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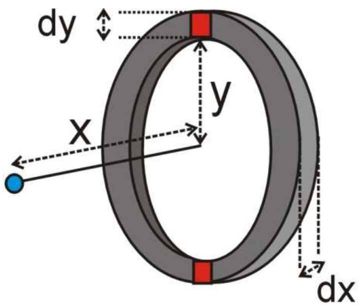
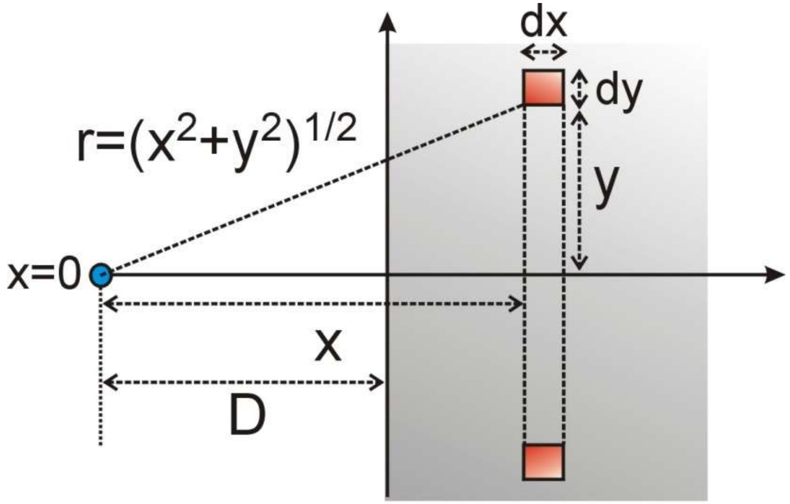
Dispersion interactions - macroscopic bodies

Force & function at the nanoscale

Detailed picture



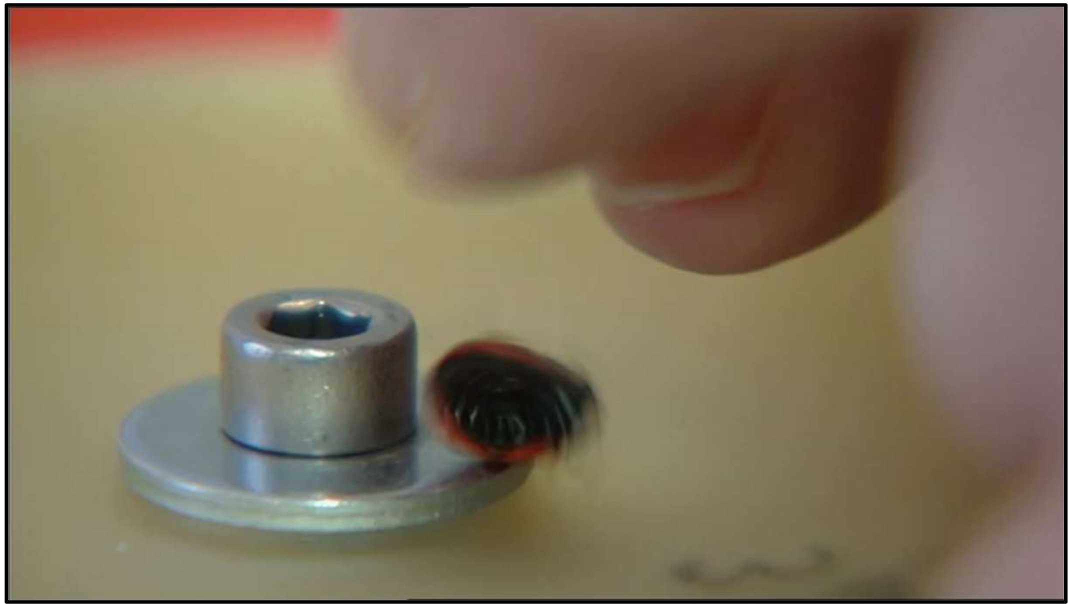
Circumference of ring = $2\pi y$
Area of ring = $2\pi y dy$
Volume of ring = $2\pi y dy dx$



$$U(x) = -\frac{C}{x^6}$$

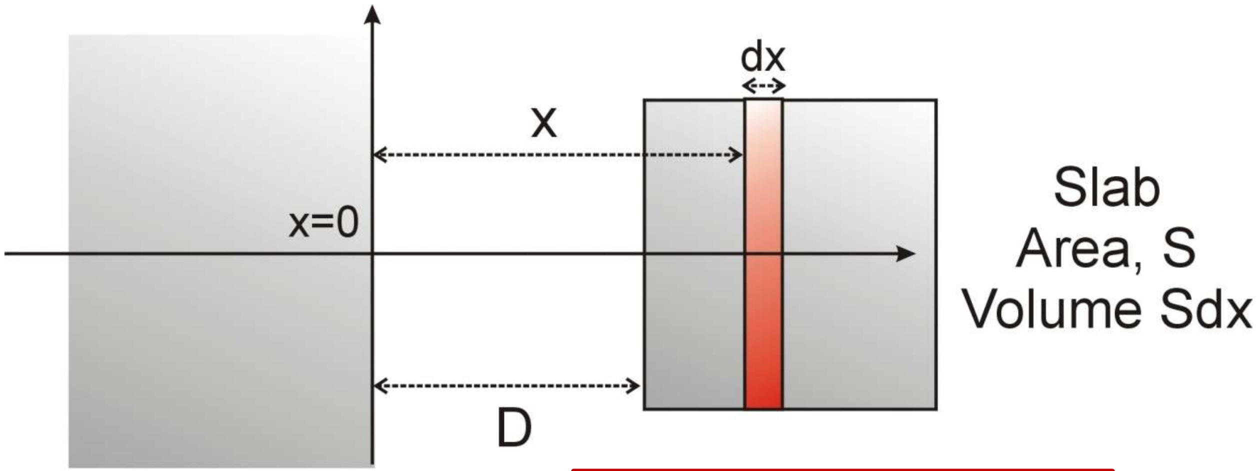
$$U(D) = -\frac{\pi n C}{6D^3}$$

Introduction



5.1 The slab & surface

Derive an expression for the dispersion forces which act between a perfectly flat slab of area S and a semi-infinite solid if the number density of atoms in the solid and slab are n_1 and n_2 respectively.



This slab is semi-infinite so extends from x=D to x=∞

$$U(D) = -\frac{n_1 n_2 \pi C S}{12 D^2}$$

The Hamaker Constant

We considered the interactions between 2 slabs. Later in the lecture we'll look at a sphere and a slab. Similar expressions exist for other geometries:

$$U(D) = -\frac{n_1 n_2 \pi C S}{12 D^2} \qquad U(D) = -\frac{n_1 n_2 \pi^2 C R}{3D}$$

The Hamaker constant provides us with an easy way to quantify the strength of interaction between two materials which is geometry independent.

$$A_{12} = n_1 n_2 \pi^2 C$$

Measured in J

Dispersion interactions and Hamaker constants

We can rewrite our expressions for the dispersion interaction energy between two macroscopic bodies in terms of the Hamaker constant

Dispersion Interaction energy between a flat slab of area, *S*, and a semi-infinite solid

$$U(D) = -\frac{n_1 n_2 \pi C S}{12 D^2} = -\frac{A_{12} S}{12 \pi D^2}$$

Dispersion Interaction energy between a sphere of radius, *R*, and a semi-infinite solid

$$U(D) = -\frac{n_1 n_2 \pi^2 C R}{3D} = -\frac{A_{12} R}{3D}$$

Dispersion Forces and Hamaker constants

We can also write the forces in terms of the Hamaker constant

Dispersion force between a flat slab of area, *S*, and a semi-infinite solid

$$F(D) = -\frac{dU}{dD} = -\frac{A_{12}S}{6\pi D^3}$$

Dispersion force between a sphere of radius, *R,* and a semi-infinite solid

$$F(D) = -\frac{dU}{dD} = -\frac{A_{12}R}{3D^2}$$

So for a given geometry we can determine the strength of the dispersion interaction A_{12} between two materials by measuring forces

How big are Hamaker constant values?

Values of A typically lie in the range 10^{-21} to 10^{-19} J
(while $kT_{300K} = 4.14 \times 10^{-21}$ J)

Medium	Dielectric Constant	Hamaker Constant (*10^{-20}J)
Liquid He	1.057	0.057
Alkanes	2	3
Benzene	2.28	5
Diamond	5.66	28.9
Silicon	11.6	18
Ethanol	26	4.2
Water	80	3.7

5.2 Force between two surfaces

We've shown that the force between a perfectly flat slab and a semi-infinite solid surface is

$$F(D) = -\frac{A_{12}S}{6\pi D^3}$$

Imagine you place your hand flat on the wall. What is the force you would need to remove it?

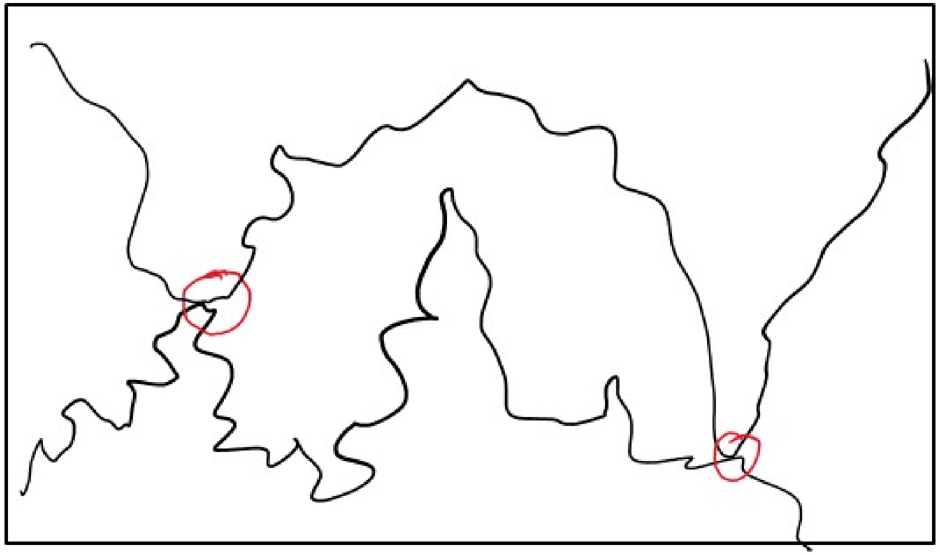
Assuming your hand has an area of $S=0.02\text{m}^2$ and $A_{12} = 10^{-21}$ J. What is the force between the slab and the surface at a separation of 0.3nm?

F ~ 39,279N (About 4 tonnes!)

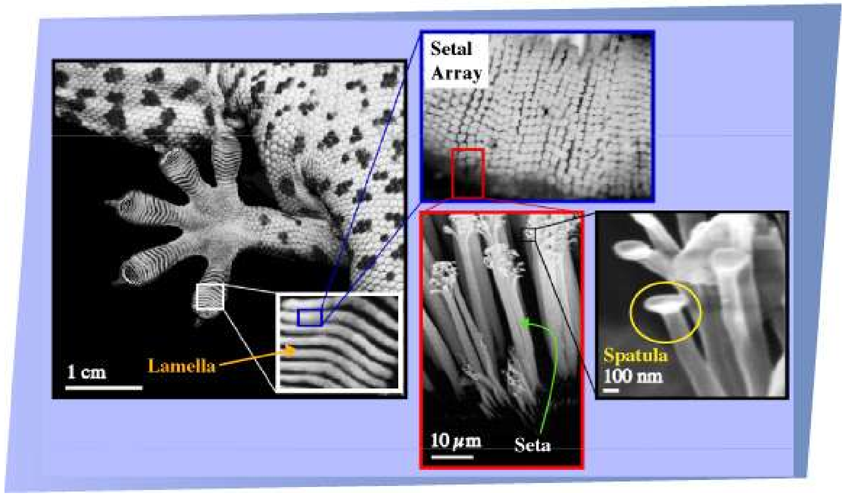
Does this seem reasonable? What's gone wrong?!

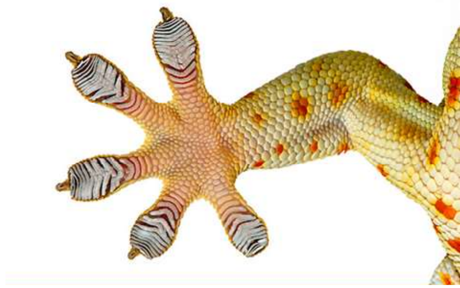
Surface Roughness

In reality all surfaces are, on the nanoscale, really rough, so that the area of “contact” between the surfaces is really small.



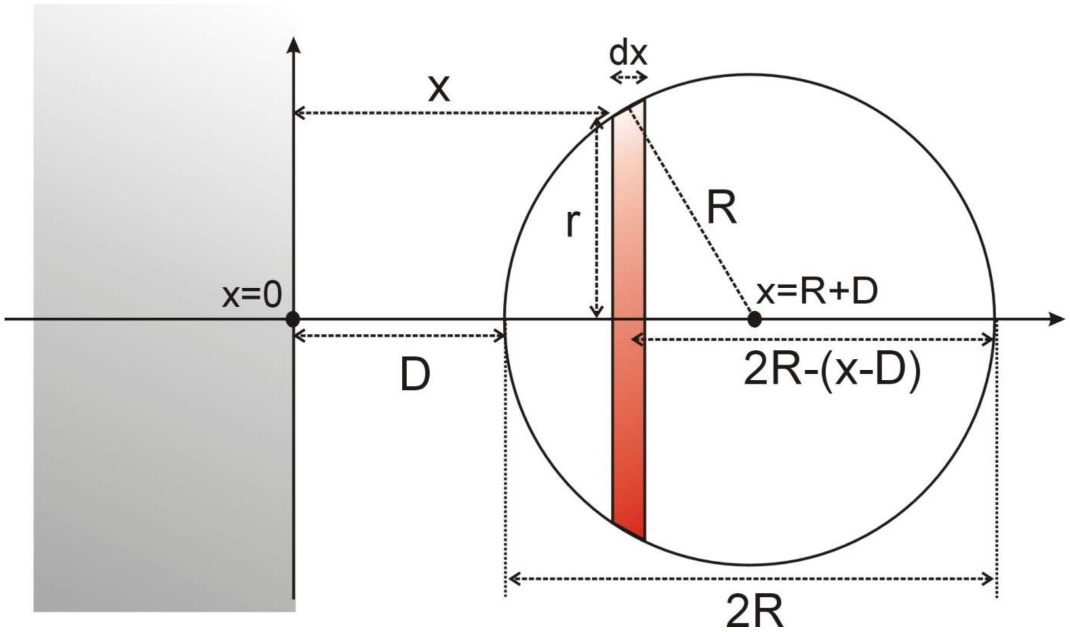
Geckos and "Biomimicry"





5.3 – The sphere and surface

Derive an expression for the dispersion forces which act between a sphere of radius R and a semi-infinite solid, for separations D>>R, if the number density of atoms in the solid and sphere are n_1 and n_2 respectively.

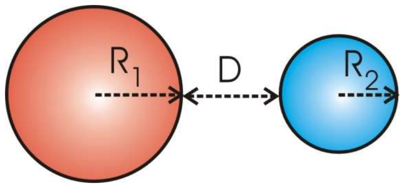


$$U(D) = -\frac{n_1 n_2 \pi^2 C R}{3D}$$

Some other important geometries

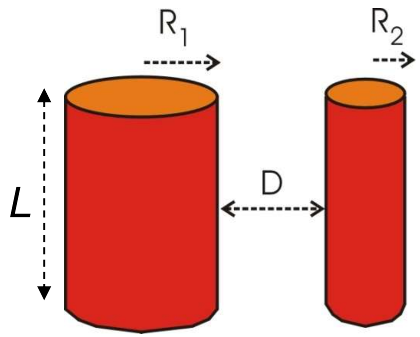
The geometry of the macroscopic bodies is important in determining the separation dependence of the dispersion interaction

Sphere-sphere



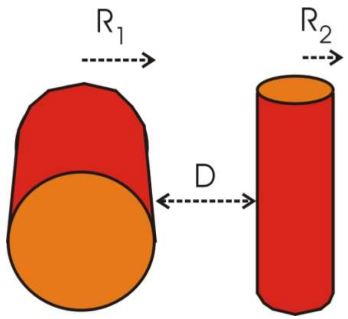
$$U(D) = -\frac{A_{12}}{3D}\frac{R_1 R_2}{R_1 + R_2}$$

Parallel cylinders



$$U(D) = -\frac{A_{12}L}{12\sqrt{2}D^{3/2}}\left(\frac{R_1 R_2}{R_1 + R_2}\right)^{1/2}$$

Perpendicular cylinders



$$U(D) = -\frac{A_{12}}{6D}\sqrt{R_1 R_2}$$

How close do you have to get to feel dispersion interactions?

We can calculate the range of the interaction by comparing dispersion and thermal energies i.e. $|U(D_{range})| \sim kT$

For a sphere of radius R and a solid surface we have

$$|U(D)| = \frac{A_{12}R}{3D_{range}} \approx kT$$

Hence

$$D_{range} \approx \frac{A_{12}R}{3kT}$$

For values of T=300K, R=10 nm and A_{12}=10^{-19}J

D_{range} ~ 10R = 100 nm

D_{range}(atoms) ~ 0.3 nm

Ok for a Gecko but not your hand

Summary of key results

Adding up dispersion interactions from individual atoms allows us to understand how macroscopic bodies interact.

The Hamaker constant provides a geometry independent way of characterising the strength of interaction between different materials

$$U(D) = -\frac{n_1 n_2 \pi C S}{12D^2}$$

Dispersion interactions between macroscopic bodies are much longer range and hence important. They are sufficiently strong to support the weight of a Gecko or ladybird….

… but maybe not if the surface spins too fast!