

Lecture: P1_Wk2_L1

Inter-Molecular Forces between a tip and a substrate

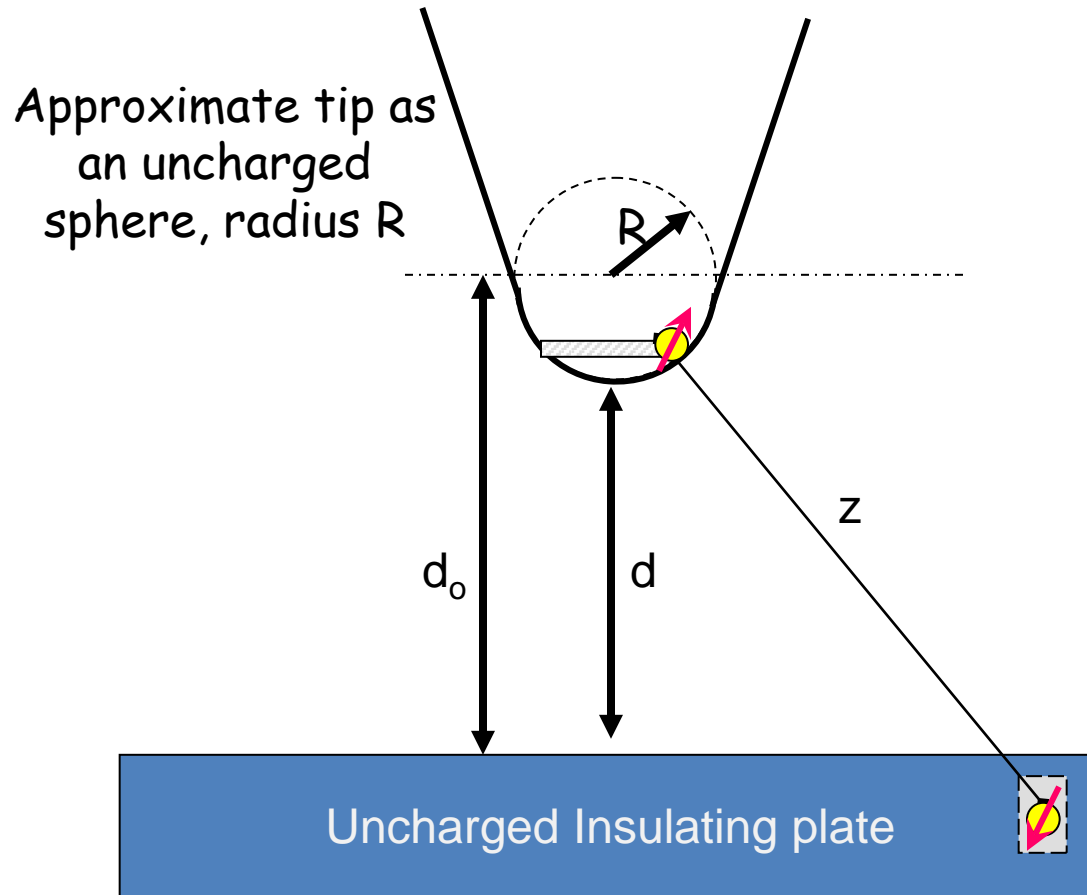
Ron Reifenberger

Birck Nanotechnology Center

Purdue University

2012

The Problem



What we know

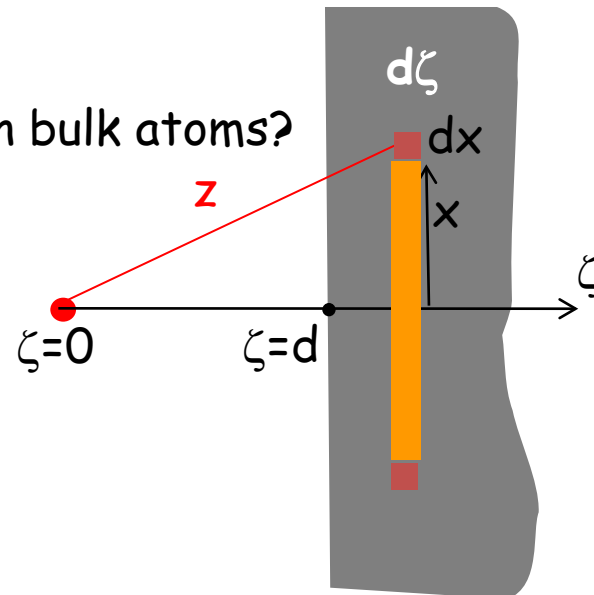
The van der Waals force is the sum of three different components of the electrostatic interaction between molecules: orientation, induction, and dispersion. Each electrostatic interaction produces a potential energy that varies as $1/z^6$, where z is the separation

- **Orientation or Keesom Force** is the angle-averaged dipole-dipole interaction between two polar molecules.
- **Debye Force** is the angle averaged dipole-induced dipole interaction between a polar and non-polar molecule
- **The London or Dispersion force** acts between all molecules with non-zero polarizability

$$\begin{aligned}U_{vdW}(z) &= U_{Keesom}(z) + U_{Debye}(z) + U_{London}(z) \\&= -\frac{2}{3} \frac{1}{k_B T} \frac{p_1^2 p_2^2}{(4\pi\kappa\epsilon_0)^2} \frac{1}{z^6} - \frac{p_1^2 \alpha_{o,2} + p_2^2 \alpha_{o,1}}{(4\pi\kappa\epsilon_0)^2} \frac{1}{z^6} - \frac{3}{2} \frac{\alpha_{o,1} \alpha_{o,2}}{(4\pi\kappa\epsilon_0)^2} \left(\frac{I_1 I_2}{I_1 + I_2} \right) \frac{1}{z^6} \\&= -\frac{C_{Keesom}}{z^6} - \frac{C_{Debye}}{z^6} - \frac{C_{London}}{z^6} \\&= -\frac{C_{vdW}}{z^6}\end{aligned}$$

One molecule interacting with a flat plane

- First consider the net interaction between an isolated atom (or molecule) and a flat material.
- Relevant separation distance will now be called "d".
- Assume that the pair potential between the isolated atom/molecule and an atom in the material is given by $U(z) = -C_{vdW}/z^6$.
- Assume additivity, that is the net interaction force will be the sum of only pair-wise molecular interactions. This means that N-body "intermediate intermolecular" interactions are ignored.
- Are surface atoms chemically different than bulk atoms?

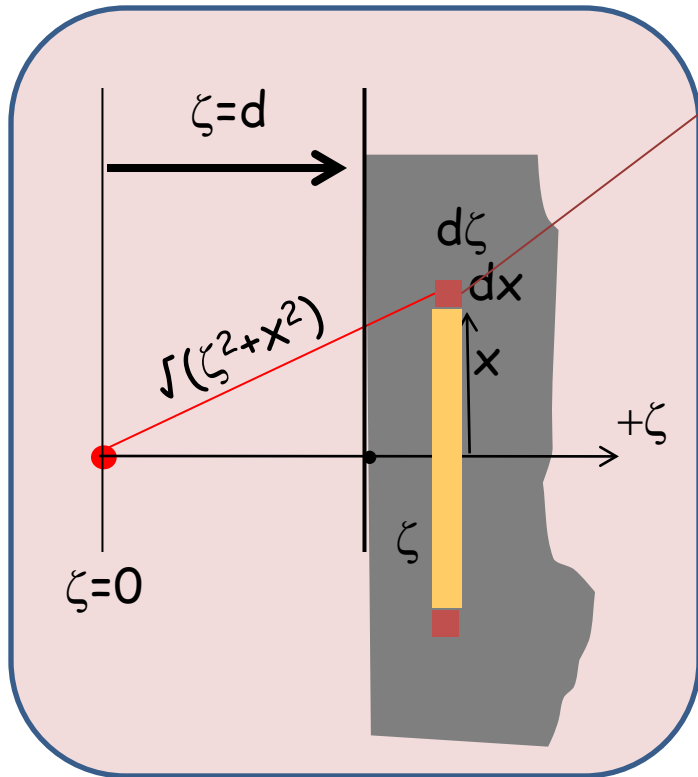


Working out the math

ρ_1 = number density of atoms/molecules in an infinitesimal ring of the material
 = $(N_{\text{Avagadro}}/m_{\text{atom or molecule}}) \times \rho_{\text{mass density}}$

ring volume is $dV = (2\pi x \, dx \, d\zeta)$

N = No. atoms/molecules in ring = $\rho_1 dV$



$$dU_{\text{ring}} = -N \frac{C_{\text{vdW}}}{(\sqrt{\zeta^2 + x^2})^6} = -\frac{2\pi\rho_1 C_{\text{vdW}} x \, dx \, d\zeta}{(\zeta^2 + x^2)^3}$$

$$U_{\text{vdW}}(d) = -2\pi\rho_1 C_{\text{vdW}} \int_{\zeta=d}^{\zeta=\infty} d\zeta \left(\int_{x=0}^{x=\infty} \frac{x \, dx}{(\zeta^2 + x^2)^3} \right)$$

$$= -2\pi\rho_1 C_{\text{vdW}} \int_{\zeta=d}^{\zeta=\infty} \left(\frac{1}{4} \cdot \frac{1}{\zeta^4} \right) d\zeta = -\frac{2\pi\rho_1 C_{\text{vdW}}}{4} \left(-\frac{1}{3\zeta^3} \right) \Big|_{\zeta=d}^{\zeta=\infty}$$

$$= -\frac{2\pi\rho_1 C_{\text{vdW}}}{4} \left(\frac{1}{3} \right) \frac{1}{d^3}$$

$$U_{\text{vdW}}(d) = \frac{-\pi\rho_1 C_{\text{vdW}}}{6d^3}$$

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.)

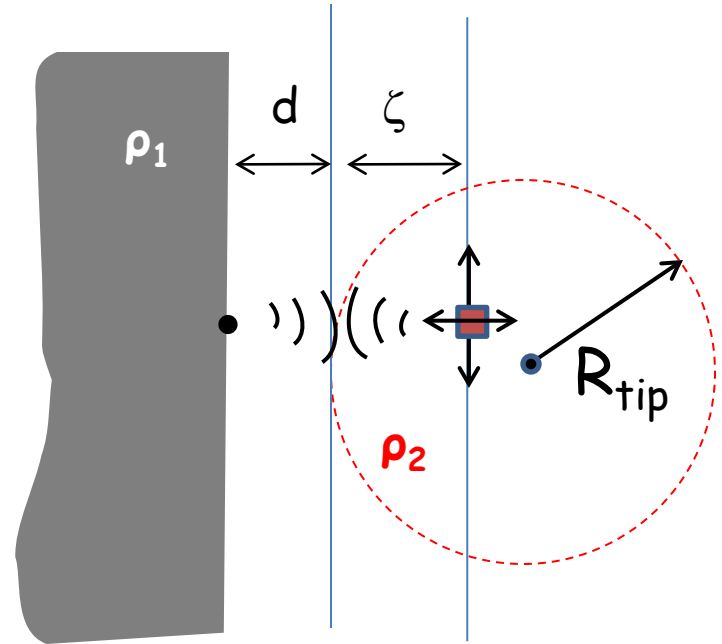
														H ^{4K}															He ^{2K}
														0.088															0.205 (at 37 atm)
Li ^{78K}		Be												B	C	N ^{20K}	O	F	Ne ^{4K}										
0.542	1.82											2.47	3.516	1.03			1.51												
4.700	12.1											13.0	17.6				4.36												
3.023	2.22												1.54			1.44	3.16												
Na ^{5K}		Mg												Al	Si	P	S	Cl ^{93K}	Ar ^{4K}										
1.013	1.74											2.70	2.33				2.03	1.77											
2.652	4.30											6.02	5.00				2.66												
3.659	3.20											2.86	2.35			2.02	3.76												
														Density in g cm ⁻³ (10 ³ kg m ⁻³)															
														Concentration in 10 ²² cm ⁻³ (10 ²⁶ m ⁻³)															
														Nearest-neighbor distance, in Å (10 ⁻¹⁰ m)															
K ^{5K}	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br ^{123K}	Kr ^{4K}												
0.910	1.53	2.99	4.51	6.09	7.19	7.47	7.87	8.9	8.91	8.93	7.13	5.91	5.32	5.77	4.81	4.05	3.09												
1.402	2.30	4.27	5.66	7.22	8.33	8.18	8.50	8.97	9.14	8.45	6.55	5.10	4.42	4.65	3.67	2.36	2.17												
4.525	3.95	3.25	2.89	2.62	2.50	2.24	2.48	2.50	2.49	2.56	2.66	2.44	2.45	3.16	2.32		4.00												
Rb ^{5K}	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe ^{4K}												
1.629	2.58	4.48	6.51	8.58	10.22	11.50	12.36	12.42	12.00	10.50	8.65	7.29	5.76	6.69	6.25	4.95	3.78												
1.148	1.78	3.02	4.29	5.56	6.42	7.04	7.36	7.26	6.80	5.85	4.64	3.83	2.91	3.31	2.94	2.36	1.64												
4.837	4.30	3.55	3.17	2.86	2.72	2.71	2.65	2.69	2.75	2.89	2.98	3.25	2.81	2.91	2.86	3.54	4.34												
Cs ^{5K}	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg ²²⁷	Tl	Pb	Bi	Po	At	Rn												
1.997	3.59	6.17	13.20	16.66	19.25	21.03	22.58	22.55	21.47	19.28	14.26	11.87	11.34	9.80	9.31														
0.905	1.60	2.70	4.52	5.55	6.30	6.80	7.14	7.06	6.62	5.90	4.26	3.50	3.30	2.82	2.67	—	—												
5.235	4.35	3.73	3.13	2.86	2.74	2.74	2.68	2.71	2.77	2.88	3.01	3.46	3.50	3.07	3.34														
Fr	Ra	Ac																											
—	—	10.07																											
		2.66	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu													
		3.76	6.77	6.78	7.00	—	7.54	5.25	7.89	8.27	8.53	8.80	9.04	9.32	6.97	9.84													
			2.91	2.92	2.93	—	3.03	2.04	3.02	3.22	3.17	3.22	3.26	3.32	3.02	3.39													
			3.65	3.63	3.66	—	3.59	3.96	3.58	3.52	3.51	3.49	3.47	3.54	3.88	3.43													
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr													
			11.72	15.37	19.05	20.45	19.81	11.87	—	—	—	—	—	—	—	—													
			3.04	4.01	4.80	5.20	4.26	2.96	—	—	—	—	—	—	—	—													
			3.60	3.21	2.75	2.62	3.1	3.61	—	—	—	—	—	—	—	—													

A sphere interacting with a flat plane

Next integrate the atom/molecule - plane vdW interaction over the volume of a spherical AFM tip. Let the number density of atoms/molecules in the tip be ρ_2 .

The vdW interaction energy for each atom/molecule inside tip is given by

$$U_{vdW}(d + \zeta) = \frac{-\pi\rho_1 C_{vdW}}{6(d + \zeta)^3}$$

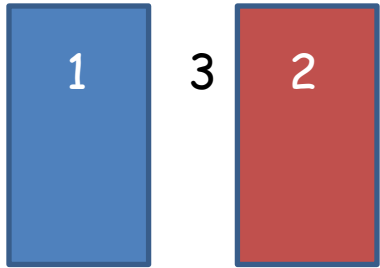


$$0 \leq \zeta \leq 2R_{tip}$$

The prior discussion focuses on integrating pair-wise interactions between molecules. Can we do better?

Lifshitz Theory - treat solids as a continuous material with BULK properties - macroscopic treatment (Dzyaloshinskii, Lifshitz and Pitaevskii, Sov. Phys. Usp. 4, 153 (1961))

- ionization energy I "replaced" by frequency dependent dielectric constant $\epsilon(i\omega)$
- polarizability a "replaced" by **static** dielectric constant ϵ
Keesom + Debye



$$H_{Lifshitz} = \frac{3}{4} k_B T \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) + \frac{3h}{4\pi} \int_{f_1}^{\infty} \left(\frac{\epsilon_1(if) - \epsilon_3(if)}{\epsilon_1(if) + \epsilon_3(if)} \right) \left(\frac{\epsilon_2(if) - \epsilon_3(if)}{\epsilon_2(if) + \epsilon_3(if)} \right) df$$

with $f_1 = \frac{2\pi}{h} k_B T$ (infrared at room temperature)

frequency dependent dielectric constant:
electrons treated as harmonically damped bound particles subject to external electric fields

textbook model: $\epsilon(i\omega) = \epsilon'(i\omega) + i\epsilon''(i\omega)$

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_{static} - \epsilon_{\infty}}{1 + \omega^2 \tau^2} \quad \epsilon'' = \frac{(\epsilon_{static} - \epsilon_{\infty}) \omega \tau}{1 + \omega^2 \tau^2}$$

ϵ_{static} = value appropriate for dc electric fields

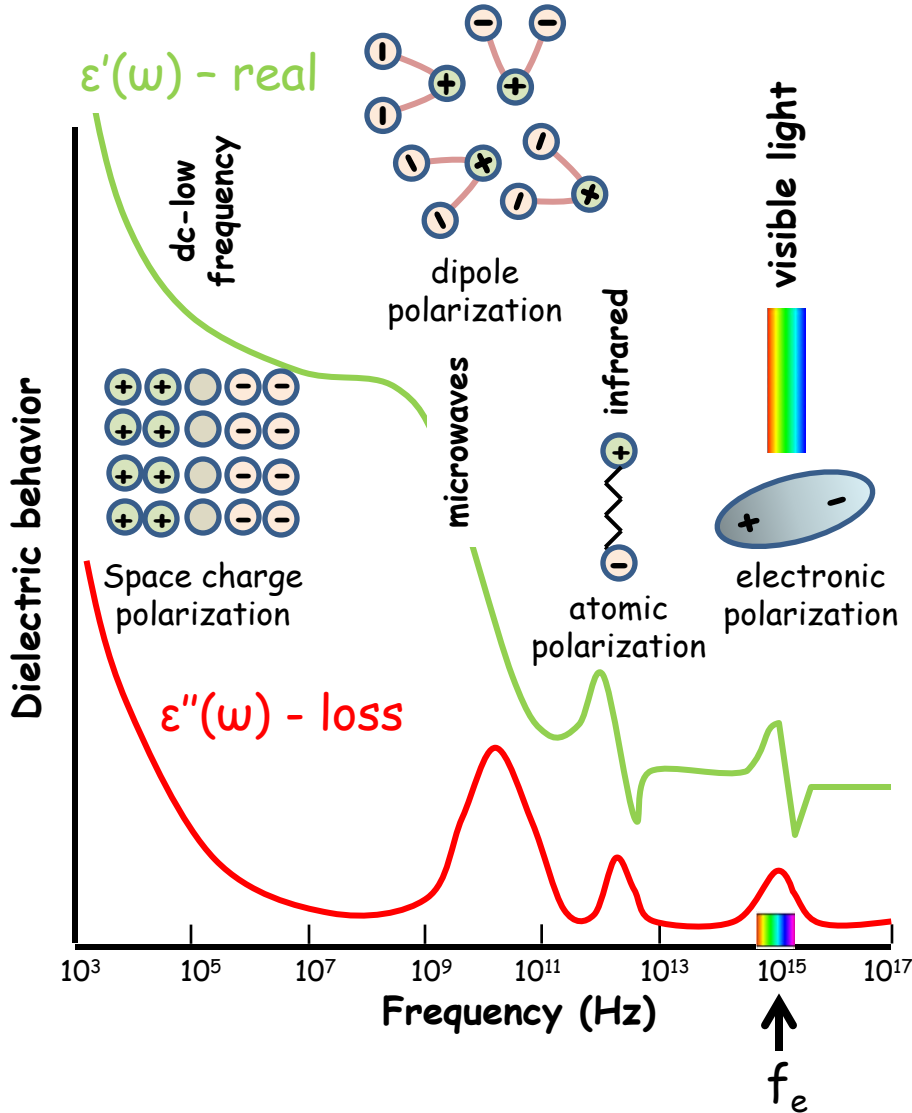
ϵ_{∞} = value appropriate for high frequency ($\sim 10^{15}$ Hz) electric fields

τ = characteristic relaxation time

The frequency dependence of the dielectric constant

How a solid responds to an electric field of frequency f

Typical behavior of $\epsilon(f) = \epsilon'(f) + i\epsilon''(f)$ for solids



for frequencies above the visible range :

$$\epsilon(f) \approx 1 + \frac{n^2 - 1}{1 + \left(\frac{f}{f_e}\right)^2}$$

where

n = refractive index

$f_e \approx$ mean ionization energy ($\sim 10^{15}$ Hz)

gives

$$H_{Lifshitz} = \frac{3}{4} k_B T \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) + \frac{3hf_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{\sqrt{n_1^2 + n_3^2} \sqrt{n_2^2 + n_3^2} (\sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2})}$$

The Lifshitz Theory provides a way to estimate the Hamaker constant for a complex material system

Example: What is the Hamaker constant for the interaction of amorphous silicon oxide (SiO_2) with amorphous silicon oxide (SiO_2) across water at 20°C ?*



Material	Static dielectric constant, κ	Index of refraction, n	Mean adsorb. frequency, f_e
SiO_2	3.82	1.46	$\sim 3.4 \times 10^{15}$ Hz
H_2O	78.5	1.33	

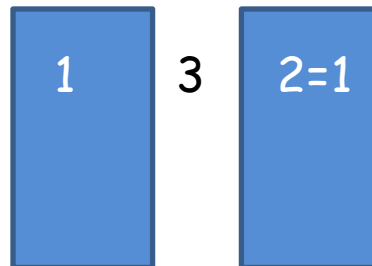
$$\begin{aligned}
 H_{Lifshitz} &= \frac{3}{4} k_B T \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) + \frac{3hf_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{\sqrt{n_1^2 + n_3^2} \sqrt{n_2^2 + n_3^2}} \cdot \frac{1}{\left(\sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2} \right)} \\
 &= 0.30 \times 10^{-21} \text{ J} \cdot \left(\frac{3.82 - 78.5}{3.82 + 78.5} \right)^2 + 5.97 \times 10^{-19} \text{ J} \cdot \frac{(1.46^2 - 1.33^2)^2}{(1.46^2 + 1.33^2)} \cdot \frac{1}{\left(2\sqrt{(1.46^2 + 1.33^2)} \right)} \\
 &= 5.4 \times 10^{-21} \text{ J}
 \end{aligned}$$

* H.-J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, 2nd ed., Wiley VCH, pg. 94 (2006).

Typical Values for Hamaker Constants

Solid	Solid-Air-Solid	Solid-Water-Solid
Quartz (crystalline)	8.8×10^{-20} J	1.7×10^{-20} J
Fused silica	$6.5^5 \times 10^{-20}$ J	$0.8^5 \times 10^{-20}$ J
Calcite	10.1×10^{-20} J	2.2×10^{-20} J
Calcium fluoride	7.2×10^{-20} J	1.0×10^{-20} J
Sapphire	15.6×10^{-20} J	5.3×10^{-20} J

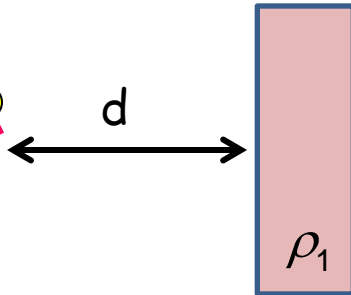
Note the reduction due to an intervening water layer.



Summary

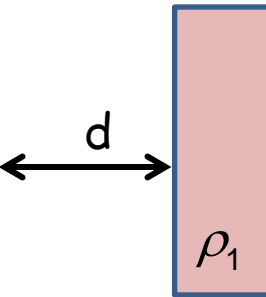
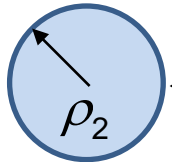


$$U_{vdW}(z) = -\frac{C_{vdW}}{z^6} \quad F_{vdW}(z) = -\frac{\partial U_{vdW}(z)}{\partial z} = -\frac{6C_{vdW}}{z^7}$$



$$U_{vdW}(d) = -\frac{\pi\rho_1 C_{vdW}}{6d^3}$$

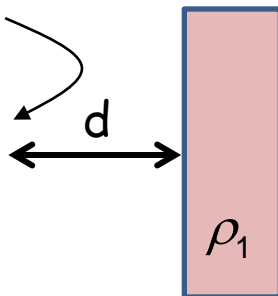
R_{tip}



$$U_{vdW}(d) = -\frac{\pi^2 \rho_2 \rho_1 C_{vdW}}{6d} R_{tip} = -\frac{H R_{tip}}{6d}$$

$$H = \pi^2 \rho_2 \rho_1 C_{vdW}$$

area A

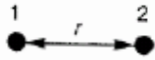

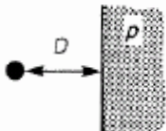

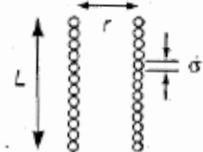
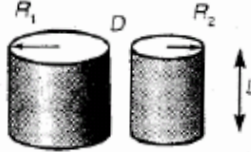
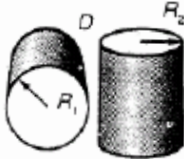
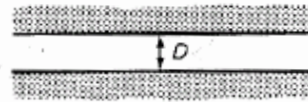


$$\frac{U_{plane-plane}(d)}{A} = -\frac{H}{12\pi d^2}$$

(see P1_Wk2_L3)

$$H = \pi^2 \rho_2 \rho_1 C_{vdW}$$

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>

Source : J. Israelachvili, "Intermolecular and surface forces", Academic Press (1992).

From intermolecular to macroscopic (micron-size) objects - some caveats

- Tip is assumed to be homogeneous also! Both tip and substrate made of "simple" atoms or molecules
- Assumes atom-atom interactions are independent of other surrounding atoms - no N-body interactions
- Perfectly smooth interacting surfaces
- Tip-surface interactions obey very different power laws compared to atom-atom laws: Molecular vdW interactions are very short ranged (z^{-6}) while vdW interactions between macroscopic bodies (e.g. sphere-plane) are long ranged (z^{-1})

Add translation slide to next lecture