


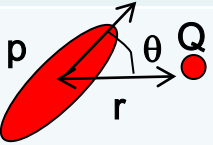
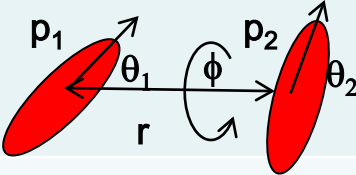
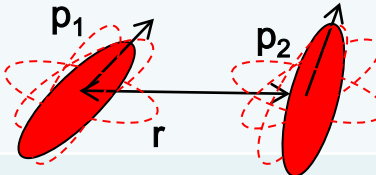
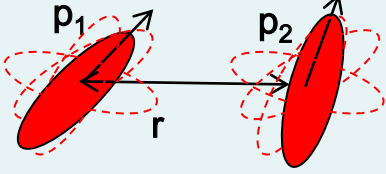
Lecture 7

Interaction forces III -

Tip-sample interaction forces

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Summary of last lecture

	Type of interaction	
	Ion-ion electrostatic	$U(r) = \frac{Q_1 Q_2}{4\pi\epsilon\epsilon_0 r}$
	Dipole-charge electrostatic	$U(r) = -\frac{Qp\cos(\theta)}{4\pi\epsilon\epsilon_0 r^2}$
	Dipole-dipole electrostatic	$U(r) = -\frac{p_1 p_2 [2\cos(\theta_1)\cos(\theta_2) - \sin(\theta_1)\sin(\theta_2)\cos(\phi)]}{4\pi\epsilon\epsilon_0 r^3}$
	Angle-averaged electrostatic (Keesom force)	$U_{Keesom}(r) = -\frac{p_1^2 p_2^2}{3(4\pi\epsilon\epsilon_0)^2 k_B T} \frac{1}{r^6}$
	Angle-averaged induced polarization force (Debye force)	$U_{Debye}(r) = -\frac{p_1^2 \alpha_{02} + p_2^2 \alpha_{01}}{(4\pi\epsilon_0 \epsilon)^2} \frac{1}{r^6}$
	Dispersion forces act between any two molecules or atoms (London force)	

$$U_{London}(r) = -\frac{3}{2} \frac{\alpha_{01}\alpha_{02}}{(4\pi\epsilon_0 \epsilon)^2} \frac{(I_1)(I_2)}{I_1 + I_2} \frac{1}{r^6}$$

Adapted from J. Israelachvili, "Intermolecular and surface forces".

From interatomic to tip-sample interactions-simple theory

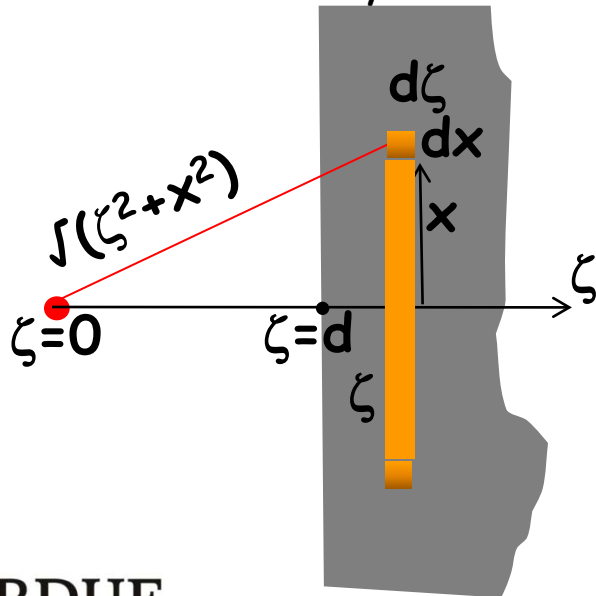
First consider the net interaction between an isolated atom/molecule and a flat surface.

Relevant separation distance will now be called "d".

Assume that the pair potential between the atom/molecule and an atom on the surface is given by $U(r) = -C/r^n$.

Assume additivity, that is the net interaction force will be the sum of its interactions with all molecules in the body - are surfaces atoms different than bulk atoms?

No. of atoms/molecules in the infinitesimal ring is $\rho dV = \rho(2\pi x dx d\zeta)$ where ρ is the number density of molecules/atoms in the surface.



$$U(d) = -2\pi C\rho \int_{\zeta=d}^{\zeta=\infty} d\zeta \left(\int_{x=0}^{x=\infty} \frac{dx}{\left(\sqrt{\zeta^2 + x^2}\right)^n} \right)$$

$$= \frac{-2\pi C\rho}{(n-2)(n-3)d^{n-3}}, \quad \text{for } n > 3$$

$$U_{vdW} = \frac{-\pi C\rho}{6d^3}, \quad \text{for } n = 6$$

Number Densities of the Elements

TABLE 4 Density and Atomic Concentration of the Elements

The data are given at atmospheric pressure and room temperature, or at the stated temperature in deg. K. (Crystal modifications as for Table 3.)

Density is in g cm^{-3} (1000 kg m^{-3})
 Concentration in 10^{23} cm^{-3} (10^{26} m^{-3})
 Nearest-neighbor distance, in \AA (10^{-10} m)

H α 0.089																	He α 0.205 (4.7°K)
Li α 0.543 4.700 3.022	Be 1.82 12.1 2.22											B 2.37 13.0	C 3.516 17.6 1.54	N α 1.02	O 1.44	F 1.71	Ne α 1.51 4.26 2.16
Na α 1.012 2.652 3.659	Mg 1.74 4.30 2.35											Al 2.70 5.32 2.85	Si 2.33 5.00 2.35	P 1.82	S 2.07	Cl α 3.02 2.02	Ar α 1.77 2.66 4.76
K α 0.860 1.482 4.525	Ca 1.53 2.30 3.96	Sc 2.99 6.27 3.26	Ti 4.51 5.65 2.89	V 5.99 7.22 2.62	Cr 7.19 8.33 2.50	Mn 7.47 8.18 2.24	Fe 7.80 8.50 2.48	Co 8.9 9.97 2.90	Ni 8.91 9.14 2.49	Cu 8.93 8.45 3.64	Zn 7.13 6.55 2.66	Ga 5.90 5.10 2.44	Ge 5.32 4.42 2.45	As 5.77 4.65 3.16	Se 4.81 3.67 2.32	Br β 4.05 2.95	Kr α 3.09 2.37 4.00
Rb α 1.628 1.148 4.037	Sr 2.58 1.76 4.30	Y 4.49 3.02 3.85	Zr 6.51 4.29 3.17	Nb 8.58 5.56 2.86	Mo 10.22 6.42 2.72	Tc 11.50 7.04 2.71	Ru 12.36 7.35 2.85	Rh 12.47 7.25 2.89	Pd 12.02 6.80 2.75	Ag 10.50 6.65 2.88	Cd 8.65 4.64 2.98	In 7.29 2.02 2.25	Sn 5.76 2.01 2.31	Sb 6.09 3.31 2.91	Te 6.25 2.94 2.85	I 4.93 2.38 3.54	Xe α 3.78 2.64 4.34
Cs α 1.907 0.905 3.235	Ba 3.89 1.80 4.35	La 6.17 2.70 3.73	Hf 13.30 4.62 3.13	Ta 16.66 5.55 2.86	W 19.35 6.30 2.74	Re 21.02 6.90 2.74	Os 22.85 7.34 2.68	Ir 22.85 7.05 2.71	Pt 21.47 6.62 2.77	Au 19.28 6.90 2.88	Hg α 14.26 4.26 3.01	Tl 11.07 3.50 3.46	Pb 11.34 3.30 2.50	Bi 9.80 2.82 2.10	Po 9.31 2.67	At —	Rn —
Fr —	Ra —	Ac 10.07 2.66 3.76	Ce 6.77 2.91 3.65	Pr 6.76 2.92 3.63	Nd 7.00 2.93 3.64	Pm —	Sm 7.54 2.02 2.59	Eu 5.25 2.04 2.96	Gd 7.89 3.02 3.55	Tb 8.27 3.22 3.52	Dy 8.53 3.17 3.51	Ho 8.80 3.22 3.49	Er 9.04 3.36 3.47	Tm 9.22 3.32 2.54	Yb 9.22 3.02 2.86	Lu 9.04 3.39 2.43	
Th 11.72 3.04 3.60	Pa 15.37 4.00 3.21	U 19.05 4.80 2.75	Np 20.45 5.20 2.62	Pu 19.80 4.26 3.1	Am 11.07 2.96	Cm —	Bk —	Cf —	Es —	Fm —	Md —	No —	Lr —				

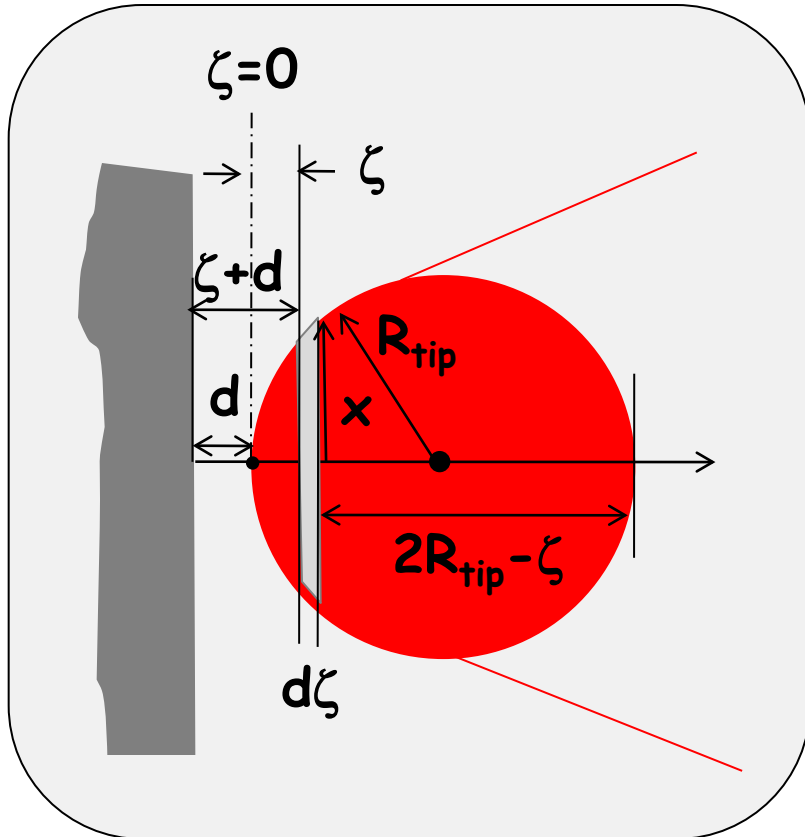
Introduction to Solid State Physics, 5th Ed. C. Kittel, pg. 32

From interatomic to tip-sample interactions-simple theory

Next integrate atom-plane interaction over the volume of all atoms in the AFM tip. Number of atoms/molecules contained within the slice shown below is

$$\pi x^2 d\zeta = \rho \pi [R^2 - (R - \zeta)^2] d\zeta = \rho \pi (2R_{\text{tip}} - \zeta) \zeta d\zeta.$$

Since all these are at the same equal distance $d + \zeta$ from the plane, the net interaction energy can be derived by using the result on the previous slide.



$$U(d) = \frac{-2\pi^2 C \rho^2}{(n-2)(n-3)} \int_{\zeta=0}^{\zeta=2R_{\text{tip}}} \frac{(2R_{\text{tip}} - \zeta) \zeta d\zeta}{(d + \zeta)^{n-3}}$$

If $d \ll R_{\text{tip}}$,

$$U(d) \sim \frac{-2\pi^2 C \rho^2}{(n-2)(n-3)} \int_{\zeta=0}^{\zeta=\infty} \frac{R_{\text{tip}} \zeta d\zeta}{(d + \zeta)^{n-3}}$$

$$= -\frac{4\pi^2 C \rho^2 R_{\text{tip}}}{(n-2)(n-3)(n-4)(n-5) d^{n-5}}$$

For $d \ll R_{\text{tip}}$, $n = 6$

$$U_{\text{vdW}}(d) \sim -\frac{\pi^2 C \rho^2 R_{\text{tip}}}{6d} = -\frac{H R_{\text{tip}}}{6d}$$

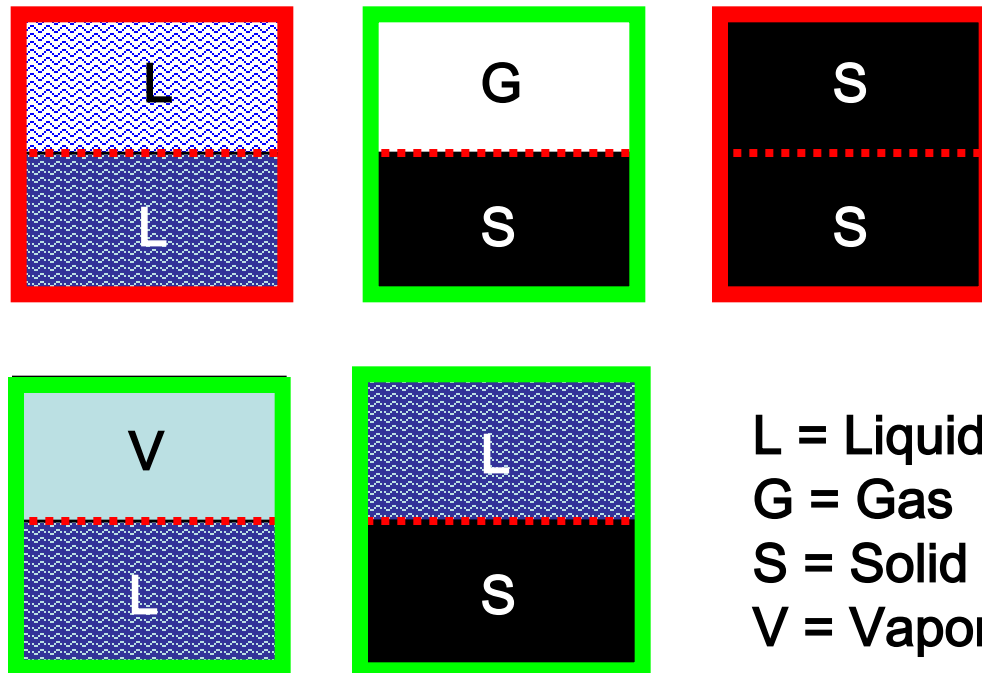
H : Hamaker's constant (also A or A_H)

From interatomic to tip-sample interactions-some caveats

- If tip and sample are made of different materials replace ρ^2 by $\rho_1\rho_2$ etc.
- Tip is assumed to be homogeneous sample also! Both made of "simple" atoms/molecules
- Assumes atom-atom interactions are independent of presence of other surrounding atoms
- Perfectly smooth interacting surfaces
- Tip-surface interactions obey very different power laws compared to atom-atom laws

Measuring Macroscopic Surface Forces

An **interface** is the boundary region between two adjacent bulk phases



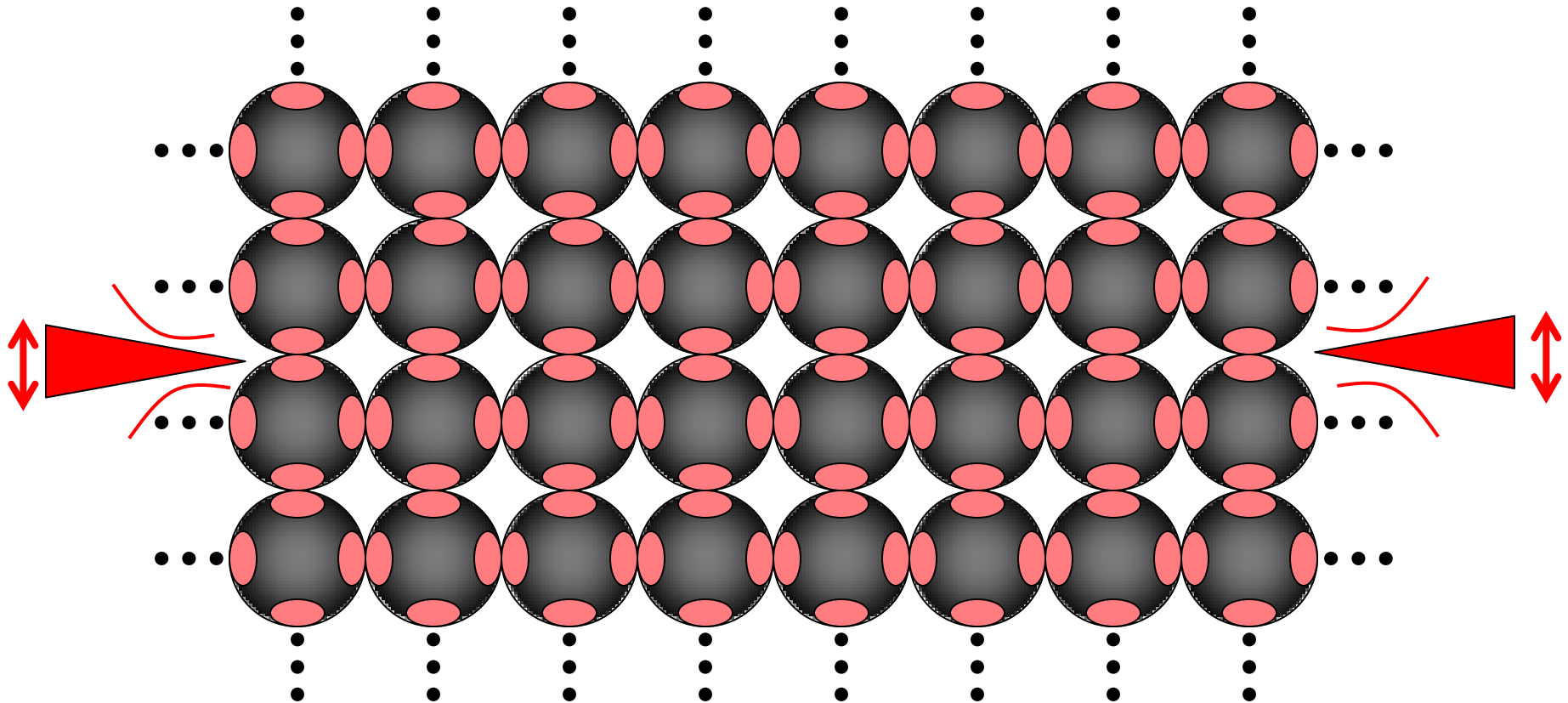
We call (S/G), (S/L), and (L/V) **surfaces**

We call (S/S) and (L/L) **interfaces**

Surface Energetics

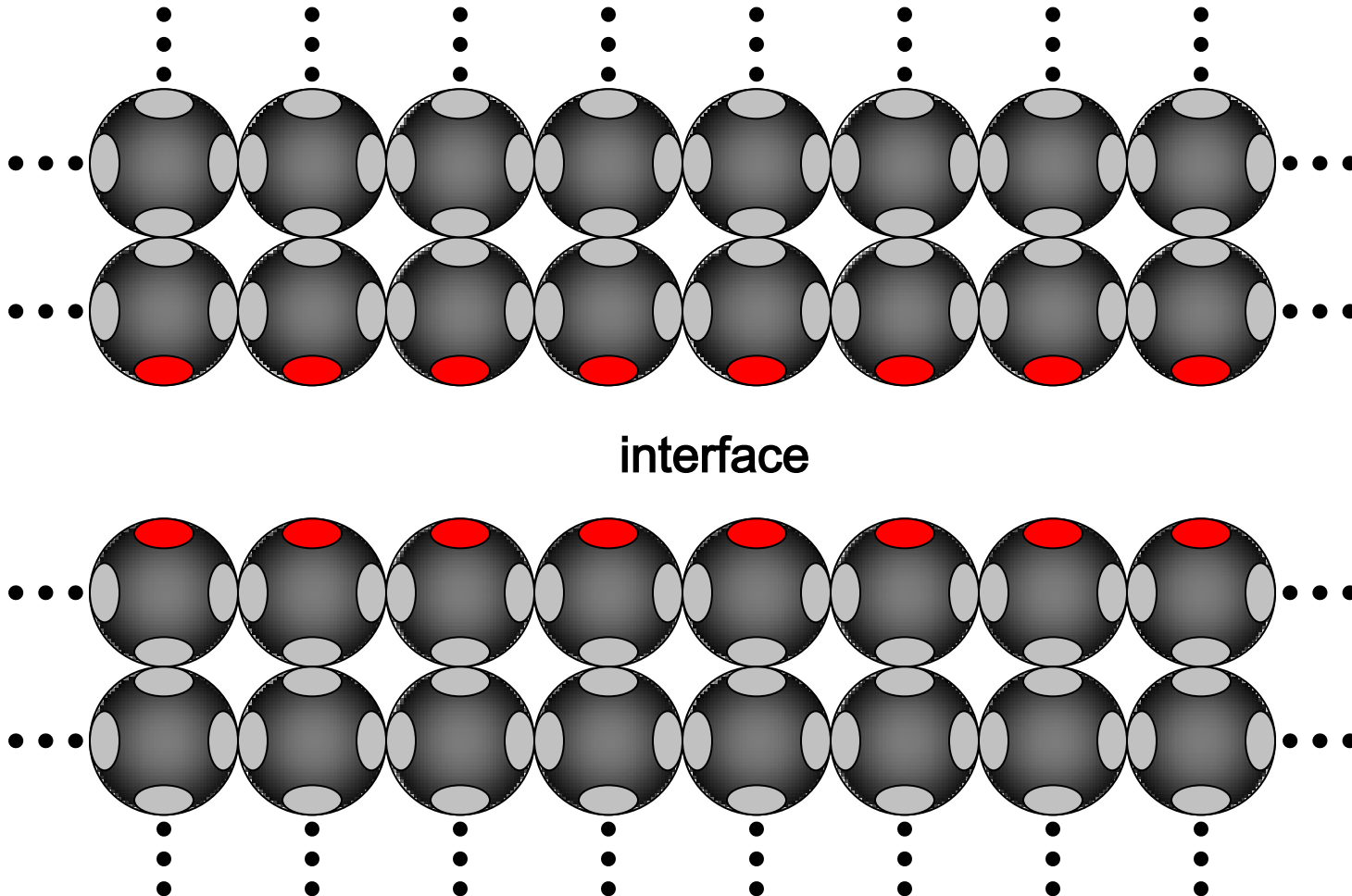
Atoms (or molecules) in the bulk of a material have a low relative energy due to nearest neighbor interactions (e.g. bonding).

Performing work on the system to create an interface can disrupt this situation...



(Excess) Surface Free Energy

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



Surface Energy

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

$$dW = \gamma \cdot dA$$

γ is the proportionality constant defined as the specific surface free energy. It is a scalar quantity and has units of energy/unit area, mJ/m^2 .

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

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

high surface energy ↔ strong cohesion ↔ high melting temperatures

Material	Surface energy (mJ/m ²)
mica	4500
gold	1000
mercury	487
water	73
benzene	29
methanol	23

Values depend on

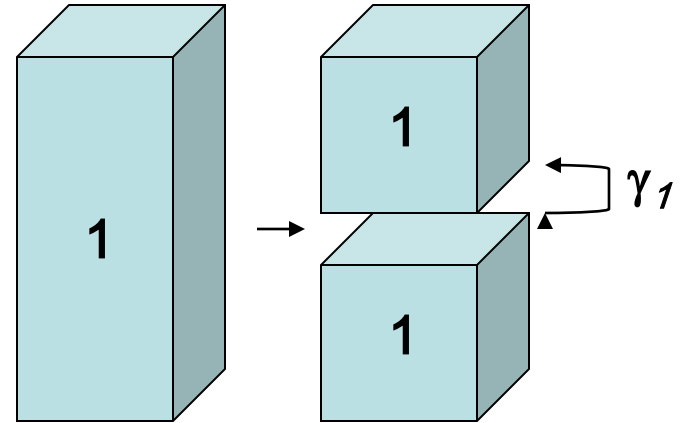
- oxide contamination
- adsorbed contaminants
- surface roughness
- etc....

**Materials with high surface energies
tend to rapidly adsorb contaminants**

Work of Cohesion and Adhesion

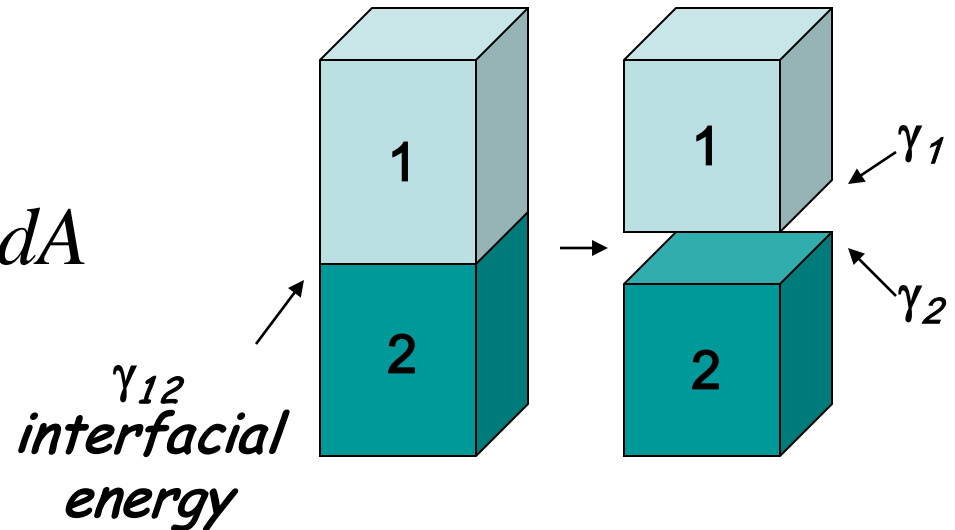
For a single solid (work of cohesion):

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



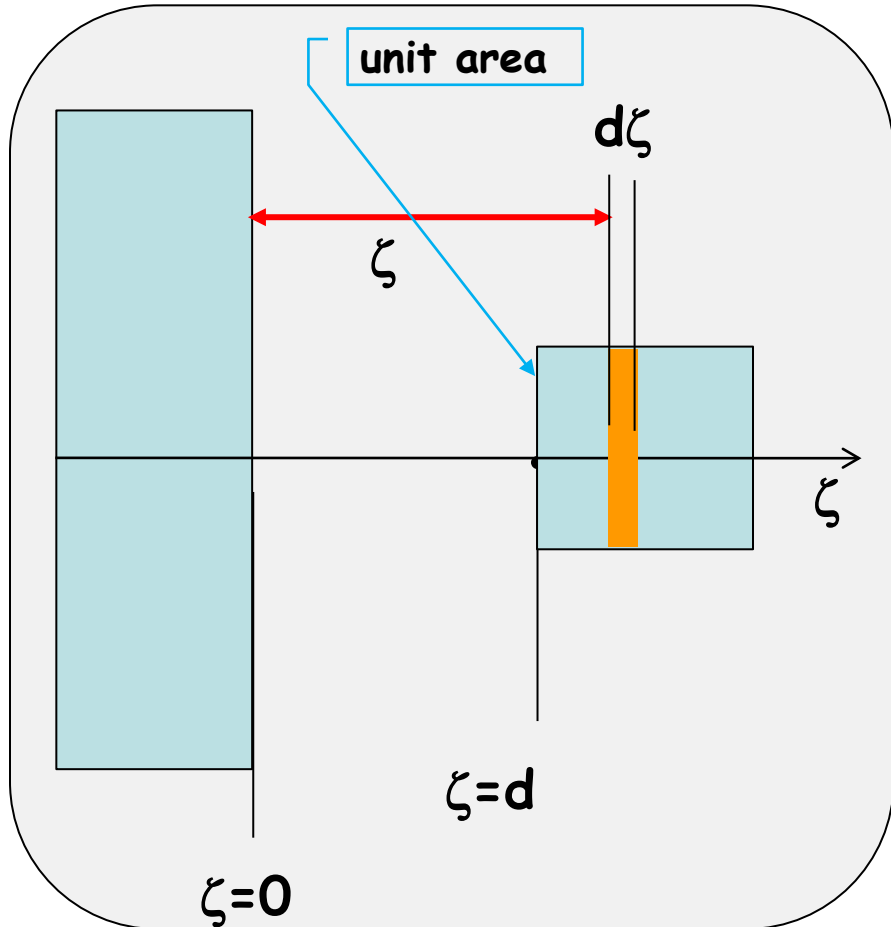
For two different solids
(work of adhesion):

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



Surface-surface interactions

Following the steps in previous slides it is possible calculate the interaction energy of two planar surfaces a distance of 'd' apart, specifically $\rho dV = \rho dA d\zeta$ for the unit area of one surface ($dA=1$) interacting with an infinite area of the other.



$$U(d) = \frac{-2\pi C\rho^2}{(n-2)(n-3)} \int_{\zeta=d}^{\zeta=\infty} \frac{d\zeta}{(\zeta)^{n-3}}$$

$$= -\frac{2\pi C\rho^2}{(n-2)(n-3)(n-4)} \frac{1}{d^{n-4}}$$

For $n=6$

$$U(d) = U(d)_{\text{plane-plane}}$$

$$= -\frac{\pi C\rho^2}{12d^2} \text{ (per unit area)}$$

$A_H = \text{Hamaker constant} \equiv \pi^2 C\rho^2$

$$U(d)_{\text{plane-plane}} = -\frac{A_H}{12\pi} \frac{1}{d^2} \text{ per unit area}$$

Typical Values for Hamaker Constant

Typically, for solids interacting across a vacuum,
 $C \approx 10^{-77} \text{ Jm}^6$ and $\rho \approx 3 \times 10^{28} \text{ m}^{-3}$

$$A_H \approx \pi^2 \cdot 10^{-77} \text{ J m}^6 \cdot \left(3 \times 10^{28} \text{ m}^{-3}\right)^2 \\ \simeq 10^{-19} \text{ J}$$

Typically, most solids have

$$A_H \simeq (0.4 - 4.0) \times 10^{-19} \text{ J}$$

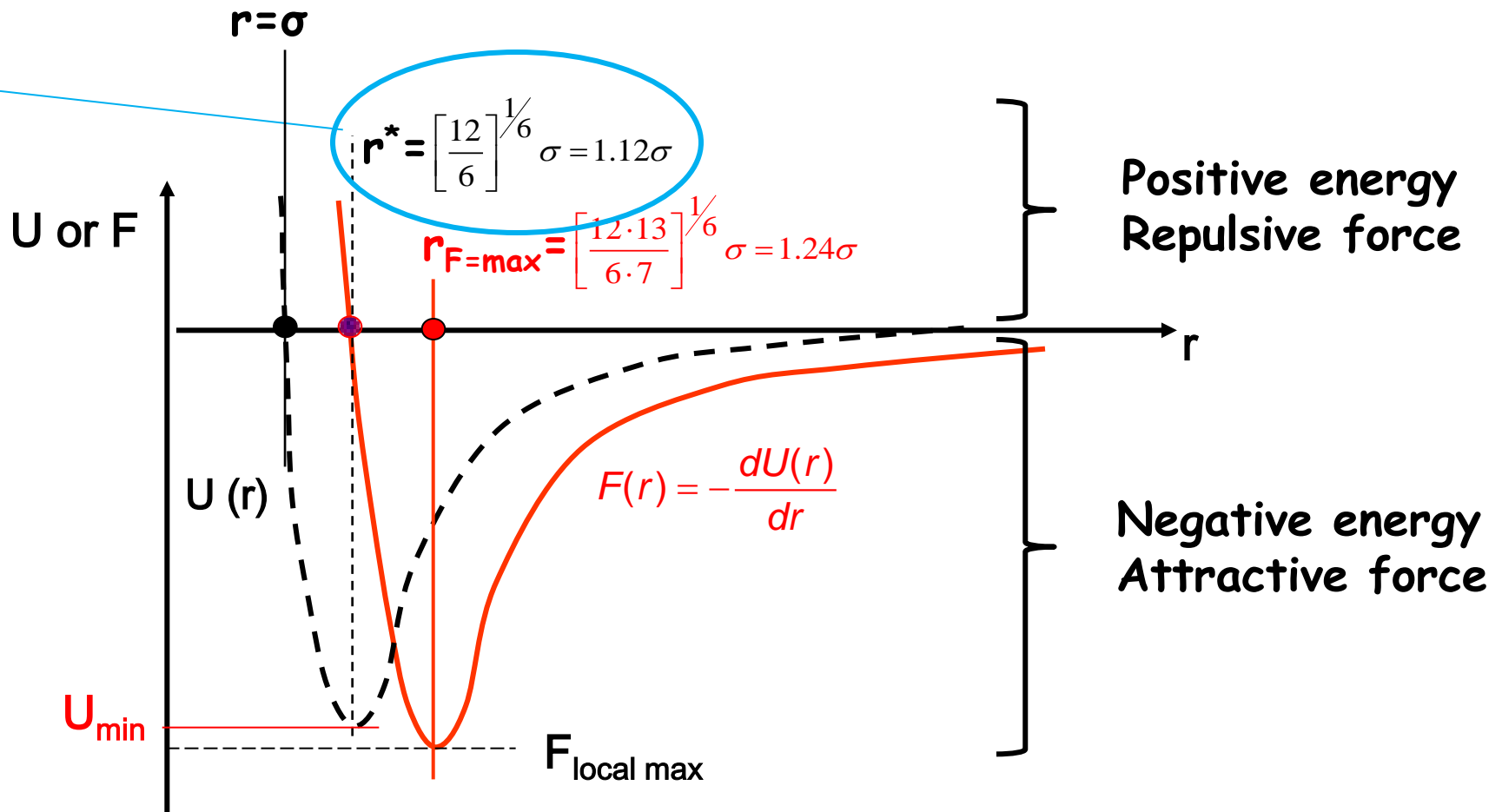
See Butt, Cappella, Kappl, Surf. Sci. Reps., **59**, 50 (2005) for more complete list

Implications

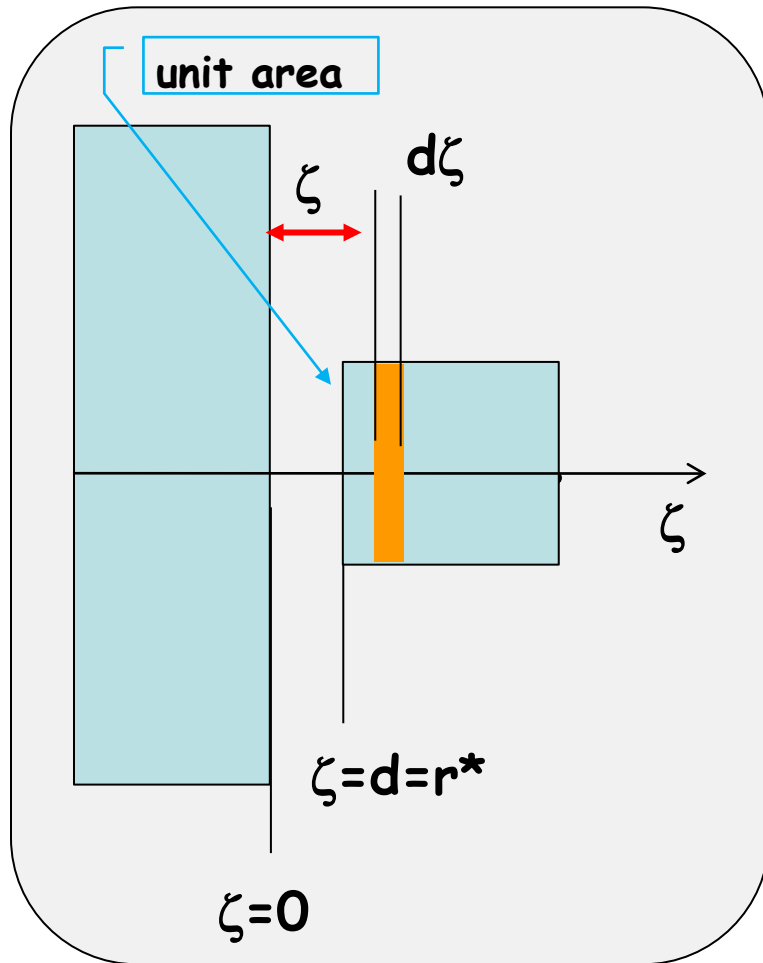
$$U(r) = 4U_0 * \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

atom-atom
interaction

Equilibrium
separation



Estimating the interfacial energy



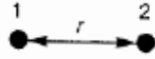

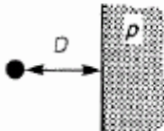

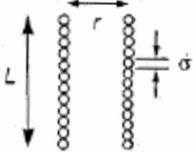
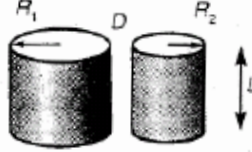

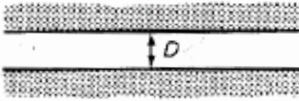
When $d \approx r^*$, then per unit area, we should have:

$$\begin{aligned} U_{vdW}(d = r^*) &= \frac{A_H}{12\pi(r^*)^2} \\ &= dW_{11} = 2\gamma_1 \end{aligned}$$

$$\gamma_1 = \frac{A_H}{24\pi(r^*)^2}$$

This approach neglects the atomicity of both surfaces. Require an "effective" r^* .

In general, vdW interactions between macroscopic objects depends on geometry

<p>Two atoms</p>  <p>$w = -C/r^6$</p>	<p>Two spheres</p>  <p>$W = \frac{-A}{6D} \frac{R_1 R_2}{(R_1 + R_2)}$</p>
<p>Atom-surface</p>  <p>$w = -\pi C \rho / 6D^3$</p>	<p>Sphere-surface</p>  <p>$W = -AR/6D$</p>
<p>Two parallel chain molecules</p>  <p>$W = -3\pi CL/8\sigma^2 r^3$</p>	<p>Two cylinders</p>  <p>$W = \frac{AL}{12\sqrt{2} D^{3/2}} \left(\frac{R_1 R_2}{R_1 + R_2} \right)^{1/2}$</p>
<p>Two crossed cylinders</p>  <p>$W = -A\sqrt{R_1 R_2}/6D$</p>	<p>Two surfaces</p>  <p>$W = -A/12\pi D^2$ per unit area</p>

The Derjaguin approximation

Plane-plane interaction energies are fundamental quantities and it is important to correlate tip-sample force to known values of surface interaction energies. For a sphere-plane interaction we saw that

$$U(d) = -\frac{4\pi^2 C \rho^2 R_{tip}}{(n-2)(n-3)(n-4)(n-5)} \frac{1}{d^{n-5}}$$
$$F(d) = -\frac{dU}{d(d)} = -\frac{4\pi^2 C \rho^2 R_{tip}}{(n-2)(n-3)(n-4)} \frac{1}{d^{n-4}}$$

Comparing with previous slides we find that

$$F(d)_{sphere-plane} = 2\pi R_{tip} U(d)_{plane-plane}$$

It can be shown that for two interacting sphere of different radii

$$F(d)_{sphere-sphere} = 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) U(d)_{plane-plane}$$

Implications of Derjaguin's approximation

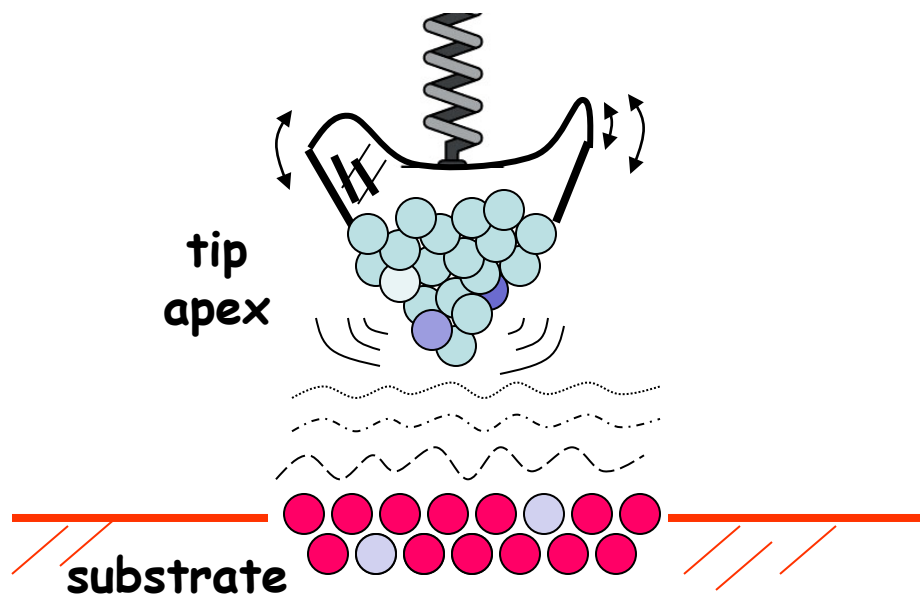
- We showed this when $U(r)=-C/r^n$ - however it is valid for any force law - attractive or repulsive or oscillatory - for two rigid spheres.
- As mentioned before, if two spheres are in contact (assuming no contamination), then $d=r^*$.
- The value of $U(d=r^*)_{\text{plane-plane}}$ is basically dW_{11} the conventional surface energy per unit area to create a solid surface. Thus:

$$F_{\text{adhesion}} \equiv F_{\text{sphere-sphere}}(d = r^*) = 2\pi \underbrace{U_{\text{plane-plane}}(d = r^*)}_{dW_{11}} \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right)^{-1}$$

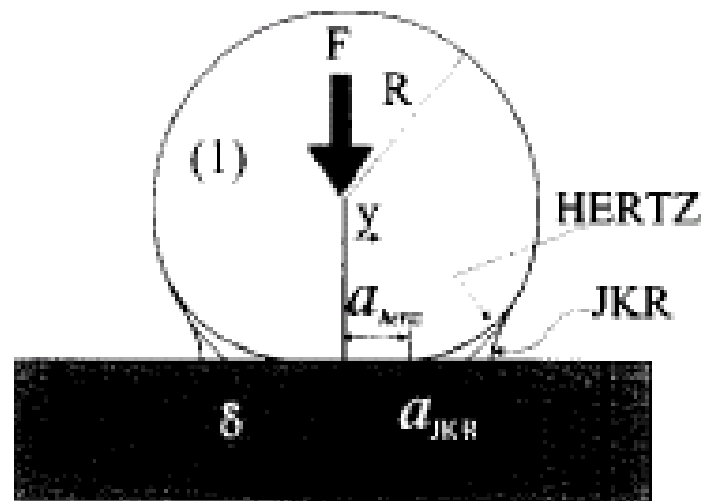
- This approximation is useful because it converts measured F_{adhesion} in AFM experiments to surface energy dW_{11}

How to Model the Repulsive Interaction at Contact?

Atom-Atom?



Sphere-Plane?



Source: Capella & Dietler

Maybe if the contact area involves tens or hundreds of atoms the description of net repulsive force is best captured by continuum elasticity models