

***Surface and Interface Science
Physics 627; Chemistry 541***

***Lectures 2
Sept 8, 2010***

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

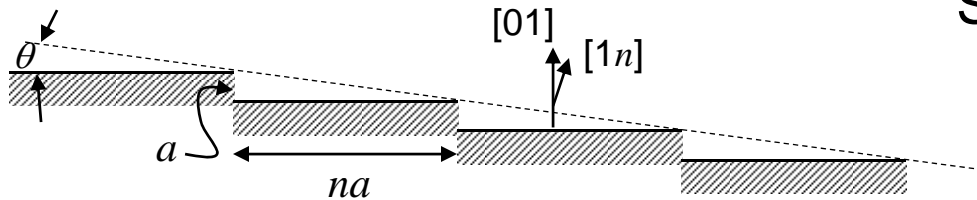
References:

- 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

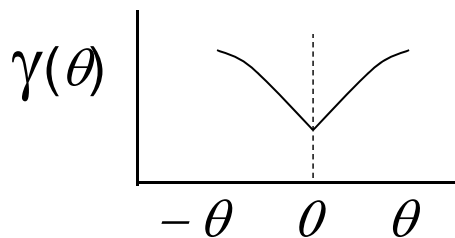


Starting from plane, addition of each step adds energy

$$\tan \theta \approx \theta \approx \frac{a}{na} \approx \frac{1}{n}$$

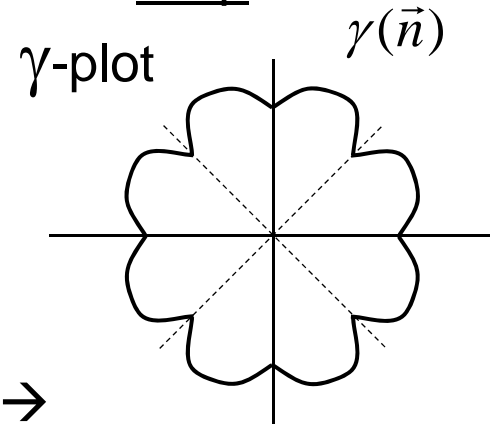
Let $\beta = \text{energy/step}$; $1/(na) = \text{steps/unit length} = \theta/a$ then: $\gamma(\theta) = \gamma(0) + \frac{\beta}{a} |\theta|$

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

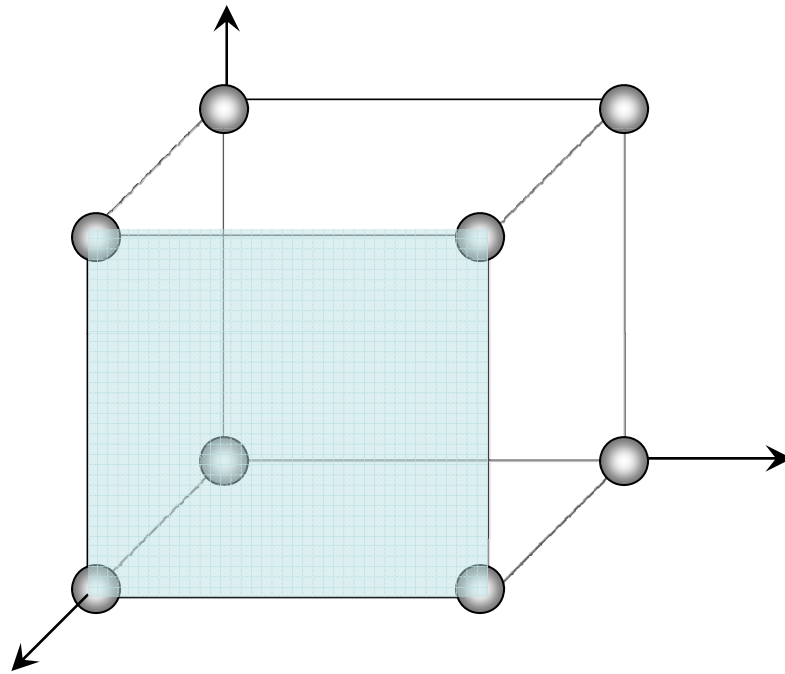


Cusps exist at every direction corresponding to a rational Miller index

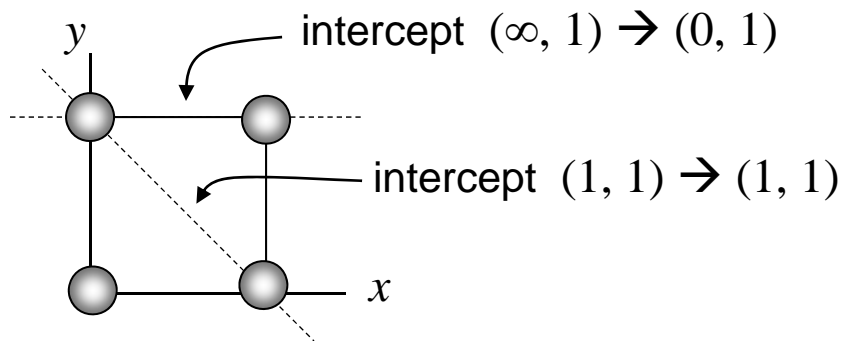
A polar plot of surface tension has many cusps \rightarrow



Aside: Miller Indices



In two dimensions (2D crystals)



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:

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

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

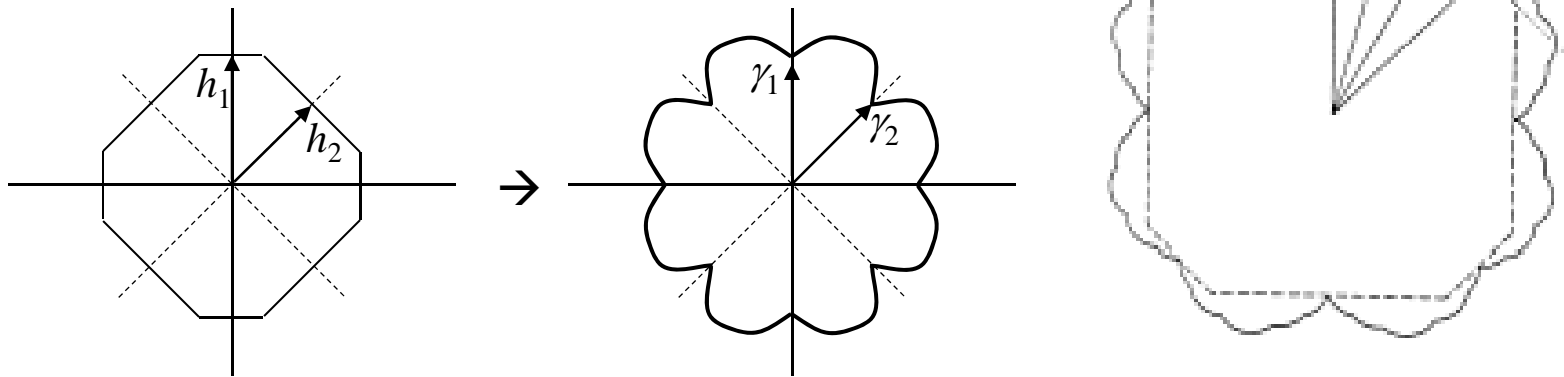
Thermodynamics of Surfaces

(f) Equilibrium crystal shape

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

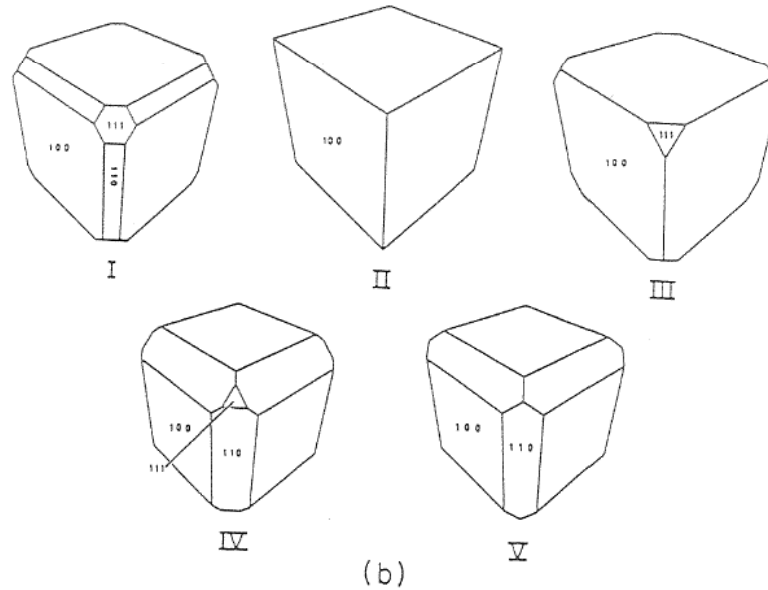
Wulff's Theorem: For a crystal at eqm. there exists a point in the interior such that its perpendicular distance, h_i , from the i^{th} face is proportional to γ_i .

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 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 $(110)(101)(011)$ corners in type V are nondegenerate while all other edges and corners in these two types are degenerate.

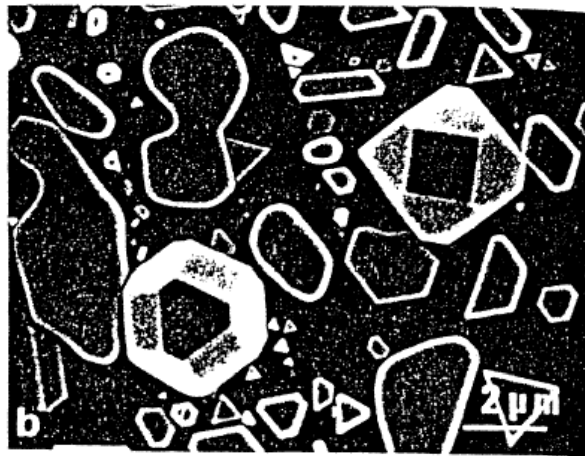


Fig 1 Growth shape of lead crystals above -120°C : (a) curved surfaces are still seen between plane faces. (b) true cuboctahedra with sharp edges.

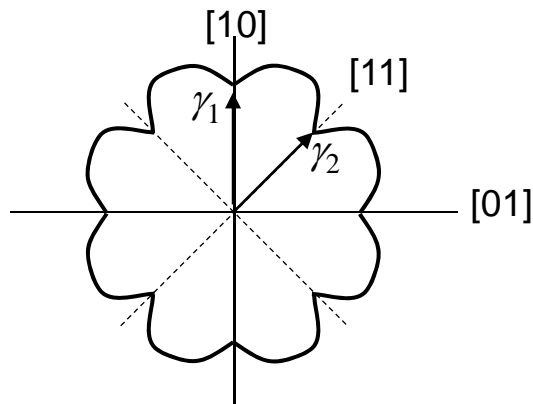
Thermodynamics of Surfaces

Dependence of ECS on degree of anisotropy:

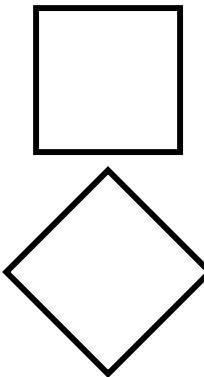
- $\Delta\gamma/\gamma < 1\%$ \rightarrow nearly spherical
- $\sim 2\% - 10\%$: Flats connected by curves
- $\sim 10\% - 20\%$: polyhedra with rounded corners
- $> 30\%$: polyhedra, flats only!!

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

Know ECS, can determine relative values of γ_i .



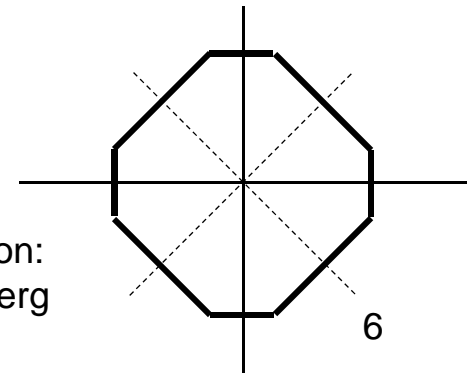
Suppose $\gamma_{10} = 250 \text{ erg/cm}$
 $\gamma_{11} = 225 \text{ erg/cm}$



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

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

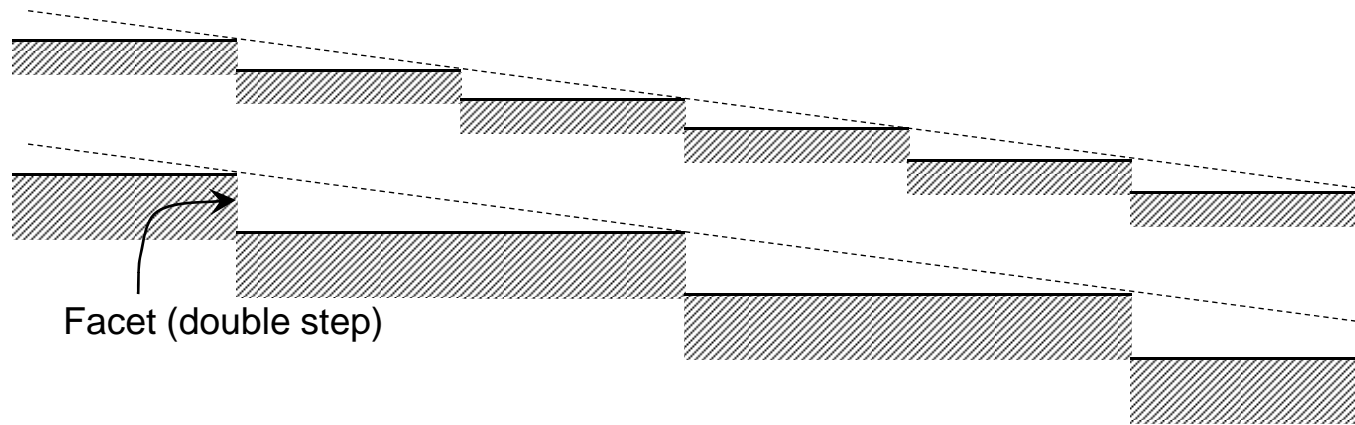
For shape generated by Wulff construction:
 $E = (4)(0.32)(225) + (4)(0.59)(250) = 851 \text{ erg}$



Thermodynamics of Surfaces

Consequences of ECS for surfaces

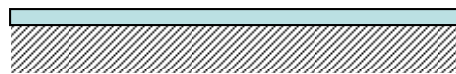
Vicinal surfaces tend to form facets due to step bunching



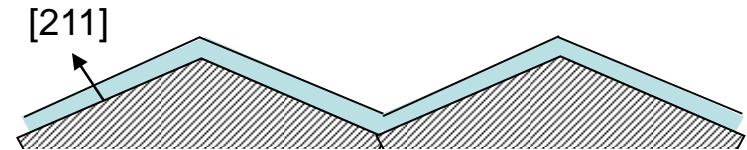
For most metals $\Delta\gamma/\gamma < 3\% \rightarrow$ no spontaneous faceting.

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

Specific surface energy (usually calculated) $u_{P,V}^s = \gamma - T \left(\frac{d\gamma}{dT}\right)$ Specific surface free energy (usually measured)

(where $\left.\frac{d\gamma}{dT}\right|_P = s^s$)

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

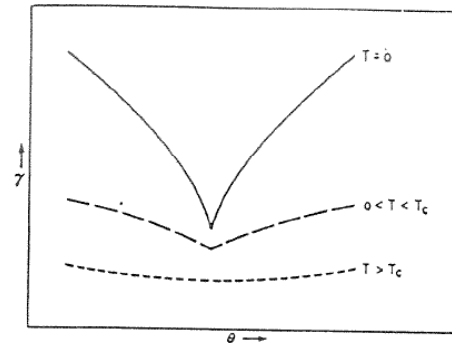
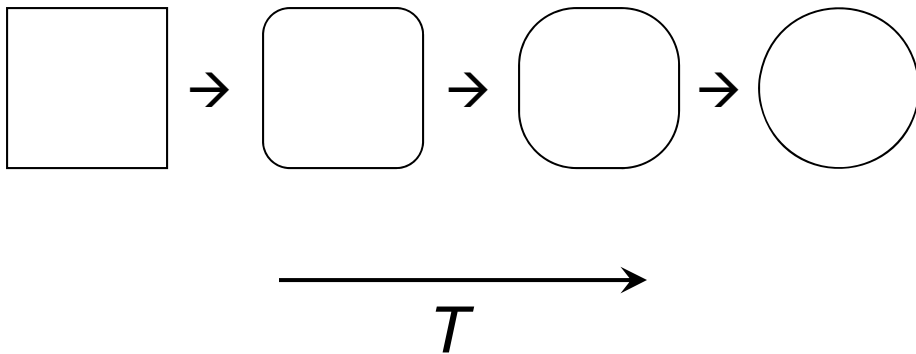


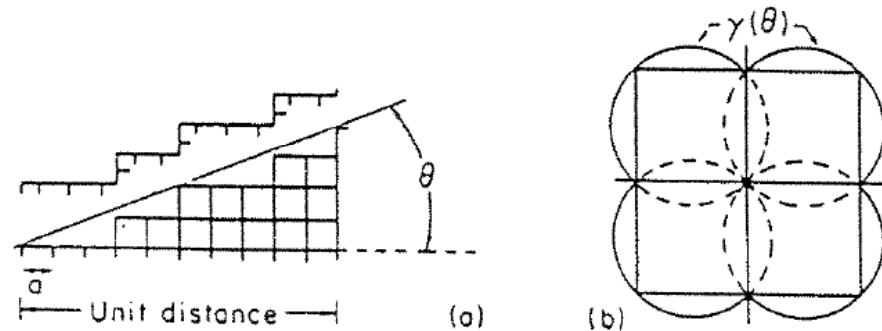
FIG. 1.—Blunting of a cusp in the γ plot with increasing temperature. Full curve: absolute zero. Dashed curve: higher temperature. Dotted curve: temperature above the critical temperature for long-range order in the position of the surface.

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



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

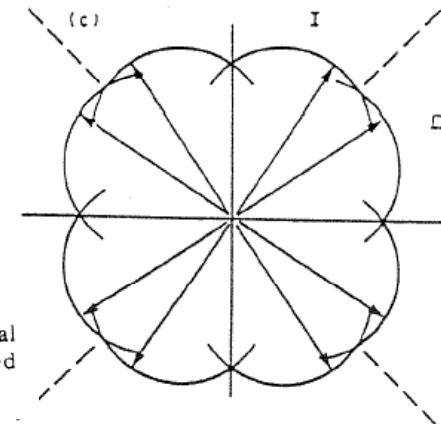


Fig. 33. (a) Simple cubic model for vicinal surface. (b) Corresponding two-dimensional Wulff plot including nearest-neighbor interactions only [86]. (c) Wulff plot calculated with first and second nearest-neighbor interactions [114].

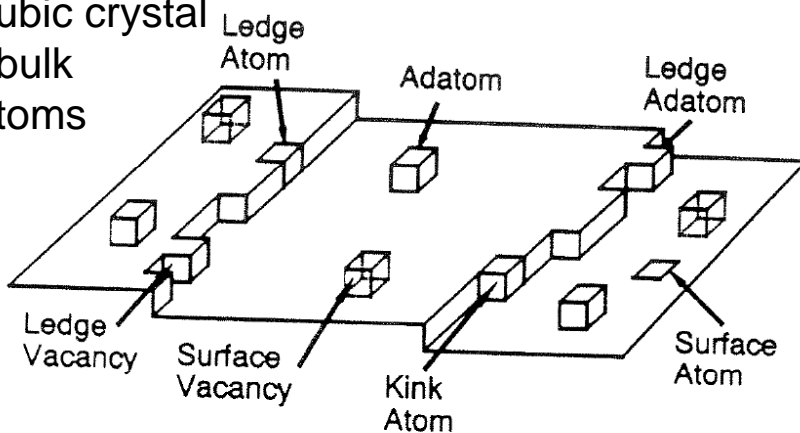
Thermodynamics of Surfaces

Consequences of γ being positive:

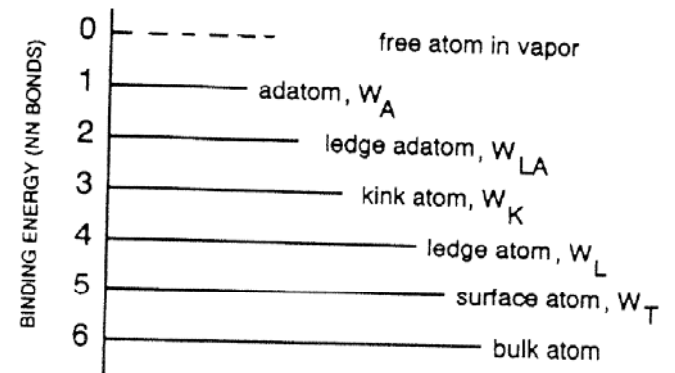
- ECS
- Surfaces easily covered by adsorbates (which lower surf. Energy)
- Alloys: Component with lower γ segregates to surface
- Adhesion best for high γ surfaces
- Self healing of organic layers

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 $T_R < T_{\text{melting}}$

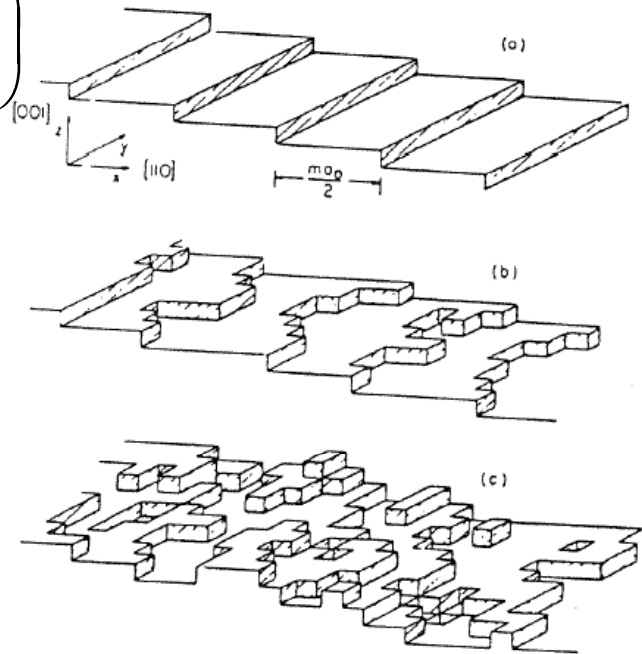


Figure 1.23 Schematic view of the surface roughening transition on an FCC (111) surface, showing (a) $T = 0$ K, (b) meandering steps, and (c) above the roughening temperature. (Source: E.H. Conrad, R.M. Aten, D.S. Kaufman, L.R. Allen, T. Engel, M. den Nijs, and E.K. Riedel, *J. Chem. Phys.* 1986;84:1015.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