



EMA5001 Lecture 12

Solidification via Homogeneous Nucleation



Phase Transformation

❑ Solid state phase transformation

- Heterogeneous transformation
 - Transformation occur at particular locations
 - Always involve creation and migration of interface
 - Often go through nucleation & growth
- Homogeneous transformation
 - Transformation everywhere in the materials
 - May or may not involve creation of interface

❑ Most phase transformation go through nucleation & growth

- Creation of interface – nucleation
- Migration of interface – growth



Classification of Nucleation & Growth Type Phase Transformation

□ Classification

Type	<i>Military</i>	<i>Civilian</i>			
Effect of temperature	Athermal	Thermal activated			
Interface type	Glissile	Non-glissile			
Composition of precipitate and parent phase	Same composition	Same composition	Different composition		
Nature of diffusion	No diffusion	Short-range diffusion	Long-range diffusion		
Rate limiting step	Interface control	Interface control	Interface control	Diffusion control	Mixed control
Examples	Martensite, Twinning	Grain growth, $\alpha \leftrightarrow \gamma$ in Fe	Bainite	Solidification	Eutectoid



Solidification & Crystallization

Applications

- Casting metal parts (e.g., iron and steel, bronze, aluminum)
- Casting of semiconductors (e.g., Si)
- Growth of single crystals (e.g., Al_2O_3)

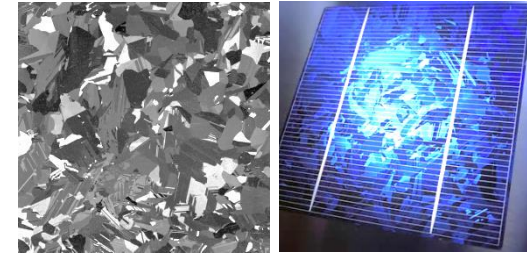
Topics

- Driving force & barrier
- Critical conditions
- Rate
- Impacts of
 - Composition
 - Processing condition (e.g., T)
 - Interfaces

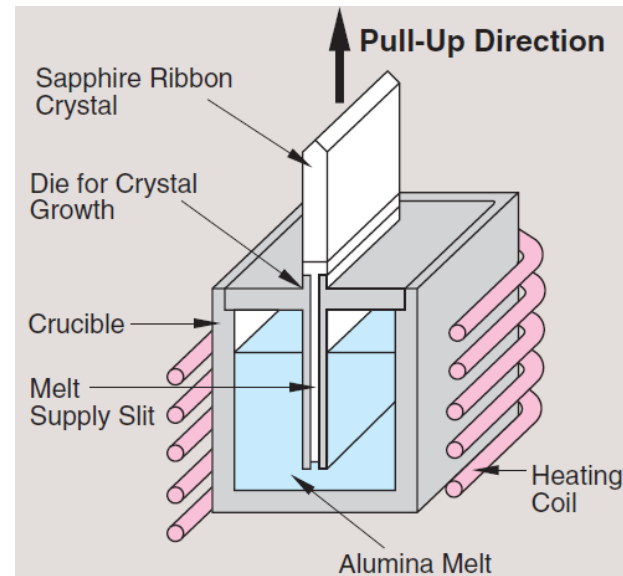


<http://pveducation.org/pvc/drom/manufacturing/multi-crystalline-silicon>

Multi-crystalline Si for solar cells

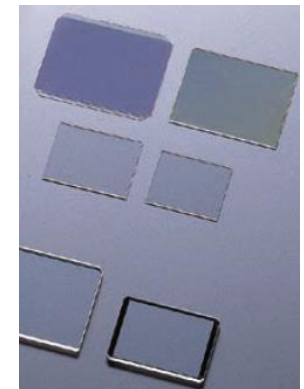


http://www.m0ukd.com/Solar_Panels/



<http://americas.kyocera.com/kicc/pdf/Kyocera%20Sapphire.pdf>

Sapphire (Al_2O_3) for advanced display and lighting

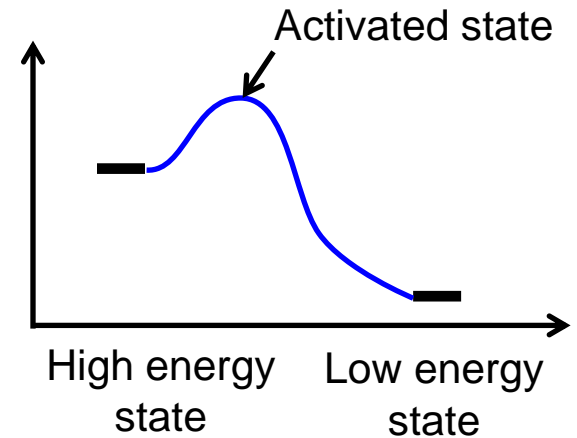




Barriers in Reactions & Phase Transformation

❑ Examples of a Process Thermodynamically Favorable yet not Readily Occurring

- Oxidation of carbohydrates at room temperature
- Complete oxidation of stainless steel or aluminum
- Liquid metal droplets undercooled below its melting point



❑ Origins of the “Barrier”

- Carbohydrate oxidation - Splitting of oxygen molecules
- Stainless steel or aluminum oxidation - Diffusion of oxygen or metal through the oxide shell to sustain the reaction
- Solidification of liquid - Creation of new surface or interfaces
 - Nucleation of solid (or a new phase) and creation of the interface
 - Growth of the nucleus and movement of the interface



Homogeneous Nucleation & Heterogeneous Nucleation

Homogeneous Nucleation

- Uniform throughout, no special location
- Need large driving force (e.g., undercooling)
- Less common

Heterogeneous Nucleation

- Occurring at special locations (local defects: interfaces, impurities, etc.)
- Small driving force (e.g., undercooling)
- Depend on features and concentration of the defects (interfaces or impurities)
- Common



Homogeneous Nucleation for Liquid Solidification (1)

□ Energy change in homogeneous nucleation

Define

V_S Volume for solid nucleus

V_L Volume for remaining liquid

G_v^L Gibbs free energy per unit volume of liquid

G_v^S Gibbs free energy per unit volume of solid

γ_{SL} Solid-liquid Interfacial energy

A_{SL} Solid-liquid Interfacial area

Total free energy of the liquid **before** nucleation

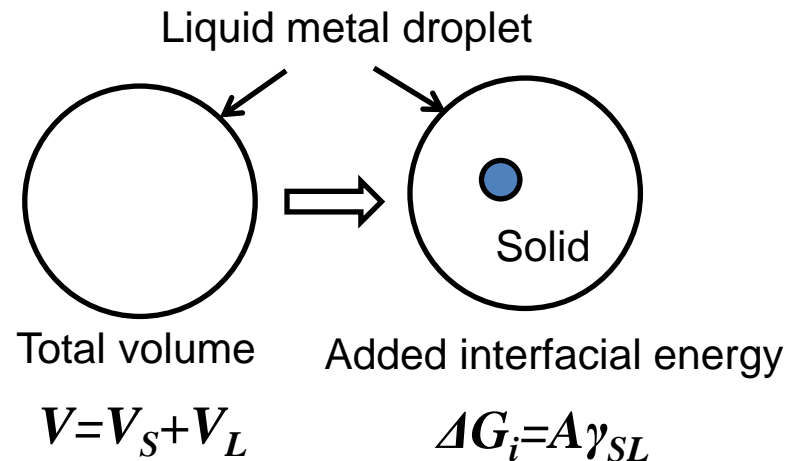
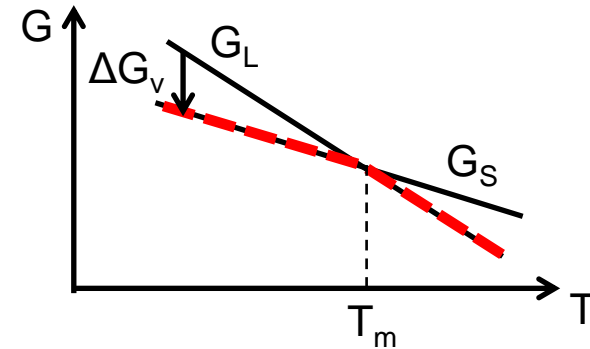
$$G_1 = (V_S + V_L)G_v^L$$

Total free energy of the **after** nucleation

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

Free energy change in this process:

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





Homogeneous Nucleation for Liquid Solidification (2)

□ Continue from p.5

We have $\Delta G = -V_S(G_v^L - G_v^S) + A_{SL}\gamma_{SL}$

Define $\Delta G_v = G_v^L - G_v^S$

We have $\Delta G = -V_S\Delta G_v + A_{SL}\gamma_{SL}$

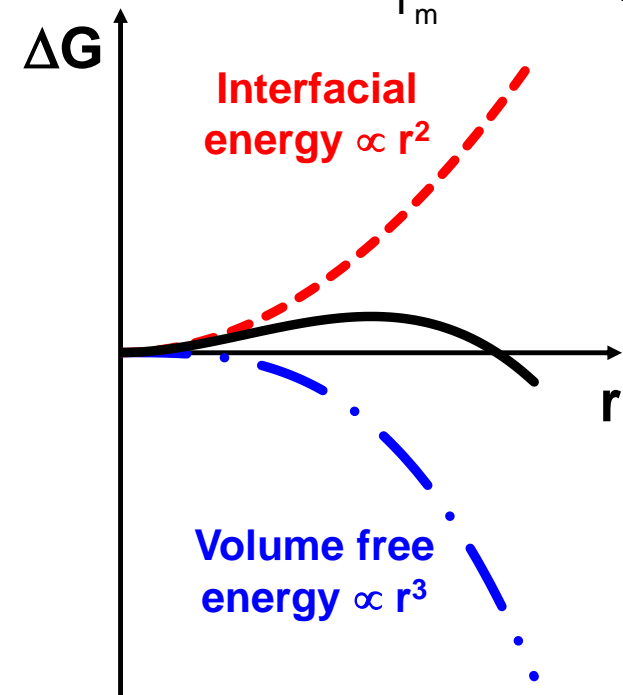
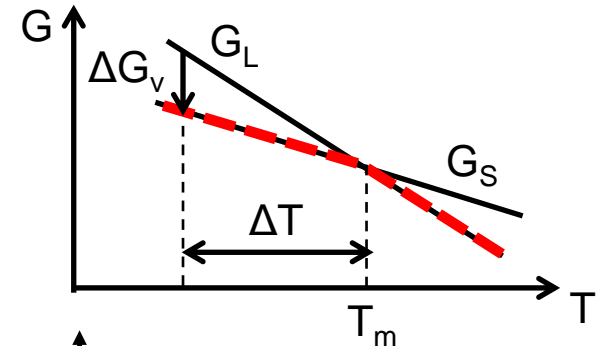
ΔG_v is a function of temperature or undercooling

L_v is the latent heat of fusion per unit volume

$$\Delta G_v = \frac{L_v \Delta T}{T_m}$$

If γ_{SL} isotropic & the nucleus takes spherical shape

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





Verification of Relationship between Volume Free Energy Change & Undercooling

□ Proof

$$\Delta G_v = \frac{L_v \Delta T}{T_m}$$

At melting point T_m : $\Delta G_v = 0 = \Delta H - T_m \Delta S = -L_v - T_m \Delta S$

Which means:

$$\Delta H = -L_v = T_m \Delta S \quad \Delta S = -\frac{L_v}{T_m}$$

At a temperature below melting point, T $\Delta G_v = \Delta H - T \Delta S$

Assuming enthalpy and entropy change in solidification do NOT change with temperature

$$\Delta G_v = \Delta H - T \Delta S = -L_v - T \Delta S = -L_v - \left(-T \frac{L_v}{T_m} \right) = \frac{T - T_m}{T_m} L_v = \frac{\Delta T}{T_m} L_v$$



Critical Radius & Free Energy Change

□ Continue from p. 6

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

Critical nucleus size r^*

$$\frac{d\Delta G}{dr} = 0$$

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

$$\Delta G^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_v)^2}$$

- $r < r^*$, nucleus shrinks; $r > r^*$, nucleus grows

Knowing

$$\Delta G_v = \frac{L_v \Delta T}{T_m}$$

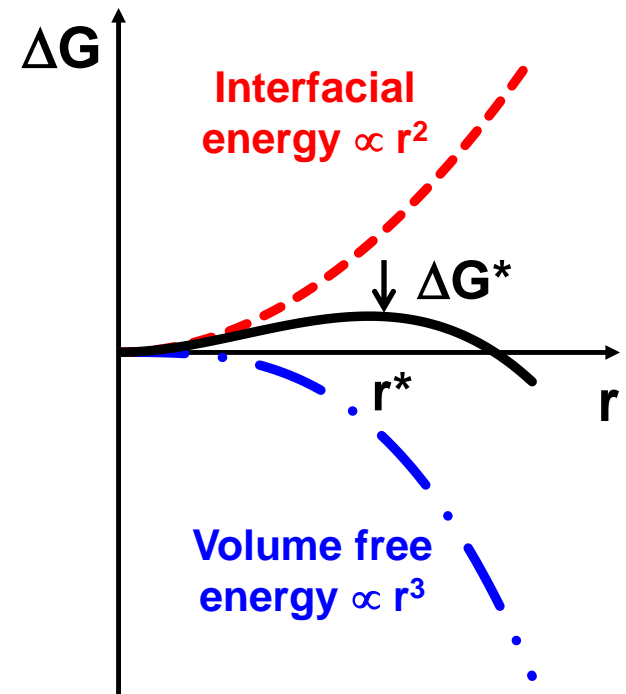
We have

$$r^* = \frac{2\gamma_{SL} T_m}{L_v} \cdot \frac{1}{\Delta T}$$

$$r^* \propto \frac{1}{\Delta T}$$

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

$$\Delta G^* \propto \frac{1}{\Delta T^2}$$



**When $\Delta T \rightarrow 0$,
 r^* and ΔG^* both $\rightarrow \infty$,
 homogeneous nucleation
 will NOT occur!**



Verification of Nucleation Barrier

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL} \quad r^* = \frac{2\gamma_{SL}}{\Delta G_v}$$

$$\Delta G = -\frac{4}{3}\pi \left(\frac{2\gamma_{SL}}{\Delta G_v}\right)^3 \Delta G_v + 4\pi \left(\frac{2\gamma_{SL}}{\Delta G_v}\right)^2 \gamma_{SL}$$

$$\Delta G = -\frac{4}{3}\pi \frac{8\gamma_{SL}^3}{(\Delta G_v)^2} + 4\pi \frac{4\gamma_{SL}^3}{(\Delta G_v)^2}$$

$$\Delta G = \left(-\frac{32}{3}\pi + 16\pi\right) \frac{\gamma_{SL}^3}{(\Delta G_v)^2}$$

$$\Delta G^* = \frac{16}{3}\pi \frac{\gamma_{SL}^3}{(\Delta G_v)^2}$$



Critical Nucleus Size & Maximum Cluster Size

□ Continue from p.7

$$r^* = \frac{2\gamma_{SL}T_m}{L_v} \cdot \frac{1}{\Delta T}$$

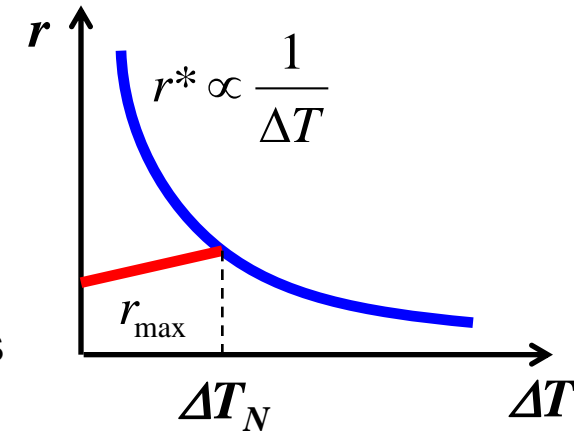
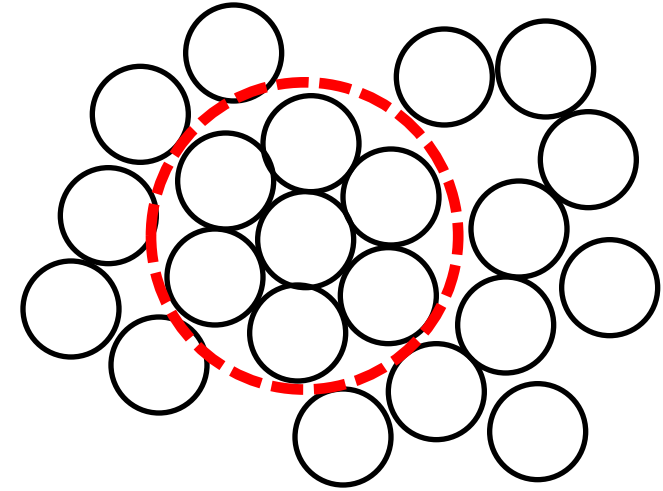
The number of solid clusters with size r , n_r

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

n_0 The total number of atoms

ΔG_r Excess energy for cluster of size r , $\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$

- For a given $\Delta T > 0$ ($\Delta G_v > 0$), when $r < r^*$:
 $r \uparrow$, $\Delta G_r \uparrow$, $n_r \downarrow$ dramatically \rightarrow
 There is effectively a **“maximum” cluster** in the liquid
- When $\Delta T \uparrow$, $\Delta G_v \uparrow \rightarrow$ for a given r , $\Delta G_r \downarrow$, $n_r \uparrow$, $r_{max} \uparrow$
- $\Delta T < \Delta T_N$, $r_{max} < r^*$, no homogeneous nucleation
- $\Delta T \geq \Delta T_N$, $r_{max} > r^*$, homogeneous nucleation occurs





Homogeneous Nucleation Rate

□ Define

C^* Number density of nucleus with size r^*

C_0 Atom density

ΔG_{hom}^* Homogeneous nucleation energy

f_0 Frequency of adding one more atom to a nucleus

Nucleation rate ($\text{m}^{-3}\text{s}^{-1}$)

$$N_{\text{hom}} = f_0 C_0 \exp\left(-\frac{\Delta G_{\text{hom}}^*}{kT}\right)$$

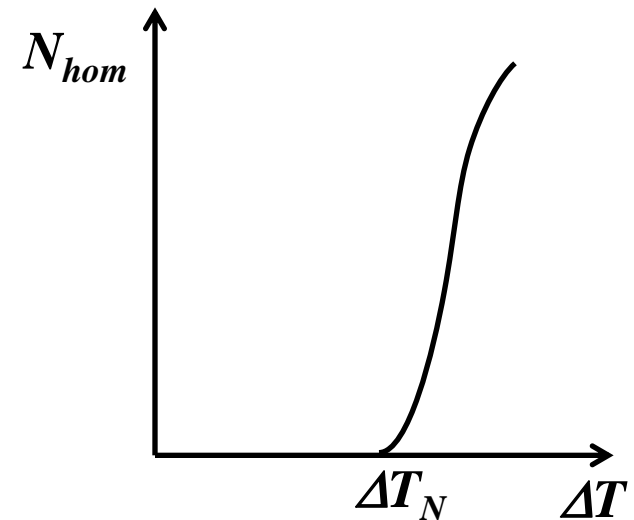
For homogeneous nucleation

$$\Delta G_{\text{hom}}^* = \Delta G^* = \frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2} \cdot \frac{1}{\Delta T^2}$$

We have

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

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



Sudden increase of nucleation rate

$$\Delta T_N \sim 0.2 T_m$$