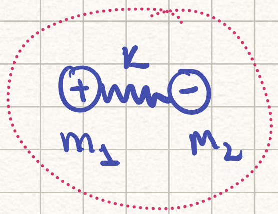
Van der Waals and Lennard-Jones potential

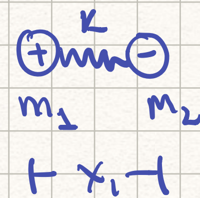


Dist. charge

Molecule

Dipole $\quad$ It's moving with velocity $\vec{v}$

Energy of Dipole



$$E = \frac{1}{2} m_1 v^2 + \frac{1}{2} m_2 v^2 + \frac{1}{2} k x_1^2$$

m : mass of the atom

$m = m_1 + m_2$

ω_0: frequency of oscillation $\qquad \omega_0 = \sqrt{\frac{k}{m}}$

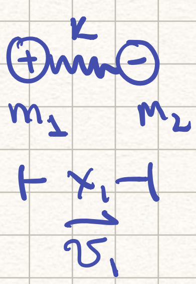
$$E = \frac{1}{2}(m_1 + m_2) v^2 + \frac{1}{2} m \omega_0^2 x_1^2 \qquad \omega_0^2 = \frac{k}{m} \Rightarrow k = m\omega_0^2$$

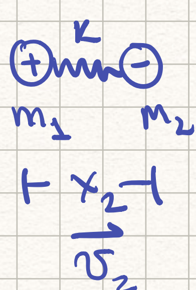
$$= \frac{1}{2} m v^2 + \frac{1}{2} m \omega_0^2 x_1^2 \qquad p = mv$$

$$p^2 = m^2 v^2$$

$$\boxed{H_0 = \frac{1}{2m} p^2 + \frac{1}{2} m \omega_0^2 x_1^2}$$

Hamiltonian of the Dipole : Total energy



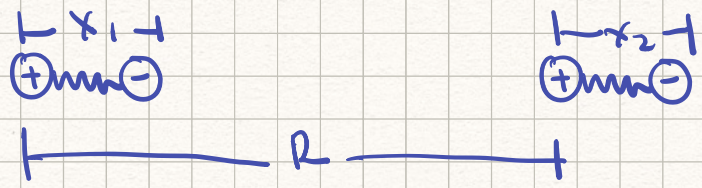


$P_1 = m v_1$

$P_2 = m v_2$

$$H_0 = \frac{1}{2m} P_1^2 + \frac{1}{2} m \omega_0^2 x_1^2 + \frac{1}{2m} P_2^2 + \frac{1}{2} m \omega_0^2 x_2^2$$

Charges feel Coulomb force $\Rightarrow H_{int}$



$$H_{int} = \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{R} + \frac{1}{R+x_2-x_1} - \frac{1}{R+x_2} - \frac{1}{R-x_1}\right]$$

$R \gg x_1, x_2$

Taylor expansion

$$\frac{1}{R \pm x} \approx \frac{1}{R} \mp \frac{x}{R^2}$$

$$\frac{1}{R+x_2-x_1} \approx \frac{1}{R} + \frac{x_1}{R^2} - \frac{x_2}{R^2} - \frac{2x_1x_2}{R^3}$$

H_{int} becomes

$$\boxed{H_{int} = -\frac{2e^2x_1x_2}{4\pi\epsilon_0 R^3}}$$

Total Hamiltonian $H_T = H_0 + H_{int}$

$$H_T = \frac{1}{2m}p_1^2 + \frac{1}{2}m\omega_0^2x_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{2}m\omega_0^2x_2^2 - \frac{2e^2x_1x_2}{4\pi\epsilon_0 R^3}$$

The H_T can be diagonalized

→ change of variable

Transformation:

$$x_1 = \frac{1}{\sqrt{2}}(x_s + x_a) \qquad p_1 = \frac{1}{\sqrt{2}}(p_s + p_a)$$

$$x_2 = \frac{1}{\sqrt{2}}(x_s - x_a) \qquad p_2 = \frac{1}{\sqrt{2}}(p_s - p_a)$$

$$P_1^2 = \frac{1}{2}\left(P_s^2 + P_a^2 + 2P_sP_a\right) \qquad x_1^2 = \frac{1}{2}\left(x_s^2 + x_a^2 + 2x_sx_a\right)$$

$$P_2^2 = \frac{1}{2}\left(P_s^2 + P_a^2 - 2P_sP_a\right) \qquad x_2^2 = \frac{1}{2}\left(x_s^2 + x_a^2 - 2x_sx_a\right)$$

$$x_1x_2 = \frac{1}{2}\left(x_s^2 - x_a^2\right)$$

$$H_T = \frac{1}{2m}P_1^2 + \frac{1}{2}m\omega_0^2x_1^2 + \frac{1}{2m}P_2^2 + \frac{1}{2}m\omega_0^2x_2^2 - \frac{2e^2x_1x_2}{4\pi\epsilon_0 R^3}$$

$$= \frac{1}{2m}\left(P_1^2+P_2^2\right) + \frac{1}{2}m\omega_0^2\left(x_1^2+x_2^2\right) - \frac{2e^2x_1x_2}{4\pi\epsilon_0 R^3}$$

$$P_1^2 + P_2^2 = P_s^2 + P_a^2 \qquad x_1^2 + x_2^2 = x_s^2 + x_a^2$$

$$= \frac{1}{2m}\left(P_s^2 + P_a^2\right) + \frac{1}{2}m\omega_0^2\left(x_s^2 + x_a^2\right) - \frac{e^2}{4\pi\epsilon_0}\frac{x_s^2 - x_a^2}{R^3}$$

$$= \frac{1}{2m}P_s^2 + \frac{1}{2}m\omega_0^2x_s^2 - \frac{e^2}{4\pi\epsilon_0}\frac{x_s^2}{R^3}$$

$$+ \frac{1}{2m}P_a^2 + \frac{1}{2}m\omega_0^2x_a^2 + \frac{e^2}{4\pi\epsilon_0}\frac{x_a^2}{R^3}$$

$$H_T = \frac{P_s^2}{2m} + \left(\frac{1}{2}m\omega_0^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{R^3}\right)x_s^2$$

$$+ \frac{P_a^2}{2m} + \left(\frac{1}{2}m\omega_0^2 + \frac{e^2}{4\pi\epsilon_0}\frac{1}{R^3}\right)x_a^2$$

$$= \frac{P_s^2}{2m} + \frac{1}{2}m\omega_s^2x_s^2 + \frac{P_a^2}{2m} + \frac{1}{2}m\omega_a^2x_a^2$$

$$\frac{1}{2}m\omega_s^2 = \frac{1}{2}m\omega_0^2 - \frac{e^2}{4\pi\epsilon_0}\frac{1}{R^3}$$

$$\omega_s^2 = \omega_0^2 - \frac{2e^2}{4\pi\epsilon_0 m R^3} = \omega_0^2\left[1 - \frac{2e^2}{4\pi\epsilon_0 m R^3\omega_0^2}\right]$$

$$\omega_a^2 = \omega_0^2\left[1 + \frac{2e^2}{4\pi\epsilon_0 m R^3\omega_0^2}\right]$$

$$\omega_{s/a} = \omega_0 \sqrt{1 \mp \frac{2e^2}{4\pi\epsilon_0 m R^3 \omega_0^2}}$$

$\sqrt{1 \pm x}$ with $x \ll 1$: Taylor expansion

$$\sqrt{1 \pm x} \approx 1 \pm \frac{x}{2} - \frac{x^2}{8} \pm \ldots$$

$$\omega_{s/a} = \omega_0 \left[1 \mp \frac{1}{2} \left(\frac{2e^2}{4\pi\epsilon_0 m R^3 \omega_0^2} \right) - \frac{1}{8} \left(\frac{2e^2}{4\pi\epsilon_0 m R^3 \omega_0^2} \right)^2 \mp \ldots \right]$$

$E_n = \hbar\omega (n + 1/2)$ $\quad E_0 = \frac{1}{2}\hbar\omega$: zero-point energy

$$\frac{1}{2}\hbar(\omega_s + \omega_a) = \frac{\hbar\omega_0}{2}\left[1 - \frac{1}{2}\left(\frac{2e^2}{4\pi\epsilon_0 m R^3 \omega_0^2} \right) - \frac{1}{8}\left(\frac{2e^2}{4\pi\epsilon_0 m R^3 \omega_0^2} \right)^2 \right]$$
$$+ \frac{\hbar\omega_0}{2}\left[1 + \frac{1}{2}\left(\frac{2e^2}{4\pi\epsilon_0 m R^3 \omega_0^2} \right) - \frac{1}{8}\left(\frac{2e^2}{4\pi\epsilon_0 m R^3 \omega_0^2} \right)^2 \right]$$
$$= \hbar\omega_0 - \frac{\hbar\omega_0}{8}\left(\frac{2e^2}{4\pi\epsilon_0 m R^3 \omega_0^2} \right)^2$$

Deviation on the energy

$$\Delta U = \frac{\hbar}{2}(\omega_s + \omega_a) - \hbar\omega_0$$
$$= -\frac{\hbar\omega_0}{8}\left(\frac{2e^2}{4\pi\epsilon_0 m R^3 \omega_0^2} \right)^2 = -\frac{\hbar\omega_0}{8}\left(\frac{2e^2}{4\pi\epsilon_0 m \omega_0^2} \right)^2 \frac{1}{R^6}$$

$$\boxed{U(R) = -\frac{A}{R^6}}$$

Van der Waals potential

- Attractive

Also known as

- London potentials
- Dipole-dipole interaction

$$A = \frac{\hbar\omega_0}{8}\left(\frac{2e^2}{4\pi\epsilon_0 m \omega_0^2} \right)^2$$

Principal attractive interaction in inert gases $\left\{ \begin{matrix} Ne & Xe \\ Ar & \\ Kr & Rn \end{matrix} \right.$

Repulsive interaction!

- Does not come from EM

→ Pauli exclusion principle ⇒ Q.M. concept

Empirically

$$U(R) = \frac{B}{R^{12}} \qquad B > 0$$

Overall

$$\boxed{U(R) = \frac{B}{R^{12}} - \frac{A}{R^6}}$$

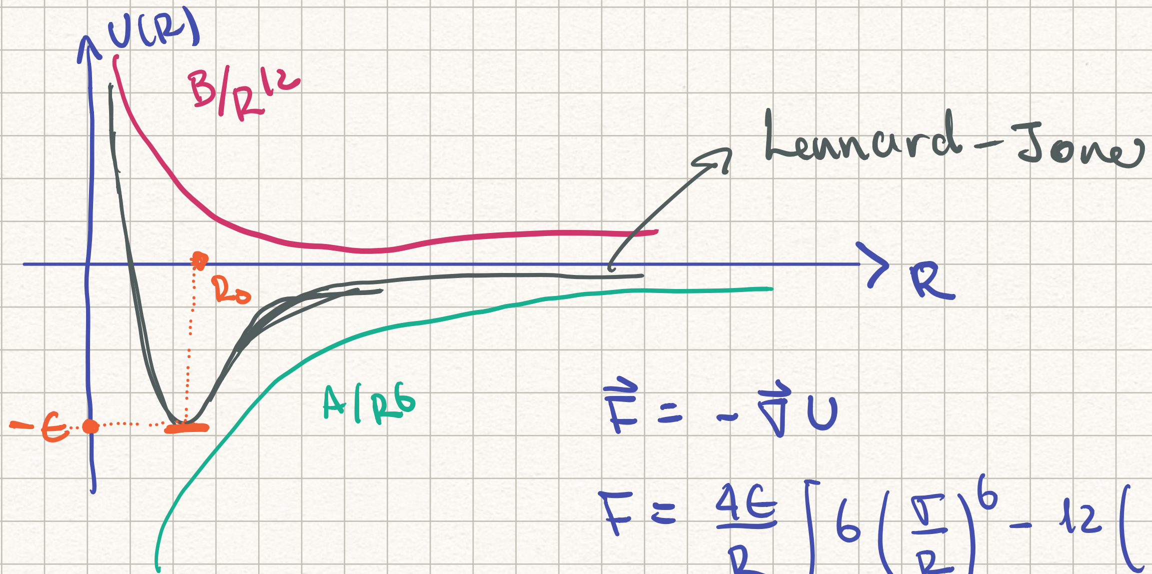
Lennard-Jones potential.

A, B can be measured for gases

$$\boxed{U(R) = 4\epsilon \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right]}$$

→ More common

$$A = 4\epsilon\sigma^6 \qquad B = 4\epsilon\sigma^{12}$$



$$\vec{F} = -\vec{\nabla} U$$

$$F = \frac{4\epsilon}{R} \left[6\left(\frac{\sigma}{R}\right)^6 - 12\left(\frac{\sigma}{R}\right)^{12} \right]$$

Force = 0 : equilibrium

$$R = 2^{1/6}\sigma = R_0$$

$$U(R_0) = -\epsilon$$