Lecture 1

Thermodynamics of Surfaces;
Equilibrium Crystal Shape

Course will primarily focus on: atomic structure and electronic properties, chemical composition and adsorption properties of surfaces

But …

Many important aspects of surface properties can be understood from the point of view of macroscopic thermodynamics

- the surface under equilibrium conditions (e.g., faceting, wetting, island growth)

References:
1) Zangwill, Chapter 1
2) Somorjai, Chapter 3
3) http://venables.asu.edu/grad/lectures.html

1.1 Surface Thermodynamic Functions

Thermodynamics (Gibbs): In equilibrium, a one-component system is characterized completely by the internal energy, U

$$U = U(S,V,N)$$

$$dU = \frac{\partial U}{\partial S}\bigg|_{V,N} dS + \frac{\partial U}{\partial V}\bigg|_{S,N} dV + \frac{\partial U}{\partial N}\bigg|_{V,S} dN$$

$$dU = TdS - PdV + \mu dN \qquad (1.1)$$

Two types of parameters:

- **Extensive** parameters

U, V, S, N, A (can be summed to give entire system value)

- **Intensive** parameters

T, P, μ_i (thermodynamic driving parameters that <u>do not add)</u>

Surface Thermodynamic Functions

Now, suppose a crystalline solid bounded by surfaces

Total Energy $U = NU_O + AU^S$ excess energy due to unit area for surface

# of atoms in solid

surface area

Similarly:

Total Entropy $S = NS_O + AS^S$

Gibbs free energy (per unit area) $G^S = H^S + TS^S$

Total free energy: $G = NG^o + AG^S$

<u>Surface</u> thermodynamic values defined as **<u>excesses</u>** over the <u>bulk</u> values

N.B.: Importance of Gibbs free energy: at equilibrium surface reactions, phase changes occur at constant T, P, where G = const $\rightarrow$ $dG = 0$

1.2 Surface Tension and Surface Energy

In 3D system to create a volume: $\delta W = P\, dV$

Similarly, to create a surface: $\delta W^S_{T,P} = \gamma\, dA$

γ is 2D analog of pressure: **<u>surface tension</u>**

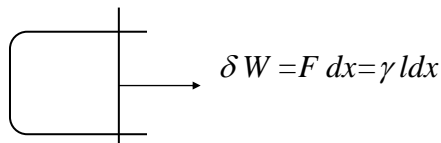e.g., for 2D liquid film, infinite work done to create additional surface area dA:

<u>Units of γ</u>:
eV/surface atom

erg/cm²   *Joules/m²*

dynes/cm   *Newtons /m*

$\delta W = F\, dx = \gamma\, l\, dx$

Note: work of crystal cleavage proportional to $\gamma\, dA$

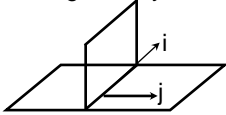# 1.3 Thermodynamics of Surfaces

$$dU = \frac{\partial U}{\partial S}\Big|_{V,N,A}dS + \frac{\partial U}{\partial V}\Big|_{S,N,A}dV + \frac{\partial U}{\partial N}\Big|_{S,V,A}dN + A\sum_{i,j}\frac{\partial U}{\partial V}\Big|_{S,V,N}d\varepsilon_{i,j} =$$

$$= TdS - PdV + \mu dN + A\sum_{i,j}\sigma_{i,j}d\varepsilon_{i,j} \quad (1.2) \quad \sigma_{i,j} \text{ and } \varepsilon_{i,j} \text{–surf. stress and strain tensors}$$

γ is independent of small strains <u>only for liquids</u>

More generally we must consider the expression (cf. Zangwill, p.11):

$$\sigma_{ij} = \gamma\delta_{ij} + \frac{d\gamma}{d\varepsilon_{ij}}\Big|_{T}$$

For liquid or solid under small strain: $\sigma = \gamma$

In solids it is convenient to denote γ as γ_i, or $\gamma(\vec{n}) = \lim\frac{\Delta W^S}{\Delta A}(\Delta A \to 0)$
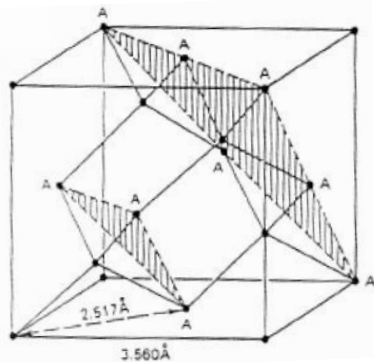
Note: $\gamma = G^S$ specific free surface energy" of one component system

<u>γ is always positive!</u>

Order of magnitude estimates of γ

Covalent bonded system:

diamond – the simplest case of bond breaking

C – C bond strength ~ 3.9 eV/bond

(bond strength in C_2H_6)

Energy = 2 γA

From crystallography:

1.85×10^{15} bonds/cm^2 for (111) surface

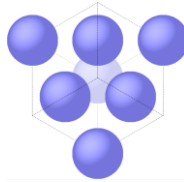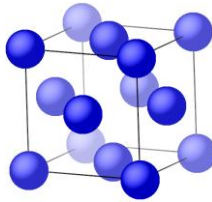$\gamma = \frac{1}{2}$ total bond energy

Order of magnitude estimates of γ

For metals: $\gamma \approx E_{coh} \dfrac{Z_S}{Z} N_S$ $\leftarrow$ # atoms/cm^2

Broken surface bonds Z_S

nearest neighbor bonds Z

Consider Cu(111) one surface atom:

Z = 12 (bulk), Z_S = 3 (surface)
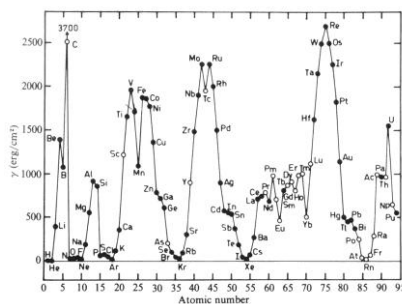
Surface tension of selected solids and liquids

Material	γ (ergs/cm^2)	T (°C)
W (solid)	2900	1727
Nb (solid)	2100	2250
Au (solid)	1410	1027
Ag (solid)	1140	907
Ag (liquid)	879	1100
Fe (solid)	2150	1400
Fe (liquid)	1880	1535
Pt (solid)	2340	1311
Cu (solid)	1670	1047
Cu (liquid)	1300	1535
Ni (solid)	1850	1250
Hg (liquid)	487	16.5
LiF (solid)	340	−195
NaCl (solid)	227	25
KCl (solid)	110	25
MgO (solid)	1200	25
CaF₂ (solid)	450	−195
BaF₂ (solid)	280	−195
He (liquid)	0.308	−270.5
Na (liquid)	9.71	−195
Xenon (liquid)	18.6	−110
Ethanol (liquid)	22.75	20
Water (liquid)	72.75	20
Benzene (liquid)	28.88	20
n-Octane (liquid)	21.80	20

Lecture 1

Order of magnitude estimates of γ
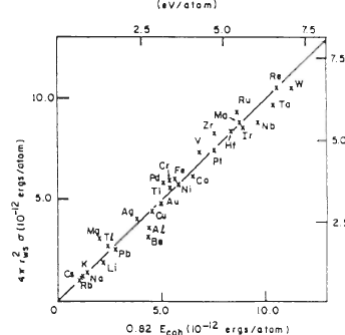
Surface tension can be regarded as an excess free energy/unit area

Fig. 1.4. Surface tension of the elements in the liquid phase (Schmit, 1974).

Relationship between surface and cohesive energy of metals (cf. A.Keijna, Metal Surf. Electron Physics, Ch.3)

changes of surface tension across the periodic table reflect <u>the variations in E$_{coh}$</u>
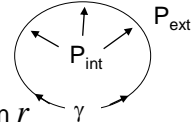
$$4\pi r_{Wigner-Seitz}^{2}\,\gamma \cong 0.82 E_{coh}$$

1.4 Curves Surfaces

For a bubble, surface tension counteracts internal pressure

$$P_{int} - P_{ext} = \frac{2\gamma}{r}$$

For curved surface of a solid, vapor pressure P_r, depends on r

• Flat surface: $\qquad r = \infty,\ P = P_O$

• Curved surface:

$$\ln\left(\frac{P_r}{P_O}\right) = \frac{2\gamma}{RT}\frac{\overline{V}_{in(specific)}}{r}$$

$\rightarrow$ Kelvin equation:

$$\frac{P_r}{P_O} = \exp\left(K\frac{\gamma}{r}\right) \quad \text{important for } r << 1000\text{Å}$$

Applied to important surface problems: melting point, nucleation and growth (e.g., "ripening":

$t = 0$ $\qquad\qquad\qquad\qquad\qquad$ $t = \infty$

For distribution of particles on surface, little ones disappear, large one grow

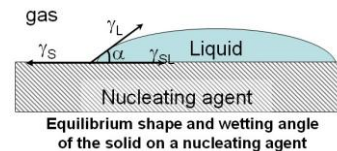9

1.5 Contact Angle

Measurements of γ for liquid:

shape of drop determined by combination of γ and g (gravity)

d_{max}

Contact angle

γ_L, γ_S – surface free energy of liquid (solid)

γ_{SL} – interface energy or tension

gas

γ_L

γ_S

α γ_{SL} Liquid

Nucleating agent

Equilibrium shape and wetting angle of the solid on a nucleating agent

Surface tension exerts force along surface at line of intersection

At equilibrium: $\gamma_L \cos\alpha = \gamma_S - \gamma_{SL}$ (Young's eq.)

$$\boxed{\cos\alpha = \frac{\gamma_S - \gamma_{SL}}{\gamma_L}}$$

Complete wetting $\qquad\qquad$ Wetting $\qquad\qquad$ No wetting

$\gamma_S > (\gamma_L + \gamma_{SL})$ $\quad$ $-\gamma_L < (\gamma_S + \gamma_{SL}) < \gamma_L$ $\quad$ $\gamma_{SL} > (\gamma_L + \gamma_S)$ $\quad$ 10

5

Need to include structural information…

The **surface energy** or the surface tension of a planar solid surface depends on the crystallographic orientation of the sample

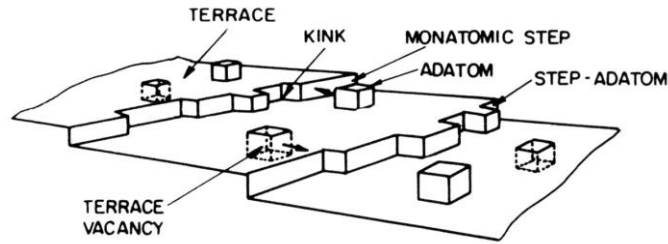Bulk energy < surface energy < step energy < kink or adatom energy

Figure 1.6. Model of a heterogeneous solid surface, depicting different surface sites. These sites are distinguishable by their number of nearest neighbors.
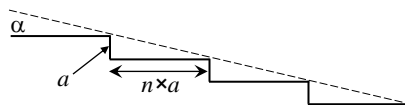
from G.A Somorjai "Chemistry in two dimensions: surfaces"

1.6 Anisotropy of surface free energy, γ

Following Zangwill (p.12) consider stepped or (vicinal) surface of 2D solid:

Starting from plane, addition of each step adds energy

Define β – energy per step

$$\tan\alpha \sim \frac{a}{na} = \frac{1}{n}$$

$$\frac{steps}{unit\_cell} = \frac{1}{na} = \frac{\tan\alpha}{a} \approx \frac{\alpha}{a}$$

$$\gamma(\alpha) = \gamma(0) + \frac{\beta}{a}|\alpha|$$

γ (α) has discontinuous derivative at α = 0 → there is a *cusp*
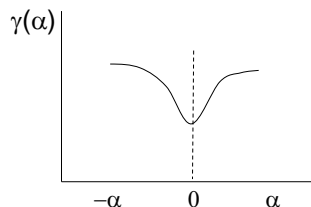
A *cusp* exists at every direction corresponding to a rational Miller index (i.e., low index plane, for example: (100), (111), (110)

γ-plot $\gamma(\vec{n})$
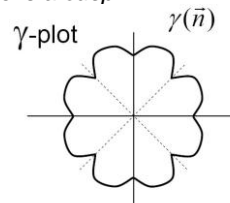
Anisotropy of the γ -plot

Fig. 1.8. Anisotropy of γ relative to $\langle 111 \rangle$ for lead as a function of temperature (Heyraud & Metois, 1983).
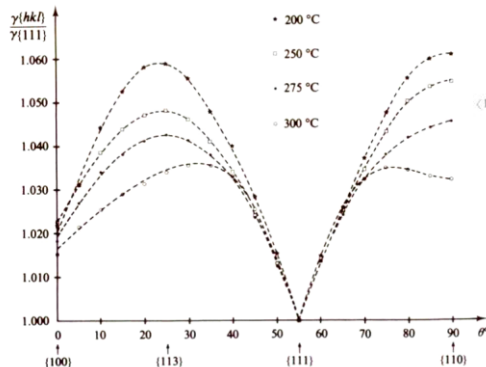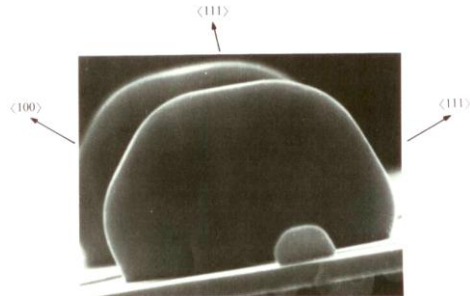
Fig. 1.7. Electron micrograph of a lead crystal at 473 K (Heyraud & Metois, 1983).
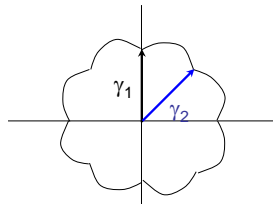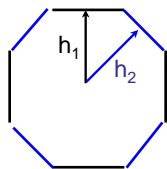

Zangwill, p.14

1.7 Equilibrium Crystal Shape (ECS)

Crystal will seek a shape determined by $\oint \gamma(\bar{n})da = \text{minimum at } V = \text{const.}$

Sphere for liquid, faceted for solids: determine shape from <u>Wulff's theorem</u>

<u>Wulff's Theorem</u>: for a crystal at equilibrium, there exists a point in the interior such that its perpendicular distance h_i from the ith face is proportional to γ_i

$$\frac{\gamma_1}{h_1} = \frac{\gamma_2}{h_2} = ...$$

<u>Procedure</u>: 1. given $\gamma(n)$, draw a set of vectors from a common origin with length *hi* proportional to γ_i, and with directions normal to plane in question

2. construct planes perpendicular to each vector

3. find the geometric figure having the smallest size with non-intersecting planes

4. this is the **ECS** (in practice - in 3D)

Equilibrium Crystal Shape (ECS)

• In equilibrium, shape of a given amount of crystal **minimizes** the total **surface energy**

• *For Liquids*: spherical shape

• *For Solids*: Equilibrium Crystal Shape (ECS) has facets

the generic ECS's (b) for the simple-cubic crystal.
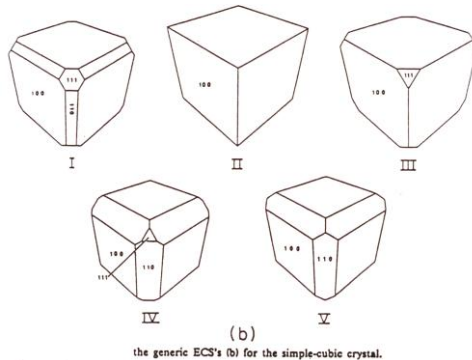
Dependence of ECS on degree of anisotropy:

$\Delta\gamma/\gamma$ < 1%   ~nearly spherical

~ 2% - 10%: flats connected by curves

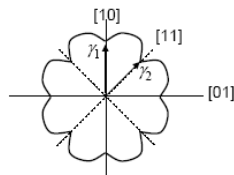~ 10% - 20%: polyhedra with rounded
> 30%   polyhedra flats only

Example of ECS for a 2D crystal

$$\oint \gamma dl = \quad \text{minimum for } \underline{\text{constant area}}$$

$\Rightarrow$ From γ (n) we can determine ECS

$\Rightarrow$ From ECS can determine relative values of γ (n)

Suppose γ - plot has only two types of cusps: (10) and (11)

Suppose γ_{10} = 250 erg/cm
           γ_{11} = 225 erg/cm
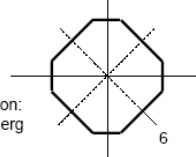
If [01] only, then E = 4x250 = 1000 erg

If [11] only, then E = 4x225 = 900 erg

For shape generated by Wulff construction:
E = (4)(0.32)(225)+(4)(0.59)(250) = 851 erg

Free-energy change *vs* radius of nucleus

$$\Delta G_{total} = \frac{4}{3}\frac{\pi r^3}{v}\Delta\mu + 4\pi r^2\gamma$$

ΔG_{total} – total free-energy change

r – radius of embryo or nucleus

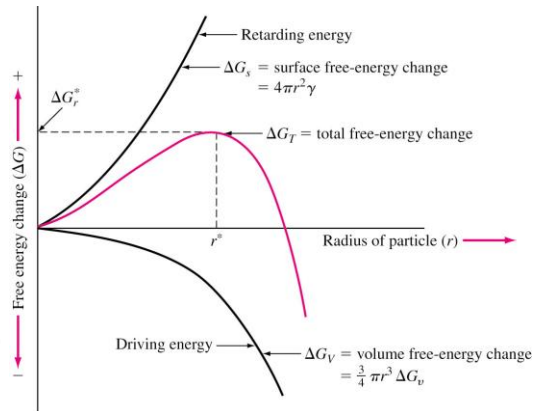$\Delta\mu$ – volume free energy

γ - specific surface free energy

Two components: (i) volume free-energy change (ΔG_V or $\Delta\mu$) and (ii) surface free-energy change (ΔG_S)

$$\Delta\mu = \mu_S - \mu_L < 0;$$
$$\mu_S < \mu_L$$

(i) is negative,

(ii) ΔG_S is positive

Retarding energy

ΔG_s = surface free-energy change $= 4\pi r^2\gamma$

ΔG_T = total free-energy change

Radius of particle (r)

Driving energy

ΔG_V = volume free-energy change $= \frac{3}{4}\pi r^3 \Delta G_v$

r* - critical radius
-if r < r*, droplet can shrink or dissolve
-if r > r*, droplet grows

Lecture 1   17

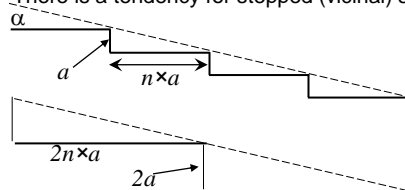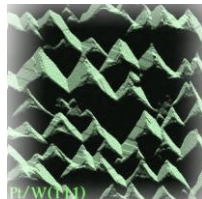
Consequences for planar surfaces

- There is a tendency for stepped (vicinal) surface to form facets by **step bunching**

Driving force → minimize edge energy

α

a

n×a

2n×a

2a

Double step

- Impurity-induced faceting: adsorb impurities (oxygen, metallic films)

e.g. bcc W(111) → Pt/W{011} and {112}

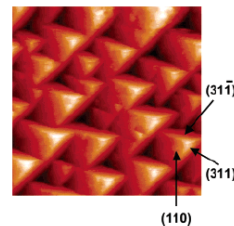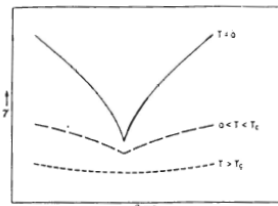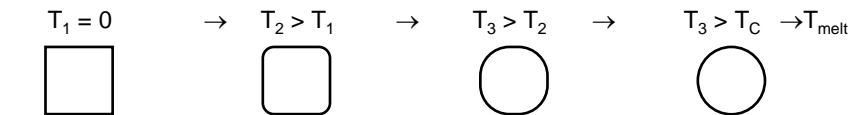**O/Ir(210) → Ir{311} and Ir (110) facets**

(31ī)

(311)

(110)

Figure 1. Scanning tunneling microscope (STM) image (100 nm × 100 nm) from oxygen-covered faceted Ir(210) showing the morphology of three-sided pyramidal facets. Faceting is induced by flashing Ir(210) in O_2 (5×10^{-8} Torr) to $T > 1700$ K and subsequent cooling in O_2 to 300 K.

Pt/W(111)

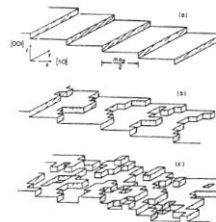**T.E.Madey, C.-H.Nien, K.Pelhos,** *Surf. Sci. 438 (1999)191-206*

Le

1.8 Temperature Dependence of γ and ECS

In general $\gamma = \gamma^o \left(1 - \dfrac{T}{T_C}\right)^n$ for metals n ~ 1 T_C – roughening temperature

ECS:

$T_1 = 0$ → $T_2 > T_1$ → $T_3 > T_2$ → $T_3 > T_C$ →T_{melt}

T = 0K

meandering steps

above T_C

Disappearing of a cusp in the γ – plot with increasing T

Terrace – Ledge - Kink (TLK) Model
also Solid on Solid (SOS) Model

Typical surface sites and defects on a simple cubic (100) surface (6 N.N. in bulk)
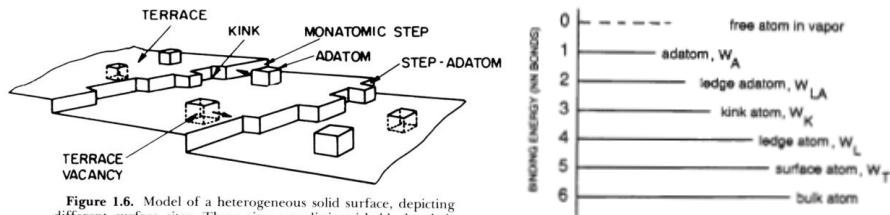

Figure 1.6. Model of a heterogeneous solid surface, depicting different surface sites. These sites are distinguishable by their number of nearest neighbors.

From Somorjai

To form vacancy in terrace and move atom to kink, break 5 bonds, remake 3

$$\Delta G_V = W_K - W_T$$

$$\frac{N_V}{N_{surf}} = \exp\left(-\frac{\Delta G_V}{kT}\right)$$

At high T, get surface roughening as vacancies interact

1.9 Consequences of γ being positive

- ECS

- Surfaces easily covered by adsorbates, which lower surface energy

- Alloys: component with lower γ segregates

- Adhesion best for high γ

- "Self-healing" of organic layers

Summary

- γ is always positive

- Order of magnitude for γ

- What defines Equilibrium Crystal Shape (ECS)

- Temperature Dependence of γ and ECS

- Terrace – Ledge - Kink (TLK) Model