

***Surface and Interface Science
Physics 627; Chemistry 542***

***Lectures 1 and 2
Jan 25, 28 2013***

***Thermodynamics of Surfaces;
Equilibrium Crystal Shape***

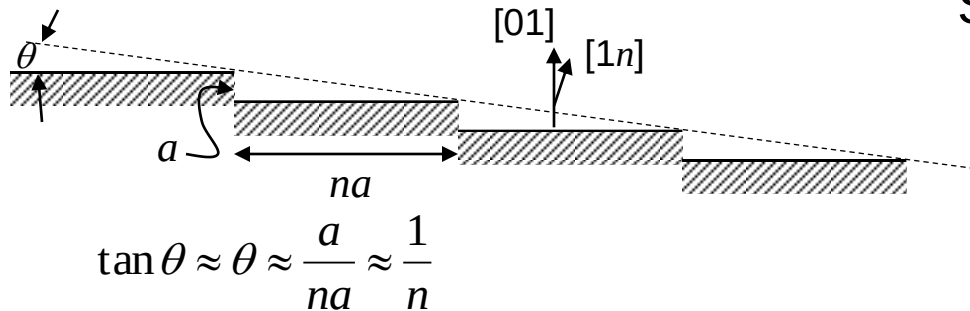
References:

- 1) Zangwill, Chapter 1
- 2) A.W. Andersen, Physical Chemistry of Surfaces, Fifth Edition (J. Wiley, New York, 1990) Chapter VII
- 3) J.M. Blakely and M Eizenberg in Vol. 1, Clean Solid Surfaces, “The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis,” ed. By D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1981) p. 1
- 4) G. A. Somorjai, Introduction to Surface Chemistry and Catalysis, Chapter 3.
- 5) A. Keijna and K.F. Wojcieckowski, Metal Surface Electron Physics, Chapter 3; Chapter 8.

Thermodynamics of Surfaces

(f) Anisotropy of γ

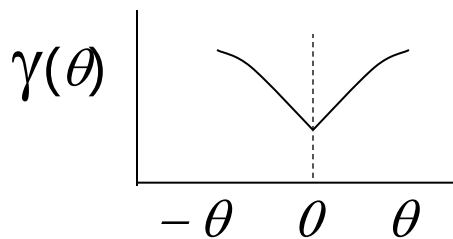
Following Zangwill, consider a vicinal surface of a 2-D solid



Starting from plane,
addition of each
step adds energy

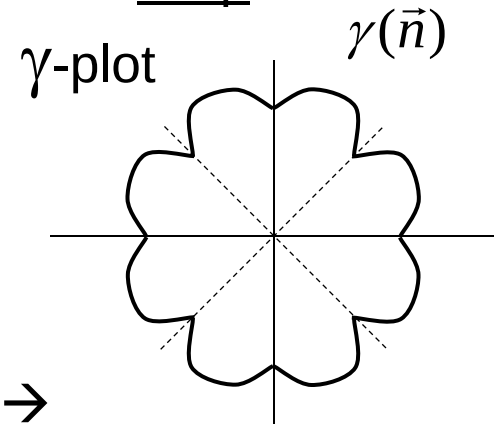
Let β = energy/step; $1/(na)$ = steps/unit length = θ/a then: $\gamma(\theta) = \gamma(0) + \frac{\beta}{a} |\theta|$

$\gamma(\theta)$ has discontinuous derivative at $\theta = 0 \rightarrow$ there is a cusp!!

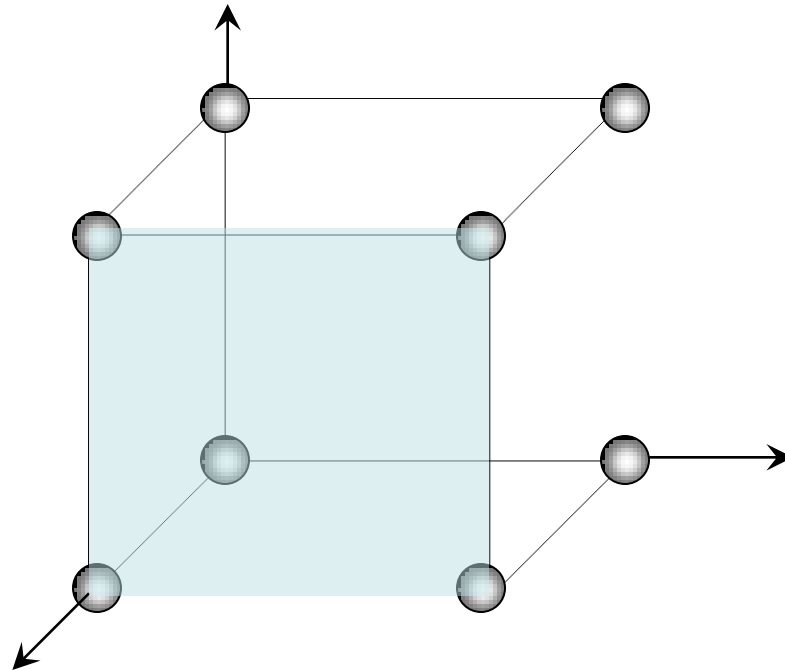


Cusps exist at every
direction corresponding to
a rational Miller index

A polar plot of surface
tension has many cusps $\rightarrow$



Aside: Miller Indices



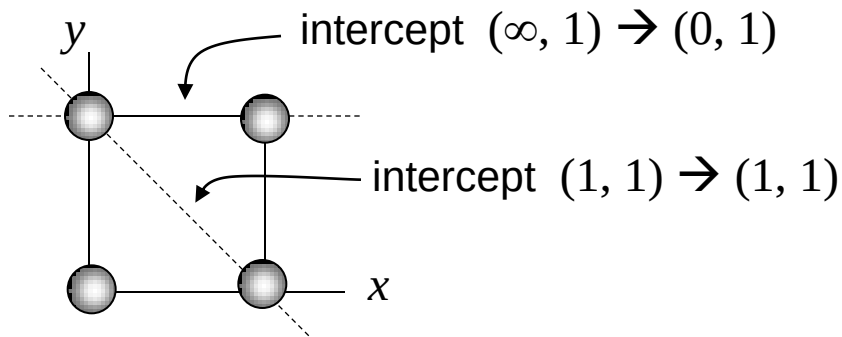
For simple cubic lattice,
consider plane that is shaded.

Vector from origin intercepts
that plane at $x, y, z = 1, \infty, \infty$

The Miller indices of this plane are:

$$\left(\frac{1}{1}, \frac{1}{\infty}, \frac{1}{\infty} \right) = (1, 0, 0)$$

In two dimensions (2D crystals)



The anisotropy of the γ -plot
determines the equilibrium
crystal shape of small
particles.

Thermodynamics of Surfaces

(f) Equilibrium crystal shape

Crystal will seek a shape determined by $\oint \gamma(\vec{n}) d\vec{a} = \text{minimum at Vol} = \text{const.}$ (sphere for liquid, faceted for solids) Determine shape from Wulff's Theorem

Wulff's Theorem: For a crystal at eqm. there exists a point in the interior such that its perpendicular distance, h_i , from the i^{th} face is proportional to γ_i .

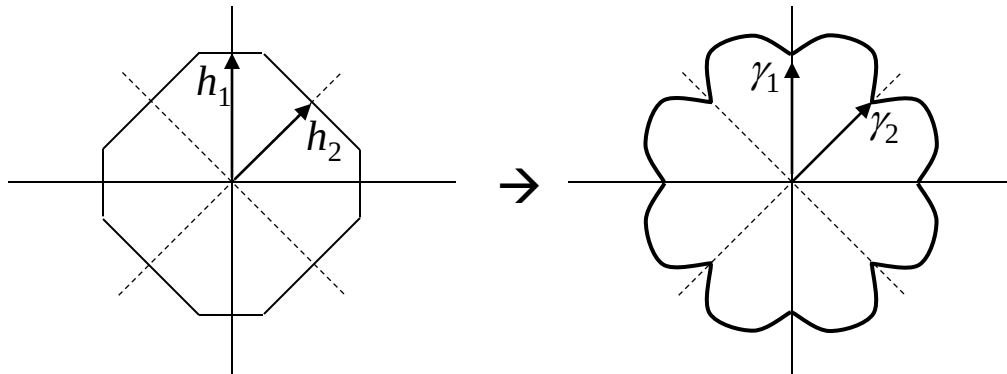
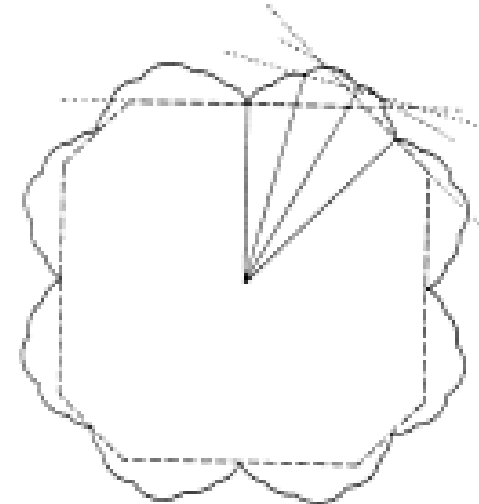
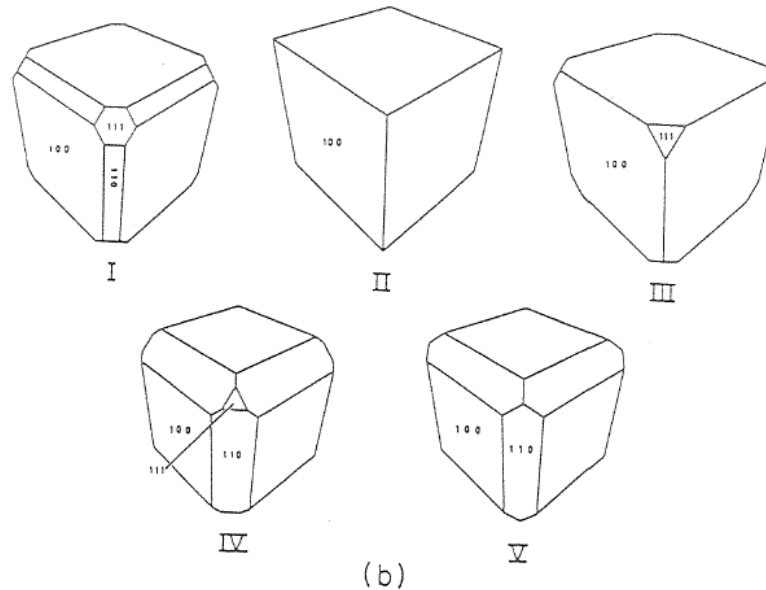


Fig. 1.6. Polar plot of the surface tension at $T=0$ (solid curve) and the Wulff construction of the equilibrium crystal shape (dashed curve) (Herring, 1951b).



Procedure: **(1)** Given $\gamma(\vec{n})$, draw set of vectors from common origin of length h_i proportional to γ_i with direction normal to plane in question; **(2)** Construct plane $\perp$ to each vector; **(3)** Find the geometric figure having smallest size with non-intersecting planes; **(4)** This is the ECS!!

Thermodynamics of Surfaces



the generic ECS's (b) for the simple-cubic crystal.

There are five generic types of shapes, designated I, II, III, IV, and V, for this system. All the edges and corners are degenerate in type I and type IV; all the edges and corners are nondegenerate in type II; the $\{100\}\{010\}$ edges in type III and the $\{110\}\{011\}$ corners in type V are nondegenerate while all other edges and corners in these two types are degenerate.

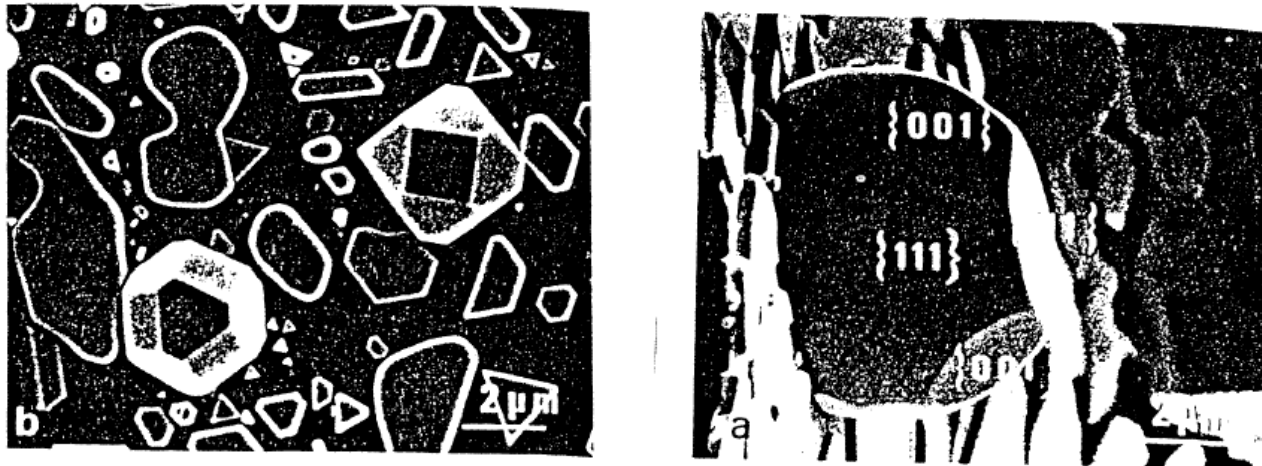


Fig. 1 Growth shape of lead crystals above -120°C : (a) curved surfaces are still seen between plane faces, (b) true cuboctahedra with sharp edges.

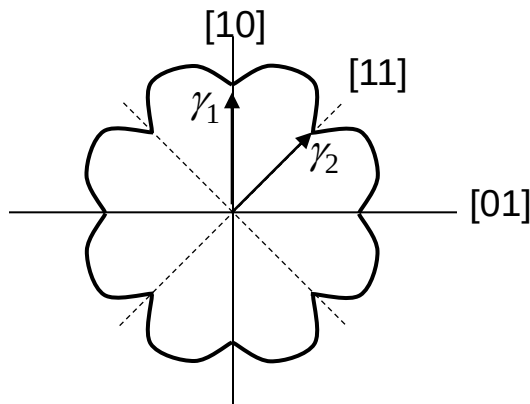
Thermodynamics of Surfaces

Dependence of ECS on degree of anisotropy:

- $\Delta\gamma/\gamma < 1\%$ $\rightarrow$ nearly spherical
- $\sim 2\% - 10\%$: Flats connected by curves
- $\sim 10\% - 20\%$: polyhedra with rounded corners
- $> 30\%$: polyhedra, flats only!!

Know $\gamma(\vec{n})$ can determine ECS.

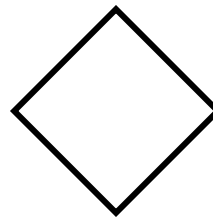
Know ECS, can determine relative values of γ_i .



Suppose $\gamma_{10} = 250 \text{ erg/cm}$
 $\gamma_{11} = 225 \text{ erg/cm}$

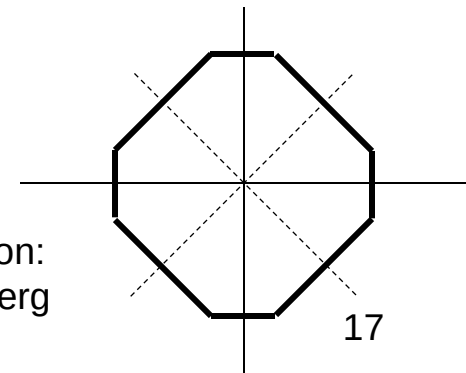


If [01] only, then $E = 4 \times 250 = 1000 \text{ erg}$



If [11] only, then $E = 4 \times 225 = 900 \text{ erg}$

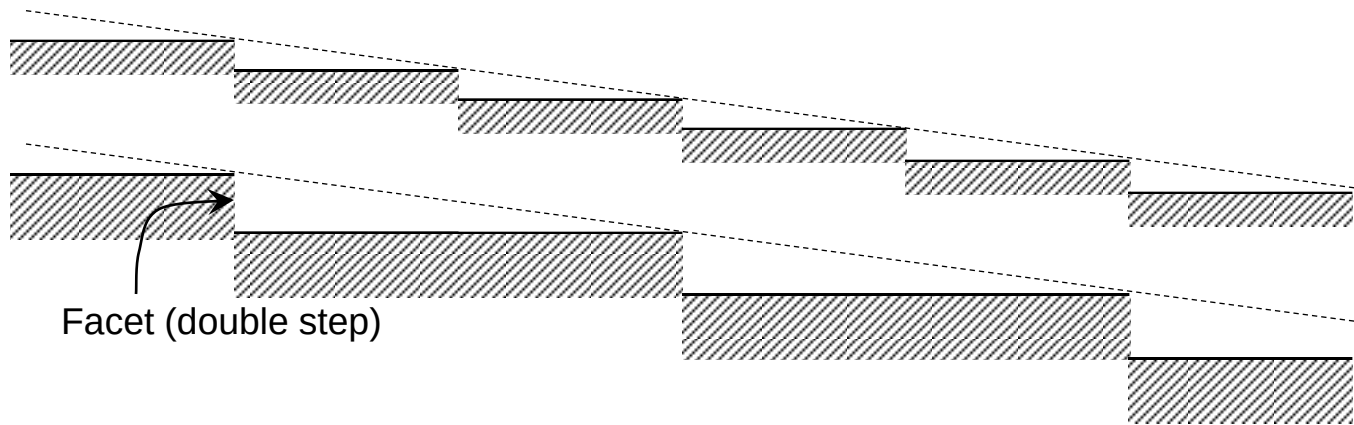
For shape generated by Wulff construction:
 $E = (4)(0.32)(225) + (4)(0.59)(250) = 851 \text{ erg}$



Thermodynamics of Surfaces

Consequences of ECS for surfaces

Vicinal surfaces tend to form facets due to step bunching



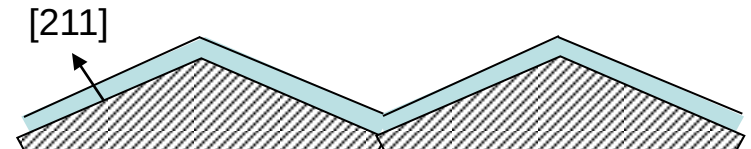
For most metals $\Delta\gamma/\gamma < 3\% \rightarrow$ no spontaneous faceting.

But: Adsorbate (oxygen, metallic film) induced faceting from increased $\Delta\gamma/\gamma$ is common

e.g., bcc(111)



$\rightarrow$
 $T > 700 \text{ K}$



Thermodynamics of Surfaces

Temperature dependence of γ and ECS

In general $\gamma = \gamma^o \left(1 - \frac{T}{T_c}\right)^n$ For metals, $n \sim 1$

Critical temperature where Interface disappears

$u_{P,V}^s = \gamma - T \left(\frac{d\gamma}{dT} \right)$ (where $\left. \frac{d\gamma}{dT} \right|_P = -s^s$)

Specific surface energy
(usually calculated)

Specific surface
free energy
(usually measured)

Since $\left. \frac{d\gamma}{dT} \right|_P < 0$, $u_{P,V}^s > \gamma$

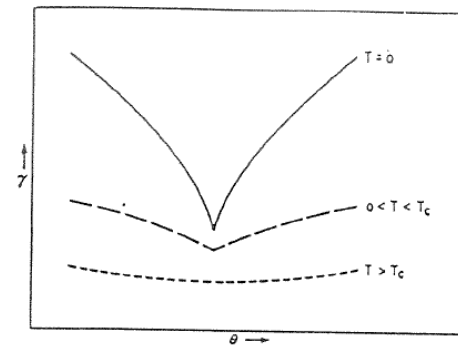
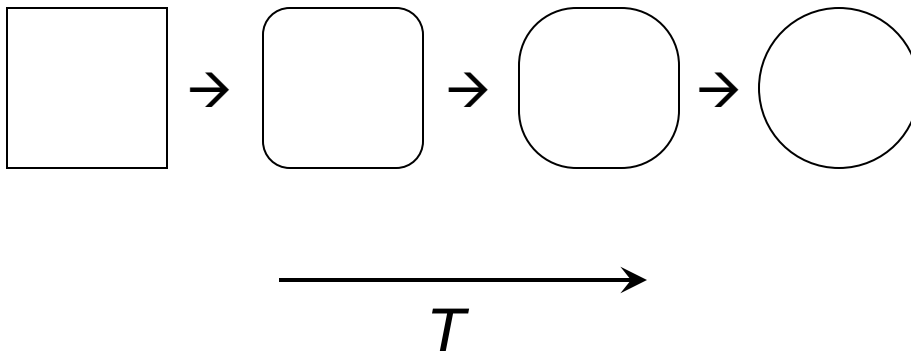


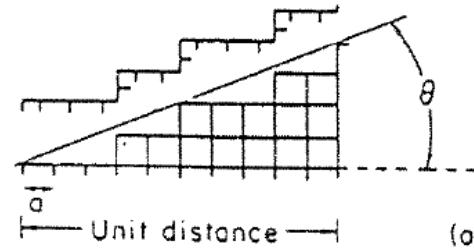
FIG. 1.—Blunting of a cusp in the γ plot with increasing temperature. *Full curve*: absolute zero. *Dashed curve*: higher temperature. *Dotted curve*: temperature above the critical temperature for long-range order in the position of the surface.

Thermodynamics of Surfaces

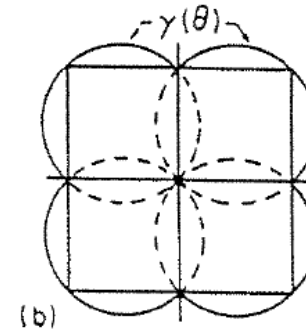
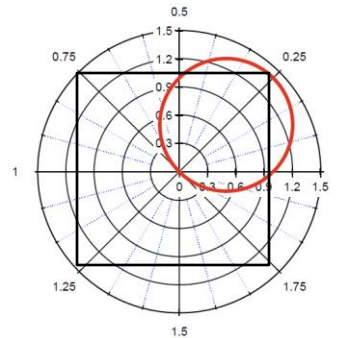
Theoretical estimates of γ

Consider 2-D crystal with pairwise interaction:

For 1st n.n. interactions only
simple cubic crystal
only 4 cusps

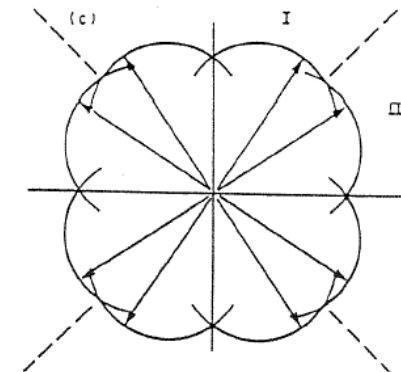


$$\gamma(\theta) \propto (\sin|\theta| + \cos|\theta|)$$



For 2nd n.n. pairwise interactions also
more cusps appear

Fig. 33. (a) Simple cubic model for vicinal surface. (b) Corresponding two-dimensional Wulff plot including nearest-neighbor interactions only [86]. (c) Wulff plot calculated with first and second nearest-neighbor interactions [114].



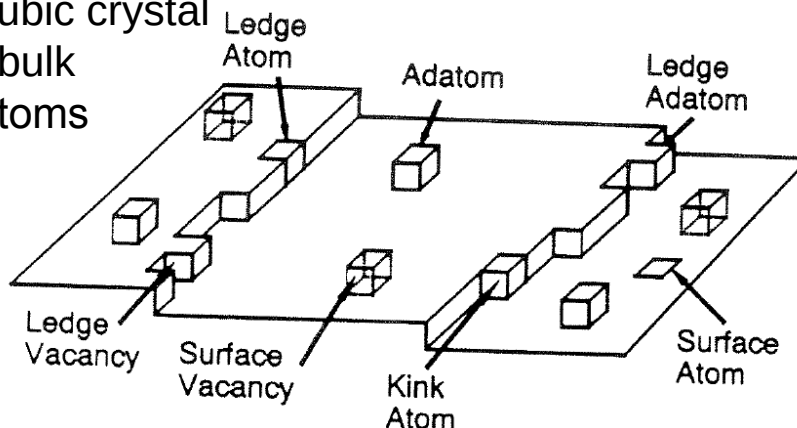
Thermodynamics of Surfaces

Consequences of γ being positive:

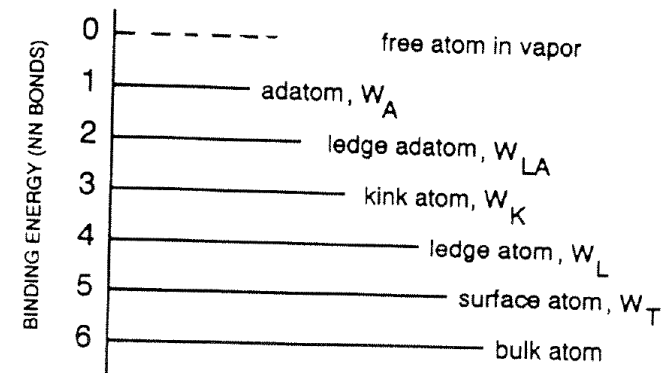
- ECS
- Surfaces easily covered by adsorbates (which lower surf. energy)
- Alloys: Component with lower γ segregates to surface
- Adhesion best for high γ surfaces
- Self healing of organic layers

Terrace – Ledge – Kink (TLK) Model, Defects:

Simple cubic crystal
6 n.n. in bulk
“cubic” atoms



Relative binding energy
scales with number of
n.n. bonds



Thermodynamics of Surfaces

Terrace – Ledge – Kink (TLK) Model, Defects (con't):

- To form vacancies in terrace and move atom to kink must break 5 bonds, remake 3:

$$\Delta G_v = W_K - W_T$$

- Equilibrium vacancies: $\frac{n_v}{M} = \exp\left(-\frac{\Delta G_v}{kT}\right)$
 Number of surface sites

- Same arguments for ledge atoms, ledge vacancies, etc.
- At high T, get surface roughening as vacancies interact
- Roughening transition temperature $T_R < T_{\text{melting}}$

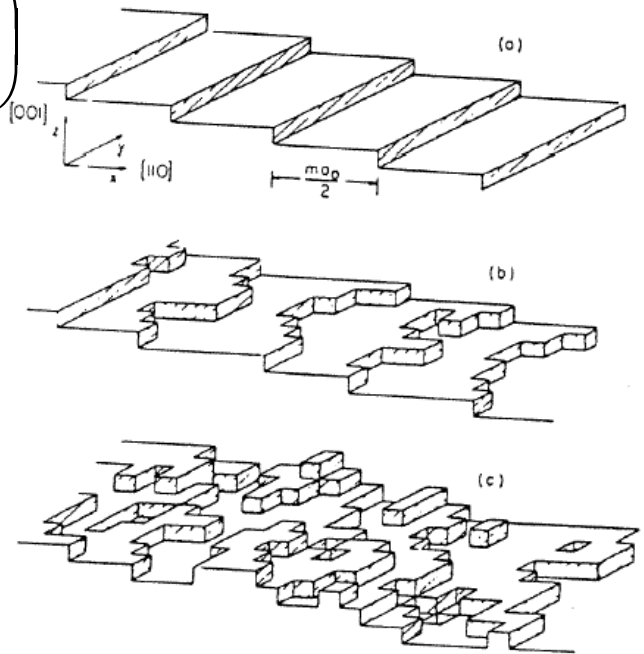


Figure 1.23 Schematic view of the surface roughening transition on an FCC (111) surface, showing (a) $T = 0$ K, (b) meandering steps, and (c) above the roughening temperature. (Source: E.H. Conrad, R.M. Aten, D.S. Kaufman, L.R. Allen, T. Engel, M. den Nijs, and E.K. Riedel, *J. Chem. Phys.* 1986;84:1015. Reprinted with permission.)