2015 Fall

"Phase Transformation *in* Materials"

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Eun Soo Park

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

Contents in Phase Transformation

Background to understand phase transformation

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

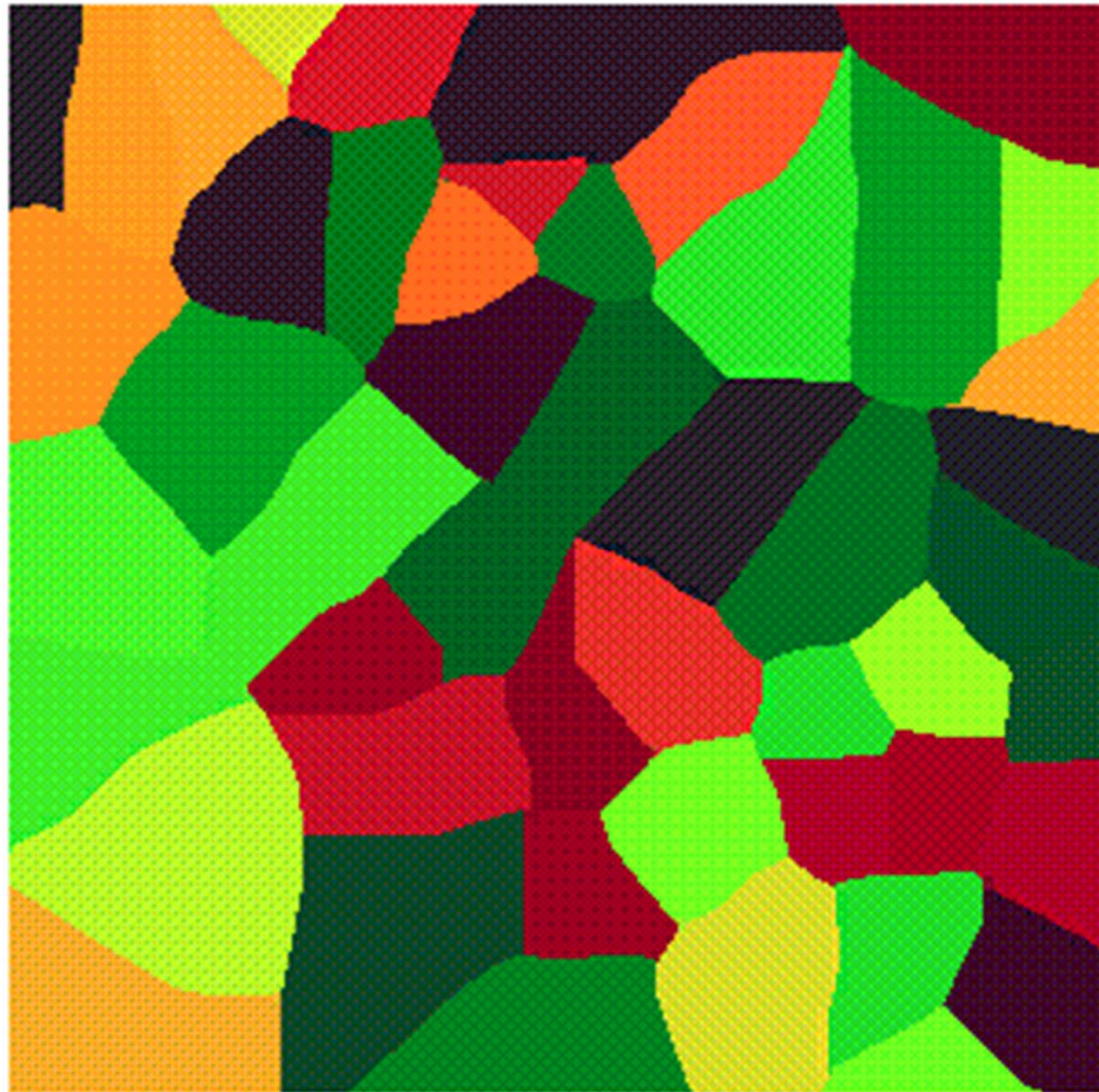(Ch3) Crystal Interface and Microstructure

Representative Phase transformation

(Ch4) Solidification: Liquid → Solid

(Ch5) Diffusional Transformations in Solid: Solid → Solid

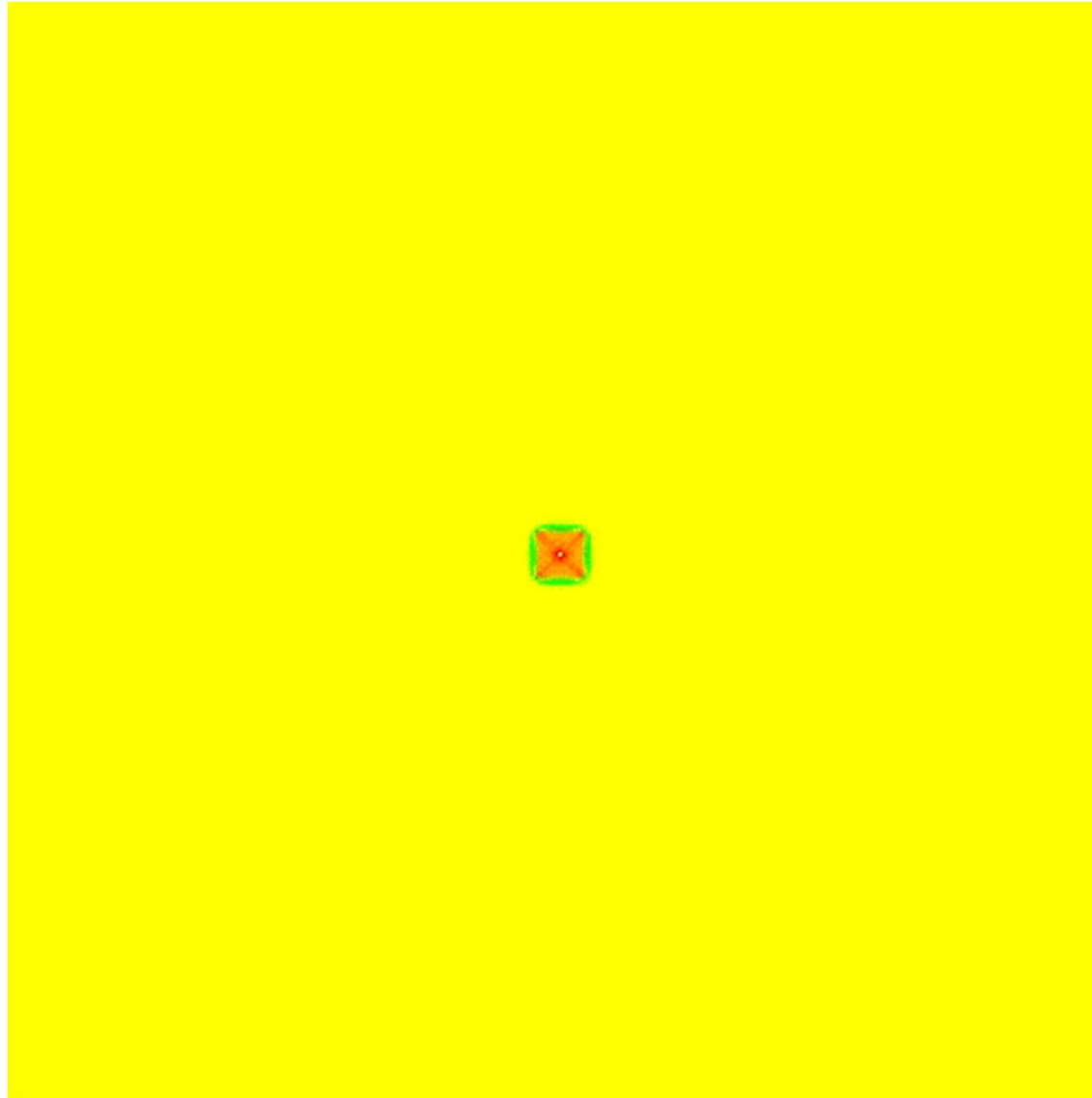(Ch6) Diffusionless Transformations: Solid → Solid

Solidification: Liquid ⟶ Solid

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

3

Solidification: Liquid ➝ Solid

4 Fold Symmetric Dendrite Array

4

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**

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Q: Undercooling of
homogenous vs heterogenous nucleation ?

Solidification: Liquid $\longrightarrow$ Solid

- casting & welding
- single crystal growth
- directional solidification
- rapid solidification
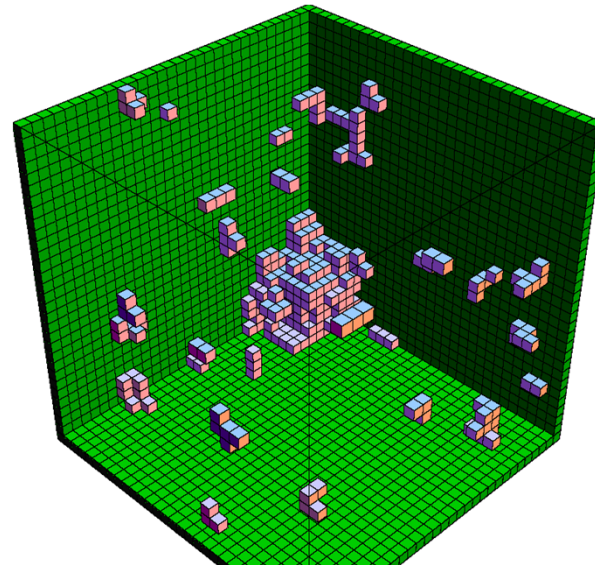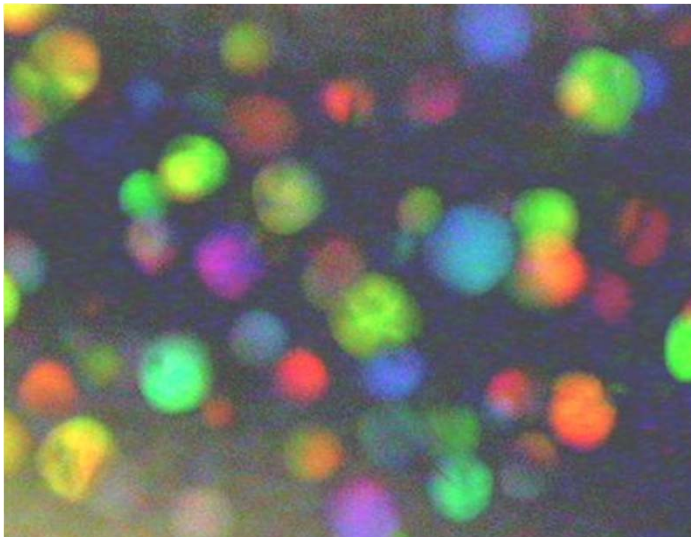
4.1. Nucleation in Pure Metals

$T_m : G_L = G_S$

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

\<Types of nucleation\>

- Homogeneous nucleation   - Heterogeneous nucleation

Electrostatic levitation in KRISS

HV (z-axis)

T : ~3000 °C
P : ~ 10^{-7} Torr

Heating laser

He-Ne laser

He-Ne laser

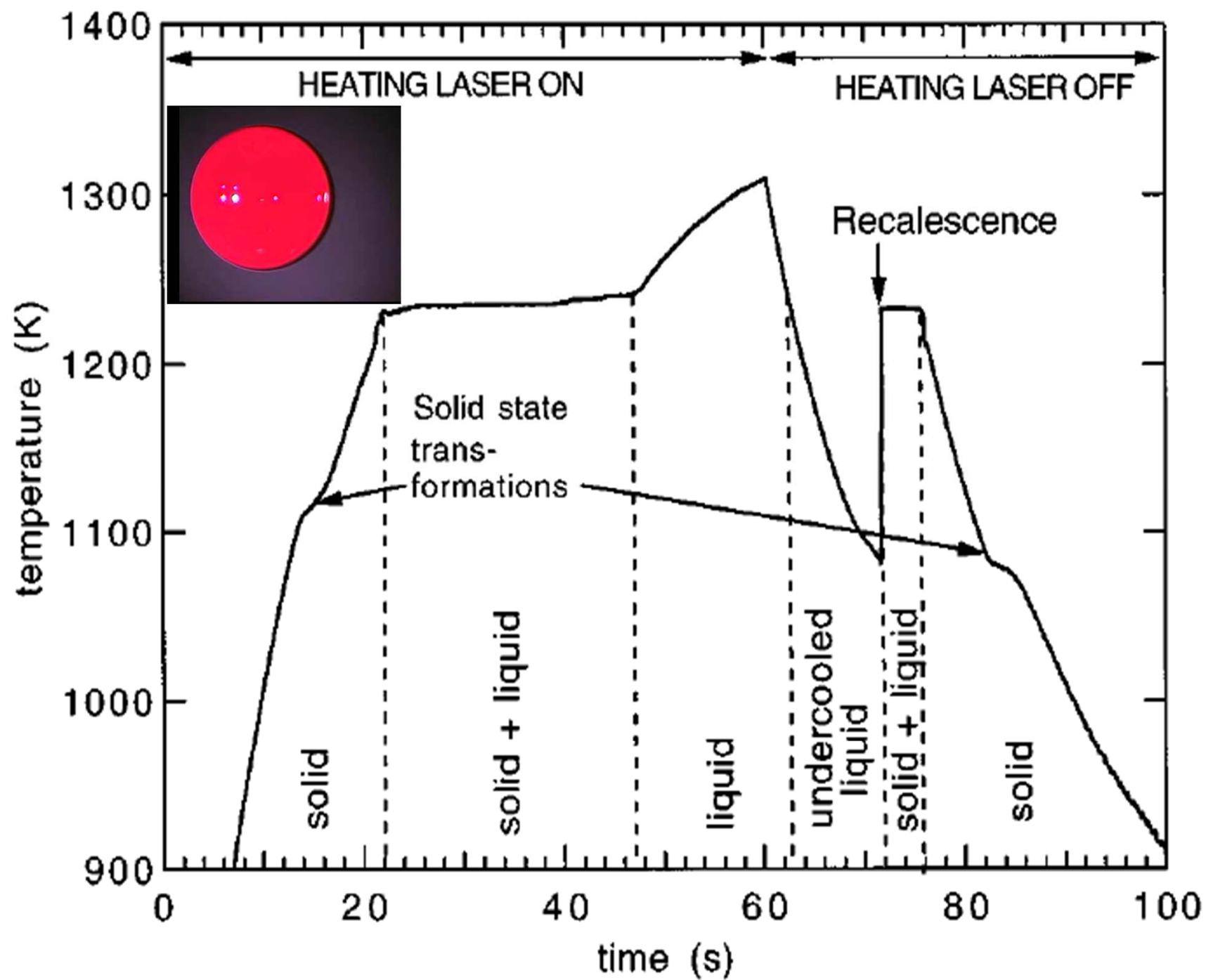Feedback

PSD (x)

PSD (y)

HV (x-axis)

HV (y-axis)

Feedback

KRISS material : Dr. G.W.Lee
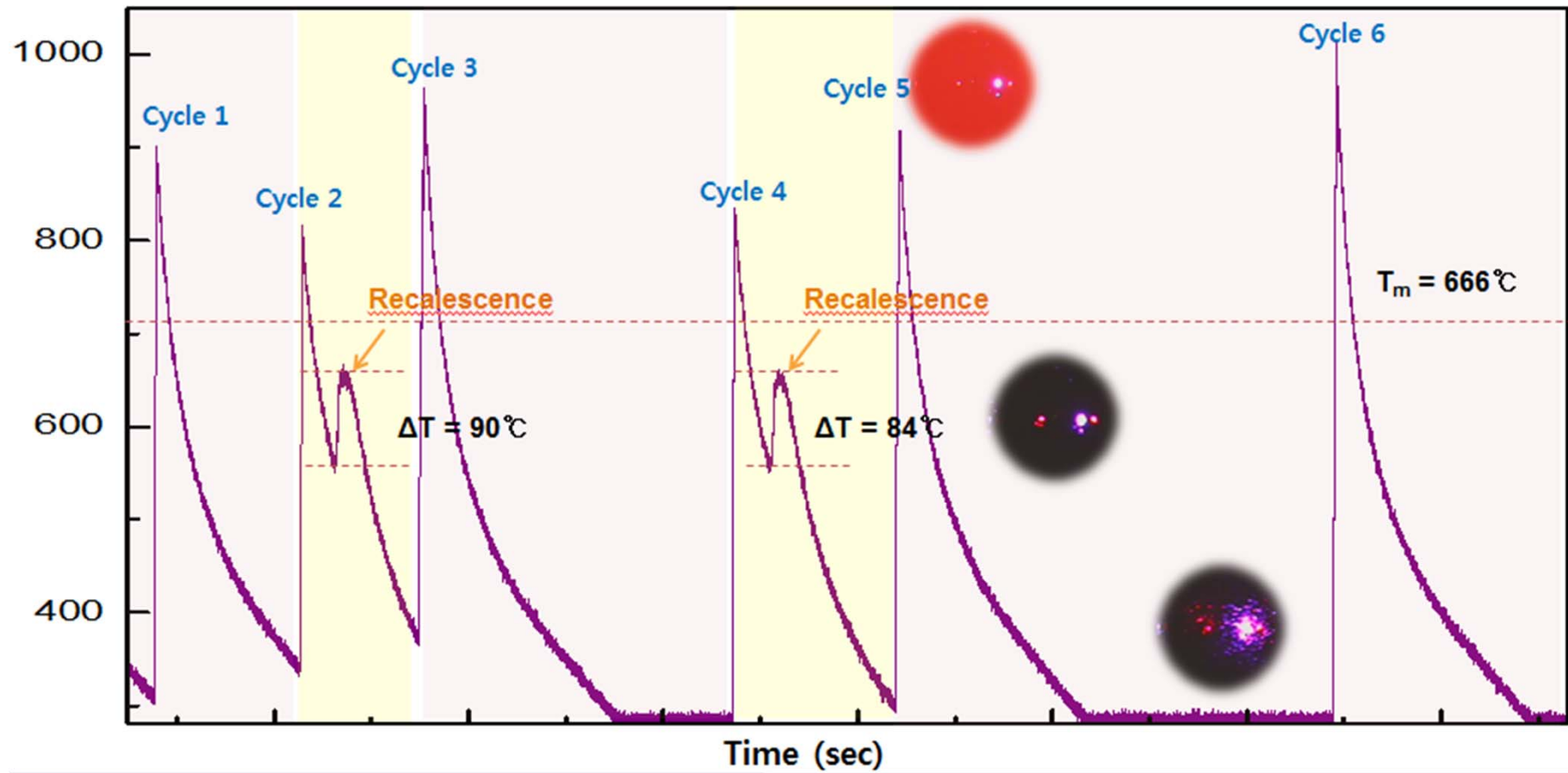
8
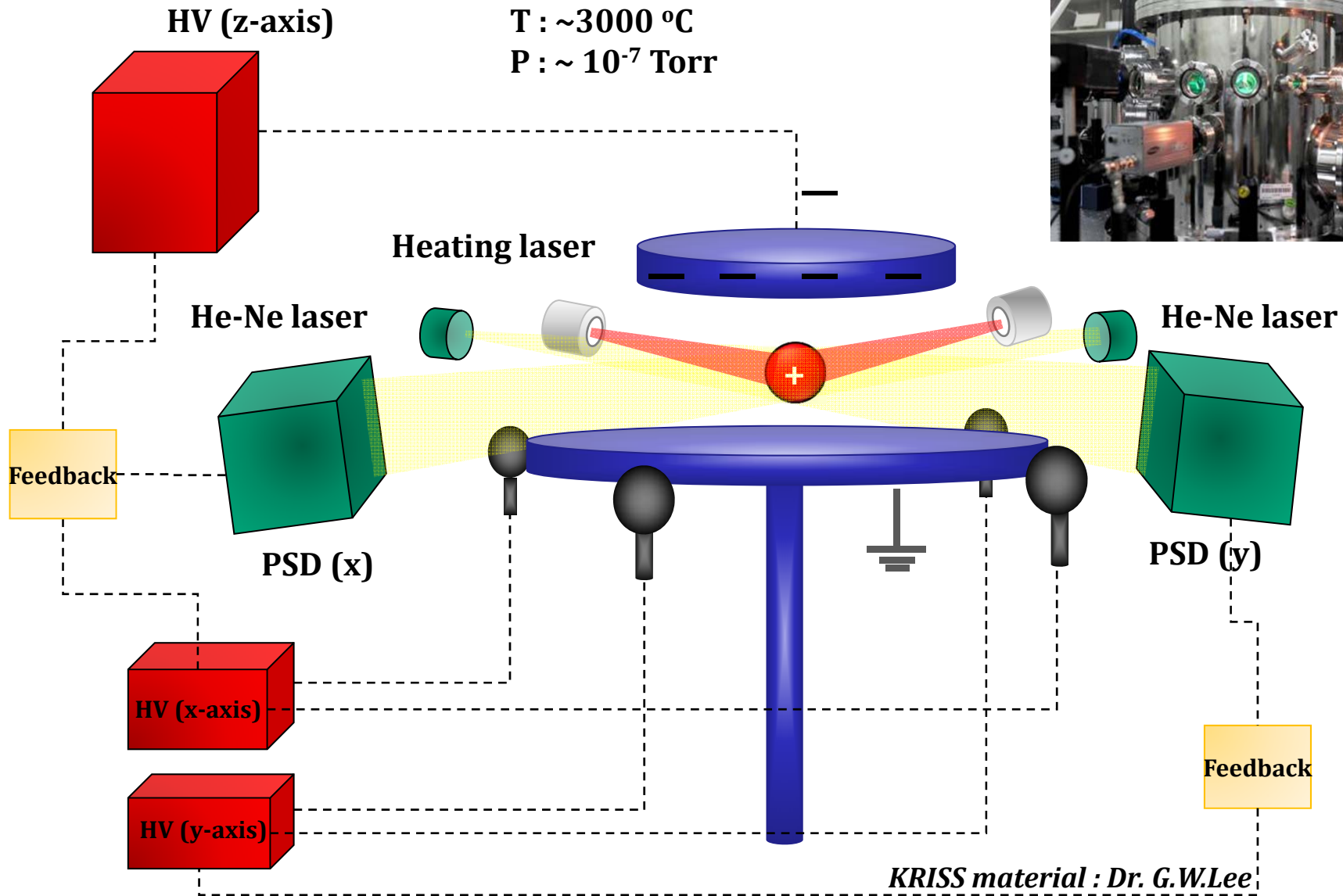
Electrostatic Levitation: cooling curve of Vitreloy 1 system

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

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

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

$$L : \Delta H = H^L - H^S$$
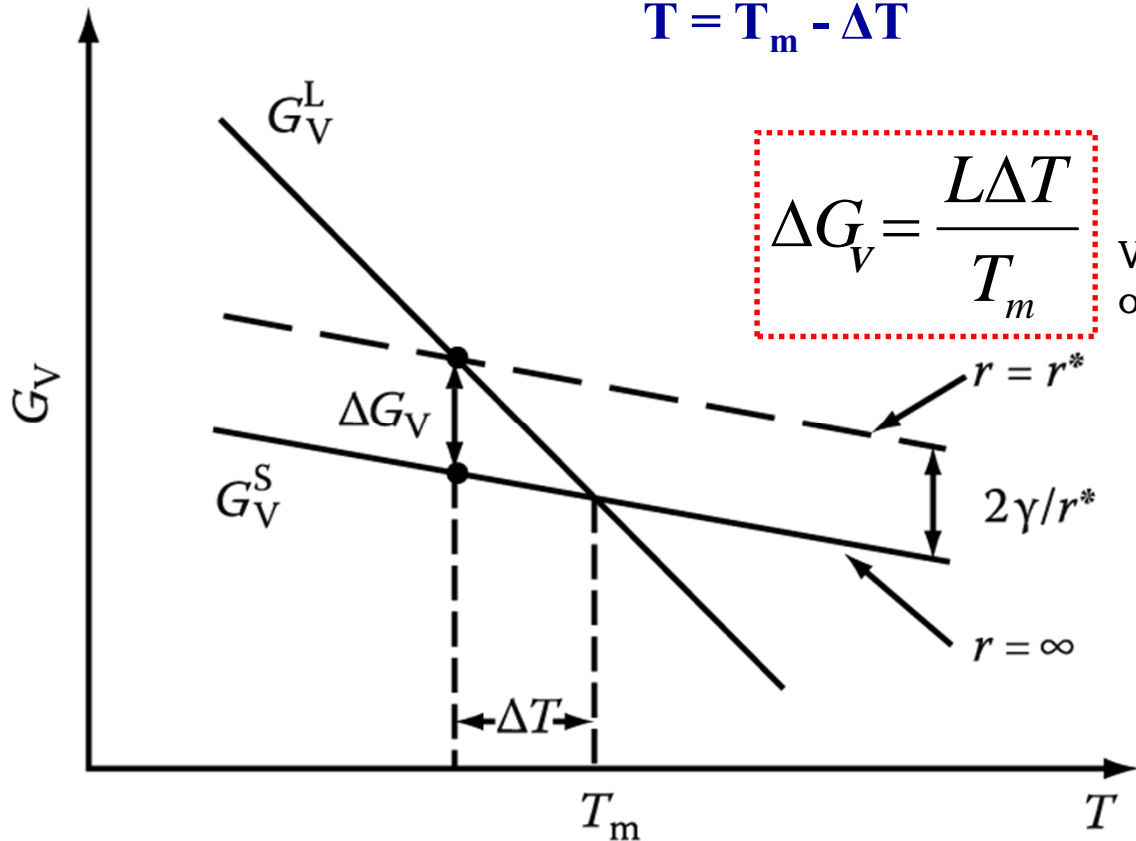$$\text{(Latent heat)}$$
$$T = T_m - \Delta T$$

$$\Delta G = 0 = \Delta H - T_m \Delta S$$
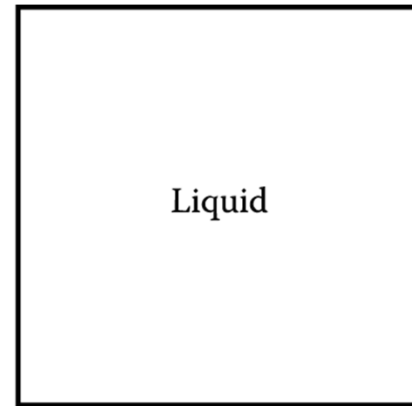$$\Delta S = \Delta H/T_m = L/T_m$$
$$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$$

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

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

4.1.1. Homogeneous Nucleation
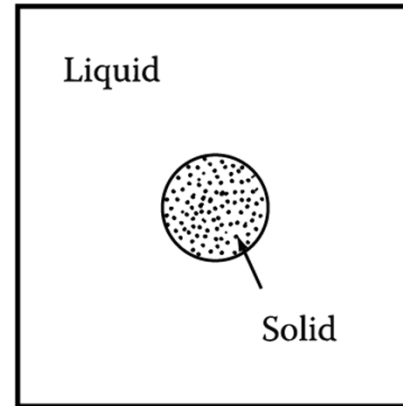
(a)　　　G_1　　　　　　　(b)　　　$G_2 = G_1 + \Delta G$

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

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

$G_V^S, \ G_V^L$: **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

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

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Calculation of critical radius, r*

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

Why r* is not defined by $\Delta G_r = 0$?
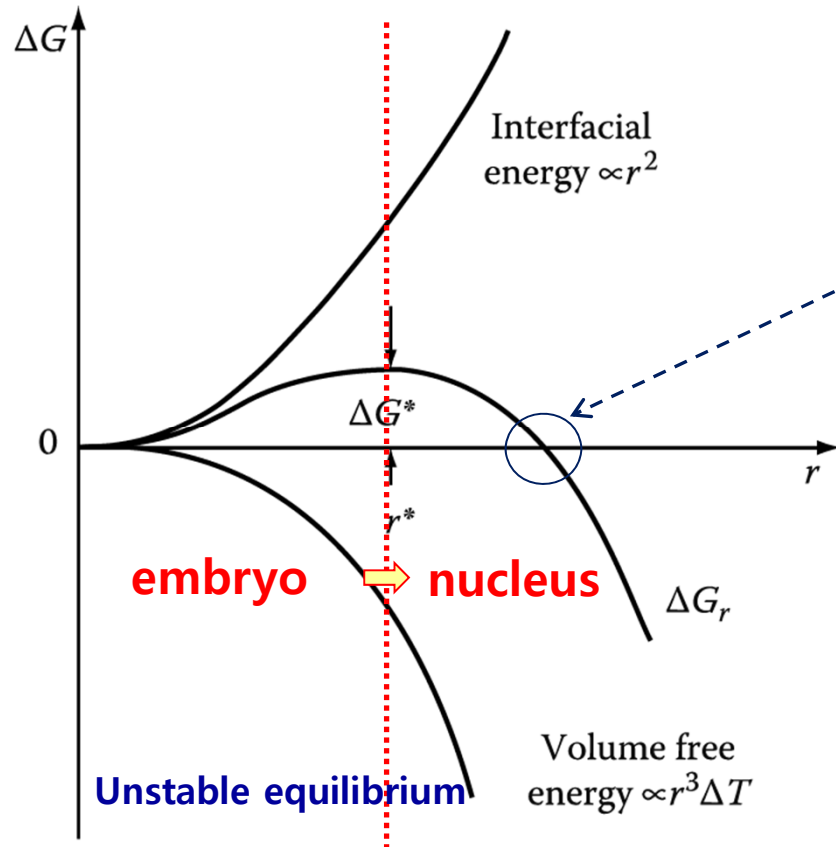
r < r* : unstable (lower free E by reduce size)

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

r* : critical nucleus size

r* $\Longrightarrow$ **dG=0**

Gibbs-Thompson Equation

Critical ΔG of nucleation at r∗

$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} \Longrightarrow \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_V^2}\right)\frac{1}{(\Delta T)^2}$$
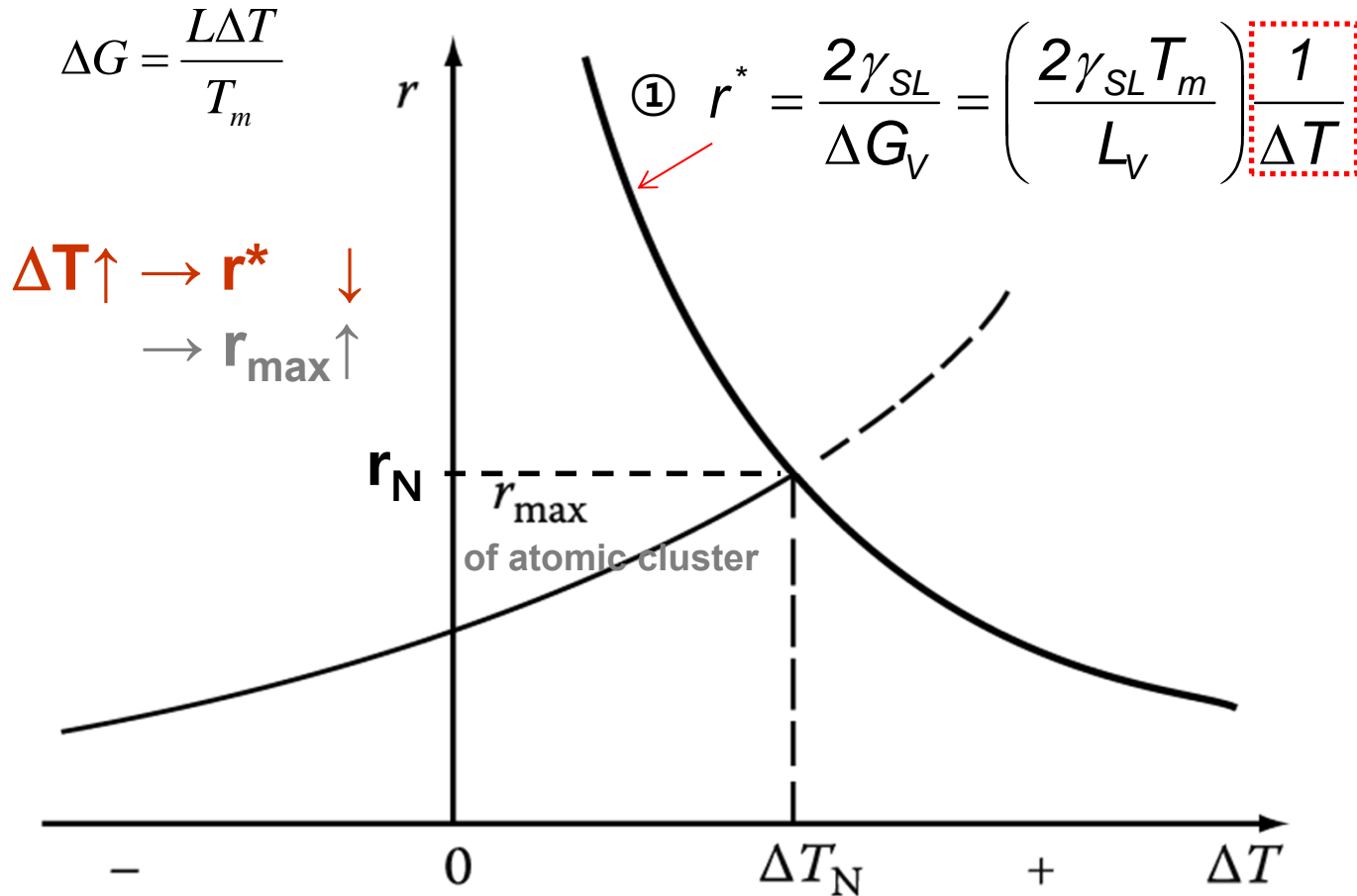
$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL} \qquad \Delta G_V = \frac{L\Delta T}{T_m}$$

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Q: How do we define ΔT_N?

The creation of a critical nucleus ~ thermally activated process

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

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

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

$\rightarrow$ **r**$_{max}\uparrow$

r$_N$

r_{max}

of atomic cluster

ΔT_N

$-$ 0 $+$ ΔT

ΔT_N is the critical undercooling for homogeneous nucleation.

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

$\rightarrow$ Condition for nucleation:
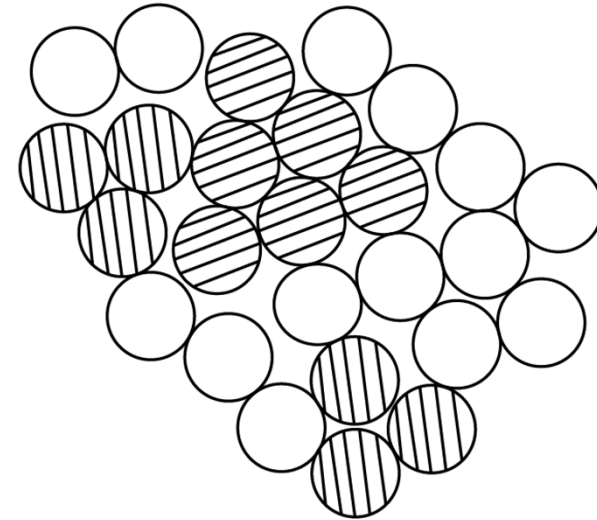   **The number of clusters with r* at T < ΔT_N is negligible.**

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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>
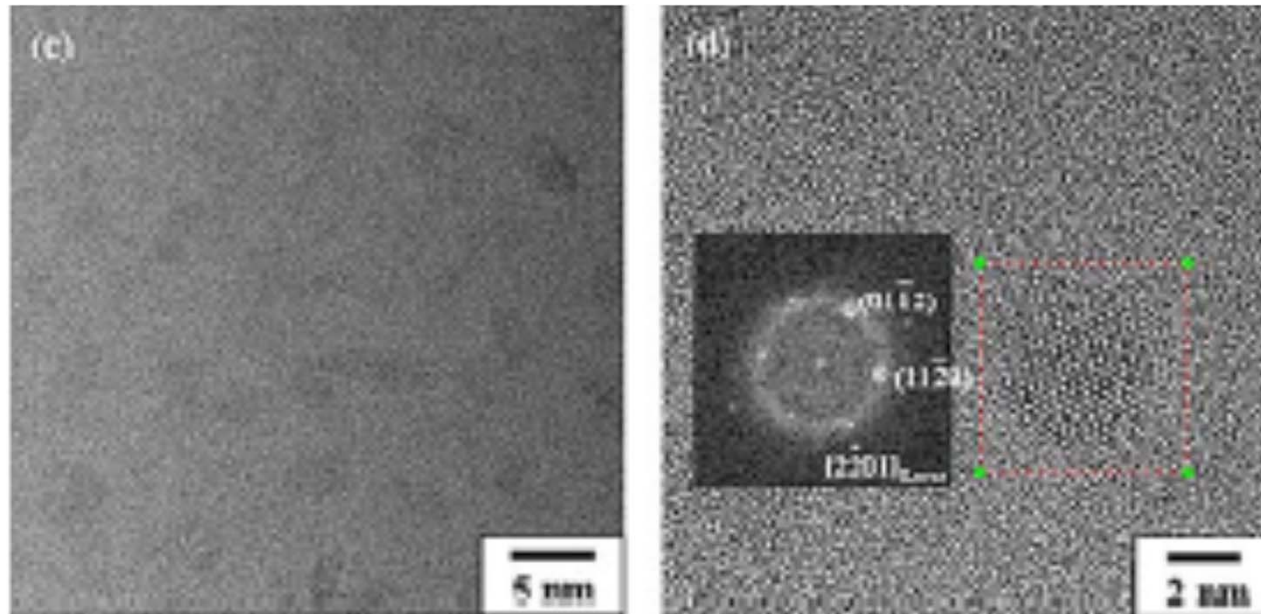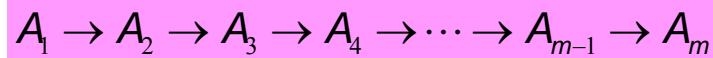
Formation of Atomic Cluster

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

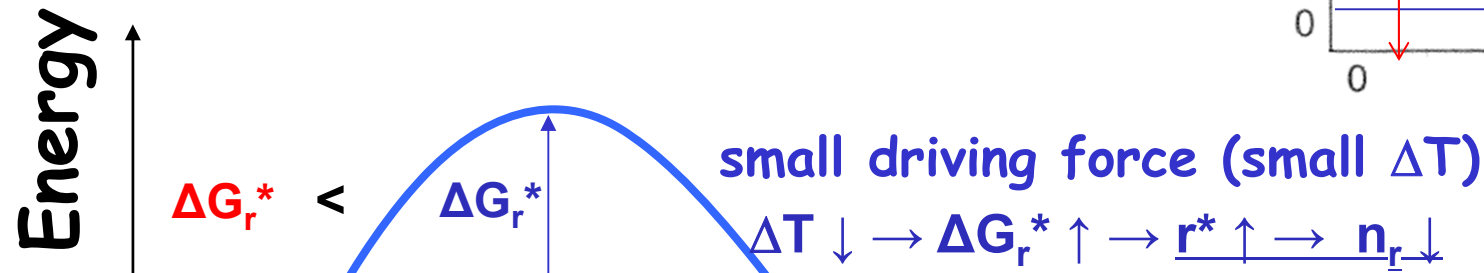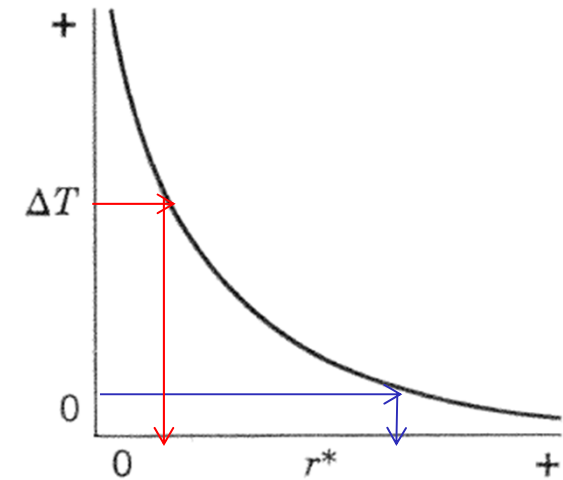$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$

n_r exponentially decreases with ΔG_r

$r \uparrow \to \Delta G_r \uparrow$

embryo ⟹ Nucleus
: no longer part of liquid

Gibbs Free Energy — *radius*

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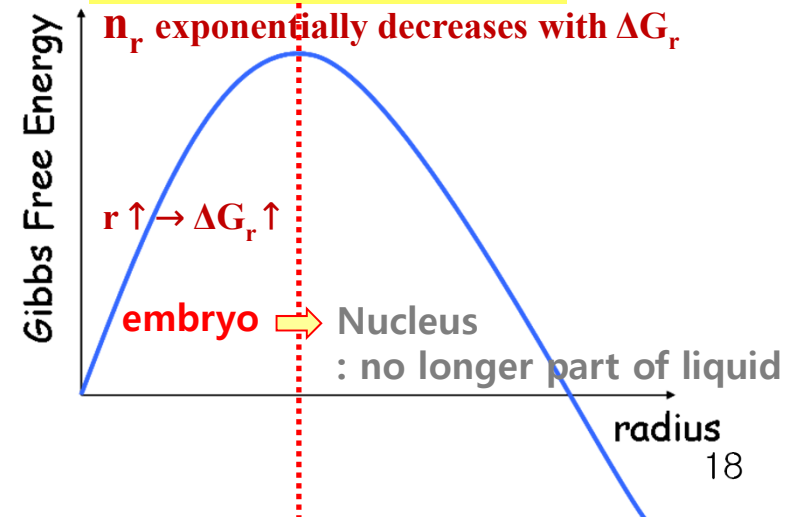
Formation of Atomic Cluster

Compare the nucleation curves between small and large driving forces.

Gibbs Free Energy

ΔG_r^* < ΔG_r^*

small driving force (small ΔT)

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

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

large driving force (large ΔT)

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

# of cluster of radius r

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

r^* < r^*

radius

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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 $\mathbf{T > T_m}$ / $\mathbf{T < T_m}$ and $\mathbf{r \leq r^*}$

Apply for all r / $r \leq r*$
($\because$ r > r*: no longer part of the liquid)

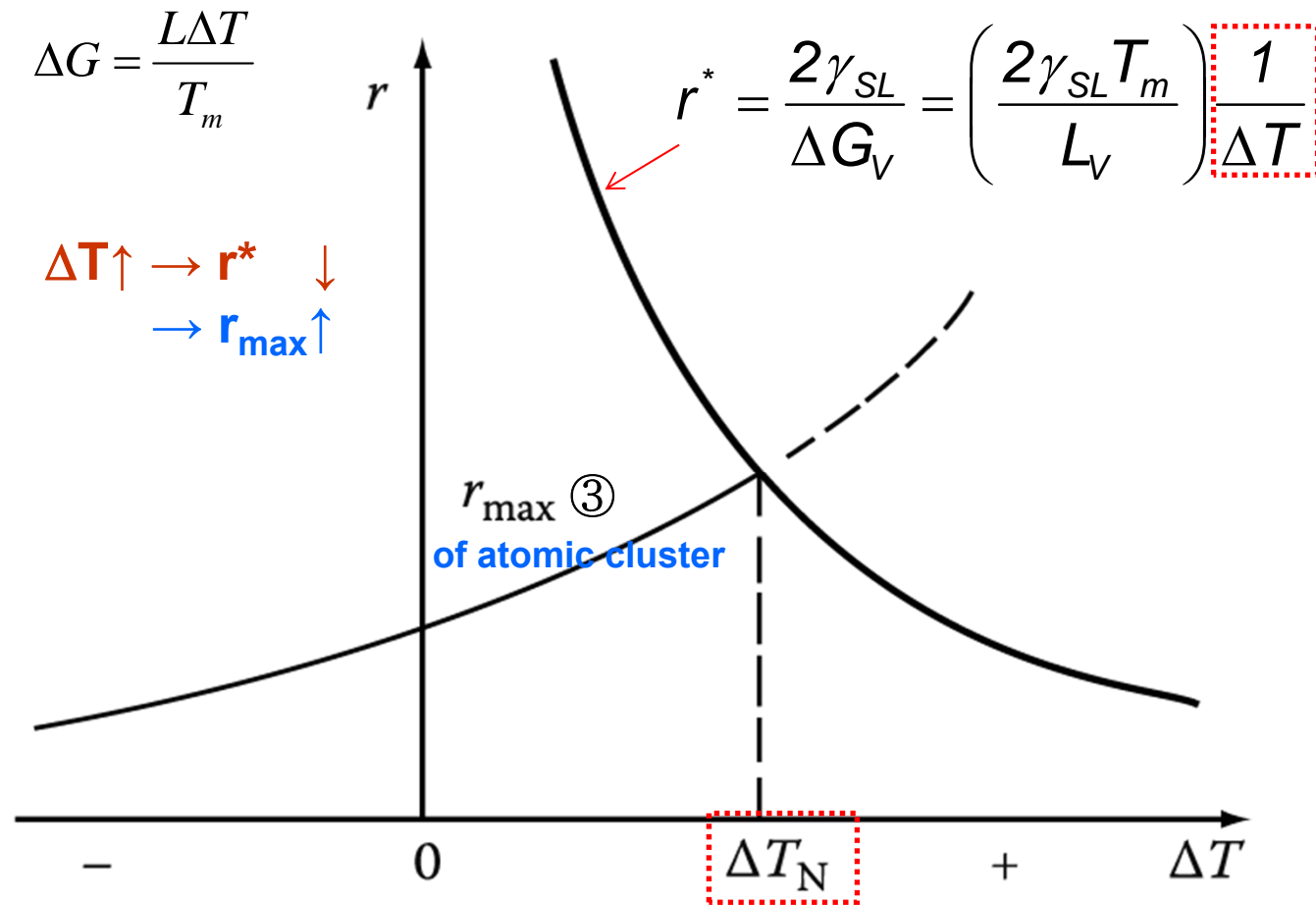- n_r exponentially decreases with ΔG_r

Ex. 1 mm^3 of copper <u>at its melting point</u> (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)

$\rightarrow$ effectively a maximum cluster size, ~ 100 atoms
$\sim 10^{-8}$ clusters mm^{-3} or <u>1 cluster in $\sim 10^7$ mm^3</u>

The creation of a critical nucleus ~ thermally activated process

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

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

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

$\rightarrow r_{max}\uparrow$

r_{max} ③
of atomic cluster

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 $T < \Delta T_N$ 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

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

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

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

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

$$\Delta G^* = \left(\frac{16\pi\gamma^3_{SL}T^2_m}{3L^2_V}\right)\frac{1}{(\Delta T)^2}$$

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

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

Reasonable nucleation rate

4.1.2. The homogeneous nucleation rate - kinetics

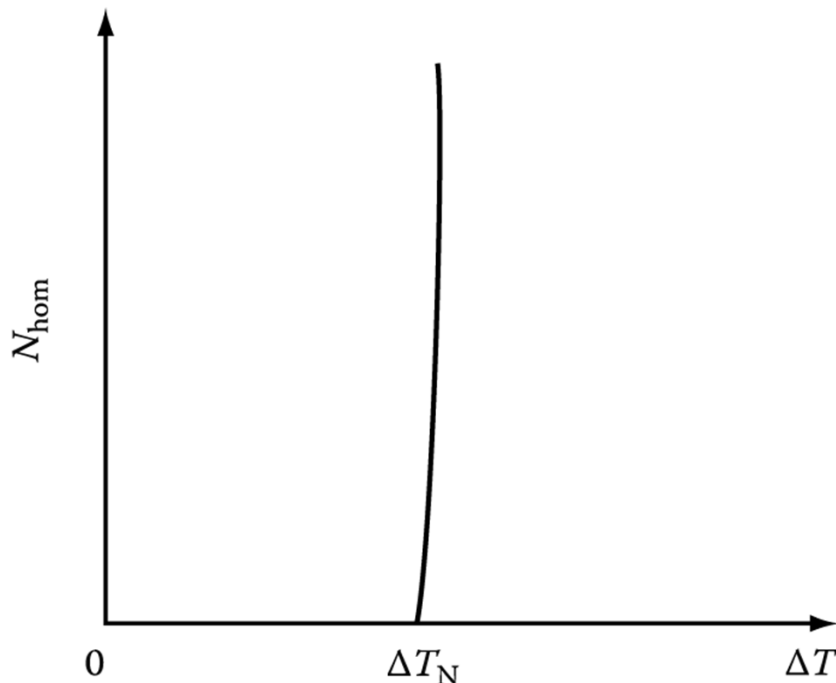$$N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\}$$

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

A = relatively insensitive to Temp.

How do we define ΔT_N?

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

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.

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* Copper Homogeneous nucleation

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

If nucleus is spherical shape,

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

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

⟹ 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.**
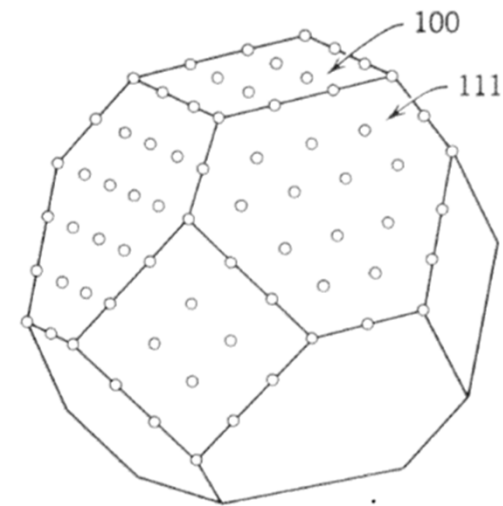

Fig. 3.11. Possible structure for the critical nucleus. (From B. Chalmers, *Physical Metallurgy*, John Wiley and Sons, New York, 1959, p. 246.)

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 <u>catalyzed by a suitable surface in contact with the liquid</u>. → "Heterogeneous Nucleation"

Ex)
liquid
——————————————
container

or

Solid thin film (such as oxide)

liquid
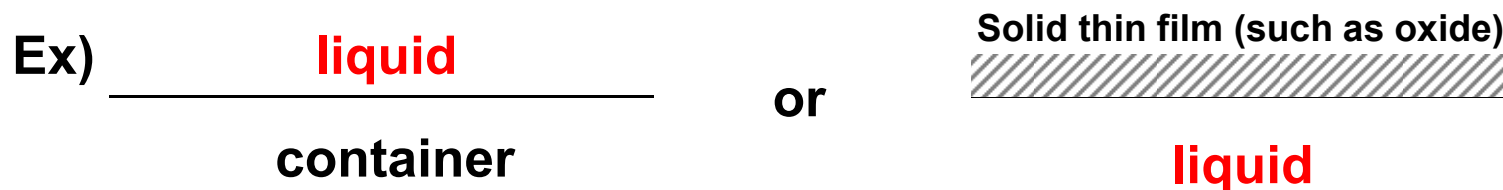
Why this happens?   What is the underlying physics?

Which equation should we examine?

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

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

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Q: Real behavior of nucleation: "Heterogeneous nucleation"

4.1.3. Heterogeneous nucleation
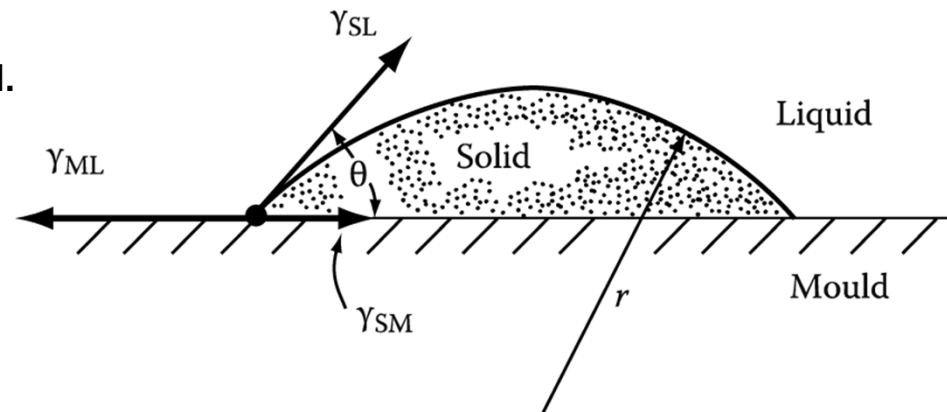
From $\quad \Delta G* = \left(\dfrac{16\pi\gamma_{SL}^3 T_m^2}{3 L_V^2} \right) \dfrac{1}{(\Delta T)^2}$

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

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

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

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

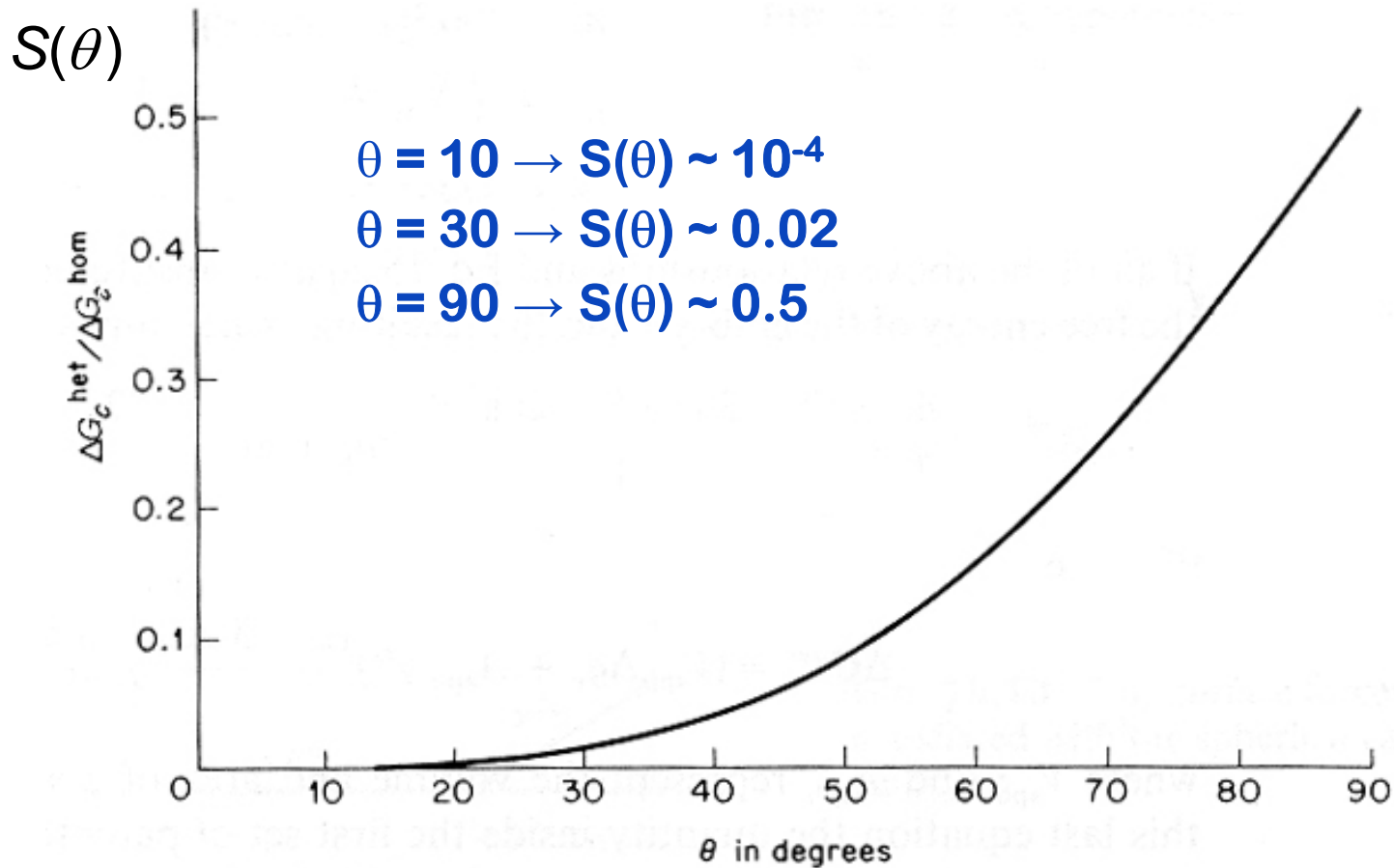$$\Delta G_{het} = -V_S \Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{ML}$$

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

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

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

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

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

$S(\theta)$

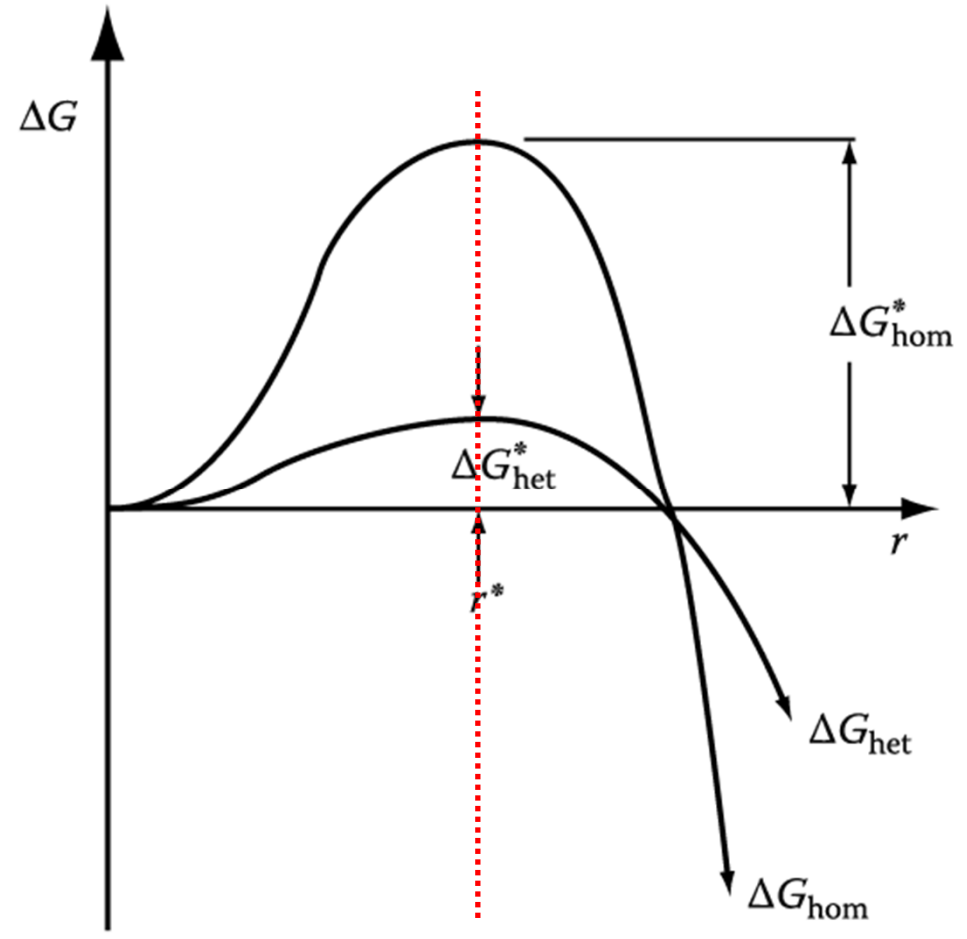$\theta = 10 \rightarrow S(\theta) \sim 10^{-4}$
$\theta = 30 \rightarrow S(\theta) \sim 0.02$
$\theta = 90 \rightarrow S(\theta) \sim 0.5$

θ in degrees

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

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

$$r* = \frac{2\,\gamma_{SL}}{\Delta G_{V}} \quad and \quad \Delta G* = \frac{16\,\pi\gamma^{3}_{SL}}{3\Delta G^{2}_{V}} \cdot S(\theta)$$

ΔG

ΔG^{*}_{hom}

ΔG^{*}_{het}

$r*$

r

ΔG_{het}

ΔG_{hom}

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

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

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

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

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.

ΔG^*_{hom}

Critical value for detectable nucleation

ΔG^*_{het}

(a)

N_{het} N_{hom}

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

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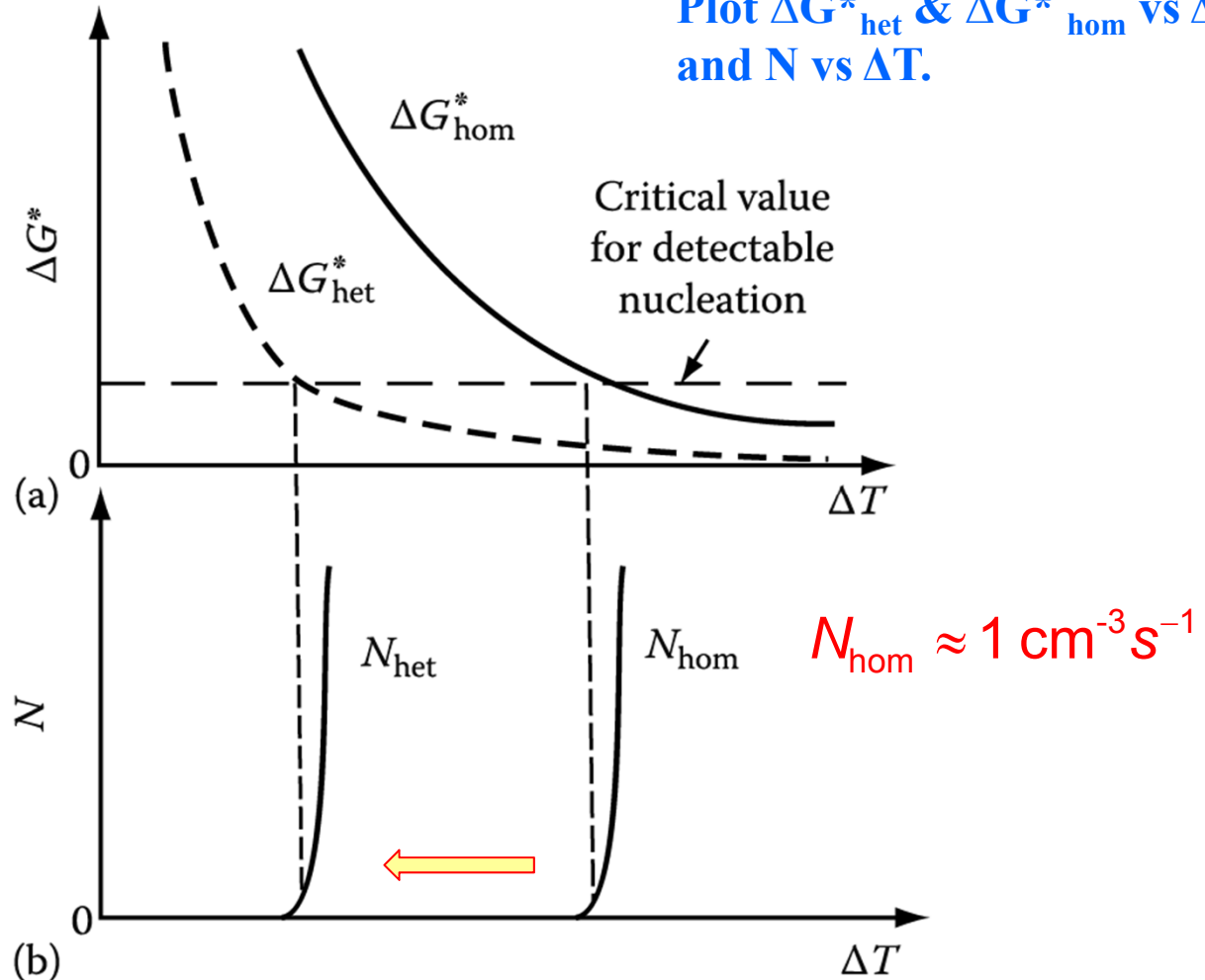
Fig. 4.9 (a) Variation of ΔG* with undercooling (ΔT) for homogeneous and heterogeneous nucleation.
(b) The corresponding nucleation rates assuming the same critical value of ΔG*

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

$\rightarrow$ **condition for heterogeneous nucleation as a function of θ**

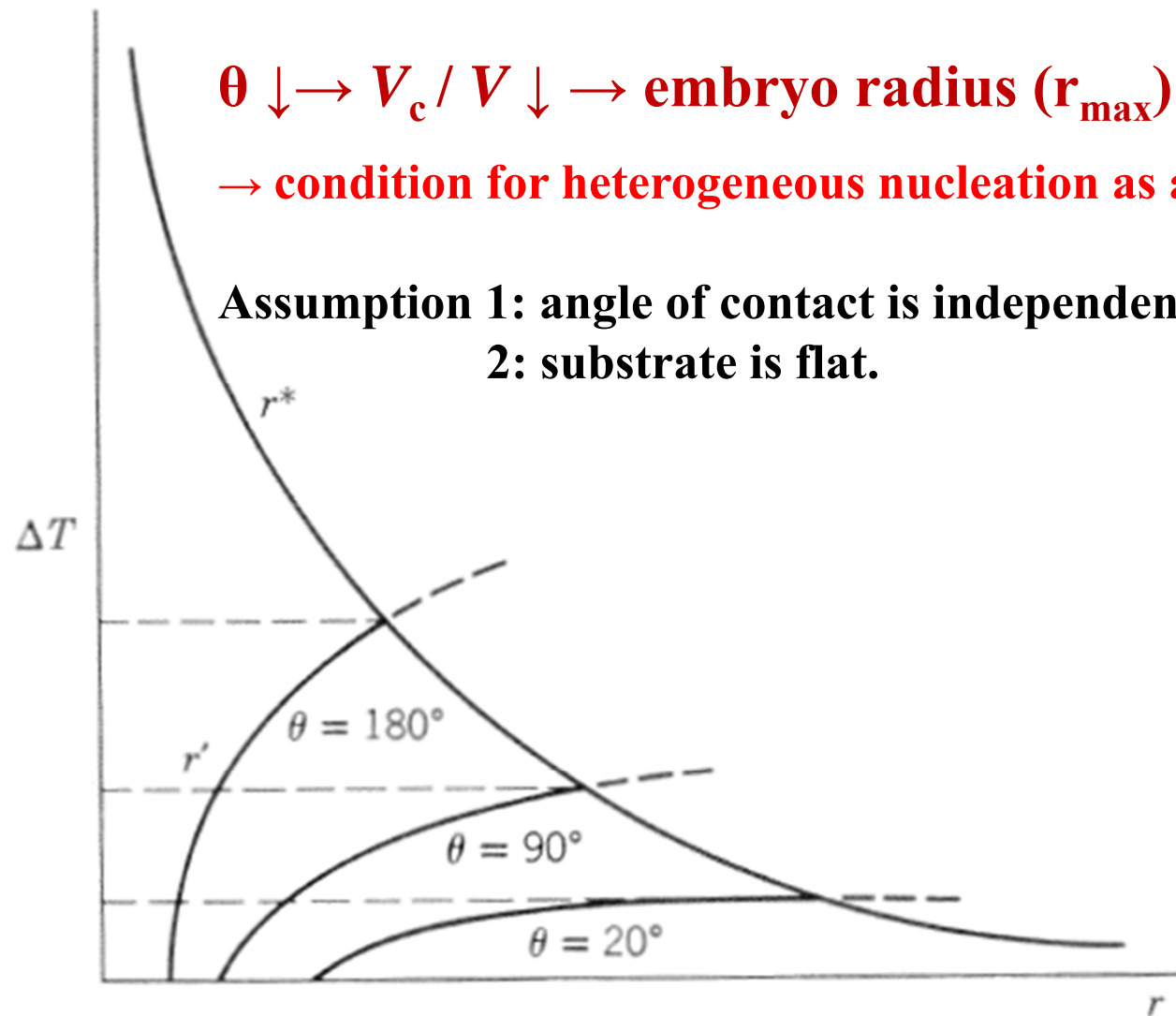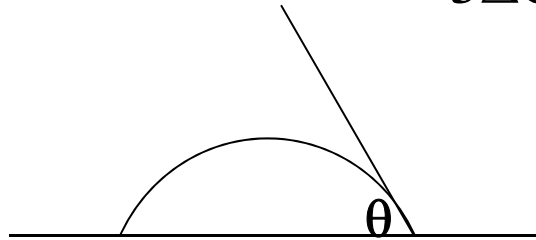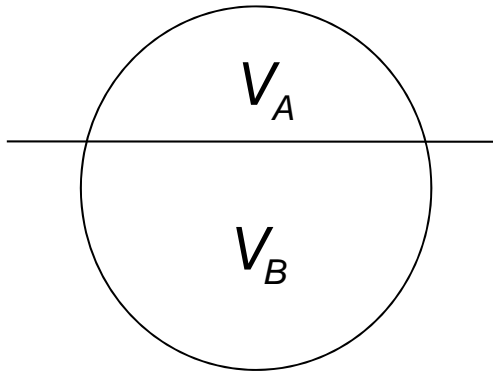**Assumption 1: angle of contact is independent of temp.**
2: substrate is flat.

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

Barrier of Heterogeneous Nucleation

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

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

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

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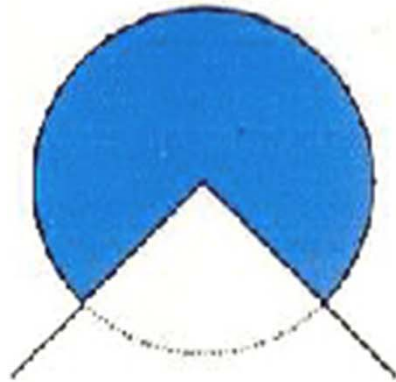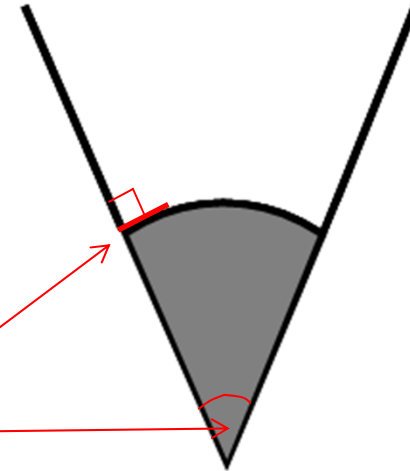
V_A

V_B

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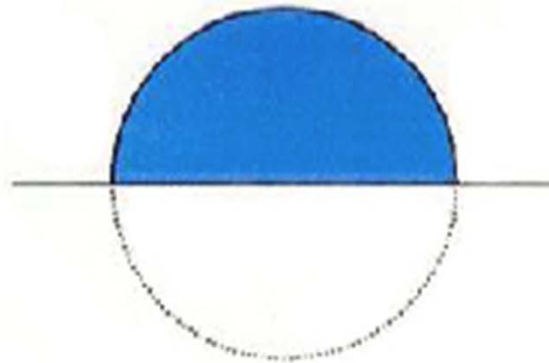
Nucleation Barrier at the crevice

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

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

contact angle = 90

groove angle = 60

$$\frac{3}{4}\Delta G^{*}_{homo}$$
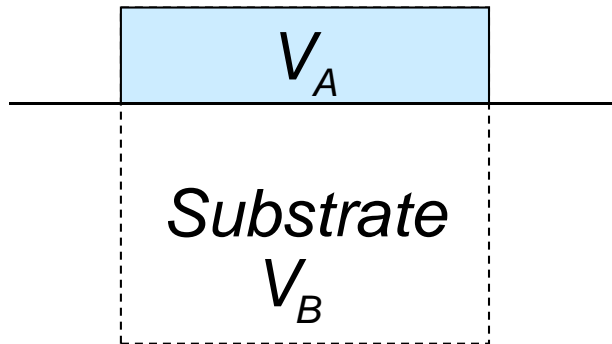
$$\frac{1}{2}\Delta G^{*}_{homo}$$

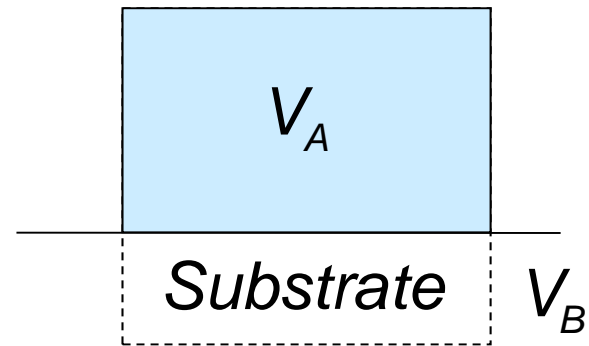$$\frac{1}{4}\Delta G^{*}_{homo}$$

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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*.

Critical radius for solid

(a)   (b)
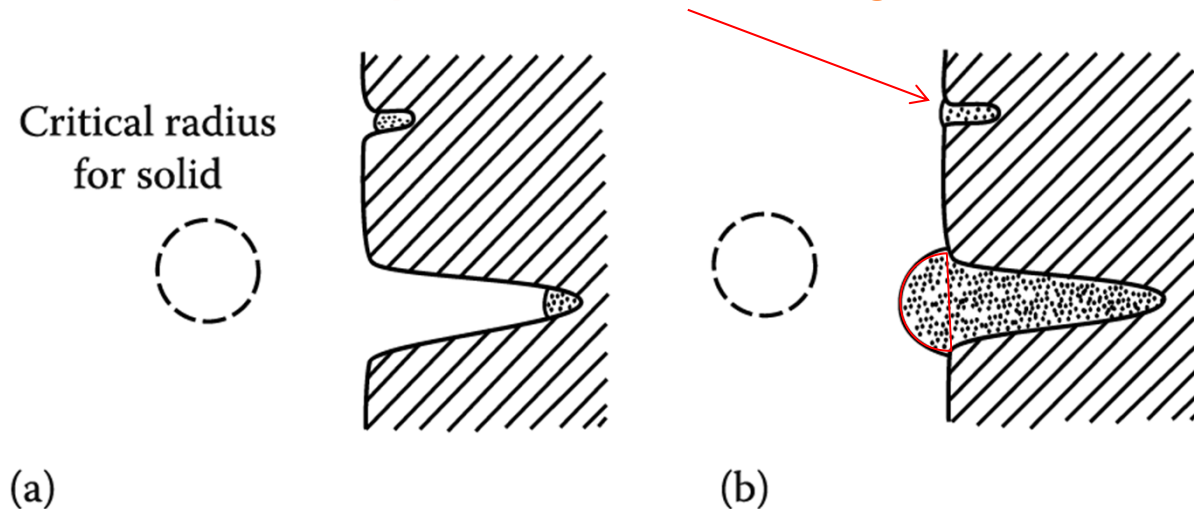
In both of the nucleation types considered so far it can be shown that

Formation of a nucleus on such a surface

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

몰드 표면에서 핵생성 될 때 필요한 에너지

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

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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?

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

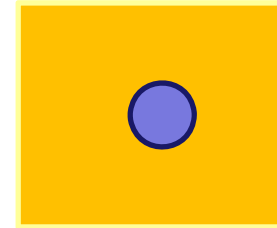**In general, wetting angle = 0** ⟹ **No superheating required!**

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid → Solid

<Thermodynamic>

• Interfacial energy ⇒ ΔT_N

Liquid T_m Undercooled Liquid   Solid

No superheating required!

• Interfacial energy ⇒ No ΔT_N

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

Melting: Liquid ← Solid

vapor

Contents for today's class

Solidification: Liquid ⟶ Solid

- **Nucleation in Pure Metals**

- **Homogeneous Nucleation**

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

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

r* & ΔG* ↓ as ΔT ↑

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

- **Heterogeneous Nucleation**

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

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

- **Nucleation of melting**

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

- **Undercooling ΔT**

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

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