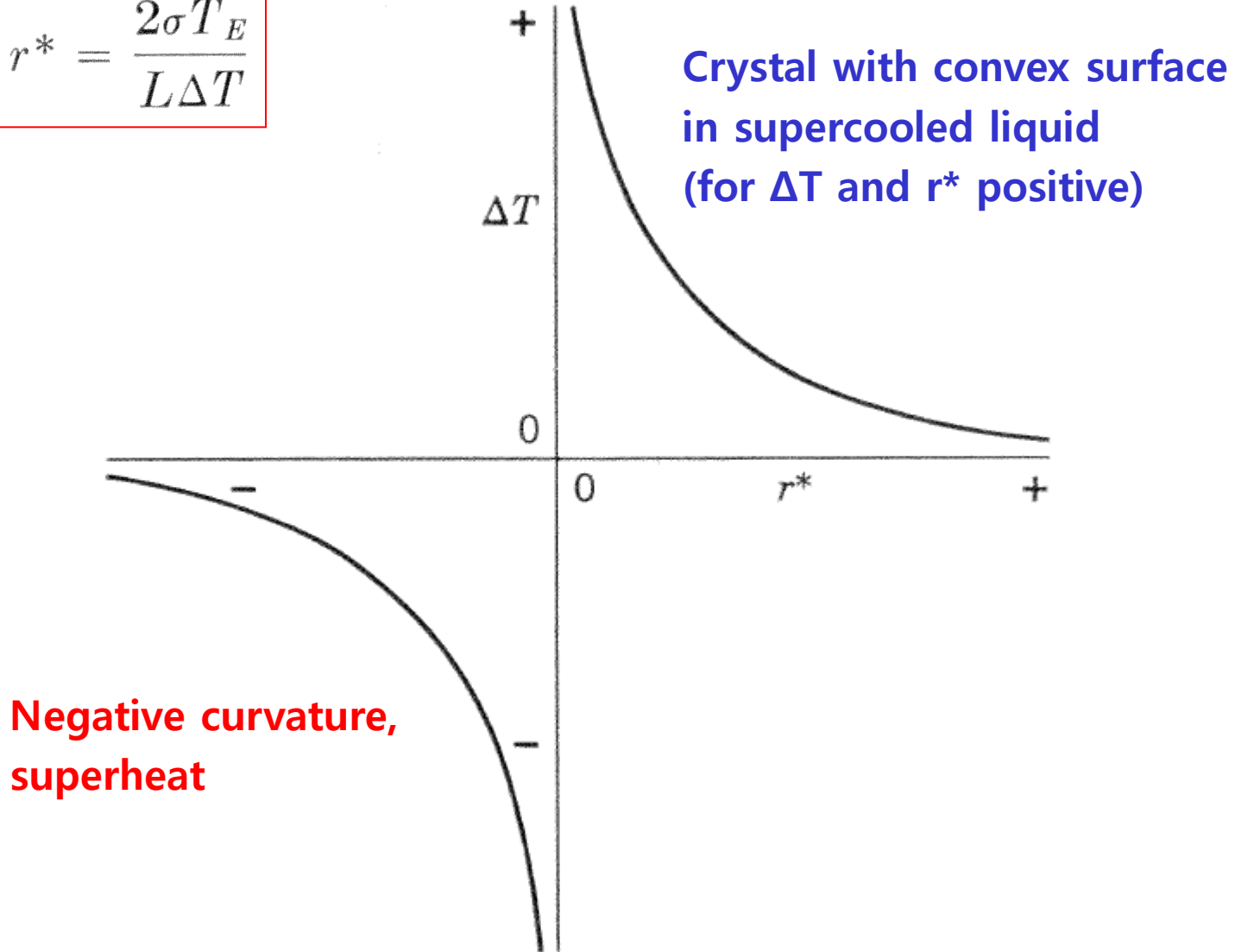
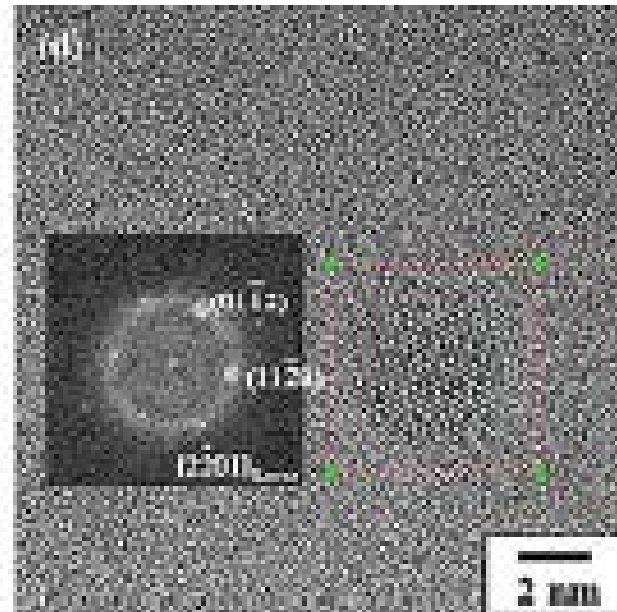
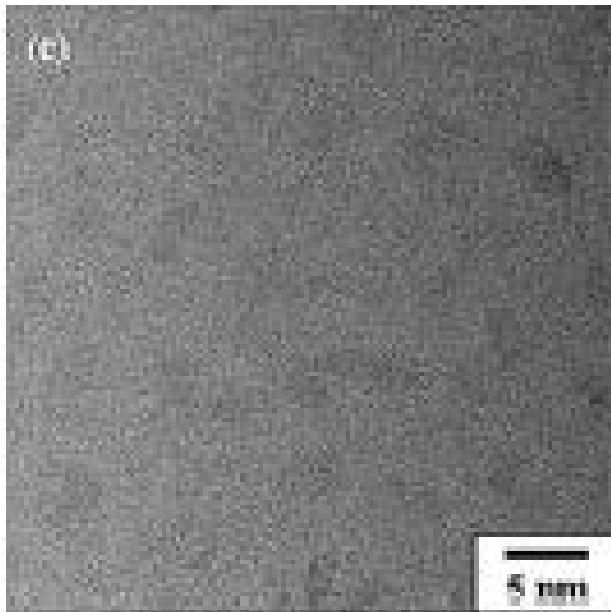
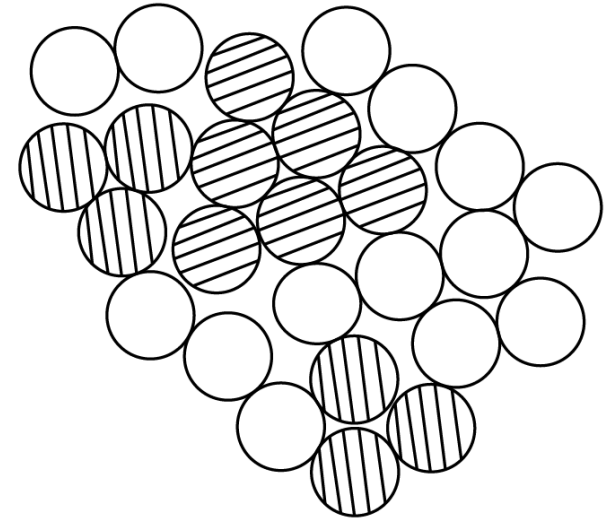


Fig. 3.3. Relationship between critical radius and supercooling. 20

Formation of Atomic Cluster

At the T_m , the liquid phase has a volume 2-4% greater than the solid.

Fig. 4.4 A two-dimensional representation of an instantaneous picture of the liquid structure. Many close-packed crystal-like clusters (shaded) are instantaneously formed.

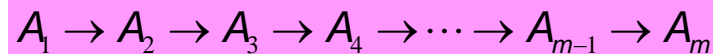


Formation of Atomic Cluster

When the free energy of the atomic cluster with radius r is by

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

how many atomic clusters of **radius r** would exist in the presence of the total number of atoms, n_0 ?



$$n_2 = n_1 \exp\left(-\frac{\Delta G^{1 \rightarrow 2}}{kT}\right) \text{ Excess free E associated with the cluster of } 1 \rightarrow 2 \text{ atoms}$$

$$n_3 = n_2 \exp\left(-\frac{\Delta G^{2 \rightarrow 3}}{kT}\right)$$

$$n_4 = n_3 \exp\left(-\frac{\Delta G^{3 \rightarrow 4}}{kT}\right)$$

$$\vdots$$

$$n_m = n_{m-1} \exp\left(-\frac{\Delta G^{m-1 \rightarrow m}}{kT}\right)$$

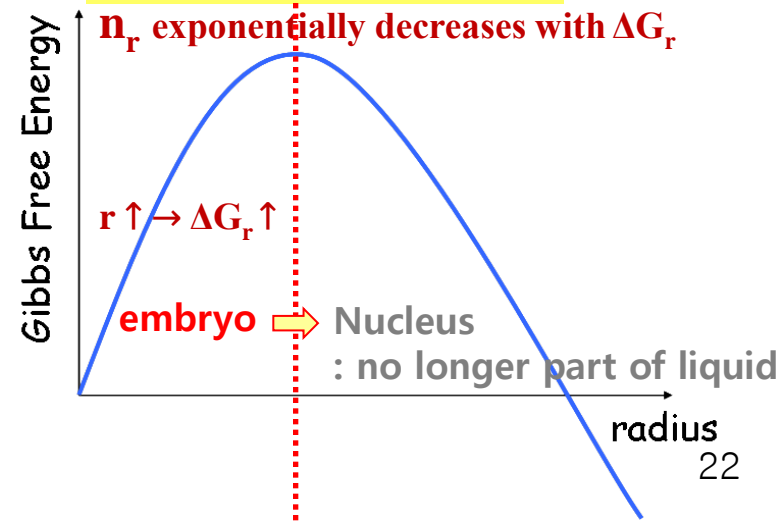
$$n_m = n_1 \exp\left(-\frac{\Delta G^{1 \rightarrow 2} + \Delta G^{2 \rightarrow 3} + \dots + \Delta G^{m-1 \rightarrow m}}{kT}\right)$$

$$n_m = n_1 \exp\left(-\frac{\Delta G^{1 \rightarrow m}}{kT}\right)$$

of spherical clusters with radius r

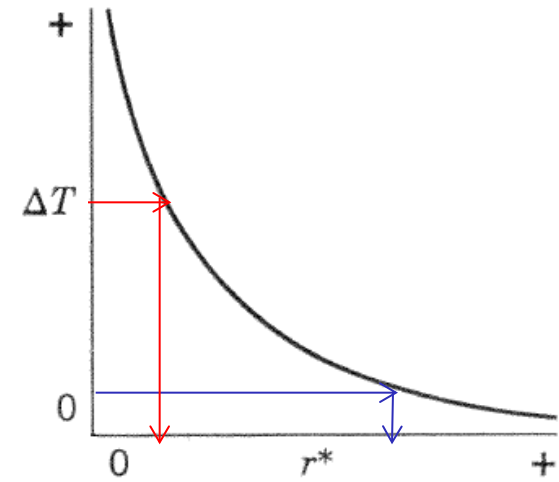
$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

of cluster of radius r

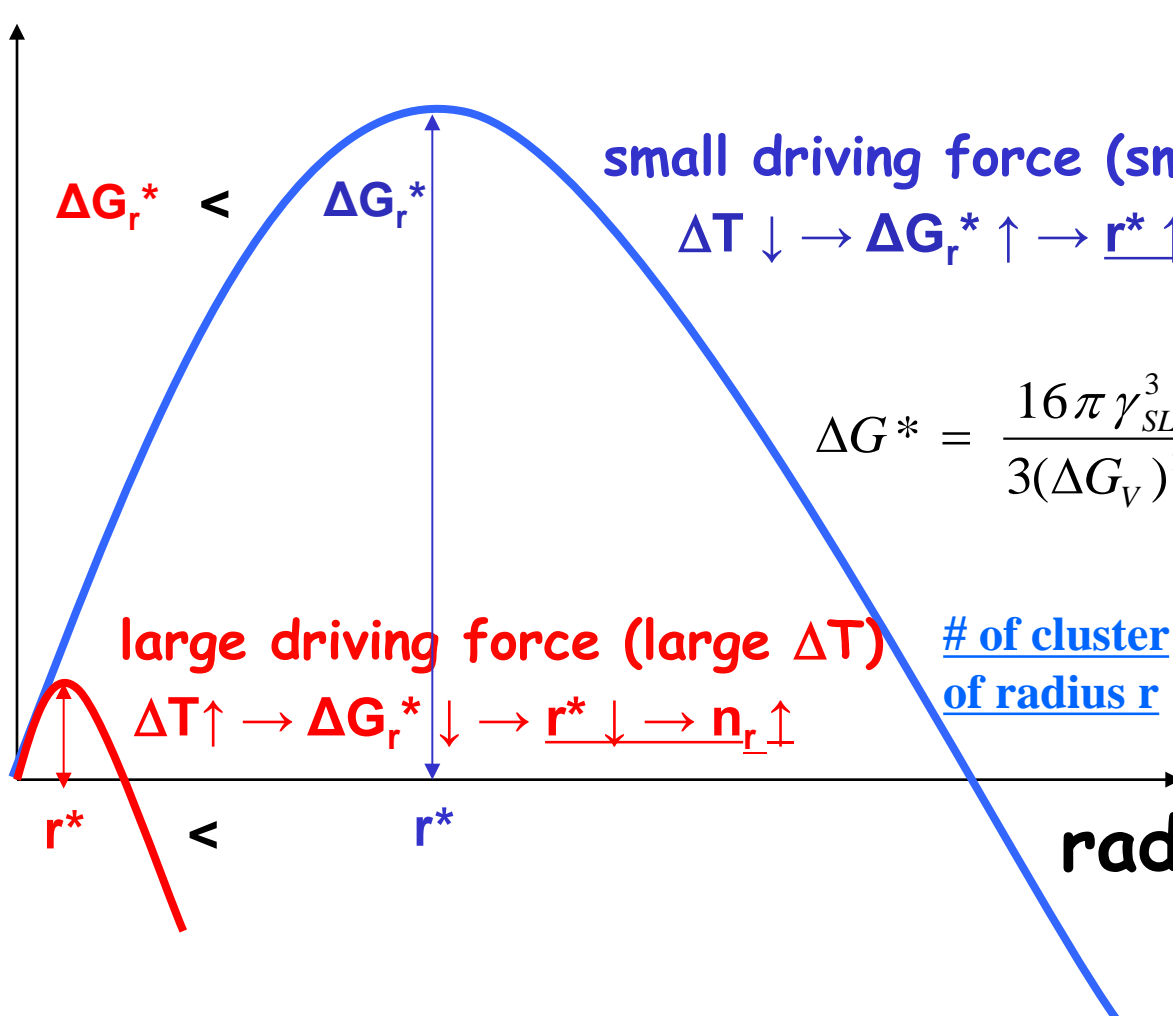


Formation of Atomic Cluster

Compare the nucleation curves between small and large driving forces.



Gibbs Free Energy



small driving force (small ΔT)

$$\Delta T \downarrow \rightarrow \Delta G_r^* \uparrow \rightarrow r^* \uparrow \rightarrow n_r \downarrow$$

large driving force (large ΔT)

$$\Delta T \uparrow \rightarrow \Delta G_r^* \downarrow \rightarrow r^* \downarrow \rightarrow n_r \uparrow$$

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

of cluster of radius r

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

Formation of Atomic Cluster

n_0 : total # of atoms.

ΔG_r : excess free energy associated with the cluster

k : Boltzmann's constant

of cluster of radius r per unit volume

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

- $\Delta G_r \neq 0 \rightarrow n_r/n \neq 0$ (맞몬 cluster with a specific size)

→ Key to nucleation : relationship btw r_{\max} and r^*

- holds for $T > T_m$ / $T < T_m$ and $r \leq r^*$

Apply for all r / $r \leq r^*$

($\because r > r^*$: no longer part of the liquid)

- n_r exponentially decreases with ΔG_r

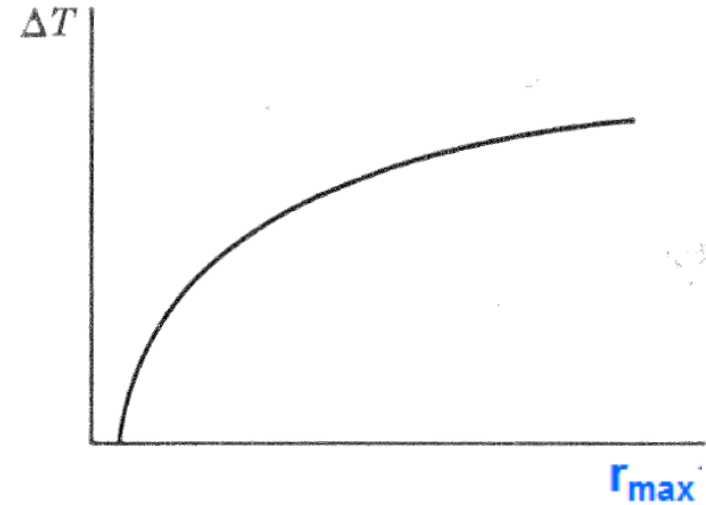


Fig. 3.5. Radius of largest embryo as a function of supercooling.

Ex. 1 mm³ of copper at its melting point (n_0 : 10^{20} atoms)

$r \downarrow \rightarrow n_r \uparrow \rightarrow \sim 10^{14}$ clusters of 0.3 nm radius (i.e. ~ 10 atoms)

$r \uparrow \rightarrow n_r \downarrow \rightarrow \sim 10$ clusters of 0.6 nm radius (i.e. ~ 60 atoms)

→ effectively a maximum cluster size, ~ 100 atoms

$\sim 10^{-8}$ clusters mm⁻³ or 1 cluster in $\sim 10^7$ mm³

2) The homogeneous nucleation rate - kinetics

How fast solid nuclei will appear in the liquid at a given undercooling?

n : atoms/unit volume

n_i^* : # of clusters with size of r^* (critical size)

$$n_i^* = n \exp\left(-\frac{\Delta G^*}{kT}\right) \text{ clusters / m}^3$$

$$\Delta G^* = 16\pi\sigma^3 / (\Delta G_P)^2$$

Excess free E of critical nucleus

The addition of one more atom to each of these clusters will convert them into stable nuclei.

Homogeneous nucleation rate
(small embryos $\rightarrow r^*$)

$$N_{\text{hom}} = I \cdot ZS^* n_i^*$$

nuclei / $\text{m}^3 \cdot \text{s}$

Net rate at which atoms travel
across the interface btw liquid
and embryo

Surface area of
Critical nucleus

Equilibrium # of
Critical nuclei

2) The homogeneous nucleation rate - kinetics

$$I = K_v \exp \left\{ - \left[(\Delta G^* + \Delta G_A) / kT \right] \right\}$$

$$K_v = n^* (a_\sigma / 9\pi kT)^{1/2} n (kT/h)$$

a: correction factor of nucleus shape (Not necessarily spherical)

n*: # of surface atoms for critical nucleus

n = # of atoms per unit volume for liquid

Assumption: "equilibrium distribution of the embryo size at all times" (ideal condition)

Vapor → liquid drop : OK but liquid → Solid : X due to low mobility

$$I = \frac{nkT}{h} \exp \left(- \frac{G_A}{kT} \right) \exp \left(- \frac{16\pi\sigma_{SL}^3 T_E^2}{3L^2 (\Delta T)^2 kT} \right)$$

→ Until ΔT reaches, the critical value I is very small.

But ΔT increases rapidly when critical value is reached

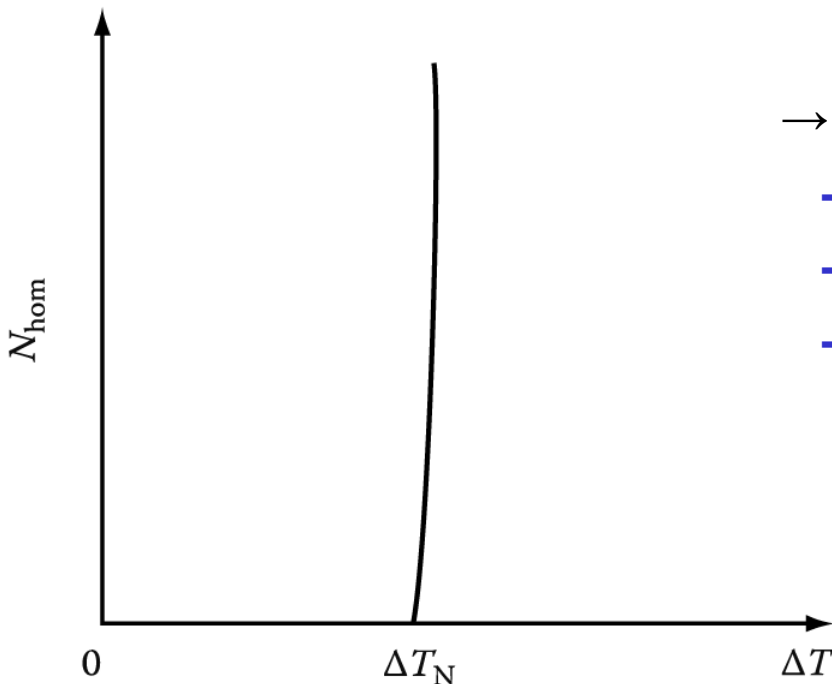
4.1.2. The homogeneous nucleation rate - kinetics

$$I = \frac{nkT}{h} \exp\left(-\frac{G_A}{kT}\right) \exp\left(-\frac{16\pi\sigma_{SL}^3 T_E^2}{3L^2(\Delta T)^2 kT}\right)$$

: insensitive to Temp.

How do we define nucleation temperature, ΔT_N ?

$$N_{\text{hom}} \sim \frac{1}{\Delta T^2}$$



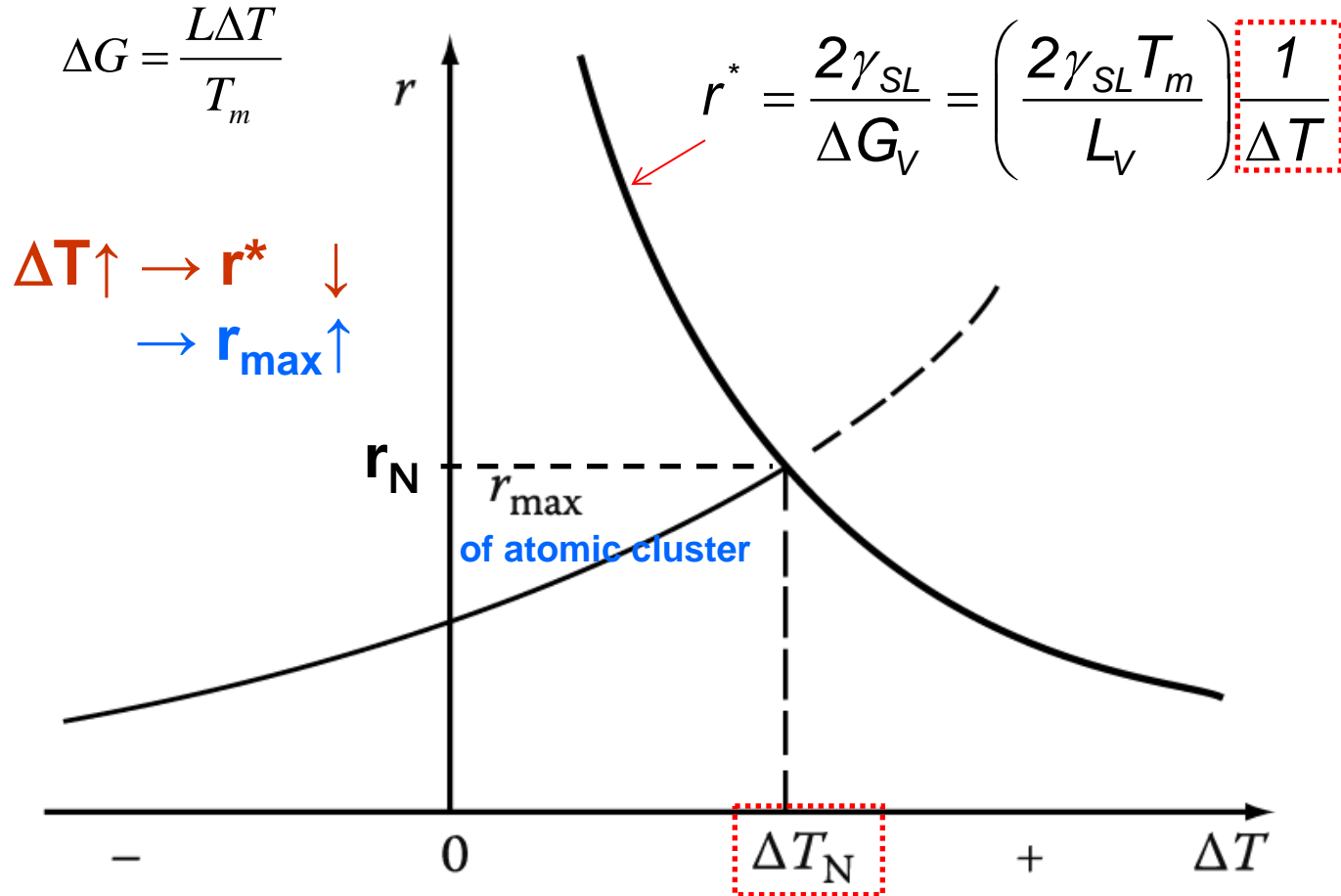
→ **critical value for detectable nucleation**

- **critical supersaturation ratio**
- **critical driving force**
- **critical supercooling**

→ **for most metals, $\Delta T_N \sim 0.2 T_m$ (i.e. $\sim 200\text{K}$)**

The homogeneous nucleation rate as a function of undercooling ΔT . ΔT_N is **the critical undercooling** for homogeneous nucleation.

The creation of a critical nucleus ~ thermally activated process



ΔT_N is **the critical undercooling** for homogeneous nucleation.

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

→ The condition for nucleation:

The number of clusters with r^* at $T < \Delta T_N$ is negligible.