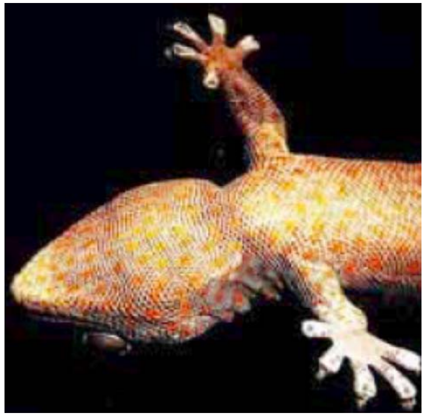
Lecture 5

Surface Forces I:
Van der Waals Forces

Surface forces

- Surface forces:
  - governs interaction between solid and liquid colloids,
  - AFM tip and the surface
  - stability of liquid films on solid surfaces and in foams etc…
- and ability of gecko to adhere to any surface

  (It is due to van der Waals attractive forces between spatulae (1 billion) on the Gecko’s leg and the wall)



Full et al. (2000), Nature 405, 681-684

Intermolecular Forces:
Contrast with gravitational forces

17th Century: Newton postulated the law of gravitation

$$W(r) = -\frac{GM_1M_2}{r} \quad \text{or} \quad F(r) = -\frac{GM_1M_2}{r^2}$$

G = Gravitational Constant, M_i (i = 1,2) Mass of bodies

r = distance of separation between centers of bodies

19th Century: Scientists postulated that one simple force law would eventually account for all intermolecular attractions

The interaction potential w(r) and force F(r) were of the form

$$W(r) = -\frac{CM_1M_2}{r^n} \quad \text{or} \quad F(r) = -\frac{dW(r)}{dr} = -\frac{nCM_1M_2}{r^{n+1}}$$

Intermolecular Forces:
Contrast with gravitational forces

$$F(r) = -\frac{nCM_1M_2}{r^{n+1}}$$

n = 1, we have gravitational forces

Argument: If Intermolecular Forces are not to extend over long ranges, then n ≥ 3. How?

For simplicity, let us express the general term for interaction potential between 2 molecules as:

$$W(r) = -\frac{C}{r^n}$$

Consider a region of space where number density of these molecules are ρ (The region can be solid/liquid/gas)

Intermolecular Forces: Contrast with gravitational forces

The summation of all interaction energies of a molecule with all other molecules in a spherical system with size L is:

$$\text{Energy} = \int_{\sigma}^{L} W(r)\rho 4\pi r^{2} dr = \int_{\sigma}^{L} -\frac{\rho C 4\pi r^{2}}{r^{n}} dr$$

σ = Molecular diameter

$$\text{Energy} = \frac{-4\pi C\rho}{(n-3)\sigma^{n-3}}\left[1-\left(\frac{\sigma}{L}\right)^{n-3}\right]$$

This expression gives us the all important relation of $n \geq 3$

Why?

Since $\left(\frac{\sigma}{L}\right) \leq 1$ Long distance contributions to Energy do not occur ONLY when $n \geq 3$

Intermolecular force potentials for $n \geq 3$

For $n < 3$, the size of the system is important (E.g. Gravity: Distant planets and stars interact)

For $n \geq 3$, intermolecular force potentials become important

It is for this reason that:

Bulk properties of material is size independent (unless in the domains of intermolecular forces)

(Boiling point of water in a test tube = boiling point of water in a bucket)

It is also for this reason that:

- As we go to sub micron size distances, properties of material changes – Intermolecular Forces Start Taking Over !

Interaction between charges

- interaction of two point charges

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$$

- e.g. for Na$^+$ and Cl$^-$ 1nm apart in vacuum:

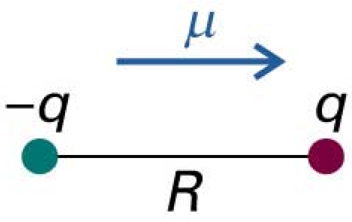
$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r} = \frac{-\left(1.6 \cdot 10^{-19}\right)^2}{4\pi \cdot 8.85 \cdot 10^{-12} \cdot 10^{-9}} = 2.3 \cdot 10^{-19}\, J$$

  - for comparison

$$k_B T = 4.12 \cdot 10^{-21}\, J$$

Electric dipole moment

- Most molecules are not charged but posess a charge distribution



1 Electric dipole

Dipole moment measured in **C·m** or in debye:

$$1D = 3.33564 \times 10^{-30}\ Cm$$

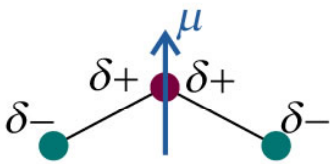
dipole moment of 2 electrons separated by 1Å:

$$4.8\text{D}{=}1.6 \times 10^{-29}\ Cm$$

- Dipole moment of a molecule can be calculated by taking into account the locations and magnitudes of the partial charges on all the atoms

$$\mu_x = \sum_j q_j x_j$$

$$\mu = \mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2$$



Ozone, O_3

Electrical dipole moment

- Charge-dipole interaction

$$V = -\frac{\mu Q \cos\theta}{4\pi\varepsilon_0 D^2}$$

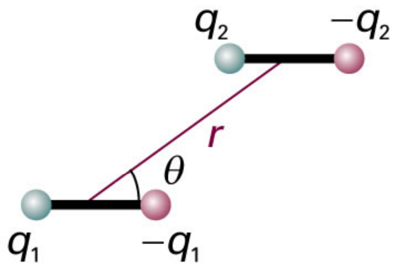
- Taking into account thermal fluctuations:

$$V = -\frac{\mu^2 Q^2}{6\left(4\pi\varepsilon_0\right)^2 k_B T D^4}$$

Interaction between two dipoles

- dipole-dipole interaction

$$V = \frac{\mu_1 \mu_2 f(\theta)}{4\pi\varepsilon_0 r^3} \qquad f(\theta) = 1 - 3\cos^2\theta$$



in case of free rotation the interaction would be zero, but as the dipoles interact the rotation is not free even in a gas phase!

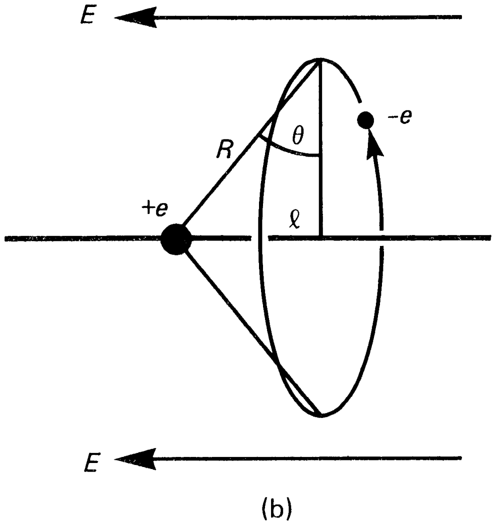
- Keesom energy: interaction between freely rotating dipoles

$$V = -\frac{{\mu_1}^2 {\mu_2}^2 Q^2}{3\left(4\pi\varepsilon_0\right)^2 k_B T D^6}$$

$$\langle V \rangle = -\frac{C}{r^6}$$

Polarizability

- Let’s consider a one-electron atom in electric field



from the force balance between the external (field) and restoring forces:

$$eE = \frac{e^2}{4\pi\varepsilon_0 R^2}\sin\theta = \frac{e\mu_{ind}}{4\pi\varepsilon_0 R^3}$$

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$$\mu_{ind} = 4\pi\varepsilon_0 R^3 E = \alpha_0 E$$

- electronic polarizability is
  - of the order of volume of a molecule
  - can be obtained by summing up contribution from the molecular bonds.

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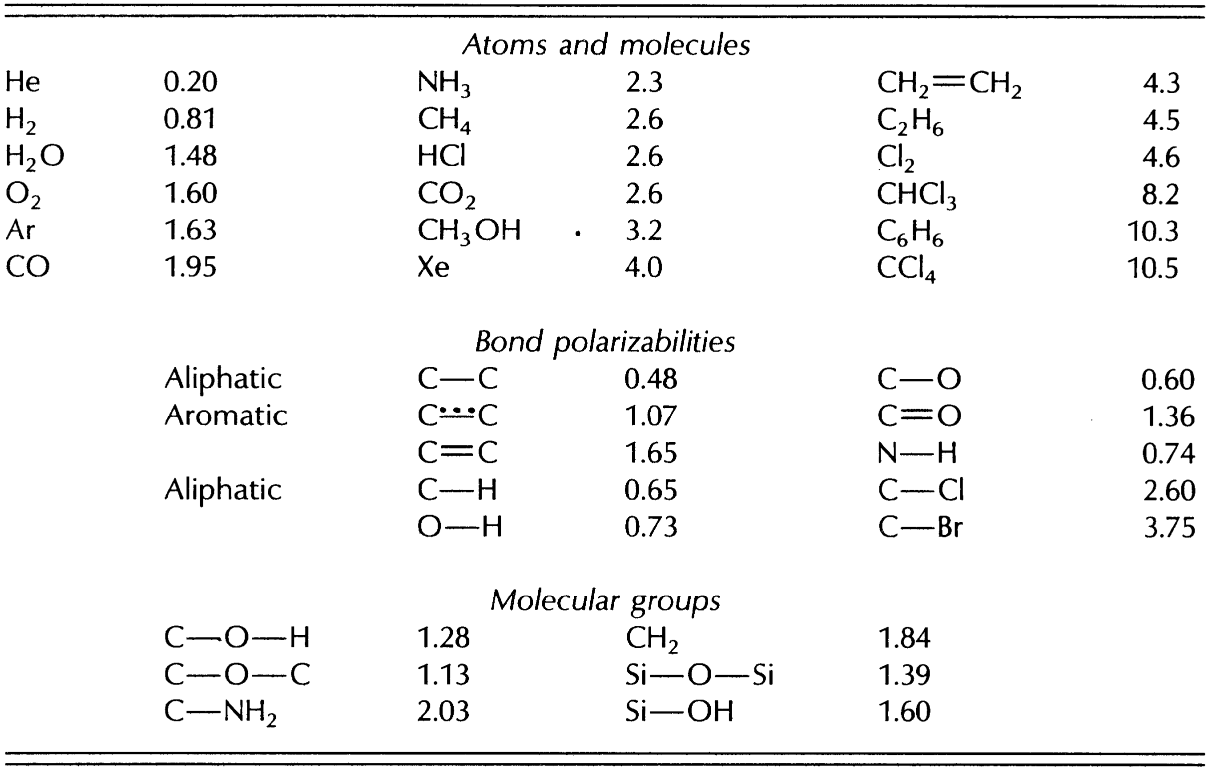


Atoms and molecules

He	0.20	NH_3	2.3	$CH_2{=}CH_2$	4.3
H_2	0.81	CH_4	2.6	C_2H_6	4.5
H_2O	1.48	HCl	2.6	Cl_2	4.6
O_2	1.60	CO_2	2.6	$CHCl_3$	8.2
Ar	1.63	CH_3OH	3.2	C_6H_6	10.3
CO	1.95	Xe	4.0	CCl_4	10.5

Bond polarizabilities

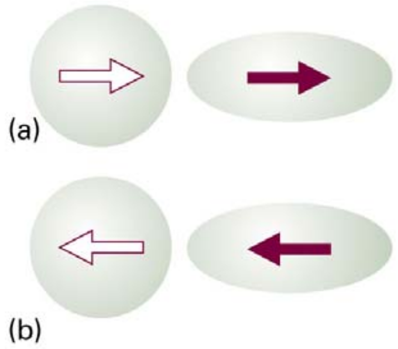
Aliphatic	C—C	0.48	C—O	0.60
Aromatic	C⋯C	1.07	C=O	1.36
	C=C	1.65	N—H	0.74
Aliphatic	C—H	0.65	C—Cl	2.60
	O—H	0.73	C—Br	3.75

Molecular groups

C—O—H	1.28	CH_2	1.84
C—O—C	1.13	Si—O—Si	1.39
$C{-}NH_2$	2.03	Si—OH	1.60

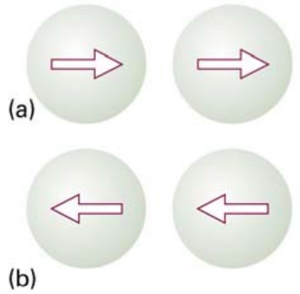
Interaction between dipoles

- dipole-induced dipole interaction



$$V = -\frac{C}{r^6} \qquad C = \frac{\mu_1^{\,2}\alpha'}{4\pi\varepsilon_0}$$

- induced dipole-induced dipole interaction
  - interaction due to transient dipoles resulting from fluctuations of electron distribution.
  - called **dispersion attraction** or **London interaction**



$$V = -\frac{C}{r^6} \qquad C = \frac{1}{2}\alpha_1'\alpha_2'\frac{I_1 I_2}{I_1 + I_2}$$

I_1, I_2 – ionization energies of the two molecules

Van der Waals interaction

- combines all dipole-dipole interactions.

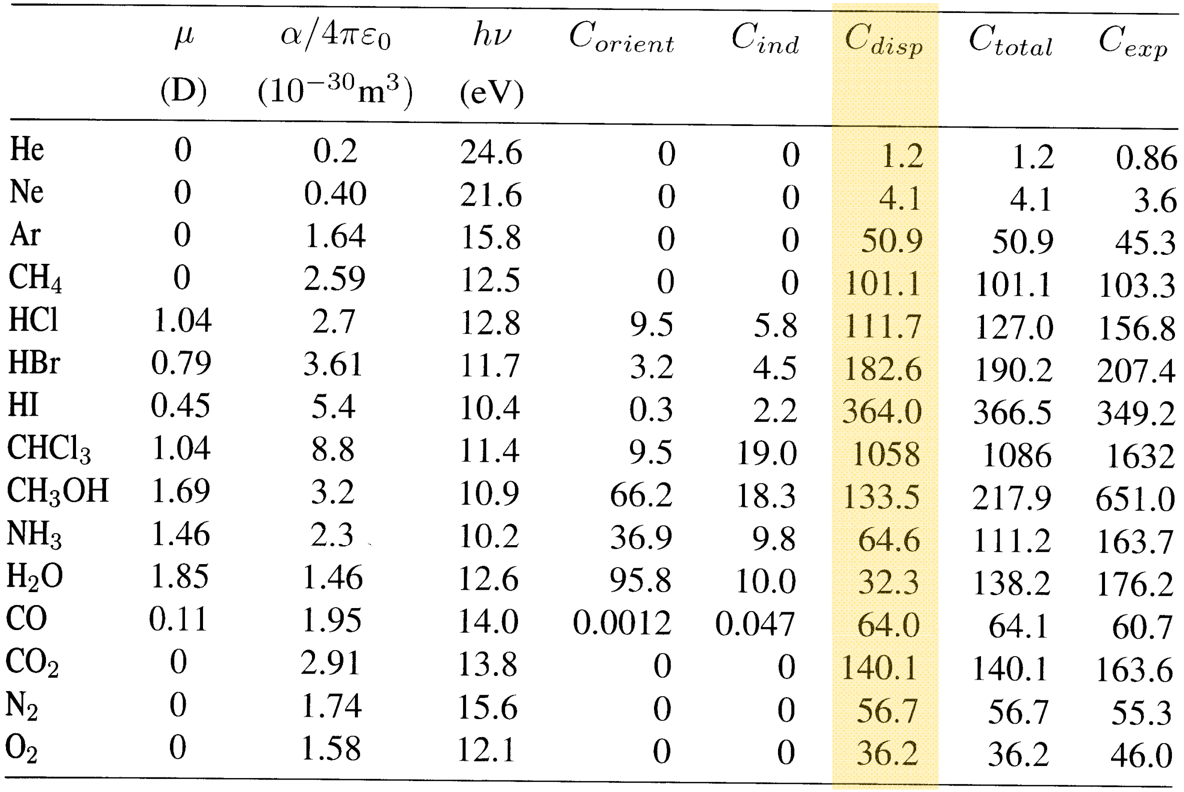
$$\frac{C_{orient} + C_{ind} + C_{disp}}{D^6}$$

Interaction Component	Origin of Interactions	Equation
Keesom	Dipole-dipole	$w(r) = -\frac{u_1^2 u_2^2}{3(4\pi\varepsilon_o\varepsilon_r)^2 k_B T}\frac{1}{r^6}$
Debye	Dipole – induced dipole	$w(r) = -\frac{u^2\alpha_o}{(4\pi\varepsilon_o\varepsilon_r)^2}\frac{1}{r^6}$
London (Dispersion)	Induced Dipole – Induced Dipole	$w(r) = -\frac{3}{2}\frac{\alpha_{o1}\alpha_{o2}}{(4\pi\varepsilon_o)^2}\frac{I_1 I_2}{(I_1 + I_2)}\frac{1}{r^6}$

- usually London dispersion dominates

Van der Waals interaction

- Contribution of the Keesom, Debye and London energies to the total van der Waals interaction



	μ (D)	$\alpha/4\pi\varepsilon_0$ (10^{-30}m^3)	$h\nu$ (eV)	C_{orient}	C_{ind}	C_{disp}	C_{total}	C_{exp}
He	0	0.2	24.6	0	0	1.2	1.2	0.86
Ne	0	0.40	21.6	0	0	4.1	4.1	3.6
Ar	0	1.64	15.8	0	0	50.9	50.9	45.3
CH_4	0	2.59	12.5	0	0	101.1	101.1	103.3
HCl	1.04	2.7	12.8	9.5	5.8	111.7	127.0	156.8
HBr	0.79	3.61	11.7	3.2	4.5	182.6	190.2	207.4
HI	0.45	5.4	10.4	0.3	2.2	364.0	366.5	349.2
$CHCl_3$	1.04	8.8	11.4	9.5	19.0	1058	1086	1632
CH_3OH	1.69	3.2	10.9	66.2	18.3	133.5	217.9	651.0
NH_3	1.46	2.3	10.2	36.9	9.8	64.6	111.2	163.7
H_2O	1.85	1.46	12.6	95.8	10.0	32.3	138.2	176.2
CO	0.11	1.95	14.0	0.0012	0.047	64.0	64.1	60.7
CO_2	0	2.91	13.8	0	0	140.1	140.1	163.6
N_2	0	1.74	15.6	0	0	56.7	56.7	55.3
O_2	0	1.58	12.1	0	0	36.2	36.2	46.0

Dispersion forces

- Long-range forces, effective from large distances (10nm) down to interatomic distances
- might be repulsive or attractive
- not only bring molecules together but also align them
- are affected by the presence of other bodies

Van der Waals forces between macroscopic solids

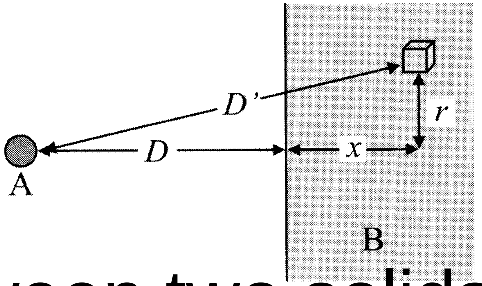
- Macroscopic approach:

  in 1937 Hamaker calculated the Van der Waals force between two macroscopic spheres

- Interaction between a molecule and a solid:

$$W_{mol-plane} = -C_{AB} \iiint_V \frac{\rho_B}{D'^6} dV$$

$$W_{mol-plane} = -\frac{\pi \rho_B C_{AB}}{6D^3}$$



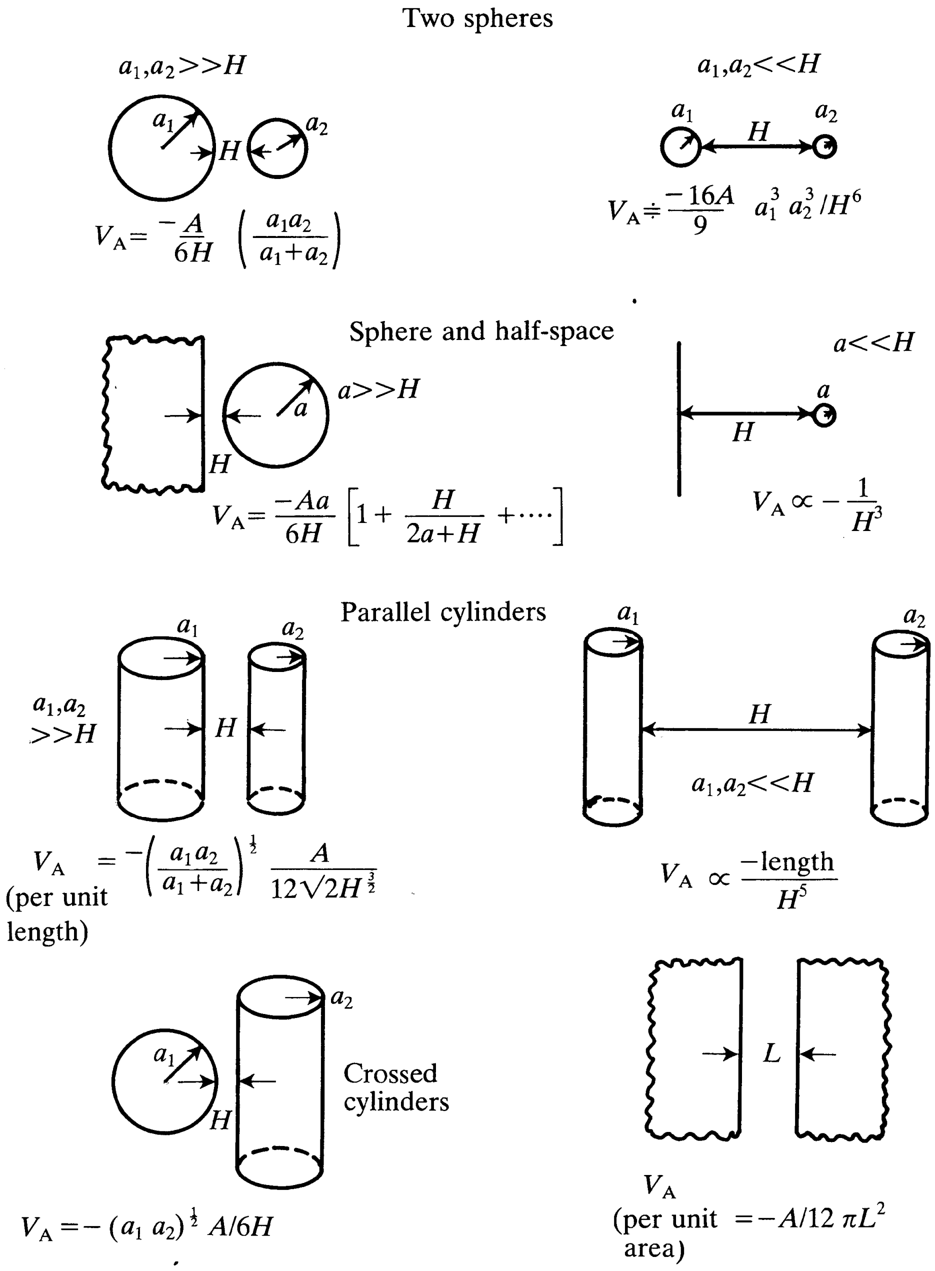
- Interaction energy per unit area between two solids separated by a gap of D

$$\frac{W_{solid-solid}}{A} = -\frac{\pi^2 \rho_B \rho_A C_{AB}}{12D^2}$$

Hamaker constant A_H.

Van der Waals energy

- for various shapes



Two spheres

$a_1,a_2>>H$

$$V_A = \frac{-A}{6H}\left(\frac{a_1a_2}{a_1+a_2}\right)$$

$a_1,a_2<<H$

$$V_A \doteq \frac{-16A}{9}\, a_1^3\, a_2^3/H^6$$

Sphere and half-space

$a>>H$

$$V_A = \frac{-Aa}{6H}\left[1+\frac{H}{2a+H}+\cdots\right]$$

$a<<H$

$$V_A \propto -\frac{1}{H^3}$$

Parallel cylinders

a_1,a_2 $>>H$

V_A (per unit length) $= -\left(\frac{a_1a_2}{a_1+a_2}\right)^{\frac{1}{2}} \frac{A}{12\sqrt{2}H^{\frac{3}{2}}}$

$a_1,a_2<<H$

$$V_A \propto \frac{-\text{length}}{H^5}$$

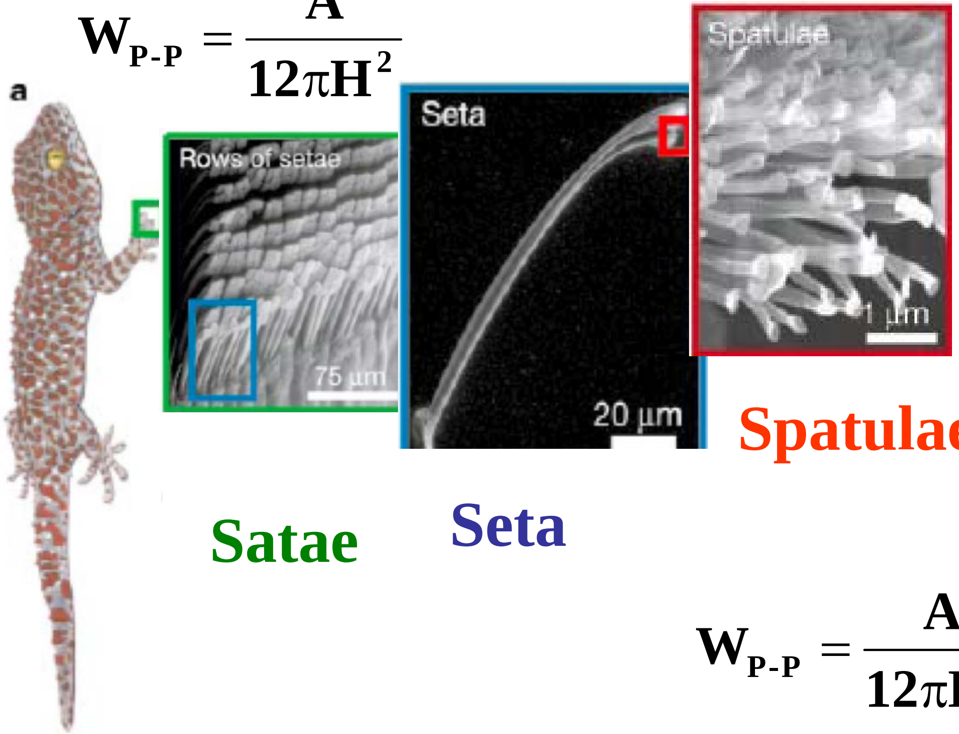
Crossed cylinders

$$V_A = -(a_1\,a_2)^{\frac{1}{2}}\,A/6H$$

V_A (per unit area) $= -A/12\,\pi L^2$

This is also why...

$$W_{P\text{-}P} = \frac{A}{12\pi H^2}$$



$$W_{M-M} = -\frac{C}{r^6}$$

Spatulae

Satae

Seta

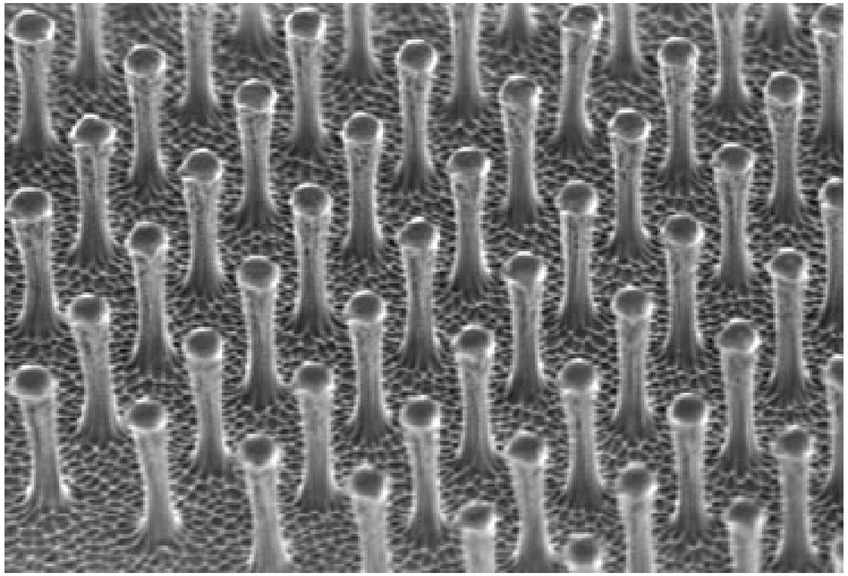
$$W_{P\text{-}P} = \frac{A}{12\pi H^2}$$

Spiderman exists only in movies !

But Seriously, can we possibly make the Spiderman costume?

Nano-Gecko

- Gecko tape: molded of poyimide polymer, each synthetic hair is 2µm high and 200nm in diameter, periodicity 1.6 µm
- Key point: flexibility that allows to bring hairs into intimate contact with the surface
- Tape is re-attachable and resist contaminations



A. Geim et al, Nature Nanomaterials

Lifshitz theory

- The vdWaals forces depend on the presence of the third bodies that was not included in our calculations
- Lifshitz approach: materials are treated as a continuum with bulk permittivity
- Result: the same dependencies, different equation for Hamaker constant

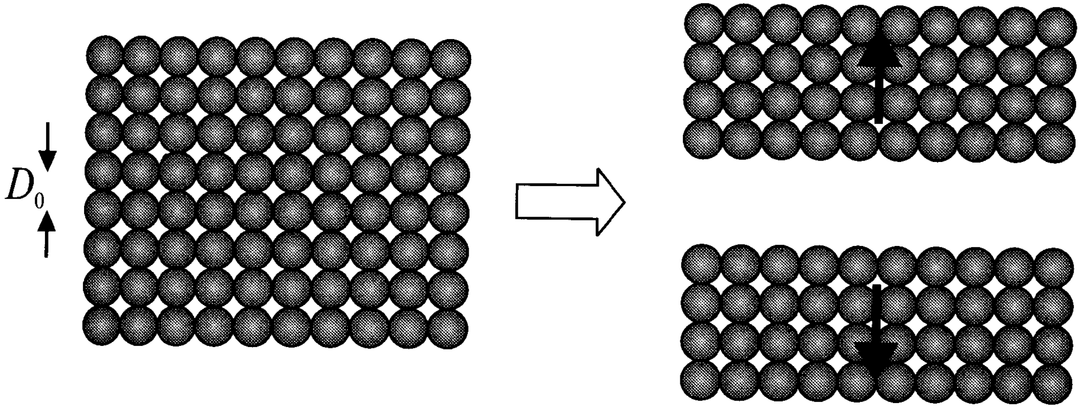
$$A_H = \frac{3}{4}kT\left(\frac{\varepsilon_1 - \overset{\substack{\text{medium}\\ \downarrow}}{\varepsilon_3}}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) +$$

$$+\frac{3h}{4\pi}\int_{v1}^{\infty}\left(\frac{\varepsilon_1(iv) - \varepsilon_3(iv)}{\varepsilon_1(iv) + \varepsilon_3(iv)}\right)\left(\frac{\varepsilon_2(iv) - \varepsilon_3(iv)}{\varepsilon_2(iv) + \varepsilon_3(iv)}\right)dv$$

$$v1 = 2\pi kT/h = 3.9\times 10^{13} \qquad (760nm)$$

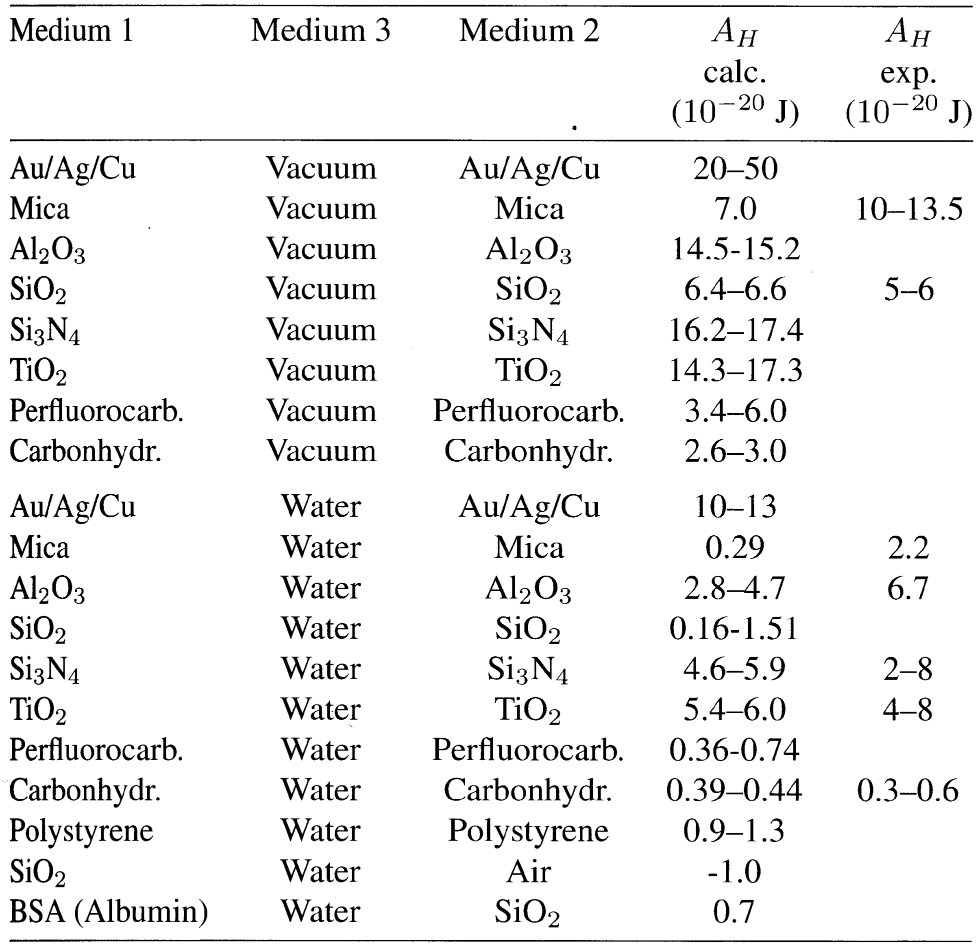
Surface energy and Hamaker constant

- The surface energy can be equated to the work of vdWaals forces required to separate two parts of solid to infinite distance



$$\gamma_S = \frac{1}{2}\frac{W}{A} = \frac{A_H}{24\pi D_0^{\,2}}$$

Hamaker constants

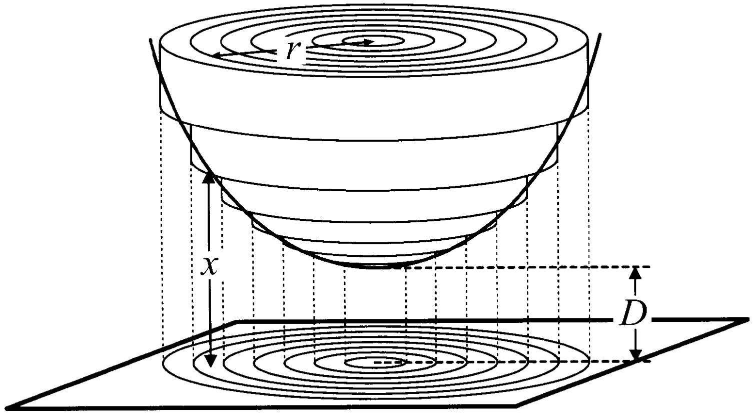


Medium 1	Medium 3	Medium 2	A_H calc. (10^{-20} J)	A_H exp. (10^{-20} J)
Au/Ag/Cu	Vacuum	Au/Ag/Cu	20–50	
Mica	Vacuum	Mica	7.0	10–13.5
Al_2O_3	Vacuum	Al_2O_3	14.5-15.2	
SiO_2	Vacuum	SiO_2	6.4–6.6	5–6
Si_3N_4	Vacuum	Si_3N_4	16.2–17.4	
TiO_2	Vacuum	TiO_2	14.3–17.3	
Perfluorocarb.	Vacuum	Perfluorocarb.	3.4–6.0	
Carbonhydr.	Vacuum	Carbonhydr.	2.6–3.0	
Au/Ag/Cu	Water	Au/Ag/Cu	10–13	
Mica	Water	Mica	0.29	2.2
Al_2O_3	Water	Al_2O_3	2.8–4.7	6.7
SiO_2	Water	SiO_2	0.16-1.51	
Si_3N_4	Water	Si_3N_4	4.6–5.9	2–8
TiO_2	Water	TiO_2	5.4–6.0	4–8
Perfluorocarb.	Water	Perfluorocarb.	0.36-0.74	
Carbonhydr.	Water	Carbonhydr.	0.39–0.44	0.3–0.6
Polystyrene	Water	Polystyrene	0.9–1.3	
SiO_2	Water	Air	-1.0	
BSA (Albumin)	Water	SiO_2	0.7	

Derjagin approximation

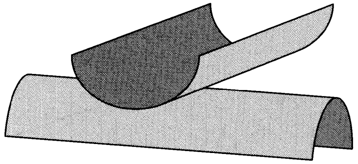
- When calculating the interaction between the two non –planar surfaces it’s convenient to use Derjagin approximation

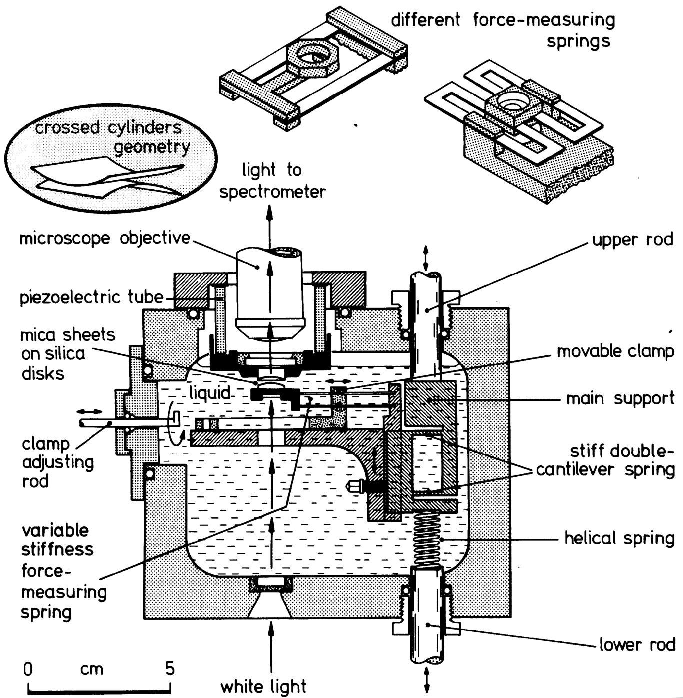
$$W(D) = \int_D^\infty w(x)\,dA = \int_D^\infty w(x)\frac{dA}{dx}dx$$



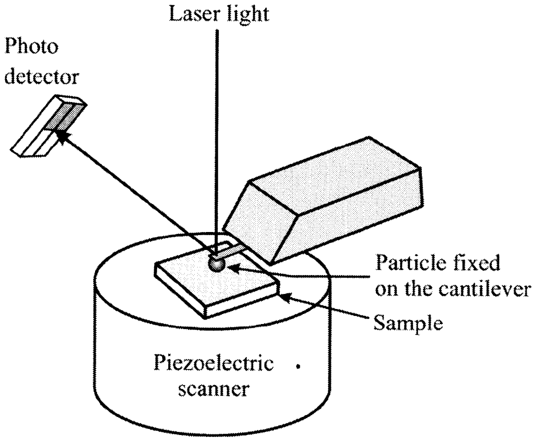
Measurement of surface forces

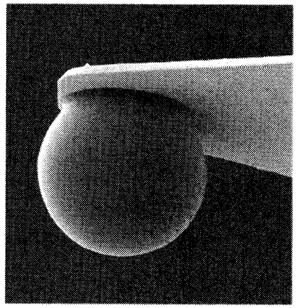
- SFA





- AFM





Problems

- 6.1. What is the van der Waals force per unit area for two planar parallel layers of molecules having surface densities of $\rho^{\sigma}{}_{A}$ and $\rho^{\sigma}{}_{B}$.
- 6.5. In atomic force microscopy the tip is approximated by a parabolic shape with curvature R in the end. Calculate vdWaals force vs distance.
- Prove equation 6.38 using Derjagin approximation.