Surface and Interface Science
Physics 627; Chemistry 542

Lectures 1
Jan 25, 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.

Aspects of Solid Surfaces

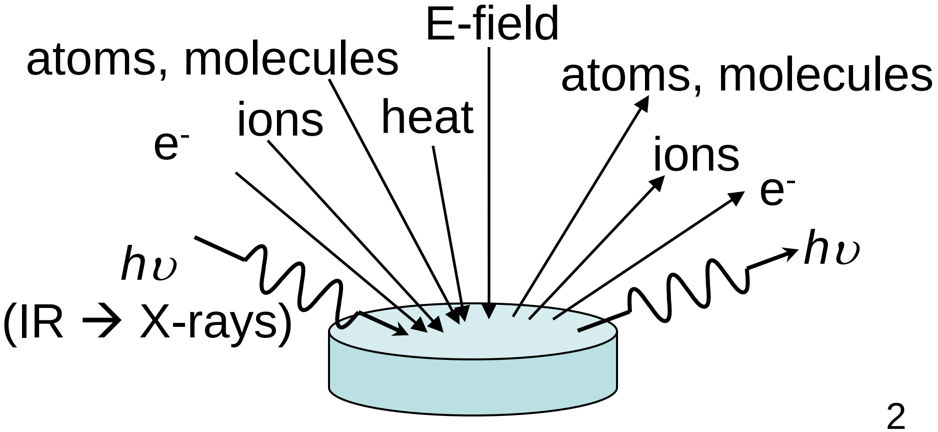
Surface Properties

- Structure
- Chemical composition
- Bonding properties
- Kinetics (adsorption, diffusion, desorption, catalysis)
- Dynamics of surface processes
- Statistical mechanics of 2-D systems

Applications of Surfaces

- Catalysis
- Corrosion
- friction, lubrication
- semiconductor devices
- electrochemistry

Probing Surface Properties



E-field

atoms, molecules

atoms, molecules

ions

heat

ions

e^-

e^-

$h\upsilon$

(IR → X-rays)

$h\upsilon$

Thermodynamics of Surfaces

Course will primarily focus on:

- Atomistic properties of surfaces
- Electronic properties
- Chemical composition
- Adsorption properties

but …

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

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

Thermodynamics of Surfaces

Introduction: Thermodynamics, Surface Thermodynamics

For system in equilibrium, two types of parameters:

Extensive parameters: U, V, N_i, A, S

(can be summed to give entire system values)

Intensive parameters: T, P, μ

(thermodynamic driving parameters that *DO NOT* add)

At eqm., for a single component bulk system:

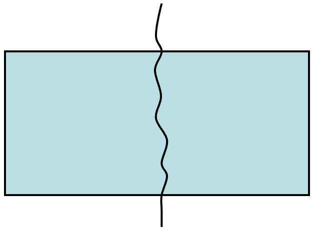
$$U = U(S, V, N)$$

Now, suppose a crystalline solid bounded by surfaces

Total Energy $U = NU_o + AU^s$

# of atoms in solid

surface area



Thermodynamics of Surfaces

Similarly:
Total Entropy $S = NS_o + AS^s$

Gibbs free energy (per unit area) $G^s = H^s - TS^s$

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

Surface thermodynamic values defined as excesses over the bulk values

NB: Importance of Gibbs free energy:
At equilibrium, surface reactions,
phase changes occur at constant T, P, where:

$$G = \text{constant} \rightarrow dG = 0$$

Thermodynamics of Surfaces

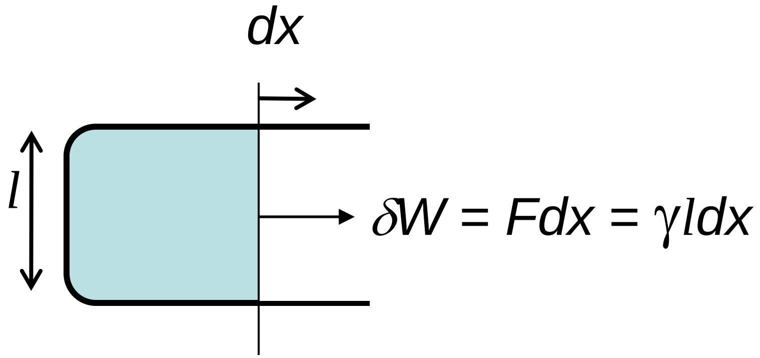
Surface Energy: (a) <u>Thermodynamics</u>

In 3-D system, to create a volume: $\delta W = PdV$

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

γ is 2D analog of pressure: surface tension

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



$\delta W = Fdx = \gamma l dx$

Units of γ:

eV/surface atom

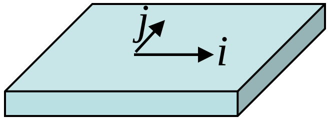
erg/cm² *Joules/m²*

dynes/cm *Newtons/m*

Note: work of crystal cleavage proportional to γdA

Thermodynamics of Surfaces

γ is independent of small strains only for liquids.
More generally, we must consider the expression:



$$\sigma_{ij} = \gamma\delta_{ij} + \frac{d\gamma}{d\varepsilon_{ij}}$$

Component of Surface stress tensor

Component of Surface strain tensor

For liquid or solid under small strain: σ = γ

In solids, it is convenient to denote γ as γ_i or $\gamma(\vec{n})$
Where

$$\gamma(\vec{n}) = \lim_{\Delta A \to 0} \frac{\Delta W^s}{\Delta A}$$

Note: γ = G^s "specific free surface energy" of one component system

γ always positive!!

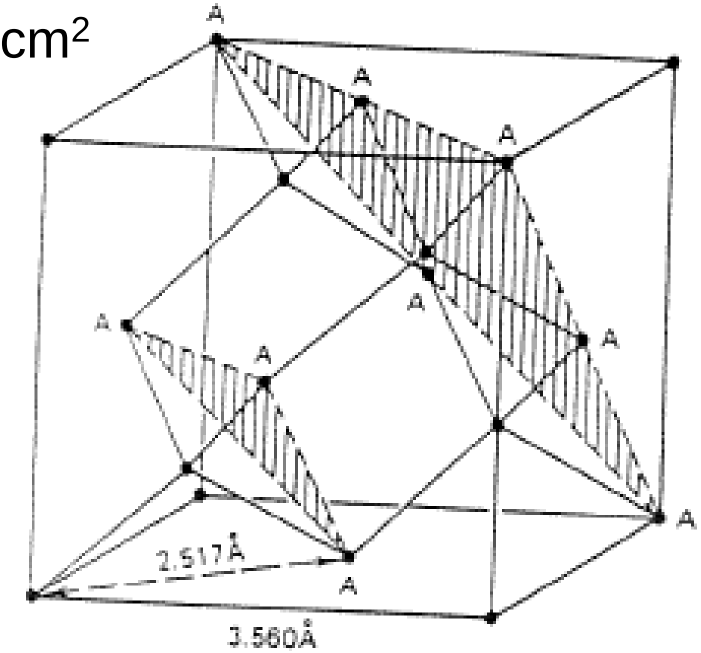
Thermodynamics of Surfaces

(b) Order of magnitude estimates of γ

(i) Covalent bonded system: diamond – simplest case of bond breaking

C – C bond ~ 3.9 eV/bond
(bond strength in C_2H_6)

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



$\gamma = ½$ (total bond energy)

$\gamma \approx 5650$ ergs/cm^2

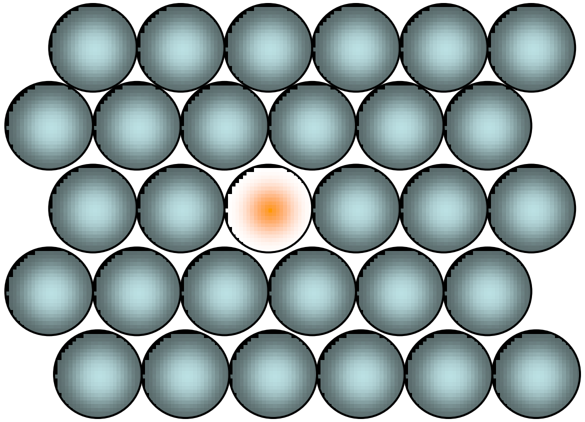
Thermodynamics of Surfaces

(b) Order of magnitude estimates of γ

(ii)For metals: $\gamma \approx E_{coh}(Z_s/Z)N_s$ # atoms/cm^2
broken surface bonds
nearest neighbor bonds

Consider Cu(111): $Z = 12$

$Z_s = 3$



$\gamma \approx$ (3.5 eV/atom)(3/12)

x(1.77 x 10^{15} atoms/cm^2) (1.6 x 10^{-12} erg/eV)

= 2480 erg/cm^2

(compare: 1670 erg/cm^2 for Cu$_s$)

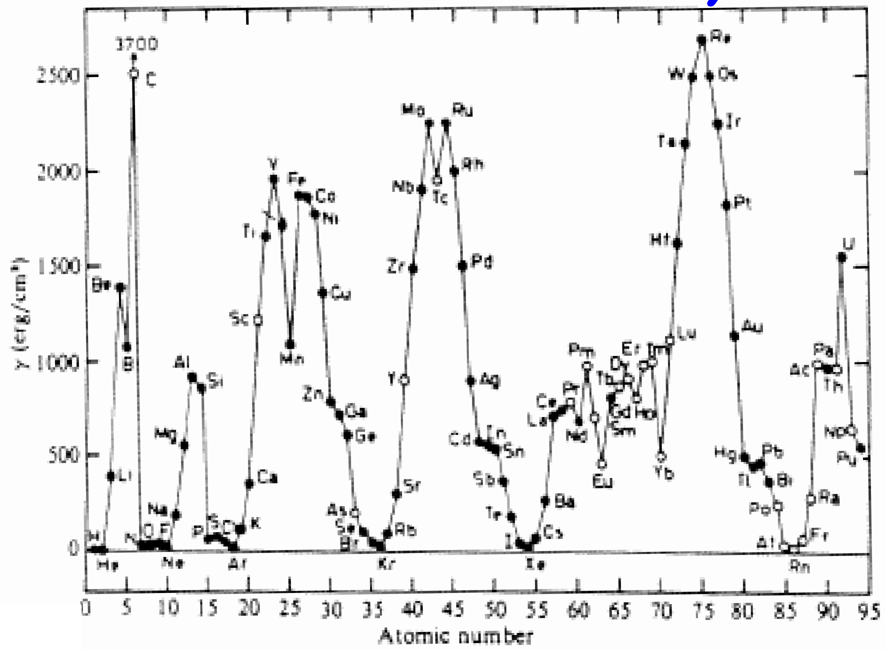
Useful correlations:

$\gamma \approx 0.16\, E_{coh}$ (energy/atom)

$4\pi r_{ws}^2\gamma = 0.82\, E_{coh}$ (energy/area)

Wigner-Seitz radius

Thermodynamics of Surfaces



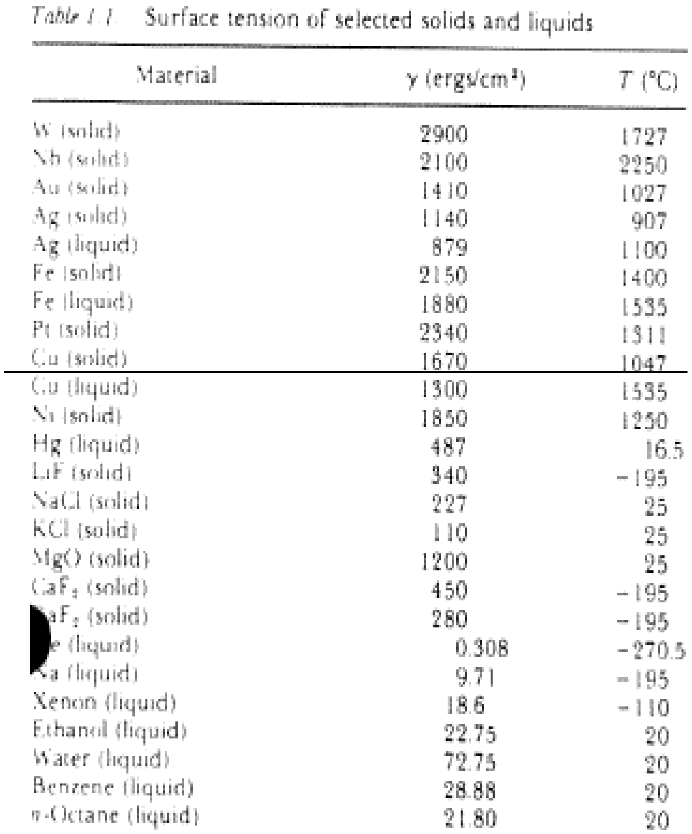
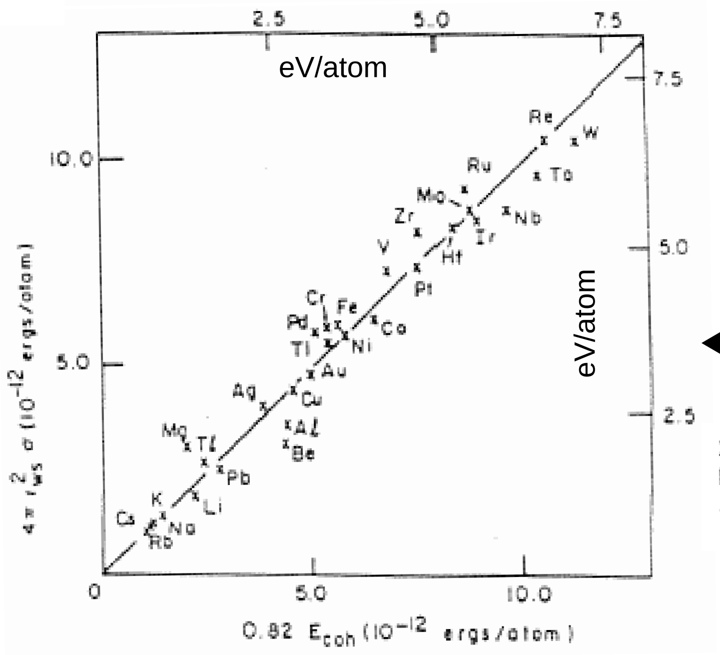


Table 1.1 Surface tension of selected solids and liquids

Material	γ (ergs/cm²)	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
CaF$_2$ (solid)	450	−195
[illegible]aF$_2$ (solid)	280	−195
[illegible]e (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



$$4\pi r_{ws}^2\gamma = 0.82\,E_{coh}\ \text{(energy/area)}$$

Fig. 18.6 Plot of the relation (18.19) between surface and cohesive energy of metals (straight line). The experimental data are denoted by the ×'s. Reprinted with permission from Rose *et al.* (1983). ©1983 The American Physical Society. cf. K+W, Ch. 18

Thermodynamics of Surfaces

(c) Curved surfaces

For a bubble, surface tension counteracts internal pressure

$$\left(P_{\text{int}} - P_{ext}\right) = \frac{2\gamma}{r}$$

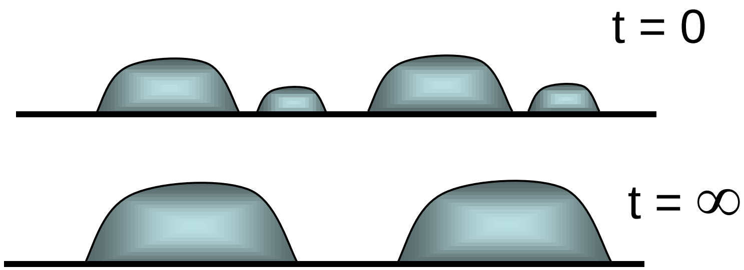
For curved surface of a solid, vapor pressure P_r, depends on r

- Flat surface: $r = \infty$, $P = P_o$

Specific volume (in cm^3/mol)

- Curved surface: $\ln\left(\frac{P_r}{P_o}\right) = \frac{2\gamma}{RT}\frac{\bar{V}_{in}}{r}$

→ Kelvin equation: $\frac{P_r}{P_o} = \exp\left(K\frac{\gamma}{r}\right)$ important for $r << 1000$ Å



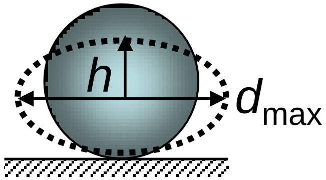
Applies to important surface problems
Melting point, nucleation and growth.
e.g., "ripening"

For a distribution of particles on the surface, small ones disappear, large ones grow

Thermodynamics of Surfaces

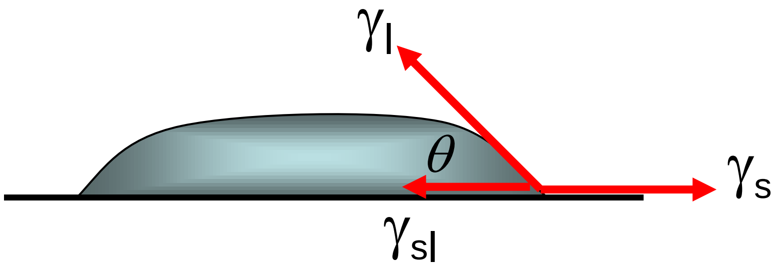
(d) Measurement of γ for liquid

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



"sessible drop"

(e) Contact angle



γ_l = surf. free energy of liq.
γ_{sl} = interface free energy
θ = contact angle

Recall: surface tension exerts force along surface at line of intersection.

At eqm. : $\gamma_l \cos\theta = \gamma_s - \gamma_{sl}$ (Young's Equation)

$\gamma_s > (\gamma_{sl} + \gamma_l)$ → complete wetting
$\gamma_{sl} > (\gamma_s + \gamma_l)$ → no wetting
$-1 < \dfrac{\gamma_s - \gamma_{sl}}{\gamma_l} < 1$ → wetting