

2018 Fall

“Phase Transformation *in* Materials”

10.16.2018

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Contents for previous class

• Substitution Diffusion

1. Self diffusion in pure material (by radioactive element)

Probability of vacancy x probability of jump

$$D_A = \frac{1}{6} \alpha^2 z v \exp\left(\frac{-(\Delta G_m + \Delta G_v)}{RT}\right)$$

$$D_A = D_0 \exp\left(-\frac{Q_{SD}}{RT}\right)$$

$$Q_{SD} = \Delta H_m + \Delta H_v$$

2. Vacancy diffusion

$$D_v = \frac{1}{6} \alpha^2 z v \exp(\Delta S_m / R) \exp(-\Delta H_m / RT)$$

Comparing D_v with the self-diffusion coefficient of A, D_A , $D_v = D_A / X_v^e$

3. Diffusion in substitutional alloys

$$X_v = X_v^e = \exp\left(\frac{-\Delta G_v}{RT}\right)$$

$$\therefore J'_B = -J'_A$$

$$J'_A = J_A + J_A^v = -\tilde{D} \frac{\partial C_A}{\partial x} = \tilde{D} \frac{\partial C_B}{\partial x}$$

$$J'_B = J_B + J_B^v = -\tilde{D} \frac{\partial C_B}{\partial x} = \tilde{D} \frac{\partial C_A}{\partial x}$$

$$\tilde{D} = X_B D_A + X_A D_B$$

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C_A}{\partial x} \right)$$

Fick's 1st law for substitutional alloy

Fick's 2nd law for substitutional alloy

The relationship between the various diffusion coefficients in the Cu-Ni system at 1273 K.

Atoms with the lower melting point possess a higher D.

D_{Cu} , D_{Ni} , (\tilde{D}) are all composition dependent, increasing as X_{Cu} increases.

* Concentration of A & B at any x after t

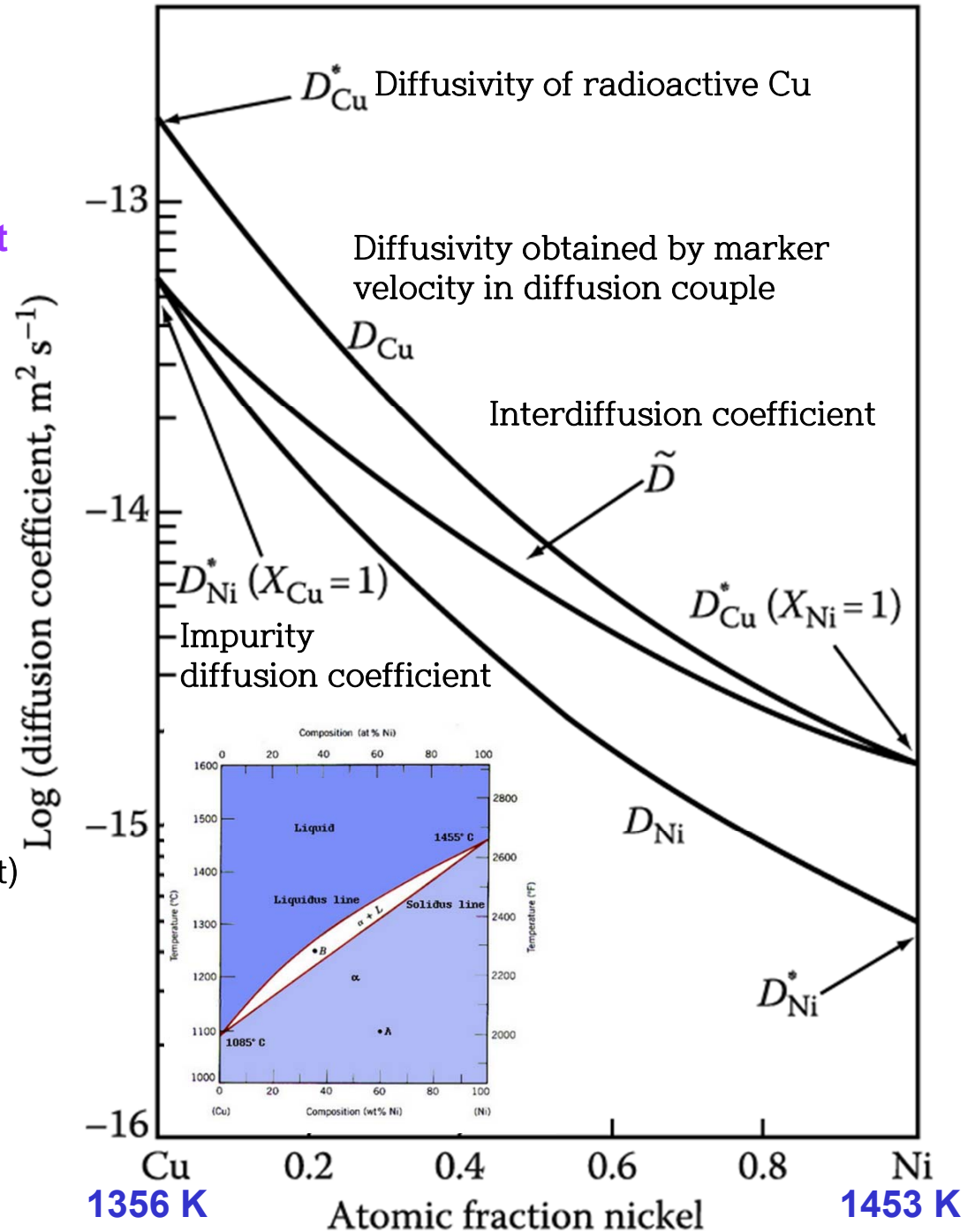
$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(\tilde{D} \frac{\partial C_A}{\partial x} \right) \quad \text{Eq. (2.53)}$$

By solving (2.53) with appropriate BCs, → Possible to obtain $C_A(x, t)$ and $C_B(x, t)$

Characteristic relaxation time for an Homogenization anneal

$$\tau = \frac{l^2}{\pi^2 \tilde{D}} \quad \tau : \text{relaxation time}$$

(The range of composition is small enough that any effect of composition on \tilde{D} can be ignored)



Contents for previous class

Fick's first law: assume that diffusion eventually stops when the concentration is the same everywhere → never true in practice due to lattice defect

- **Atomic Mobility** $D_B = M_B RTF$ $F = \left(1 + \frac{d \ln \gamma_B}{d \ln X_B}\right)$

both the concentration gradient and the gradient of the interaction energy

Thermodynamic factor

- **Tracer Diffusion in Binary Alloys** $\tilde{D} = X_B D_A + X_A D_B = F(X_B D_A^* + X_A D_B^*)$

D_{Au}^* gives the rate at which Au* (or Au) atoms diffuse in a **chemically homogeneous** alloy, whereas D_{Au} gives the diffusion rate of Au when **concentration gradient** is present.

Contents for today's class I

- Interstitial Diffusion / Substitution Diffusion
- Atomic Mobility
- **Tracer Diffusion in Binary Alloys**
- **High-Diffusivity Paths**
 1. Diffusion along Grain Boundaries and Free Surface
 2. Diffusion Along Dislocation
- **Diffusion in Multiphase Binary Systems**

Q: How do the compositions of ternary A and B alloys of diffusion couple change with time?

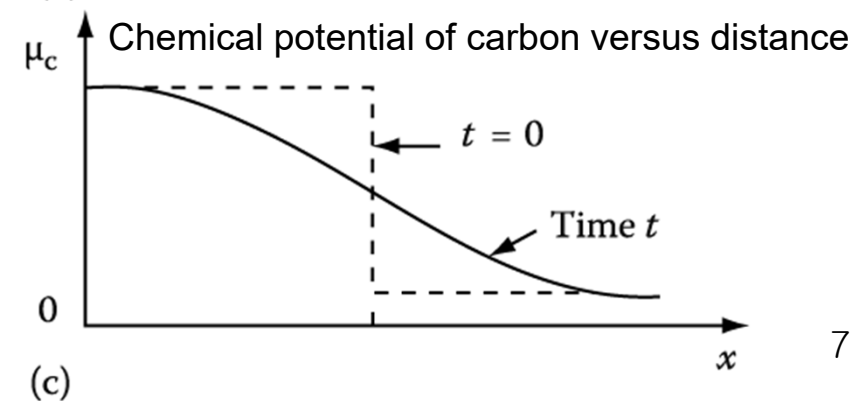
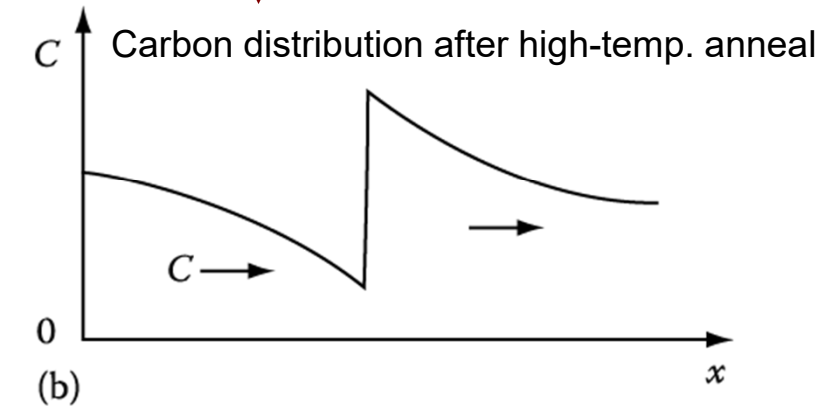
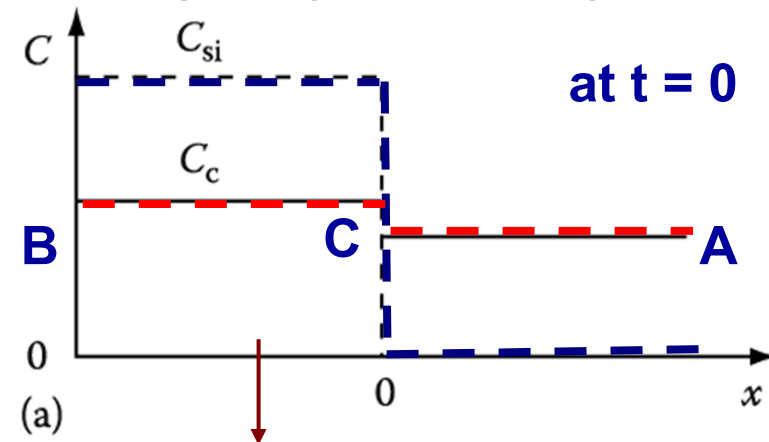
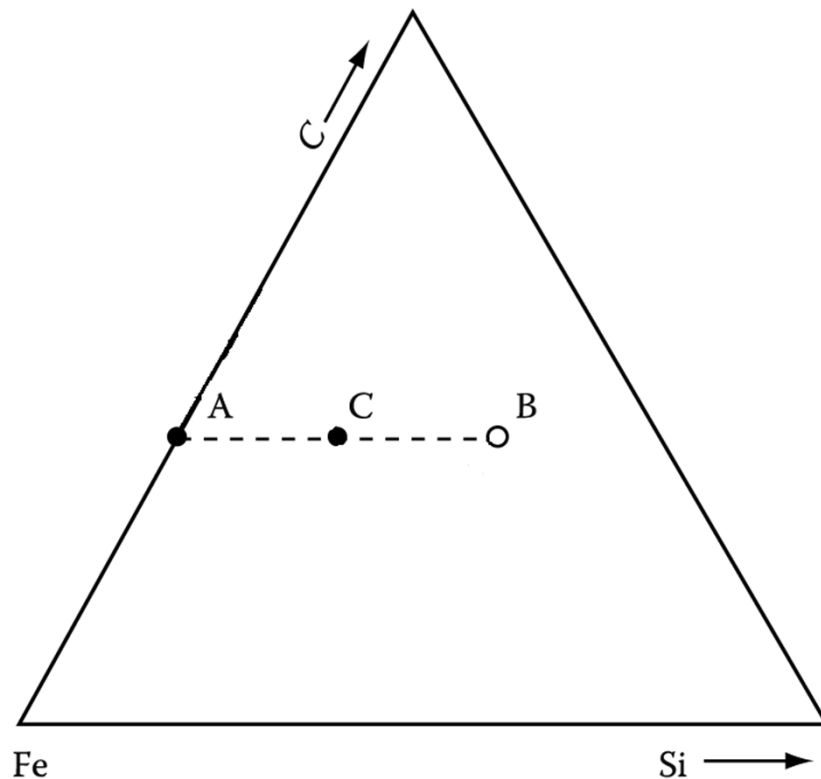
2.6 Diffusion in ternary alloys: Additional Effects

Example) Fe-Si-C system (Fe-3.8%Si-0.48%^BC) vs. (Fe-0.44%^AC) at 1050°C austenitized

- ① Si raises the μ_C in solution.
(chemical potential of carbon)

C 이동: 고농도 → 저농도 영역 & Si-rich → Si 적은 영역

- ② $M_{Si} \text{ (sub.)} \ll M_C \text{ (interstitial solute)}$,
(M : mobility)



How do the compositions of A and B change with time?

- 1) **Carbon atom migration $B \rightarrow A$**
 - ~ equilibrate the activity, or chemical potential, of carbon in both sides
 - ~ only partial equilibrium of chemical potential of the carbon & not for the silicon

- 2) **Silicon atom migration $B \rightarrow A$**
 - ~ over sufficient time
 - ~ the carbon atoms will continually redistribute themselves to maintain a constant chemical potential.

- 3) **The concentrations of carbon and silicon are uniform everywhere. C**

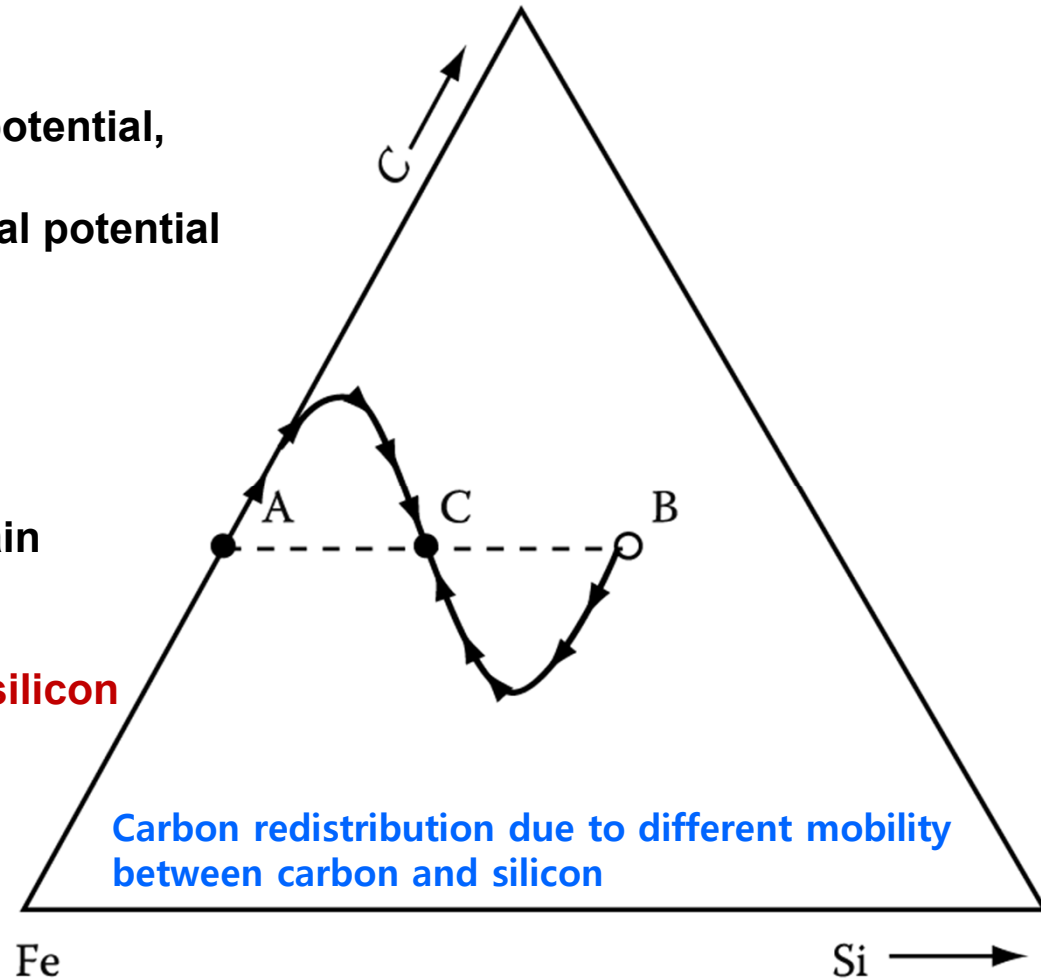


Fig. 2.24. Schematic diagram showing the change in composition of two points (A and B) on opposite sides of the diffusion couple

Q: What conditions high-diffusivity paths' (grain boundary, dislocation) diffusion is important?

$$D_s > D_b > D_l \longleftrightarrow A_l > A_b > A_s$$

1. Diffusion along Grain Boundaries and Free Surface

Grain boundary diffusion makes a significant contribution

only when $D_b \delta > D_l d$.

($T < 0.75 \sim 0.8 T_m$)

$$D_{app} = D_l + D_b \frac{\delta}{d}$$

2. Diffusion Along Dislocation

At low temperatures, ($T < \sim 0.5 T_m$)

gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

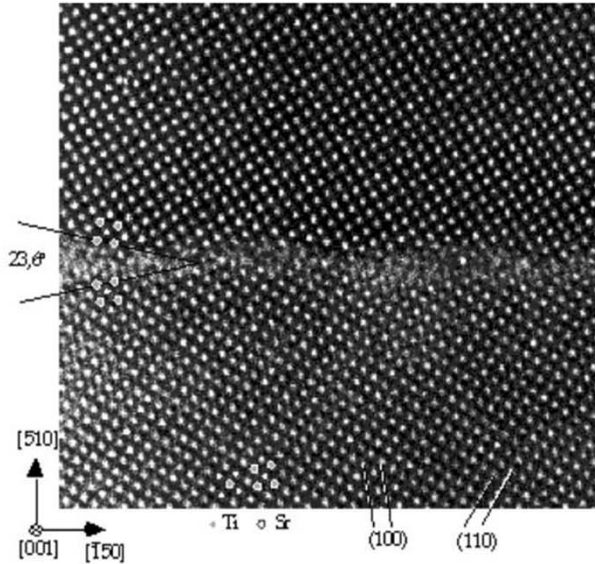
2.7.1 High-diffusivity paths

Real materials contain **defects**.

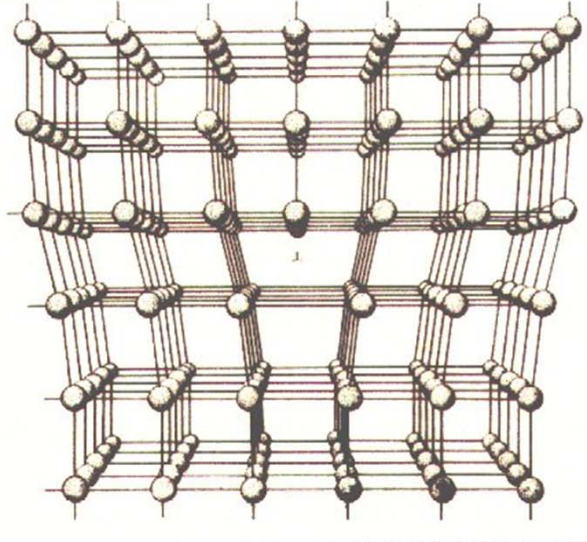
= more open structure → fast diffusion path.

원자들의 도약 진동수가 큼

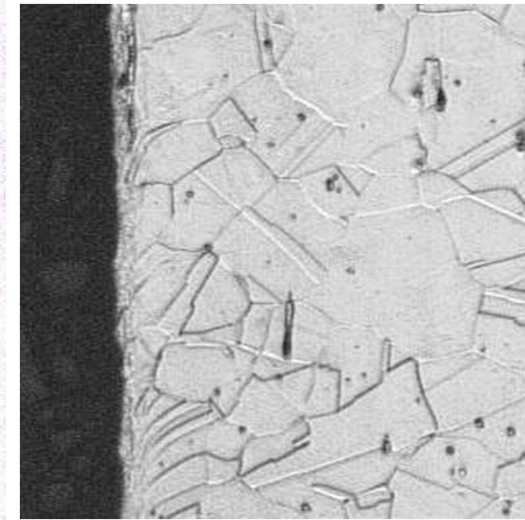
확산의 주요한 행로



Grain boundary



dislocation



surface

$$D_s > D_b > D_l$$

Diff. along lattice

$$D_l = D_{l0} \exp\left(-\frac{Q_l}{RT}\right)$$

Diff. along grain boundary

$$D_b = D_{b0} \exp\left(-\frac{Q_b}{RT}\right)$$

Diff. along free surface

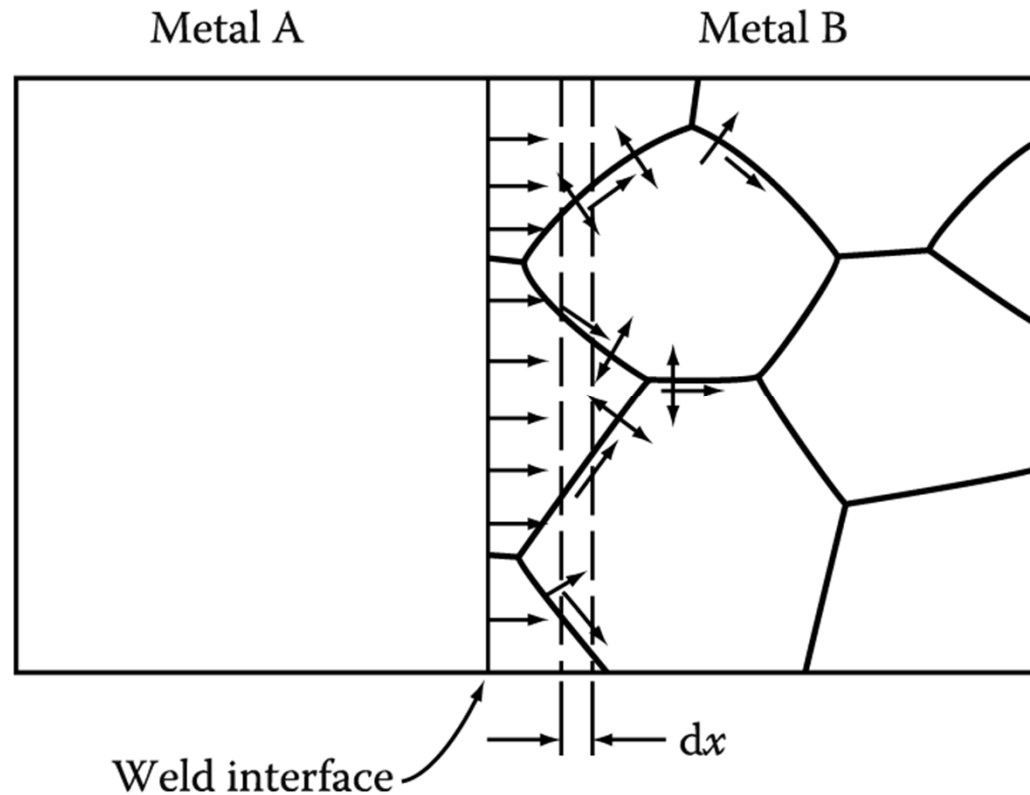
$$D_s = D_{s0} \exp\left(-\frac{Q_s}{RT}\right)$$

But area fraction → **lattice** > **grain boundary** > **surface**

Diffusion along grain boundaries

Atoms diffusing along the boundary will be able to **penetrate much deeper** than atoms which only diffuse through the lattice.

In addition, as the concentration of solute builds up in the boundaries, atoms will also **diffuse from the boundary into the lattice**.



Composite between plastic matrix and a continuous network of Al sheets

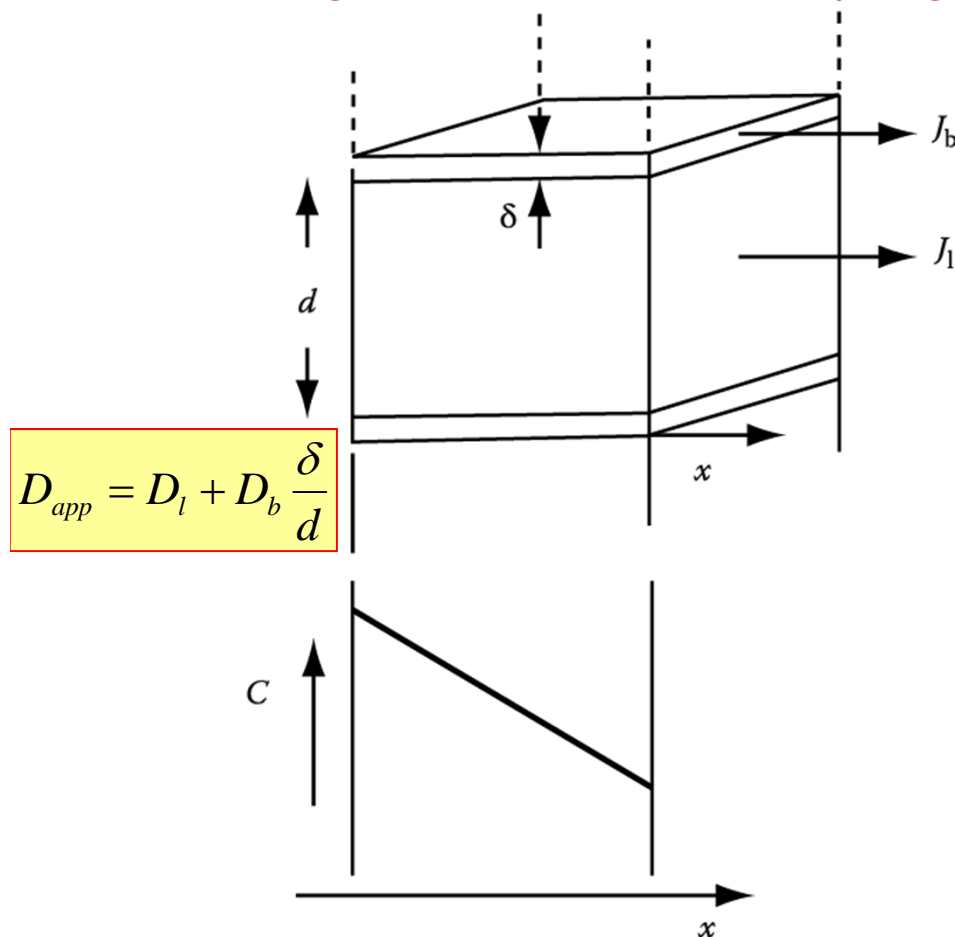
Fig. 2.25. The effect of grain boundary diffusion combined with volume diffusion.

: Rapid diffusion along the grain boundaries

→ increase in the apparent diffusivity in the materials as a whole

Combined diffusion of grain boundary and lattice : What conditions grain boundary diffusion is important?

Assumption: GBs are perpendicular to the sheet, steady-state diffusion, Concentration gradients in the lattice and along the GB are identical,



$$D_{app} = D_l + D_b \frac{\delta}{d}$$

$$J_l = -D_l \frac{dC}{dx}$$

$$J_b = -D_b \frac{dC}{dx}$$

$$J = (J_b \delta + J_l d) / d = -D_{app} \frac{dC}{dx}$$

δ : grain boundary thickness $\approx 0.5\text{nm}$

d : grain size

D_{app} : apparant diffusivity

$$D_{app} = D_l + D_b \frac{\delta}{d}$$

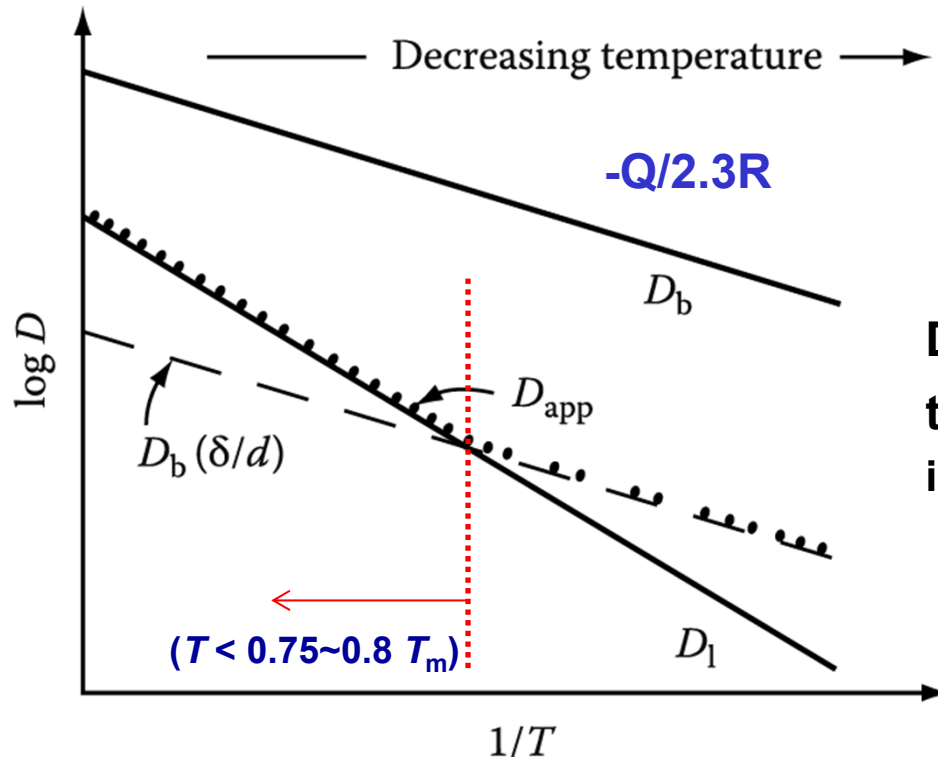
Fig. 2.26 Combined lattice and boundary fluxes during steady-state diffusion through a thin slab of material.

Thus, grain boundary diffusion makes a significant contribution

only when $D_b \delta > D_l d$.

The relative magnitudes of $D_b\delta$ and $D_l d$ are most sensitive to **temperature**.

$$D_b = D_{b0} \exp\left(-\frac{Q_b}{RT}\right) \quad D_l = D_{l0} \exp\left(-\frac{Q_l}{RT}\right)$$



$$D_b > D_l \text{ at all temp.}$$

Due to $Q_b < Q_l$, ($Q_b = 0.5Q_l$)
the curves for D_l and $D_b\delta/d$ cross
in the coordinate system of $\ln D$ versus $1/T$.

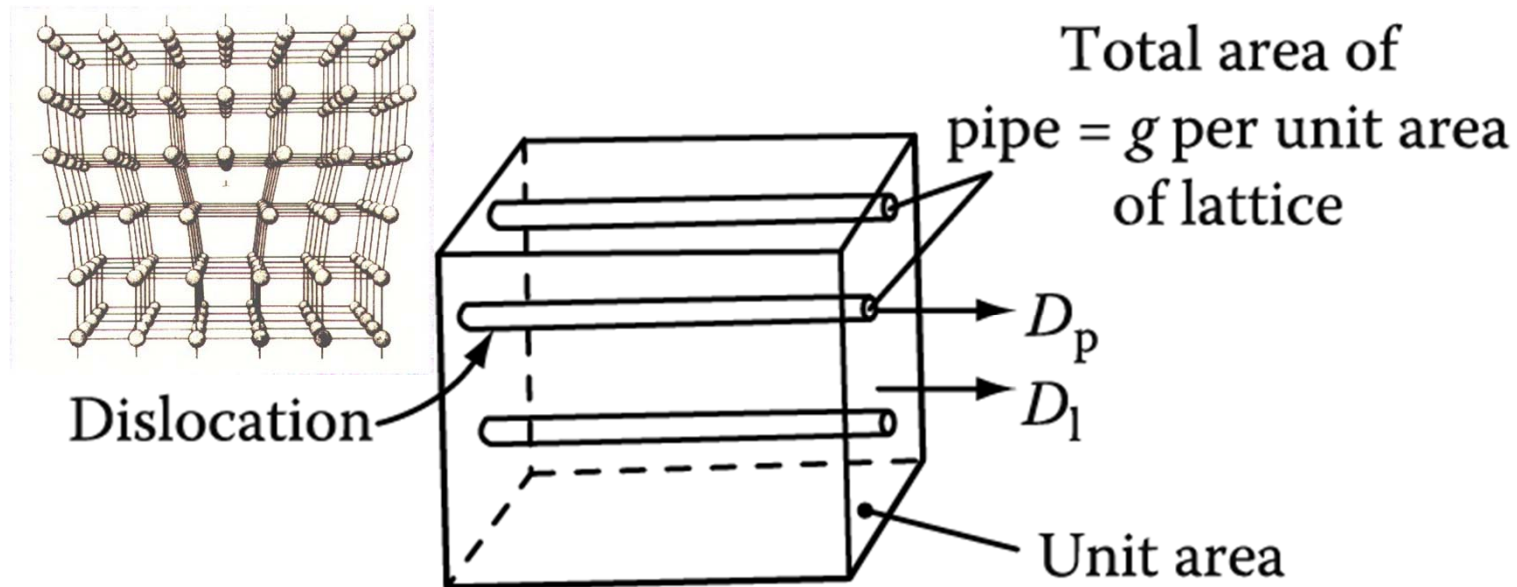
Fig. 2.27 Diffusion in a polycrystalline metal.

➔ Therefore, the grain boundary diffusion becomes predominant at temperatures lower than the crossing temperature.

$$(T < 0.75 \sim 0.8 T_m)$$

The diffusion rate depends on the atomic structure of the individual boundary = orientation of the adjoining crystals and the plane of the boundary. Also, the diffusion coefficient can vary with direction within a given boundary plane.

2.7.2 Diffusion along dislocations



Composite between plastic matrix and Al wires

Fig. 2.28. Dislocations act as a high conductivity path through the lattice.

$D_{app} = ?$ hint) 'g' is the cross-sectional area of 'pipe' per unit area of matrix.
파이프와 기지의 횡단면적

$$D_{app} = D_l + g \cdot D_p \quad \rightarrow \quad \frac{D_{app}}{D_l} = 1 + g \cdot \frac{D_p}{D_l}$$

ex) annealed metal $\sim 10^5$ disl/mm²; one dislocation(\perp) accommodates 10 atoms in the cross-section; matrix contains 10^{13} atoms/mm².

$$g = \frac{10^5 * 10}{10^{13}} = \frac{10^6}{10^{13}} = 10^{-7}$$

g = cross-sectional area of 'pipe' per unit area of matrix

At high temperatures,

diffusion through the lattice is rapid and gD_p/D_l is very small so that the dislocation contribution to the total flux of atoms is very small.

Due to $Q_p < Q_l$,

the curves for D_l and gD_p/D_l cross in the coordinate system of $\ln D$ versus $1/T$.

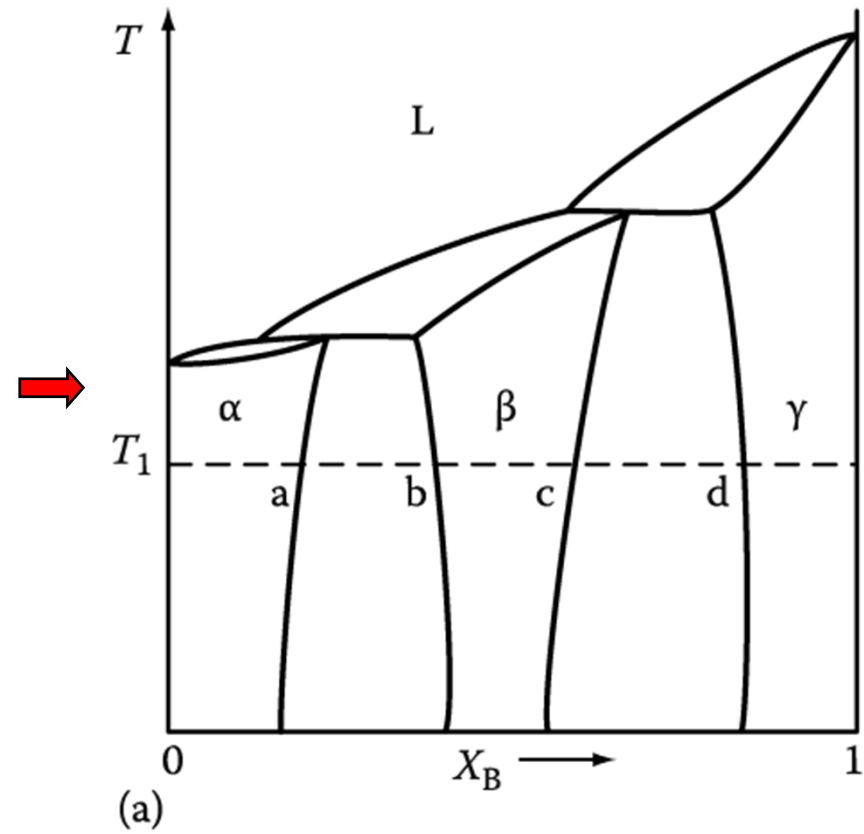
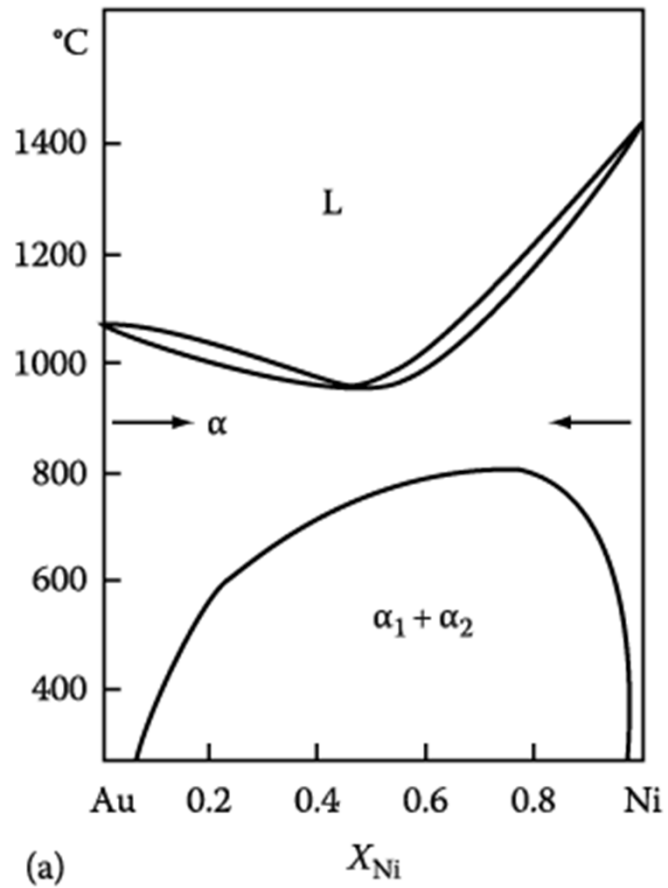
At low temperatures, ($T < \sim 0.5 T_m$)

gD_p/D_l can become so large that the apparent diffusivity is entirely due to diffusion along dislocation.

Q: How can we formulate the interface (α/β , β/γ) velocity in multiphase binary systems?

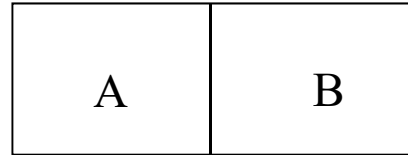
$$v = \frac{dx}{dt} = \frac{1}{(C_B^\beta - C_B^\alpha)} \left\{ \tilde{D}(\alpha) \frac{\partial C_B^\alpha}{\partial x} - \tilde{D}(\beta) \frac{\partial C_B^\beta}{\partial x} \right\} \quad \text{(velocity of the } \alpha/\beta \text{ interface)}$$

2.8 Diffusion in multiphase binary systems (다상 2원계의 확산)



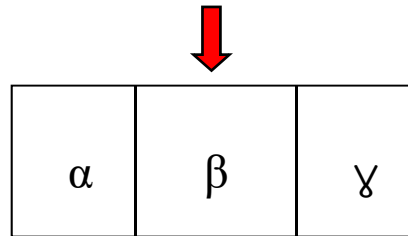
2.8 Diffusion in multiple binary system

A diffusion couple made by welding together pure A and pure B

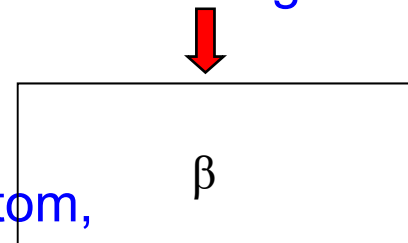


What would be the microstructure evolved after annealing at T_1 ?

→ a layered structure containing α , β & γ .



Draw a phase distribution and composition profile in the plot of distance vs. X_B after annealing at T_1 .

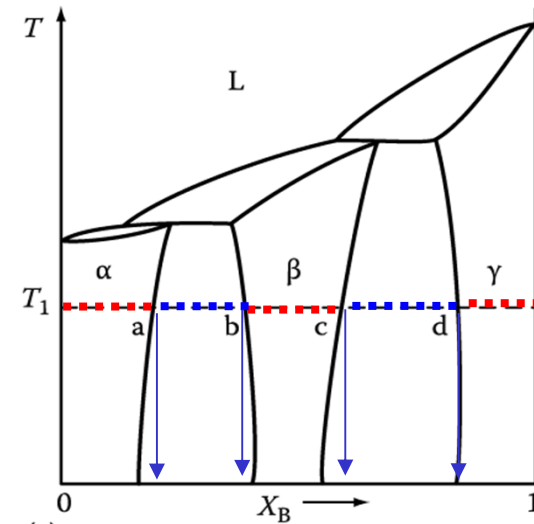


Draw a profile of activity of B atom, in the plot of distance vs. a_B after annealing at T_1 .

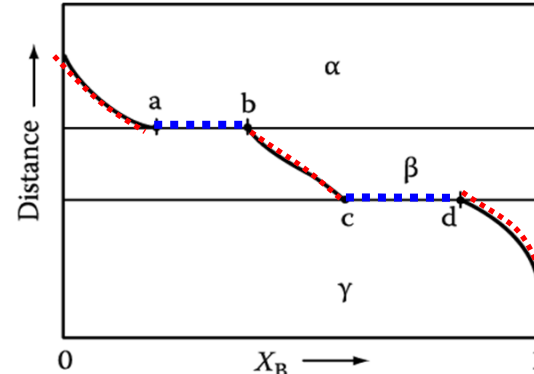
A or B atom → easy to jump interface (local equil.)

→ $\mu_A^\alpha = \mu_A^\beta, \mu_A^\beta = \mu_A^\gamma$ at interface

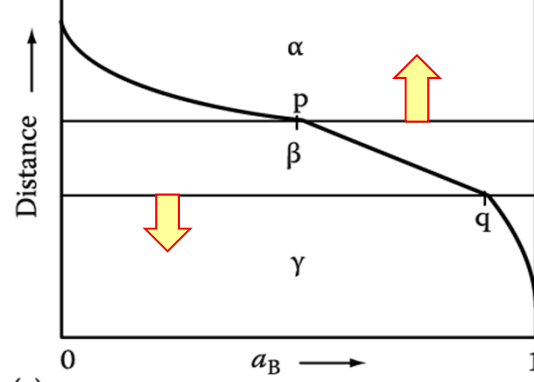
$(a_A^\alpha = a_A^\beta, a_A^\beta = a_A^\gamma)$



(a)



(b)



(c)

Complete solution of the diffusion equations for this type of diffusion couple is complex. However an expression for the rate at which the boundaries mover can be obtained as follows.

How can we formulate the interface (α/β , β/γ) velocity?

If unit area of the interface moves a distance dx , a volume ($dx \cdot 1$) will be converted from α containing C_B^α atoms/ m^3 to β containing C_B^β atoms/ m^3 .

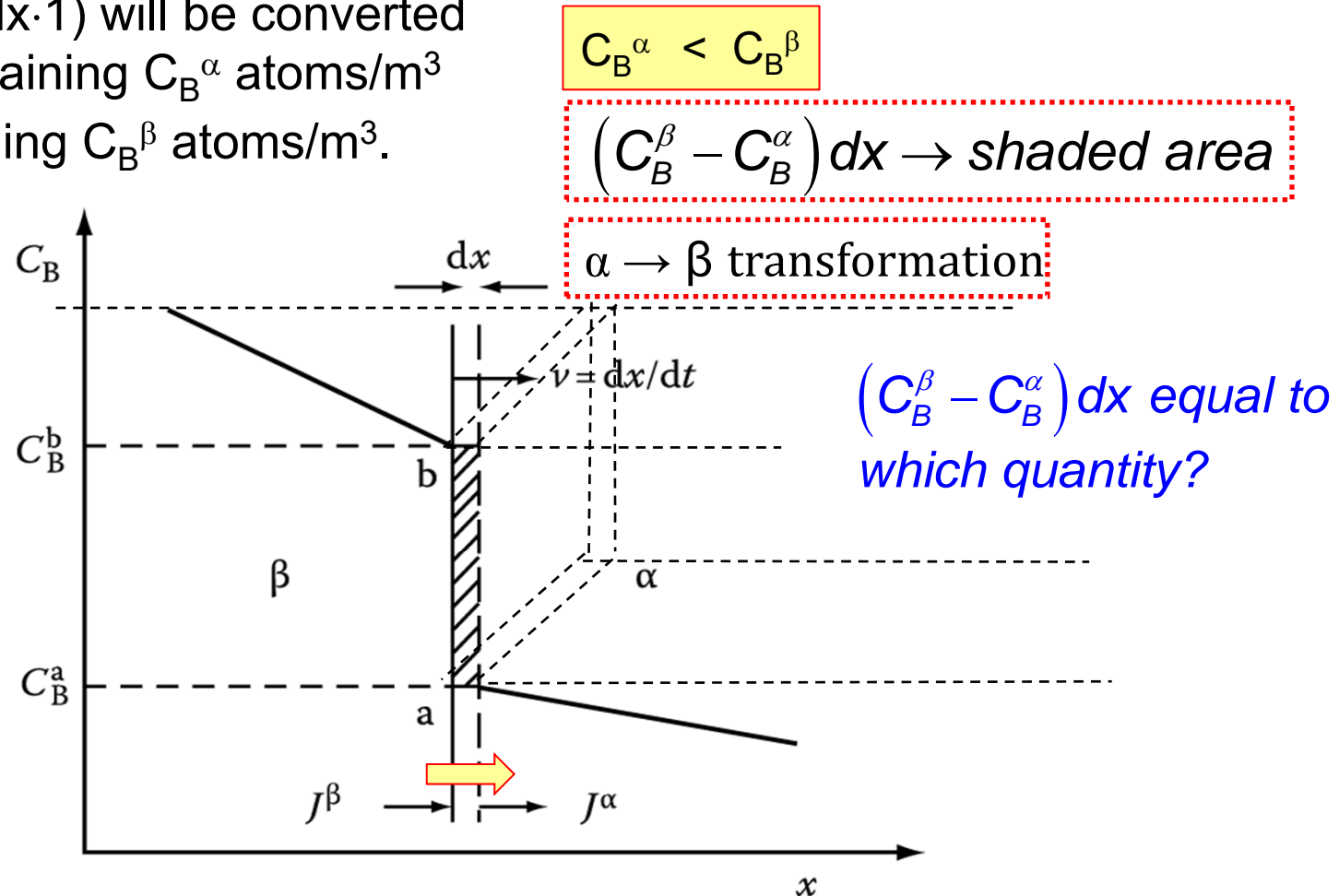


Fig. 2.30. Concentration profile across the α/β interface and its associated movement assuming diffusion control.

Local equilibrium is assumed.

a flux of B towards the interface from the β phase

$$J_B^\beta = -\tilde{D}(\beta) \frac{\partial C_B^\beta}{\partial x}$$

a flux of B away from the interface into the α phase

$$J_B^\alpha = -\tilde{D}(\alpha) \frac{\partial C_B^\alpha}{\partial x}$$

In a time dt , there will be an accumulation of B atoms given by

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2}$$



$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x}$$

$$- [J_B - J_A] dt$$

$$dC dx$$

$$\left\{ - \left(\tilde{D}(\beta) \frac{\partial C_B^b}{\partial x} \right) - \left(-\tilde{D}(\alpha) \frac{\partial C_B^a}{\partial x} \right) \right\} dt = (C_B^b - C_B^a) dx$$

Accumulation of B atoms during dt

$$v = \frac{dx}{dt} = \frac{1}{(C_B^b - C_B^a)} \left\{ \tilde{D}(\alpha) \frac{\partial C_B^a}{\partial x} - \tilde{D}(\beta) \frac{\partial C_B^b}{\partial x} \right\}$$

(velocity of the α/β interface)

Contents for today's class

- Atomic Mobility

$$D_B = M_B RTF$$

Thermodynamic factor

$$F = \left(1 + \frac{d \ln \gamma_B}{d \ln X_B}\right)$$

- Tracer Diffusion in Binary Alloys

$$\tilde{D} = X_B D_A + X_A D_B = F (X_B D_A^* + X_A D_B^*)$$

D_{Au}^* gives the rate at which Au* (or Au) atoms diffuse in a **chemically homogeneous** alloy, whereas D_{Au} gives the diffusion rate of Au when **concentration gradient** is present.

- High-Diffusivity Paths

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1. Diffusion along Grain Boundaries and Free Surface

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- Diffusion in Multiphase Binary Systems

$$v = \frac{dx}{dt} = \frac{1}{(C_B^\beta - C_B^\alpha)} \left\{ \tilde{D}(\alpha) \frac{\partial C_B^\alpha}{\partial x} - \tilde{D}(\beta) \frac{\partial C_B^\beta}{\partial x} \right\}$$

(velocity of the α/β interface)

*** Homework 3 : Exercises 2 (pages 111-114)**

until 25 October

Good Luck!!

Contents in Phase Transformation

Background
to understand
phase
transformation

(Ch1) Thermodynamics and Phase Diagrams

(Ch2) Diffusion: Kinetics

(Ch3) Crystal Interface and Microstructure

Representative
Phase
transformation

(Ch4) Solidification: Liquid \rightarrow Solid

(Ch5) Diffusional Transformations in Solid: Solid \rightarrow Solid

(Ch6) Diffusionless Transformations: Solid \rightarrow Solid

Contents for today's class II

Chapter 3 Crystal Interfaces and Microstructure

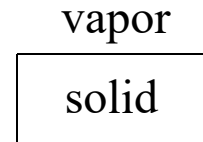
- Interfacial Free Energy
- Solid/Vapor Interfaces

Q: Types of interface in metallic system?

• Types of Interface

Basically three different types of interface are important in metallic system:

1. Free surface (solid/vapor interface)



: Important in vaporization and condensation transformations

2. Grain boundary (α/α interfaces)

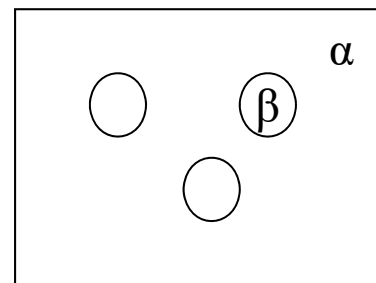
> same composition, same crystal structure

> different orientation

: Important in recrystallization, i.e. the transformation of a highly deformed grain structure into new undeformed grains, and following grain coarsening and grain growth

3. inter-phase boundary (α/β interfaces) : “Important role in determining the kinetics of phase transformation/ complex”

> different composition & crystal structure



⇒ defect

⇒ energy ↑


→ First, consider simple interfaces, (1) and (2) in this chapter

Q: Interfacial free energy, γ vs Surface tension, F ?

3.1. Interfacial free energy

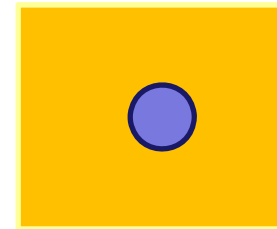
Interfacial energy ($\gamma : \text{J/m}^2$)

→ Gibbs free energy of a system containing an interface of area A

→ $G_{\text{bulk}} + G_{\text{interface}}$  → $G = G_0 + \gamma A$ (excess free E arising from the fact that some material lies in or close to the interface)

Melting and Crystallization are Thermodynamic Transitions

Solidification: Liquid \rightarrow Solid



<Thermodynamic>

• Interfacial energy $\Rightarrow \Delta T_N$

Liquid

T_m

Undercooled Liquid

Solid

No superheating required!

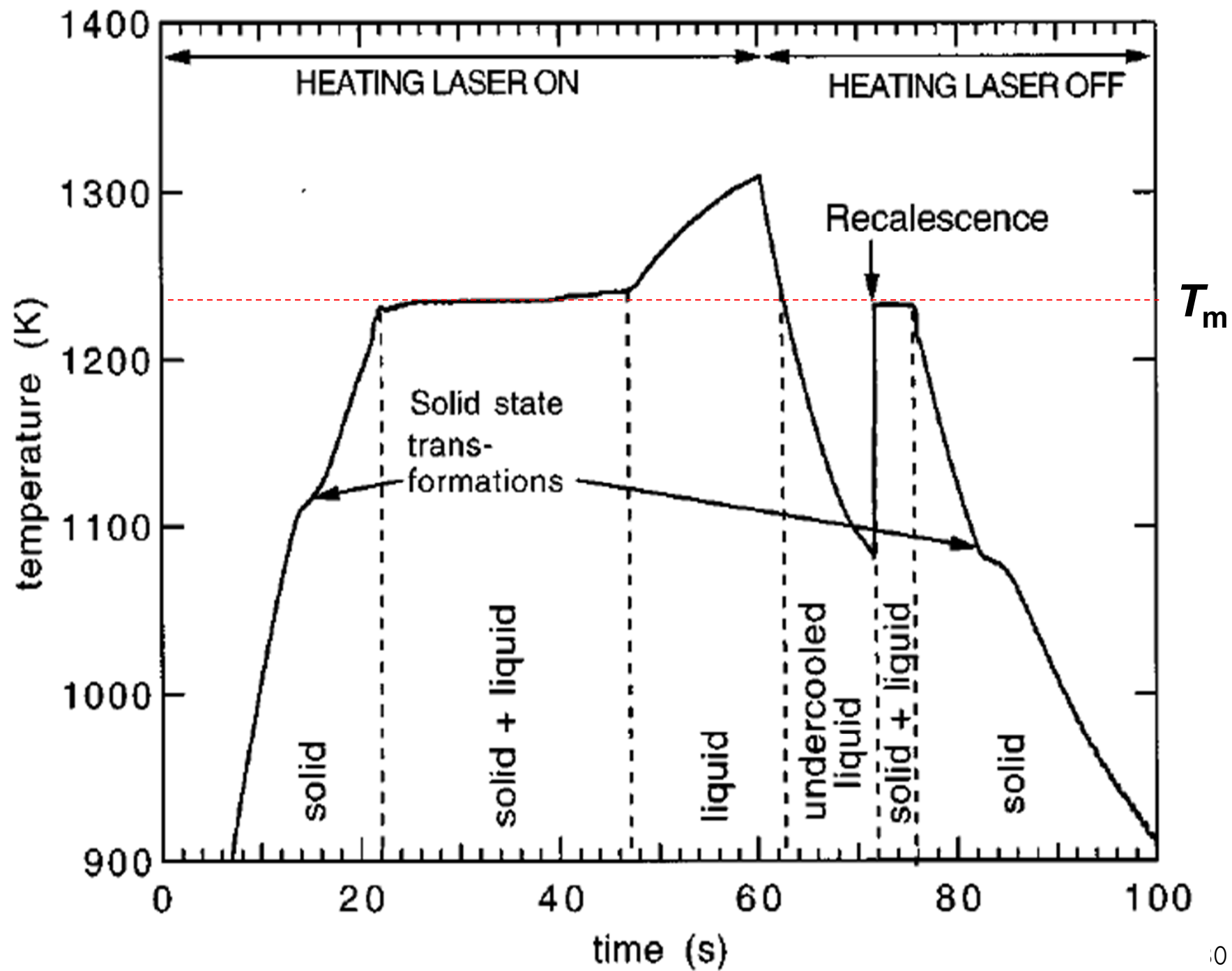
• Interfacial energy \Rightarrow No ΔT_N

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

vapor



Melting: Liquid \leftarrow Solid



3.1. Interfacial free energy

Interfacial energy (γ : J/m²)

→ Gibbs free energy of a system containing an interface of area A

→ $G_{\text{bulk}} + G_{\text{interface}}$ vapor
solid → $G = G_0 + \gamma A$ (excess free E arising from the fact that some material lies in or close to the interface)

Interfacial energy (γ) vs. surface tension (F: a force per unit length)

1) work done : $F dA = dG$

2) $dG = \gamma dA + A d\gamma$

→ $F = \gamma + A d\gamma / dA$

In case of a liq. film, $d\gamma / dA = 0$, $F = \gamma$ (N/m = J/m²)

Ex) liq. : $d\gamma / dA = 0$ Why? Maintain a constant surface structure by rearrangement
(independent of A)

sol. : $d\gamma / dA \neq 0$, but, very small value

At near melting temperature $d\gamma / dA = 0$ → $F = \gamma$ (N/m = J/m²)
(high enough atomic mobility)

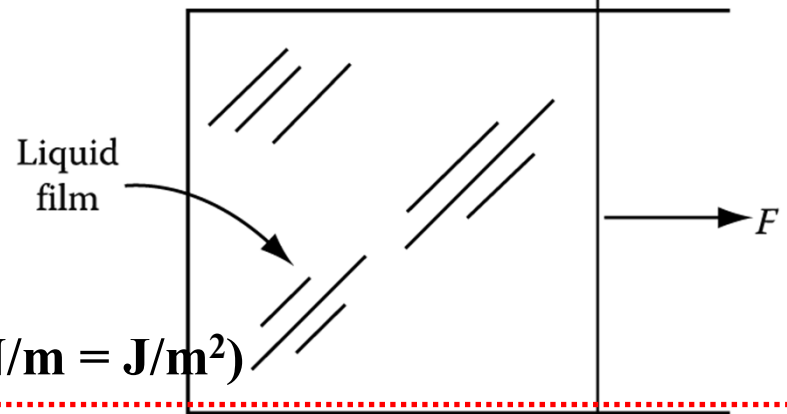


Fig. 3.1 A liquid film on a wire frame.

Q: Free surface (solid/vapor interface)?

(a) E_{sv} vs γ ?

Extra energy per atom on surface: 표면 에너지

- The measured γ values for pure metals near the melting temperature

$$E_{sv} = 3 \epsilon / 2 = 0.25 L_s / N_a \quad \Rightarrow \quad \gamma_{sv} = 0.15 L_s / N_a \quad \text{J / surface atom}$$

(\because surface free E averaged over many surface plane, S effect at high T)

(b) Equilibrium shape: Wulff surface

: Polyhedron with the largest facets having the lowest interfacial free energy

3.2 Solid / Vapor Interfaces

* **Assumption: S/V interface** → **Hard sphere model/ uncontaminated surface**
 (In real systems surfaces will reduce their free energies by the adsorption of impurities.)

- **Fcc : density of atoms in these planes decreases as $(h^2+k^2+l^2)$ increases**

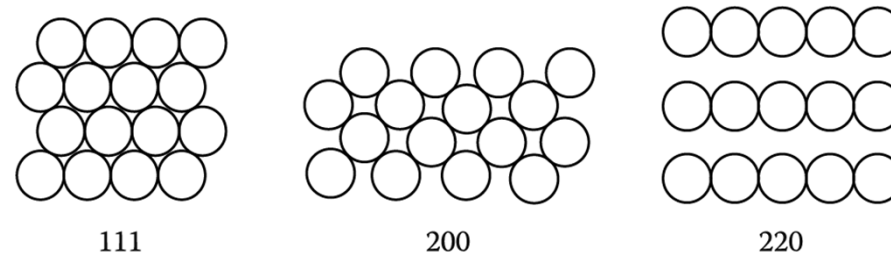
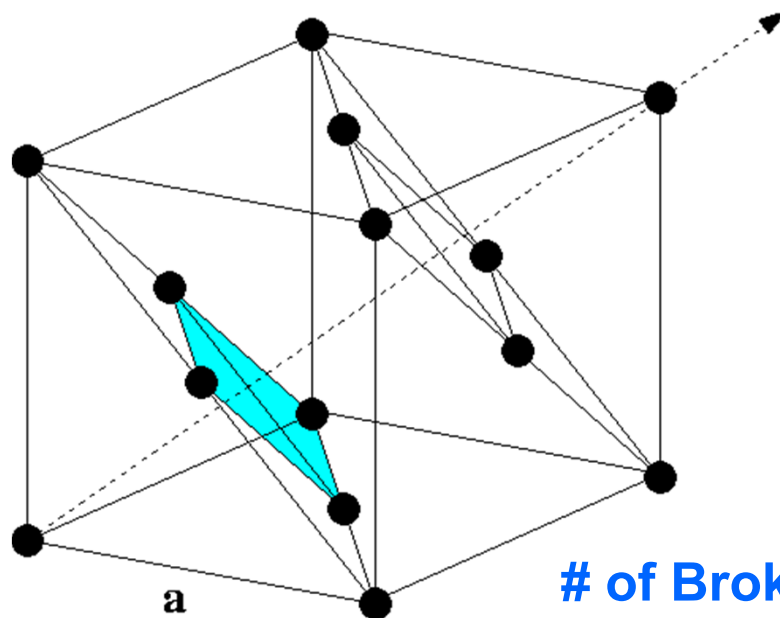


Fig. 3.2 Atomic configurations on the three closest-packed planes in fcc crystals; (111), (200), and (220).

(notation $\{200\}$ and $\{220\}$ plane has been used instead of $\{100\}$ and $\{110\}$ because the spacing of equivalent atom planes is than given by $a/(h^2+k^2+l^2)^{1/2}$ where a is the lattice parameter.)

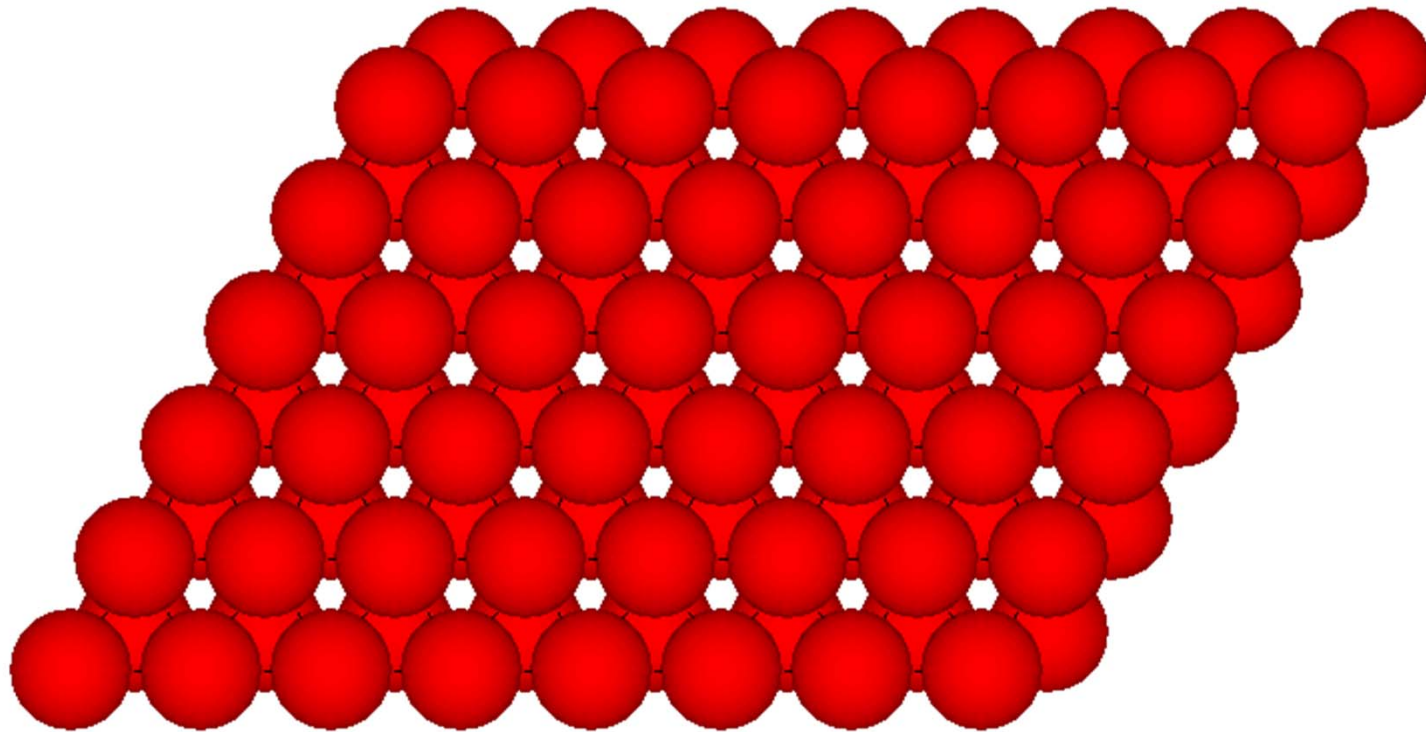
For (111) plane CN=12 **[111]**



of Broken Bonds per atom at surface?

of Broken Bonds per atom at surface? → 3 per atom

2005 - S.G. Podkolzin



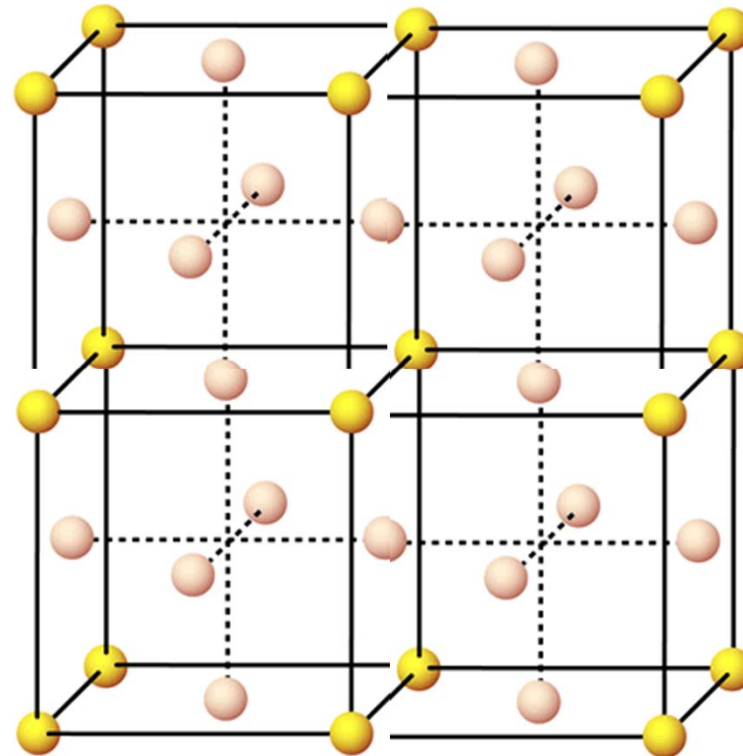
For (111) plane

of broken bond at surface : 3 broken bonds

Bond Strength: ϵ \rightarrow for each atom : $\epsilon/2$

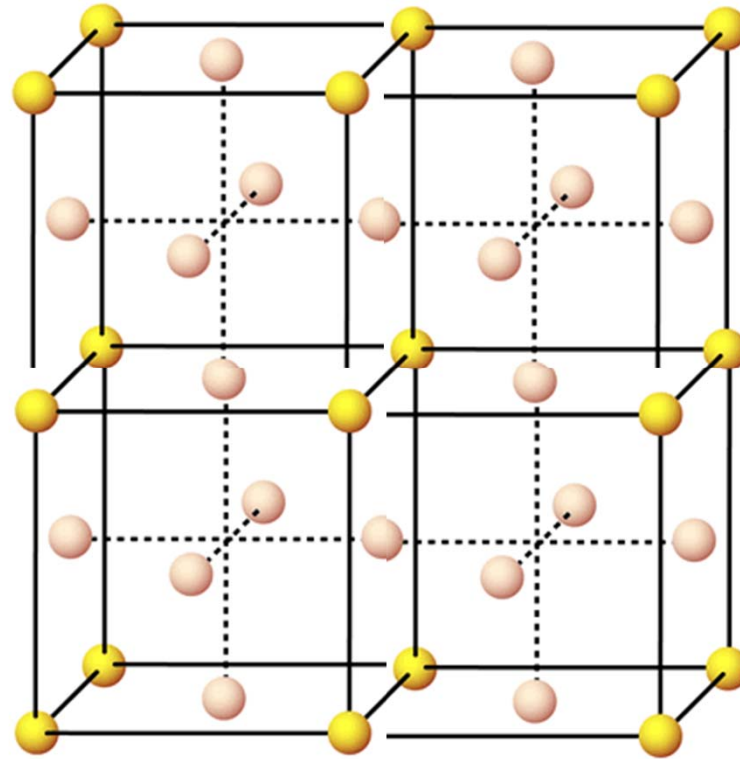
Excess internal energy over that of the atoms in the bulk: $3\epsilon/2 \uparrow$

For (200) plane CN=12



of Broken Bonds per atom at surface?

For (200) plane CN=12



of Broken Bonds per atom at surface?

of broken bond at surface : 4 broken bonds

Bond Strength: $\epsilon \rightarrow$ for each atom : $\epsilon/2$

Excess internal energy over that of the atoms in the bulk: $4\epsilon/2 \uparrow_{36}$

(excess internal energy of $4\epsilon/2$ over that of the atoms in the bulk)

For (111) plane

of broken bond at surface : **3 broken bonds**

Bond Strength: $\epsilon \rightarrow$ for each atom : $\epsilon/2$

Extra energy per atom on surface: $3\epsilon/2$

Heat of Sublimation (승화) in terms of ϵ ? $\rightarrow L_s = 12 N_a \epsilon/2$
(Latent heat of melting + vaporization) (1 mole of solid = $12 N_a$)

Energy per atom of a {111} Surface?

$$E_{sv} = 3 \epsilon/2 = 0.25 L_s / N_a \quad (\frac{1}{4} \text{ of } L_s/N_a) \quad \Rightarrow E_{sv} \text{ vs } \gamma ?$$

"Approximated value" due to assumptions, 1) 2nd nearest neighbors have been ignored and 2) strengths of the remaining bonds in the surface are unchanged from the bulk values.

γ interfacial energy = surface free energy \leftarrow Gibb's free energy (J/m²)

$$\rightarrow \gamma = G = H - TS$$

$$= E + PV - TS \quad (\text{if PV is ignored}) \quad (E_{sv} \uparrow \rightarrow \gamma \uparrow)$$

$$\rightarrow \gamma = E_{sv} - TS_{sv} \quad (S_{sv} \text{ thermal entropy, configurational entropy})$$

surface > bulk Extra configurational entropy due to vacancies

$$\rightarrow \partial\gamma / \partial T = -S : \text{surface free energy decreases with increasing T}$$

$0 < S < 3 \text{ (mJ/m}^2\text{K}^{-1})$ due to increased contribution of entropy

* E_{sv} vs γ ?

- The measured γ values for pure metals near the melting temperature

$$E_{sv} = 3 \epsilon / 2 = 0.25 L_s / N_a \quad \Rightarrow \quad \gamma_{sv} = 0.15 L_s / N_a \quad \text{J / surface atom}$$

(\because surface free E averaged over many surface plane, S effect at high T)

• Average Surface Free Energies of Selected Metals

Crystal	T_m (°C)	γ_{sv} (mJ m ⁻²)
Sn	232	680
Al	660	1080
Ag	961	1120
Au	1063	1390
Cu	1084	1720
δ -Fe	1536	2080
Pt	1769	2280
W	3407	2650

측정 어려움, near T_m

γ of Sn : 680 mJ/m² (T_m : 232°C)

γ of Cu : 1720 mJ/m² (T_m : 1083°C)

cf) G.B. energy γ_{gb} is about one third of γ_{sv}

* Higher T_m \rightarrow stronger bond (large L_s) \rightarrow larger surface free energy (γ_{sv})

high T_m \rightarrow high L_s \rightarrow high γ_{sv}

Surface energy for high or irrational {hkl} index

Closer surface packing → smaller number of broken bond → lower surface energy
 # of broken bonds will increase through the series {111} {200} {220} → γ_{SV} will increase along the same series (if different entropy term is ignored)

A crystal plane at an angle θ to the close-packed plane will contain broken bonds in excess of the close-packed plane due to the atoms at the steps.

Surface with high {hkl} index

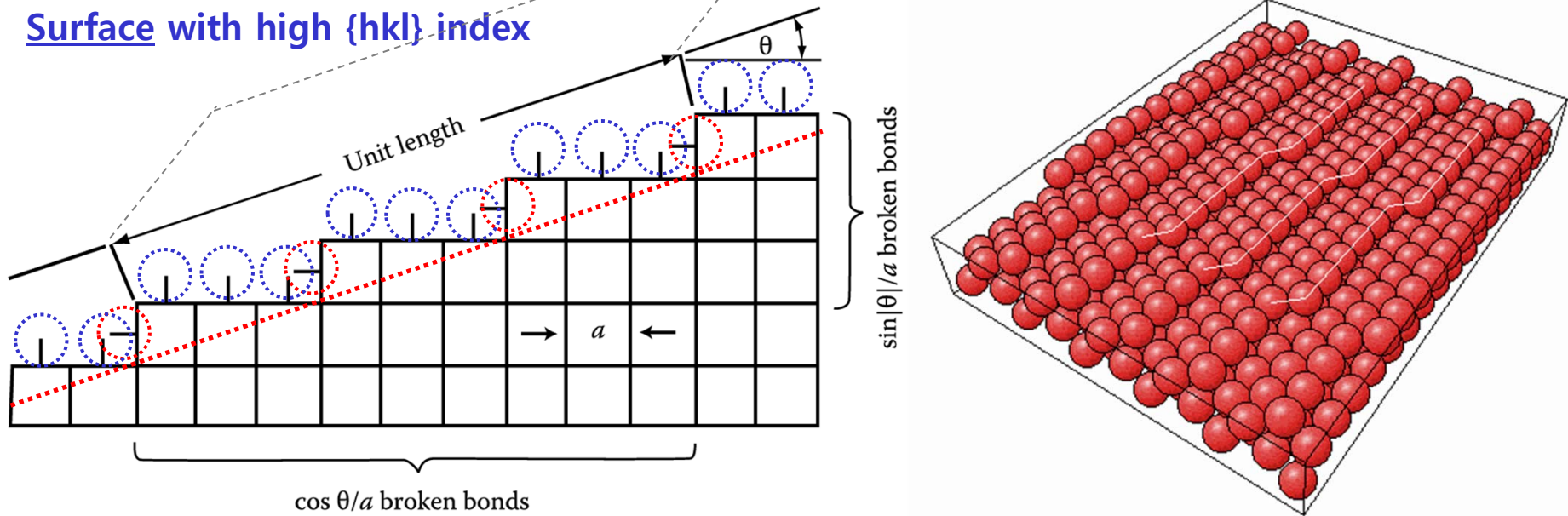


Fig. 2.2 The 'broken-bond' model for surface energy.

**$(\cos\theta/a)(1/a)$: broken bonds
 from the atoms on the steps**

**$(\sin|\theta|/a)(1/a)$: additional broken bonds
 from the atoms on the steps**

Surface energy for high or irrational {hkl} index

$(\cos\theta/a)(1/a)$: broken bonds from the atoms on the steps

$(\sin|\theta|/a)(1/a)$: additional broken bonds from the atoms on the steps

Attributing $\varepsilon/2$ energy to each broken bond,

$$E_{sv} = \frac{1}{1 \times a} \frac{\varepsilon}{2} \left(\frac{\cos\theta}{a} + \frac{\sin|\theta|}{a} \right)$$

$$= \frac{\varepsilon(\cos\theta + \sin(|\theta|))}{2a^2}$$

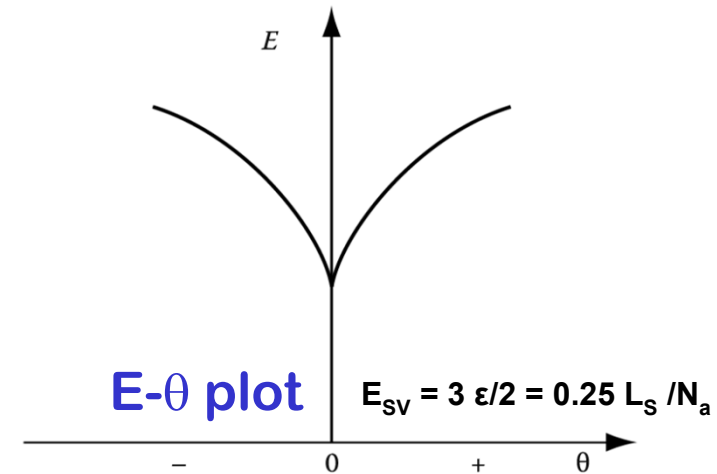


Fig. 3.4 Variation of surface energy as a function of θ

- **The close-packed orientation ($\theta = 0$) lies at a cusped minimum in the E plot.**
- Similar arguments can be applied to any crystal structure for rotations about any axis from any reasonably close-packed plane.
- **All low-index planes should therefore be located at low-energy cusps.**
- If γ is plotted versus θ similar cusps are found (γ - θ plot), but as a result of **entropy effects** they are **less prominent than in the E- θ plot**, and for the higher index planes they can even disappear.

Q: Free surface (solid/vapor interface)?

(a) E_{SV} vs γ ?

Extra energy per atom on surface

- The measured γ values for pure metals near the melting temperature

$$E_{SV} = 3 \epsilon/2 = 0.25 L_S / N_a \quad \Rightarrow \quad \gamma_{SV} = 0.15 L_S / N_a \quad \text{J / surface atom}$$

(\because surface free E averaged over many surface plane, S effect at high T)

(b) Equilibrium shape: Wulff surface

: Polyhedron with the largest facets having the lowest interfacial free energy

Equilibrium shape: Wulff surface

* A convenient method for plotting the variation of γ with surface orientation in 3 dimensions

* **Distance from center** : γ_{sv}

→ Construct the surface using γ_{sv} value as a distance between the surface and the origin when measured along the normal to the plane

Several plane A_1, A_2 etc. with energy γ_1, γ_2

Total surface energy : $A_1\gamma_1 + A_2\gamma_2 \dots$

= $\sum A_i \gamma_i \rightarrow$ minimum

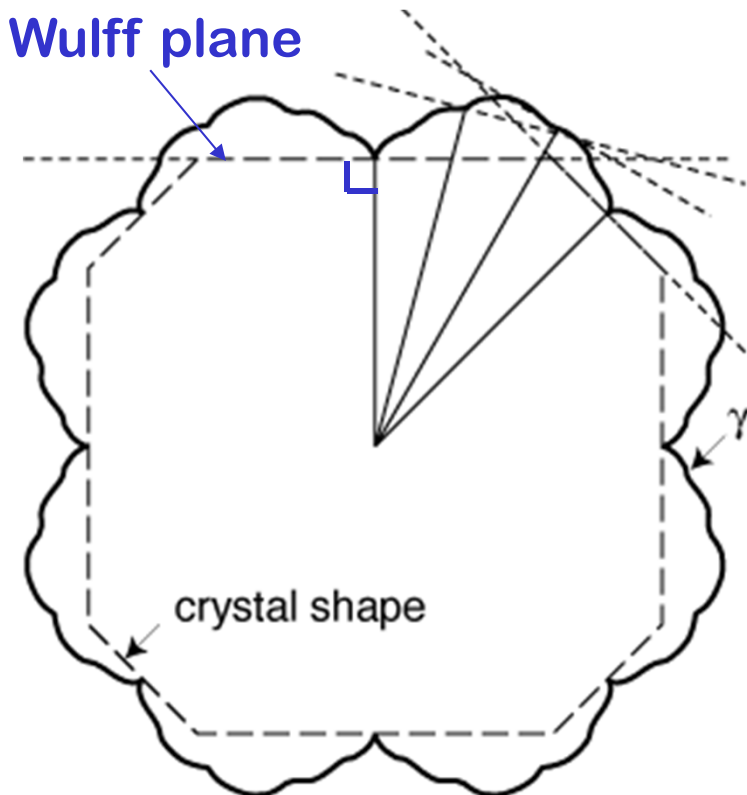
→ equilibrium morphology

: can predict the equilibrium shape of
an isolated single crystal

How is the equilibrium shape
determined?

$$\sum_{i=1}^n A_i \gamma_j = \text{Minimum}$$

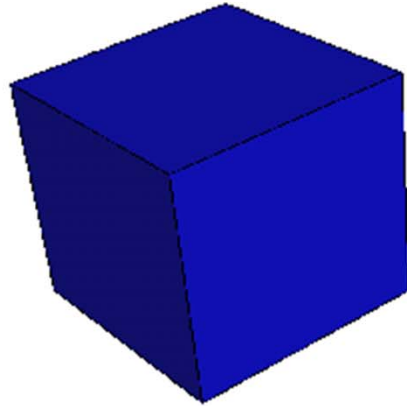
Wulff plane



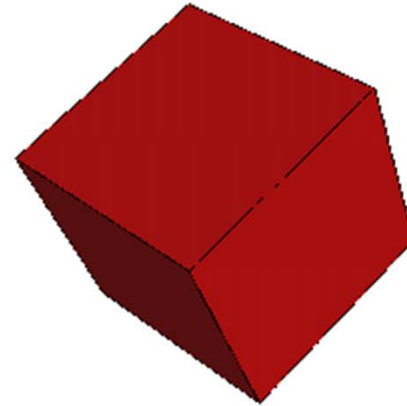
γ - θ plot

Due to entropy effects the plot are less prominent than in the E_{sv} - θ plot, and for the higher index planes they can even disappear

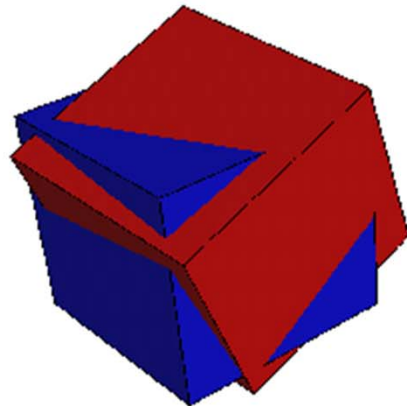
Process of Wulff shape intersection for two cubic Wulff shapes
: Polyhedron with the largest facets having the lowest interfacial free energy



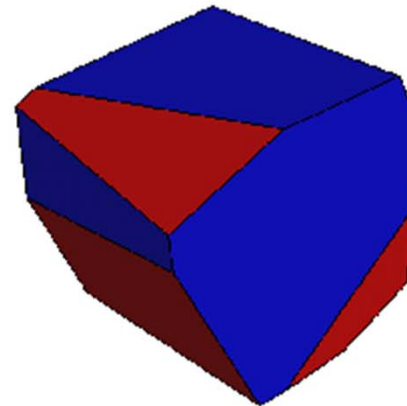
(a) Wulff Shape I



(b) Wulff Shape II



(c) Union of I and II



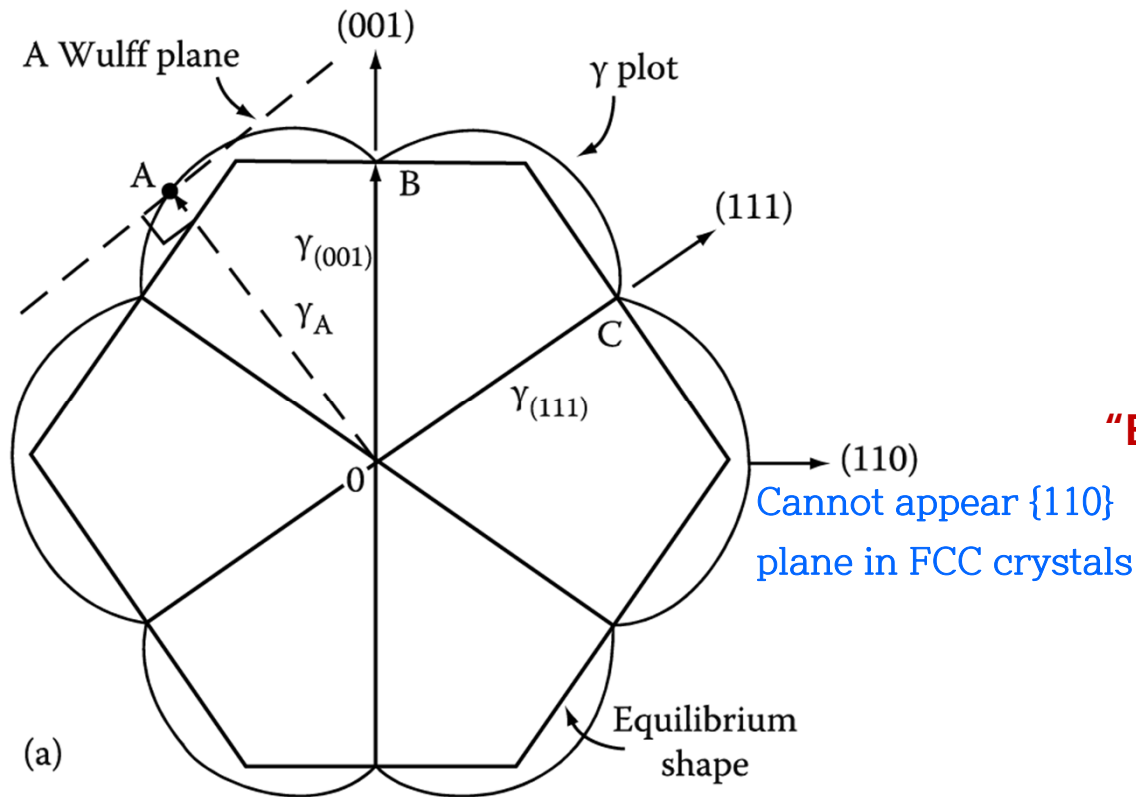
(d) Intersection of I and II

Figure 1: The process of Wulff shape intersection for two cubic Wulff shapes with displaced origins and rotated coordinate systems. Each individual shape has cubic symmetry $m\bar{3}m$ and $[100]$ facets.

Equilibrium shape: Wulff surface

Equilibrium shape can be determined experimentally by annealing small single crystals at high temperatures in an inert atmosphere, or by annealing small voids inside a crystal.

Of course **when γ is isotropic**, as for liquid droplets, both the γ -plots and equilibrium shapes are **spheres**.



“Equilibrium shape of FCC crystals”

- 1) Square faces $\{100\}$ and
- 2) Hexagonal faces $\{111\}$

The length OA represents the free energy of a surface plane whose normal lies in the direction OA.

A possible $(\bar{1}10)$ section through the γ -plot of an fcc crystal