2009 fall

Advanced Physical Metallurgy

“Phase Equilibria in Materials”

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Contents for previous class

- **Interphase Interfaces in Solid (α/β)**

  - **Glissil Interfaces** : 전위의 이동에 의해 전진할 수 있는 반정합계면

    Shockley partial dislocation sliding ➡ Stacking fault region

    평활 이동 전위가 있는 계면의 중요한 특징: 그 면들이 결정의 모양을 변화시킬 수 있다는 것.

  - **Solid/Liquid Interfaces**

    Faceted interface > $L_f / T_m \approx 4R$ > Diffusion interface : 대부분의 금속 ~ R

    1 원자층 두께의 매우 좁은 천이대

    몇 개의 원자층에 걸쳐서 천이가 일어남

  Types of Interface

  - **Glissile Interface:** Athermal, Shape change → Military transformation
  - **Non-Glissile Interface:** Thermal, 원자들의 불규칙 도약 → Civilian transformation

- **Interphase migration**

  1) 부정합 계면처럼 계면 이동도가 매우 높다면,

  High Mobility: $\Delta\mu_B^i$ small, $X_i \approx X_e$; Diffusion-Control

  2) 계면 이동도가 낮은 경우,

  Low Mobility: $\Delta\mu_B^i$ must be large; Mixed-Control

  3) 계면 이동도가 매우 낮은 경우,

  Very low Mobility: $X_i \approx X_o$, $\left(\dfrac{\partial C}{\partial X}\right)_{intrface} \approx 0$; Interface-Control

  $\Delta\mu_B^i$ 는 최대

Contents in Phase Transformation

상변태를
이해하는데
필요한 배경

(Ch1) 열역학과 상태도: Thermodynamics

(Ch2) 확산론: Kinetics

(Ch3) 결정계면과 미세조직

대표적인 상변태

(Ch4) 응고: Liquid → Solid

(Ch5) 고체에서의 확산 변태: Solid → Solid (Diffusional)

(Ch6)고체에서의 무확산 변태: Solid → Solid (Diffusionless)

Contents for today's class

Solidification: Liquid → Solid

< Nucleation >

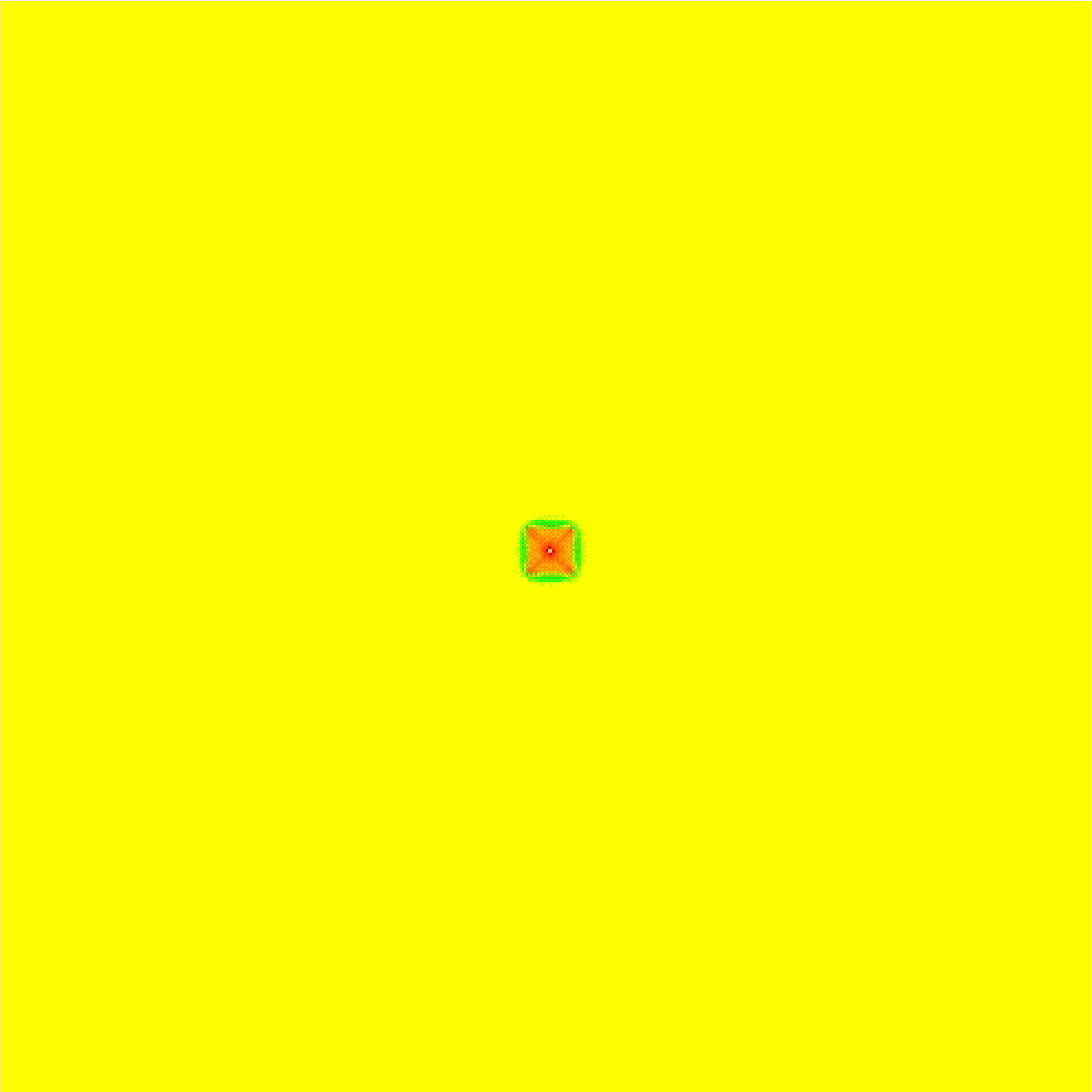
- Nucleation in Pure Metals
- Homogeneous Nucleation
- Heterogeneous Nucleation
- Nucleation of melting

&

< Growth >

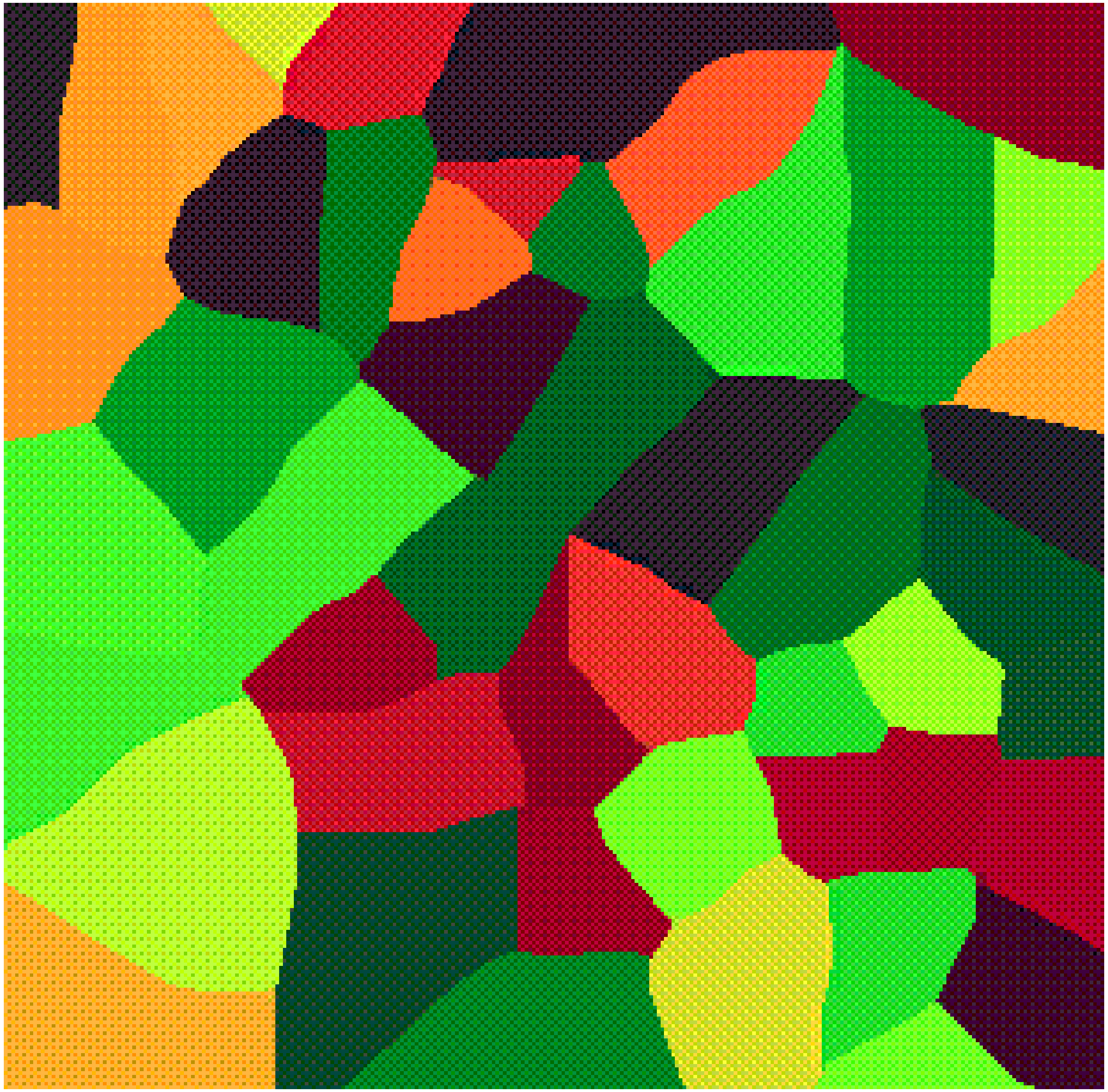
- Equilibrium Shape and Interface Structure on an Atomic Scale
- Growth of a pure solid
  1) Continuous growth
  : Atomically rough or diffuse interface
  2) Lateral growth
  : Atomically flat of sharply defined interface
- Heat Flow and Interface Stability

Solidification: Liquid → Solid



4 Fold Symmetric Dendrite Array

Solidification: Liquid → Solid



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

Solidification: Liquid → Solid

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

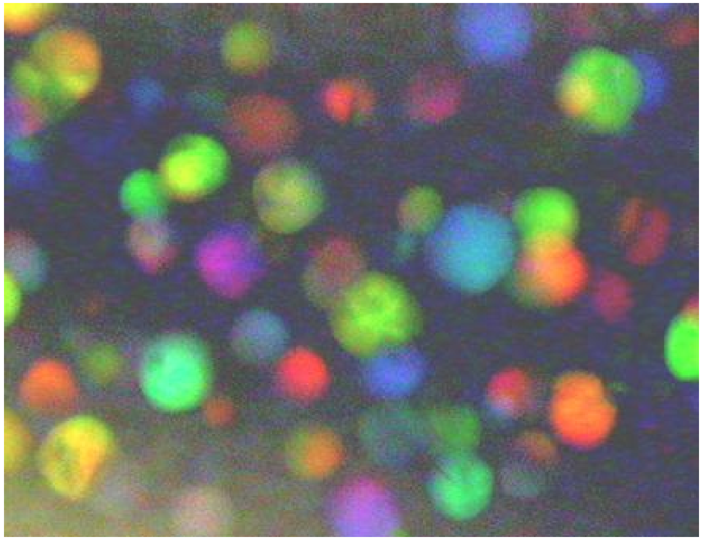
4.1. Nucleation in Pure Metals

$T_m : G_L = G_S$

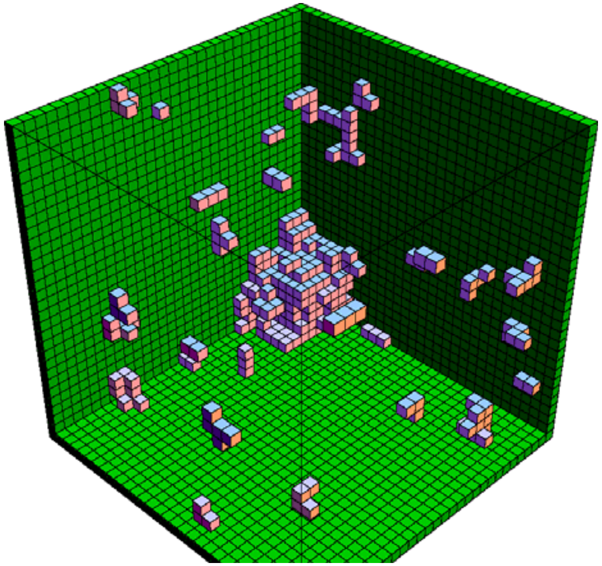
- Undercooling (supercooling) for nucleation: 250 K ~ 1 K

<Types of nucleation>

- **Homogeneous nucleation**



- **Heterogeneous nucleation**



4.1.1. Homogeneous Nucleation

Driving force for solidification

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

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

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

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

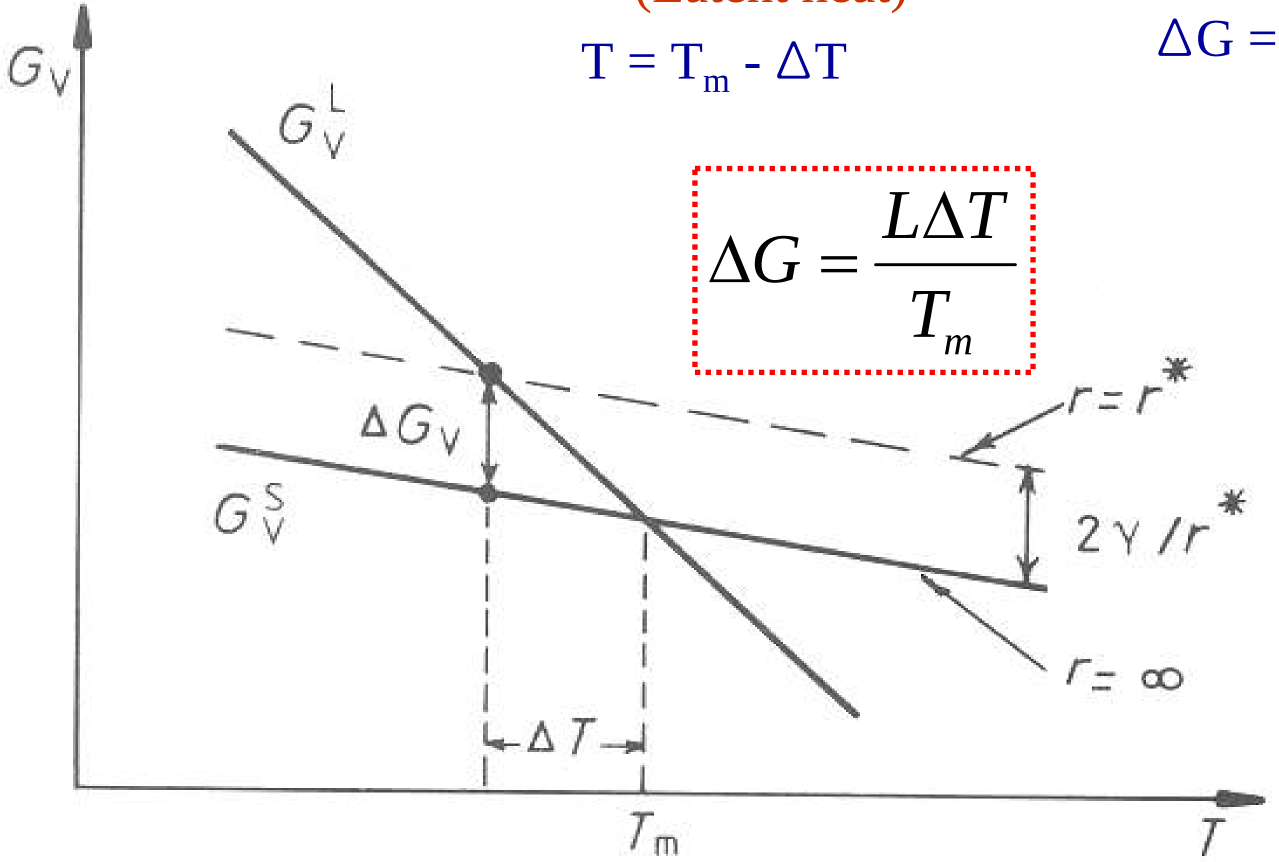
(Latent heat)

$T = T_m - \Delta T$

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

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

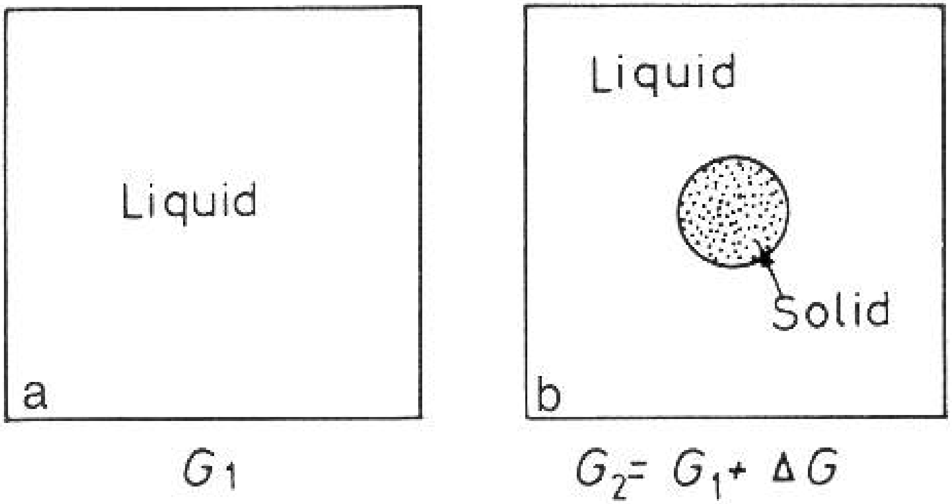
$\Delta G = L - T(L/T_m) \approx (L\Delta T)/T_m$



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

,

4.1.1. Homogeneous Nucleation



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

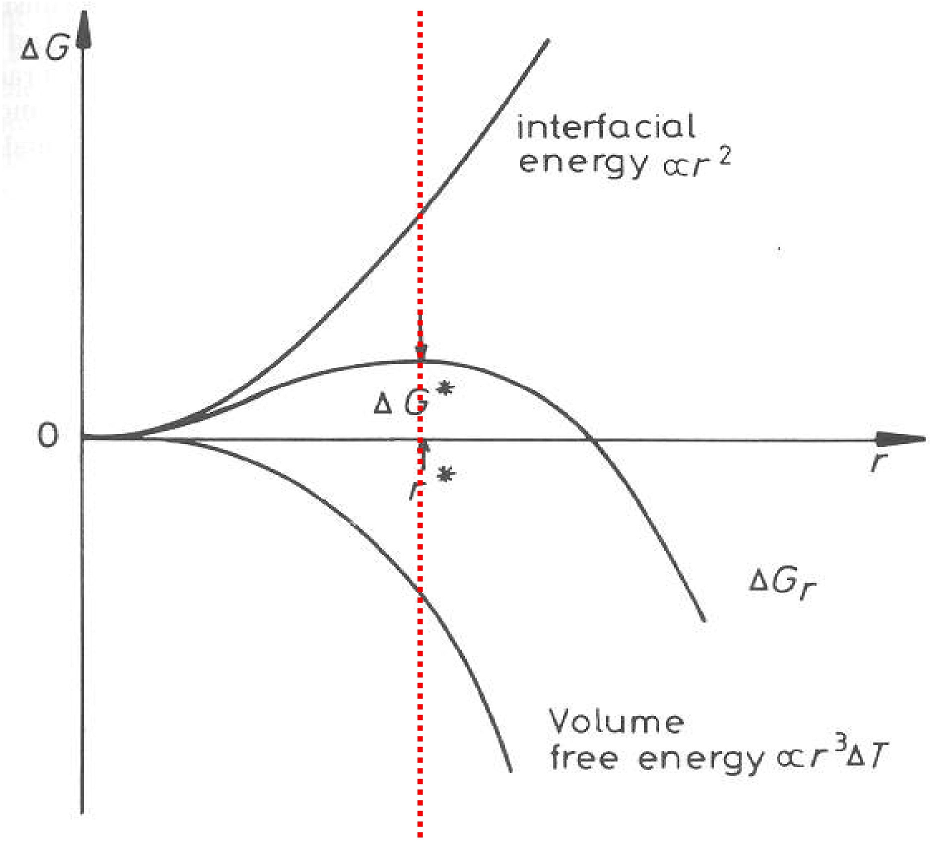
$G_V^S,\ G_V^L$ **: free energies per unit volume**

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

for spherical nuclei (isotropic) of radius : r

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

4.1.1. Homogeneous Nucleation



Unstable equilibrium

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^* ⇨ **$dG=0$**

Fig. 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

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

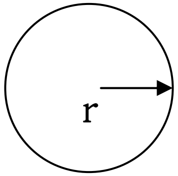
ΔG of a supersaturated solute in liquid in equilibrium with a particle of radius, r

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

Equil. condition for open system

→ Δμ should be the same.

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



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

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

r*: in (unstable) equilibrium with surrounding liquid

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

The creation of a critical nucleus ~ thermally activated process

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

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

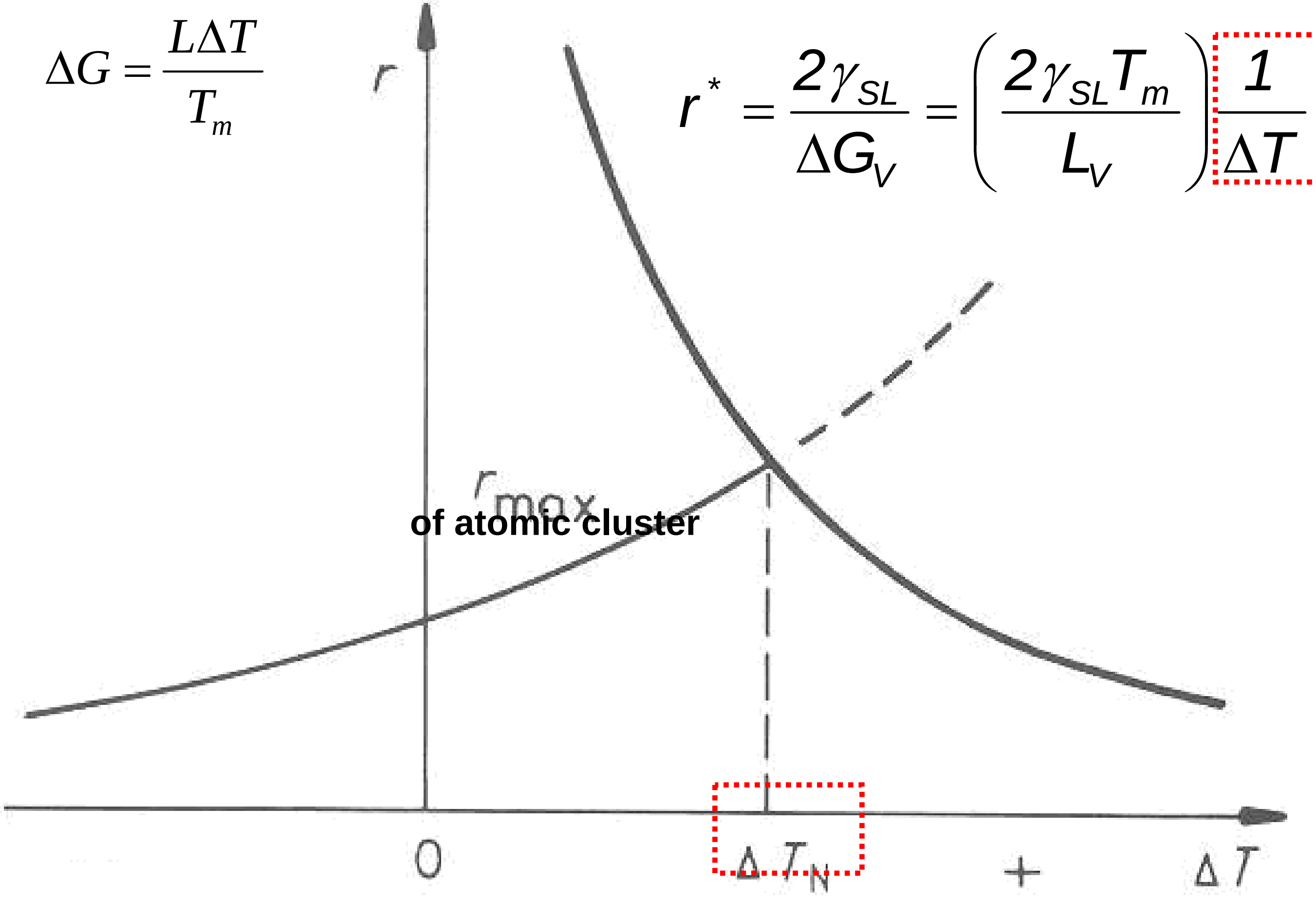


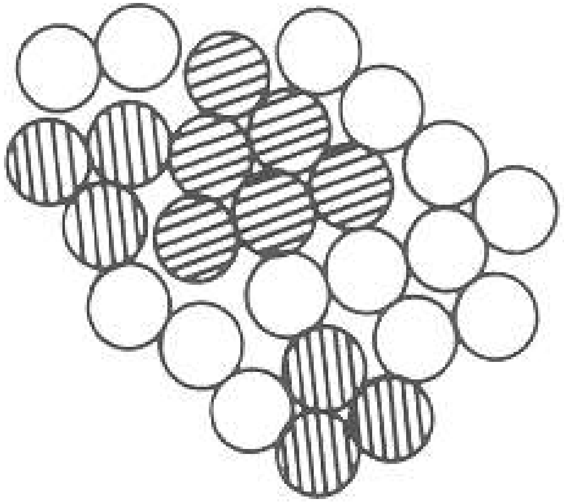
Fig. 4.5 The variation of r* and r_{max} with undercooling ΔT

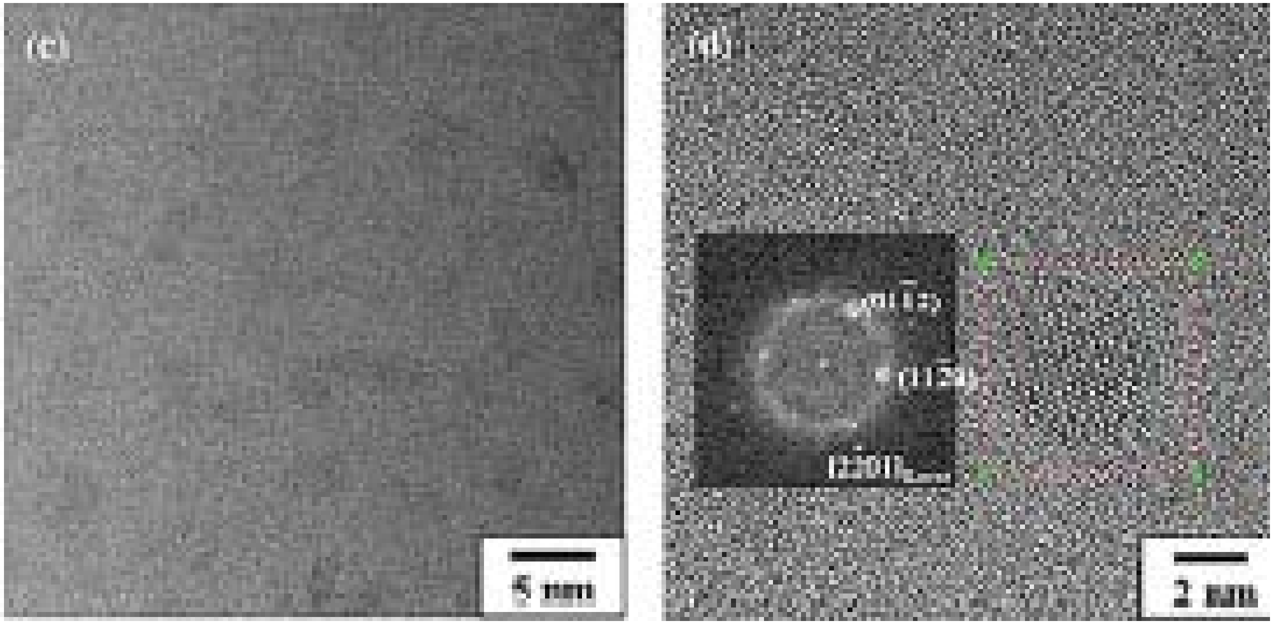
The number of clusters with r^* at < ΔT_N is negligible.

Formation of Atomic Cluster

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

Fig. 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?

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

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

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

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

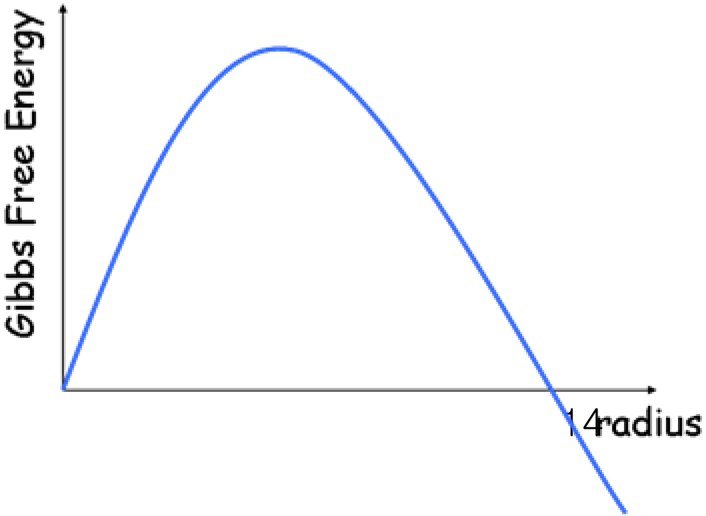
$$\vdots$$

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

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

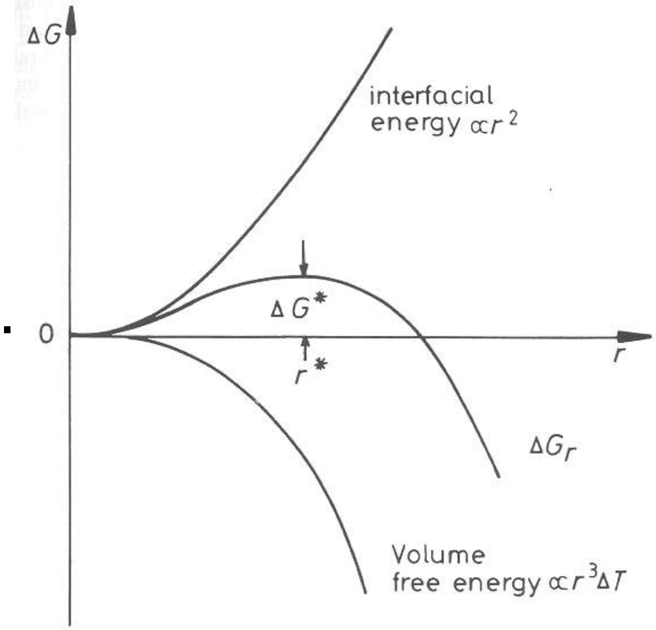
$$n_m = n_1 \exp\left(-\frac{\Delta G^{1\rightarrow m}}{kT}\right)$$

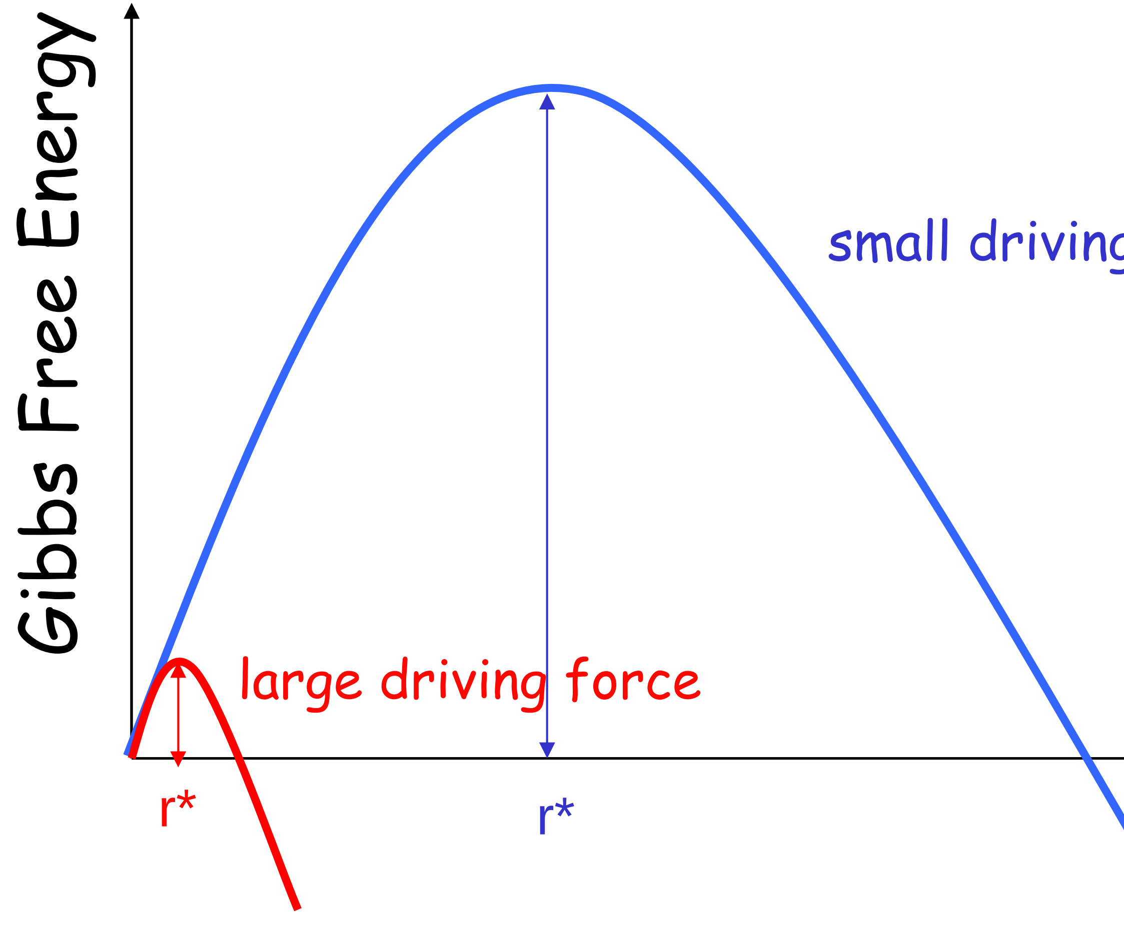
$$n_r = n_0 \exp\left(-\frac{\Delta G_r}{kT}\right)$$



Formation of Atomic Cluster

Compare the nucleation curves between small and large driving forces.





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

Formation of Atomic Cluster

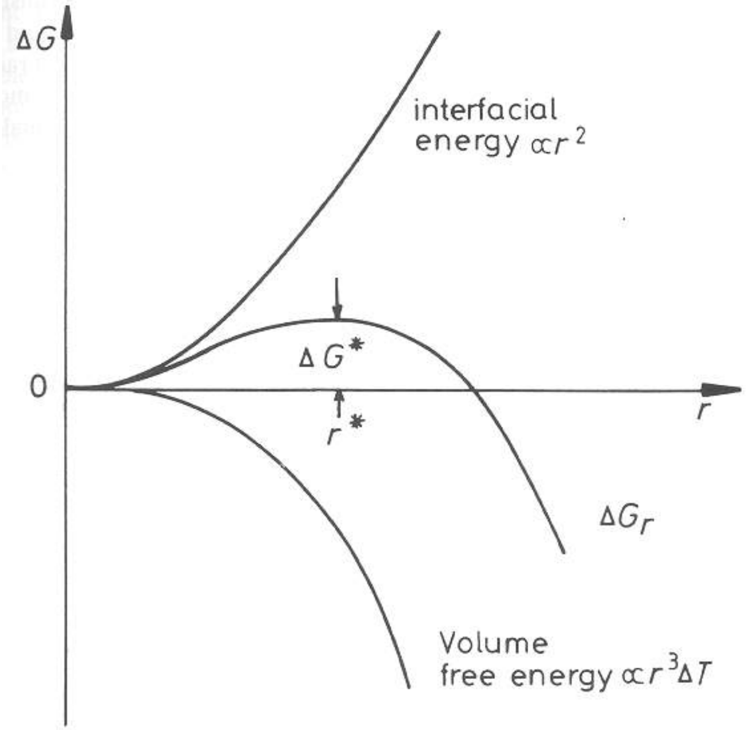
n_o : total # of atoms.

ΔG_r : excess free energy associated with the cluster

# of cluster of radius r

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

- holds for T > T_m or T < T_m and r ≤ r*
- n_r exponentially decreases with ΔG_r



Ex. 1 mm^3 of copper at its melting point (no: 10^{20} atoms)

→ ~10^{14} clusters of 0.3 nm radius (i.e. ~ 10 atoms)

→ ~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

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

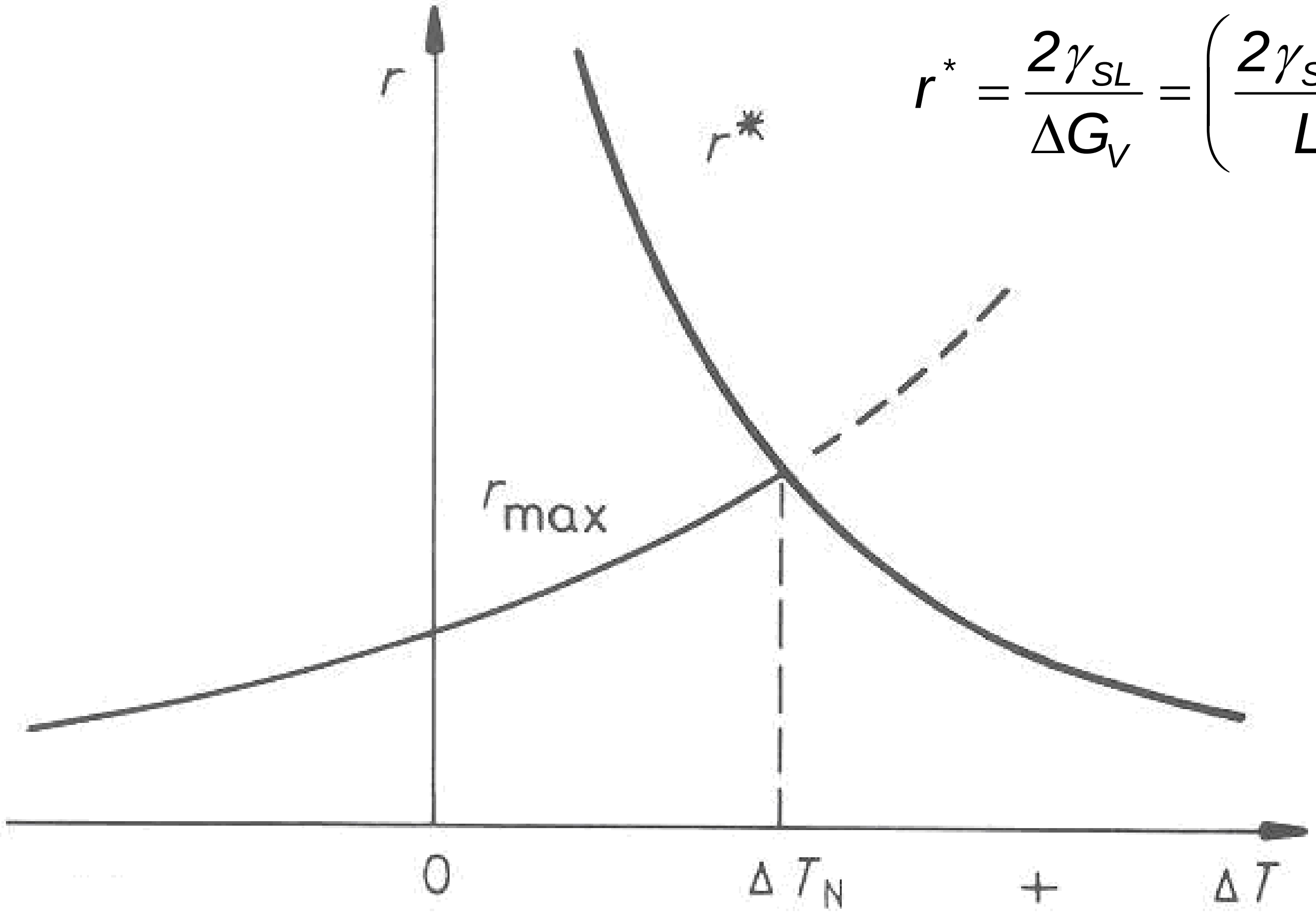


Fig. 4.5 The variation of r* and r_{max} with undercooling ΔT

The number of clusters with r^* at $< \Delta T_N$ 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)

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

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

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

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

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

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

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

4.1.2. The homogeneous nucleation rate - kinetics

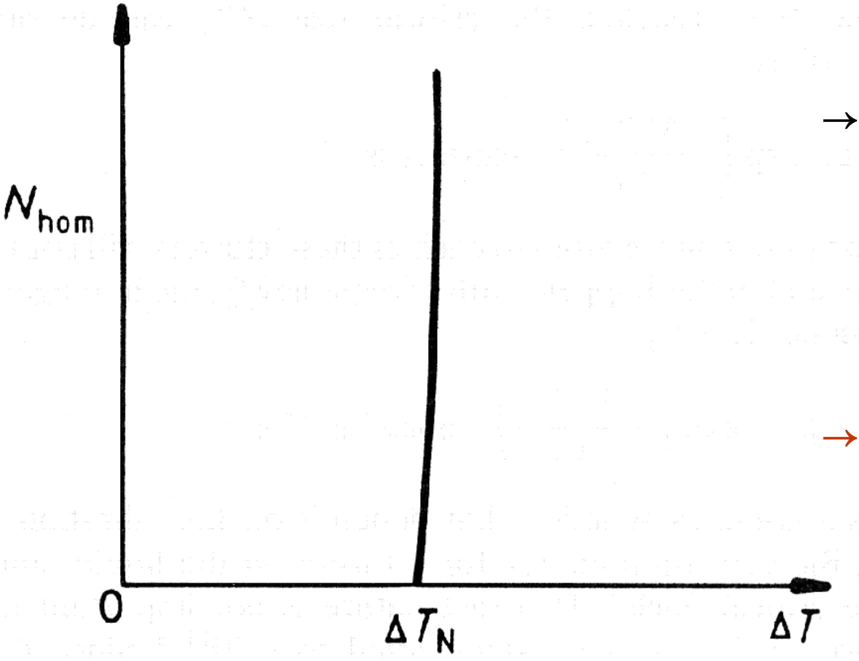
$$N_{\text{hom}} \approx f_0 C_o \exp\{-\frac{A}{(\Delta T)^2}\}$$

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

: insensitive to Temp

How do we define 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. ~200K)

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

Real behavior of nucleation

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.

In the refrigerator, however, water freezes even ~ 1 K below zero.

In winter, we observe that water freezes ~ a few degrees below zero.

Why this happens? What is the underlying physics?

Which equation should we examine?

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

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

Normally undercooling as large as 250 K are not observed.

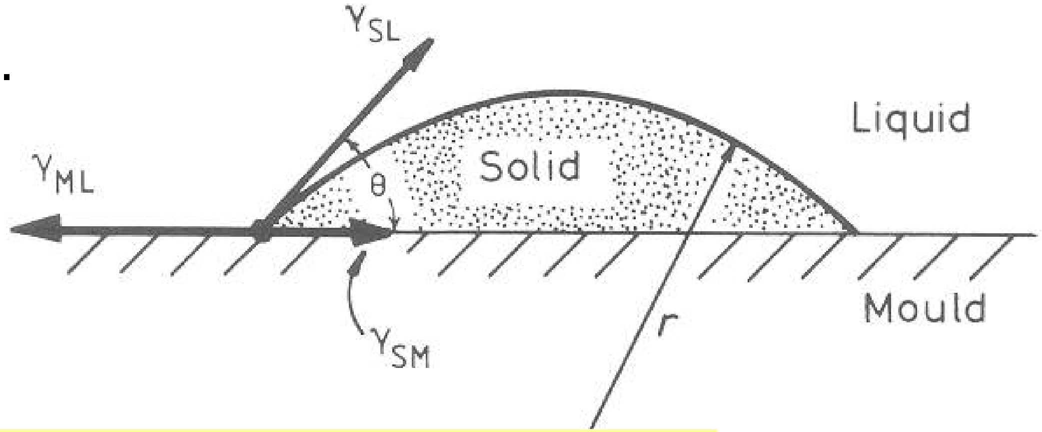
The nucleation of solid at undercooling of only ~ 1 K is common.

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

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



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

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

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

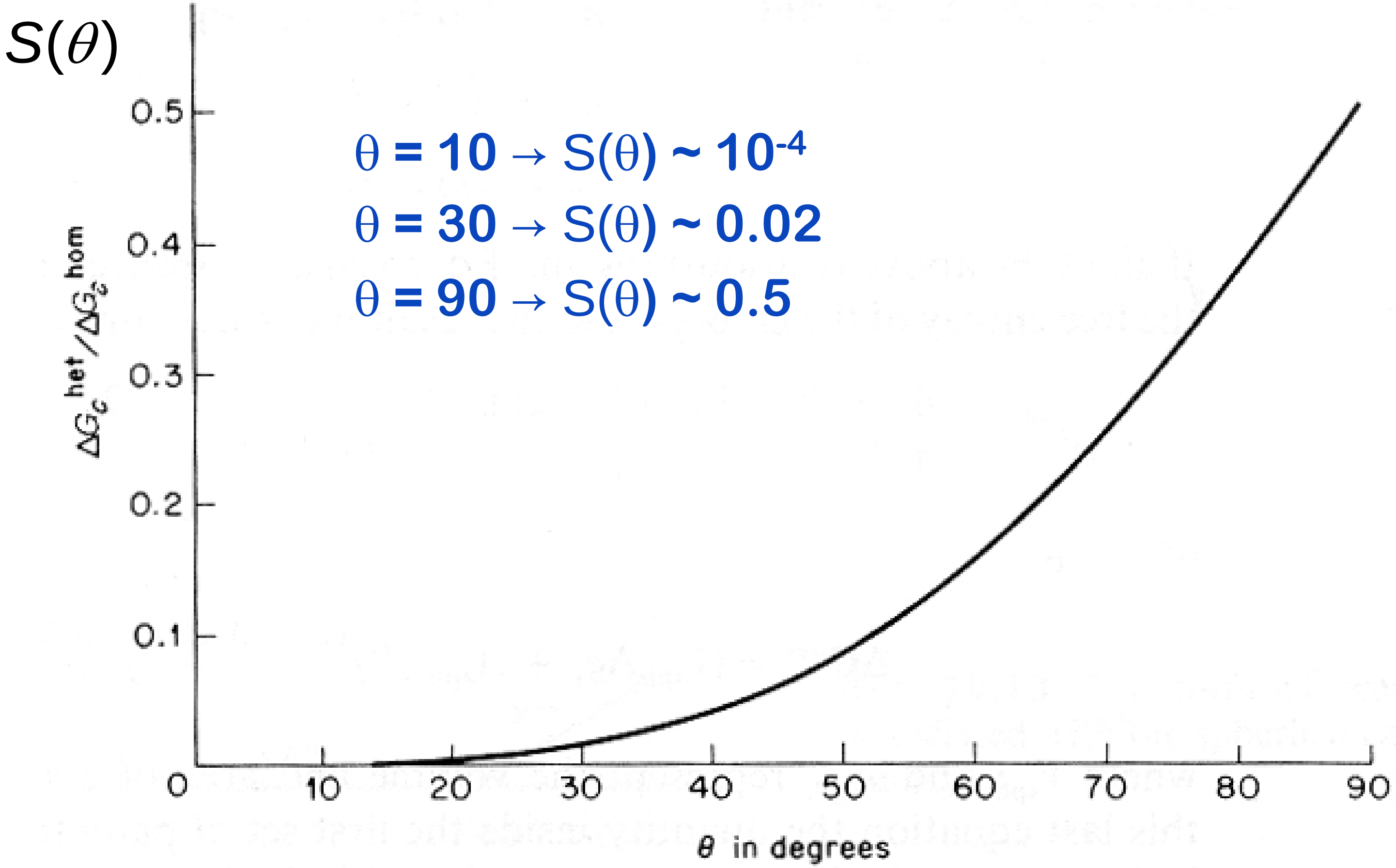
In terms of the wetting angle (θ) and the cap radius (r) **(Exercies 4.6)**

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

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)

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



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)

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

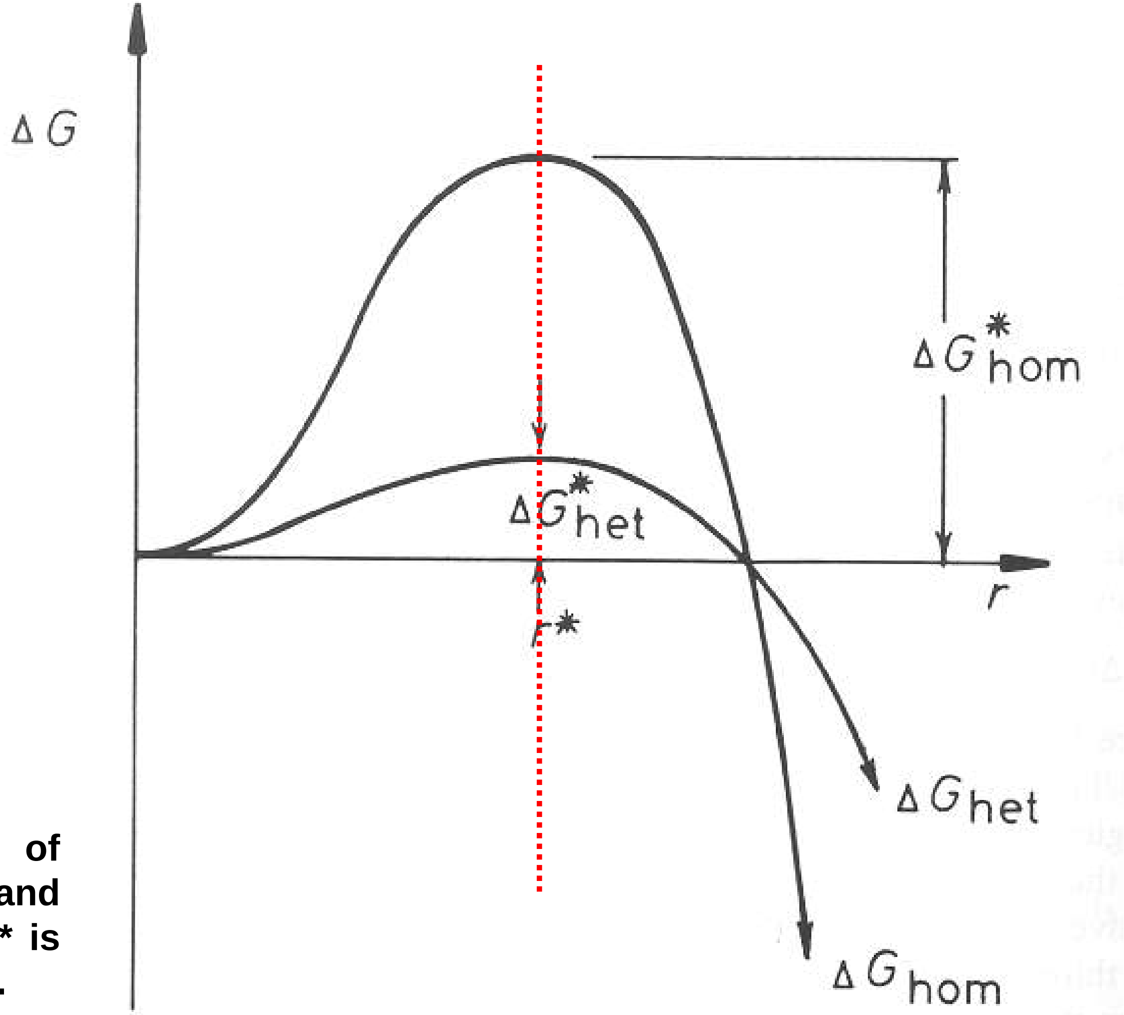
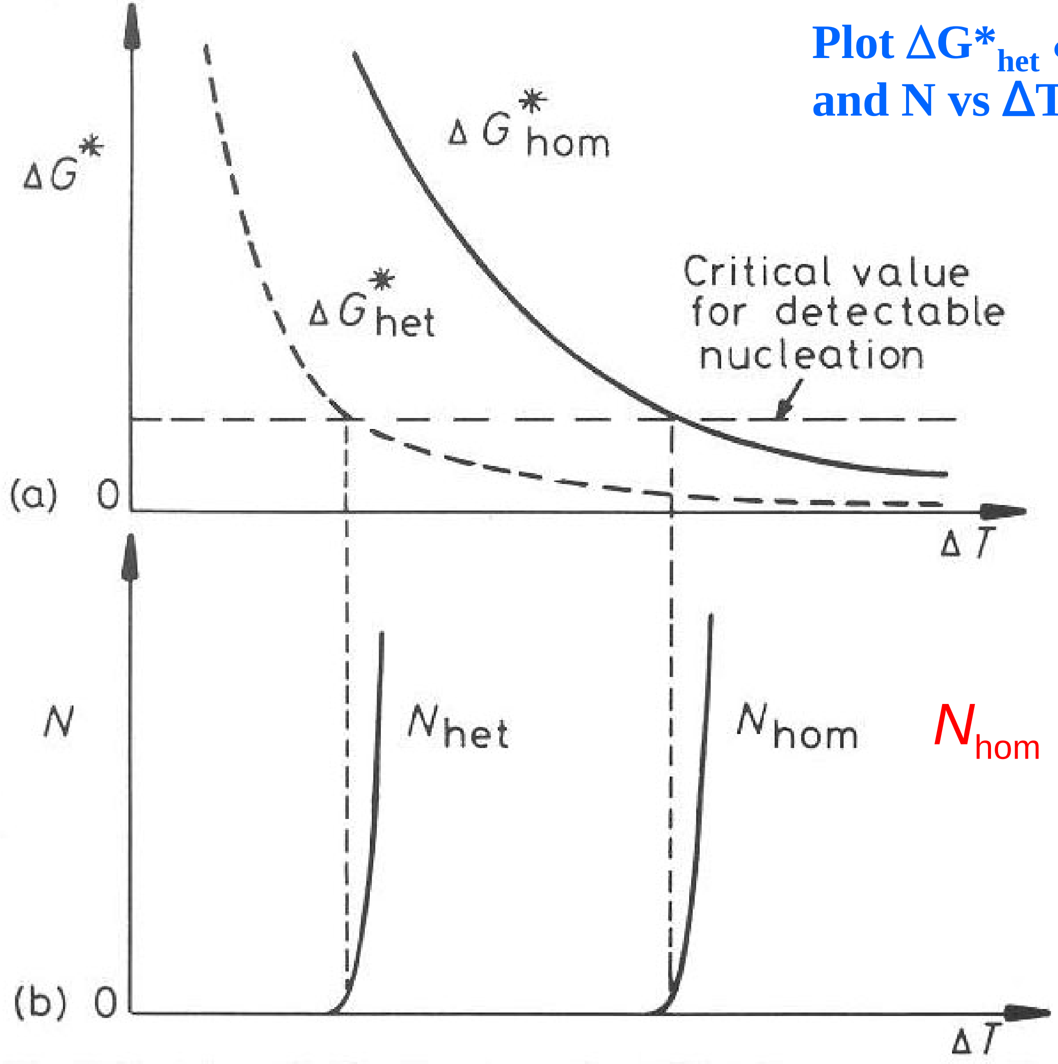


Fig. 4.8 The excess free energy of solid clusters for homogeneous and heterogeneous nucleation. Note r* is independent of the nucleation site.

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

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

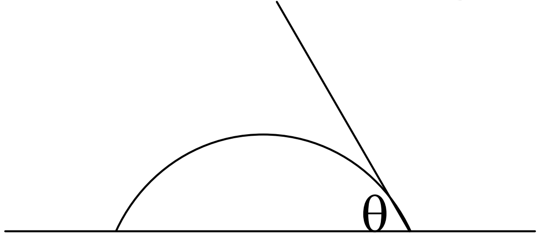


$N_{hom} \approx 1\,\text{cm}^{-3}s^{-1}$

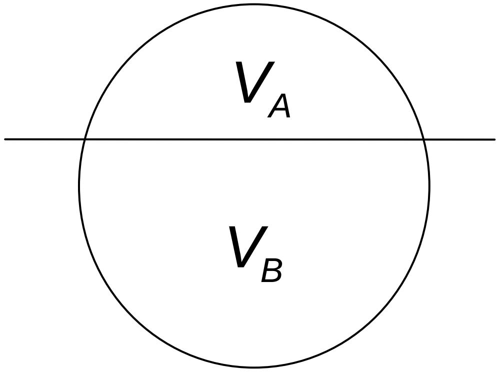
Fig. 4.9 (a) Variation of ΔG^* with undercooling (ΔT) for homogeneous and heterogeneous nucleation. (b) The corresponding nucleation rates assuming the same critical value of ΔG^*

Barrier of Heterogeneous Nucleation

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



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



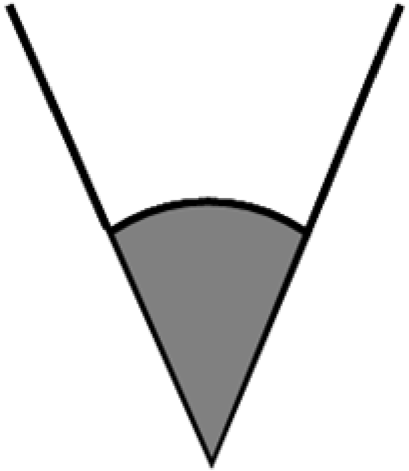
$$\Delta G_{sub}^* = \Delta G_{homo}^* \left(\frac{2-3\cos\theta+\cos^3\theta}{4}\right)$$

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

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

Nucleation Barrier at the crevice

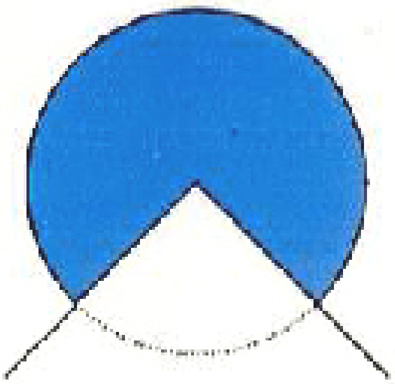
What would be the shape of nucleus and the nucleation barrier for the following conditions?



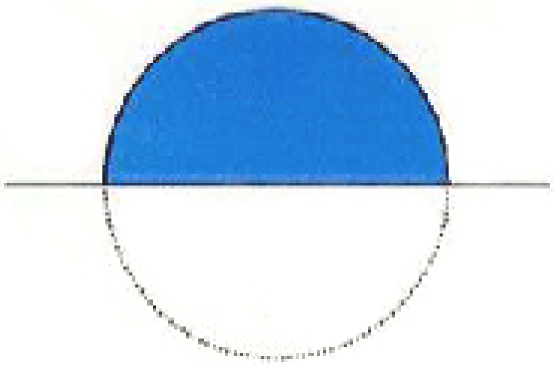
contact angle = 90

groove angle = 60

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



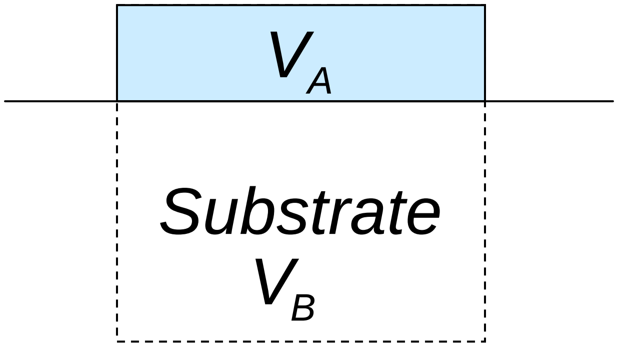
$$\frac{3}{4}\Delta G^{*}_{\text{homo}}$$



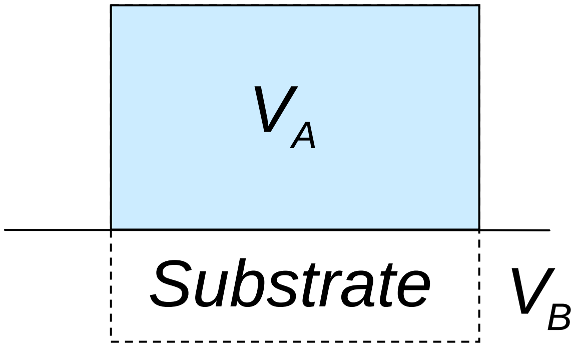
$$\frac{1}{2}\Delta G^{*}_{\text{homo}}$$

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

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

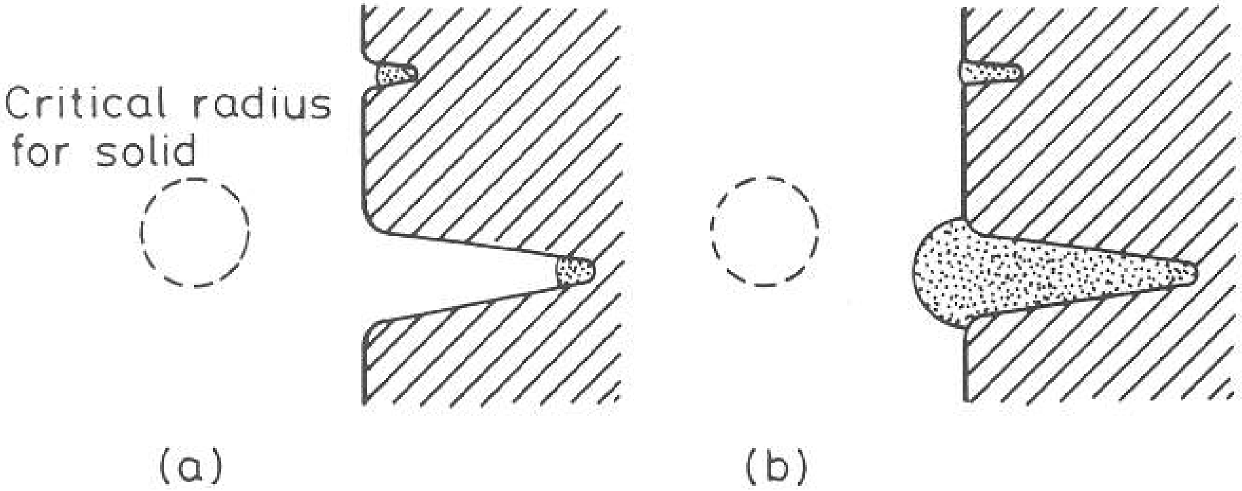
Nucleation inside the crevice

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

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

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

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 inteface decreasing below r*.



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

4.1.4. 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.

Why?

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

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