# EMA5001 Lecture 9
# Surface Energy

# Types of Interfaces for Solids

❑ **By the materials on each side of the interface**

- Surface
  - Between solid and vapor (or vacuum)
  - Always present
  - Matters in vaporization, condensation, wetting, fracture, etc.

- Grain boundaries
  - Separate solids with same composition and same crystal structure but different orientation
  - Can be absent
  - Matters in recrystallization, grain growth, mechanical strength, hardness, etc.

- Interphase interfaces
  - Separate two phases with different crystal structure and/or compositions
  - Matters in phase transformation, mechanical properties, etc.
  - Most complex and least understood

# Interfacial Free Energy & Surface Tension

❑ **For a system with interface area $A$ and free energy per unit interface area $\gamma$, the total free energy is**

$$G = G_0 + A\gamma$$

- $G_0$ is free energy of system assuming all material has the bulk properties
- $\gamma$ reflects the **excess** free energy of material on surface, equaling the work that must be done at constant $T$ and $P$ to create unit area of surface from bulk material

❑ **At constant T and P, if interface area increase by $dA$, system free energy change**

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

❑ **For liquid**

$F$ is surface tension

$$dG = dW = FdA$$

Therefore,

$$F = \gamma + A\frac{d\gamma}{dA}$$

For liquid, $\quad \dfrac{d\gamma}{dA} = 0 \qquad F = \gamma$

# Energy of a Particular Surface Plane (1)

❑ **Example of (111) plane as surface of FCC crystal**

- $\varepsilon$  Bond strength
- If a bond is broken, the energy of one of the atom is raised by $\dfrac{1}{2}\varepsilon$

Compared with bulk, every surface atom on (111) surface plane has lost **three (3)** of the nearest neighboring atoms

- **<u>Excess</u>** internal energy for each of the (111) surface atom over an atom in the bulk is $3 \times \dfrac{1}{2}\varepsilon$

- If $L_S$ is the measured sublimation energy per mole, For FCC structure, $N_a$ is Avogadro's number.  Therefore

$$L_S = 12 N_a \cdot \frac{1}{2}\varepsilon$$

$$\varepsilon = L_S / 6 N_a$$

- (111) surface (solid-vapor interface) excess internal energy **per surface atom** is

$$E_{sv}(1\,1\,1) = \frac{3}{2}\varepsilon = \frac{3}{2}\cdot\frac{L_S}{6 N_a} = \frac{L_S}{4 N_a}$$

- Assumptions:
    - Consider only nearest neighbors
    - Strength of remaining bonds unchanged
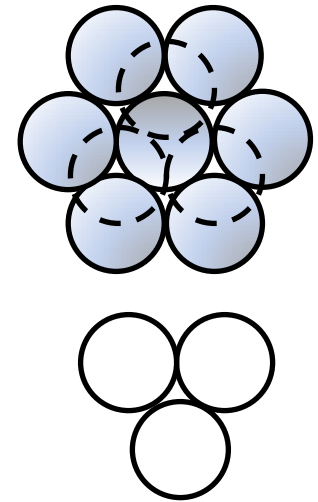
# Energy of a Particular Surface Plane (2)

For **FCC**

❑ **Continue from p.4**

Excess energy **per atom** on a (111) surface plane

$$E_{sv}(111) = \frac{3}{2}\varepsilon = \frac{3}{2}\cdot\frac{L_S}{6N_a} = \frac{L_S}{4N_a}$$

Excess surface energy **per unit area** (if neglecting entropy term)
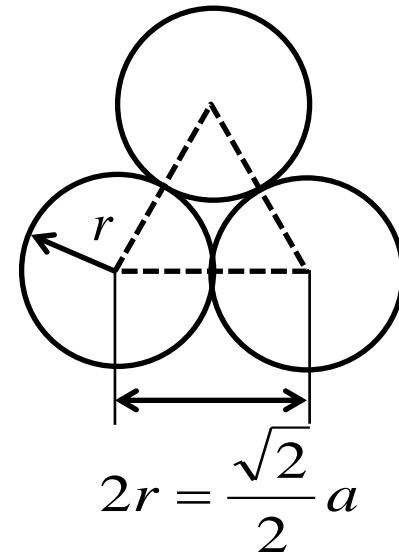
$$\gamma_{(111)} = E_{sv}\cdot n_{(111)}$$

$n$ is atom number density on (111) plane

$$n_{(111)} = \frac{0.5}{0.5\cdot(2r)\cdot\sqrt{3}r} = \frac{1}{2\sqrt{3}r^2} = \frac{1}{2\sqrt{3}\left(\dfrac{\sqrt{2}}{4}a\right)^2} = \frac{4}{\sqrt{3}}\cdot\frac{1}{a^2}$$

$$2r = \frac{\sqrt{2}}{2}a$$

Therefore,

$$\gamma_{(111)} = E_{sv}\cdot n_{(111)} = \frac{L_S}{4N_a}\cdot\frac{4}{\sqrt{3}}\cdot\frac{1}{a^2} = \frac{1}{\sqrt{3}}\cdot\frac{L_S}{N_a a^2} \approx 0.58\frac{L_S}{N_a a^2}$$

# Energy of a Particular Surface Plane (3)

## ❑ Surface energy of other planes

- Broken bond excess energy $\varepsilon / 2$
- We have $\varepsilon = L_S / 6N_a$

Atom on (002) surface plane lost **four (4)** of the nearest neighbors
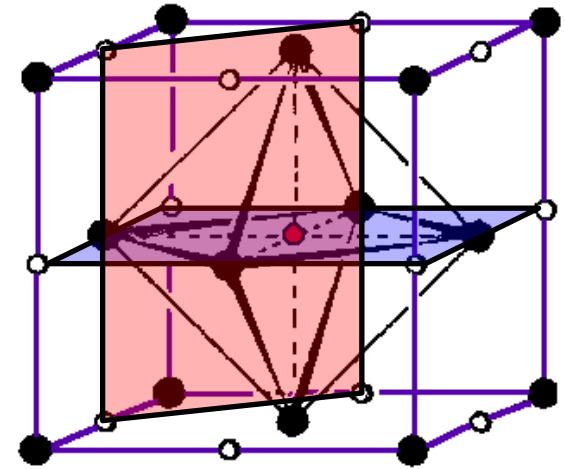
$$E_{sv}(002) = 4 \cdot \frac{\varepsilon}{2} = \frac{4}{2} \cdot \frac{L_S}{6N_a} = \frac{L_S}{3N_a}$$

$$\gamma(002) = \frac{L_S}{3N_a} \cdot \frac{1}{\left(\frac{\sqrt{2}}{2}a\right)^2} = \frac{2}{3} \cdot \frac{L_S}{N_a a^2} = 0.67 \frac{L_S}{N_a a^2}$$

http://www.tf.uni-kiel.de/matwis/amat/def_en/kap_1/ illustr/t1_3_3.html

Atom on (220) surface plane lost **five (5)** of the nearest neighbors

$$E_{sv}(220) = 5 \cdot \frac{\varepsilon}{2} = \frac{5}{2} \cdot \frac{L_S}{6N_a} = \frac{5L_S}{12N_a}$$

$$\gamma(220) = \frac{5}{12} \cdot \frac{L_S}{N_a} \cdot \frac{1}{a \cdot \frac{\sqrt{2}}{2}a} = \frac{5}{6\sqrt{2}} \cdot \frac{L_S}{N_a a^2} = 0.59 \frac{L_S}{N_a a^2}$$

**Surface energy (excess energy with respect to bulk) change with different crystal planes**

# Surface Energy & Surface Orientation (1)

□ **If a <u>3D</u> crystal surface at an angle $\theta$ to close packed (001) plane for a simple cubic lattice structure**
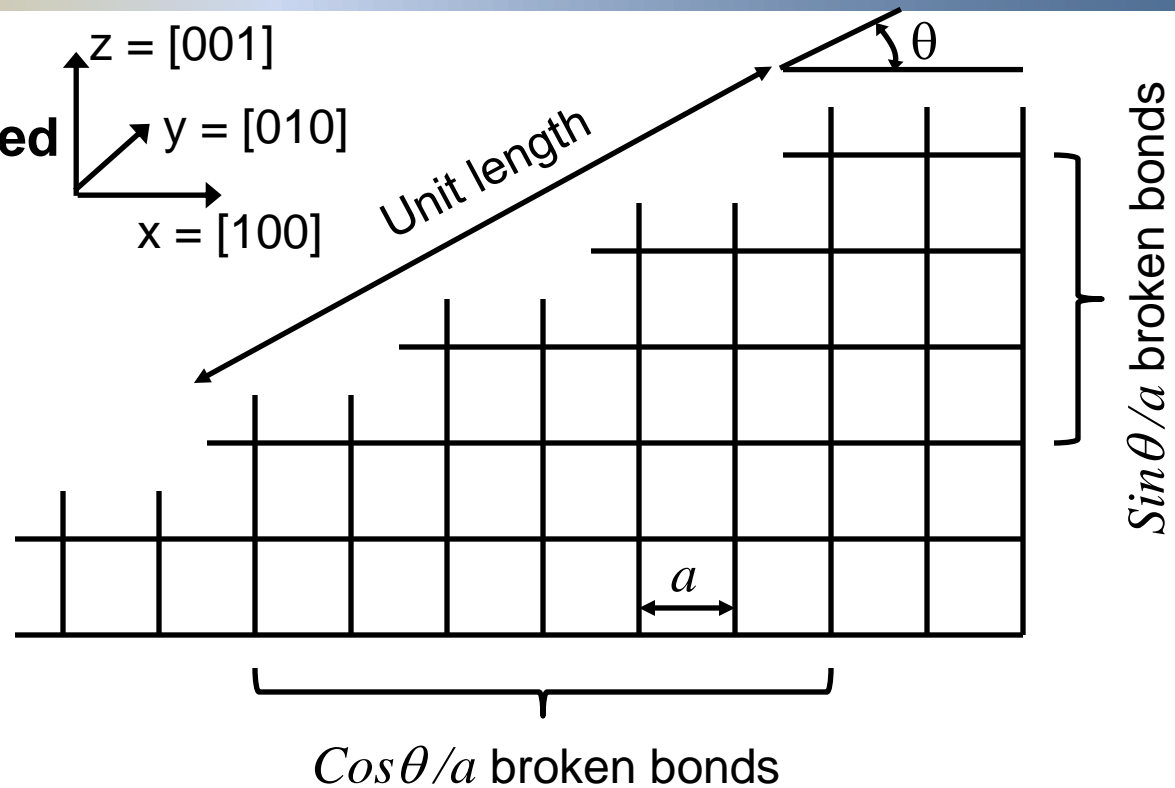
- Number of broken bonds along (001) plane

$$\frac{Cos\,\theta}{a} \cdot \frac{1}{a}$$

- Number of broken bonds along (100) plane

$$\frac{Sin|\theta|}{a} \cdot \frac{1}{a}$$

z = [001]

y = [010]

x = [100]

Unit length

$\theta$

$Sin\,\theta/a$ broken bonds

$a$

$Cos\,\theta/a$ broken bonds

- Energy associated with each broken bond $\varepsilon/2$
- Total excess surface internal energy (with respect to the bulk) per unit area

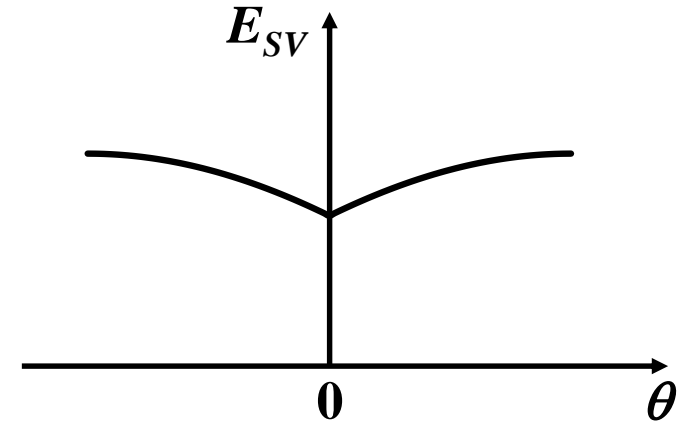$$E_{sv}(\theta) = \frac{Cos\,\theta + Sin|\theta|}{a^2} \cdot \frac{\varepsilon}{2}$$

# Surface Energy & Surface Orientation (2)

☐ **Continue from p.7**

$$E_{sv}(\theta) = \frac{Cos\,\theta + Sin\,|\theta|}{a^2} \cdot \frac{\varepsilon}{2}$$

☐ **Plotting $E_{SV}$ vs. $\theta$**

- Closed packed orientation lie at energy minimum (cusp or trough) positions



☐ **Example of $\gamma$ in <u>polar coordination</u> system for simple cubic lattice**

- $\theta$ angle to close packed {100} type planes, for $0 \leq \theta \leq 90^\circ$

$$\gamma = (Cos\,\theta + Sin\,\theta) \cdot \frac{\varepsilon}{2a^2} = \left[ Cos\,\theta \cdot \frac{1}{\sqrt{2}} - Sin\,\theta \cdot \left( -\frac{1}{\sqrt{2}} \right) \right] \cdot \frac{\sqrt{2}\varepsilon}{2a^2}$$

$$\gamma = Cos\left( \theta - \frac{\pi}{4} \right) \cdot \frac{\varepsilon}{\sqrt{2}a^2}$$

# Wulff Planes & Equilibrium Shape

❑ **Continue from p.7**

$$\gamma = Cos\left(\theta - \frac{\pi}{4}\right) \cdot \frac{\varepsilon}{\sqrt{2}a^2}$$

A circle off by 45º and **<u>diameter</u>** of $\dfrac{\varepsilon}{\sqrt{2}a^2}$

❑ **Plotting $\gamma(\theta)$ in polar system**

As function of $\theta$ and absolute value of surface excess energy, yielding schematic

❑ **Equilibrium shape of a crystal determined by**

- Minimization of the total surface energy

$$\sum \gamma_i A_i$$

- **<u>Wulff Theorem</u>**

"The equilibrium shape is bonded by those parts of Wulff planes that can be reached from the origin without crossing any other Wulff planes"

J. W. Martin, et al. Stability of microstructure in metallic systems, Cambridge Univ. Press, 2nd ed, Cambridge, UK (1997), p. 234