



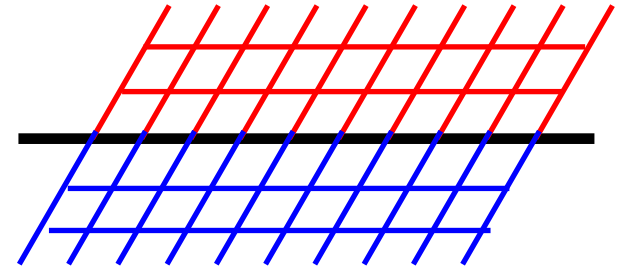
# **EMA5001 Lecture 11 (Interphase) Interfaces & Precipitates Shape**



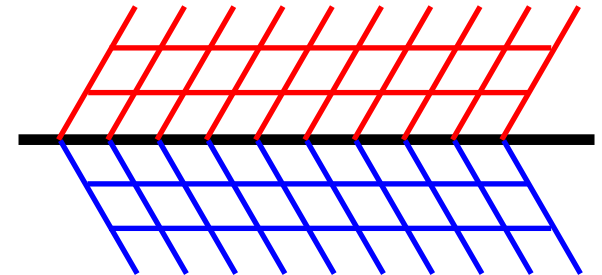
# Coherent Interfaces (1)

❑ Two crystals match very well at the interface plane

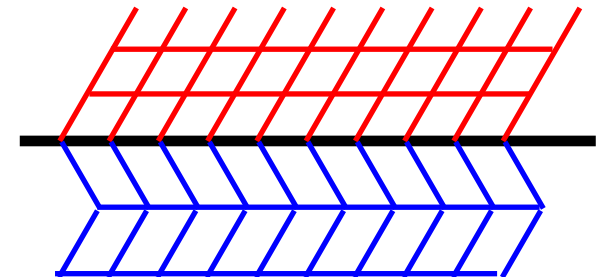
- Same lattice structure and same orientation



- Same lattice structure but different orientation



- Different lattice structure

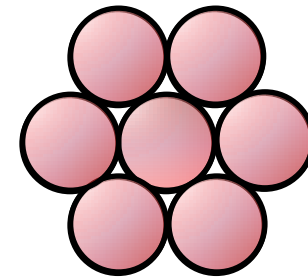
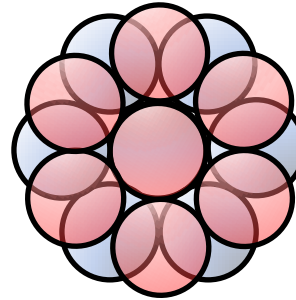
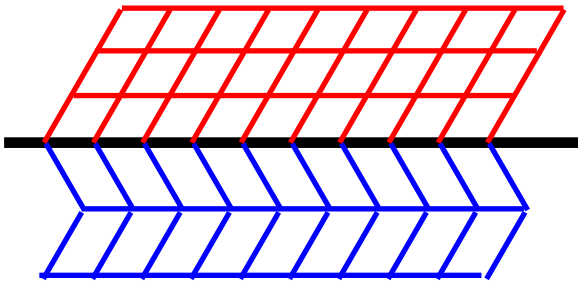




# Coherent Interfaces (2)

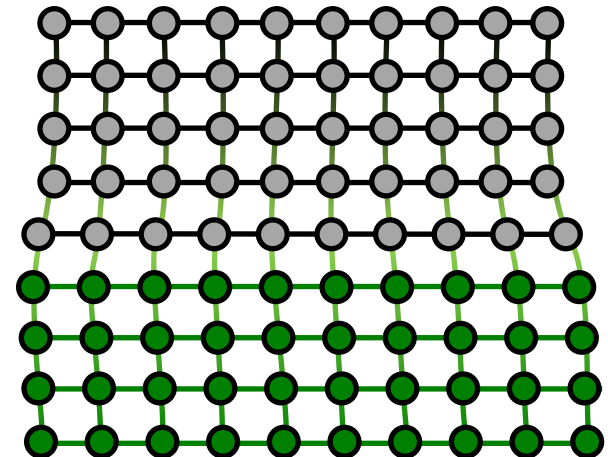
## □ Geometric match at the interface

- Match of 2D lattice structure (typically closed packed plane)
- Match of close-packed direction



## □ Interfacial energy

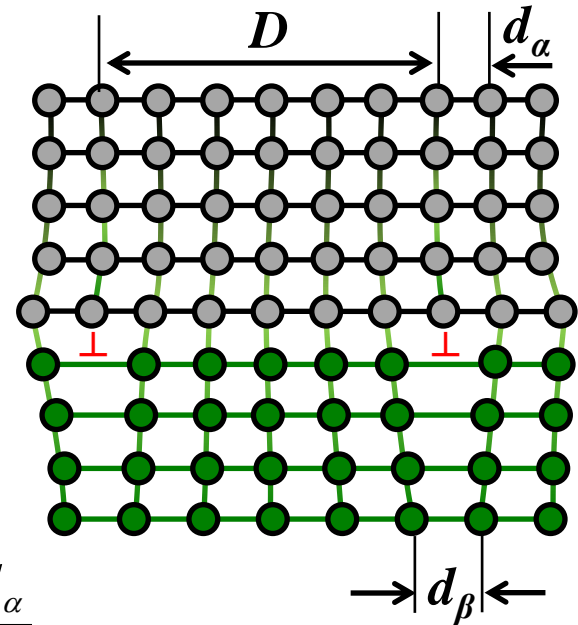
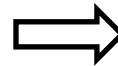
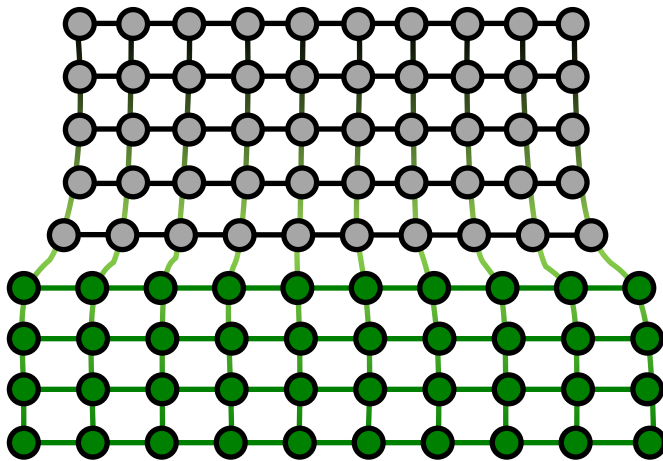
- If perfect match
  - Coherent interface energy comes only from chemical bonding to the “wrong” atoms:  
 $\gamma_{ch}$  Chemical contribution
- If small geometric mismatch ( $< \sim 5\%$ )
  - Strain energy term appears



# Semicoherent Interfaces (1)

## □ Larger mismatch in lattice parameter (e.g., > ~5%)

- Energetically more favorable to have semi-coherent interface w/ dislocations than w/ huge strain energy



Misfit between two phases defined by  $\delta = \frac{d_\beta - d_\alpha}{d_\alpha}$

The distance between two dislocations  $D$  will satisfy  $\frac{D}{d_\beta} \cdot (d_\beta - d_\alpha) = d_\beta$

i.e.,  $D \cdot \delta = d_\beta$   
Therefore, we have  $D = \frac{d_\beta}{\delta}$



# Semicoherent Interfaces (2)

## □ Continue from p.5

- Relationship between relative mismatch and dislocation spacing  $D = \frac{d_\beta}{\delta}$   
Considering Burger's vector

$$b \approx \frac{d_\alpha + d_\beta}{2}$$

We have  $D \approx \frac{b}{\delta}$

- For mismatch in two different directions,  $D_1 \approx \frac{b_1}{\delta_1}$   $D_2 \approx \frac{b_2}{\delta_2}$

## □ Interfacial energy come from two contributions

- $\gamma_{ch}$  Chemical contribution
  - $\gamma_{st}$  Structural misfit contribution
- $$\gamma_{semicoherent} \approx \gamma_{ch} + \gamma_{st}$$

For small misfit  $\delta$  ( $5\% < \delta < 25\%$ ),  $\gamma_{st} \propto \frac{1}{D} \propto \delta$

For large misfit of  $\delta > 25\%$ ,  $D = \frac{d_\beta}{\delta} < 4d_\beta$ , too much misfit  $\rightarrow$  Incoherent interface



# Incoherent Interfaces

## ❑ Large mismatch of the two adjacent phases

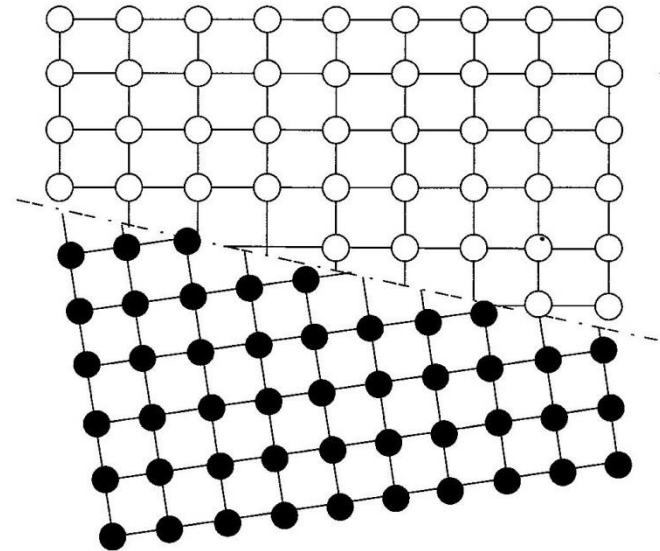
- Different lattice structure that don't have matching planes

Or

- Large mismatch of lattice constant

## ❑ Interfacial energy for incoherent interfaces

- Large interfacial energy
- Not sensitive to orientation





# Interfacial Energy on Precipitate Shape (1)

## □ Simplest cases

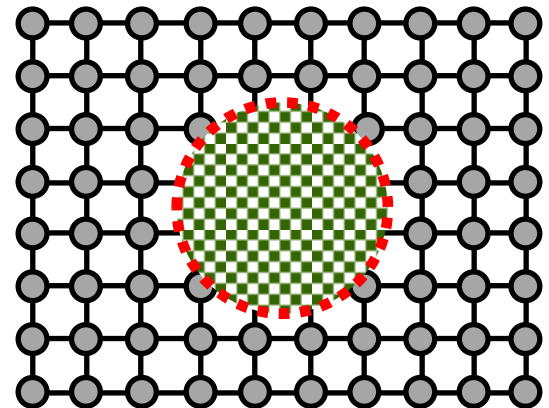
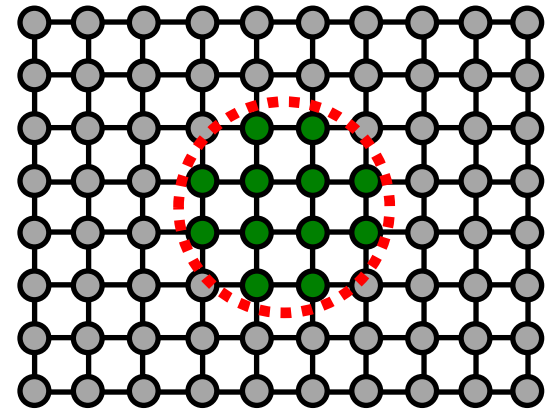
- $\beta$  precipitates in  $\alpha$  single crystal
- **Strain free**
- Shape & orientation determined by minimization of  $\sum A_i \gamma_i$

## □ Fully coherent precipitate / GP Zone

- $\beta$  precipitate has the same crystal structure and similar lattice constant as  $\alpha$ ;
- Matching (parallel) orientation
- Shape: spherical

## □ Incoherent precipitate

- $\beta$  precipitate has very different crystal structure and no match of any crystal plane
- Shape
  - Spherical
  - Other shape – does not indicate coherency





# Interfacial Energy on Precipitate Shape (2)

## □ Partially coherent precipitate

- $\beta$  precipitate has different crystal structure from  $\alpha$  but w/ good match of only one crystal plane
- Shape
  - If no other match: **disk-shaped** precipitates

Define

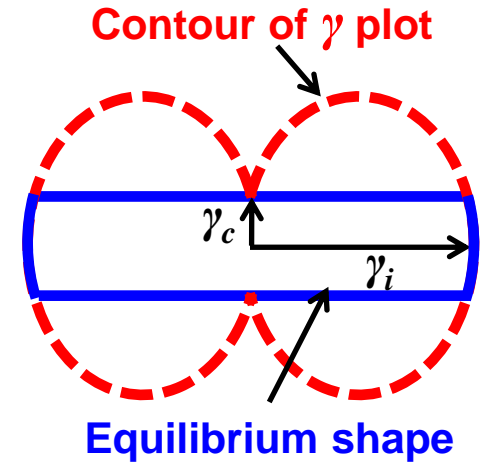
$r$  Plate radius

$h$  Plate thickness

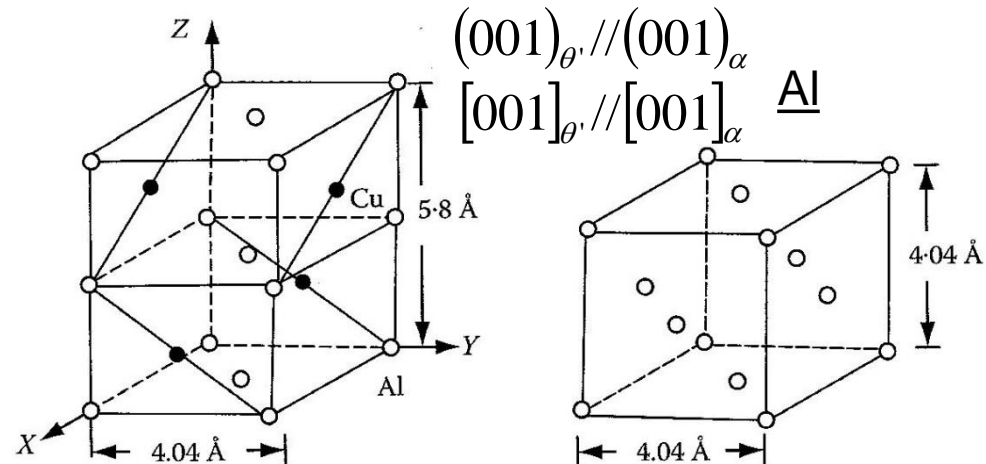
Geometry of the plate satisfy

$$\frac{2r}{h} = \frac{\gamma_i}{\gamma_c}$$

- If other cups exist - Other shapes



## $\theta'$ precipitate in Al-Cu



Phase Transformations in Metals & Alloys, Porter, 3<sup>rd</sup> Ed, 2008, p. 155





# Interfacial Energy on Precipitate Shape (3)

□ To prove the relationship for plate-like precipitate shape

Define total interfacial energy for the plate-like precipitate:

$$G = \sum A_j \gamma_j = 2\pi r^2 \gamma_c + 2\pi r h \gamma_i$$

Because total volume of the plate-like precipitate is fixed, i.e.,

$$\pi r^2 h = V \quad \rightarrow \quad h = V / \pi r^2$$

Therefore,

$$G = 2\pi r^2 \gamma_c + 2\pi r \frac{V}{\pi r^2} \gamma_i = 2\pi r^2 \gamma_c + 2 \frac{V}{r} \gamma_i$$

For total interfacial energy to reach minimum,

$$\frac{dG}{dr} = 4\pi r \gamma_c - 2 \frac{V}{r^2} \gamma_i = 0$$

$$\text{We have } 4\pi r \gamma_c = 2 \frac{V}{r^2} \gamma_i = 2 \frac{\pi r^2 h}{r^2} \gamma_i$$

Therefore

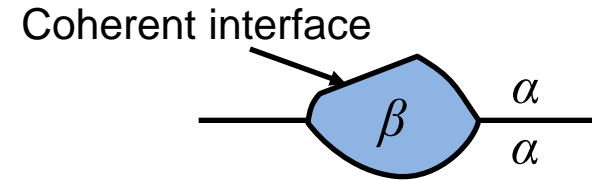
$$2r \gamma_c = h \gamma_i \quad \text{or} \quad \frac{2r}{h} = \frac{\gamma_i}{\gamma_c}$$



# Precipitates on Grain Boundaries

## □ Precipitates on grain boundaries with a coherent interface

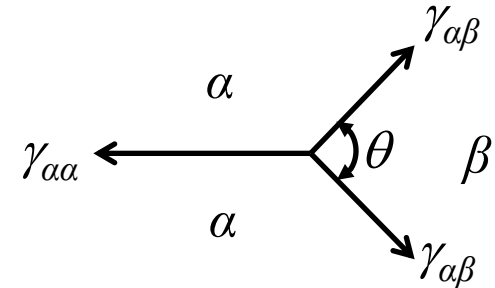
- Planar (coherent) interface on one side
- Curved (incoherent) interface on other sides



## □ Precipitates on grain boundaries without any coherent interfaces

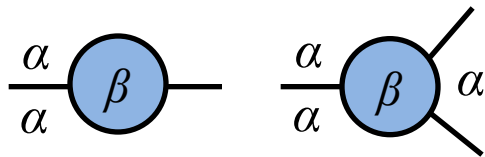
- $\gamma_{\alpha\alpha}$  Grain boundary energy in  $\alpha$  matrix
- $\gamma_{\alpha\beta}$  Incoherent interface energy
- $\theta$  Interphase angle

We have 
$$\gamma_{\alpha\alpha} = 2\gamma_{\alpha\beta} \cos \frac{\theta}{2}$$



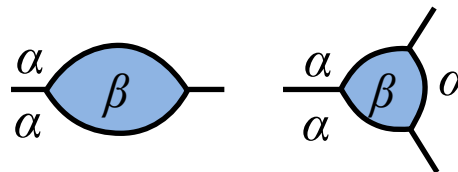
$$\gamma_{\alpha\alpha} \ll \gamma_{\alpha\beta}$$

$$\theta = 180^\circ$$



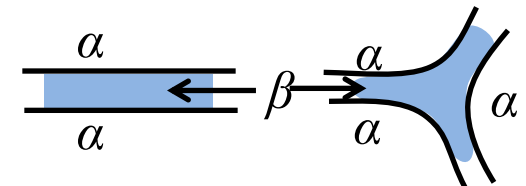
$$\gamma_{\alpha\alpha} = \gamma_{\alpha\beta}$$

$$\theta = 120^\circ$$



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

$$\theta = 0^\circ$$





# Misfit Strain on Precipitate Shape

## □ General precipitates

- Shape determined by minimization of  $\sum A_i \gamma_i + \Delta G_s$ 
  - $\Delta G_s$  Strain energy term

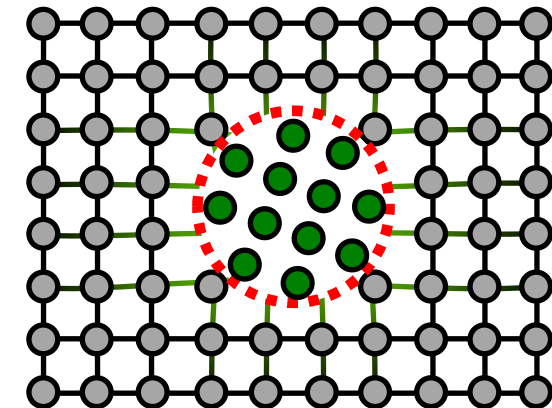
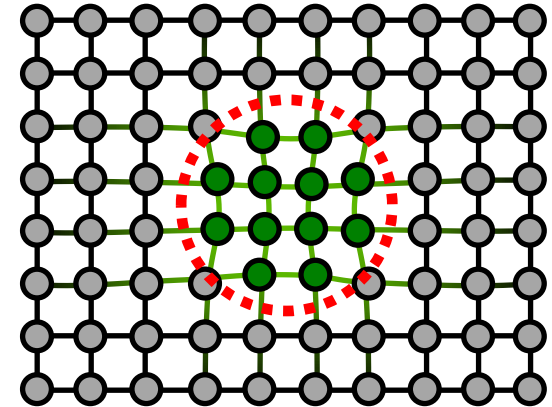
## □ Coherent precipitate

- Conservation of lattice sites
- Shape of precipitates depends on
  - Matrix: isotropic vs. anisotropic
  - Precipitates: hard vs. soft
  - Misfit: <5% vs. >5%
- For isotropic matrix and the same elastic modules

$$\Delta G_s = 4\mu\delta^2 \cdot V$$

## □ Incoherent precipitate

- Lattice sites do not have to remain unchanged
- No coherency strain
- Strain due to volume misfit  $\Delta$  may exist





# Loss of Coherency during Precipitate Growth

## □ Continue from p.11

For isotropic matrix, if volume misfit exist:

$$\Delta G_s = \frac{2}{3} \mu \Delta^2 \cdot V \cdot f(c/a)$$

$f(c/a)$  shape effect factor

Incoherent precipitates usually oblate spheroid

## □ Loss of coherency during precipitation

For coherent spherical precipitate

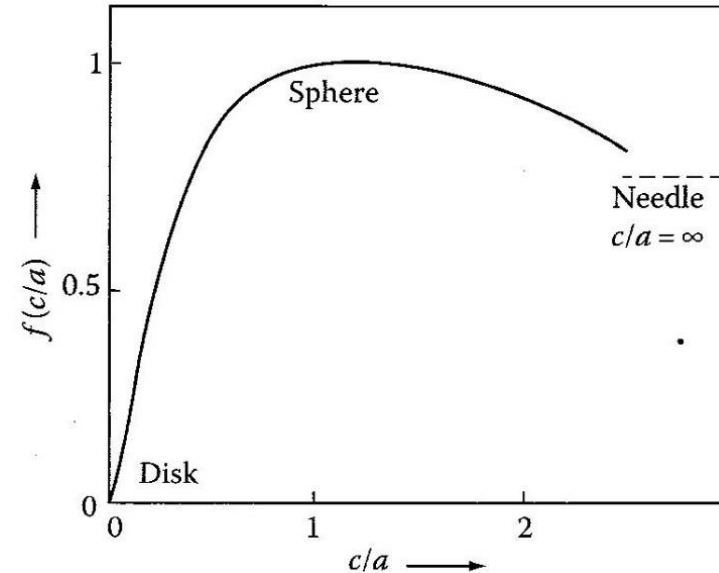
$$\Delta G_{coherent} = A\gamma_{ch} + \Delta G_s = 4\pi r^2 \gamma_{ch} + 4\mu\delta^2 \cdot \frac{4}{3} \pi r^3$$

For semi-coherent precipitate (assume no volume misfit)

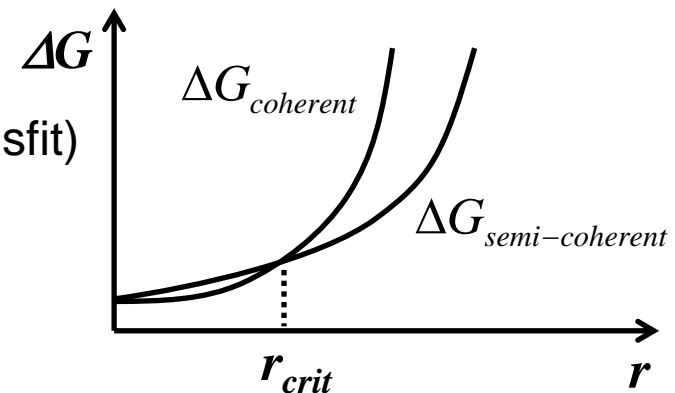
$$\Delta G_{semi-coherent} = A(\gamma_{ch} + \gamma_{st}) = 4\pi r^2 (\gamma_{ch} + \gamma_{st})$$

We have 
$$r_{criti} = \frac{3\gamma_{st}}{4\mu\delta^2} \propto \frac{1}{\delta^2}$$

$r < r_{criti}$ : coherent;  $r > r_{criti}$ , semi-coherent



Phase Transformations in Metals & Alloys, Porter, 3<sup>rd</sup> Ed, 2008, p. 163





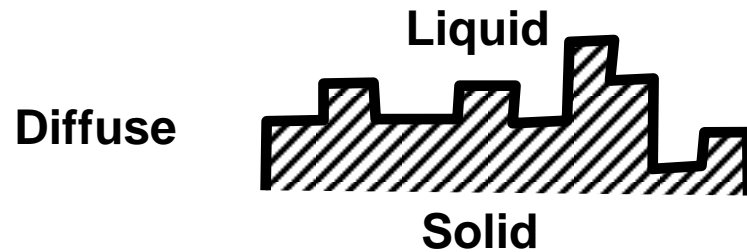
# Solid Liquid Interfaces

□ Two types of solid-liquid interfaces



$$\frac{L_f}{T_m} \geq \sim 4R$$

Si, Ge, and nonmetals



$$\frac{L_f}{T_m} \approx R$$

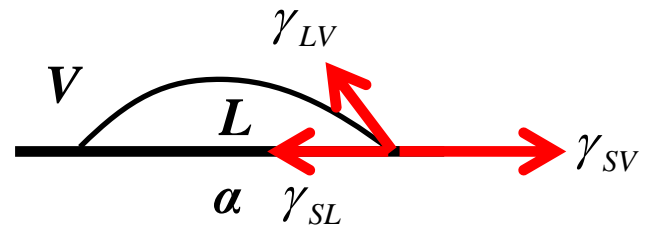
Most metals

□ Relationship between  $\gamma_{SV}$ ,  $\gamma_{SL}$  and  $\gamma_{LV}$

- $\gamma_{SL} \approx 0.45\gamma_b$      $\gamma_b = 0.3\gamma_{SV}$

- $\gamma_{SL} \approx 0.15\gamma_{SV}$

- For the same material in solid and liquid states,  $\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$





# Expectations about Surface & Interfaces

- Understand that surface or interface free energy are the excess energy with respect to bulk
- Be able to estimate the surface free energy for low index crystal surface in cubic lattices
- Understand why surface energy change with orientation
- Understand the impact of surface energy on crystal shape
- Be able to name types of low angle grain boundaries and explain how grain boundary energy change with misorientation angle
- Understand why certain special high angle grain boundaries (e.g., twin boundary) have low energy
- Understand what determines the shapes of grains and grain boundaries and the driving forces for grain boundary movement
- Understand the origin of grain boundary segregation and the relationship between grain boundary and bulk molar fraction of solute

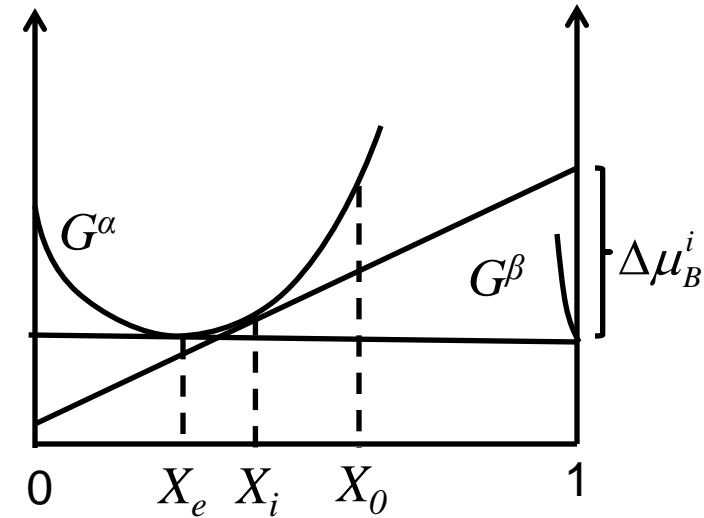
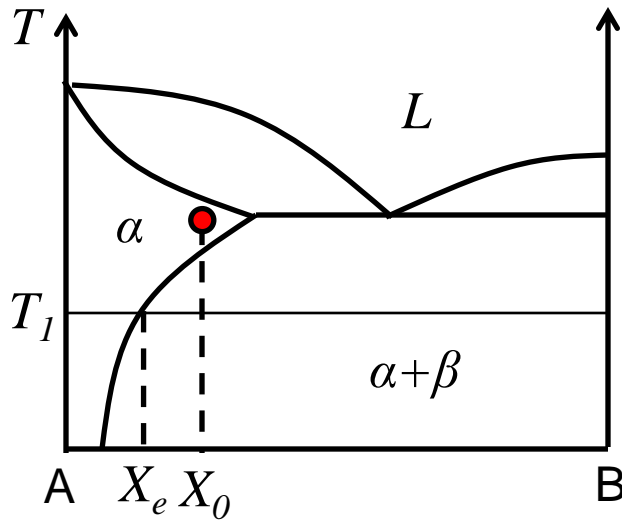


# Expectations about Surface & Interfaces

- Be able to qualitatively describe coherent, semi-coherent, and incoherent interfaces
- Understand that the precipitate shape is determined by minimization of interface energy and strain energy and be able to derive geometric relationship for simple case when strain energy is omitted
- Understand how grain boundaries impact precipitate shape
- Understand from energy point of view the origin of the loss of coherency for a precipitate as it grows



# Interface Control vs. Diffusion Control



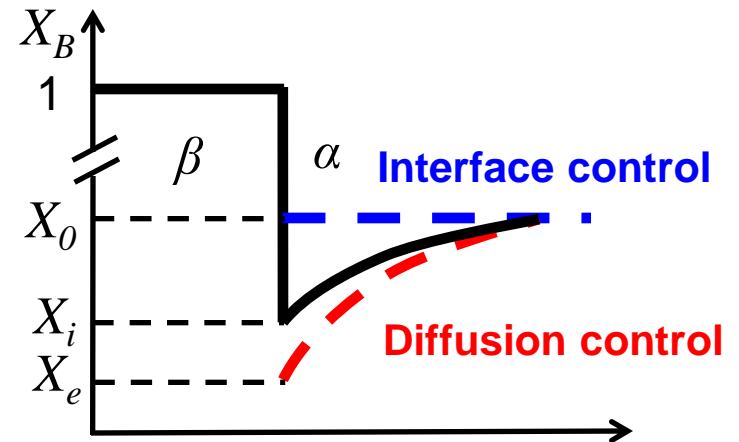
## ☐ Interface controlled

- Low interface mobility
- Relative fast diffusion

## ☐ Diffusion controlled

- High interface mobility
- Local equilibrium at interface

## ☐ Mixed controlled







# Porter exercise 3.3

□ Total “surface” free energy

$$G_{surface} = \sum A_i \gamma_i = l_1 \gamma_1 + l_2 \gamma_2$$

□ Shape of the 2D crystal determined by minimization of the total “surface” energy

□ The total area is a constant  $l_1 \cdot l_2 \equiv A$

□ Therefore, for minimization of  $G_{surface} = \sum A_i \gamma_i = l_1 \gamma_1 + l_2 \gamma_2$

$$\frac{dG_{surface}}{dl_1} = \frac{d(l_1 \gamma_1 + \frac{A}{l_1} \gamma_2)}{dl_1} = \gamma_1 - \frac{A}{l_1^2} \gamma_2 = \gamma_1 - \frac{l_1 l_2}{l_1^2} \gamma_2 = \gamma_1 - \frac{l_2}{l_1} \gamma_2 = 0$$

□ Therefore,

$$\frac{l_1}{l_2} = \frac{\gamma_2}{\gamma_1}$$