



EMA5001 Lecture 17

Nucleation in Precipitation



Precipitation

□ Precipitation

- Change in solubility with temperature
- Often used for strengthening of Al alloys

□ Two different mechanisms for precipitation

- Nucleation & Growth
 - Need thermal activation
 - Nucleus reach critical size
 - With defined interface between new phase and matrix
- Spinodal decomposition
 - Need composition fluctuation
 - No nucleation
 - No defined interfaces

Foundation of Materials Science (Chinese), Pan, Tong, and Tian, 1st Ed, 1998, p. 549-556



Homogeneous Nucleation in Solids (1)

□ Precipitation reaction $\alpha \rightarrow \alpha + \beta$

- Local composition fluctuation
- Re-arrangement atoms from α to β

□ Energetics for homogeneous nucleation

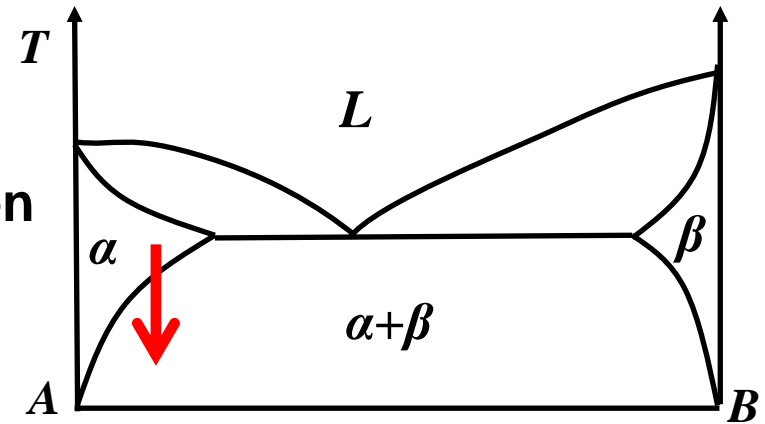
- Driving force
 - Volume free energy change ΔG_v
- Barriers
 - Added α/β interface energy γ_i for different interfaces (may not be isotropic)
 - Volume strain energy ΔG_s

Consider

- V is nucleus volume
- A_i is nucleus interface area for interface i

Total free energy change in nucleation

$$\Delta G = -V\Delta G_v + \sum A_i\gamma_i + V\Delta G_s$$





Homogeneous Nucleation in Solids (2)

□ Continue from p.3

$$\Delta G = -V\Delta G_v + \sum A_i \gamma_i + V\Delta G_s$$

Assuming isotropic interface and spherical nucleus

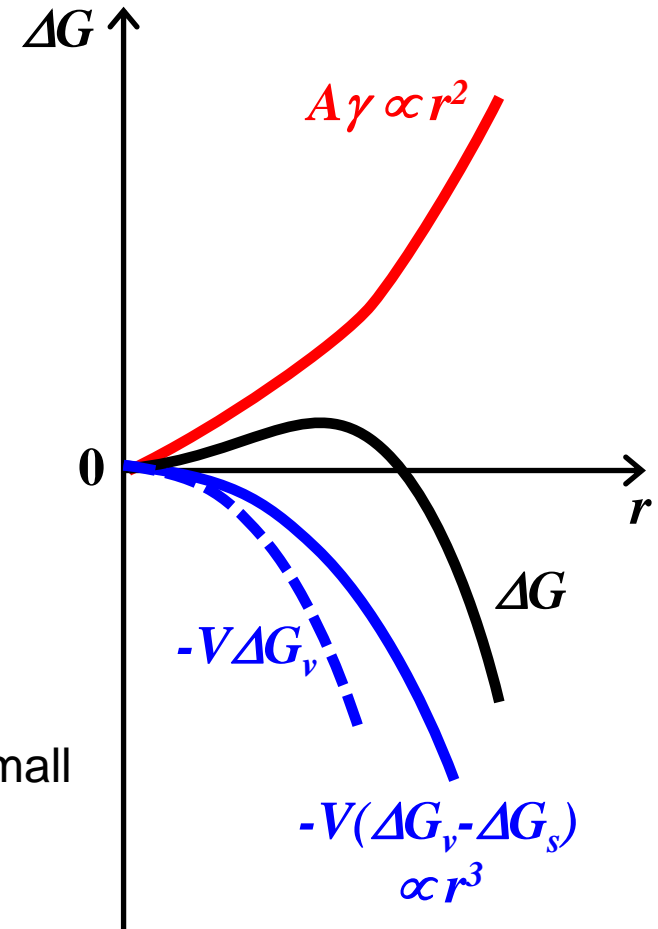
$$\Delta G = -\frac{4}{3}\pi r^3 (\Delta G_v - \Delta G_s) + 4\pi r^2 \gamma$$

Similar to homogeneous nucleation for solidification

$$r^* = \frac{2\gamma}{\Delta G_v - \Delta G_s} \quad \Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v - \Delta G_s)^2}$$

Consider the beginning of precipitation, ΔG_s is very small

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





Driving Force for Homogeneous Nucleation in Solids

- ❑ Molar free energy change for the entire phase transformation process is ΔG_0
- ❑ ΔG_0 is NOT the driving force for nucleation: i.e., the very first bit of β precipitating out of α matrix
- ❑ Driving force for nucleation (per mole of precipitate)

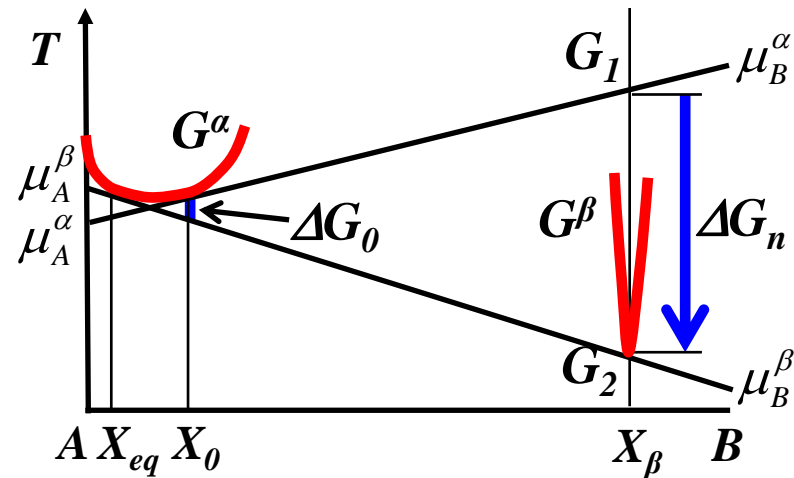
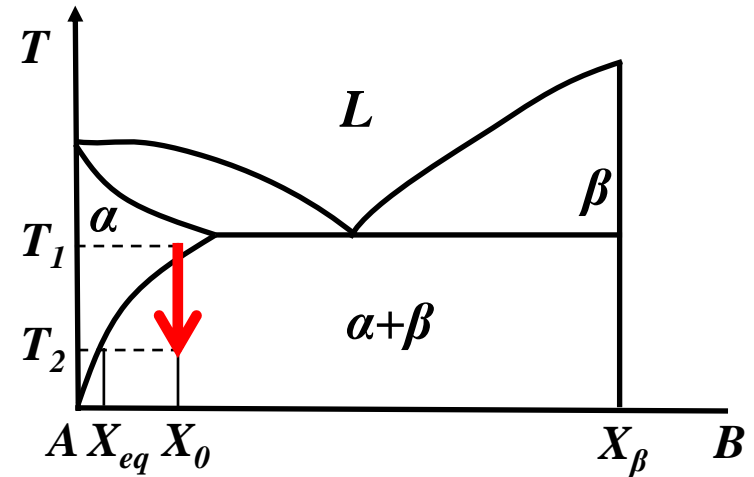
G_1 Molar free energy of material with composition X_B^β and structure of α

$$G_1 = \mu_A^\alpha X_A^\beta + \mu_B^\alpha X_B^\beta = \mu_A^\alpha (1 - X_B^\beta) + \mu_B^\alpha X_B^\beta$$

G_2 Molar free energy of material with composition X_B^β and structure of β

$$G_2 = \mu_A^\beta X_A^\beta + \mu_B^\beta X_B^\beta = \mu_A^\beta (1 - X_B^\beta) + \mu_B^\beta X_B^\beta$$

$$\Delta G_n = G_2 - G_1$$





Driving Force for Homogeneous Nucleation in Solids

□ Continue from p.5

$$\Delta G_n = G_2 - G_1$$

Driving force per unit volume (volume free energy change)

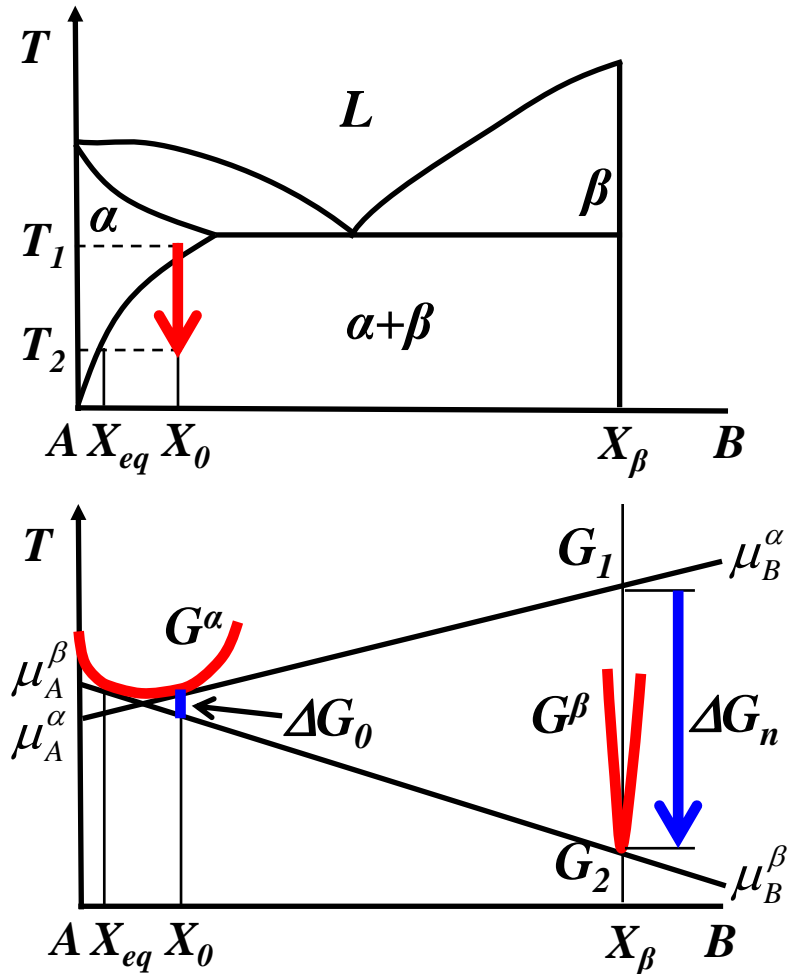
$$\Delta G_v = \frac{\Delta G_n}{V_m}$$

For the very beginning,

$$\Delta G_n \propto (X_0 - X_{eq})$$

- The driving force is proportional to supersaturation
- The driving force is also proportional to undercooling

$$\Delta G_n \propto \Delta T$$





Nucleation Rate in Homogeneous Precipitation

□ Similar to discussion of nucleation rate for liquid solidification

C^* Number density of nucleus with size r^* $C^* = C_0 \exp\left(-\frac{\Delta G^*}{kT}\right)$
 C_0 Atom density

ΔG_{hom}^* Homogeneous nucleation barrier, decreases with decreasing T

f Frequency of adding one more atom to a nucleus to make it “supercritical”

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

$$N_{\text{hom}} = fC^* = fC_0 \exp\left(-\frac{\Delta G_{\text{hom}}^*}{kT}\right)$$

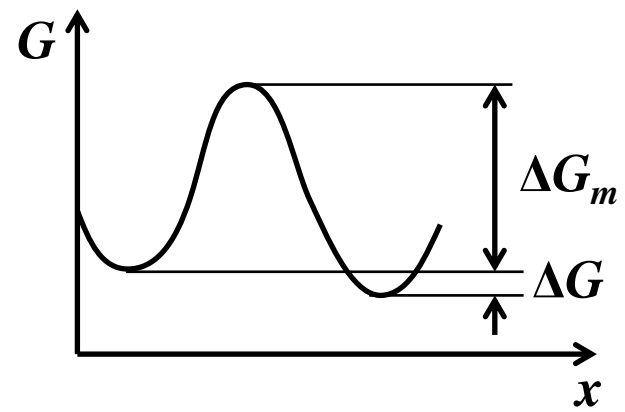
For solid precipitation

$$f = \omega \exp\left(-\frac{\Delta G_m}{kT}\right)$$

ω Pre-exponential factor

ΔG_m Migration energy barrier (temperature independent)

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

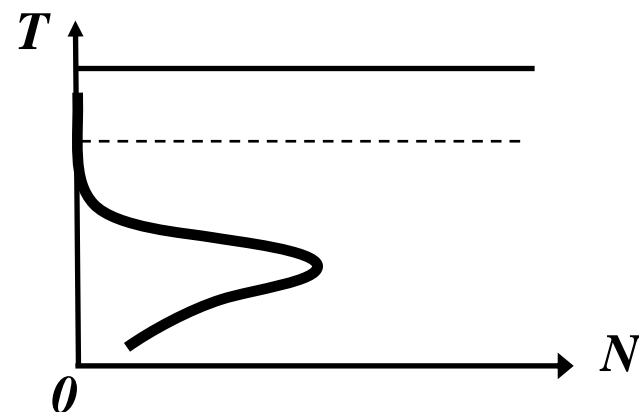
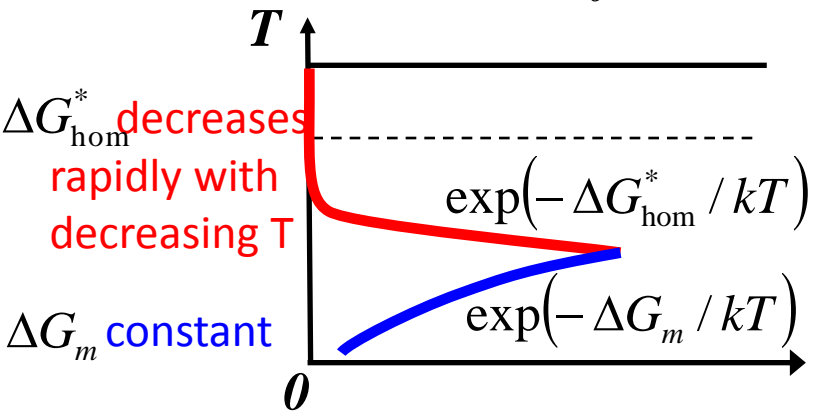
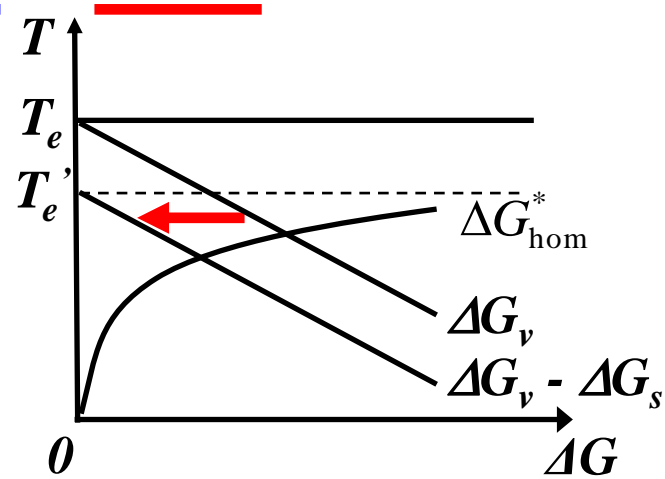
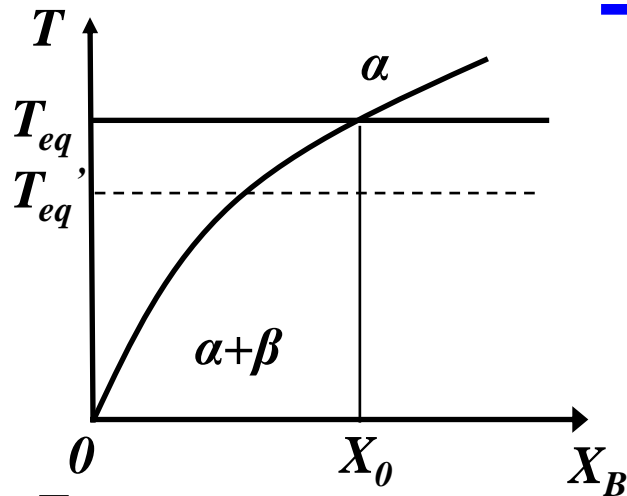




Nucleation Rate in Homogeneous Precipitation

□ Continue from p. 7

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





Other Considerations in Homogeneous Precipitation

❑ Impacts of solubility /equilibrium temperature

❑ Nucleation rate changes in precipitation process due to

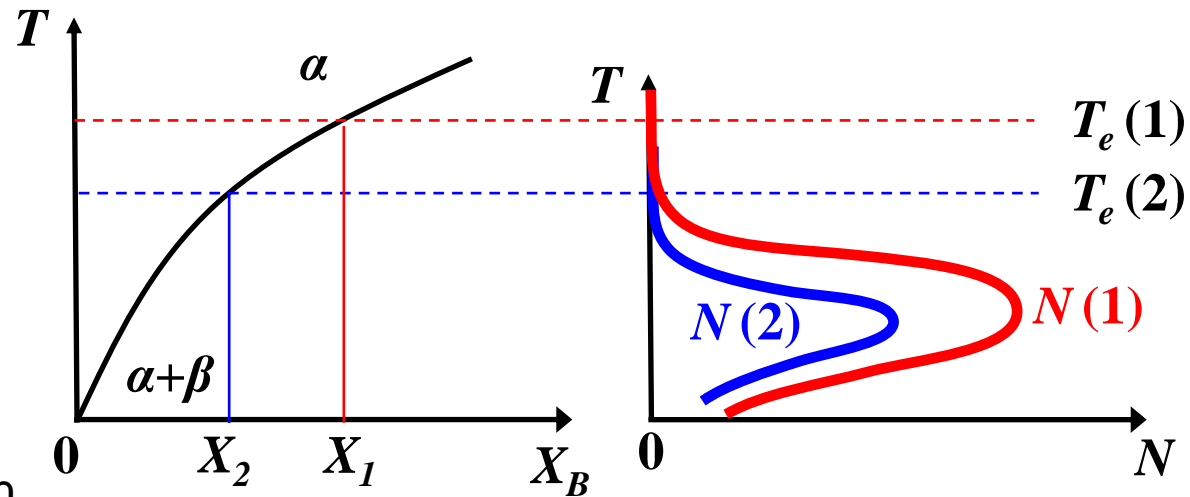
- Change in supersaturation

❑ Nucleus shape often NOT spherical

- Preferred match of certain orientation to lower interfacial energy

❑ Precipitation of meta-stable phase is common

- Less driving force but also less barrier





Heterogeneous Precipitation

❑ Defects sites in solids often have excess energy associated with it compared with the defect-free bulks

❑ If nucleation leads to removal of defects sites → Release of excess energy associated with the defects → Lower barrier to nucleation

$$\Delta G = -V(\Delta G_v - \Delta G_s) + A\gamma - \Delta G_d$$

❑ Heterogeneous nucleation at grain boundaries

Energy change (assuming no strain energy)

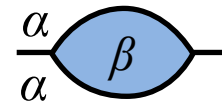
$$\Delta G = -V\Delta G_v + A_{\alpha\beta}\gamma_{\alpha\beta} - A_{\alpha\alpha}\gamma_{\alpha\alpha}$$

Critical nucleus size

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

Nucleation energy satisfy

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



$$\gamma_{\alpha\alpha} = 2\gamma_{\alpha\beta} \cos\theta$$



Heterogeneous Precipitation

□ Heterogeneous nucleation at grain boundaries (continued)

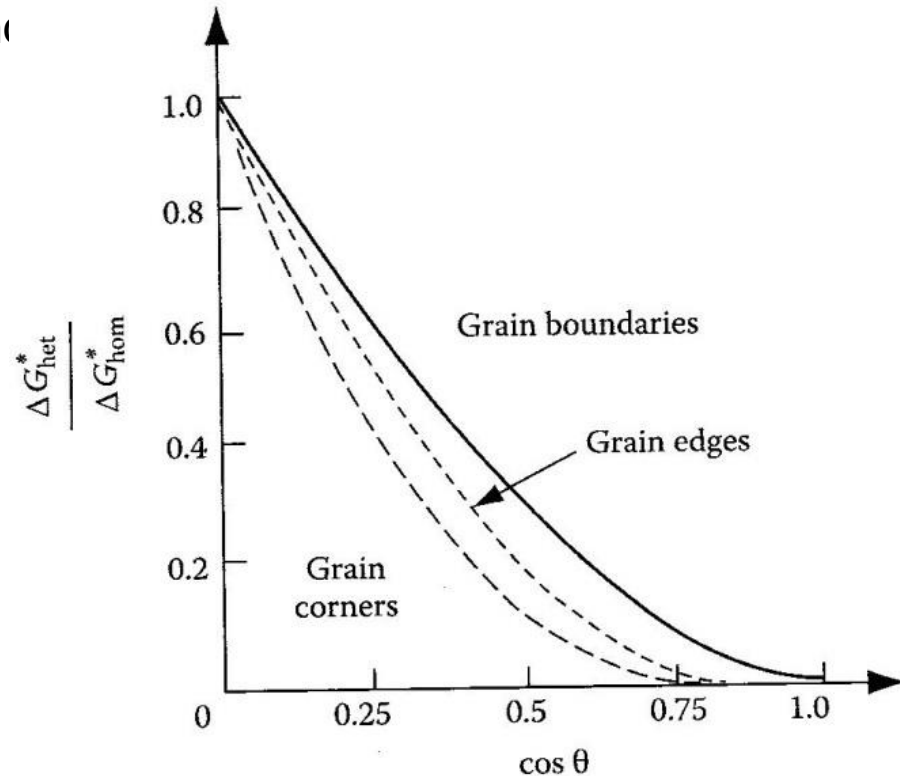
- Nucleation at grain edges (3 grains) and grain corners (4 grains) reduces the critical nucleation energy further
- Matching of certain crystal plane could reduce energy further
- Similar for free surfaces and inclusion-matrix interfaces

□ Nucleation at dislocations

- Helps release strain energy
- Solute segregation leading to local enrichment

□ Nucleation at vacancies

- Increases diffusion rate
- Releases strain energy



Phase Transformations in Metals & Alloys, Porter, 3rd Ed, 2008, p. 272



Rate of Heterogeneous Nucleation in Solid

□ Heterogeneous nucleation rate depend on two factors

Critical nucleation energy ΔG^* DECREASES



Homogeneous sites

Vacancies

Dislocations

Stacking faults

Grain boundaries/
interphase interfaces

Free surface



Nucleation sites (defects) density C_d DECREASES

□ Heterogeneous nucleation rate

$$N_{het} = \omega C_d \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G_{het}^*}{kT}\right)$$

□ Assuming similar migration barrier

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