

Phase Transformation of Materials

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Chapter 4.

Solidification

1. Nucleation in pure metals



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Liquid → Solid

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



Homogeneous nucleation

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

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

$$\Delta G_{1 \rightarrow 2} = G_2 - G_1$$

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

$$= V_S \Delta G_V^{L \rightarrow S} + A_{SL} \gamma_{SL}$$

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

For spherical nuclei (isotropic) of radius : r

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

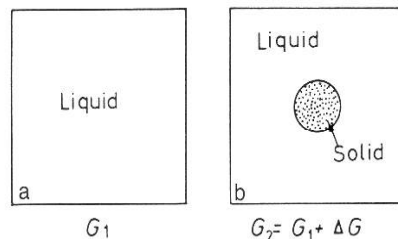


Fig. 4.1 Homogeneous nucleation.



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

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

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

$r < r^*$: unstable
(ΔG decreases by dissolving)

$r > r^*$: stable
(ΔG decreases by growing)

r^* : critical nucleus size

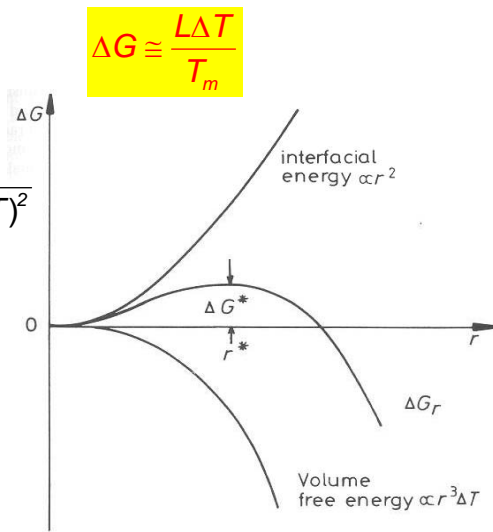


Fig. 4.2 The free energy change associated with homogeneous nucleation of a sphere of radius r .



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

$$\Delta G_V = \frac{2\gamma}{r} \rightarrow r = \frac{2\gamma}{\Delta G_V}$$



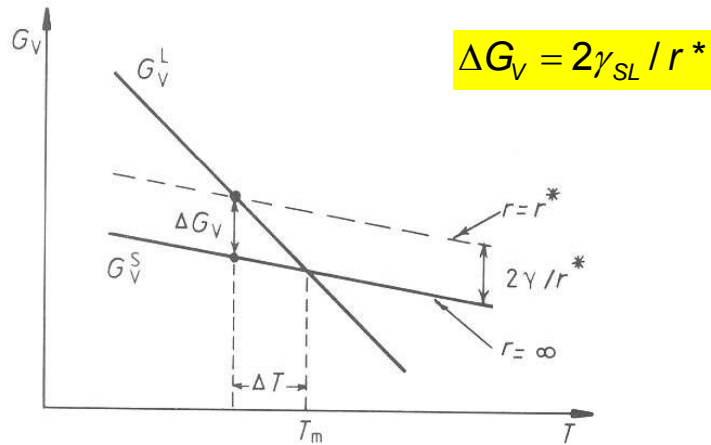


Fig. 4.3 Volume free energy as a function of temperature for solid and liquid phases, showing the origin of ΔG_V and r^* .



Formation of Atomic Cluster

At the melting point the liquid phase has a volume 2-4% greater than the solid.

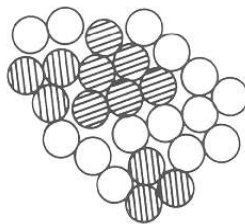


Fig. 4.4

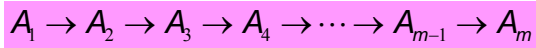
A two-dimensional representation of an instantaneous picture of the liquid structure. Many close-packed crystal-like clusters (shaded) are present.

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 ?





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

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

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

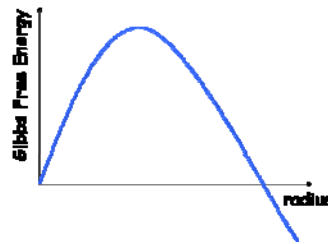
⋮

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

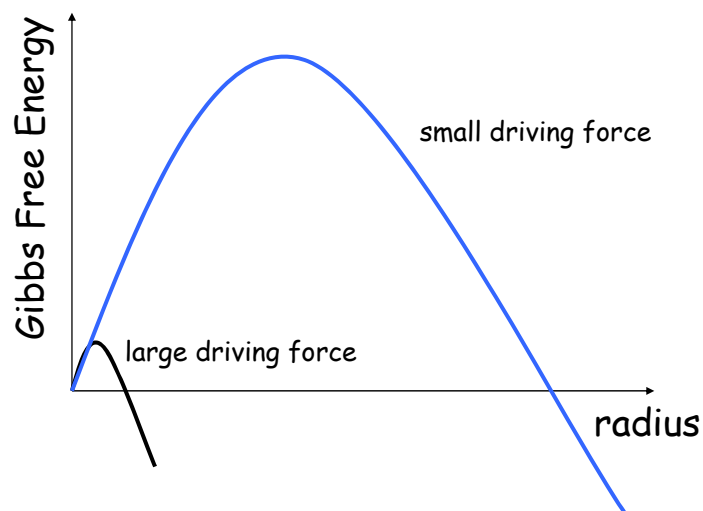
$$n_m = n_1 \exp\left(-\frac{\Delta G^{1 \rightarrow 2} + \Delta G^{2 \rightarrow 3} + \dots + \Delta G^{m-1 \rightarrow m}}{kT}\right)$$

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

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



Compare the nucleation curves between small and large driving forces.



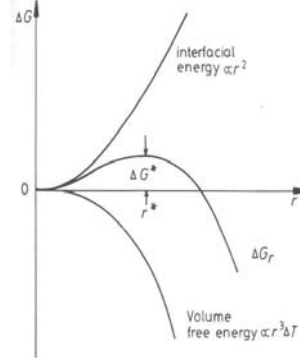
n_0 : total # of atoms.

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 $r \leq r^*$
- n_r exponentially decreases with ΔG_r



1 mm³ of copper at its melting point ($\sim 10^{20}$ atoms)

→ $\sim 10^{14}$ 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**

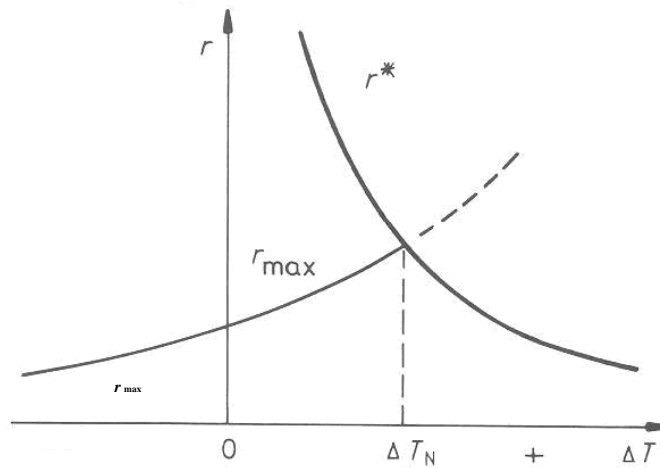


Fig. 4.5 The variation of r^* and r_{\max} with undercooling ΔT

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



4.1.2 The homogeneous nucleation rate

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

C_0 : atoms/unit volume.

C^* : # of clusters w/ size of C^* (critical size)

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

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

$$N_{\text{hom}} = f_0 C_0 \exp\left(-\frac{\Delta G_{\text{hom}}^*}{kT}\right) \quad \text{nuclei / m}^3 \cdot \text{s} \quad \Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_V)^2} = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3 L_V^2}\right) \frac{1}{(\Delta T)^2}$$



$$N_{\text{hom}} \approx f_0 C_0 \exp\left\{-\frac{A}{(\Delta T)^2}\right\}$$

$$A = \frac{16\pi\gamma_{SL}^3 T_m^2}{3 L_V^2 kT} \quad : \text{insensitive to Temp}$$

How do we define ΔT_N ?

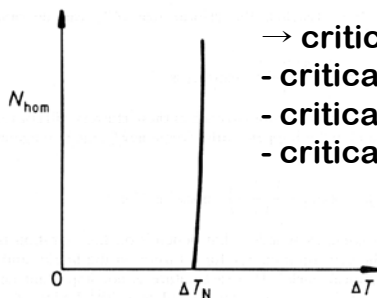
$$N_{\text{hom}} \approx 1 \text{ cm}^{-3} \text{ s}^{-1} \quad \text{when } \Delta G^* \sim 78 \text{ kT}$$

f_0 : frequency \propto

- The vibration frequency of the atoms,
- The activation energy for diffusion in the liquid,
- The surface area of the critical nuclei

$$f_0 \sim 10^{11}$$

$$C_0 \sim 10^{29} \text{ atoms/m}^3$$



- critical value for detectable nucleation
- critical supersaturation ratio
 - critical driving force
 - critical supercooling

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



Problems that will be asked in the next class

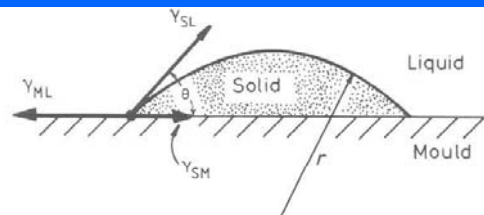
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Nucleation on the wall

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

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



When nucleation takes place on the mould wall as shown in the figure, the free energy change for nucleation can be written as follows.

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

Here, V_s is the volume of the nucleus with a shape of a spherical cap and A_{SL} and A_{SM} are areas of solid-liquid and solid-mould interfaces, respectively.

Express V_s , A_{SL} and A_{SM} in terms of the wetting angle (θ) and the cap radius (r). And using these expressions, derive the new simplified expression of ΔG_{het} .

