2018 Fall

“Phase Transformation *in* Materials”

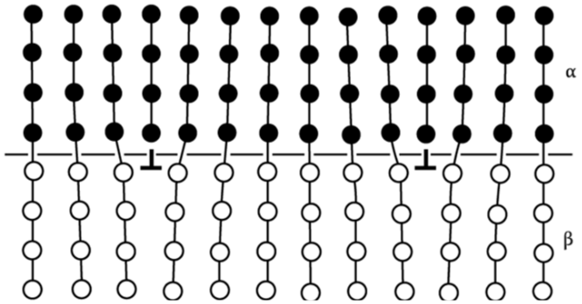
11.01.2018

Eun Soo Park

Office: 33-313
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Interphase Interfaces in Solid (α/β)

1) Glissile Interfaces (평활 이동 계면)



: epitaxial; Can't move forward or backward

(interface//burgers vector) → **Non-glissile interface**

: Glide of the interfacial disl. cannot cause the interface to advance

: Glissile; Boundary moves toward α or β

: semi-coherent interfaces which can advance by the coordinated glide of the interfacial disl.

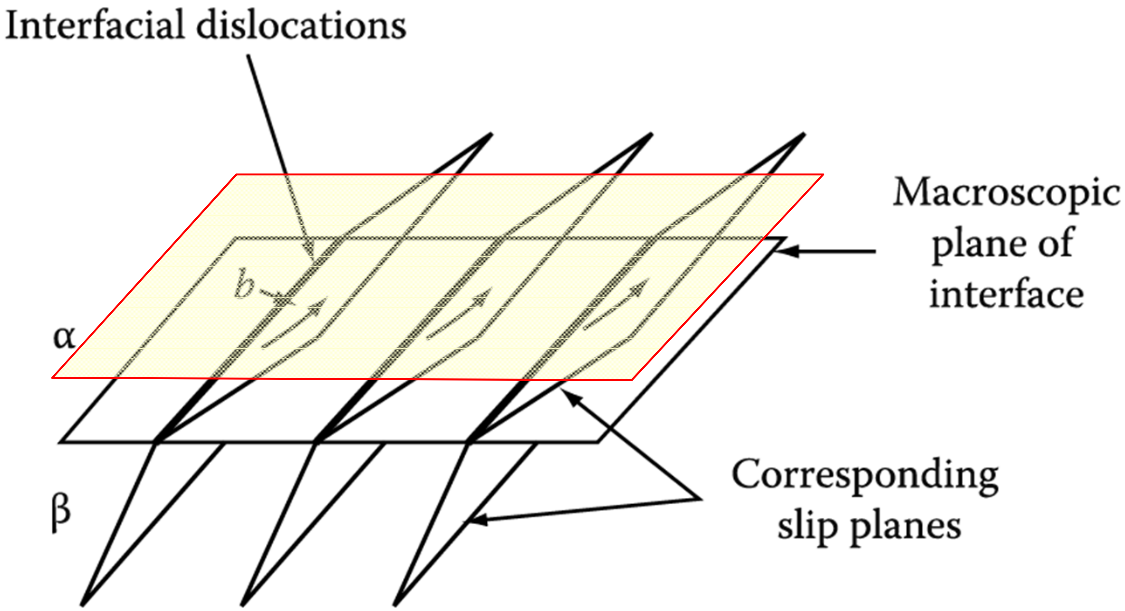


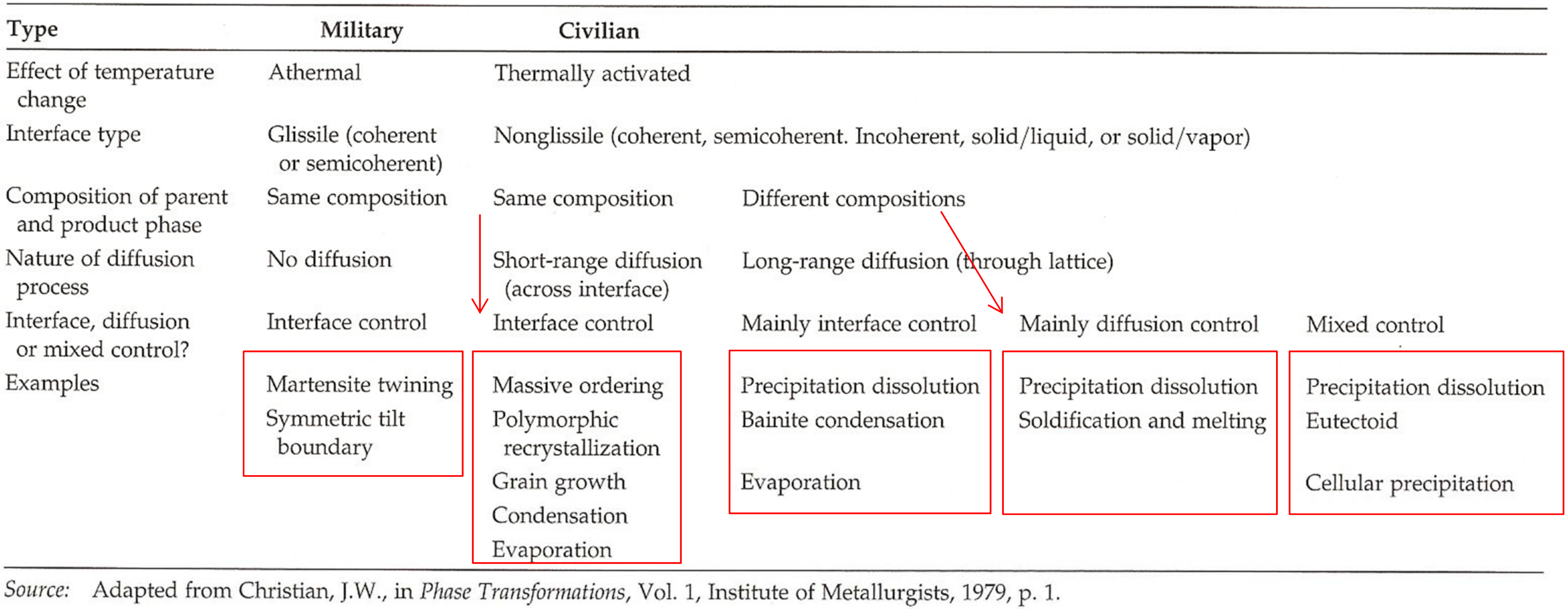
Fig. 3. 55 The nature of a glissile interface.

The dislocations have a Burgers vector that can glide on matching planes in the adjacent lattices.

Slip planes : continuous across the interface

Gliding of the dislocation : α is sheared into the β structure.

Classification of Heterogeneous (Nucleation and Growth) Transformation



Type	Military	Civilian			
Effect of temperature change	Athermal	Thermally activated			
Interface type	Glissile (coherent or semicoherent)	Nonglissile (coherent, semicoherent. Incoherent, solid/liquid, or solid/vapor)			
Composition of parent and product phase	Same composition	Same composition	Different compositions		
Nature of diffusion process	No diffusion	Short-range diffusion (across interface)	Long-range diffusion (through lattice)		
Interface, diffusion or mixed control?	Interface control	Interface control	Mainly interface control	Mainly diffusion control	Mixed control
Examples	Martensite twining Symmetric tilt boundary	Massive ordering Polymorphic recrystallization Grain growth Condensation Evaporation	Precipitation dissolution Bainite condensation Evaporation	Precipitation dissolution Soldification and melting	Precipitation dissolution Eutectoid Cellular precipitation

Source: Adapted from Christian, J.W., in *Phase Transformations*, Vol. 1, Institute of Metallurgists, 1979, p. 1.

exception) bainite transformation: thermally activated growth/ shape change similar to that product by the motion of a glissile interface

(need to additional research)

Contents in Phase Transformation

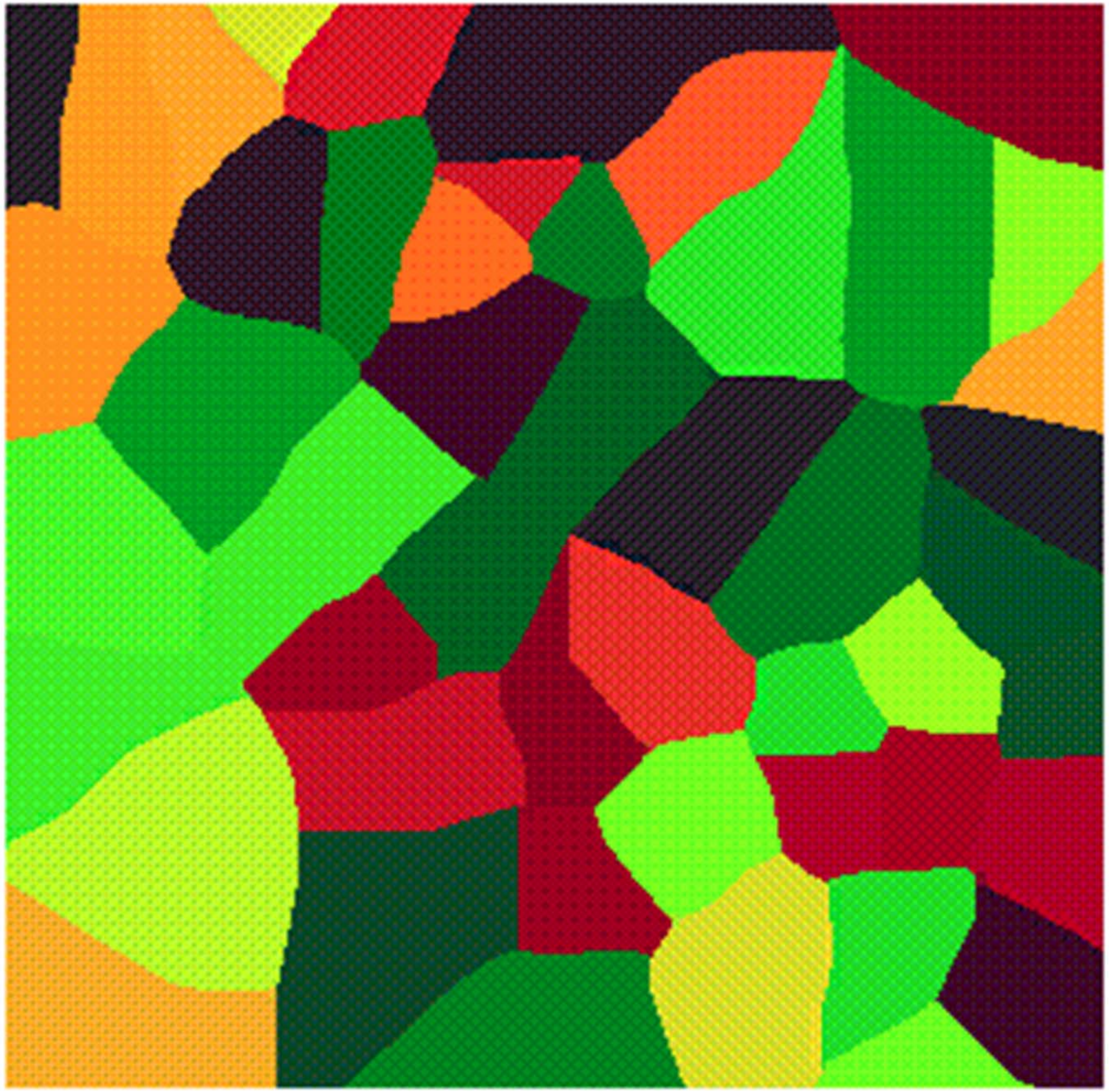
Background to understand phase transformation

- (Ch1) Thermodynamics and Phase Diagrams
- (Ch2) Diffusion: Kinetics
- (Ch3) Crystal Interface and Microstructure

Representative Phase transformation

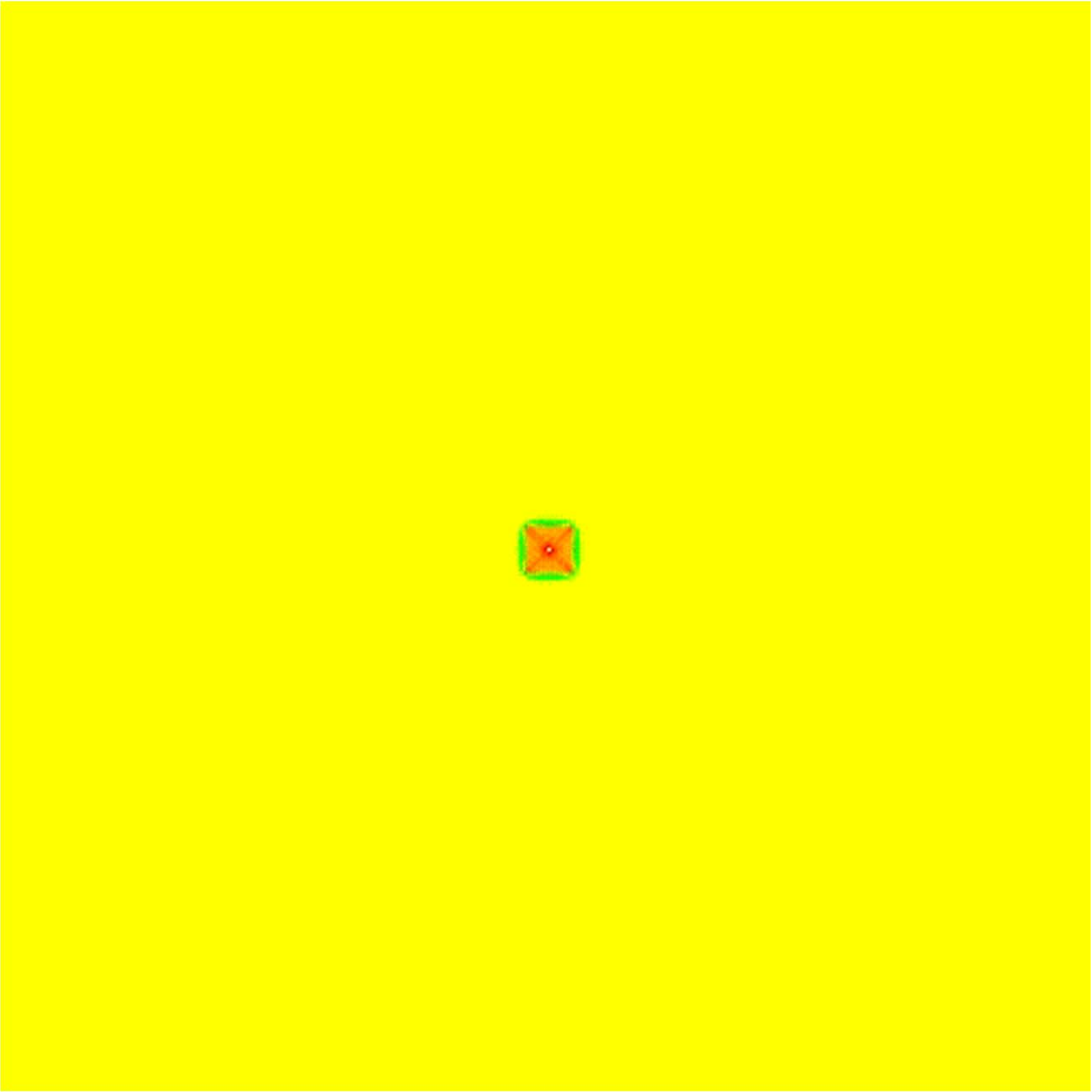
- (Ch4) Solidification: Liquid → Solid
- (Ch5) Diffusional Transformations in Solid: Solid → Solid
- (Ch6) Diffusionless Transformations: Solid → Solid

Solidification: Liquid → Solid



4 Fold Anisotropic Surface Energy/2 Fold Kinetics, Many Seeds

Solidification: Liquid ⟶ Solid



4 Fold Symmetric Dendrite Array

Contents for today's class

Solidification: Liquid → Solid

< Nucleation >

- Nucleation in Pure Metals
- Homogeneous Nucleation
- Heterogeneous Nucleation
- Nucleation of melting

&

< Growth >

- Equilibrium Shape and Interface Structure on an Atomic Scale
- Growth of a pure solid
  - 1) Continuous growth
    : Atomically rough or diffuse interface
  - 2) Lateral growth
    : Atomically flat of sharply defined interface
- Heat Flow and Interface Stability

Q: Undercooling of homogenous vs heterogenous nucleation ?

Solidification: Liquid → Solid

- casting & welding
- single crystal growth
- directional solidification
- rapid solidification

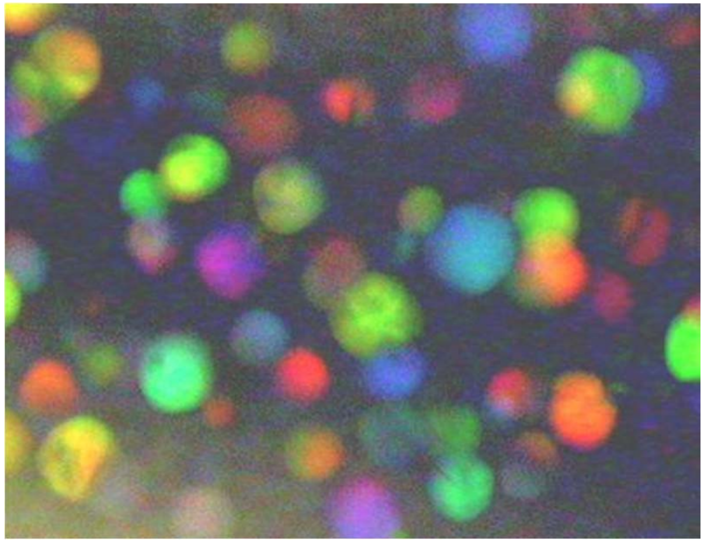
4.1. Nucleation in Pure Metals

T_m : $G_L = G_S$

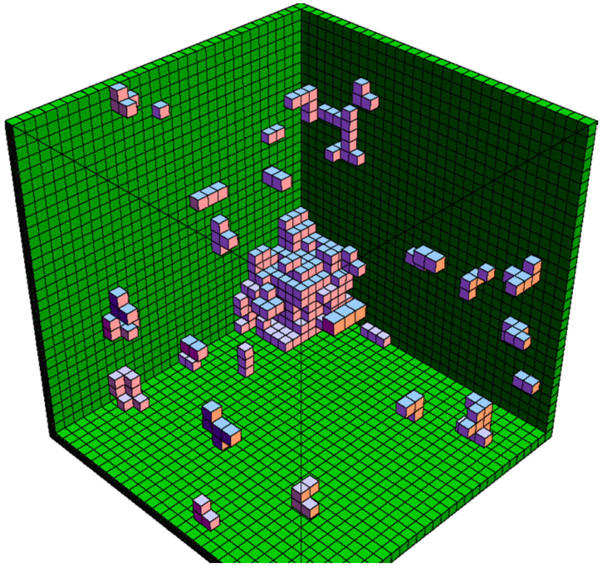
- Undercooling (supercooling) for nucleation: 250 K ~ 1 K

<Types of nucleation>

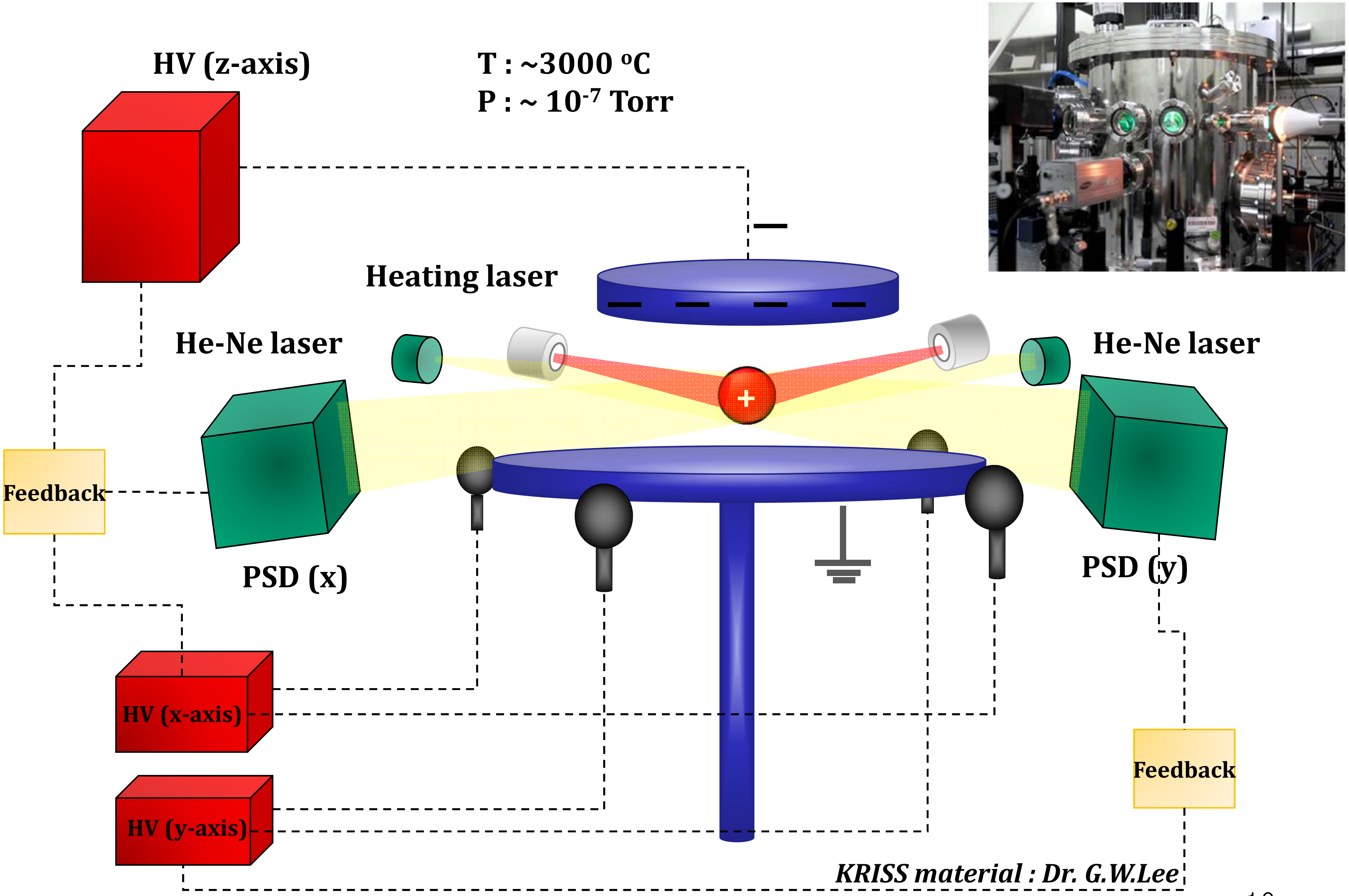
- Homogeneous nucleation



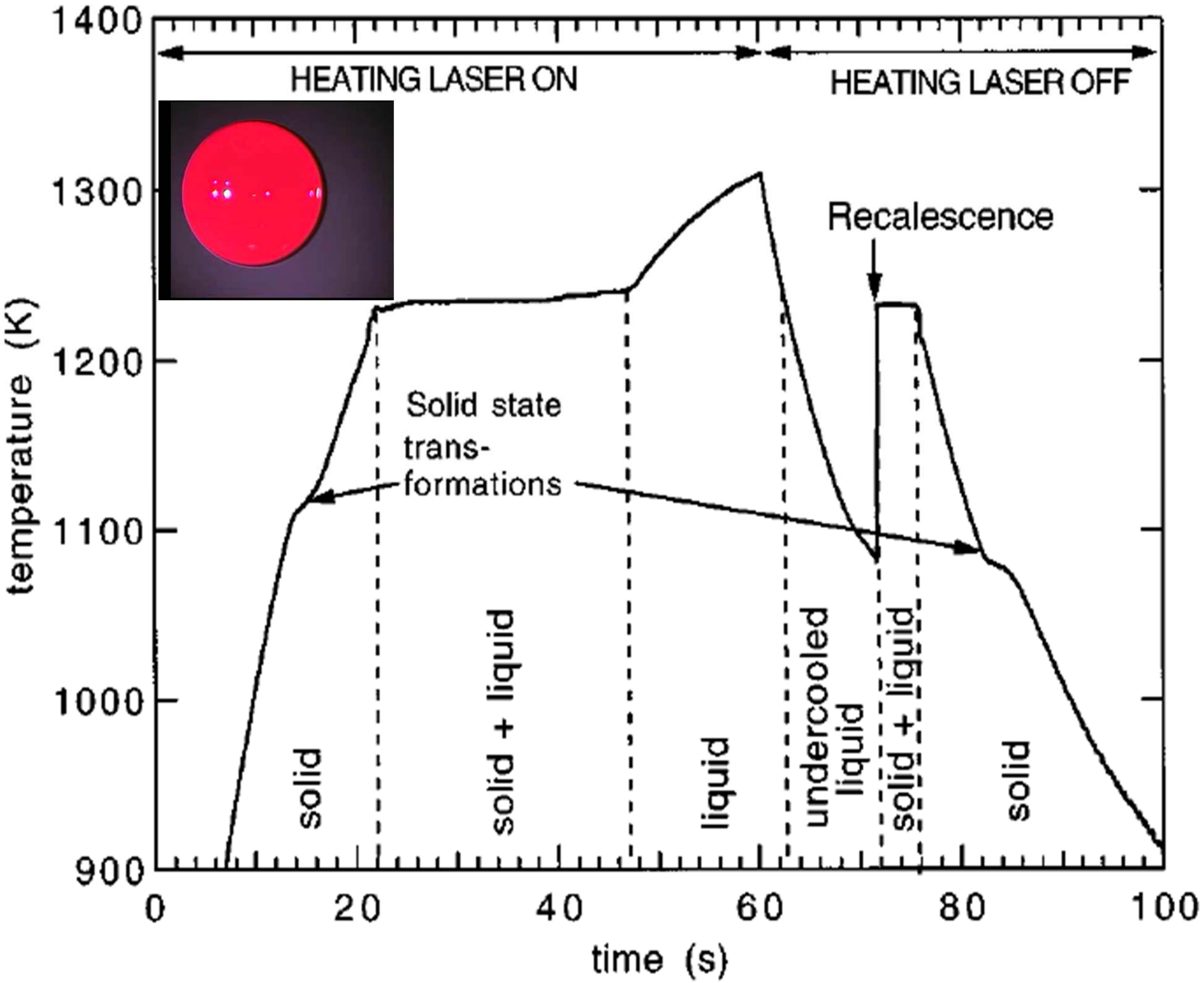
- Heterogeneous nucleation



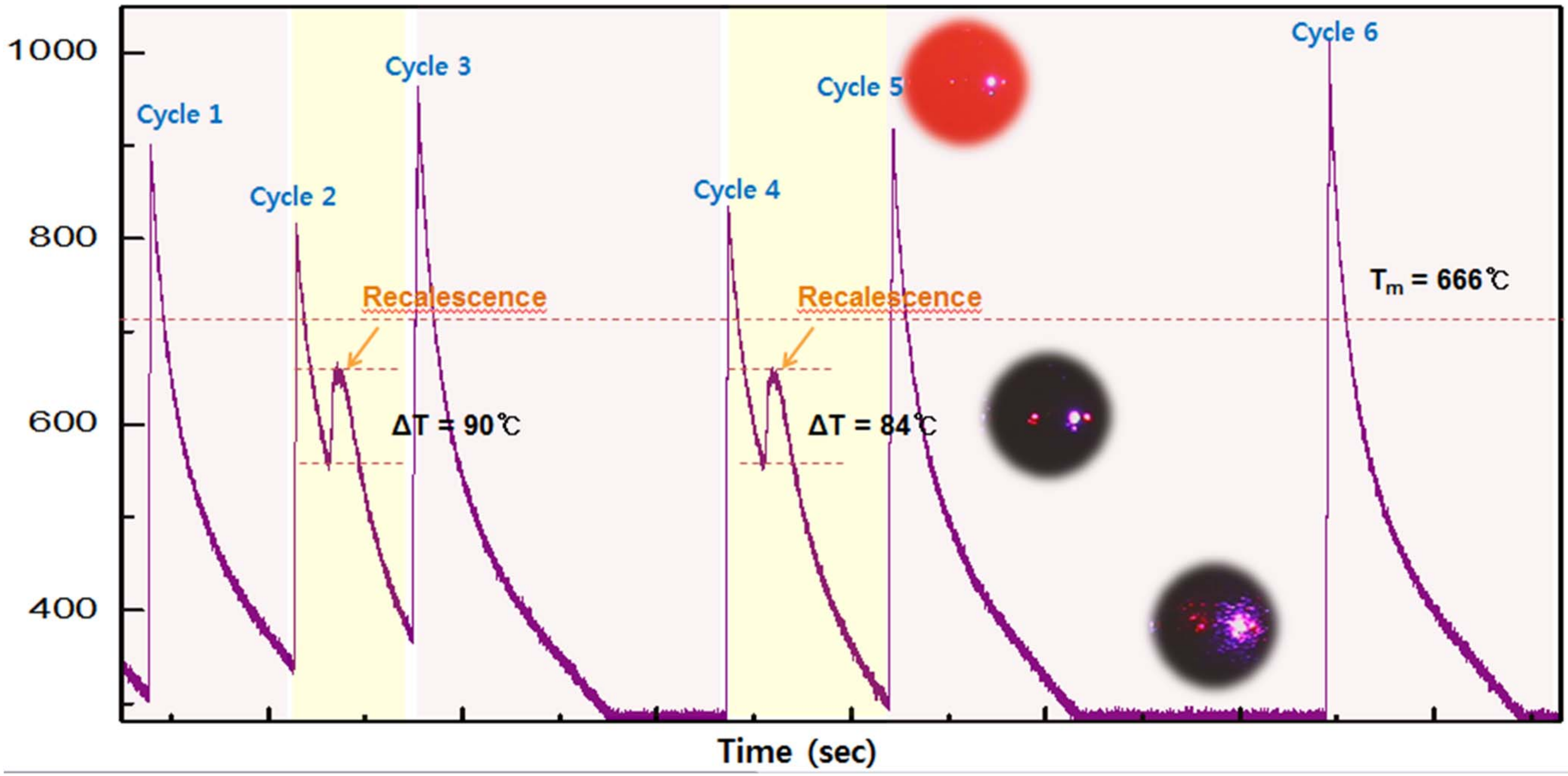
Electrostatic levitation in KRISS



KRISS material : Dr. G.W.Lee


1400
1300
1200
1100
1000
900
temperature (K)
0
20
40
60
80
100
time (s)
HEATING LASER ON
HEATING LASER OFF
Recalescence
Solid state trans- formations
solid
solid + liquid
liquid
undercooled liquid
solid + liquid
solid

Electrostatic Levitation: cooling curve of Vitreloy 1 system



Q: Homogenous nucleation

(a) Driving force for solidification, ΔG_v

(b) Calculation of ΔG_r , r*, ΔG*

4.1.1. Homogeneous Nucleation

Driving force for solidification

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

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

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

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

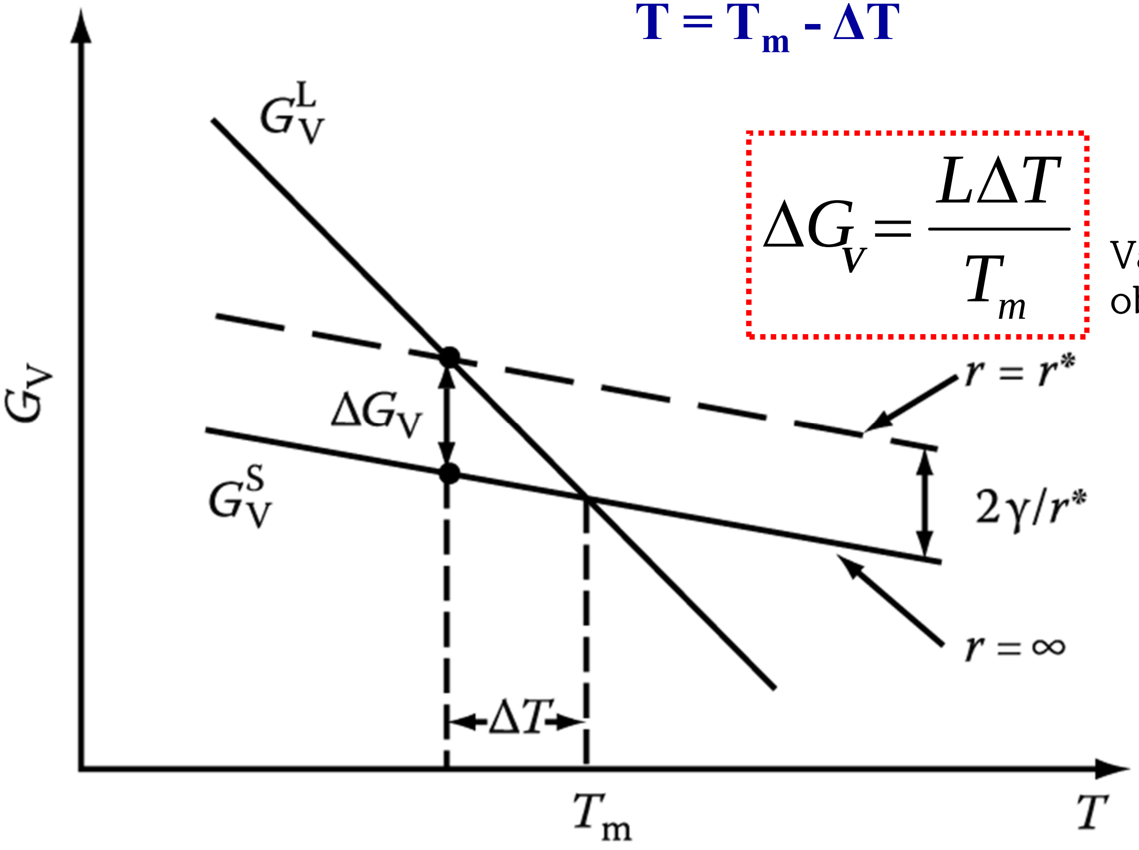
(Latent heat)

$T = T_m - \Delta T$

$\Delta G = 0 = \Delta H - T_m \Delta S$

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

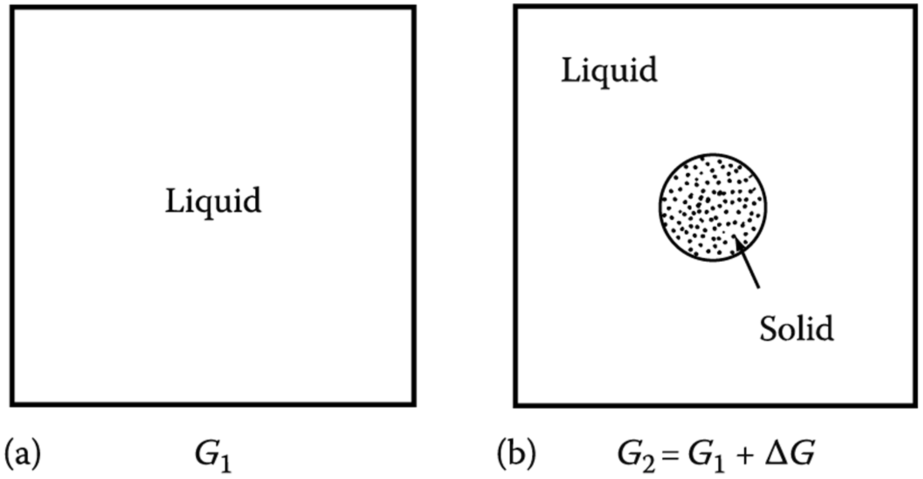
$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$



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

Variation of free energy per unit volume obtained from undercooling (ΔT)

4.1.1. Homogeneous Nucleation



$$G_1 = (V_S + V_L) G_V^L \qquad G_2 = V_S G_V^S + V_L G_V^L + A_{SL}\gamma_{SL}$$

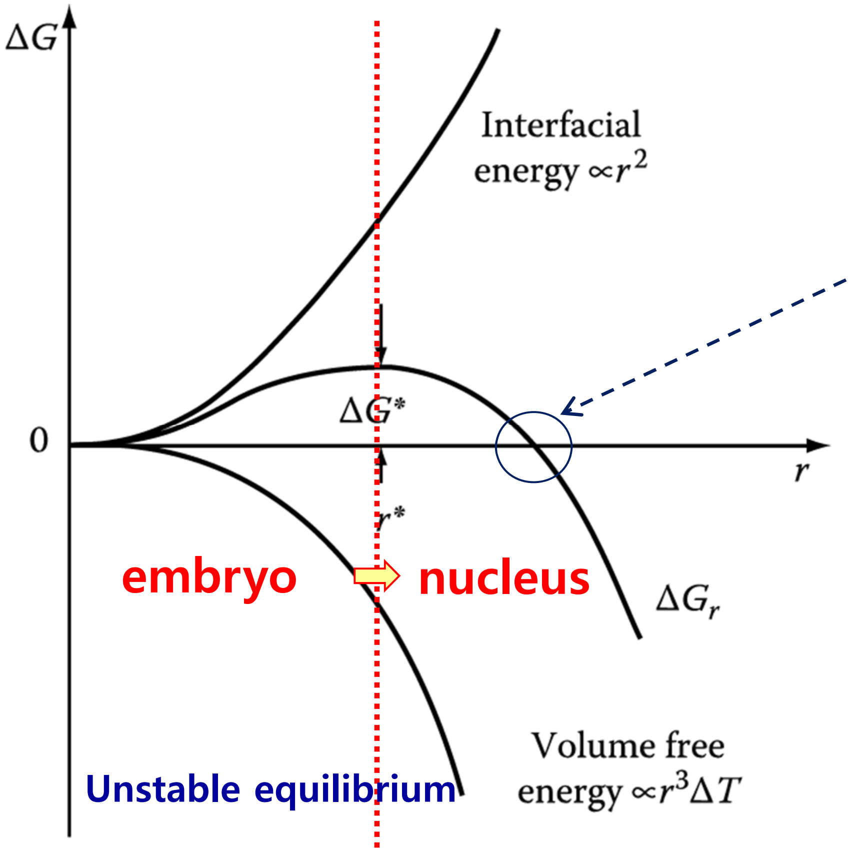
G_V^S, G_V^L : **free energies per unit volume**

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

for spherical nuclei (isotropic) of radius : r

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

Calculation of critical radius, r*



embryo ⇨ **nucleus**

Unstable equilibrium

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

Why r^* is not defined by $\Delta G_r = 0$?

r < r* : unstable (lower free E by reduce size)

r > r* : stable (lower free E by increase size)

r* : critical nucleus size

r* ⇒ **dG=0**

Gibbs-Thompson Equation

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

⇒

Critical ΔG of nucleation at r*

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

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

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

Q: How do we define ΔT_N?

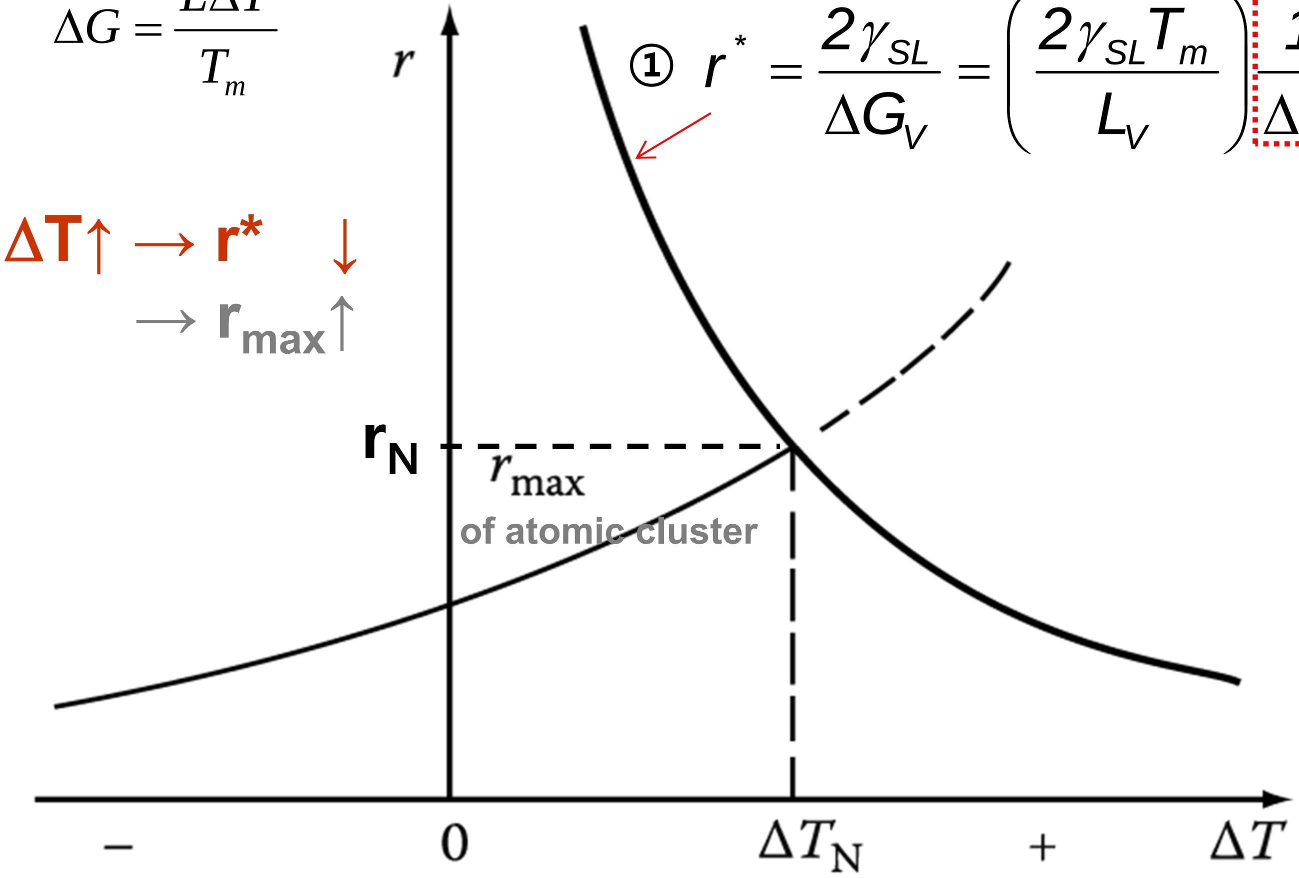
The creation of a critical nucleus ~ thermally activated process

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

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

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

$\rightarrow r_{max}\uparrow$



ΔT_N is the critical undercooling for homogeneous nucleation.

Fig. 4.5 The variation of r* and r_{max} with undercooling ΔT

→ Condition for nucleation:

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

② Formation of Atomic Cluster

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

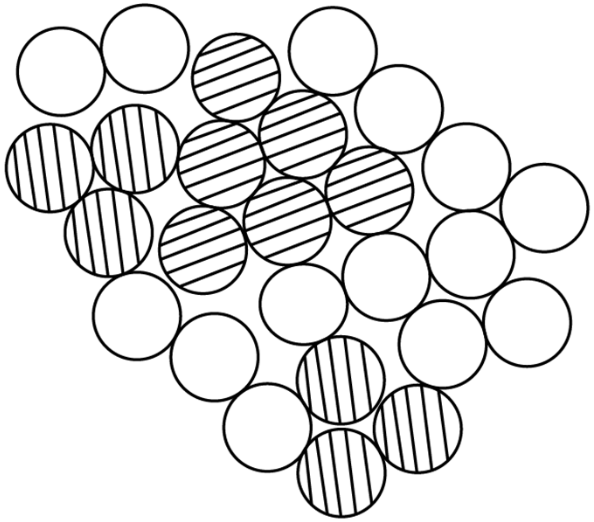
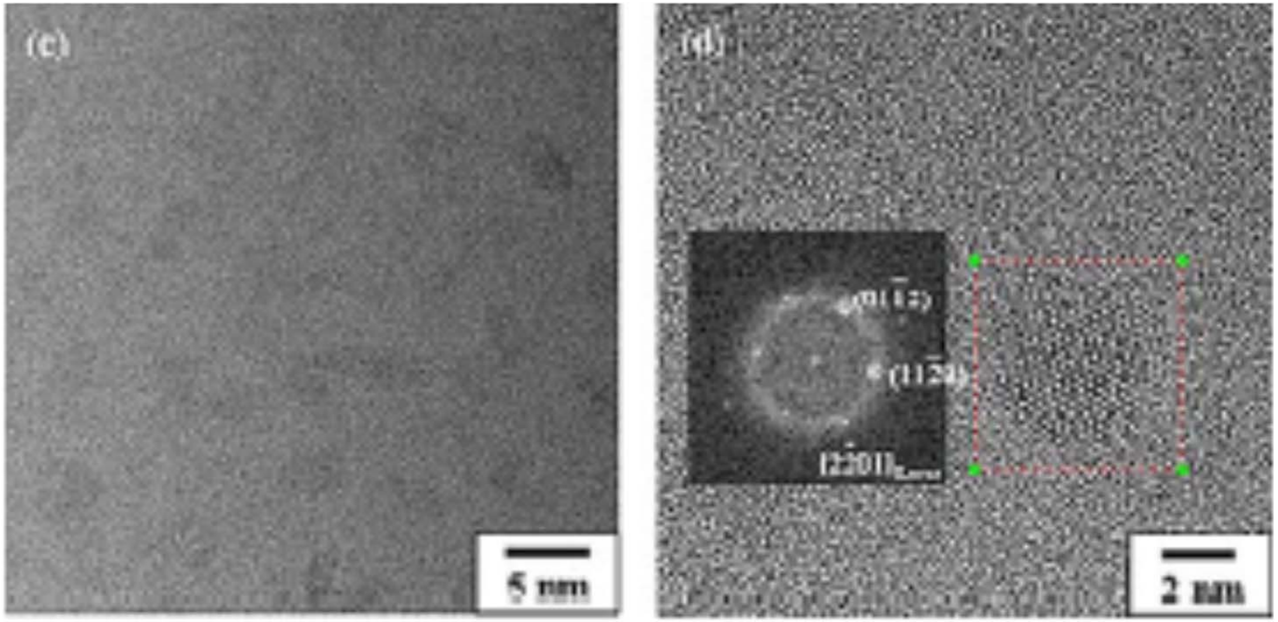


Fig. 4.4 **<u>A two-dimensional representation of an instantaneous picture of the liquid structure. Many close-packed crystal-like clusters (shaded) are instantaneously formed.</u>**



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?

$$A_1 \to A_2 \to A_3 \to A_4 \to \cdots \to A_{m-1} \to A_m$$

$$n_2 = n_1 \exp\left(-\frac{\Delta G^{1\to 2}}{kT}\right)$$

Excess free E associated with the cluster of 1→2 atoms

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

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

$$\vdots$$

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

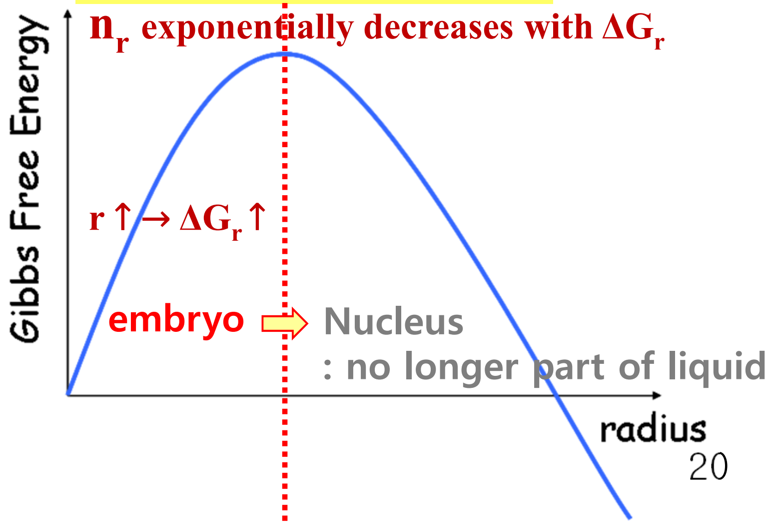
$$n_m = n_1 \exp\left(-\frac{\Delta G^{1\to 2} + \Delta G^{2\to 3} + \cdots + \Delta G^{m-1\to m}}{kT}\right)$$

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

반지름 r인 구상의 군집체 수

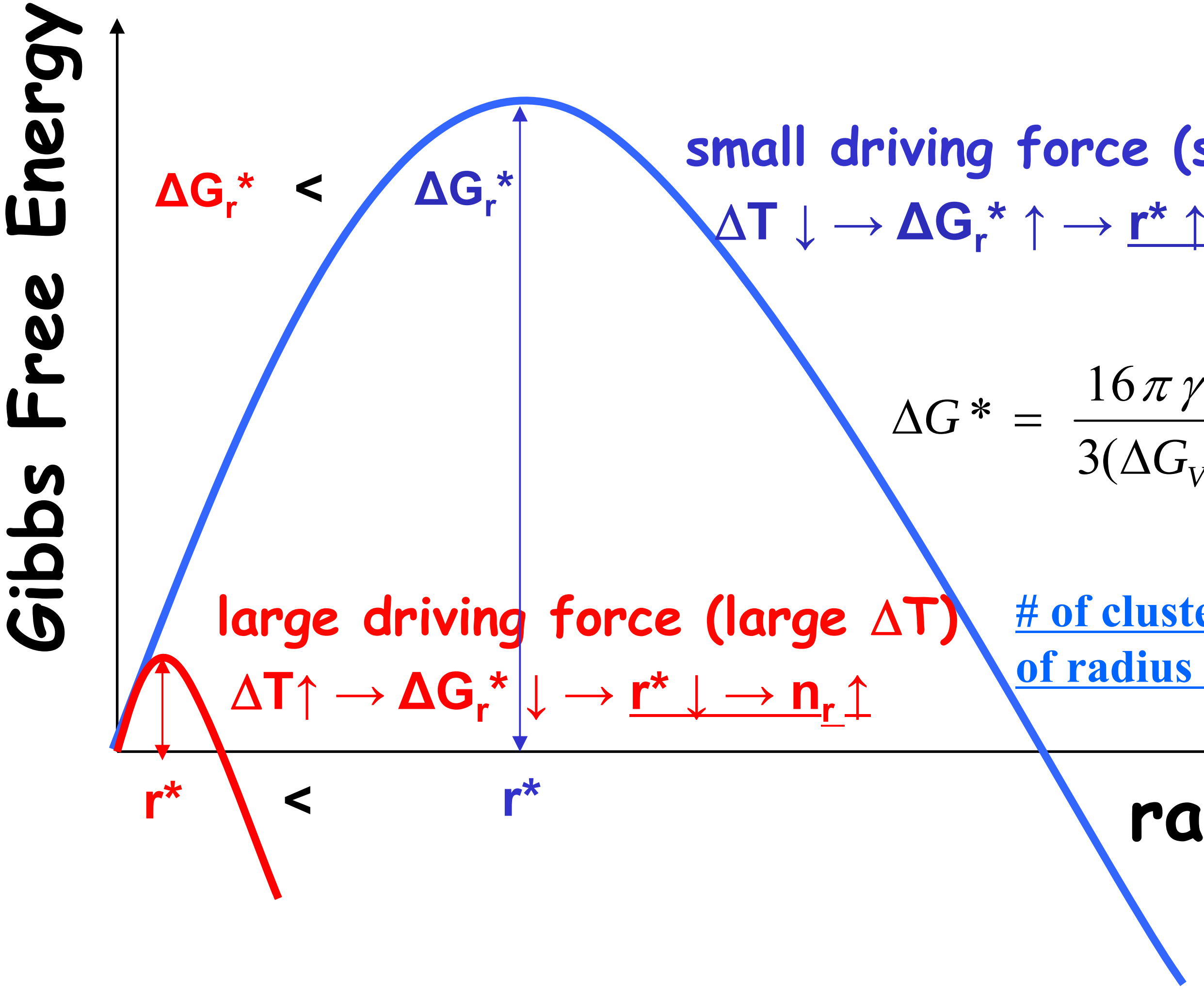
# of cluster of radius r

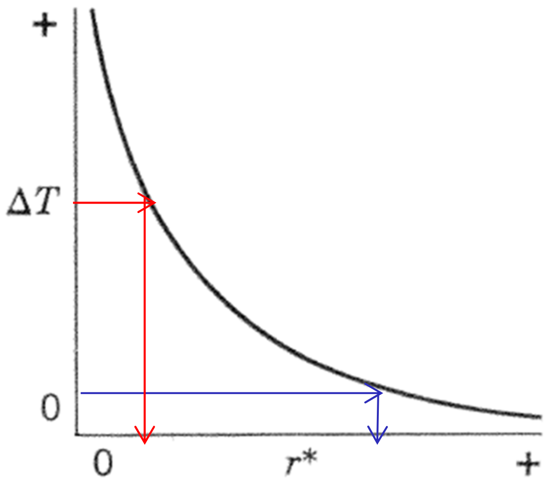
$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$



Formation of Atomic Cluster

Compare the nucleation curves between small and large driving forces.





small driving force (small ΔT)

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

large driving force (large ΔT)

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

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

<u>**# of cluster of radius r**</u>

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

Formation of Atomic Cluster

n_o : total # of atoms.
ΔG_r : excess free energy associated with the cluster
k : Boltzmann's constant

# of cluster of radius r

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

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

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

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

- **n_r exponentially decreases with ΔG_r**

Ex. 1 mm^3 of copper at its melting point (n_0: 10^{20} atoms)

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

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

→ effectively a maximum cluster size, ~ 100 atoms
~ 10^{-8} clusters mm^{-3} or 1 cluster in ~ 10^7 mm^3

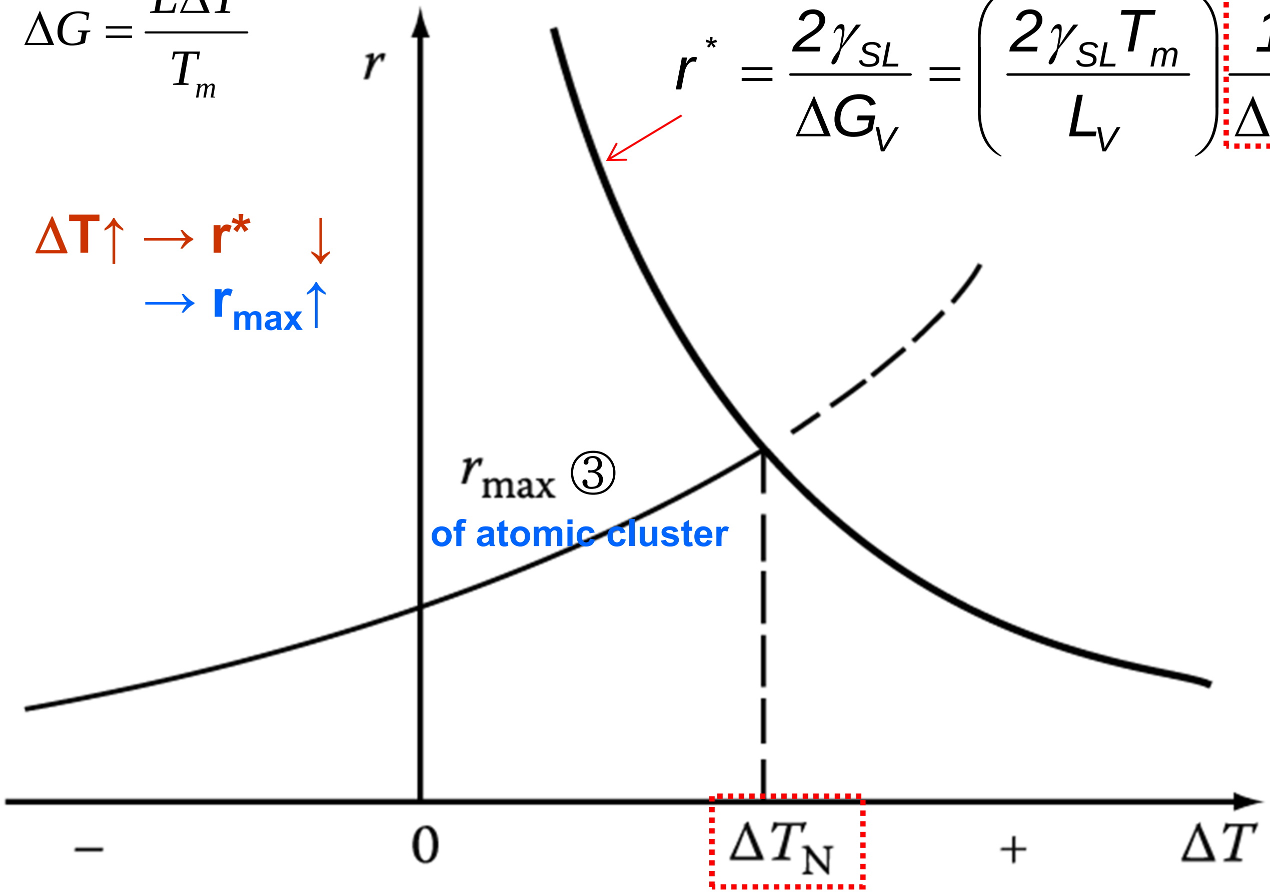
The creation of a critical nucleus ~ thermally activated process

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

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

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

$\rightarrow r_{max}\uparrow$



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

Fig. 4.5 The variation of r* and r_{max} with undercooling ΔT

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

4.1.2. The homogeneous nucleation rate - kinetics

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

C_0 : atoms/unit volume
C^* : # of clusters with size of C* (critical size) 임계핵 크기의 cluster 수

$$C^* = C_0 \exp\left(-\frac{\Delta G^*_{\text{hom}}}{kT}\right)$$ **clusters / m^3**

The addition of one more atom to each of these clusters will convert them into stable nuclei. 한 개 원자 추가로 확산시 핵생성

Homogeneous Nucleation rate

$$N_{\text{hom}} = f_0 C_o \exp\left(-\frac{\Delta G^*_{\text{hom}}}{kT}\right)$$ **nuclei / $m^3 \cdot s$**

$f_o \sim 10^{11}\ s^{-1}$: frequency ∝ vibration frequency energy of diffusion in liquid surface area (const.)

$C_o \sim$ typically 10^{29} atoms/m^3

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

$$N_{\text{hom}} \approx 1\ cm^{-3}s^{-1} \text{ when } \Delta G^* \sim 78\,kT$$

Reasonable nucleation rate

4.1.2. The homogeneous nucleation rate - kinetics

$$\boxed{N_{\mathrm{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\}}$$

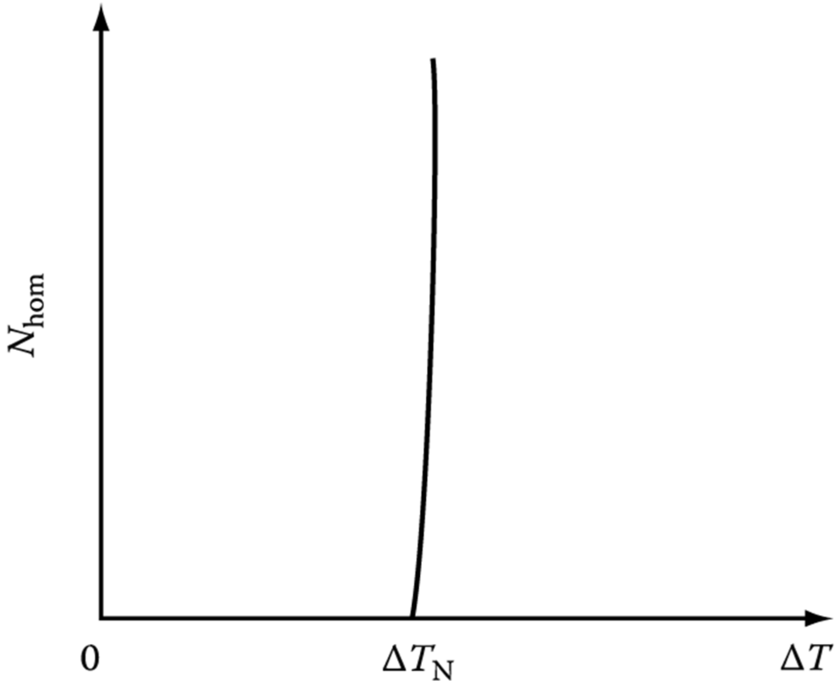
where $A = \frac{16\pi\gamma_{SL}^3 T_m^2}{3 L_V^2 kT}$

A = relatively insensitive to Temp.

How do we define ΔT_N?

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

Changes by orders of magnitude from essentially zero to very high values over a very narrow temperature range



→ **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. ~200K)**

Fig. 4.6 The homogeneous nucleation rate as a function of undercooling ΔT. ΔT_N is the critical undercooling for homogeneous nucleation.

∗ Copper Homogeneous nucleation

$\Delta T = 230\ K \rightarrow r* \sim 10^{-7}\ cm < 4 * $ (Diameter of Cu atom)

If nucleus is spherical shape,

$V = 4.2 * 10^{-21}\ cm^3 \sim 360$ atoms ($\because$ one Cu atom $1.16 * 10^{-23}\ cm^3$)

"Typically in case of metal" $\Delta T* \sim 0.2\ T_E$ / $\sigma_{SL} \sim 0.4\ L$

⇨ r∗ (critical nucleus for homogeneous nucleation) of metal ~ 200 atoms

But, if cluster radius ~ (only 4 ∗ atom diameter),

"no spherical shape"

(large deviation from spherical shape) →

→ Possible structure for the critical nucleus of Cu

: bounded only by {111} and {100} plane

- **σ_{SL} may very with the crystallographic nature of the surface.**
- **The faces of this crystal are close to their critical size for 2D nucleation at the critical temp for the nucleus as a whole.**

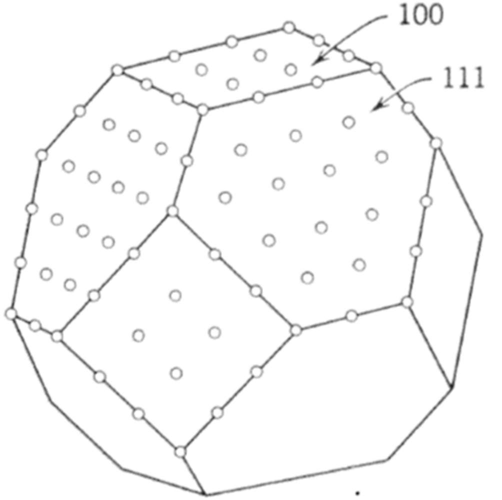


Fig. 3.11. Possible structure for the critical nucleus. (From B. Chalmers, *Physical Metallurgy*, John Wiley and Sons, New York, 1959, p. 246.)

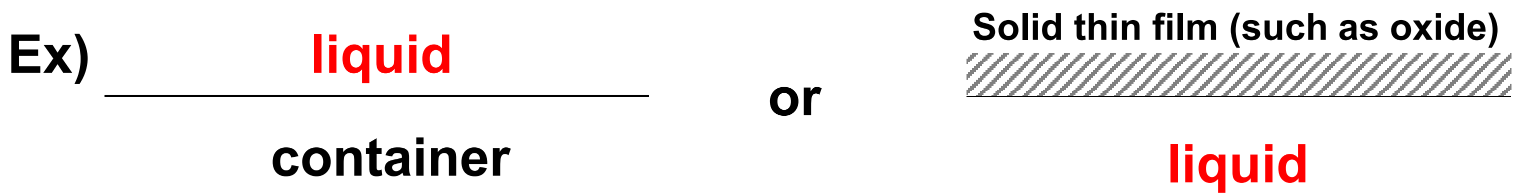
Real behavior of nucleation: metal $\Delta T_{bulk} < \Delta T_{small\ drop}$

Under suitable conditions, liquid nickel can be undercooled (or supercooled) to 250 K below T_m (1453°C) and held there indefinitely without any transformation occurring.

Normally undercooling as large as 250 K are not observed.

The nucleation of solid at undercooling of only ~ 1 K is common.

The formation of a nucleus of critical size can be catalyzed by a suitable surface in contact with the liquid. → "Heterogeneous Nucleation"



Why this happens? What is the underlying physics?

Which equation should we examine?

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

$$N_{hom} = f_0 C_o \exp\left(-\frac{\Delta G_{hom}^*}{kT}\right)$$

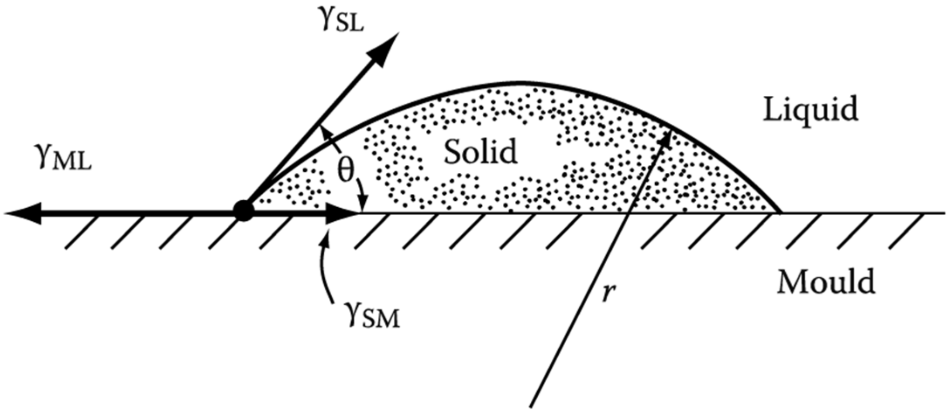
Q: Real behavior of nucleation: “Heterogeneous nucleation”

4.1.3. Heterogeneous nucleation

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

Nucleation becomes easy if $\gamma_{SL}\downarrow$ by forming nucleus from mould wall.

Fig. 4.7 Heterogeneous nucleation of spherical cap on a flat mould wall.



$$\boxed{\gamma_{ML} = \gamma_{SL}\cos\theta + \gamma_{SM}}$$

$$\cos\theta = (\gamma_{ML} - \gamma_{SM})/\gamma_{SL}$$

$$\Delta G_{het} = -V_S\Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{ML}$$

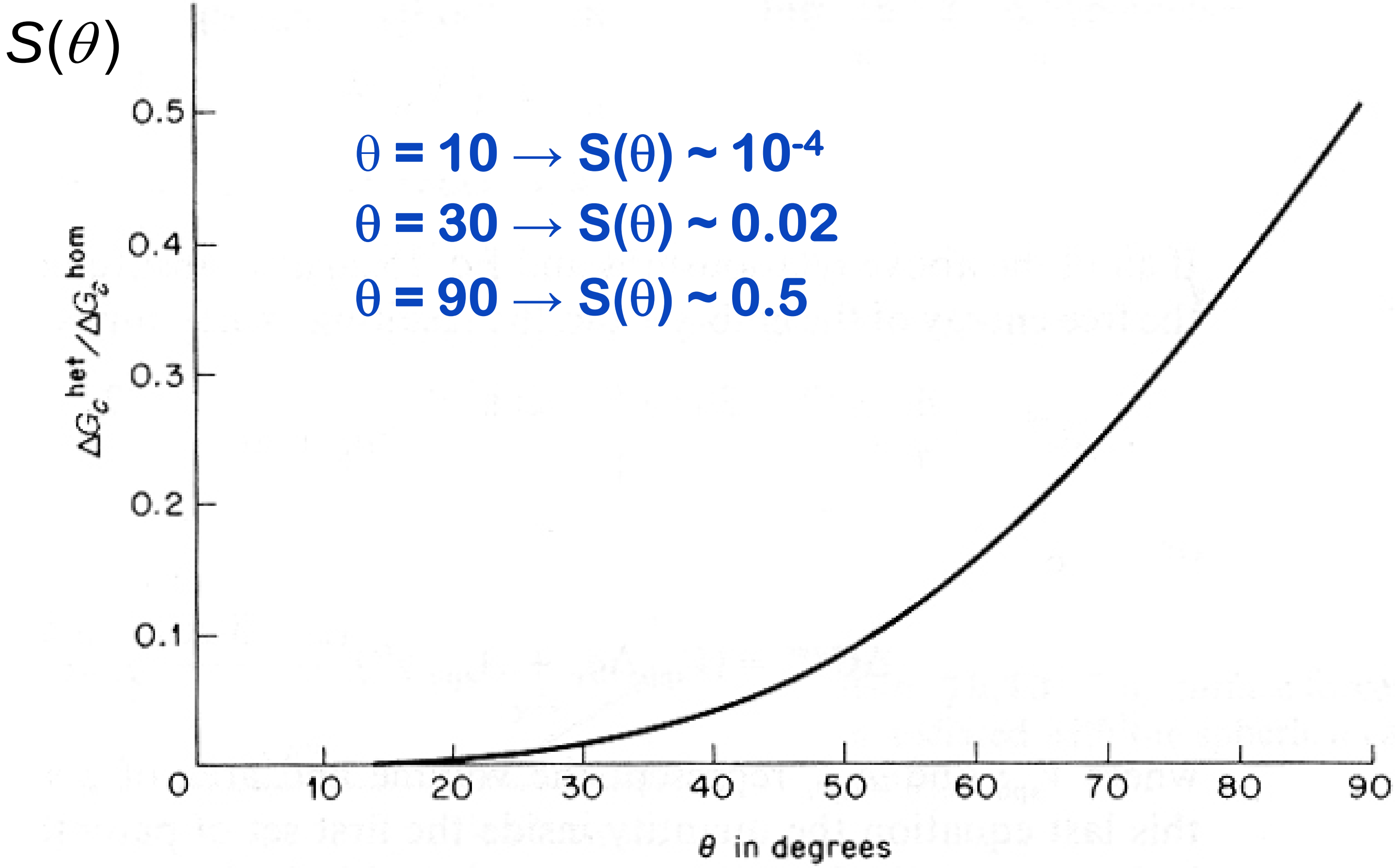
In terms of the wetting angle (θ) and the cap radius (r) **(Exercies 4.6)**

$$\boxed{\Delta G_{het} = \left\{-\frac{4}{3}\pi r^3\Delta G_V + 4\pi r^2\gamma_{SL}\right\}S(\theta)}$$

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

S(θ) has a numerical value ≤ 1 dependent only on θ (the shape of the nucleus)

$$\boxed{\Delta G^*_{het} = S(\theta)\Delta G^*_{\mathrm{hom}}} \quad \Rightarrow \quad r^* = \frac{2\,\gamma_{SL}}{\Delta G_V} \quad and \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot S(\theta)$$



θ = 10 → S(θ) ~ 10^{-4}

θ = 30 → S(θ) ~ 0.02

θ = 90 → S(θ) ~ 0.5

S(θ) has a numerical value ≤ 1 dependent only on θ (the shape of the nucleus)

$$\Delta G^*_{het} = S(\theta)\Delta G^*_{hom}$$

⇨

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} \quad \text{and} \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta)$$

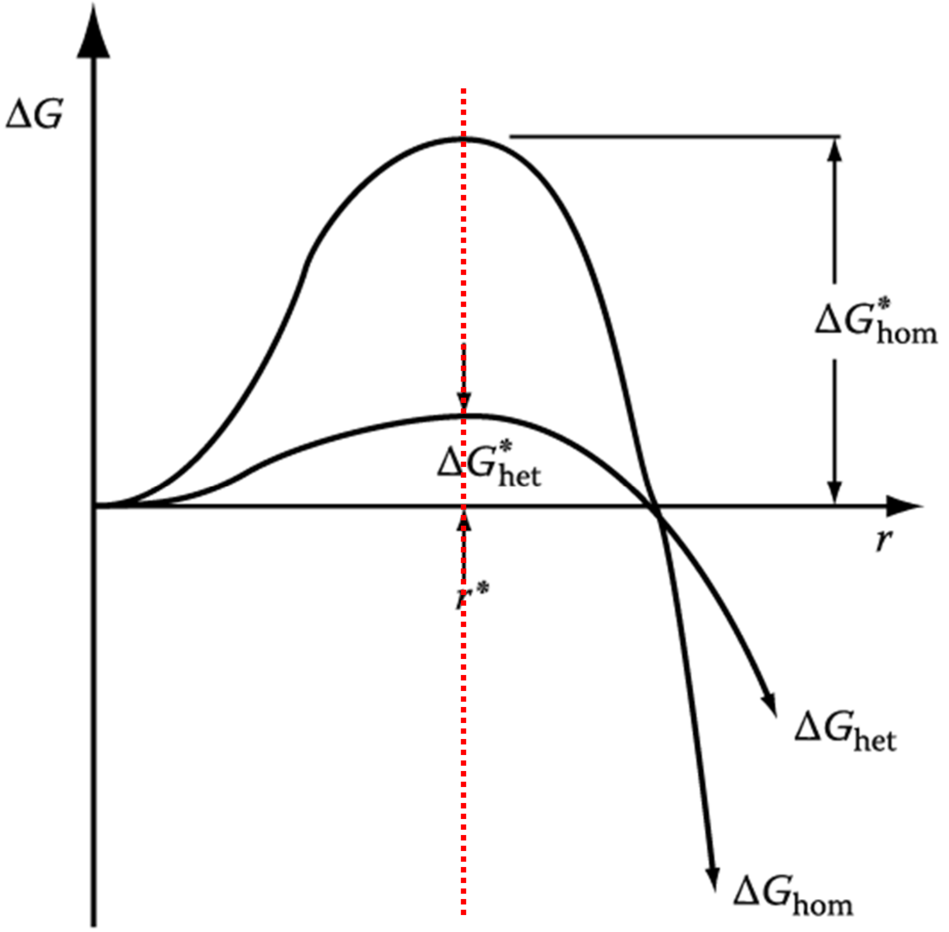


Fig. 4.8 The excess free energy of solid clusters for homogeneous and heterogeneous nucleation. Note r* is independent of the nucleation site.

The Effect of ΔT on ΔG^*_{het} & ΔG^*_{hom}?

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

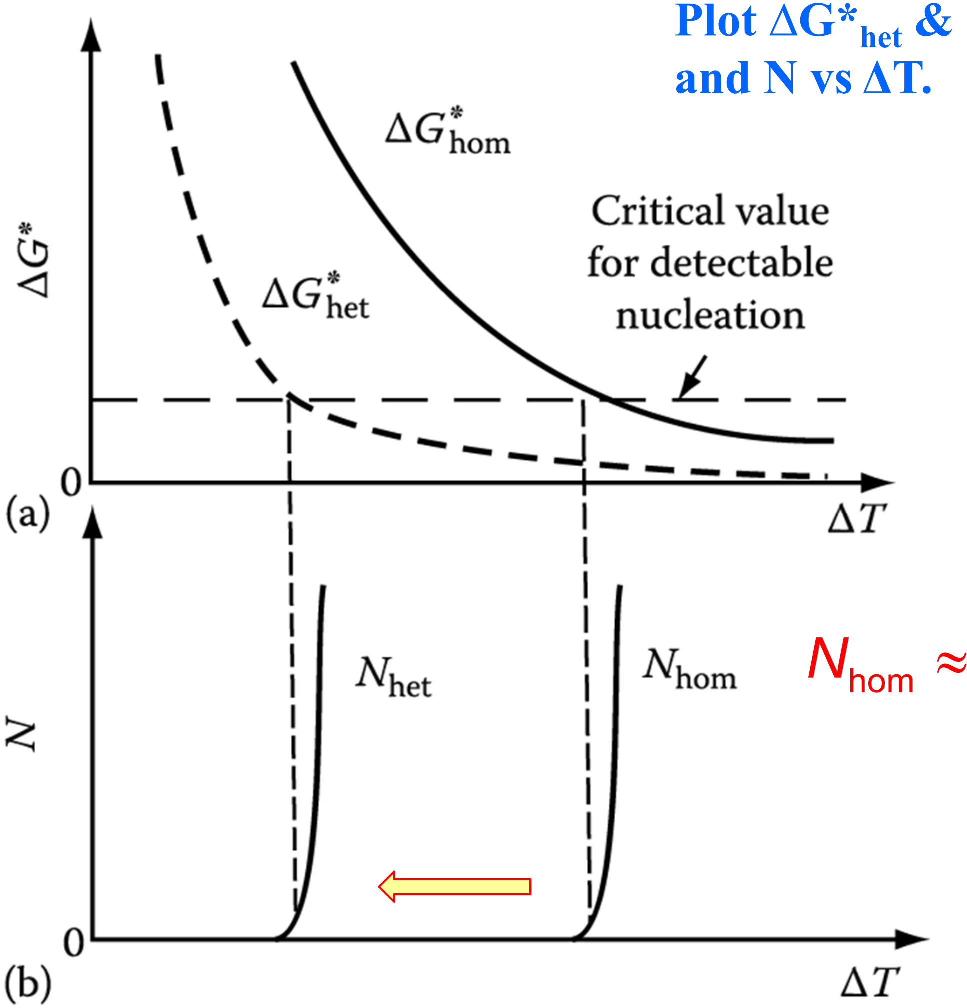
$$\Rightarrow\ \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot S(\theta)$$

n_1 atoms in contact with the mold wall

$$n^* = n_1 \exp\left(-\frac{\Delta G^*_{het}}{kT}\right)$$

$$N_{het} = f_1 C_1 \exp\left(-\frac{\Delta G^*_{het}}{kT}\right)$$

Plot ΔG^*_{het} & ΔG^*_{hom} vs ΔT and N vs ΔT.



$N_{hom} \approx 1\ \mathrm{cm}^{-3}\mathrm{s}^{-1}$

Fig. 4.9 (a) Variation of ΔG* with undercooling (ΔT) for homogeneous and heterogeneous nucleation. (b) The corresponding nucleation rates assuming the same critical value of ΔG*

$\theta \downarrow \rightarrow V_c / V \downarrow \rightarrow$ embryo radius (r_{max}) ↑

→ condition for heterogeneous nucleation as a function of θ

Assumption 1: angle of contact is independent of temp.
2: substrate is flat.

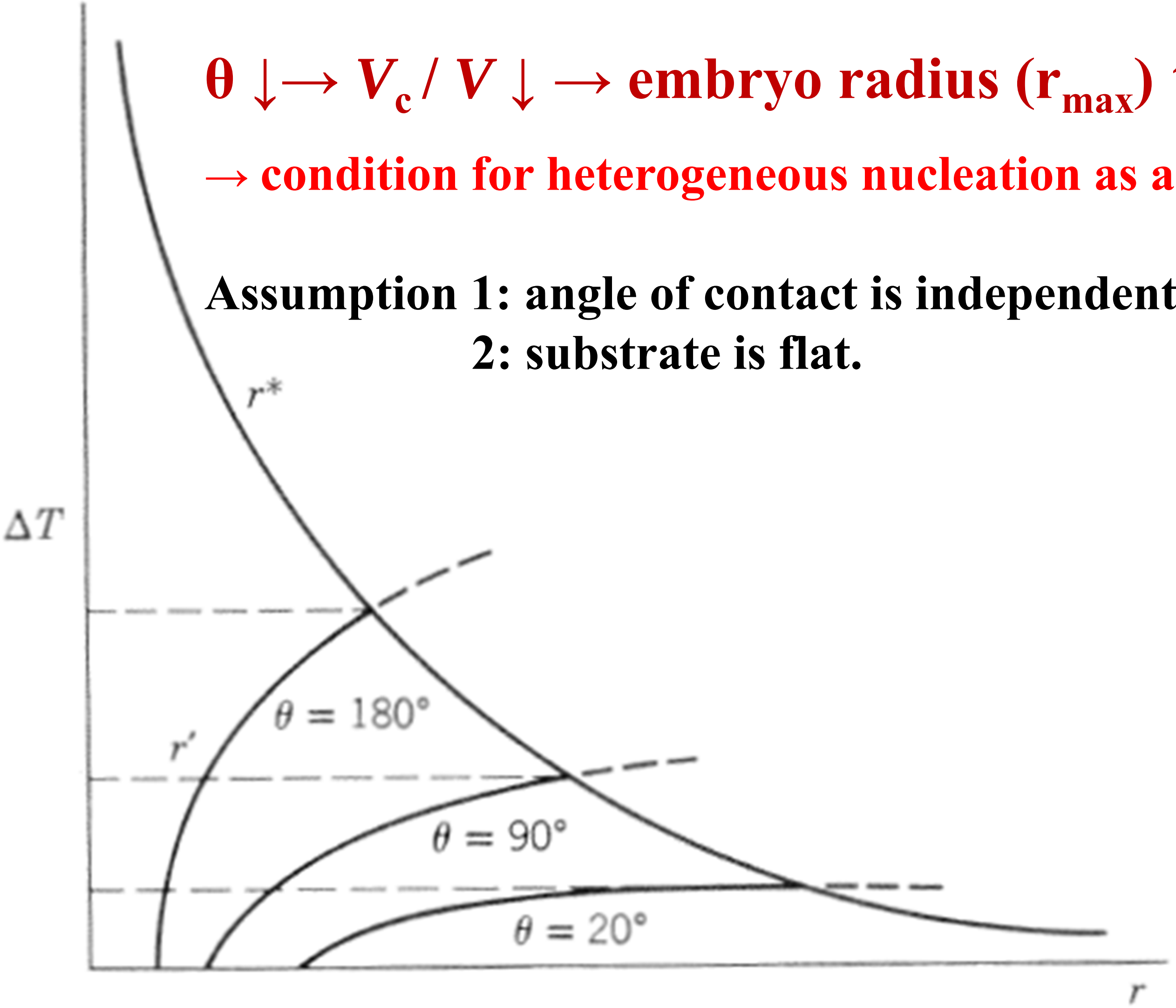
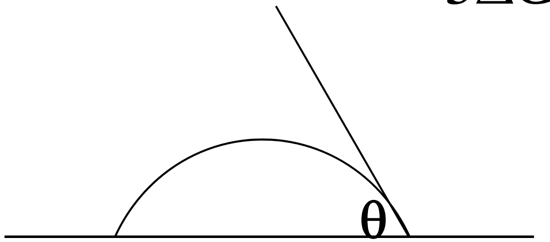


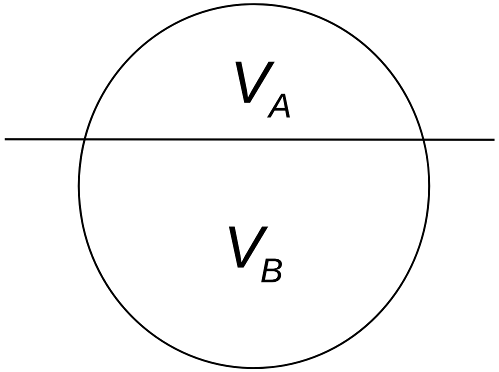
Fig. 3.15. Condition for heterogeneous nucleation (schematic).

Barrier of Heterogeneous Nucleation

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot S(\theta) = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2}\cdot\frac{(2-3\cos\theta+\cos^3\theta)}{4}$$



$$\boxed{\Delta G^*_{het} = S(\theta)\Delta G^*_{\text{hom}}}$$



$$\Delta G^*_{sub} = \Delta G^*_{homo}\left(\frac{2-3\cos\theta+\cos^3\theta}{4}\right)$$

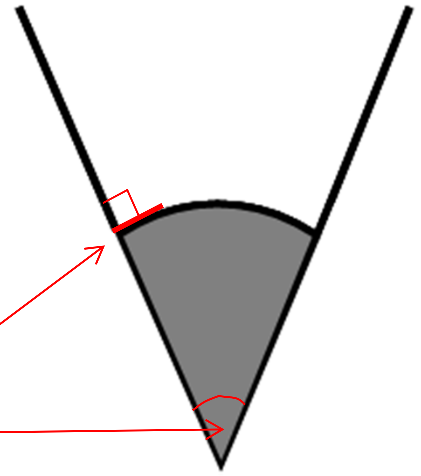
$$\boxed{\frac{V_A}{V_A+V_B} = \frac{2-3\cos\theta+\cos^3\theta}{4} = S(\theta)}$$

How about the nucleation at the crevice or at the edge?

Nucleation Barrier at the crevice

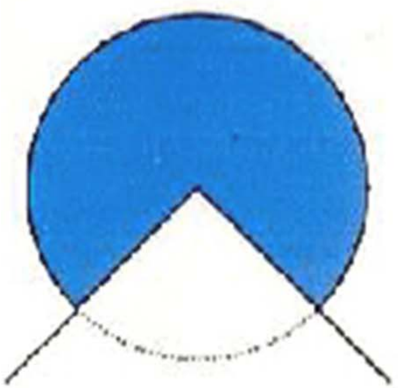
What would be the shape of nucleus and the nucleation barrier for the following conditions?

$$\frac{1}{6}\Delta G^*_{\mathrm{homo}}$$

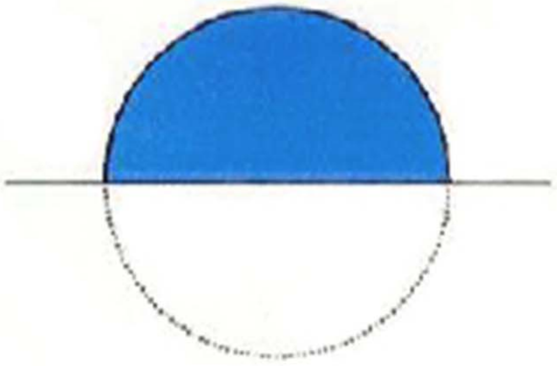


contact angle = 90

groove angle = 60



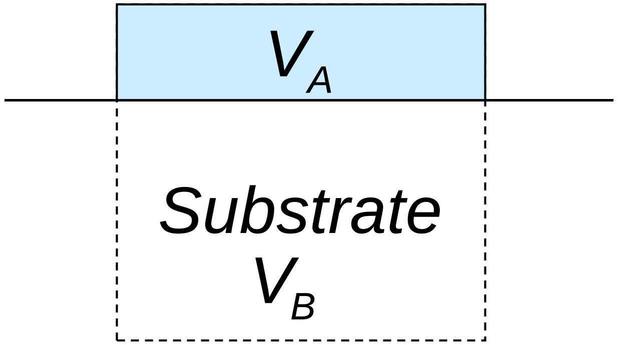
$$\frac{3}{4}\Delta G^*_{\mathrm{homo}}$$



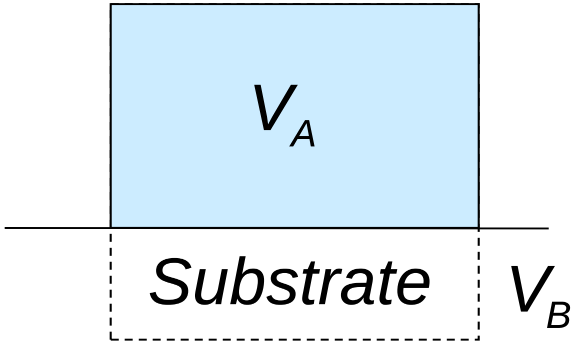
$$\frac{1}{2}\Delta G^*_{\mathrm{homo}}$$

$$\frac{1}{4}\Delta G^*_{\mathrm{homo}}$$

How do we treat the non-spherical shape?



Good Wetting



Bad Wetting

$$\Delta G^*_{sub} = \Delta G^*_{homo}\left(\frac{V_A}{V_A + V_B}\right)$$

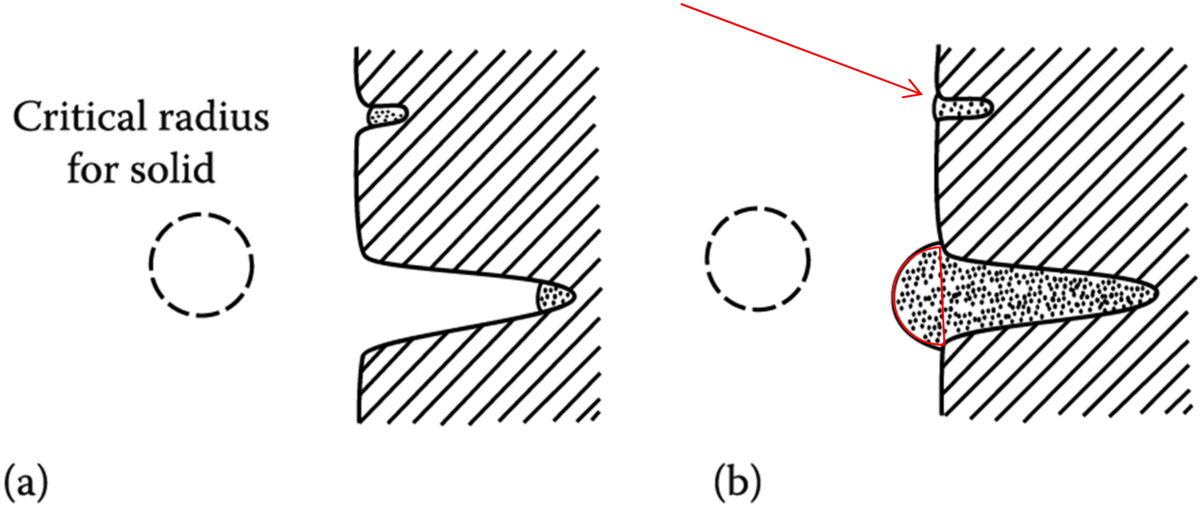
Effect of good and bad wetting on substrate

Extreme form of a concave substrate: Nucleation inside the crevice

So far it has been assumed that the mold wall is microscopically flat.

In practice, however, it is likely to contain many microscopic cracks or crevices.

Nucleation from cracks or crevices should be able to occur at very small undercoolings even when the wetting angle θ is relatively large. However, that for the crack to be effective the crack opening must be large enough to allow the solid to grow out without the radius of the solid/liquid interface decreasing below r*.



In both of the nucleation types considered so far it can be shown that

Formation of a nucleus on such a surface

$$\boxed{\Delta G^* = \frac{1}{2} V^* \Delta G_V}$$

몰드 표면에서 핵생성 될 때 필요한 에너지

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

Inoculants ~ low values of θ → low energy interface, fine grain size

3.7 The Nucleation of Melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating.

Because, melting can apparently, start at crystal surfaces without appreciable superheating.

Why?

$$\boxed{\gamma_{SL} + \gamma_{LV} < \gamma_{SV}}$$ **(commonly)**

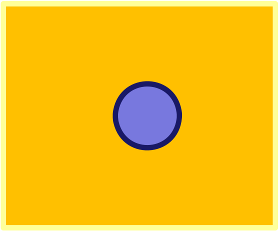
In the case of gold,

γ_{SL}	solid-liquid	132 ergs/cm
γ_{LV}	liquid-vapor	1128 ergs/cm
γ_{SV}	solid-vapor	1400 ergs/cm

In general, wetting angle = 0 ⇨ No superheating required!

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid



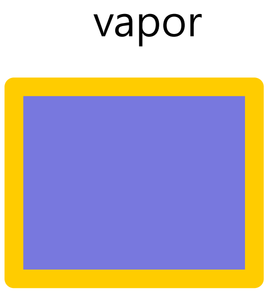
<Thermodynamic>

- Interfacial energy ⇨ ΔT_N

No superheating required!

- Interfacial energy ⇨ No ΔT_N

$$\boxed{\gamma_{SL} + \gamma_{LV} < \gamma_{SV}}$$



Melting: Liquid ← Solid

Contents for today's class

Solidification: Liquid ⟶ Solid

- **Nucleation in Pure Metals**
- **Homogeneous Nucleation**

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

r* & ΔG* ↓ as ΔT ↑

$$\boxed{N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\} \sim \frac{1}{\Delta T^2}}$$

- **Heterogeneous Nucleation**

$$\boxed{\Delta G_{het}^* = S(\theta)\Delta G_{\text{hom}}^*}$$

$$\boxed{\frac{V_A}{V_A + V_B} = \frac{2 - 3\cos\theta + \cos^3\theta}{4} = S(\theta)}$$

- **Nucleation of melting**

$$\boxed{\gamma_{SL} + \gamma_{LV} < \gamma_{SV}} \quad \textbf{(commonly)}$$

- **Undercooling ΔT**
- **Interfacial energy**

  γ_{SL} / S(θ) wetting angle