

24 sept.

Intermolecular forces

Interactions between dipoles.

a permanent electric dipole: $\begin{matrix} \leftarrow & l & \rightarrow \\ -q & & q \end{matrix}$

the dipole moment: $\vec{\mu} = q \cdot \vec{l}$,

Still reported in a non-SI unit; Debye

$$\begin{aligned} 1 \text{ D} &= 3.33564 \cdot 10^{-30} \text{ C} \cdot \text{m} \\ &= 1.602 \cdot 10^{-19} \text{ C} \cdot \text{\AA} \Rightarrow \\ &= \underline{1.602 \cdot 10^{-19} \text{ C}} \cdot \underline{2.082 \cdot 10^{-11} \text{ m}} \end{aligned}$$

examples:

	μ/D	$\alpha'/10^{-30} \text{ m}^3$
<chem>CCl4</chem>	0	10.5
<chem>H2</chem>	0	0.819
<chem>H2O</chem>	1.85	1.48
<chem>HCl</chem>	1.08	2.63
<chem>HI</chem>	0.42	5.45
	dipole moment	polarizability

An induced dipole moment

an applied electric field can distort a molecule as well as aligning its permanent μ . The induced dipole moment, μ^* , is in proportion to the field strength (ϵ).

$$\mu^* = \alpha \cdot \epsilon$$

A derived quantity is more often used.

$$\alpha' = \frac{\alpha}{4\pi\epsilon_0} \quad (\text{dimensions of volume: } 10^{-30} \text{ m}^3)$$

(5)

the potential energy of interaction:

the system; a dipole and an electric charge.



$$V = - \frac{\mu_1 \cdot q_2}{4\pi\epsilon_0 r^2}, \quad \mu_1 = q_1 \cdot l, \quad \text{because}$$

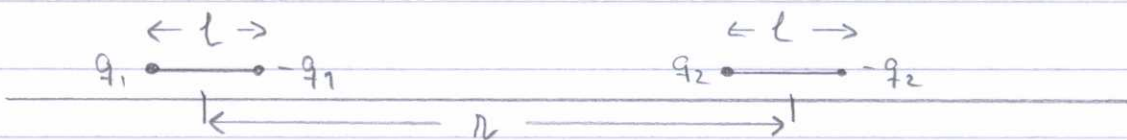
$$V = \frac{1}{4\pi\epsilon_0} \left(- \frac{q_1 \cdot q_2}{r - \frac{l}{2}} + \frac{q_1 \cdot q_2}{r + \frac{l}{2}} \right), \quad \text{assume } l \ll r$$

$$= \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r} \left(- \frac{1}{1-x} + \frac{1}{1+x} \right), \quad x \equiv \frac{l}{2r}$$

$$\approx \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r} \left\{ - (1+x \dots) + (1-x \dots) \right\}, \quad \text{expanding}$$

$$= - \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r} \cdot 2x = - \frac{q_1 \cdot q_2 \cdot l}{4\pi\epsilon_0 r^2} = - \frac{\mu_1 \cdot q_2}{4\pi\epsilon_0 r^2}$$

the system; two interacting dipoles.



the potential energy:

$$V = \frac{1}{4\pi\epsilon_0} \left(- \frac{q_1 \cdot q_2}{r+l} + \frac{q_1 \cdot q_2}{r} + \frac{q_1 \cdot q_2}{r} - \frac{q_1 \cdot q_2}{r-l} \right)$$

$$= \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r} \left(\frac{1}{1+x} - 2 + \frac{1}{1-x} \right); \quad x \equiv \frac{l}{r}$$

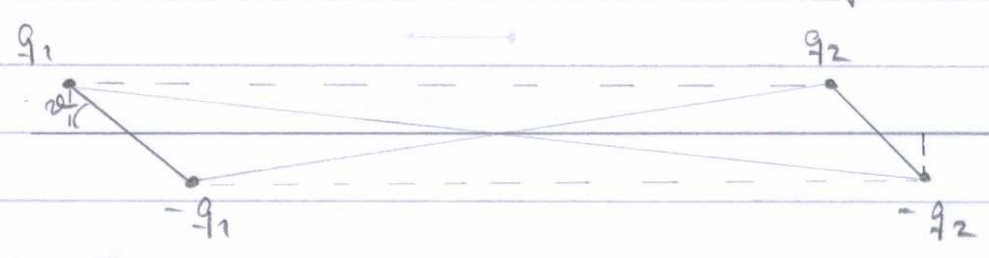
Expanding;

$$\frac{1}{1+x} \approx 1 - x + x^2 + \dots$$

$$\frac{1}{1-x} \approx 1 + x + x^2 + \dots$$

$$V = - \frac{q_1 \cdot q_2}{4\pi\epsilon_0 r} \cdot 2x^2 = - \frac{\mu_1 \cdot \mu_2}{4\pi\epsilon_0} \cdot \frac{2}{r^3}$$

When the dipoles makes an angle



$$V = \frac{1}{4\pi\epsilon_0} \left(- \frac{q_1 \cdot q_2}{rD} + \frac{q_1 \cdot q_2}{r} + \frac{q_1 \cdot q_2}{r} - \frac{q_1 \cdot q_2}{rd} \right)$$

$$\approx - \frac{\mu_1 \cdot \mu_2}{4\pi\epsilon_0 r^3} (1 - 3 \cos^2 \theta)$$

D: distance between q_1 and $-q_2$
 d: - " - $-q_1$ and q_2

$$D = 2 \sqrt{\left(\frac{r}{2}\right)^2 + \left(\frac{l}{2}\right)^2 - 2 \cdot \frac{l}{2} \cdot \frac{r}{2} \cdot \cos(\pi - \theta)}$$

$$d = 2 \sqrt{\left(\frac{r}{2}\right)^2 + \left(\frac{l}{2}\right)^2 - 2 \cdot \frac{l}{2} \cdot \frac{r}{2} \cdot \cos \theta}$$

which is Taylor expanded.

LONDON FORCES; van der Waals forces
the system



- Each electron is bound in an harmonic potential

$$V(x) = \frac{1}{2} k \cdot x^2$$

- In addition there is dipole interaction

$$V(x_1, x_2) = \frac{e^2}{n^3} \cdot x_1 \cdot x_2 \quad \left(\frac{1}{4\pi\epsilon_0} \equiv 1 \right)$$

$$\text{Total potential : } V = \frac{1}{2} k x_1^2 + \frac{1}{2} k x_2^2 + \frac{e^2}{n^3} \cdot x_1 \cdot x_2$$

the force constant is replaced by st. polarizability;

the electron is displaced in an external field:

$$k \cdot x = e \cdot E$$

$$\mu (\text{dipole moment}) = e \cdot x = e \frac{eE}{k} = \frac{e^2}{k} \cdot E \equiv \alpha \cdot E$$

$$\alpha = \frac{e^2}{k}$$

$$\text{Substitution: } X_D = \frac{1}{\sqrt{2}} (x_1 + x_2); \quad X_A = \frac{1}{\sqrt{2}} (x_1 - x_2)$$

$$\Rightarrow V = \frac{1}{2} f_D \cdot X_D^2 + \frac{1}{2} f_A \cdot X_A^2, \quad \text{where}$$

$$f_D \equiv f \left(1 + \frac{2\alpha}{n^3} \right), \quad f_A \equiv f \left(1 - \frac{2\alpha}{n^3} \right)$$

Schrödinger eq.

$$\frac{\partial^2 \psi}{\partial X_D^2} + \frac{\partial^2 \psi}{\partial X_A^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} f_D \cdot X_D^2 - \frac{1}{2} f_A \cdot X_A^2 \right) \psi = 0$$

The energy eigenvalues:

$$E = (m_0 + \frac{1}{2}) \hbar f_0 + (m_1 + \frac{1}{2}) \cdot \hbar f_1$$

The lowest eigenvalue: $E_0 = \frac{1}{2} \hbar (f_0 + f_1)$

The lowest energy of the independent osc.

$$E'_0 = 2 \left(\frac{1}{2} \hbar f \right)$$

Gain in ground state energy.

$$\begin{aligned} \Delta E_0 &\equiv E - E'_0 = \frac{1}{2} \hbar (f_0 + f_1) - \hbar f \\ &\approx - \frac{\hbar f \cdot d^2}{2 n^6} \end{aligned}$$

going to three dimensions:

$$\Delta E_0 = - \frac{3}{2} \cdot \frac{\hbar \cdot f \cdot d^2}{2 n^6}$$