

ECE5320

Lecture #1-2

Basic Thermodynamics Functions

$$H = U + pV \quad [J]$$

$$h = u + pv_m \quad [J/mol]$$

Enthalpy

$$G = U - TS + pV = H - TS \quad [J]$$

$$g = u - Ts + pv_m = h - Ts \quad [J/mol]$$

Gibbs Free Energy

$$F = U - TS \quad [J]$$

$$f = u - Ts \quad [J/mol]$$

Helmholtz Free Energy

First and Second Law of Thermodynamics

$$dU = dQ + dW \quad (1\text{st LTD})$$

$$dS = \frac{dQ}{T} \quad (2\text{nd LTD})$$

Mechanical Work

$$dW = -pdV$$

Surface Work

$$dW = -\gamma dA$$

γ – surface free energy, $[\text{J}/\text{m}^2]$

Electrical Work

$$dW = -EdZ$$

(Z - Charge, $[\text{C}]$)

Magnetic Work

$$dW = -HdM$$

Chemical Work

$$dW = \sum \mu_i dn_i$$

(μ - chemical potential, $[\text{J}/\text{mol}]$)

Back to Basic Thermodynamics Functions

From 1st and 2nd LTD and basic definitions we get:

$$dU = TdS - pdV$$

$$dH = TdS - Vdp$$

$$dG = -SdT + Vdp$$

$$dF = -SdT - pdV$$

Heat Capacities

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v \Rightarrow U = C_v \int_{T_1}^{T_2} dT$$

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \Rightarrow H = C_p \int_{T_1}^{T_2} dT$$

Phase Equilibrium

Two phases, A and B

$$\mu_A = \left(\frac{\partial G_A}{\partial n_A} \right)_{p,T} ; \mu_B = \left(\frac{\partial G_B}{\partial n_B} \right)_{p,T}$$

$$\mu_A(p, T) = \mu_B(p, T) - \text{equilibrium}$$

$$\mu_A + d\mu_A = \mu_B + d\mu_B$$

$$\Rightarrow d\mu_A(p, T) = d\mu_B(p, T)$$

Phase Equilibrium

$$dG = -SdT + Vdp$$

$$d\mu = -sdT + v_m dp$$

$$-s_A dT + v_{m,A} dp = -s_B dT + v_{m,B} dp$$

$$s_A - s_B = \Delta s;$$

$$v_{m,A} - v_{m,B} = \Delta v;$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta s}{\Delta v};$$

$$ds = \frac{dh}{T} (T, P = \text{const})$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta h}{T\Delta v}$$

Clapeyron

Phase Equilibrium

$\Delta s_m, \Delta v_m, \Delta h_m$; -melting

$\Delta s_{ev}, \Delta v_{ev}, \Delta h_{ev}$; -evaporation

$\Delta s_{sb}, \Delta v_{sb}, \Delta h_{sb}$; -sublimation

$$\Delta v_{ev} \approx v_g = \frac{RT}{p}$$

and

$$\Delta v_{sb} \approx v_g = \frac{RT}{p}$$

$$\Rightarrow \frac{d \ln p}{dT} = \frac{\Delta h_{ev}}{RT^2}$$

and

$$\Rightarrow \frac{d \ln p}{dT} = \frac{\Delta h_{sb}}{RT^2}$$

Clausius-Clapeyron

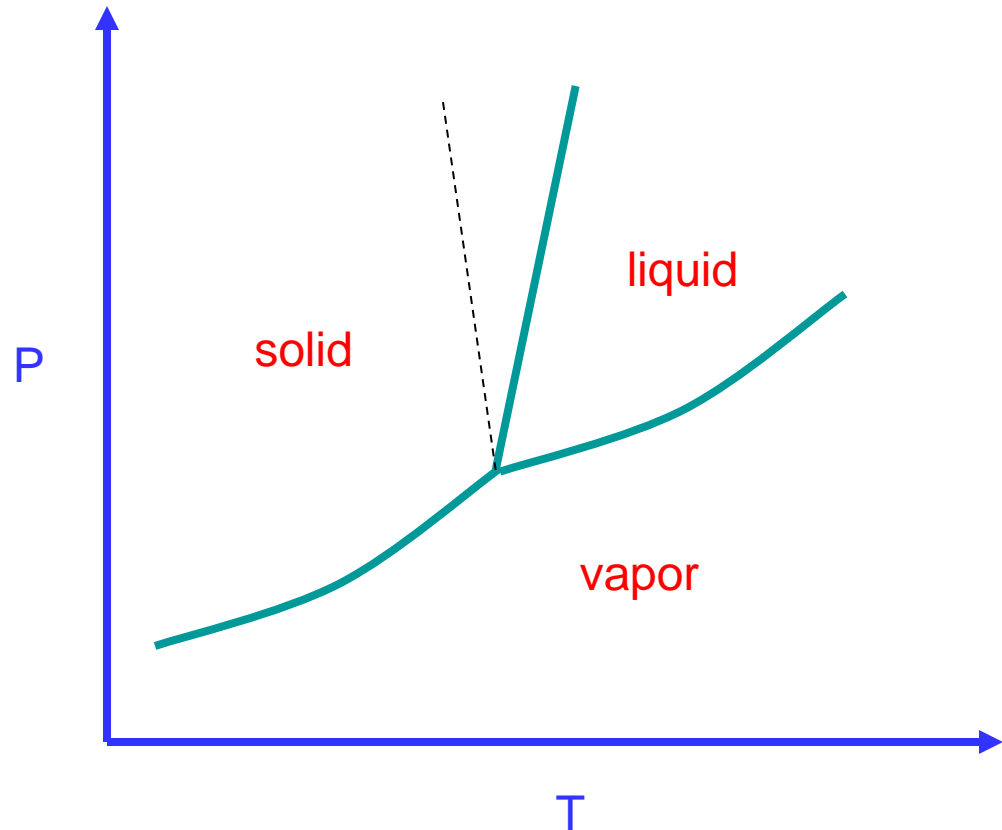
$$p = p_0 \cdot \exp \left[-\frac{\Delta h_{ev, sb}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right]$$

Phase Equilibrium

$$\frac{dp}{dT} = \frac{\Delta h}{T\Delta v};$$

$$p - p_0 = \frac{\Delta h}{\Delta v} \ln\left(\frac{T}{T_0}\right);$$

What about dotted line?



Saturation

Thermodynamic driving force for phase change / transformation from one phase into another is the difference in chemical potentials between these two phases at particular pressure p and temperature T .

$$\Delta\mu = \mu_A(p, T) - \mu_B(p, T);$$

$$T = \text{const.}$$

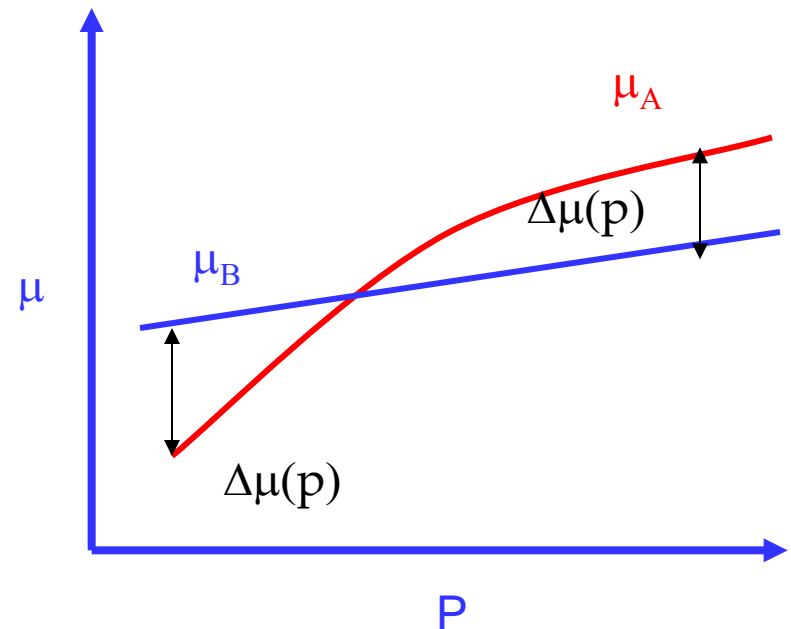
$$\mu_A(p_0) = \mu_B(p_0)$$

$$\Delta\mu = [\mu_A(p) - \mu_A(p_0)] - [\mu_B(p) - \mu_B(p_0)]$$

$$\Delta\mu \approx \int_{p_0}^p \frac{\partial\mu_A}{\partial p} dp - \int_{p_0}^p \frac{\partial\mu_B}{\partial p} dp$$

$$\text{recalling : } d\mu = v_m dp; T = \text{const}$$

$$\Rightarrow \frac{\partial\mu}{\partial p} = v_m;$$



Saturation, Cont.

$$\Delta\mu \approx \int_{p_0}^p (v_{m,A} - v_{m,B}) dp;$$

$$(v_{m,A} - v_{m,B}) \approx v_g = \frac{RT}{p}$$

crystal growth from gas phase

$$\Rightarrow \Delta\mu = \int_{p_0}^p \frac{RT}{p} dp$$

$$\Delta\mu = RT \ln \left(\frac{p}{p_0} \right)$$

$$\Delta\mu = RT \ln \left(\frac{C}{C_0} \right)$$

case of crystal growth from solution

$$\Delta\mu = -zF\eta \quad (\eta = E - E_0)$$

case of electrocrystalization

Laplace / Capillary Pressure

$T = \text{const.}$

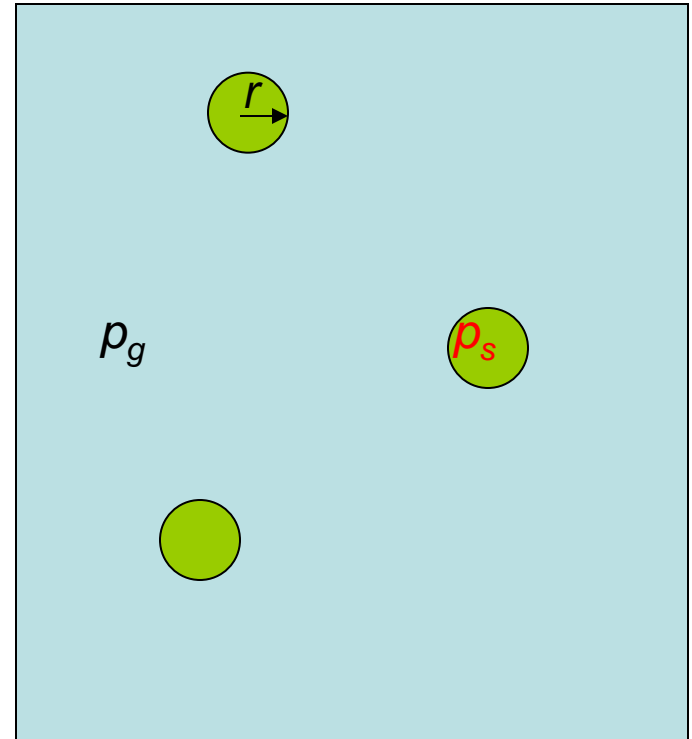
at equilibrium:

$$dF = -p_g dV_g - p_s dV_s + \gamma_s dA$$

$$V_{\text{total}} = V_g + V_s = \text{const.}$$

$$\Rightarrow dV_g = -dV_s$$

$$\Rightarrow p_s - p_g = \gamma_s \frac{dA}{dV_s}$$



Laplace / Capillary Pressure, Cont...

Force Balance:

$$A = 4r^2\pi;$$

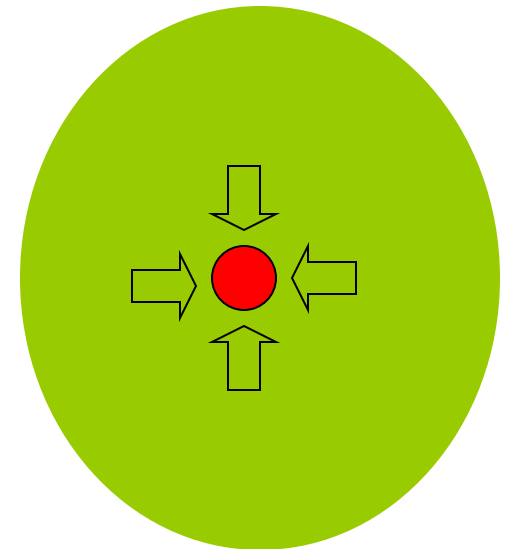
$$V_s = \frac{4r^3\pi}{3};$$

$$\Rightarrow \frac{dA}{dV_s} = \frac{2}{r}$$

$$\Rightarrow p_s - p_g = \frac{2\gamma_s}{r} \quad (\text{gas-liquid})$$

$$\Rightarrow p_s - p_g = \frac{2f_s}{r} \quad (\text{gas-solid, } f\text{-surface stress})$$

$$4r^2\pi \cdot p_g + 8r\pi \cdot \gamma = 4r^2\pi \cdot p_s$$



Gibbs-Thomson Equation

$$T = \text{const}, P = \text{const}$$

$$dG = \mu_A dn_A + \mu_B dn_B + \gamma_B dA = 0$$

$$n_A + n_B = \text{const}, \Rightarrow dn_A = -dn_B$$

$$\Rightarrow \mu_A - \mu_B = \gamma_B \frac{dA}{dn_B}$$

$$n_B = \frac{V_B}{v_{m,B}} \Rightarrow dn_B = \frac{4r^2 \pi dr}{v_{m,B}}; dA = 8r \pi dr$$

$$\Rightarrow \mu_A - \mu_B = 2\gamma_B v_{m,B} \frac{1}{r};$$

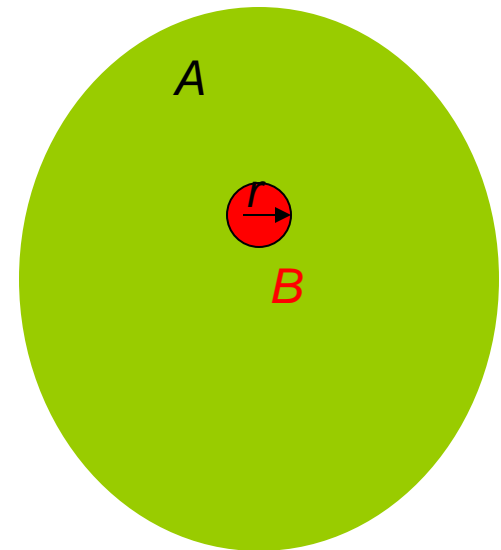
or

$$\mu_g - \mu_s = 2\gamma_s v_{m,s} \frac{1}{r};$$

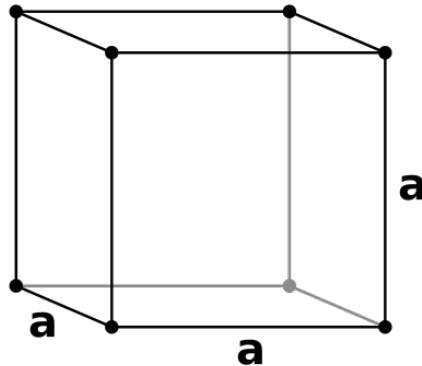
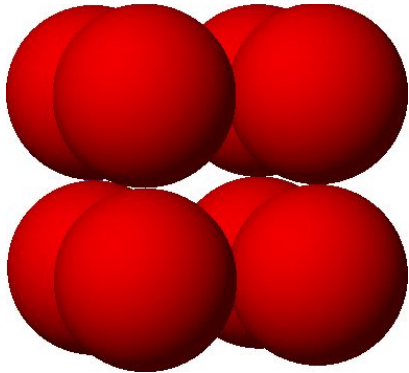
Re-statement:

$$(p_g - p_s) \cdot \frac{V_s}{n_s} = \mu_g - \mu_s$$

$$\frac{2\gamma_s}{r} \cdot v_{m,s} = \mu_g - \mu_s$$



Basic Crystal Structure: SC

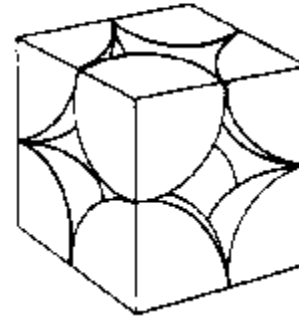


Type of Packing

Packing Efficiency

Coordination Number

Simple cubic (sc)

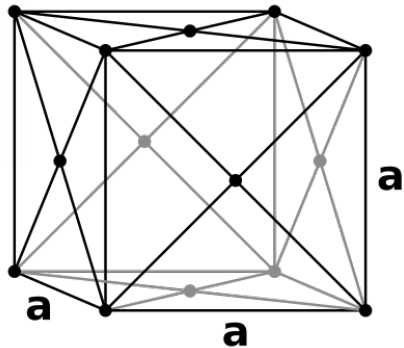
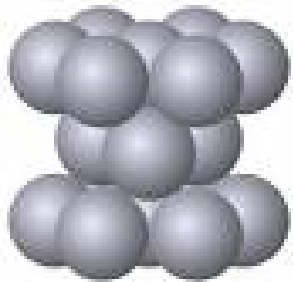
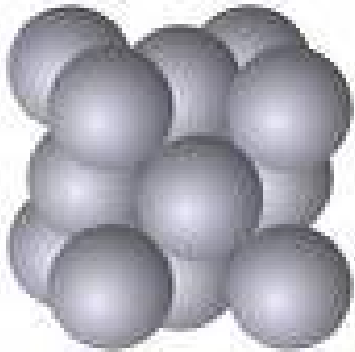


52%

6

$$\frac{\#atoms}{cell} = \frac{1}{8} \cdot corner\ atoms \frac{8}{8} = 1$$

Basic Crystal Structure: FCC & HCP



Type of Packing	Packing Efficiency	Coordination Number
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Hexagonal close-packed (hcp)

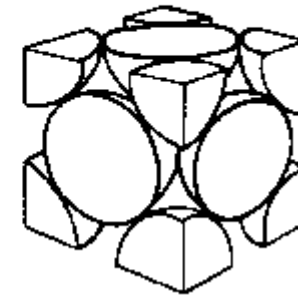
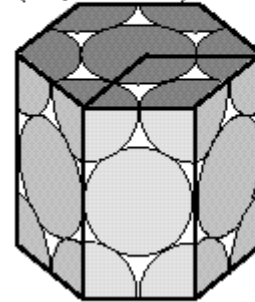
74%

12

Cubic close-packed (ccp or fcc)

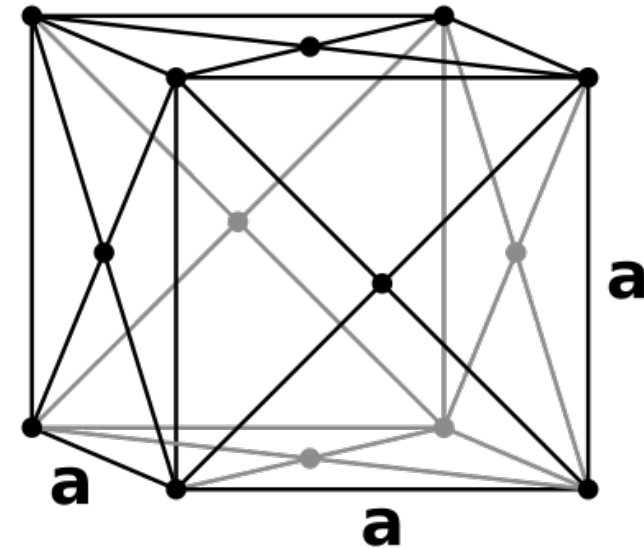
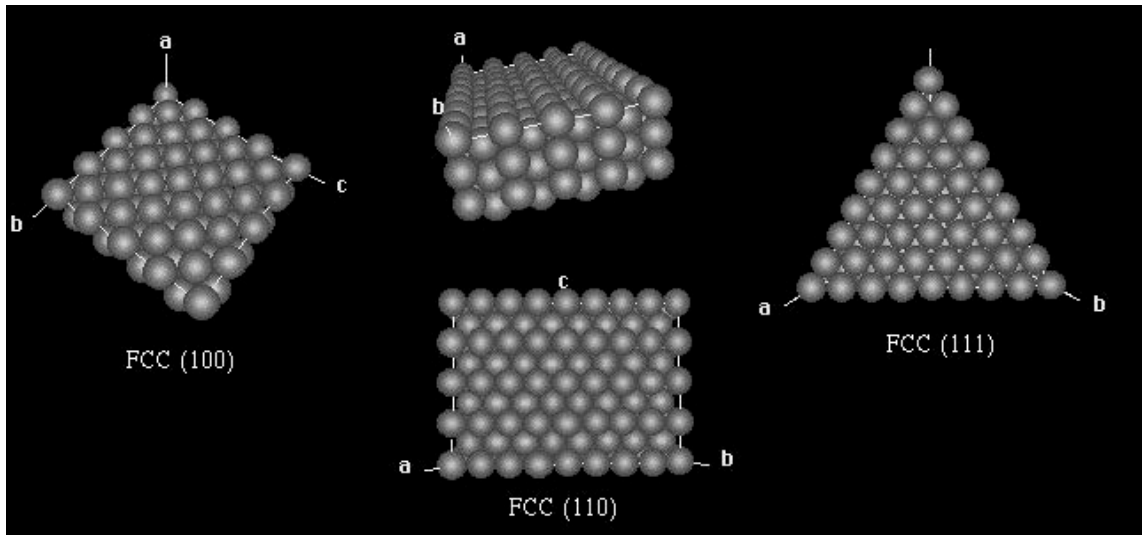
74%

12



$$\frac{\#atoms}{cell} = \frac{1}{8} \cdot corner\ atoms + \frac{1}{2} \cdot face\ atoms = \frac{8}{8} + \frac{6}{2} = 4$$

Basic Crystal Structure: FCC Low Index Planes

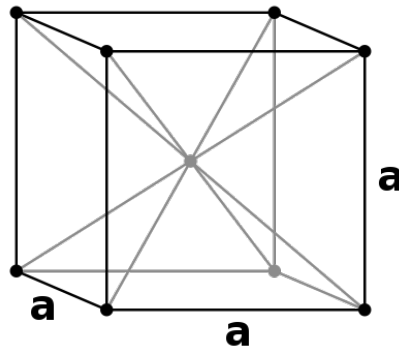
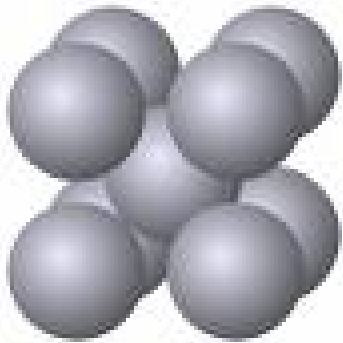


$$a\sqrt{2}; a\sqrt{3}$$

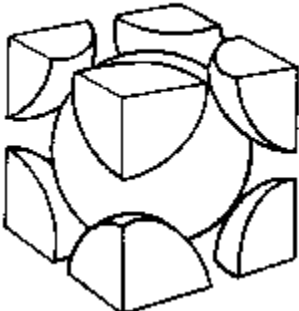
$$(111), (110), (100), (h, k, l), [h, k, l]$$

$$\{111\}, [111]$$

Basic Crystal Structure: BCC

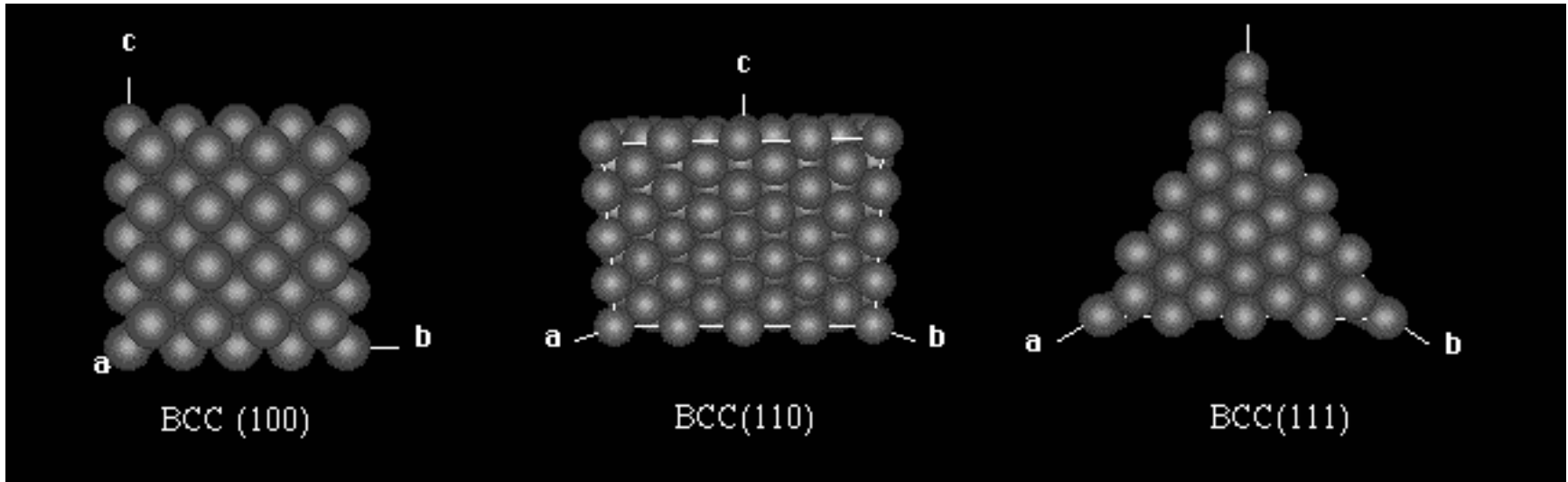


Type of Packing	Packing Efficiency	Coordination Number
Body-centered cubic (bcc)	68%	8

A 3D diagram showing the packing of atoms in a BCC structure. The atoms are represented as gray spheres, and the unit cell is outlined as a cube. The central atom is surrounded by eight corner atoms.

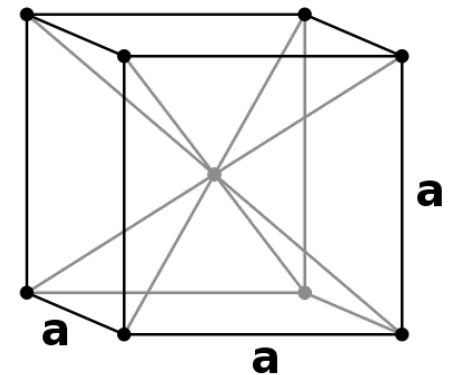
$$\frac{\#atoms}{cell} = \frac{1}{8} \cdot \text{corner atoms} + 1 \cdot \text{body atoms} = \frac{8}{8} + 1 = 2$$

Basic Crystal Structure: BCC

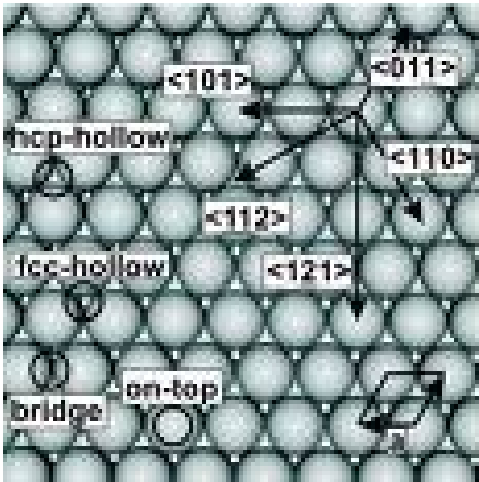


$(111), (110), (100), (h, k, l), [h, k, l]$

$\{111\}, [111]$



Basic Relations



Planes/directions are perpendicular:

$$(hkl), [uvw]$$

$$h = u, k = v, l = w$$

Direction/plane are parallel (direction is in plane):

$$hu + kv + lw = 0$$

Two planes or directions are normal:

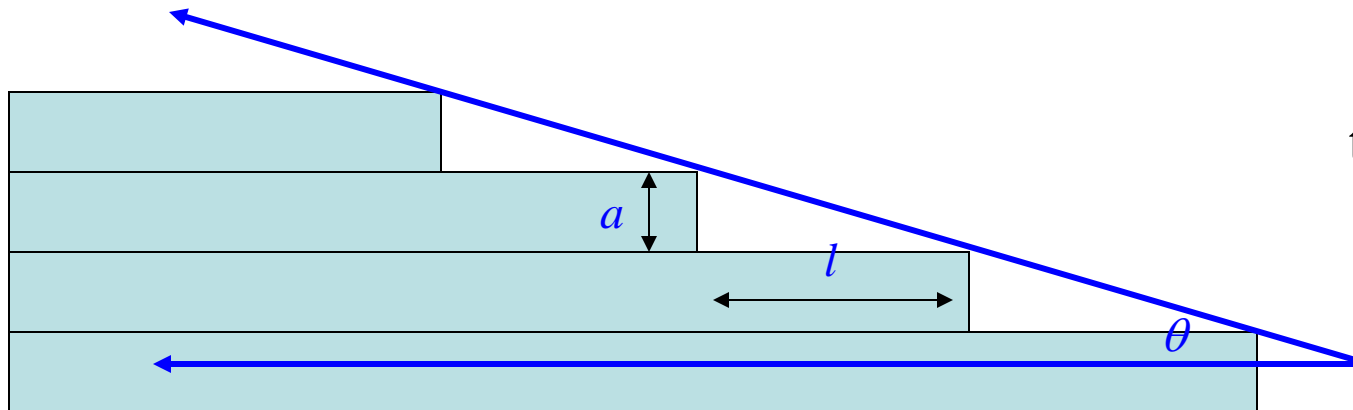
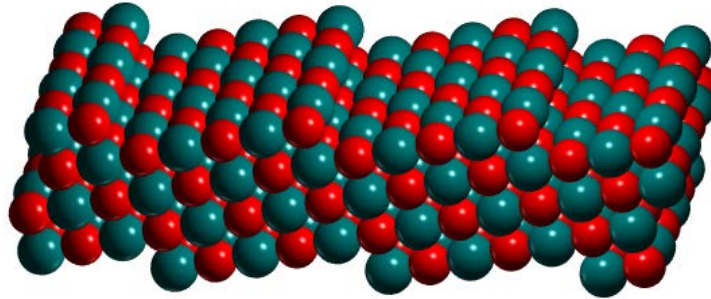
$$h_1h_2 + k_1k_2 + l_1l_2 = 0$$

$$u_1u_2 + v_1v_2 + w_1w_2 = 0$$

Angle between two planes or directions :

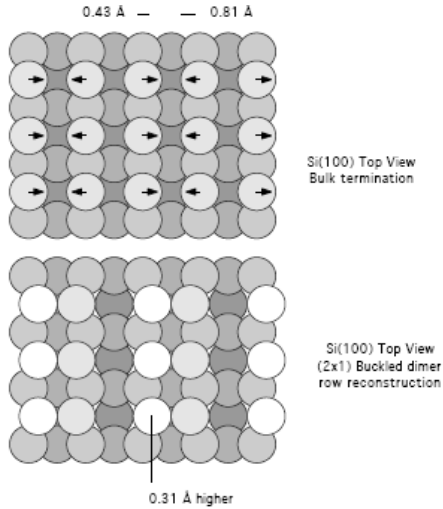
$$\cos \theta = \frac{h_1h_2 + k_1k_2 + l_1l_2}{\sqrt{h_1^2 + k_1^2 + l_1^2} \cdot \sqrt{h_2^2 + k_2^2 + l_2^2}}$$

Vicinal Surfaces



$$\tan \theta = \frac{a}{l}$$

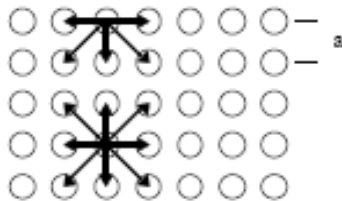
Surface Relaxation



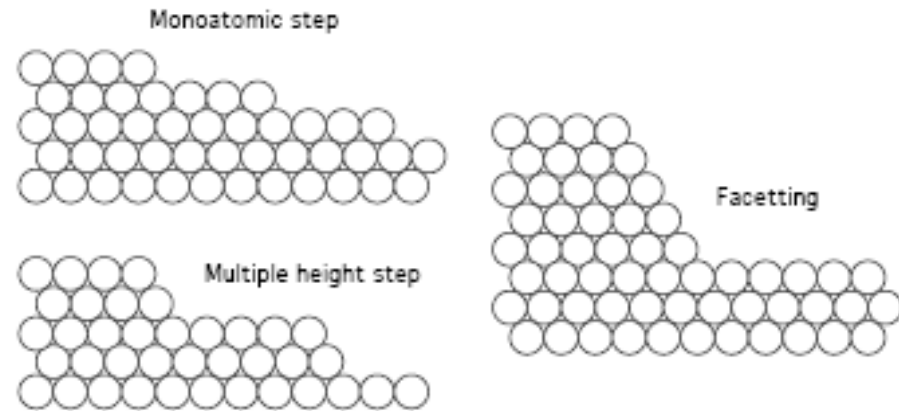
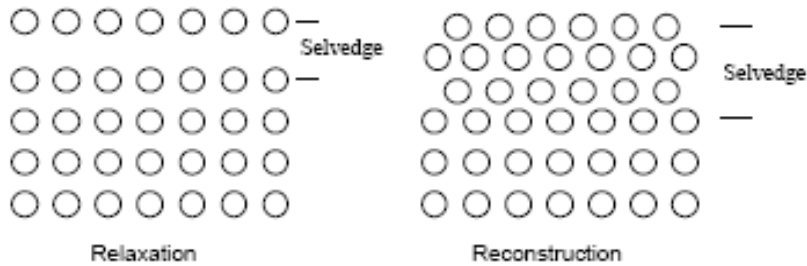
$$\gamma_{100} / \epsilon_{bulk} = 0.224$$

$$\gamma_{100} / \epsilon_{bulk} = 0.235$$

$$\gamma_{111} / \epsilon_{bulk} = 0.212$$

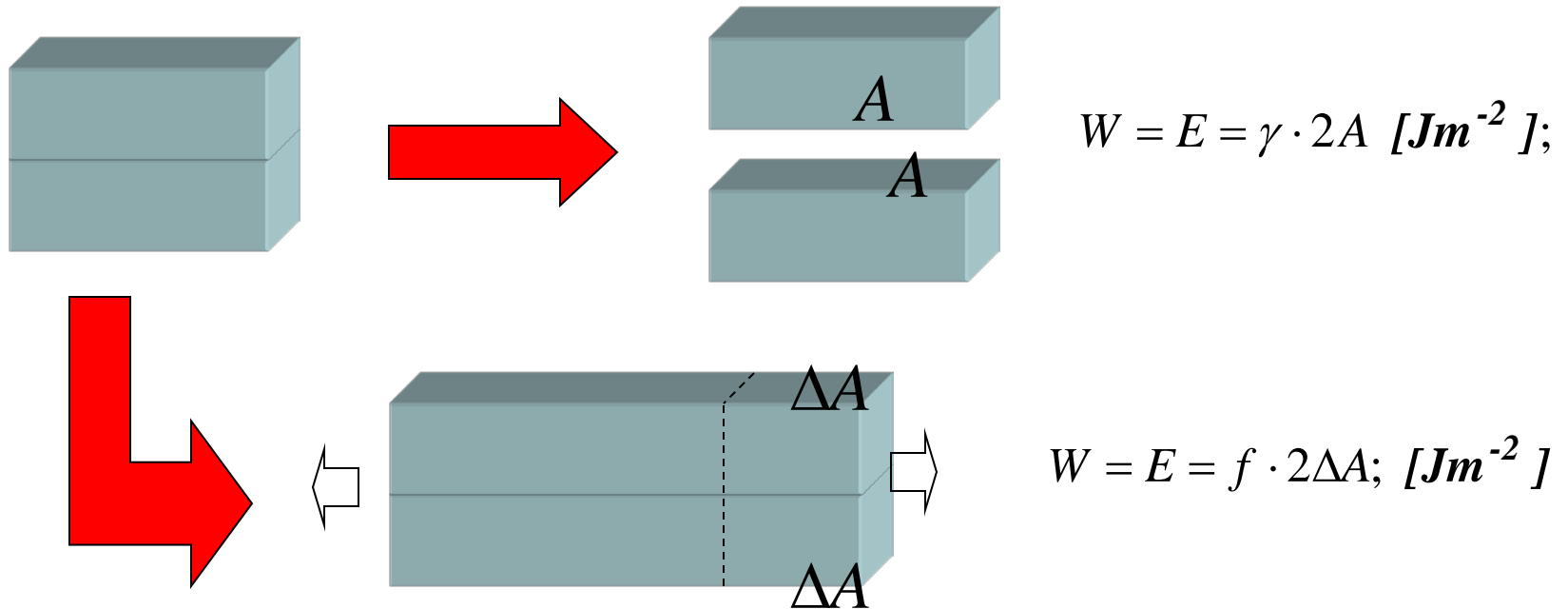


In extreme cases (adsorbate-induced or clean) may get *facetting*



Surface Energy and Surface Stress

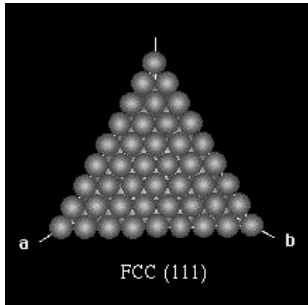
Energy/work required to create a new surface, *Gibbs* :



Tensors :
$$f_{ij} = \delta_{ij} \gamma_{ij} + \frac{\partial \gamma_{ij}}{\partial \varepsilon_{ij}} \approx \gamma + \frac{\partial \gamma}{\partial \varepsilon}$$

Surface Energy

Broken Bonds (111) plane?:



$$\gamma_{100} / \varepsilon_{bulk} = 0.224$$

$$\gamma_{100} / \varepsilon_{bulk} = 0.235$$

$$\gamma_{111} / \varepsilon_{bulk} = 0.212$$

$$\gamma = n_{bb} N_s \varepsilon_b$$

Surface Energy/Heat of Sublimation:

$$\frac{E_s / AN_s}{\Delta E_s / N_A} = \frac{\frac{1}{4} n_c N_A \varepsilon_b}{\frac{1}{2} n_c N_A \varepsilon_b} = \frac{1}{2}$$

Potential Energy of an atom (LJ model):

$$\varphi(r) = \varepsilon_b \cdot \left[\left(\frac{a_o}{r} \right)^{12} - 2 \left(\frac{a_o}{r} \right)^6 \right];$$

equilibrium:

$$\varphi(a_o) = -\varepsilon_b$$

Binding Energy:

$$E_b = \frac{1}{2} n_c N_A \varepsilon_b$$

Heat of Sublimation:

$$\Delta E_s = \frac{1}{2} n_c N_A \varepsilon_b$$

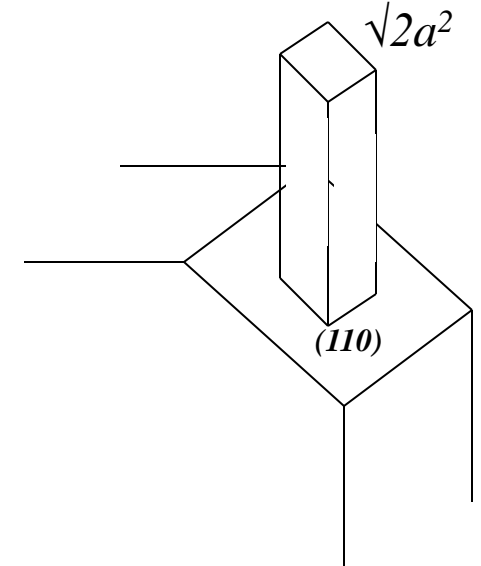
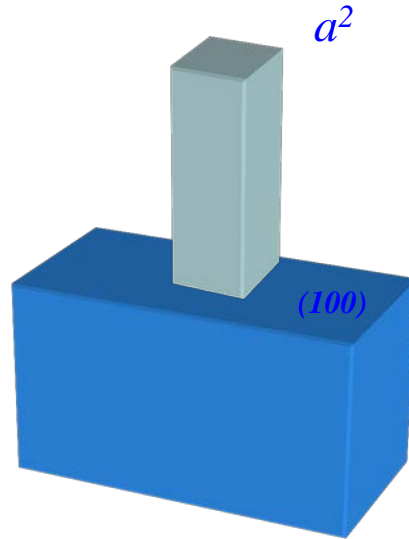
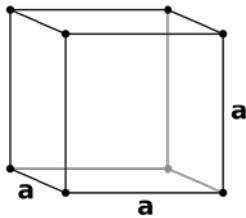
Surface Energy

Material	$\gamma / \text{J}\cdot\text{cm}^{-2}\times 10^{-7}$	T / C°
Au	1410	1027
Ag	1140	907
Fe	2150	1100
Pt	2340	1311
Cu	1670	1047
Ni	1850	1250
CaF2	450	25
KCl	110	25

$$\gamma = \gamma_0 - T \frac{d\gamma}{dT}$$

Equilibrium Shape of Crystals

Kossel Crystal (SB-Polonium)



$$\gamma_{100} = \frac{\varepsilon_{b,1} + 4\varepsilon_{b,2} + 4\varepsilon_{b,3}}{2a^2}; \quad \gamma_{100} = \frac{2\varepsilon_{b,1} + 6\varepsilon_{b,2} + 4\varepsilon_{b,3}}{2a^2\sqrt{2}}$$

$$\gamma_{110} = \frac{1}{a^2} \cdot \left(\frac{1}{2}\varepsilon_{b,1} + 2\varepsilon_{b,2} + 2\varepsilon_{b,3} \right); \quad \gamma_{110} = \frac{1}{a^2} \cdot \left(\frac{1}{\sqrt{2}}\varepsilon_{b,1} + \frac{3}{\sqrt{2}}\varepsilon_{b,2} + \sqrt{2}\varepsilon_{b,3} \right)$$

$$\Rightarrow \gamma_{100} < \gamma_{110};$$

$$\gamma_{hkl} = \frac{\sum_{i=1}^3 n_{bbi} \cdot \varepsilon_{b,i}}{2A_{hkl}}$$

In general for Kossel Crystal

$$\gamma_{100} < \gamma_{110} < \gamma_{111} < \dots$$

Gibbs –Wulff –Curie Theorem

Recalling :

$$V_{total} = const, T = const$$

$$dF_{total} = -SdT - pdV_{total} = 0;$$

equilibrium gas - crystal :

$$dF_g = -SdT - p_g dV_g$$

$$dF_c = -SdT - p_c dV_c + \sum_n \gamma_{hkl} dA_n$$

$$dF_c + dF_g = dF_{total} = 0$$

$$\Rightarrow p_g dV_g - p_c dV_c + \sum_n \gamma_{hkl} dA_n$$

$$dV_{total} = d(V_c + V_g) = 0; \Rightarrow dV_c = -dV_g$$

$$-(p_c - p_g) dV_c + \sum_n \gamma_{hkl} dA_n = 0$$

Gibbs –Wulff –Curie Theorem

$$-(p_c - p_g)dV_c + \sum_n \gamma_{hkl}dA_n = 0;$$

$$V_c = \frac{1}{3} \sum_1^n h_n A_n; \quad dV_c = \frac{1}{3} \sum_1^n (h_n dA_n + A_n dh_n)$$

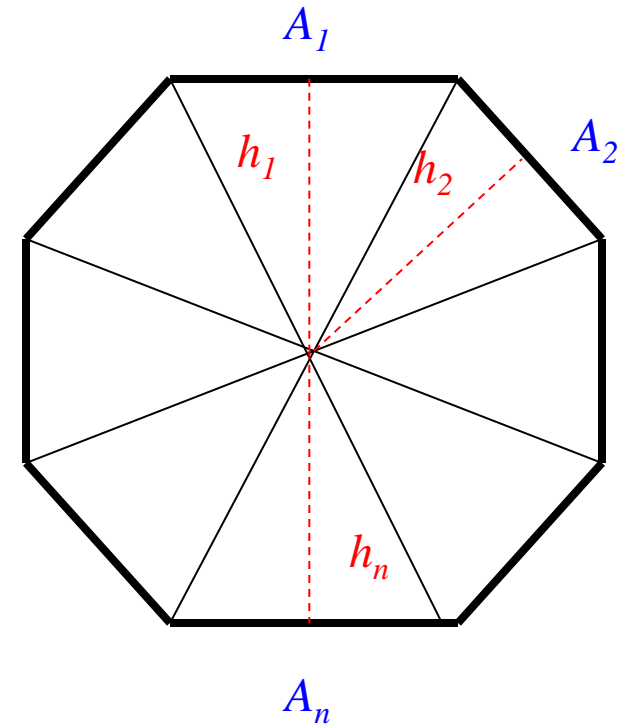
It is also valid that :

$$V_c = \sum_1^n A_n dh_n$$

$$\Rightarrow dV_c = \frac{1}{2} \sum_1^n h_n dA_n$$

$$\Rightarrow \sum_1^n \left(\gamma_{hkl} - \frac{1}{2} (p_c - p_g) h_n \right) dA_n = 0$$

$$\Rightarrow p_c - p_g = \frac{2\gamma_{hkl}}{h_n}$$

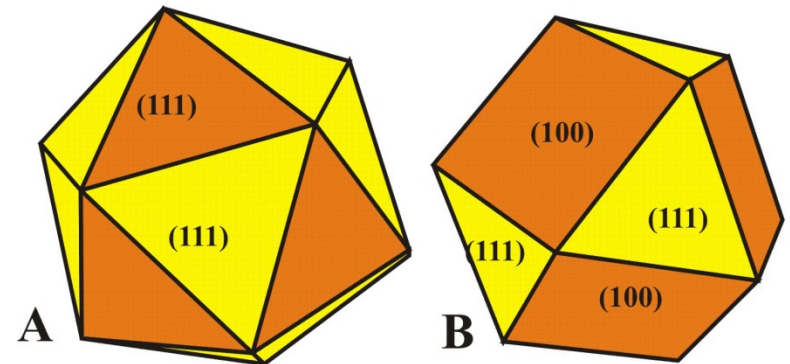


Gibbs –Wulff –Curie Theorem

$$p_c - p_g = \text{const}$$

$$\Rightarrow \frac{\gamma_{hkl}}{h_n} = \text{const}$$

$$\frac{\gamma_{100}}{h_1} = \frac{\gamma_{110}}{h_2} = \frac{\gamma_{111}}{h_3} \dots$$



In equilibrium, the distance of the crystal faces from a common point with in the crystal (Wulff point) is proportional to the corresponding specific surface energies of these faces.

Gibbs –Wulff –Curie Theorem

Re - statment :

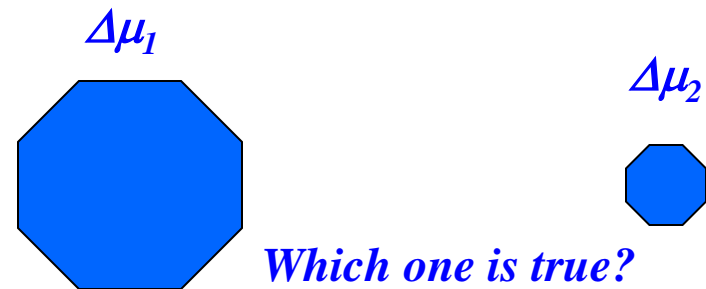
$$(p_c - p_g) = \frac{2\gamma_{hkl}}{h_n}$$

recalling $d\mu = v_m dp$; $T = const$

$$(p_c - p_g) \cdot v_m = \Delta\mu$$

$$\Rightarrow \Delta\mu = \frac{2\gamma_{hkl}}{h_n} \cdot v_m = const$$

The supersaturation/saturation has the one and same value of the crystal surfaces. The equilibrium size of the crystal is determined by the supersaturation.

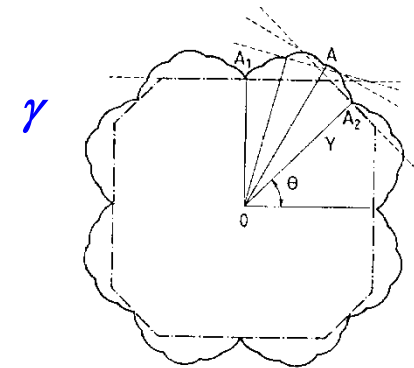
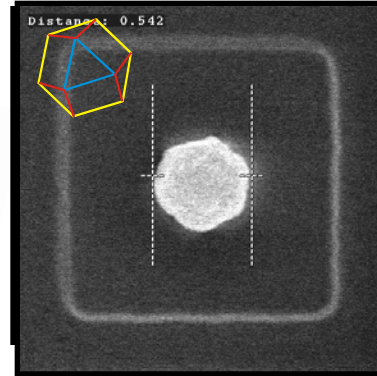
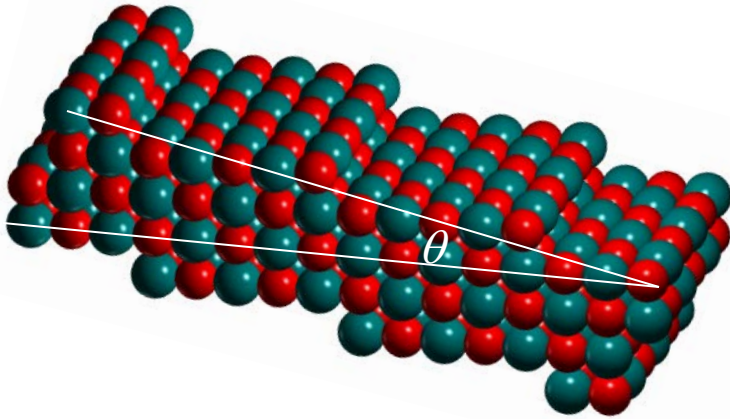


$$\Delta\mu_1 > \Delta\mu_2$$

or

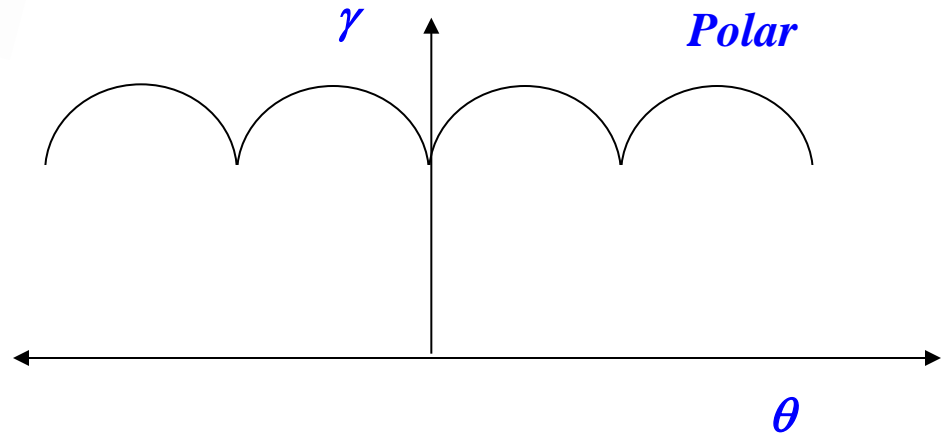
$$\Delta\mu_1 < \Delta\mu_2$$

Polar Diagram of Surface Energy



$$\gamma(\theta) = \frac{\kappa}{l} \sin(\theta) + \gamma_{hkl} \cos(\theta)$$

$$\gamma(-\theta) = -\frac{\kappa}{l} \sin(\theta) + \gamma_{hkl} \cos(\theta)$$



Cartesian