재료상변태

Phase Transformation of Materials

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Contents for previous class

- Tracer Diffusion in Binary Alloys
- Diffusion in Ternary Alloy
- High-Diffusivity Paths

  1) Diffusion along Grain Boundaries and Free Surface

  2) Diffusion Along Dislocation
- Diffusion in Multiphase Binary Systems

Contents for today's class

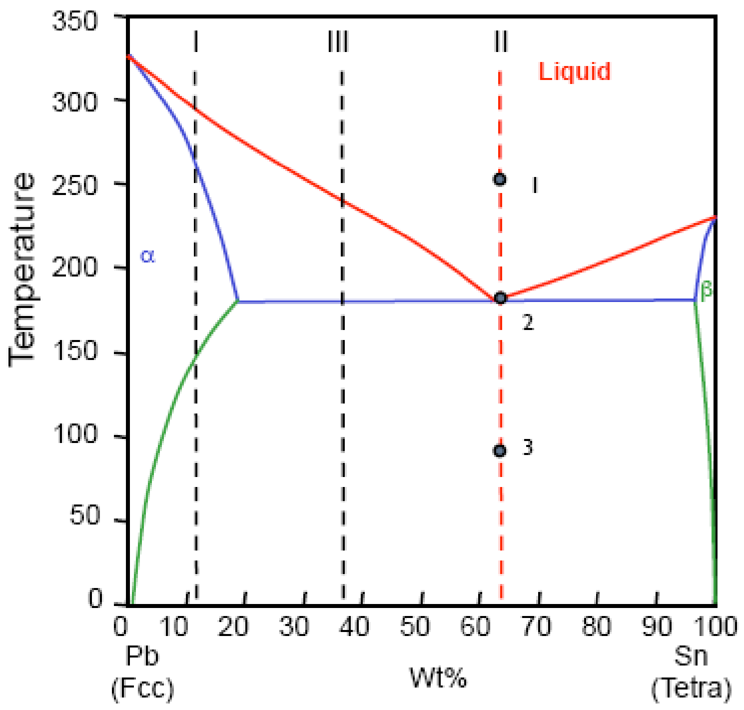
- Diffusion in multiphase binary system

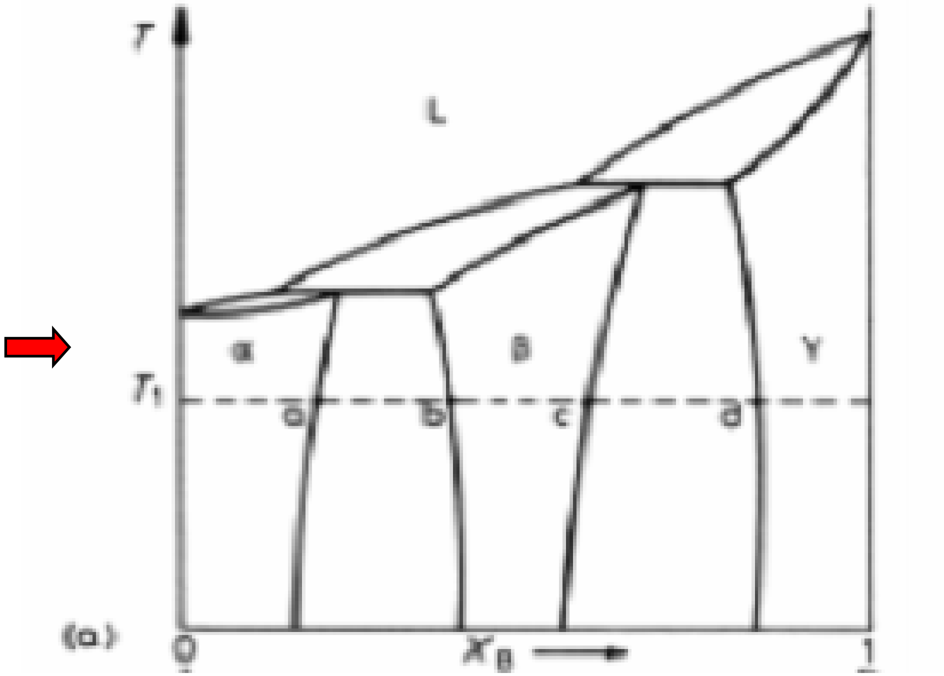
Chapter 3 Crystal Interfaces and Microstructure

- Interfacial Free Energy
- Solid/Vapor Interfaces

2.8 Diffusion in multiple binary system

Pb-Sn phase diagram



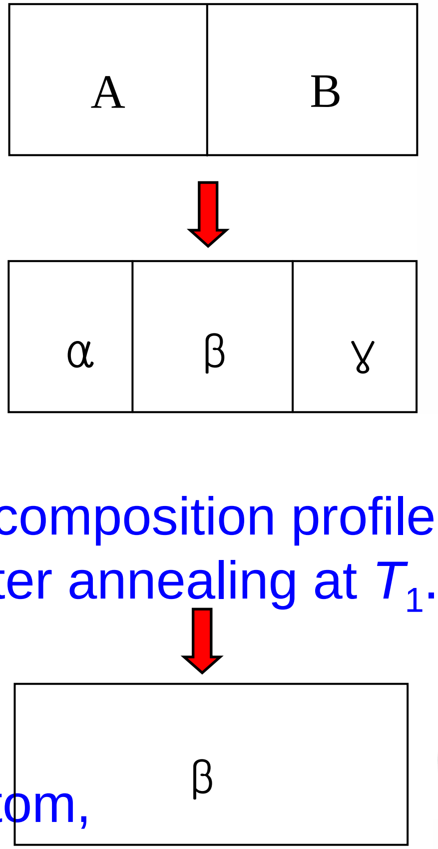


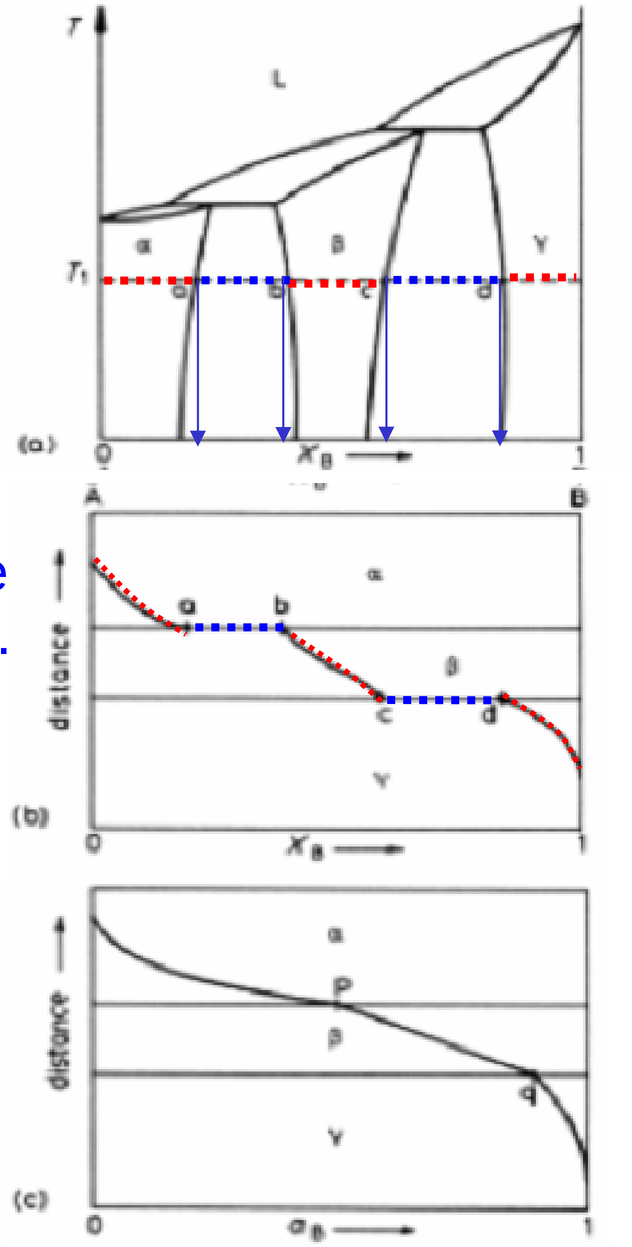
2.8 Diffusion in multiple binary system

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 & ɣ.





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.)

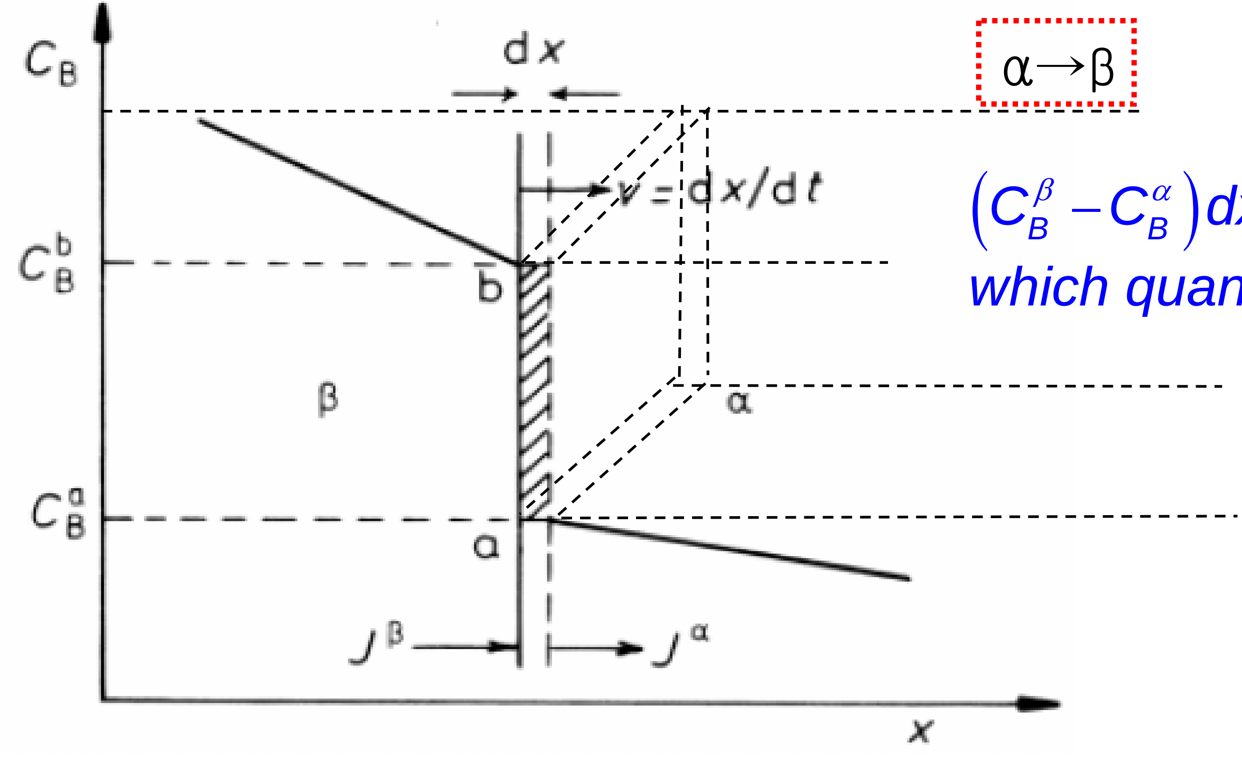
$$\rightarrow \mu_A^{\alpha} = \mu_A^{\beta},\ \mu_A^{\beta} = \mu_A^{\gamma} \text{ at interface}$$

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

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

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

$$\boxed{\left(C_B^{\beta} - C_B^{\alpha}\right)dx \rightarrow shaded\ area}$$



$\boxed{\alpha \rightarrow \beta}$

$\left(C_B^{\beta} - C_B^{\alpha}\right)dx$ equal to which quantity?

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

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

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

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

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

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

➡

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

$- [J_B - J_A]\, dt$

$dCdx$

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

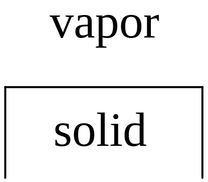
$$v = \frac{dx}{dt} = \frac{1}{(C_B^{\ b} - C_B^{\ a})}\left\{\tilde{D}(\alpha)\frac{\partial C_B^{\ a}}{\partial x} - \tilde{D}(\beta)\frac{\partial C_B^{\ b}}{\partial x}\right\}$$

(velocity of the α/β interface)

3. Crystal interfaces and microstructure

- **Types of Interface**

1. Free surface (solid/vapor interface)



2. Grain boundary (α/ α interfaces)

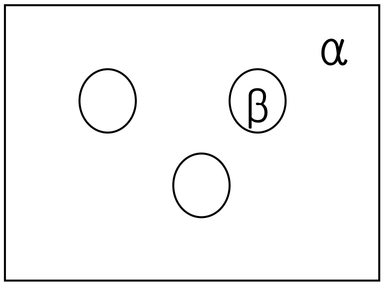
> same composition, same crystal structure

> different orientation

3. inter-phase boundary (α/β interfaces)

> different composition &

crystal structure



⇨ defect

⇨ energy ↑

3.1 Interfacial Free Energy

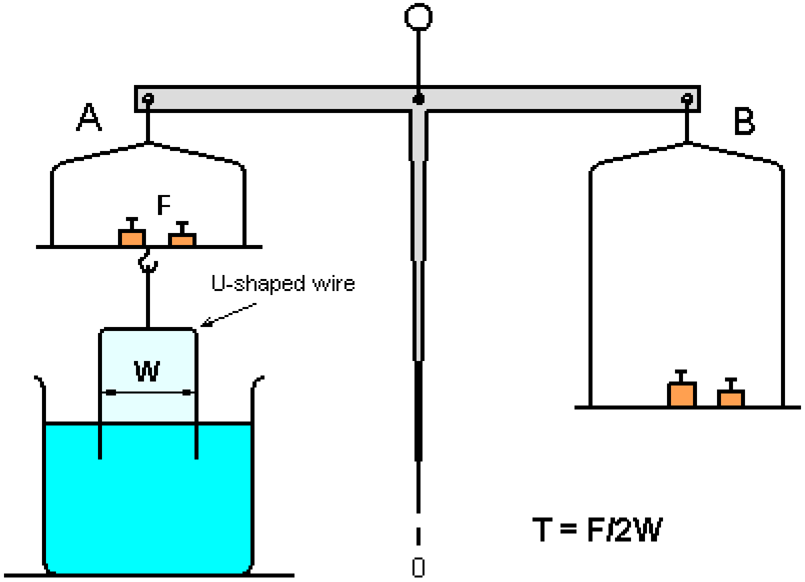


Figure 5 - Experimental device to measure the surface tension of a liquid.

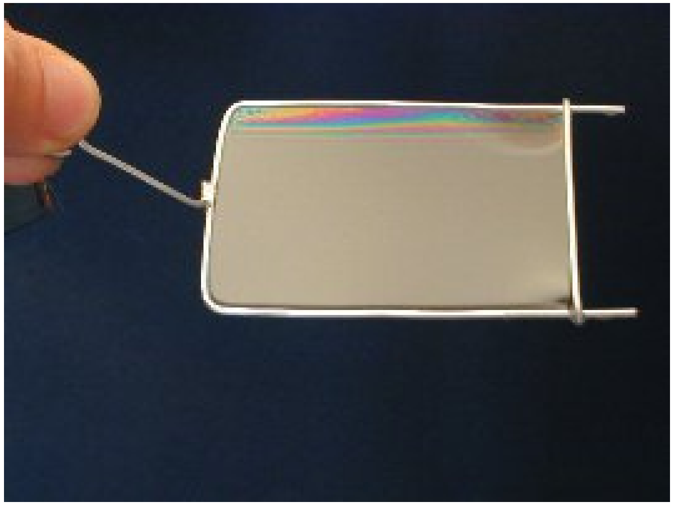


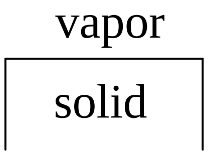
Figure 6 - "U" frame in the liquid under examination.

3.1. Interfacial free energy

Interfacial energy (γ : J/m^2)

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

→ $G_{bulk} + G_{interface}$



→ $G = G_0 + \gamma A$

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/m^2)

Ex) liq. : $d\gamma / dA = 0$ *Why?* **Rearrangement**

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

At near melting temperature $d\gamma / dA = 0$

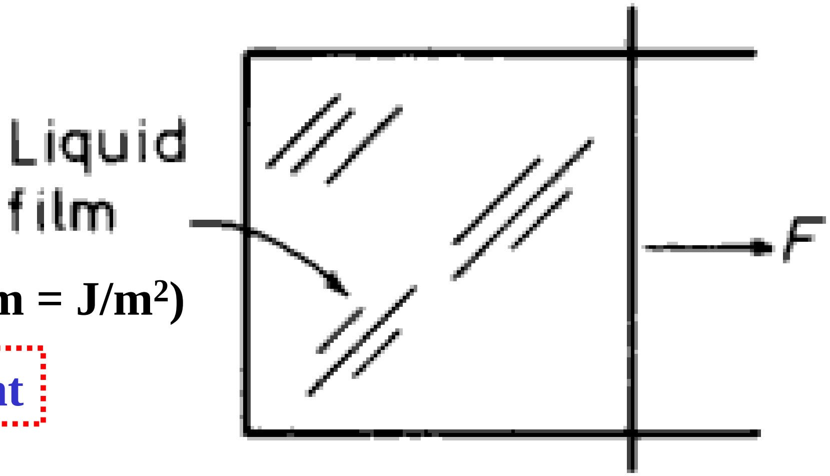


Fig. 3.1 A liquid film on a wire frame.

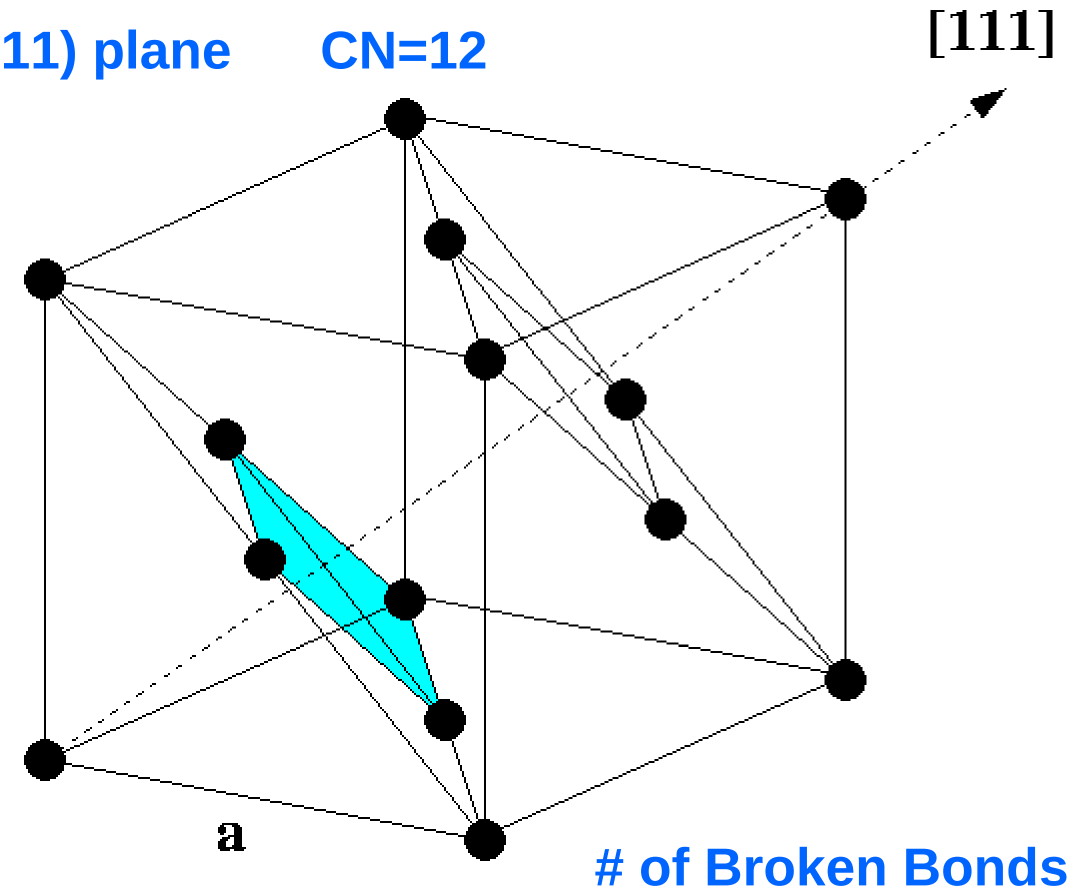
3.2 Solid / Vapor Interfaces

*** Hard sphere model**

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

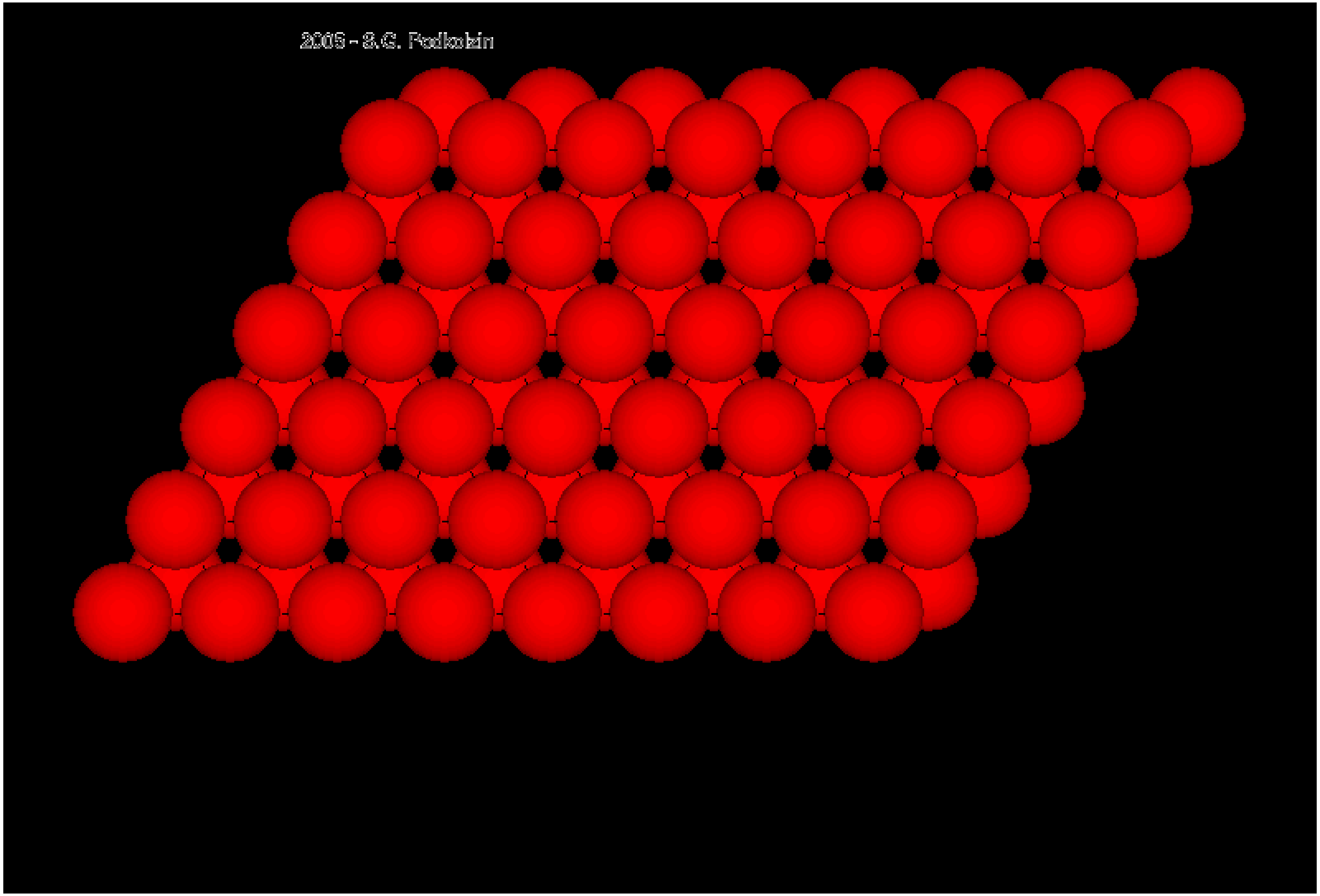
Origin of the surface free energy? → Broken Bonds

For (111) plane CN=12



# of Broken Bonds per atom at surface?

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



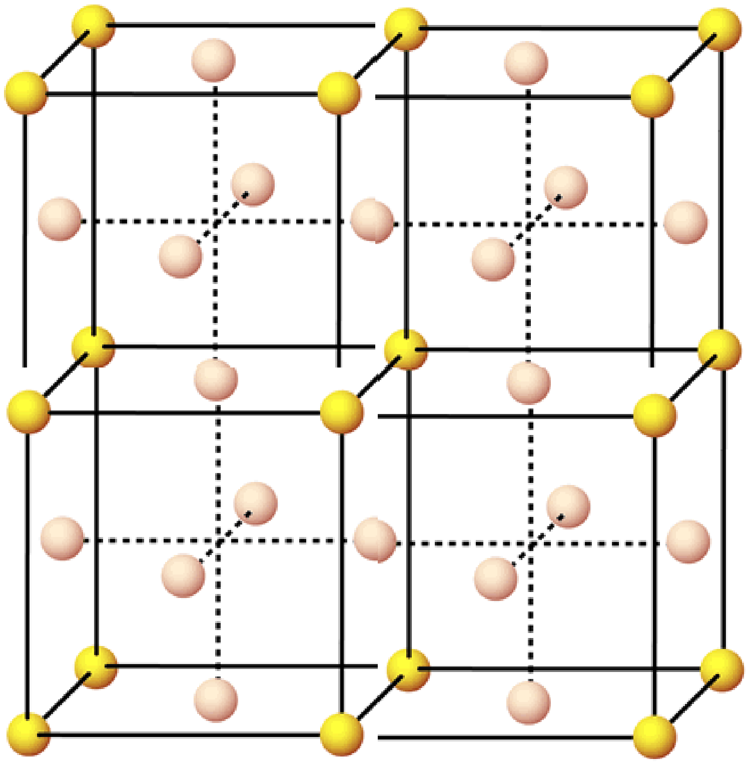
For (111) plane

of broken bond at surface : 3 broken bonds

Bond Strength: ε >> for each atom : ε/2

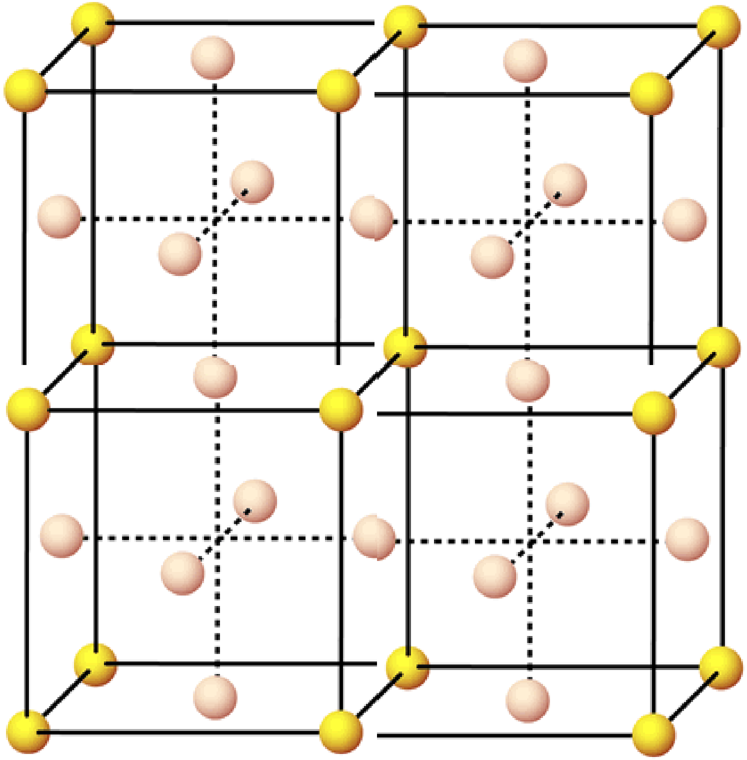
Lowering of Internal Energy per Bond: 3ε/2 ↓

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: ε **>> for each atom :** $\varepsilon/2$

Lowering of Internal Energy per Bond: $4\varepsilon/2$ ↓

For (100) plane

# of broken bond at surface : 3 broken bonds

Bond Strength: ε >> for each atom : $\varepsilon/2$

Lowering of Internal Energy per Bond: $3\varepsilon/2$

Heat of Sublimation in terms of ε? $\rightarrow L_S = 12\,N_a\,\varepsilon/2$

Energy per atom of a {111} Surface?

$E_{SV} = 3\,\varepsilon/2 = 0.25\,L_S\,/N_a$

E_{SV} vs γ ?

γ interfacial energy = free energy (J/m²)

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

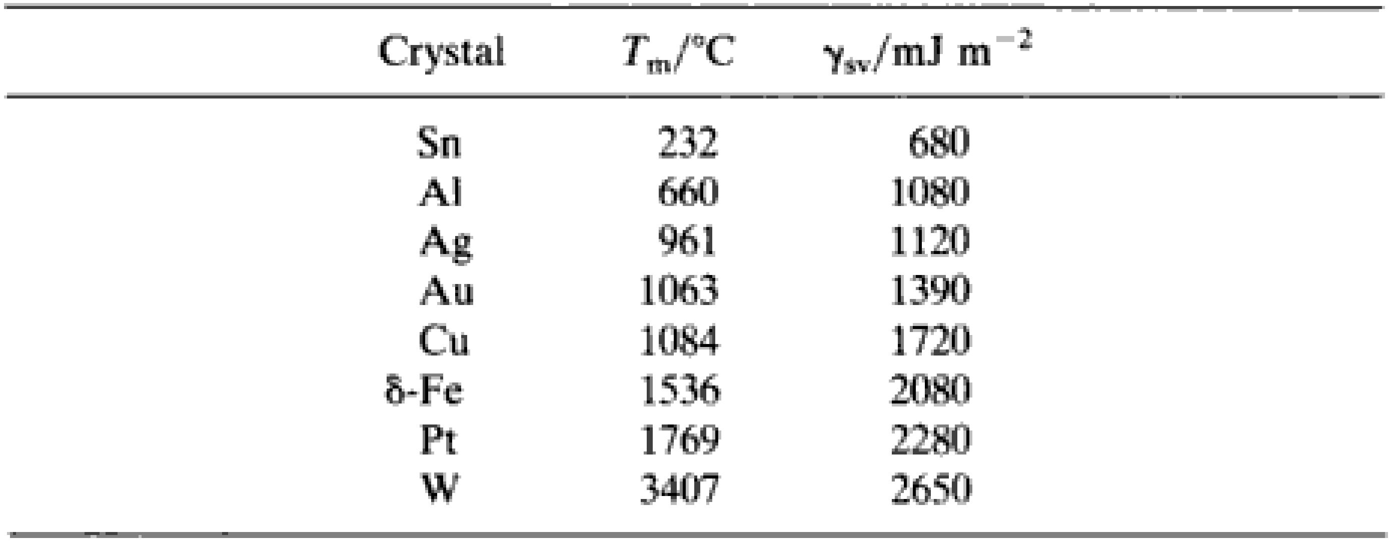
$= E + PV - TS$ **(: PV is ignored)**

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

$\rightarrow \boxed{\partial\gamma\,/\partial T = -S}$ **: surface energy decreases with increasing T**

due to increased contribution of entropy

- **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

γ of Sn : 680 mJ/m^2 (T_m : 232°C)
γ of Cu : 1720 mJ/m^2 (T_m : 1083°C)

C.F. G.B. energy γ_{gb} is about one third of γ_{sv}

Higher T_m,
>> stronger bond (large negative bond energy)
>> larger surface energy

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

$$\gamma_{SV} = 0.15\ L_S / N_a \quad \text{J / surface atom}$$

$$high\ T_m \rightarrow high\ L_s \rightarrow high\ \gamma_{sv}$$

Surface energy for high or irrational {hkl} index

Closer surface packing, >> smaller number of broken bond
>> lower surface energy

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.

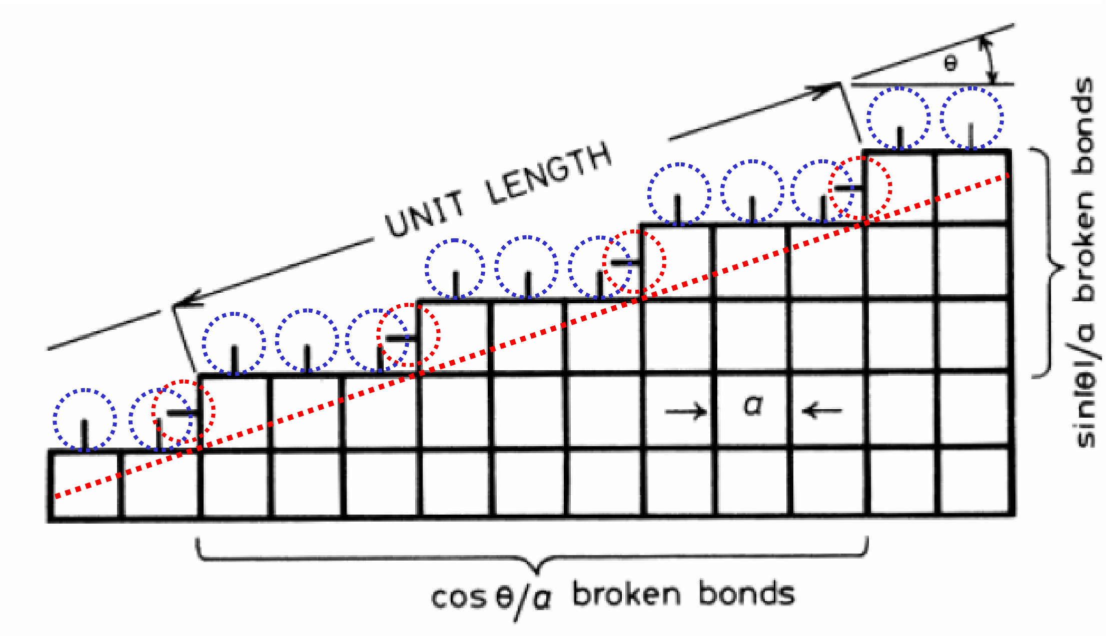
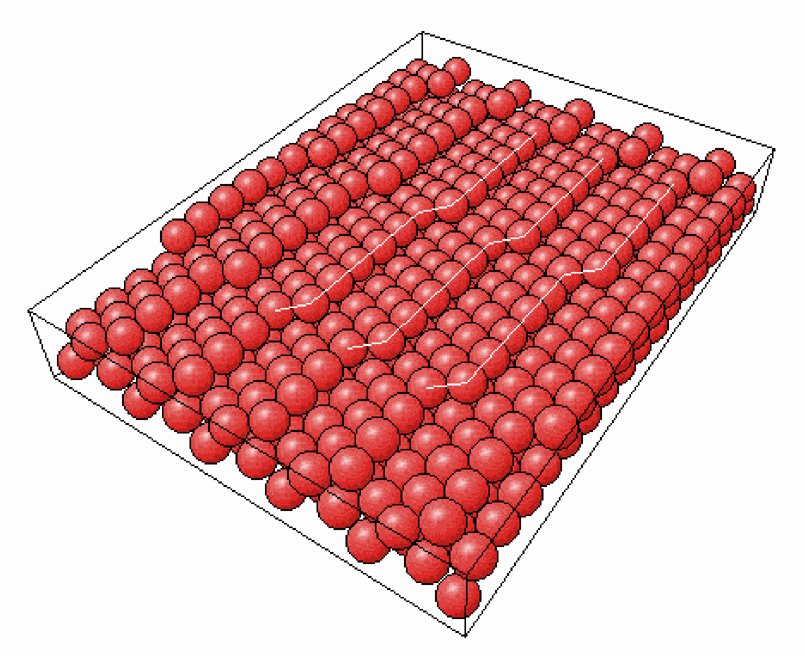


Fig. 3.3 The 'broken-bond' model for surface energy.



$(\cos\Theta/a)(1/a)$: **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

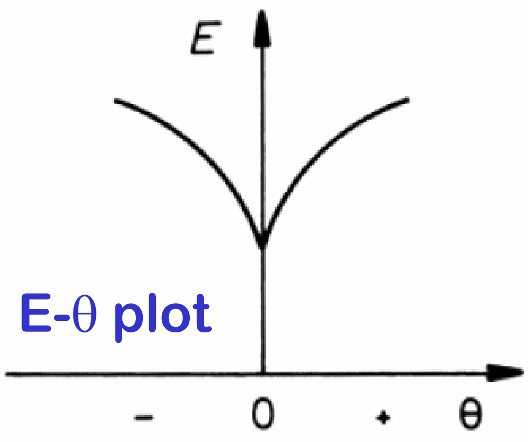
(cosΘ/a)(1/a) : **broken bonds from the atoms on the steps**

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

Attributing ε/2 energy to each broken bond,

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

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



E-θ plot

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

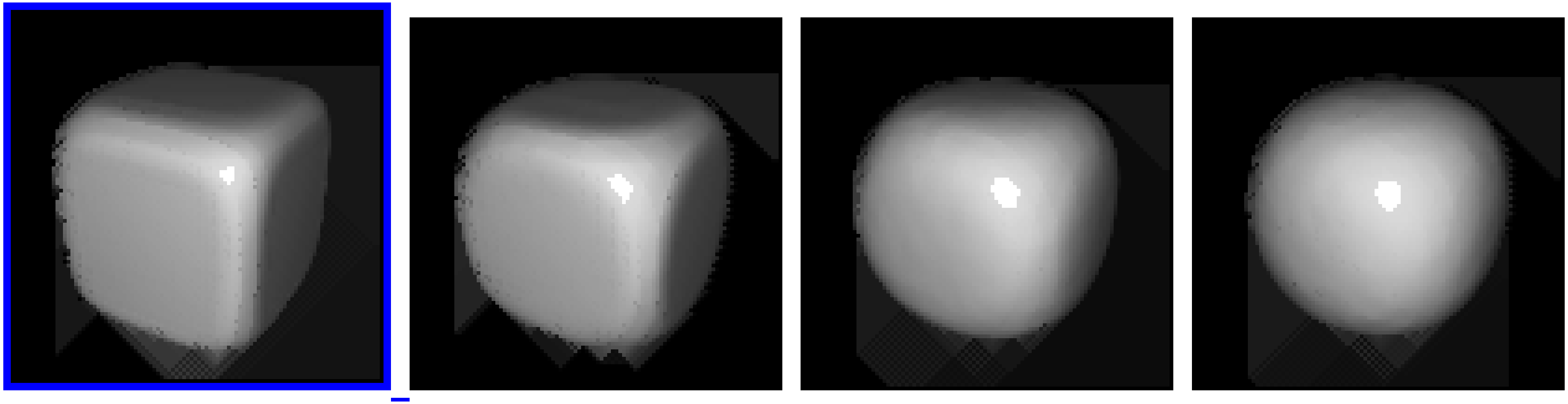
- **The close-packed orientation (θ = 0) lies at a cusped minimum in the E plot.**
- **Similar arguments can be applied to any crystal structure for rotations about any axis from any reasonably close-packed plane.**
- **All low-index planes should therefore be located at low-energy cusps.**

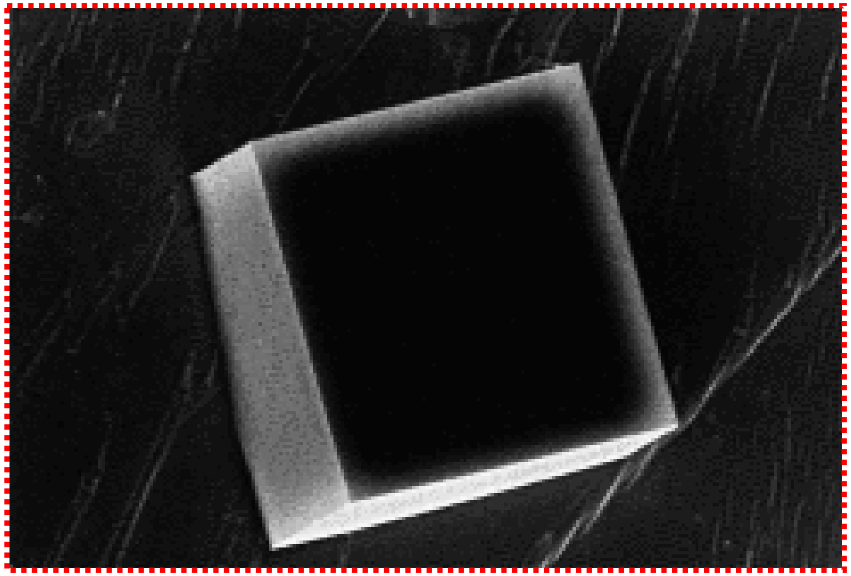
Equilibrium shape of a crystal?

- 기지와 β 입자와의 평형을 고려함에 있어서,

-자유에너지는 입자 모양이 고정된 경우는 입자의 크기에 대해 최소화된다.

-그러나 입자의 크기가 고정화 된다면 자유에너지는 모양에 대해 최소값을 가질 것이다.





Equilibrium shape: Wulff surface

Distance from center : γ_{sv}

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

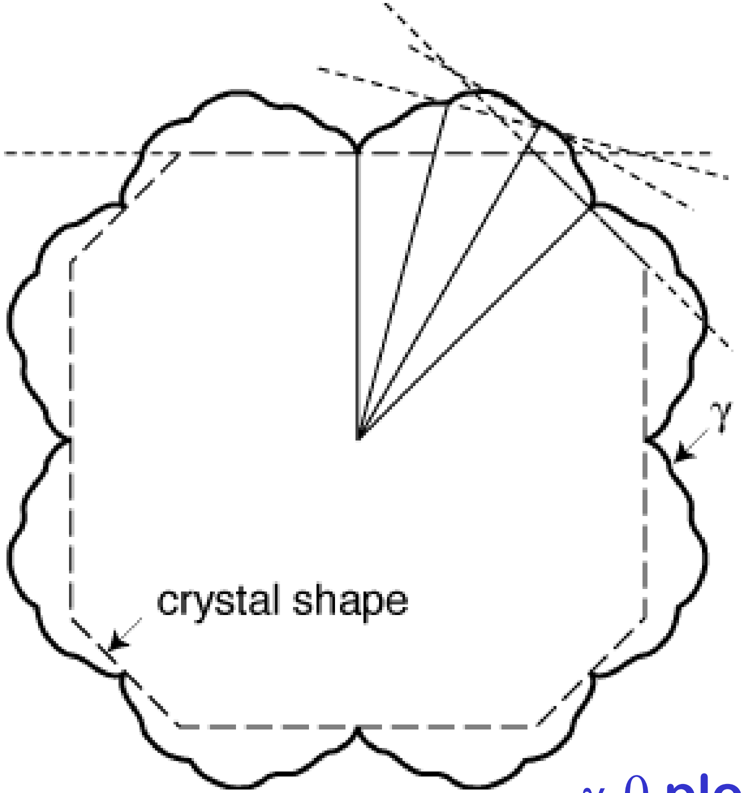
Total surface energy : $A_1\gamma_1 + A_2\gamma_2 \ldots$

$= \sum A_i \gamma_i \rightarrow$ minimum

→ equilibrium morphology

Analytical solution in 2D is reported

How is the equilibrium shape determined?



γ-θ plot

Equilibrium shape: Wulff surface

(a) Wulff Shape I

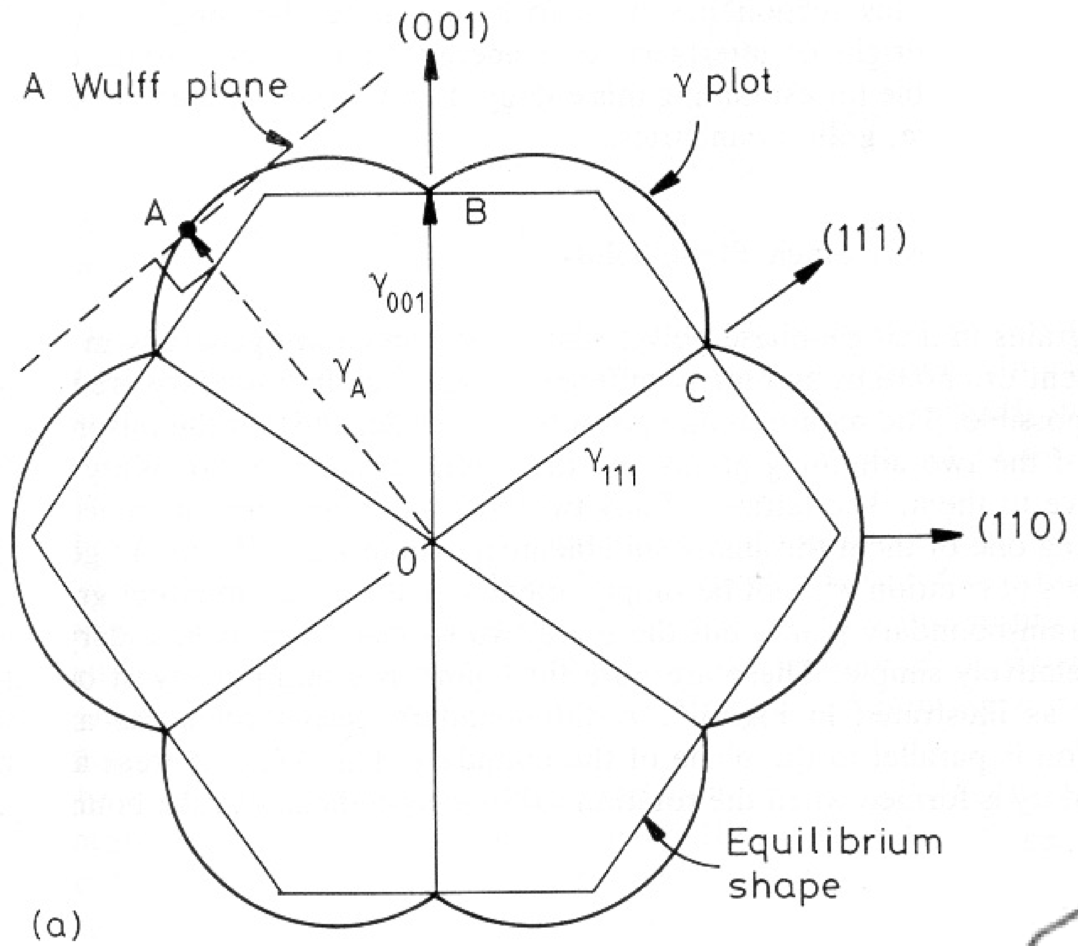
(b) Wulff Shape II

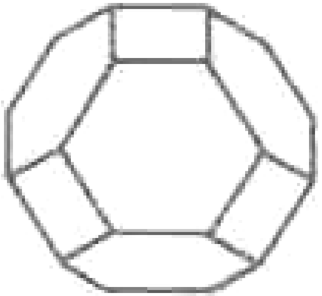
(c) Union of I and II

(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 *m3m* and **[100]** facets.

Equilibrium shape: Wulff surface





Equilibrium shape can be determined experimentally

by annealing small single crystals (high T, inert atmosphere)