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 (~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 Schrödinger’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 \( n \geq 3 \) 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:

\[ W = \text{potential} = \int \frac{w}{\rho} \, dV \]

\[ \text{total} = \left( \frac{\text{potential/particle}}{\text{particle}} \right) (M \text{ particles}) \]

\[ W = -\frac{c}{r^n}, \text{ per particle} \]

\[ r = \sqrt{x^2 + z^2} \]

\[ \rho = \text{density of particles in solid} \]

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

\[ \int \frac{1}{(x^2 + z^2)^{n/2}} \, dx = \frac{2\pi r^n}{(n-2)D} \]

\[ \frac{2\pi r^n c}{(n-2)D} \left( \frac{1}{\frac{1}{n-3}} \right) \left( \frac{1}{D} \right) \]

\[ \Rightarrow \text{always } D > 3 \]

or attraction is infinite for finite bodies.
for now forces, \( n = 6 \)

\[
-W(D) = -\frac{\Pi f c}{6 D^2} \quad \Leftrightarrow \text{ molecule to plane}
\]

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 \( dV \) the "slice" shown at right,

for a unit area of surface, the # of molecules = \( \int dV \)

\[
dV = \text{(unit area)}(d\tau)
\]

total energy = \( \int \text{(unit area)}(p)(d\tau)(\text{particle - surface energy}) \)

\[
= -\frac{2\pi c p^2}{(n-2)(n-3)} \int_D \frac{d\tau}{D^{n-3}}
\]

\[
= -\frac{2\pi c p^2}{(n-2)(n-3)(n-4)} \left( \frac{1}{D^{n-4}} \right)
\]
which for vdW forces, \( n = 6 \)

\[
W(d) = -\frac{\pi c \rho^2}{12d^2}
\]

plane - plane

recall \( F = \frac{dW}{dz} = \frac{dW}{dD} \)

for molecule - plane:

\[
F = \frac{d}{dD} \left( -\frac{\pi c \rho^2}{6d^3} \right) = -\frac{\pi c \rho^2}{2D^4}
\]

plane - plane:

\[
F = \frac{-\pi c \rho^2}{6D^3}
\]

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: \( w(D) = \frac{-\pi^4 \rho c R}{6D}, \) for \( R > D \)

\[ \text{"effective interaction area" for sphere-plate: model the sphere-plate as 2 plates, 1 of effective area } A_{\text{eff}}. \]

\( w(D) \text{ plates } (A_{\text{eff}}) = w(D) \text{ sphere-plate} \)

\( \frac{-\pi^4 \rho c^2}{(2D^2)} A_{\text{eff}} = \frac{-\pi^4 \rho c^2 R}{6D} \)

\[ \Rightarrow A_{\text{eff}} = \frac{2\pi R D}{\rho c^2} \text{ Langbein approximation} \]

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

Accordingly, the Debye-Hückel approximation:

\[ F(D)_{\text{curved}} = 2\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right) w(D)_{\text{planes}} \]

\[ \Rightarrow \text{work of adhesion} \]

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

used in practice with the surface force apparatus.
van der Waals force based on Hamaker constant, defined as

\[ A = \pi^2 C \rho_1 \rho_2 \rho_3 \]

* assumes volume

before we assumed \( \rho_1 = \rho_2 \)

\[ D = \frac{A}{\pi^4 \rho_1 \rho_2} \]

typically \( A = 10^{-19} \text{ J} \) in vacuum

example: 2 surfaces in "contact", \( D = 2 \text{ nm} \) (roughness of polished m.)

\[ F_{\text{plane-plane}} = \frac{\pi C \rho_1}{6 \rho_3^3} = \frac{A}{\pi^4 \rho_1 \rho_2} \left( \frac{\rho_3^3}{6 \rho_3^3} \right) = \frac{A}{6 \pi \rho_3^3} \]

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

\[ = 7 \text{ GPa} \]

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 point charge interactions but we use the $A$ values determined by Lifschitz theory.

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

\[
\begin{pmatrix}
1 \\
2 \\
3
\end{pmatrix}
\]

- Interacting across vacuum:
  \[ A_{12} \equiv \sqrt{A_{11} A_{22}} \]

- Interacting across medium:
  \[ A_{13} \equiv (\sqrt{A_{11}} - \sqrt{A_{33}})^2 \]

- May be $> 0$ or $\leq 0$:
  \[ A_{13} \equiv \pm \sqrt{A_{131} A_{232}} \]

\[ \approx (\sqrt{A_{11}} - \sqrt{A_{22}})(\sqrt{A_{22}} - \sqrt{A_{33}}) \]

For any 2 bodies in vacuum - always attractive.

- Some materials across any medium - always attractive.
- Different materials across a medium - may be attractive or repulsive.