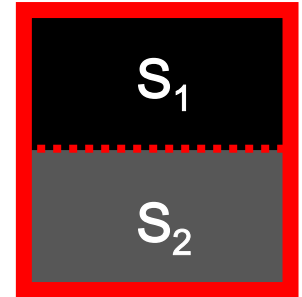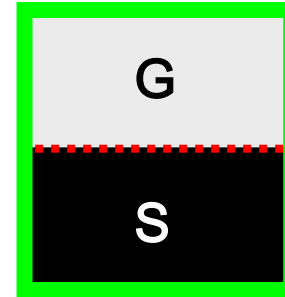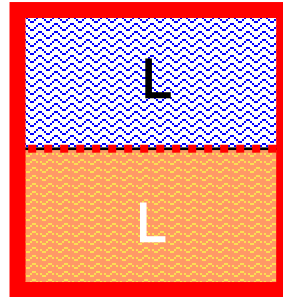Lecture: P1_Wk2_L2

Surface Energy and Adhesion

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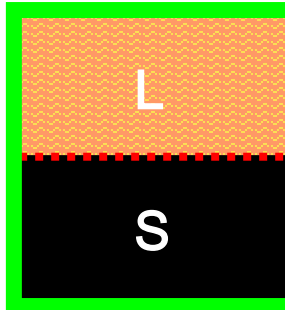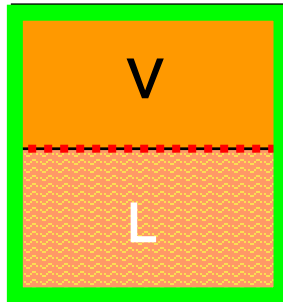2012

Surfaces and Interfaces

The boundary region between two adjacent phases

We call the boundary between (G/S), (V/L), and (L/S)
surfaces

We call the boundary between (S/S) and (L/L)
interfaces

L
L

G
S

S_1
S_2

V
L

L
S

L = Liquid
G = Gas
S = Solid
V = Vapor

The physical and chemical processes occurring at surfaces and interfaces depend on the strength and range of interaction between relevant atoms/molecules in the two phases. The processes are often dominated by defects.

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A Fundamental Quantity - (Excess) Surface Energy

Atoms (or *molecules*) at an interface are in a state of higher energy than those in the bulk due to the lack of nearest neighbor interactions.

~(few) a_o
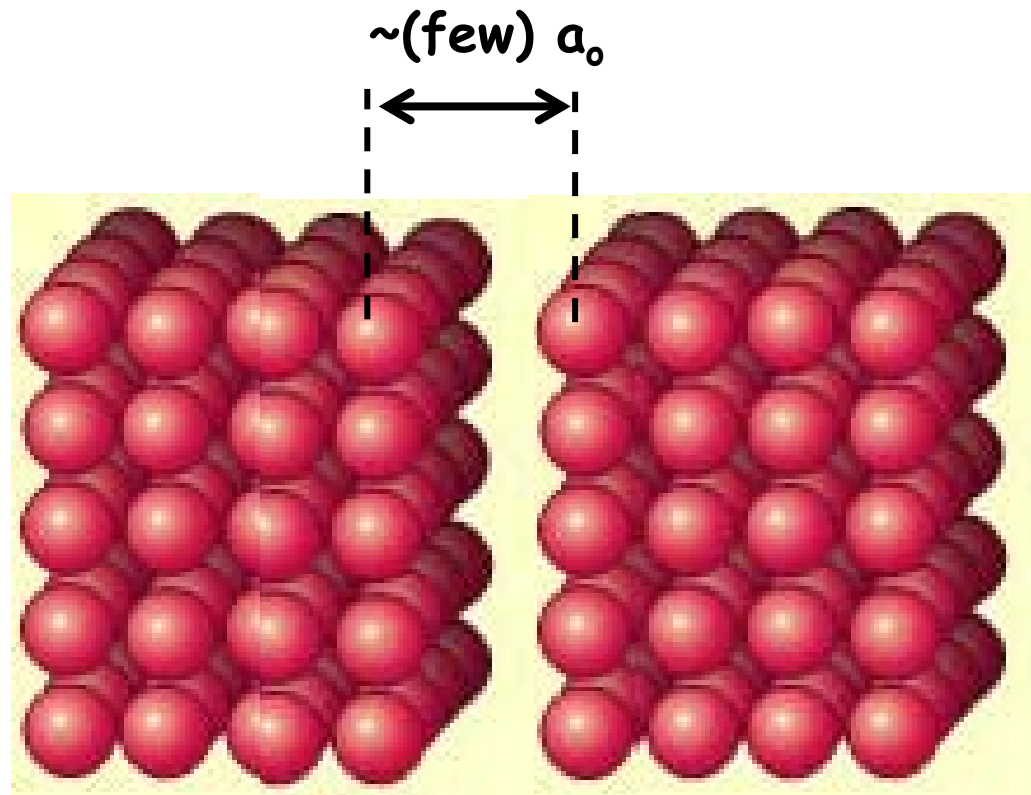
Atoms at surface tend to be under compression or tension

Surface Energy – Empirical Law (Thomas Young 1805)

The work (dW) to create a new surface of area dA is proportional to the number of atoms/molecules at the surface and must there fore be proportional to the surface area (dA):

$$dW \propto dA$$

$$dW = \gamma \cdot dA$$

γ is the proportionality constant defined as the specific <u>surface energy</u>. γ is a <u>scalar</u> quantity and has units of energy/unit area, (mJ/m^2).

γ acts as a restoring force to resist an increase in area. For liquids γ is numerically equal to the surface tension which is a <u>vector</u> and has units of force/unit length, mN/m.

Surface tension acts to decrease the surface energy of the system and leads to some well-known effects like liquid droplets forming spheres and meniscus formation in small capillaries.

Calculating Surface Energies

Create surface

Relax surface
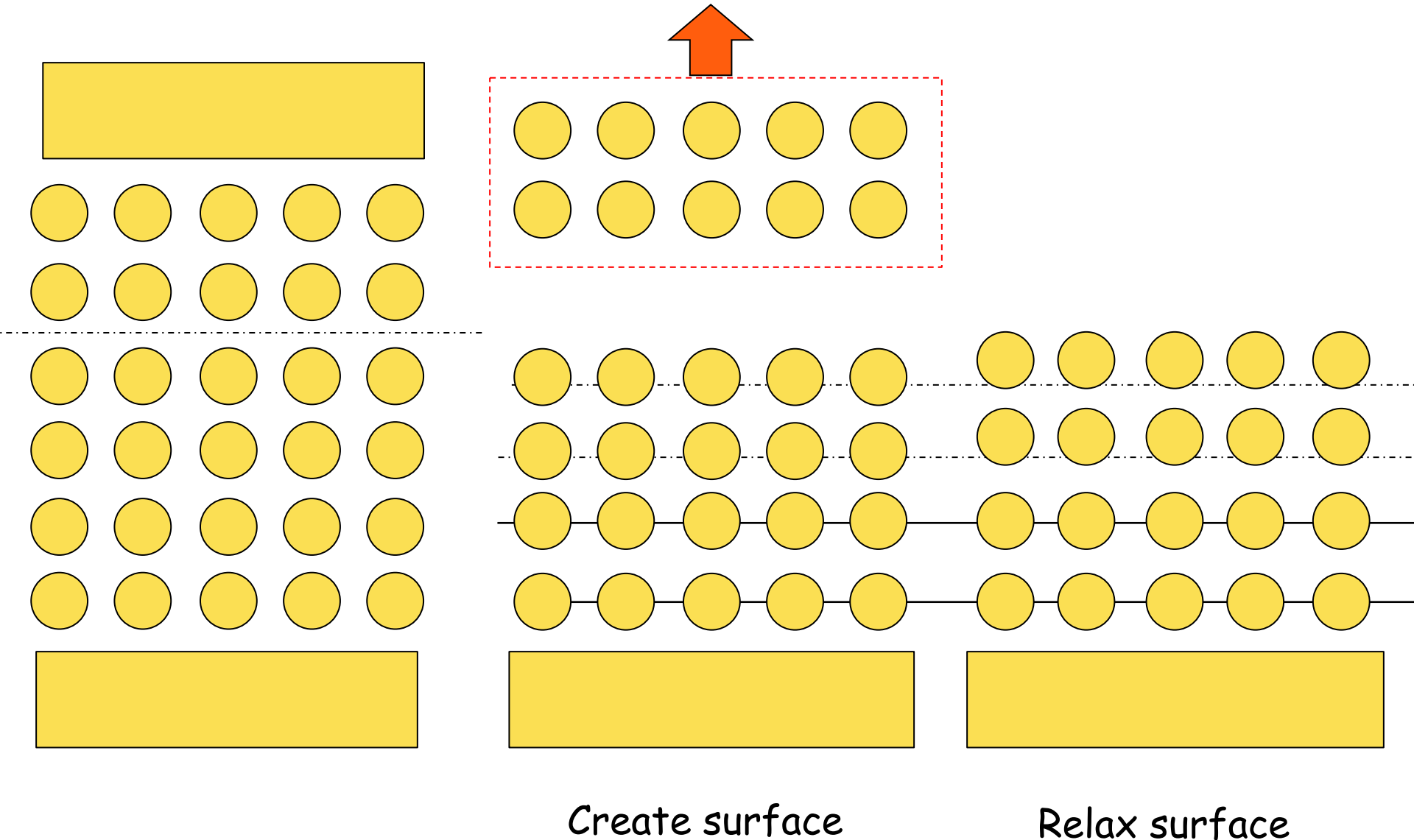
Measuring Surface Energies

(mostly indirect methods)

For low energy solids like polymers, use contact angle
 measurements – depends on surface roughness

Measure lattice spacing of atoms at surfaces (LEED, STM)

Measure work to cleave a crystal – inaccurate because of
mechanical deformations

Adsorption isotherms – how to measure exact amount
of material adsorbed – quartz microbalance, ellipsometry

Mechanical (bi-metallic cantilevers) deflection as
temperature is varied

high surface energy ↔ strong cohesion ↔ high melting temperatures

Solids	Surface energy (mJ/m^2)	Liquids	Surface energy (mJ/m^2)
mica (vacuum)	4500		
copper	1100		
gold	1000		
aluminum	840	mercury	487
glass	40-100		
nylon	46	water	73
polystyrene	41	benzene	29
acrylic	38	acetone	25
polyethylene	31	methanol	23
teflon	18	ethanol	22

Materials with high surface energies tend to rapidly adsorb contaminants. Exact values depend on surface oxides, adsorbates, surface roughness, surface treatment, etc….

Why do different materials stick to one another?

• **Mechanical adhesion** - adhesive material fills voids or pores and holds the surfaces together by mechanical interlocking.
✓ **Chemical adhesion** – formation of a chemical bond across an interface, involves molecules from each surface.
✓ **Dispersive adhesion** – molecules from each surface attract one another by van der Waals forces. In surface science, the term "adhesion" almost always refers to dispersive adhesion. (also known as physisorption)
• **Electrostatic adhesion** - exchange of electrons across an interface, producing an interfacial structure similar to a capacitor.
• **Diffusive adhesion** – polymer-like molecules entangle at an interface by diffusion. Requires molecules of both materials to be mobile and soluble in each other.
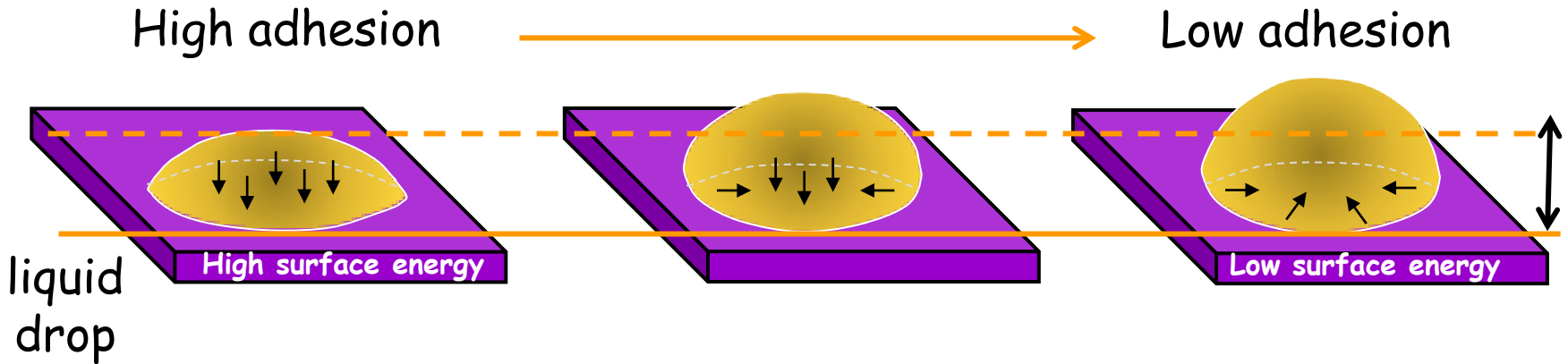
It follows that there may be many contributions to γ, and some contributions may be zero for certain systems.

$$\gamma = \gamma_{dispersion} + \gamma_{ion} + \gamma_{H\,Bonding} + ...$$

$$example: \quad \gamma_{water} = \gamma_{dispersion} + \gamma_{H\,Bonding}$$

$$= 22\,mJ/m^2 + 50.8\,mJ/m^2 = 72.8\,mJ/m^2$$

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Adhesion is determined by the molecular force of attraction between unlike materials

High adhesion → Low adhesion

High surface energy
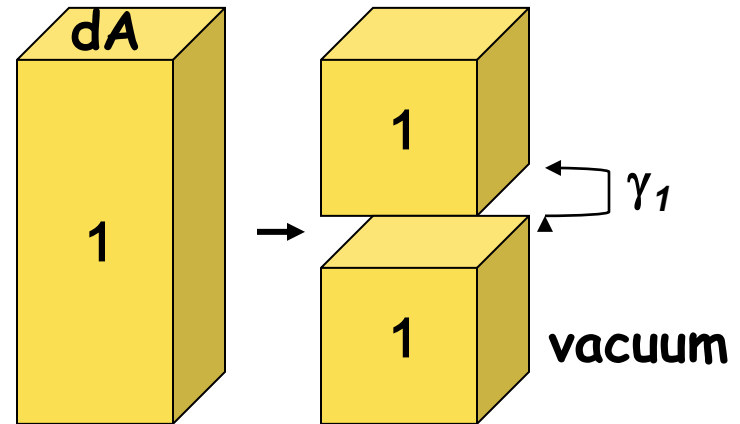
Low surface energy

liquid drop

The strength of attraction is determined by the surface energy of the material. The higher the surface energy, the greater the molecular attraction. The lower the surface energy, the weaker the attractive adhesive forces.

Work of Cohesion and Work of Adhesion

For a single solid (work of cohesion):

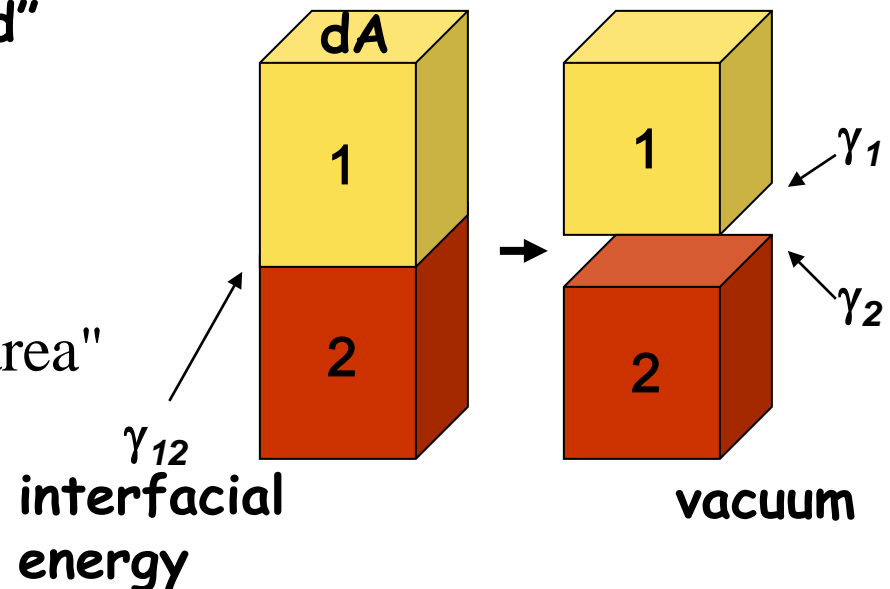$$dW_{11} = \gamma_1 \cdot 2\, dA = 2\gamma_1 dA$$

For two different solids (work of adhesion):
"surface 1 created, surface 2 created, interface between 1 and 2 destroyed"

$$dW_{12} = (+\gamma_1 - \gamma_2)dA$$

$$\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{12}$$

$$= \text{"work of adhesion per unit area"}$$

How to determine γ_{12}??

The Lifshitz theory provides a <u>rough</u> empirical rule for estimating interfacial surface energy γ_{12}

$$H_{Lifshitz} \propto \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right)$$

in vacuum (or air), $\varepsilon_3 = \varepsilon_o$

$$H_{Lifshitz} \propto \left(\frac{\varepsilon_1 - \varepsilon_o}{\varepsilon_1 + \varepsilon_o}\right)\left(\frac{\varepsilon_2 - \varepsilon_o}{\varepsilon_2 + \varepsilon_o}\right) = \frac{\left(\varepsilon_1 - \varepsilon_o\right)\left(\varepsilon_2 - \varepsilon_o\right)}{\varepsilon_1\varepsilon_2 + \varepsilon_o\varepsilon_2 + \varepsilon_o\varepsilon_1 + \varepsilon_o^2}$$

$$= \frac{\varepsilon_o^2\left(\dfrac{\varepsilon_1}{\varepsilon_o} - 1\right)\left(\dfrac{\varepsilon_2}{\varepsilon_o} - 1\right)}{\varepsilon_o^2\left(\dfrac{\varepsilon_1\varepsilon_2}{\varepsilon_o^2} + \dfrac{\varepsilon_2}{\varepsilon_o} + \dfrac{\varepsilon_1}{\varepsilon_o} + 1\right)} = \frac{\left(\kappa_1 - 1\right)\left(\kappa_2 - 1\right)}{\kappa_1\kappa_2 + \kappa_1 + \kappa_2 + 1}$$

when both materials are the same, then material 1 = material 2, and

$$\gamma_{11} \equiv 2\gamma_1 \propto H_{11} \propto \frac{\left(\kappa_1 - 1\right)^2}{2\kappa_1 + \kappa_1^2 + 1}$$

$$\gamma_{22} \equiv 2\gamma_2 \propto H_{22} \propto \frac{\left(\kappa_2 - 1\right)^2}{2\kappa_2 + \kappa_2^2 + 1}$$

$$\left. \rule{0pt}{4em} \right\} \quad \textbf{see P1\_Wk2\_L3, slide 8}$$

$$\therefore \quad \gamma_{12} \propto \frac{\left(\kappa_1 - 1\right)\left(\kappa_2 - 1\right)}{\kappa_1\kappa_2 + \kappa_1 + \kappa_2 + 1} \approx \frac{\sqrt{\gamma_{11}} \cdot \sqrt{\gamma_{22}} \cdot \sqrt{2\kappa_1 + \kappa_1^2 + 1} \cdot \sqrt{2\kappa_2 + \kappa_2^2 + 1}}{\kappa_1\kappa_2 + \kappa_1 + \kappa_2 + 1}$$

$$\simeq \left(\sqrt{\gamma_{11}} \cdot \sqrt{\gamma_{22}}\right)\left[\frac{\sqrt{2\kappa_1 + \kappa_1^2 + 1} \cdot \sqrt{2\kappa_2 + \kappa_2^2 + 1}}{\kappa_1\kappa_2 + \kappa_1 + \kappa_2 + 1}\right] = \left[\Gamma\right]\sqrt{\gamma_{11}} \cdot \sqrt{\gamma_{22}} = \left[\Gamma\right]\sqrt{2\gamma_1 \cdot 2\gamma_2} \simeq 2\sqrt{\gamma_1 \cdot \gamma_2}$$

The **term in square brackets** [Γ] is strictly equal to 1 when $\kappa_1 = \kappa_2$, so the scaling law for estimating γ_{12} works best when the dielectric constants are approximately equal.

The interfacial physics/chemistry at a S/S interface is probed every time
an AFM tip makes contact with a substrate