

Lecture 16

Intermolecular Forces:

In formulating equation of state for real gas it was assumed that molecules do interact with each other i.e. there exists different kinds of intermolecular forces.

There exists different kinds of interaction between molecules:

1. Ion-Dipole interaction

Not present for neutral molecules

2. Ion-Induced Dipole interaction

3. Dipole – Dipole interaction (Keesom interaction, W. H. Keesom, 1922)

4. Dipole – Induced Dipole interaction (Debye interaction)

5. Induced Dipole – Induced Dipole interaction (London Dispersion interaction, Fritz London (German), 1930)

6. H-bonding etc.

Ion-Dipole interaction:

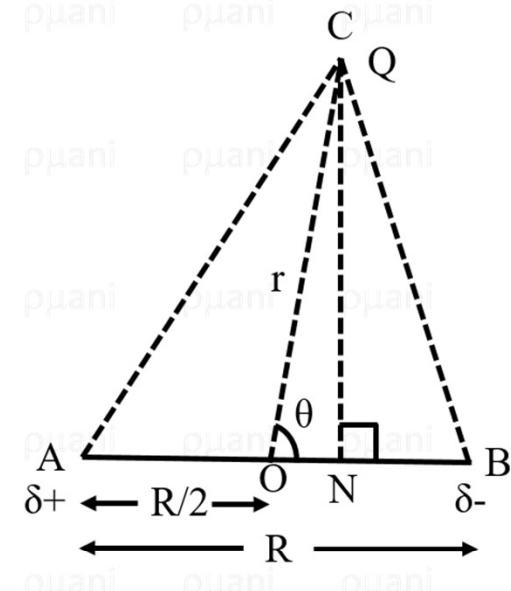
The corresponding interaction energy $u_{\text{ion-Dipole}} = (-) \frac{\mu_1 Q \cos \theta}{(4 \pi \epsilon_0) \times r^2}$

When the ion with the charge Q is collinear with the axis of the dipole:

The corresponding interaction energy $u_{\text{ion-Dipole}} = (-) \frac{\mu_1 Q}{(4 \pi \epsilon_0) \times r^2}$

Note that $r \gg R$

Negative sign in the above expressions means that the interaction is attractive in nature.



If the electronic charge and protonic charge are separated by a distance of 1\AA , then the dipole moment is defined as:

$$\mu = e \times r = (4.8 \times 10^{-10}) \times (1 \times 10^{-8}) \text{ esu. cm} = 4.8 \times 10^{-18} \text{ esu. cm}$$

$$1\text{Debye} = 1 \times 10^{-18} \text{ esu. cm}$$

Thus, $\mu = 4.8 \text{ Debye}$

$$\mu = e \times r = (1.6 \times 10^{-19}) \times (1 \times 10^{-10}) \text{ C m} = 1.6 \times 10^{-29} \text{ C m}$$

Dipole-Dipole interaction (W. H. Keesom interaction (1922))

When the molecule is polar: This means that there exists electrical asymmetries. This means there exists positively and negatively charged centroid (both equally charged in magnitude) within the molecule. When polar molecules come close to each other they try to orient themselves in such a manner that oppositely charged centres attract one another. The potential energy for such interaction has been shown to be inversely proportional to sixth power of distance between the molecules i.e.

$$U_{\text{int-orientation}} = -A_1 \times r^{-6}$$

[(-)ve sign is given for attraction]

$$A_1 (\text{identical}) = \frac{2 \mu^4}{(4 \pi \epsilon_0)^2 \times 3 k_B T}$$

$$A_1 (\text{non-identical}) = \frac{2 \mu_1^2 \mu_2^2}{(4 \pi \epsilon_0)^2 \times 3 k_B T}$$

Dipole-dipole interaction
(Keesom force)



More likely

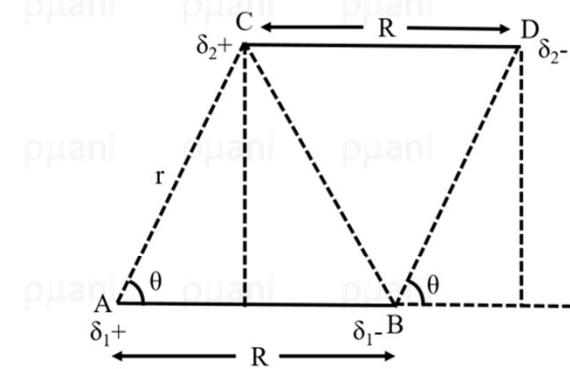


Less likely

Here, μ = dipole moment of the molecule and ϵ_0 = permittivity of free space

$$U_{\text{int-orientation}} (\text{identical}) = (-) \frac{2 \mu^4}{(4 \pi \epsilon_0)^2 \times 3 k_B T \times r^6}$$

$$U_{\text{int-orientation}} (\text{non-identical}) = (-) \frac{2 \mu_1^2 \mu_2^2}{(4 \pi \epsilon_0)^2 \times 3 k_B T \times r^6}$$



These are known as *Keesom interaction energy* which arises because of *orientation effect*. The negative sign means that the interaction is attractive in nature. Note its temperature dependence.

Dipole-Induced dipole interaction (Debye force):

In addition to orientation effect, polar molecules tend to induce a moment on each other. This is known as induction effect. Thus, potential energy of interaction because of induction effect is

$$U_{\text{int-induction}} = -A_2 \times r^{-6}$$

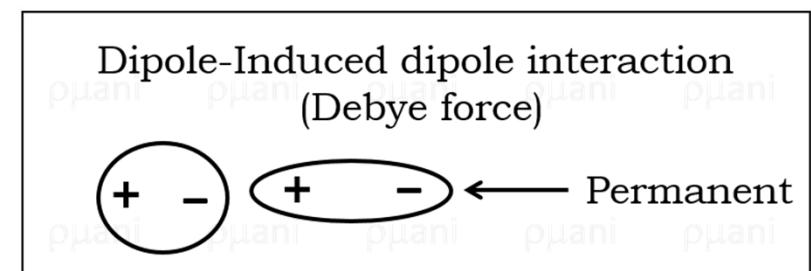
$$A_2 (\text{identical}) = \frac{2 \mu^2 \alpha}{(4 \pi \epsilon_0)^2}$$

$$A_2 (\text{non-identical}) = \frac{\mu_1^2 \alpha_2 + \mu_2^2 \alpha_1}{(4 \pi \epsilon_0)^2}$$

Here, α = polarizability
 $(\mu_{\text{induced}}) = \alpha E$

$$\frac{\alpha}{4 \pi \epsilon_0} = \text{polarizability volume}$$

A_2 magnitude depends on dipole moment and polarizability of the molecules.



$$U_{\text{int-induction}} (\text{identical}) = (-) \frac{2 \mu^2 \alpha}{(4 \pi \epsilon_0)^2 \times r^6}$$

$$U_{\text{int-induction}} (\text{non-identical}) = (-) \frac{\mu_1^2 \alpha_2 + \mu_2^2 \alpha_1}{(4 \pi \epsilon_0)^2 \times r^6}$$

The negative sign means that the force or energy or interaction is attractive in nature.

London dispersion force (London Dispersion interaction (1930)):

When the molecule is non-polar: A molecule is nonpolar because of no net electrical asymmetry. However, it is now known that the net zero moment is because of net result of large number of instantaneous and electrical asymmetric arrangements which are momentarily polar. Those fleeting/transient (quickly vanishing) polar configurations do induce moment to neighbouring molecules and in consequence attractive force originates. Potential energy out of this kind of attraction is known as dispersion energy.

$$U_{\text{int-dispersion}} = -A_3 \times r^{-6}$$

$$A_3 (\text{identical}) = \frac{3}{4} I_E \left(\frac{\alpha}{4\pi\epsilon_0} \right)^2$$

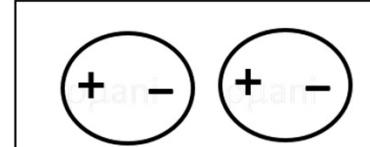
$$A_3 (\text{non-identical}) = \frac{3}{2} \left(\frac{I_1 I_2}{I_1 + I_2} \right) \frac{\alpha_1 \alpha_2}{(4\pi\epsilon_0)^2}$$

[Note: no permanent dipole moment term]

This interaction energy increases with increase in size (I_2 is solid, Br_2 liquid)

Here, I_E = Ionisation energy ; α = polarizability

Constant A_3 depends on polarizability and ionisation energy of the molecules.



↑
London dispersion force
Fritz London (German)

Combining above three equations, potential energy due to attraction is given by:

$$U_{\text{attraction}} = -(A_1 + A_2 + A_3) \times r^{-6} = -A \times r^{-6}$$

Lennard – Jones potential:

$$u(r) = \frac{B}{r^{12}} - \frac{A}{r^6}$$

For identical molecules, $A = \frac{2 \mu^4}{(4 \pi \epsilon_0)^2 \times 3 k_B T} + \frac{2 \alpha \mu^2}{(4 \pi \epsilon_0)^2} + \frac{3}{4} \frac{I \alpha^2}{(4 \pi \epsilon_0)^2}$

Attractive potential:

(Keesom)	(Debye)	(London)
$\frac{2 \mu_1^2 \mu_2^2}{(4 \pi \epsilon_0)^2 \times 3 k_B T}$	$\frac{\mu_1^2 \alpha_2 + \mu_2^2 \alpha_1}{(4 \pi \epsilon_0)^2}$	$\frac{3}{2} \left(\frac{I_1 I_2}{I_1 + I_2} \right) \frac{\alpha_1 \alpha_2}{(4 \pi \epsilon_0)^2}$
Dipole-dipole	Dipole – Induced dipole	Induced dipole – induced dipole
(Keesom)	(Debye)	(London)

(Keesom, Debye, London forces are known as van der Waals forces – all attractive in nature!)

When the molecules are sufficiently close, then individual electron density encroach upon each other, and thus repulsive force starts to operate. The interaction energy because of repulsion was shown (by John Edward Lennard-Jones (1924)) to be

$$U_{\text{int-repulsion}} = +B \times r^{-n} \quad [n \text{ varies between 9 and 15}]$$

An average of $n = 12$ is taken, then $U_{\text{repulsion}} = +B \times r^{-12}$

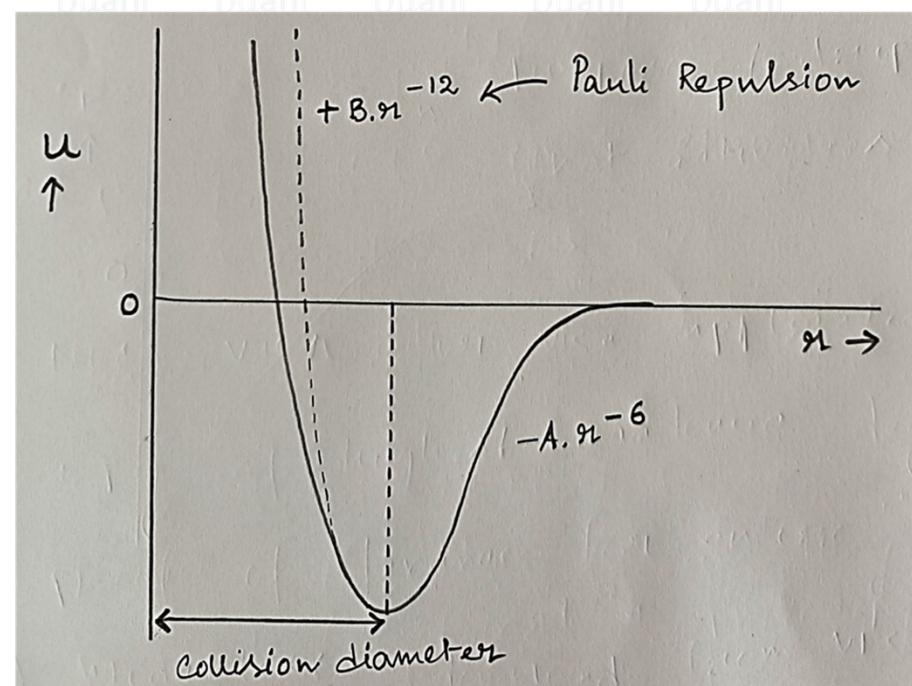
Thus, the total interaction energy, $u = u_{\text{attraction}} + u_{\text{repulsion}}$

$$\text{Thus, } u = -A \times r^{-6} + B \times r^{-12}$$

This is Lennard-Jones 6-12 potential

Thus at sufficiently large (!) distance, the interaction energy is almost nil. As distance decreases, attractive interaction energy dominates, thus interaction energy decreases. When the distance is very small, then repulsive interaction energy dominates and thus interaction energy increases.

Because of the two opposite interaction a minimum is observed. At this point of intersection, where attraction and repulsive interaction balance each other. The corresponding distance (r) is known as collision diameter.



Interaction energy for a pair of molecules

$$u(r) = 4 \varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

$$\Rightarrow \frac{du}{dr} = 4 \varepsilon \left[\frac{-12\sigma^{12}}{r^{13}} + \frac{6\sigma^6}{r^7} \right] = 0$$

$$\Rightarrow \frac{6\sigma^6}{r_{\min}^7} = \frac{12\sigma^{12}}{r_{\min}^{13}}$$

$$\Rightarrow r_{\min}^6 = 2\sigma^6$$

$$\boxed{r_{\min} = 2^{\frac{1}{6}} \times \sigma}$$

$$\Rightarrow r_{\min} = 1.12 \times \sigma$$

Putting this value in equation (1) we get

$$u(r_{\min}) = 4 \varepsilon \left[\left(\frac{\sigma}{2^{\frac{1}{6}} \times \sigma} \right)^{12} - \left(\frac{\sigma}{2^{\frac{1}{6}} \times \sigma} \right)^6 \right]$$

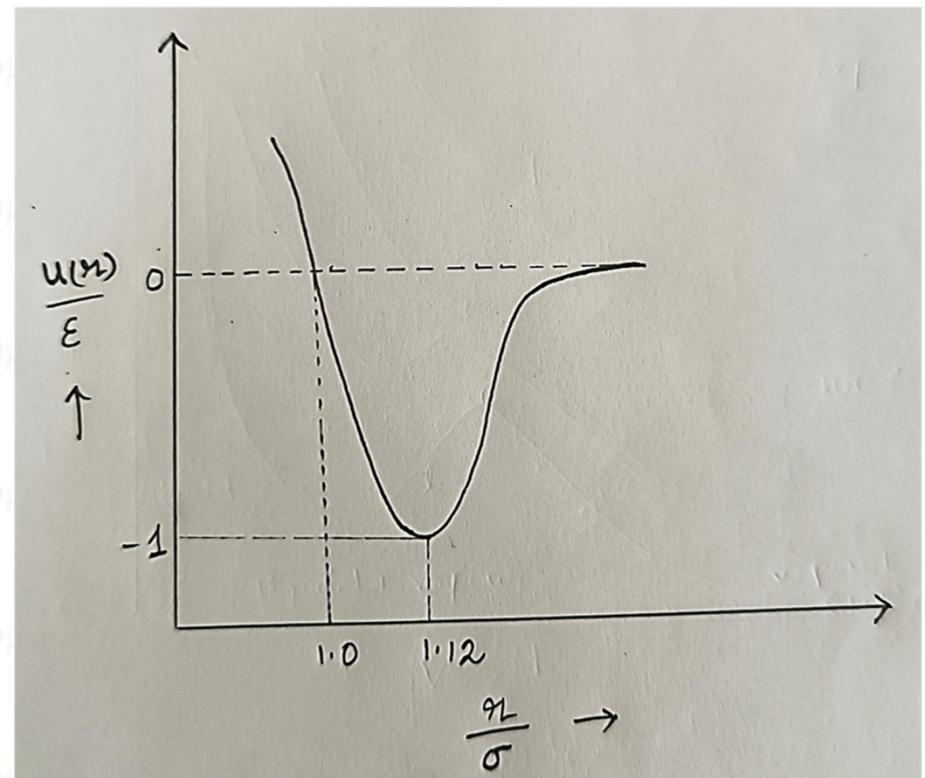
$$= 4 \varepsilon \times \left[\frac{1}{4} - \frac{1}{2} \right] = (-) \varepsilon$$

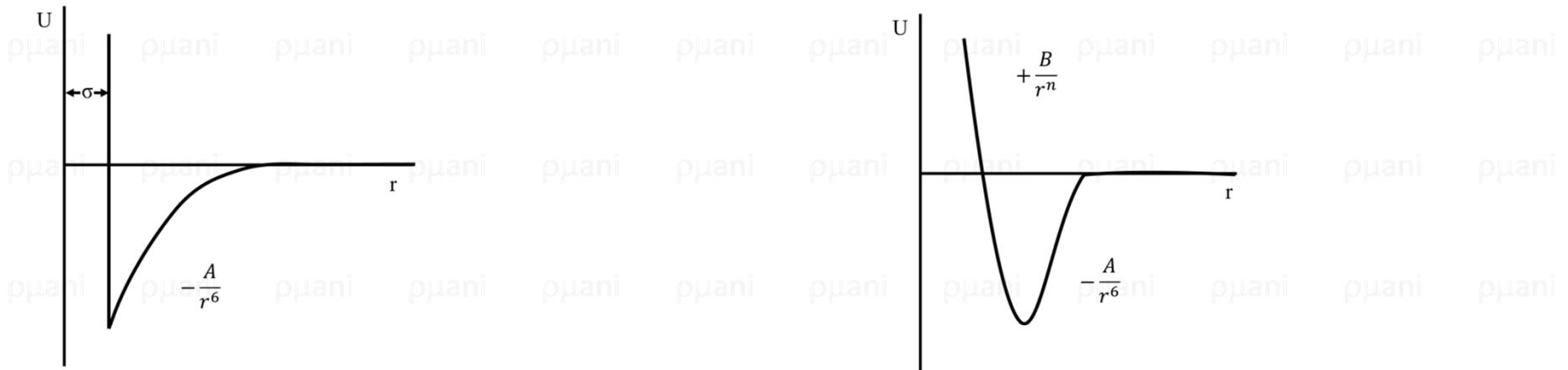
$\varepsilon \rightarrow$ depth of the potential well

$\sigma \rightarrow$ distance at which $u(r) = 0$

$\varepsilon \rightarrow$ measure of how strongly the molecules attract each other

$\sigma \rightarrow$ measure of size of the molecule





(van der Waals potential)
 (attractive) (hard sphere model)

$n = 8$ considering the quadrupole consideration or higher terms considering higher multipoles.

(Lennard Jones potential)
 (both attractive and repulsive)
 (Diffuse electron cloud model)

$n = 12$ in general.

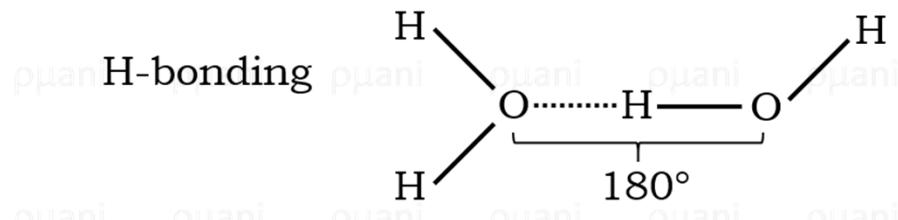
You will learn other potential energy functions e.g. Morse potential, Mie potential etc. at higher classes.

Question: What are the dimensions of the attractive and repulsive forces?

Question: Where are the minima for van der Waals and Lennard-Jones potentials?

Question: What are the physical significances of the van der Waals constants (a and b)?

Ion-induced dipole similar to dipole-induced dipole type where ion is present in place of dipole.



Ion-dipole > dipole-dipole

Ion-induced dipole > dipole-induced dipole

Ion-dipole ~50-200 kJ/mol or ~10-50 kcal/mol

Bond	Energy (kcal/mol)
Ionic lattice energy	250-4000
Covalent	30-250
Ion-dipole	10-50
London	1-15
Dipole-dipole	0.5-2
H-bonding	1-12 (Pauling)

van der Waals interactions in common molecules at 25°C:

Molecule	Dipole Moment (D)	Dipole – Dipole interaction energy (Orientation effect) (Keesom interaction) ($A_1 \times 10^{60}$ in erg cm ⁶ unit)	Dipole – Induced Dipole interaction energy (Induction effect) (Debye interaction) ($A_2 \times 10^{60}$ in erg cm ⁶ unit)	Induced Dipole – Induced Dipole interaction energy (Dispersion effect) (London interaction) ($A_3 \times 10^{60}$ in erg cm ⁶ unit)
Ar				50
N ₂				58
C ₆ H ₆				1086
HCl	1.03	22	6	106
SO ₂	1.63	114	20	205
H ₂ O	1.8	190	11	38
HCN	2.98	1277	46	111

Value Source: Physical Chemistry by Ira Levine

- For non-polar molecules only London-dispersion interaction is present
- For highly polar molecules Keesom interaction is generally larger than the Debye interaction
- Debye interaction is generally quite small in magnitude