

Nanomanufacturing

University of Michigan

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Lecture 07 – Intermolecular and surface forces

Supplement to lecture slides

Forces keep the universe together. As stated by Israelachvili, There are three main types of forces:

- Intermolecular and surface forces, which are caused by electromagnetic interactions;
- Nuclear forces (“strong” and “weak”), which act over very short ($\sim 10^{-5}$ nm) ranges;
- Gravitational forces, which act over very long ranges.

The ancient Greeks said that there are only two forces—love and hate—explain everything. We will not consider these forces!

In principle, we could write Schrodinger’s equation for a prescribed geometry and then determine the interaction forces by solving for the electrostatic fields. However, it is impossible to do this exactly even for just a pair of hydrogen atoms. Instead, we will consider pairwise interaction potentials.

Recall the interatomic potential from the lecture on mechanical properties. Here we will consider more general features of this potential, which is a superposition of repulsive (short range) and attractive (long range) interactions. We saw then that the potential (denoted U, V, or W; with units of energy, e.g., [J] typically has a minimum at a particular spacing, denoting the equilibrium spacing between two atoms. Now we consider that assemblies of atoms, e.g., particles or surfaces, also have interaction potentials which can be derived by a superposition of the atomic interaction potentials.

Recall that, by taking derivatives, potential [J] \rightarrow force [J/m = N] \rightarrow stiffness [N/m]. Today we will derive the interaction potentials for simple bodies, and once again take the derivative to find the force as a function of the distance between the bodies.

Typically, an interaction potential has the form

$$U = \frac{C}{r^n},$$

where $n > 3$ guarantees that the potential will be finite over infinite distances. We will see this arise quantitatively later.

This understanding began to develop in 1873 when JD van der Waals proposed deviations from the ideal gas law to account for interactions between molecules, and for the finite size of the molecules. Then, in 1903, Mie proposed a “pair potential”,

$$U(r) = -\frac{A}{r^n} + \frac{B}{r^m}.$$

This adds the attractive and repulsive potentials. Today, we primarily discuss van der Waals forces which are considered “long range”. Next week, we will meet electrostatic forces. Together, van der Waals forces and electrostatic forces will let us build a simple picture of colloid stability. We will also learn about surface energy and capillary forces. Altogether these forces will help build our understanding of self-assembly.

interaction between a particle and a surface: ("molecule and surface")

$$W = \text{potential} = \int \frac{w}{r^n} dV$$

$$\text{total} = (\text{potential/particle}) (\# \text{ particles})$$

$$w = -c/r^n \text{ per particle}$$

$$r = \sqrt{x^2 + z^2}$$

$\rho = \#$ density of particles in solid.

$$\Rightarrow \int \frac{w}{r^n} dV = -2\pi\rho c \int_D dz \int_0^\infty \frac{x}{(\sqrt{x^2 + z^2})^n} dx$$

$$dV = 2\pi x dx dz$$

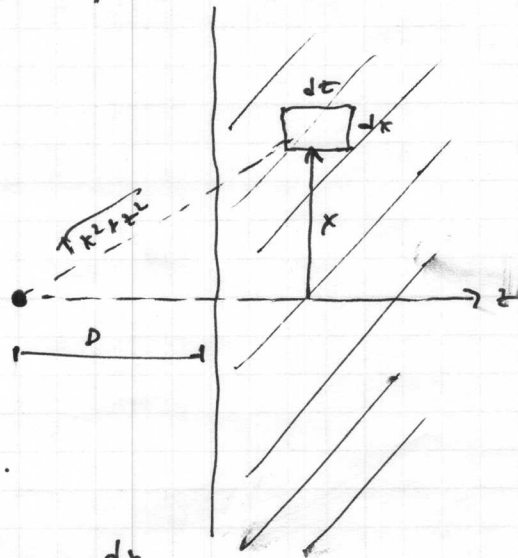
$$\int \frac{x}{(x^2 + z^2)^{n/2}} dx = \frac{1}{(n-2)(x^2 + z^2)^{n/2-1}}$$

$$\Rightarrow W = -2\pi\rho c \int_D dz \left(\frac{1}{(n-2)(x^2 + z^2)^{n/2-1}} \right) = \frac{2\pi\rho c}{n-2} \int_D \frac{1}{z^{n-2}}$$

$$= \frac{2\pi\rho c}{n-2} \left(\frac{1}{n-3} \right) \left(\frac{1}{z^{n-3}} \right)_D$$

$$= \frac{-2\pi\rho c}{(n-2)(n-3)} \left(\frac{1}{D^{n-3}} \right) \Rightarrow \text{always } D > 3$$

or attraction is infinite for finite bodies

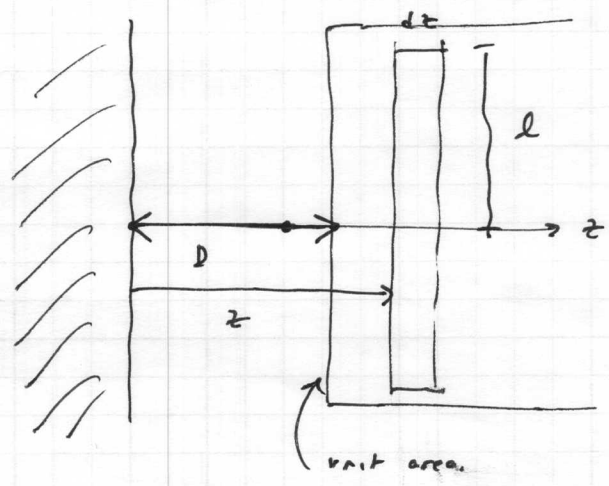


for row forces, $n = 6$

$$\Rightarrow w(D) = \frac{-\pi p c}{6 D^3} \quad \leftarrow \text{molecule to plane}$$

now consider a surface - surface interaction, simplest case is two flat surfaces

We just derived a molecule + surface, so now we simply sum the interactions for all molecules in the surface.



consider dz = the "slice" shown at right,

for a unit area of surface, the # of molecules = ρdz

$$dV = (\text{unit area}) (dz)$$

$$\text{total energy} = \int_V (\text{unit area}) (\rho) (dz) (\text{particle-surface energy})$$

$$= \frac{-2\pi c \rho^2}{(n-2)(n-3)} \int_D^\infty \frac{dz}{z^{n-3}}$$

$$= \frac{-2\pi c \rho^2}{(n-2)(n-3)(n-4)} \left(\frac{1}{D^{n-4}} \right)$$

which for vdw forces, $n = 6$

$$\Rightarrow w(D) = \frac{-\pi c \rho^2}{12 D^2} \quad \leftarrow \text{plane-plane}$$

recall $F = \frac{dw}{dz} = \frac{dw}{dD}$

for molecule-plane: $F = \frac{d}{dD} \left(\frac{-\pi \rho c}{6 D^3} \right) = \frac{-\pi \rho c}{2 D^4}$

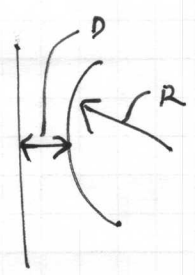
plane-plane: $F = \frac{-\pi c \rho^2}{6 D^3}$

note these "body-body" interactions decay much more slowly than the constituent particle-particle or molecule-molecule

forces, e.g. $\frac{1}{D^2}$ or $\frac{1}{D^3}$ vs $\frac{1}{D^6}$

see table of interaction potentials for typical solid bodies

for a sphere-plate: $w(D) = \frac{-\pi^2 \rho c R}{6D}$, for $R \gg D$
 radius } spring



"effective interaction area" for sphere-plate: Model the sphere-plate as 2 plates, 1 of effective area A_{eff} .

$$w(D)_{plates} (A_{eff}) = w(D)_{sphere-plate}$$

$$\frac{-\pi c \rho^2}{(2D)^2} A_{eff} = \frac{-\pi^2 c \rho^2 R}{6D}$$

$$\Rightarrow \underline{A_{eff} = 2\pi R D} \leftarrow \text{Langhein approximation}$$

in many experiments we can measure the force between curved surfaces but want to relate it to the interaction energy between planar surfaces.

Accordingly the Derjaguin approximation:

$$F(D)_{curved} = 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) w(D)_{planes} \equiv \text{work of adhesion}$$

at some separation D

applies to any force law as long as $D \ll (R_1, R_2)$

used in practice with the surface force apparatus

VDW forces based on Hamaker constant, defined as

$$A = \pi^2 C \rho_1 \rho_2$$

~~X~~ # atoms / volume.

before we assumed $\rho_1 = \rho_2$

$$\Rightarrow C = \frac{A}{\pi^2 \rho_1 \rho_2}$$

typically $A \approx 10^{-19}$ J in vacuum

example: 2 surfaces in "contact", $D = 2$ nm (roughness of polished \approx polished \approx).

$$F_{\text{plane-plane}} = \frac{\pi C \rho^2}{60^3} = \frac{A}{\pi^2 \rho^2} \left(\frac{\rho^2 \pi}{60^3} \right) = \frac{A}{6 \pi D^3}$$

$$= 7 \times 10^8 \text{ N/m}^2$$

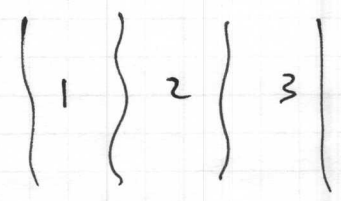
$$= 7000 \text{ atm!}$$

Must consider all atom-atom interactions in calculating A, not just independent pairwise interactions

Accordingly, Lifshitz theory calculates A based on bulk material properties - dielectric constant and index of refraction.

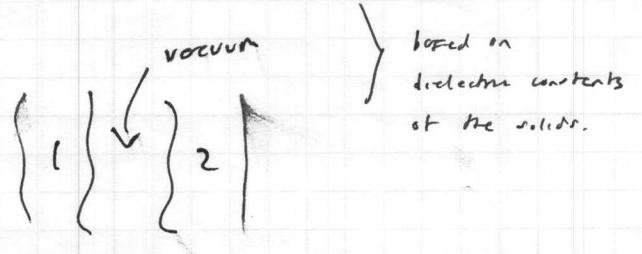
We can still use the relations calculated based on pairwise interactions but we use the A values determined by Lifshitz theory

further, we can combine Hamaker constants to account for different materials and interaction media



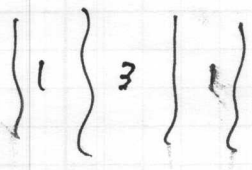
always > 0

→ $A_{12} \equiv \sqrt{A_{11} A_{22}}$
 interacting across vacuum



always > 0

→ $A_{131} \equiv (\sqrt{A_{11}} - \sqrt{A_{33}})^2$
 interacting across medium 3



may be > 0 or < 0

→ $A_{132} \cong \pm \sqrt{A_{131} A_{232}}$
 $= (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$

any 2 bodies in vacuum - always attractive

same material across any medium - always attractive

different materials across a medium ~ may be attractive or repulsive.