Chapter 4. Solidification

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- ✓ Heat flow and interface stability

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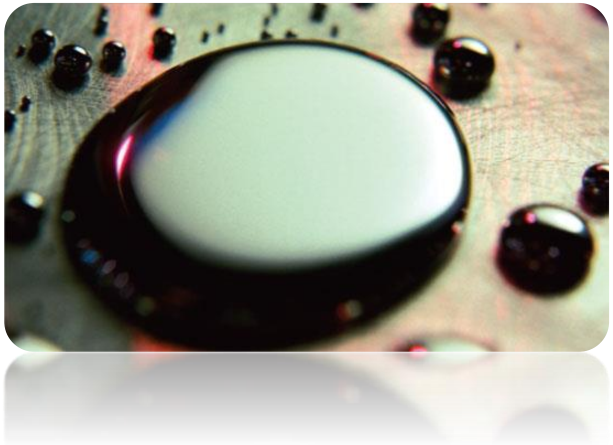
Solidification

Liquid



Solidification

Solid

- Casting
- Single crystal growth
- Directional solidification
- Rapid solidification
- ….

4.1 Nucleation in Pure Metals

T_m : $G_L = G_S$

Undercool (supercool) for nucleation : 250K ~ 1K

Homogeneous nucleation, Heterogeneous nucleation.

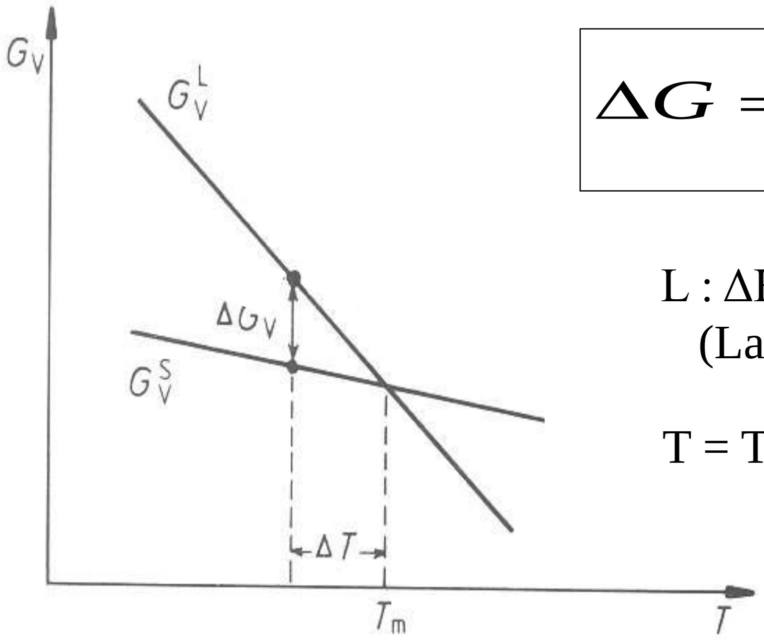
4.1.1 Homogeneous Nucleation

- Driving force for solidification

(Ch.1.2.3)

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

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

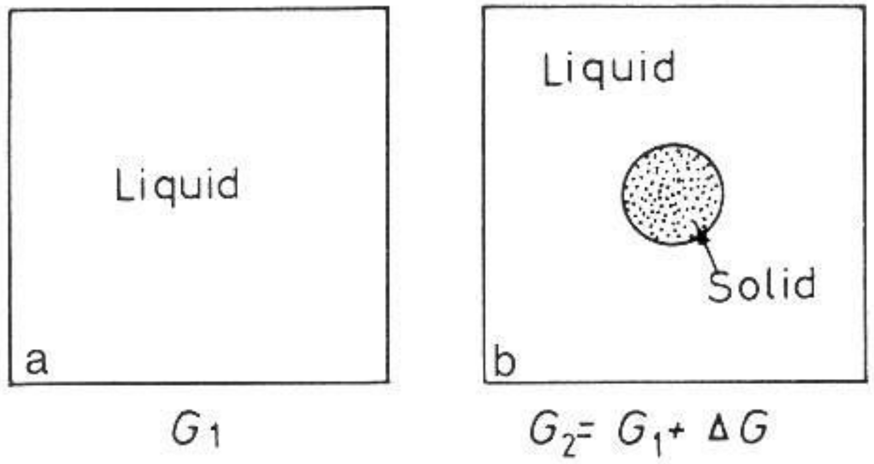


$$\boxed{\Delta G = \frac{L \Delta T}{T_m}}$$

L : $\Delta H = H^L - H^S$
(Latent Heat)

$T = T_m - \Delta T$

4.1 Nucleation in Pure Metals



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

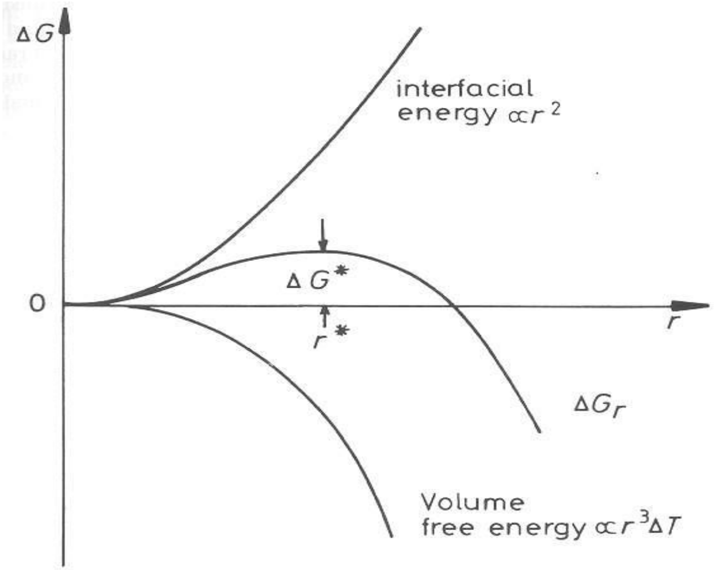
$G_V^S,\ G_V^L$: free energies per unit volume

$$\Delta G = G_2 - G_1 = -V_S\,\underbrace{(G_V^L - G_V^S)}_{\Delta G = \frac{L\Delta T}{T_m} > 0} + A_{SL}\gamma_{SL}$$

for spherical nuclei (isotropic) of radius : r

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

4.1 Nucleation in Pure Metals



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

r < r* : unstable
(lower free E by reduce size)
r > r* : stable
(lower free E by increase size)
r* : critical nucleus size

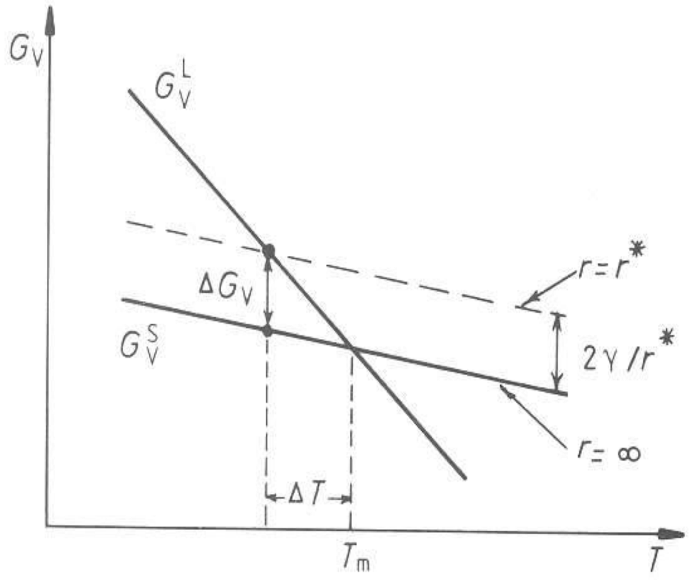
$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL} T_m}{L_V}\right)\frac{1}{\Delta T}$$

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

r* , ΔG ↓ as ΔT ↑

4.1 Nucleation in Pure Metals

- **Also from Gibbs-Thompson Eq. (Eq1.58)**
  - ✓ r* : the radius of the solid sphere that is in (unstable) equilibrium with surrounding liquid.
  - ✓ Solid sphere and liquid have the same energy.

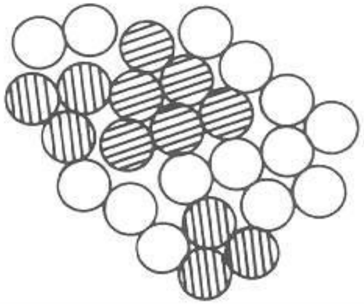


$$\frac{2\gamma V_m}{r} \ / \ \text{mol} \qquad \text{or} \qquad \frac{2\gamma}{r} \ / \ \text{unit volume}$$

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

4.1 Nucleation (Atomistic View)

- **Formation of atomic cluster**
  - ✓ Liquid 2~4% larger volume than solid.
  - ✓ Instantaneously form many close-packed cluster of atoms (same crystalline array of solid).
- **The average # of clusters of radius r**



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

n_0 : total # of atoms.
ΔG_r : excess free energy associated w/ the cluster (Eq. 4.4)

- ✓ $T > T_m$: holds for all value of r
  $T < T_m$: $r \leq r^*$
- ✓ n_r exponentially decrease with ΔG_r → Increase rapidly with r
- ✓ r이 커지면 cluster를 발견할 확률은 급속히 감소

4.1 Nucleation (Atomistic View)

- **Example**

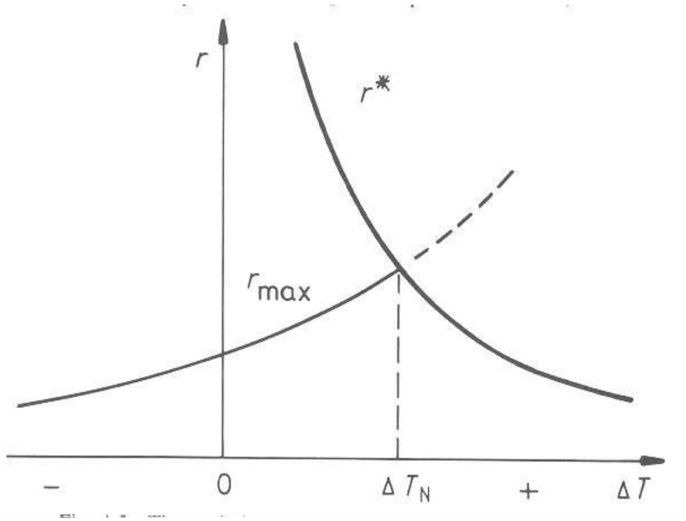
1mm^3 of Cu n_o : ~ 10^{20} atoms

at T_m 0.3nm clusters (~10 atoms) ~ 10^{14} clusters.

0.6nm clusters (~60 atoms) ~ 10 clusters

(cluster의 수는 size에 매우 sensitive)

practically, maximum cluster size r_{max} (~100 atoms)



Under cooling

$$\Delta T = T_m - T$$

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

ΔT가 증가하면 감소

ΔT_N: homogeneous nucleation이 현실적으로 가능한 supercooling temperature

4.1.2 Homogeneous Nucleation Rate

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

clusters/m^3

C_o : atoms/unit volume

C^* : # of clusters with size of C* (critical size)

Addition of one more atom to each cluster will convert to stable nuclei

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

nuclei / $m^3 \cdot s$

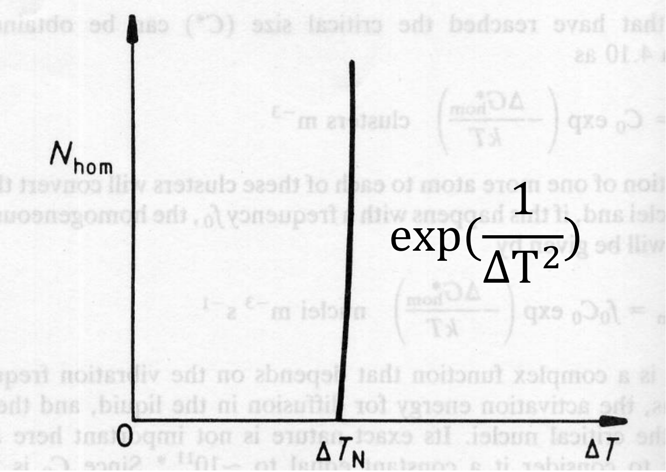
f_o : frequency ∝ (vibrational freq.), (E_a of diff. in liquid), (surface area of C*)

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

$f_0 \sim 10^{11}$

where $A = \dfrac{16\pi\gamma_{SL}{}^3 T_m{}^2}{3L_V{}^2 kT}$ ← Relatively insensitive to temperature

4.1.2 Homogeneous Nucleation Rate



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

'Explosion' of nuclei

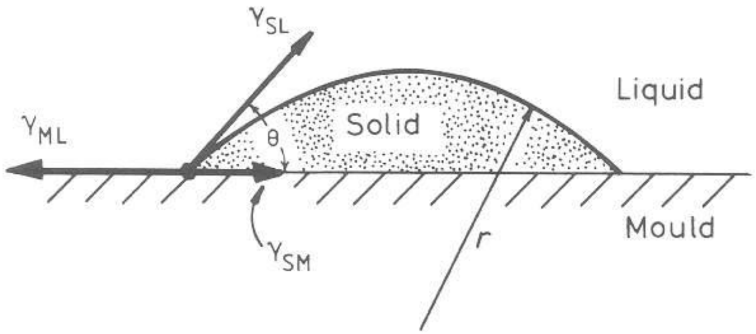
ΔT_N ~ 0.2 T_m (i.e., ~200K) for most metals

4.1.3 Heterogeneous Nucleation

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

Nucleation becomes easy if

$\gamma_{SL} \downarrow$ by forming nucleus from mould wall



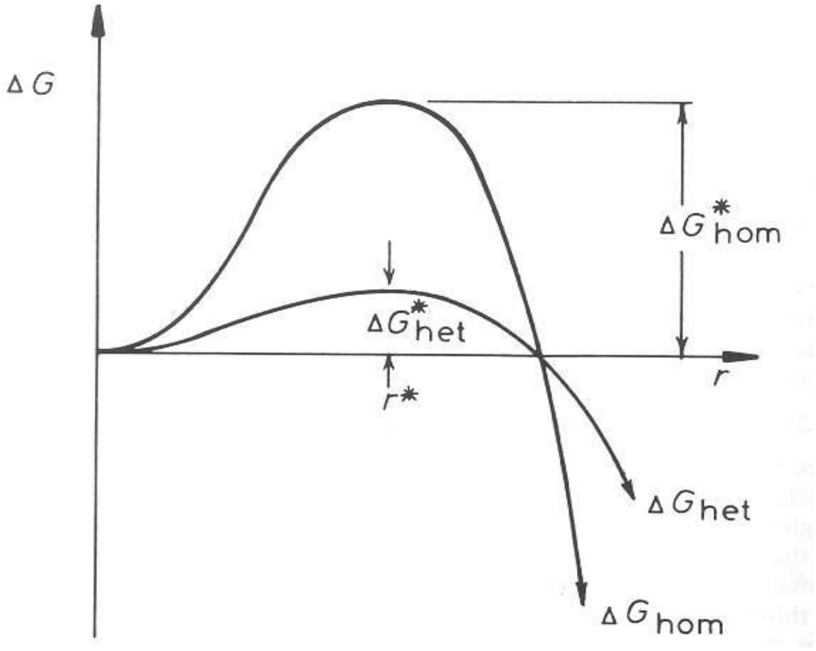
$$\gamma_{ML} = \gamma_{SL}\cos\theta + \gamma_{SM} \quad , \quad \cos\theta = (\gamma_{ML} - \gamma_{SM})/\gamma_{SL}$$

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

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

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

4.1.3 Heterogeneous Nucleation

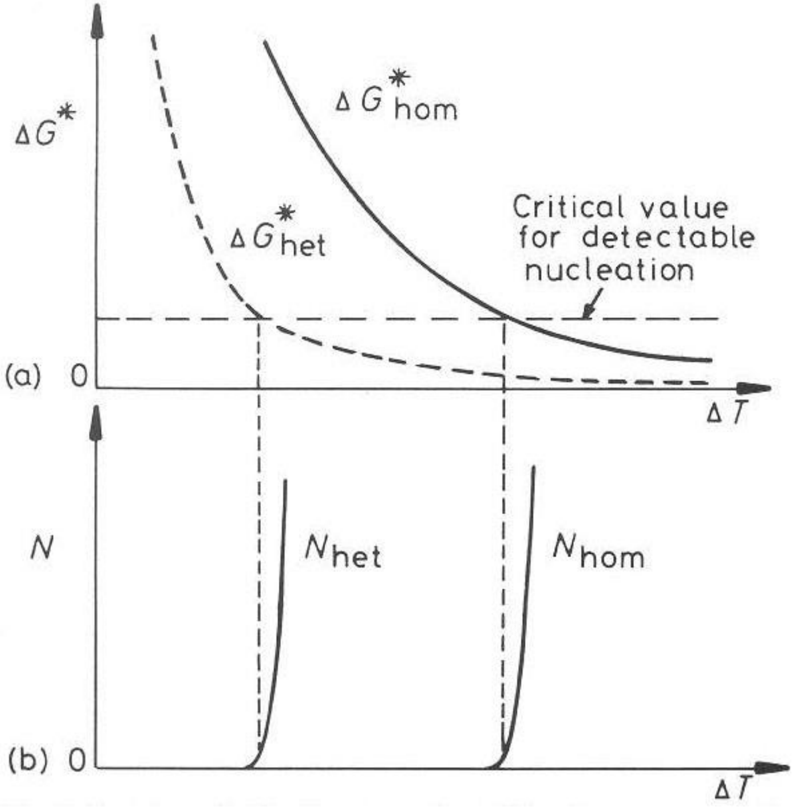


$$r^* = \frac{2\gamma_{SL}}{\Delta G_V} \quad \text{and} \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3\Delta G_V^2} \cdot S(\theta)$$

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

4.1.3 Heterogeneous Nucleation

- **The effect of ΔT on ΔG_{het}^* & ΔG_{hom}^***



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

$n*$: the number of nuclei,
n_1 : atoms in contact with the mold wall

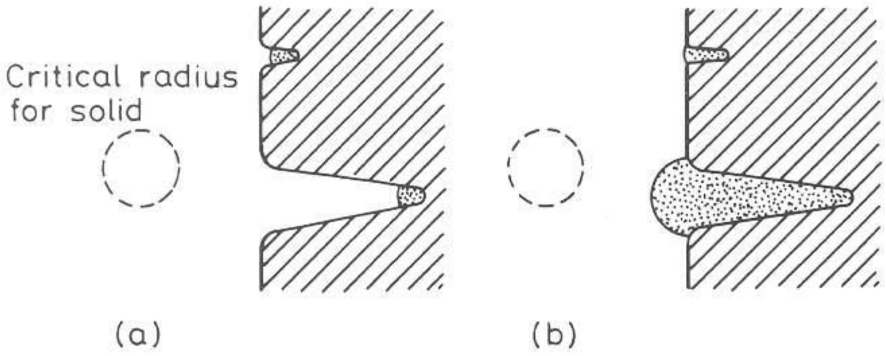
$$N_{het} = f_1 C_1 \exp\left(-\frac{\Delta G^*_{het}}{kT}\right)$$

f_1: frequency factor
C_1: # of atoms in contact with hetero nucleation sites/unit vol. of liquid

4.1.3 Heterogeneous Nucleation

만일 mould wall이 microscopically flat하지 않다면 cracks crevices

- **Nucleation inside crevices**



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

V^* : volume of critical nucleus

(cap or sphere)

Wetting angle이 크더라도 nucleation이 가능 할 수 있다.

(그러나 crack의 입구는 critical radius 보다 커야 함.)

4.1.4 Nucleation of Melting

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

일반적으로 wetting angle (θ)=0 → No superheating required!

Solid metal close to T_m

liquid/vapor + solid/vapor + solid/liquid