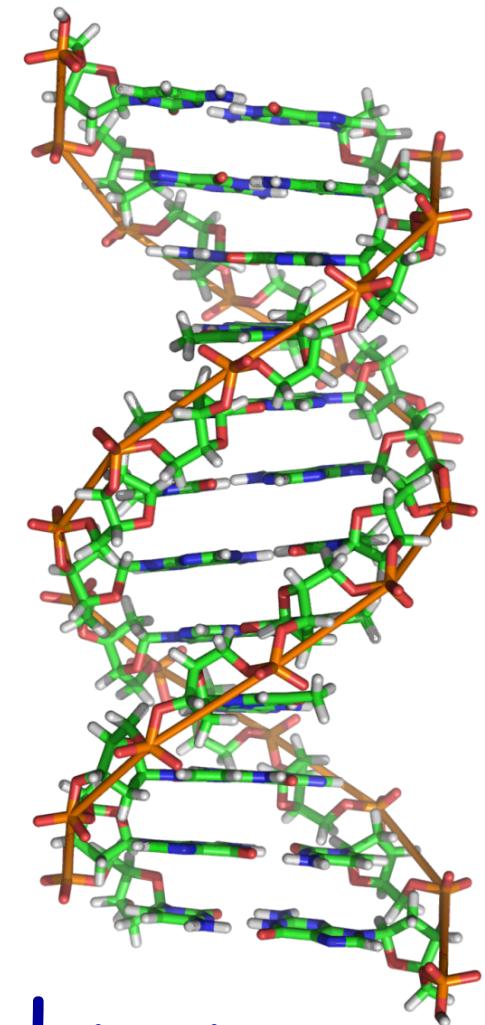
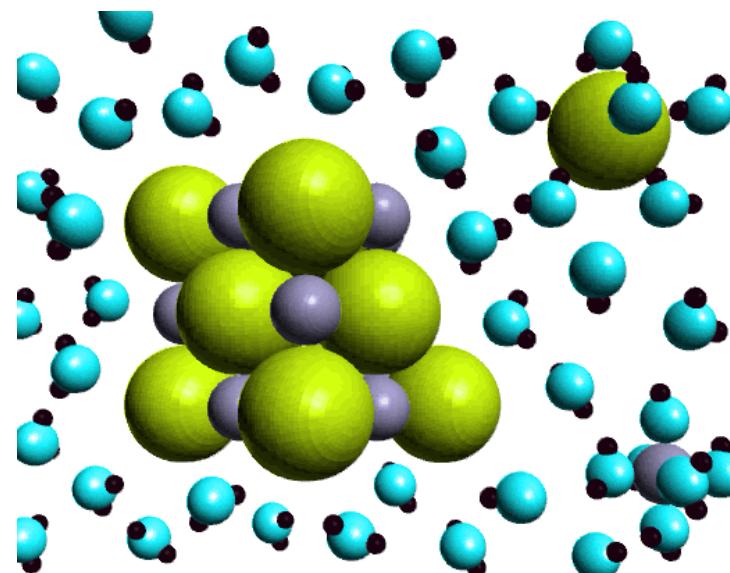
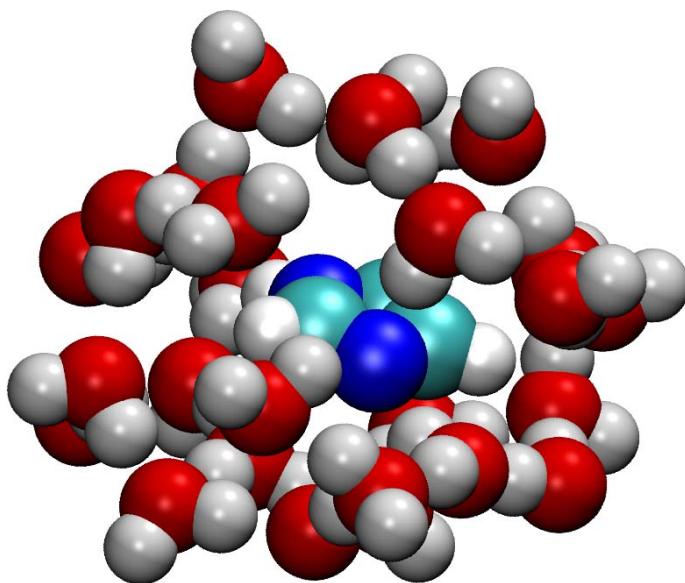
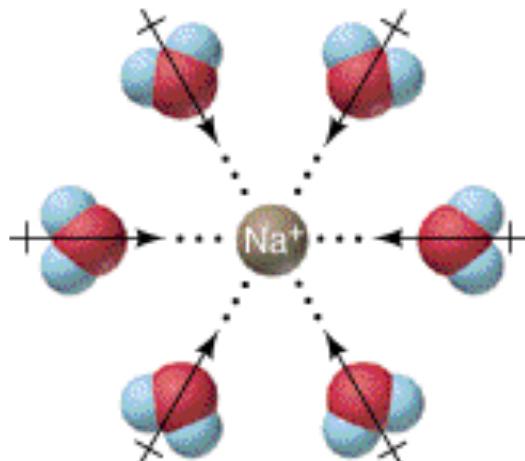


# Intermolecular Forces

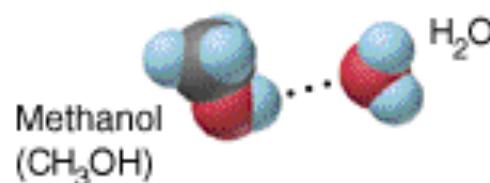


Forces that bind individual non-reacting molecules in gases/liquids

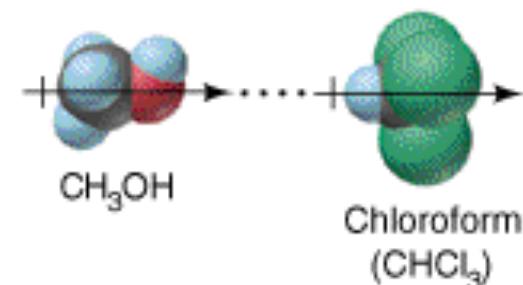
# Various categories of intermolecular interactions (forces)



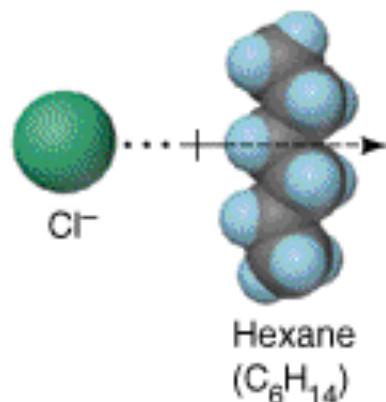
Ion-dipole



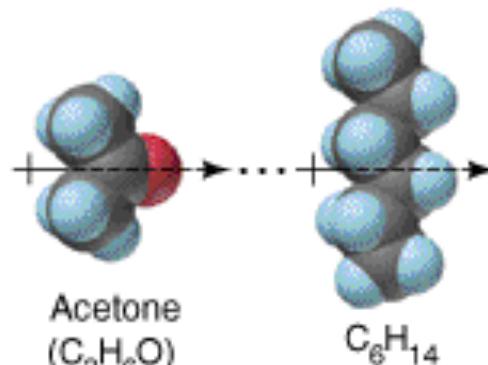
H bond



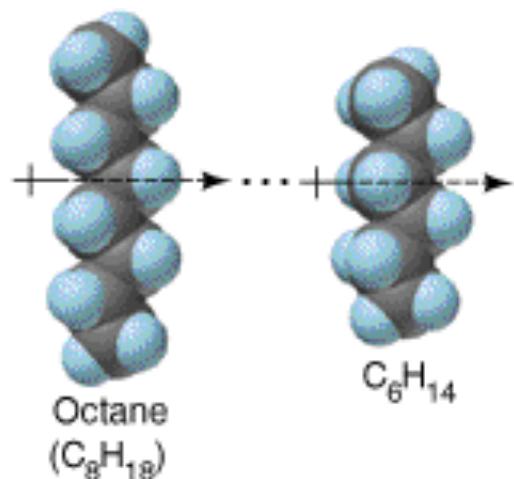
Dipole -dipole



Ion-induced dipole

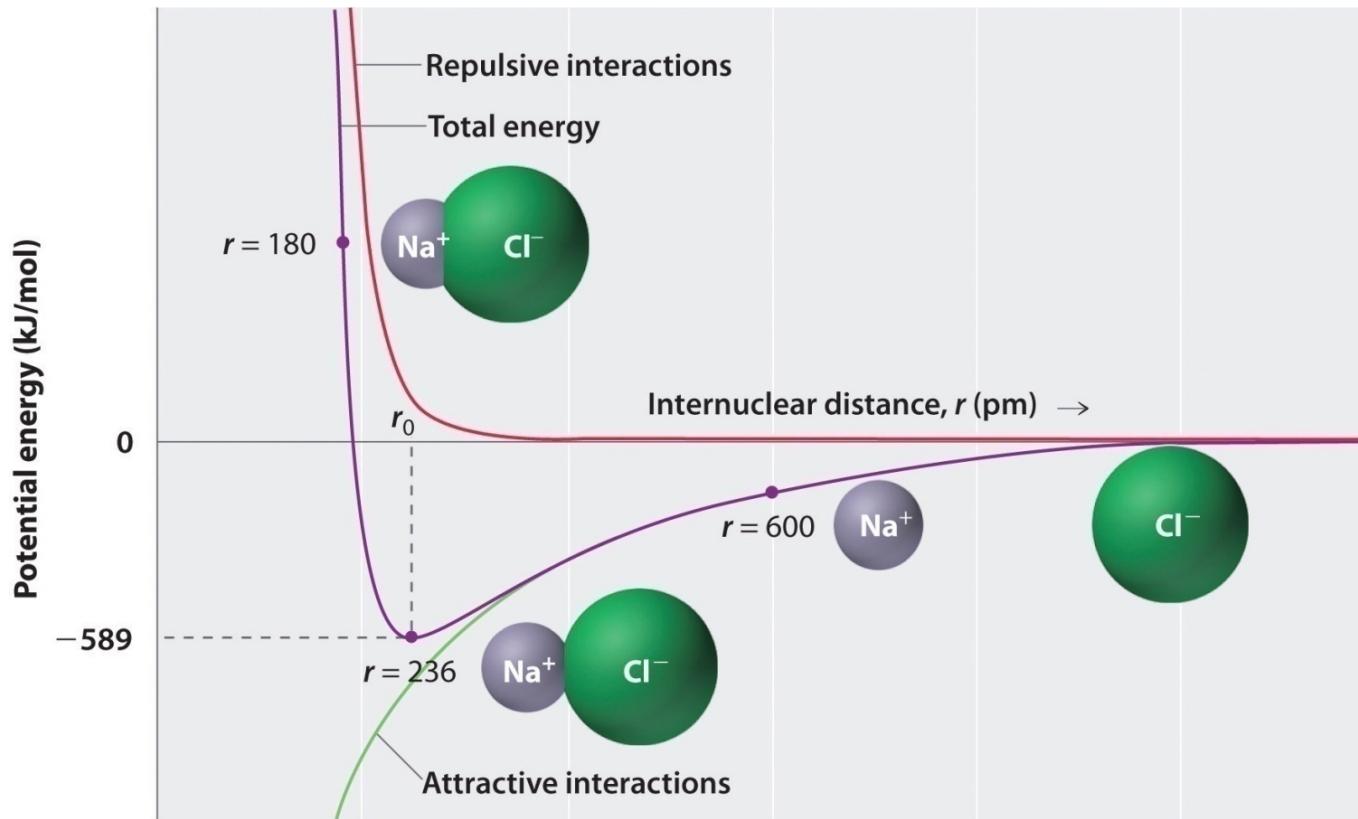


Dipole-Induced dipole

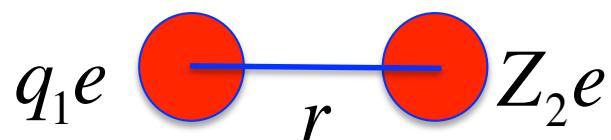


Dispersion

# Ion-Ion Interaction for Charged molecules: Coulomb Potential

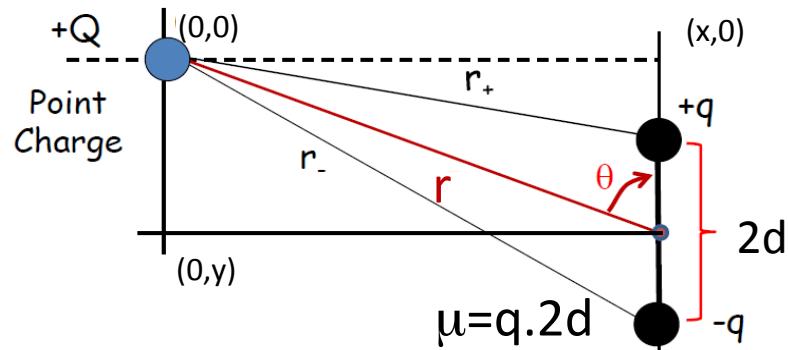
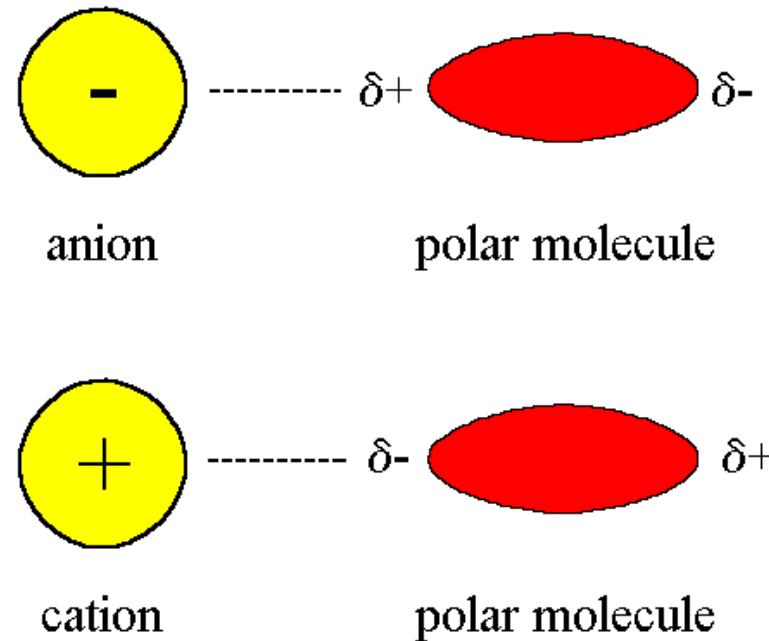
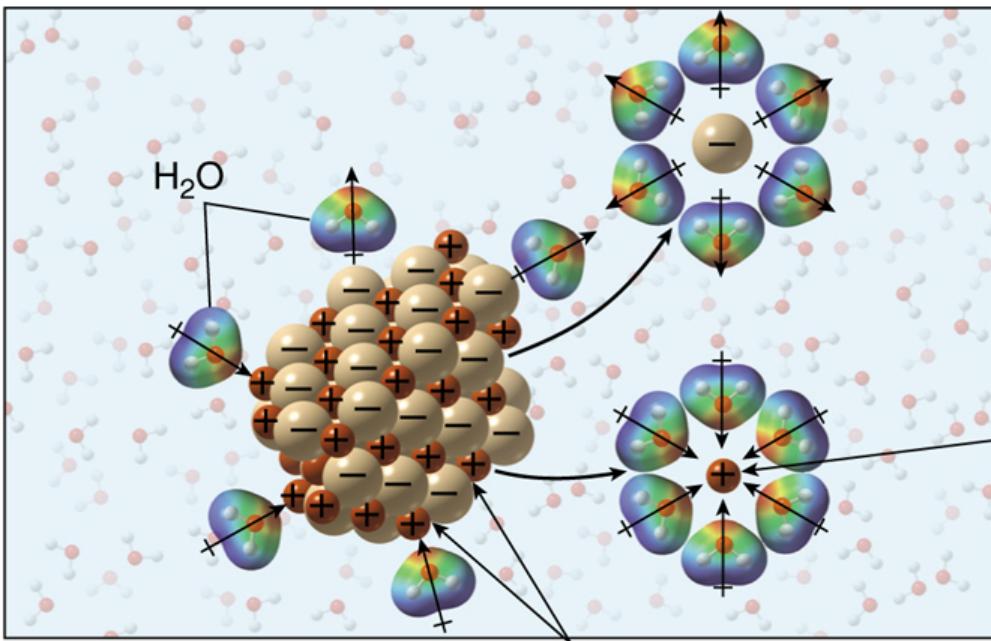


Interaction via Coulomb potential



$$V(r) = \frac{(q_1 e)(q_2 e)}{4\pi\epsilon_0 r}$$

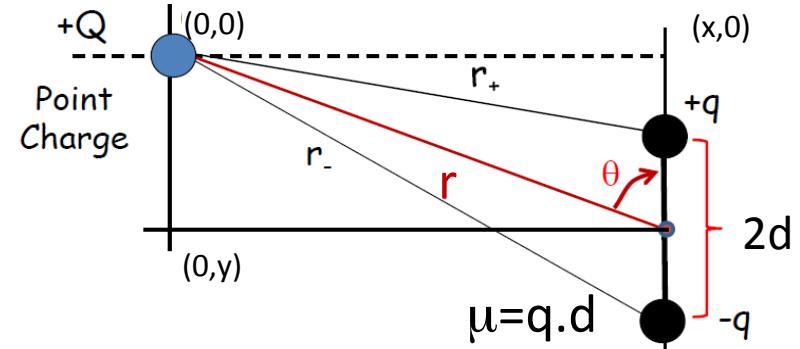
# Monopole (Ion)-dipole interaction



$$V(r, \theta)_{ion-dipole} = \vec{\mu}_j \cdot \vec{E} = \frac{\vec{\mu}_j q_i \cos\theta}{r^2}$$

## Ion - Dipole Interaction

$$V = \frac{1}{4\pi\epsilon_0} \cdot Q \cdot \left( \frac{q}{r_+} - \frac{q}{r_-} \right)$$



$$r_-^2 = x^2 + (y + d)^2$$

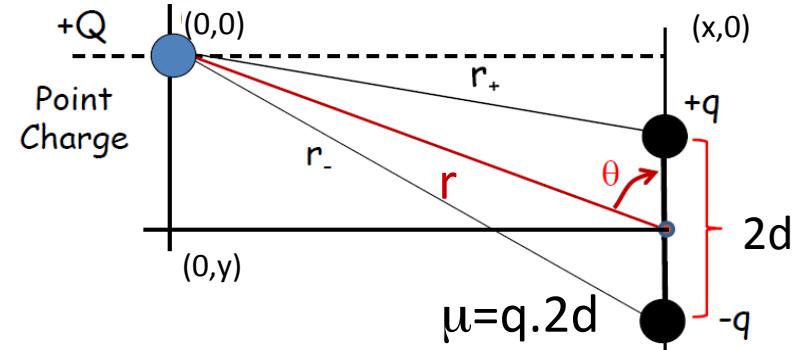
$$\frac{1}{r_-} = \left[ x^2 + (y + d)^2 \right]^{-1/2} = \left[ x^2 + y^2 + d^2 + 2yd \right]^{-1/2} = \left[ r^2 + d^2 + 2yd \right]^{-1/2}$$

$$\frac{1}{r_-} = \frac{1}{r} \left[ 1 + \left( \frac{d}{r} \right)^2 + \frac{2yd}{r^2} \right]^{-1/2} \approx \frac{1}{r} \left[ 1 + \frac{2yd}{r^2} \right]^{-1/2} \quad r \gg 2d$$

$$\frac{1}{r_-} = \frac{1}{r} \left[ 1 - \frac{yd}{r^2} \right] \quad \frac{1}{r_+} = \frac{1}{r} \left[ 1 + \frac{yd}{r^2} \right]$$

## Ion - Dipole Interaction

$$V = \frac{1}{4\pi\epsilon_0} \cdot Q \cdot q \left( \frac{1}{r_+} - \frac{1}{r_-} \right)$$



$$\frac{1}{r_-} = \frac{1}{r} \left[ 1 - \frac{yd}{r^2} \right] \quad \frac{1}{r_+} = \frac{1}{r} \left[ 1 + \frac{yd}{r^2} \right]$$

$$\left( \frac{1}{r_+} - \frac{1}{r_-} \right) = \frac{1}{r} \left[ 1 + \frac{yd}{r^2} \right] - \frac{1}{r} \left[ 1 - \frac{yd}{r^2} \right] = \frac{2yd}{r^3}$$

$$V = \frac{1}{4\pi\epsilon_0} \cdot Q \cdot q \cdot \frac{2yd}{r^3} = \frac{1}{4\pi\epsilon_0} \cdot \frac{Q \cdot q \cdot 2d}{r^2} \cdot \frac{y}{r} = \frac{1}{4\pi\epsilon_0} \cdot \frac{Q\mu}{r^2} \cdot \cos\theta$$

# Monopole-dipole interaction

$$V(r, \theta)_{ion-dipole} = \vec{\mu}_j \cdot \vec{E} = \frac{\vec{\mu}_j q_i \cos\theta}{r^2}$$

Simple average over all  $\theta$ :  $\int_0^\pi \cos\theta \sin\theta d\theta = \int_0^\pi \cos\theta d(\cos\theta) = 0$

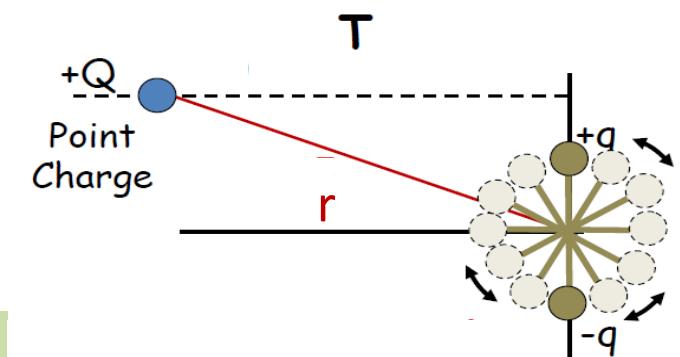
$$\langle V(r, \theta)_{ion-dipole} \rangle = 0 !!!$$

Are all orientations equally probable?

No! Orientations with lower energy are slightly favored!

Dictated by Boltzmann Distribution

$$P(Orientation) \sim \exp\left(-\frac{V(r, \theta)}{k_B T}\right)$$



Need to calculate the average over all orientations weighted by Boltzmann factor  $\rightarrow$  Boltzman Average!

# Boltzmann Average over all orientations

$$\left\langle V(r,\theta)_{ion-dip} \right\rangle_{BA} = \left\langle \frac{\vec{\mu}_j q_i \cos\theta}{r^2} \cdot \exp\left(-\frac{V(r,\theta)}{k_B T}\right) \right\rangle = \frac{\vec{\mu}_j q_i}{r^2} \cdot \left\langle \cos\theta \exp\left(-\frac{V(r,\theta)}{k_B T}\right) \right\rangle$$

Analytically difficult, numerically easy!

Assume :  $V(r,\theta) \ll k_B T \rightarrow$  interaction energy between monopole and dipole is small compared to the thermal energy ( $k_B T$ )

expand exponential function       $\exp(-x) = 1 - x + \frac{x^2}{2!} - \dots \approx 1 - x$

$$\begin{aligned} \left\langle \cos\theta \exp\left(-\frac{V(r,\theta)}{k_B T}\right) \right\rangle &\approx \left\langle \cos\theta \left(1 - \frac{V(r,\theta)}{k_B T}\right) \right\rangle \\ &= \langle \cos\theta \rangle - \left\langle \cos\theta \frac{V(r,\theta)}{k_B T} \right\rangle = - \left\langle \frac{V(r,\theta) \cos\theta}{k_B T} \right\rangle \end{aligned}$$

# Orientation-Averaged potential for ion-dipole interactions

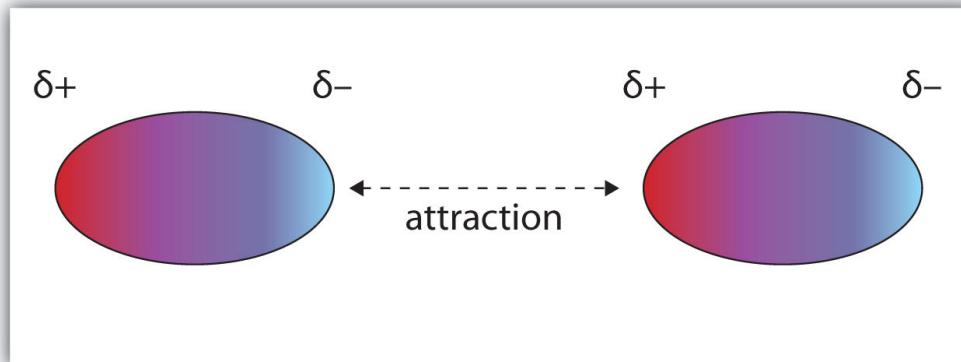
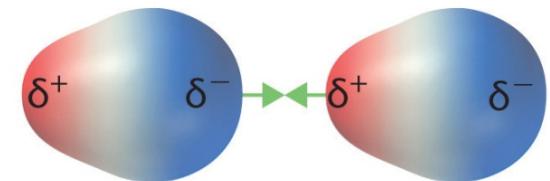
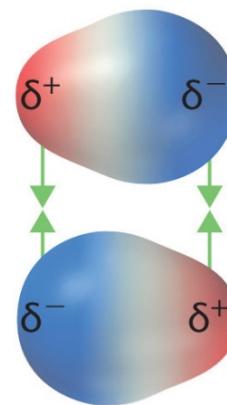
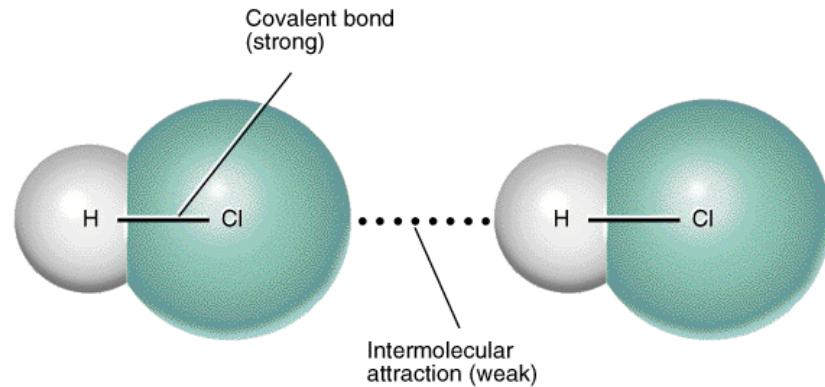
$$\begin{aligned}\left\langle V(r,\theta)_{ion-dipole} \right\rangle_{Boltzman} &= \frac{\vec{\mu}_j q_i}{r^2} \times \left\{ - \left\langle V(r,\theta) \times \frac{\cos\theta}{k_B T} \right\rangle \right\} \\ &= - \frac{\vec{\mu}_j q_i}{r^2} \times \left\langle \frac{\vec{\mu}_j q_i \cos\theta}{r^2} \times \frac{\cos\theta}{k_B T} \right\rangle\end{aligned}$$

$$\left\langle V(r,\theta)_{ion-dipole} \right\rangle_{Boltzman} = - \left( \frac{\vec{\mu}_j q_i}{r^2} \right)^2 \times \frac{1}{k_B T} \times \left\langle \cos^2\theta \right\rangle$$

$$\left\langle \cos^2\theta \right\rangle = \int_0^\pi \cos^2\theta \sin\theta d\theta = \int_0^\pi \cos^2\theta [-d(\cos\theta)] = - \frac{\cos^3\theta}{3} \Big|_0^\pi = \frac{2}{3} \neq 0$$

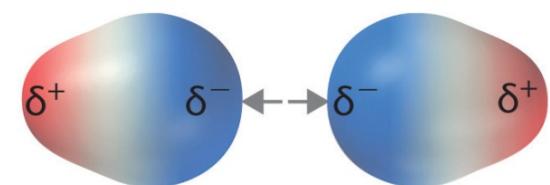
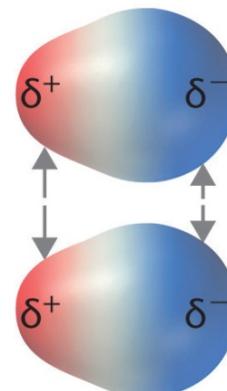
$$\left\langle V(r)_{ion-dipole} \right\rangle_{Boltzman} \sim - \frac{1}{3k_B T} \frac{\left( \vec{\mu}_j q_i \right)^2}{r^4} \sim - \frac{const.}{r^4}$$

# Interactions between two dipoles!



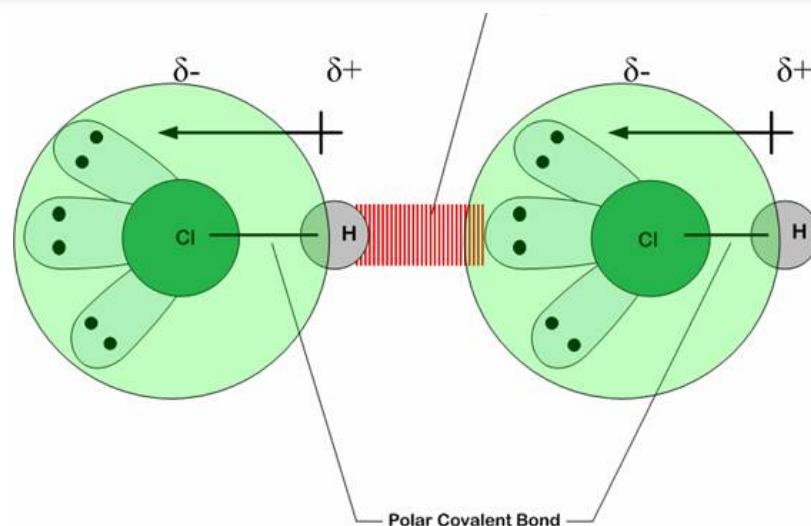
(a) Attraction

(b) Attraction



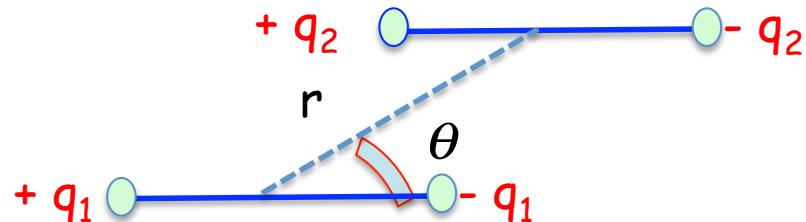
(c) Repulsion

(d) Repulsion



Depending on the relative Orientation - magnitude and Sign of force will vary

# Dipole-dipole interaction potential



$$V(r) = \frac{\mu_1 \mu_2 f(\theta)}{4\pi\epsilon_0 r^3}$$

Consider parallel dipoles (simplified)

$$f(\theta) = 1 - 3\cos^2 \theta$$

Orientation-averaged potential energy of two dipoles

$$\langle V(r) \rangle = \frac{\mu_1 \mu_2 \langle f(\theta) \rangle}{4\pi\epsilon_0 r^3}$$

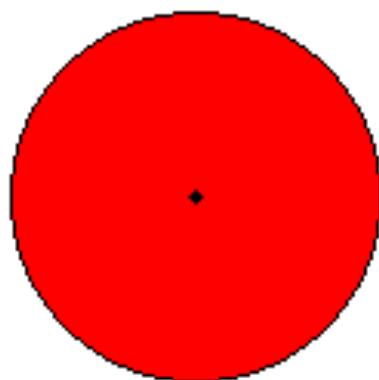
Take a Boltzmann average !!

attractive

$$V_{d-d}(r) = -\frac{2\mu_1^2 \mu_2^2}{3k_B T (4\pi\epsilon_0)^2 r^6} \sim \frac{1}{r^6}$$

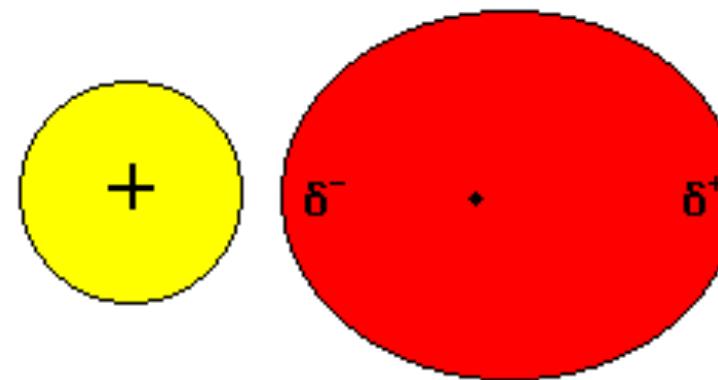
Temperature  
Dependent!

# Interaction of Ion and Induced-Dipole



Spherical atom with no dipole.  
The dot indicates the location  
of the nucleus.

Presence of a nearby Ion  
(charge) will affect the  
Electronic distribution of  
An atom or a neutral  
(non-polar) molecule

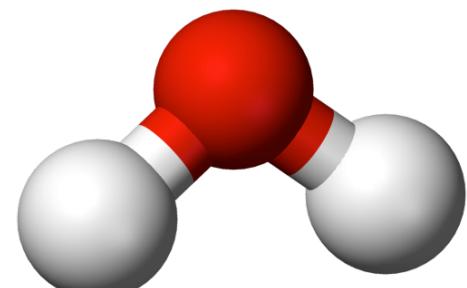
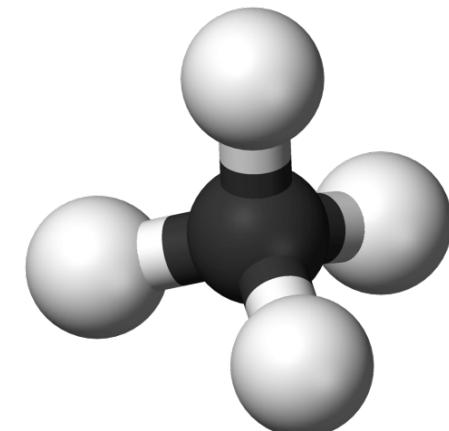
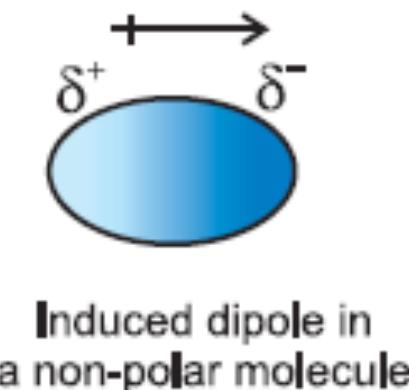
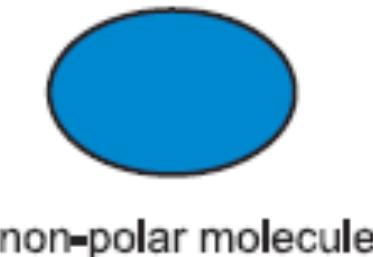
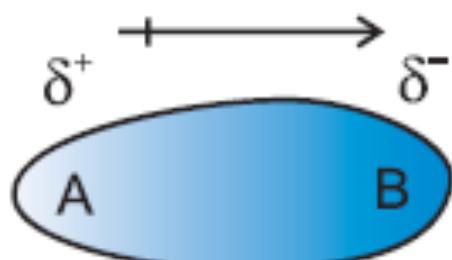
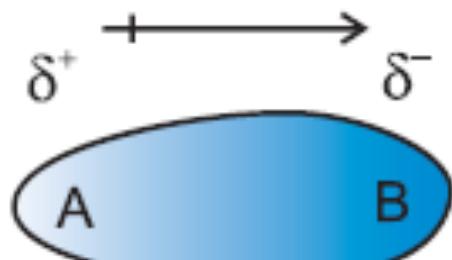


Upon approach of a charged ion,  
electrons in the atom respond and  
the atom develops a dipole.

Induced Dipole moment is  
generated, magnitude of  
Which depends on the  
Polarizability ( $\alpha$ )!

$$\langle V(r) \rangle_{ion-ind\_dipole} = -\frac{\alpha q_i^2}{2r^4} \sim \frac{\alpha}{r^4}$$

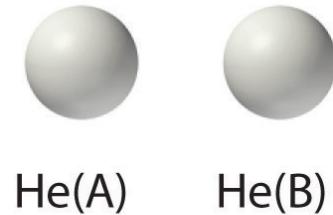
# Dipole Induced-Dipole Interaction



$$\langle V(r) \rangle_{dipole-ind\_dipole} = -\frac{\mu_1^2 \alpha}{4\pi^2 \epsilon_0^2 r^6} \sim \frac{\alpha}{r^6}$$

Not a thermal  
Or Boltzman  
Average: No  
temperature  
dependence

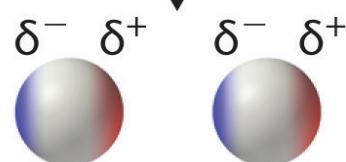
# Instantaneous electronic fluctuations - transient dipoles!



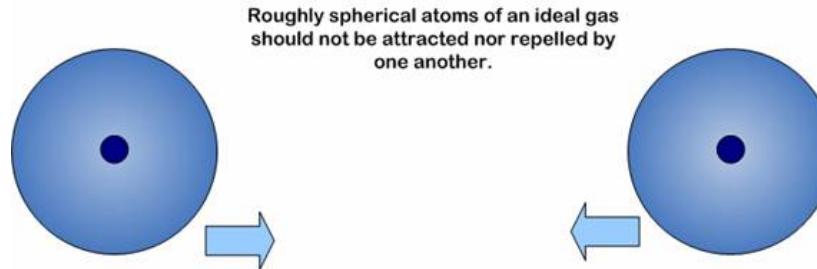
No polarization  
 $\delta^-$   $\delta^+$



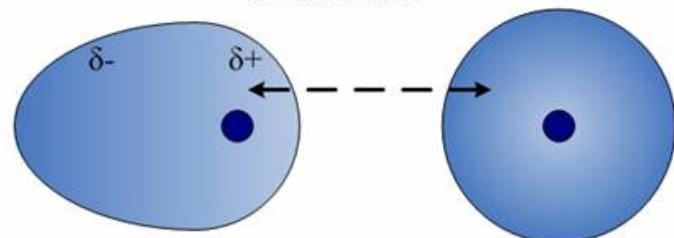
Instantaneous  
dipole on atom A



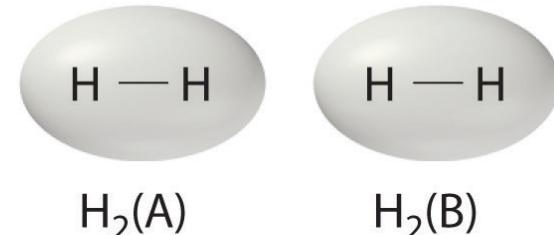
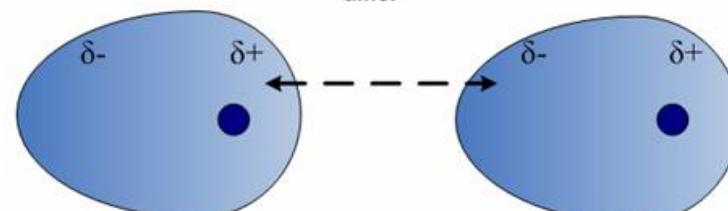
Induced dipole  
on atom B



A real gas atom can have an instantaneous dipole. Partial charges on one atom cause a neighboring atom to distort due to the electrostatic attractions/repulsions of their electron clouds.



Attractions between opposite partial charges of neighboring induced dipoles cause atoms to "stick together" for a very short time.

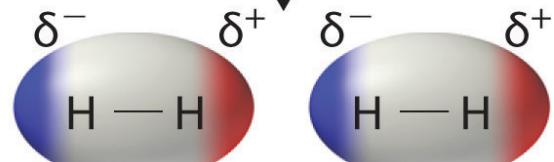


No polarization  
 $\delta^-$   $\delta^+$



H<sub>2</sub>(A)      H<sub>2</sub>(B)

Instantaneous dipole  
on molecule A



H<sub>2</sub>(A)      H<sub>2</sub>(B)

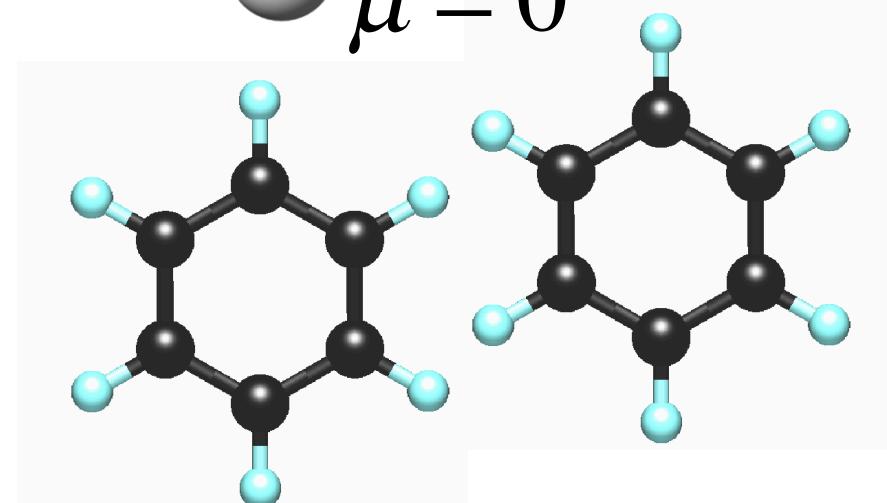
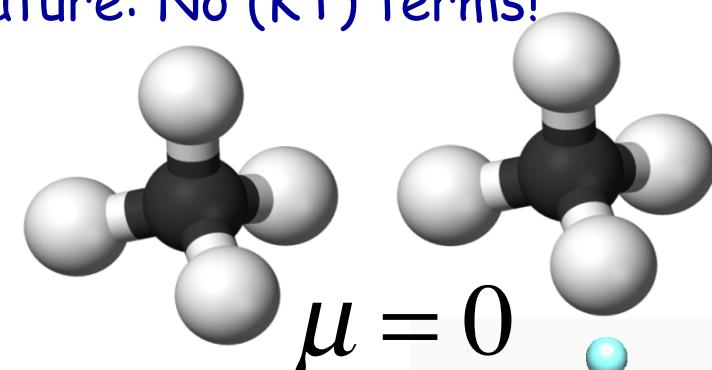
Induced dipole on  
molecule B

# Induced Dipole-Induced Dipole Interaction (Dispersion force)

Transient induced-dipole moments - electronic polarizabilities has to be involved - Due to correlated motion of electrons

$$V_{id-id}(r) \sim \frac{\alpha_i \alpha_j}{r^6}$$

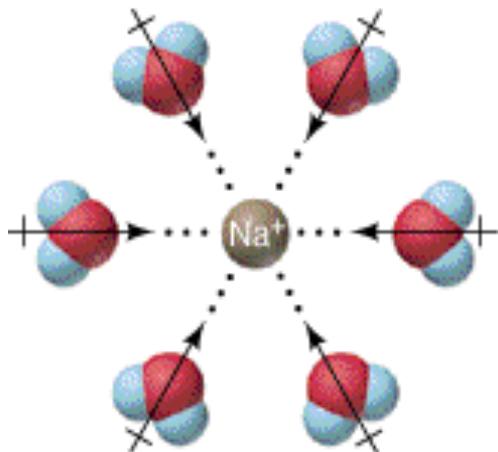
Independent of Orientation and Temperature: No (KT) terms!



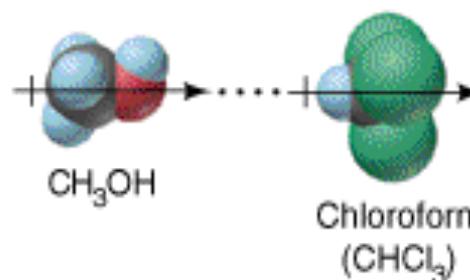
Termed London Forces, or dispersion! core of a quantum-mechanical effect!

Can be extremely strong force if a large number of molecules are involved - higher alkanes are solid at 300K

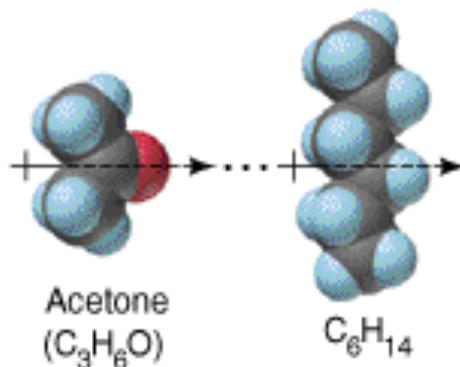
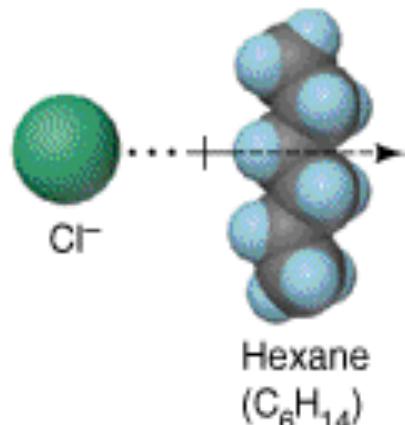
# Attractive Potentials for Various Intermolecular forces



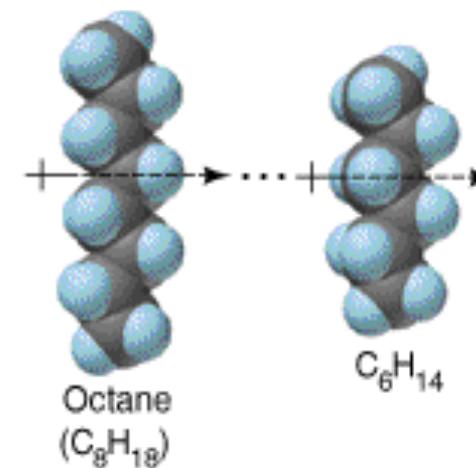
$$\langle V(r) \rangle \sim \frac{(\vec{\mu}_j q_i)^2}{r^4}$$



$$\langle V(r) \rangle \sim \frac{(\vec{\mu}_i \vec{\mu}_j)^2}{r^6}$$



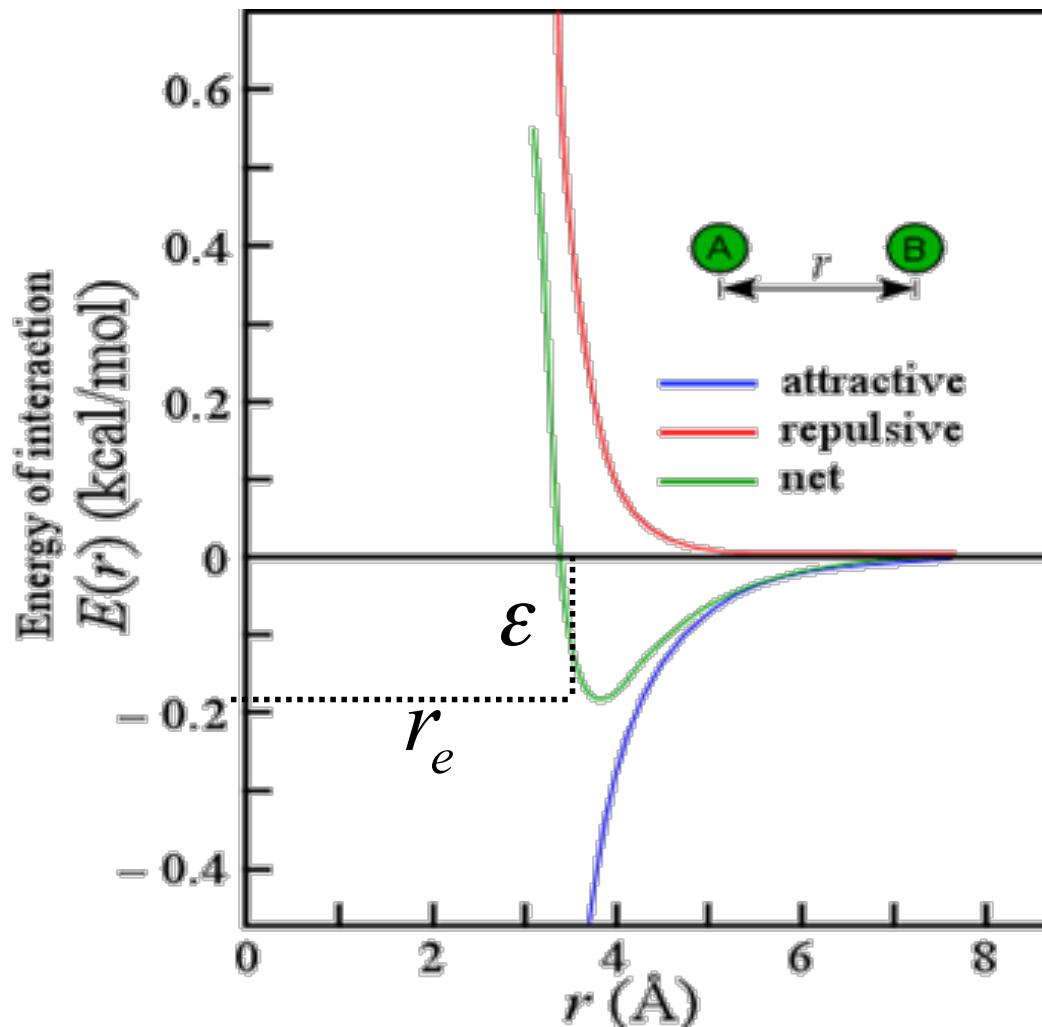
$$\langle V(r) \rangle \sim \frac{\mu_i \alpha_j}{r^6}$$



$$V_{id-id}(r) \sim \frac{\alpha_i \alpha_j}{r^6}$$

$$\langle V(r) \rangle \sim \frac{\alpha}{r^4}$$

# LJ: Good potential to model intermolecular interactions



Lennard-Jones Potential\*  
very suitable as a model  
for van der waals' forces

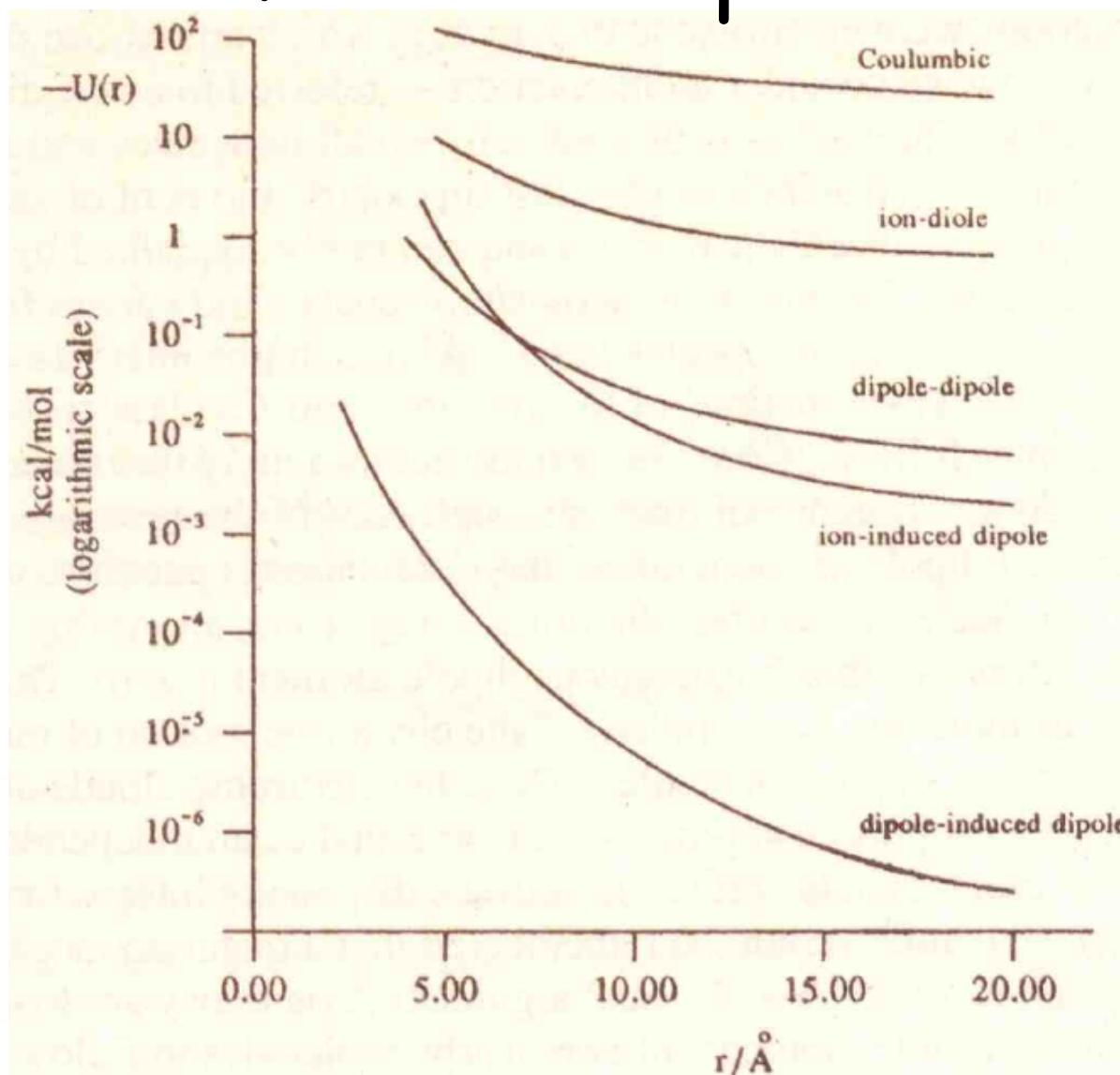
$$V_{LJ} = \epsilon \left[ \left( \frac{r_e}{r} \right)^{12} - 2 \left( \frac{r_e}{r} \right)^6 \right]$$

\* Did Lennard and Jones come up with this potential function independently or they worked together??

# Comparison of Various Interactions

Ion-dipole		Ion charge–dipole charge	40–600	$\text{Na}^+ \cdots \text{O}-\text{H}$
Dipole-dipole		Dipole charges	5–25	$\text{I}-\text{Cl} \cdots \text{I}-\text{Cl}$
Ion-induced dipole		Ion charge–polarizable $e^-$ cloud	3–15	$\text{Fe}^{2+} \cdots \text{O}_2$
Dipole-induced dipole		Dipole charge–polarizable $e^-$ cloud	2–10	$\text{H}-\text{Cl} \cdots \text{Cl}-\text{Cl}$
Dispersion (London)		Polarizable $e^-$ clouds	0.05–40	$\text{F}-\text{F} \cdots \text{F}-\text{F}$
H bond	$-\overset{\delta^-}{\text{A}}-\overset{\delta^+}{\text{H}} \cdots : \overset{\delta^-}{\text{B}}-$	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	$\begin{array}{c} \ddot{\text{O}} \\   \\ \text{H} \end{array} - \text{H} \cdots \begin{array}{c} \ddot{\text{O}} \\   \\ \text{H} \end{array} - \text{H}$

# Distance dependence of intermolecular potentials



After modification by all the constants involved

# Distance dependence of various intermolecular potentials

Typical Energies / kcal mol<sup>-1</sup>

Type of interaction	$r_{ij} = 5 \text{ \AA}$	$r_{ij} = 10 \text{ \AA}$	$r_{ij} = 15 \text{ \AA}$
ion-ion	- 66.41		- 22.14
ion-dipole	- 4.15		- 0.46
dipole-dipole	- 0.52		- 0.019
ion-induced dipole	- 0.79		- 0.0098
dipole-induced dipole	- 0.0124		- 0.000017

$$\langle V \rangle_{Ion-Dip} \sim \frac{1}{r^4}$$

$$\langle V \rangle_{dip-dip} \sim \frac{1}{r^6}$$

$$\langle V \rangle_{ion-ind\_dip} \sim \frac{1}{r^4}$$

$$\langle V \rangle_{dip-ind\_dip} \sim \frac{1}{r^6}$$

# Revisiting Electronic Polarizability!

Induced dipole moment in a atom or molecule due to the polarization of charge distribution

$$\vec{\mu}_{Induced}(\vec{E}) = \alpha \vec{E}$$

$\alpha \rightarrow$  Electronic Polarizability (molecular property)

Polarizability of a molecule (or atom) is a measure of its ability to respond to an uniform electric field and acquire an (induced) dipole moment (a vector!)

$$\vec{\mu}_I = \vec{\mu}_{Ix} + \vec{\mu}_{Iy} + \vec{\mu}_{Iz}$$

While (induced) dipole moment is a vector, Polarizability is a tensor - No specific direction, but has directionality !!

# The Polarizability tensor: 3x3 matrix

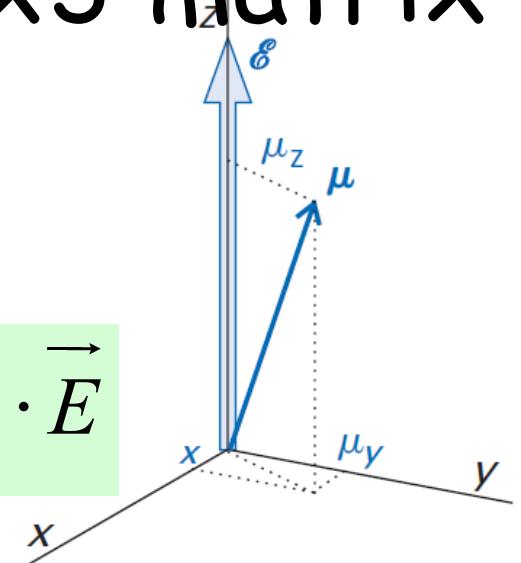
$$\rightarrow \quad \rightarrow \quad \rightarrow$$

$\mu_{Ix}, \mu_{Iy}, \mu_{Iz}$  : may not be the same

$$\langle \mu_{Iz} \rangle = \alpha_{zz} \cdot \vec{E}$$

$$\langle \mu_{Ix} \rangle = \alpha_{xx} \cdot \vec{E}$$

$$\langle \mu_{Iy} \rangle = \alpha_{yy} \cdot \vec{E}$$



Applied electric field can induce a dipole moment which may not be parallel to the field. Induced dipole depends on all the elements of the polarizability matrix!

$$\bar{\alpha} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

Non-centrosymmetric molecules

$$\alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz}$$

Polarizability is a 3x3 matrix (tensor or rank 2)

# Estimate relative magnitudes of polarizability components

$$\vec{\mu}_{Ind} = \vec{\mu} \xrightarrow{E} - \vec{\mu} \xrightarrow{E=0} = \vec{\alpha} E$$

$$\begin{pmatrix} \vec{\mu}_{Ix} \\ \vec{\mu}_{Iy} \\ \vec{\mu}_{Iz} \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} \vec{E}_x \\ \vec{E}_y \\ \vec{E}_z \end{pmatrix}$$

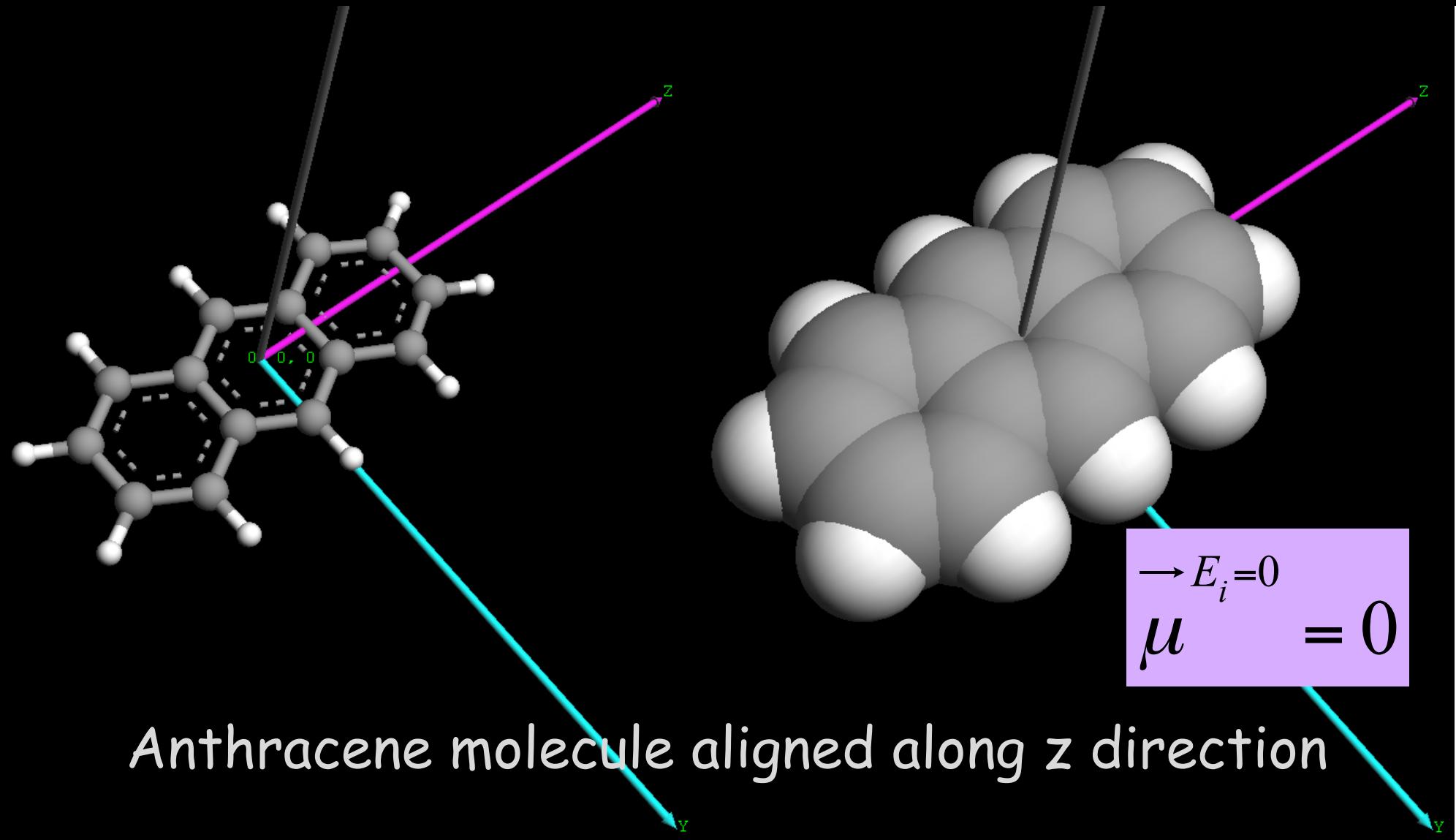
Average of the electronic Polarizability  $\sim 1/3 \times$  Trace of matrix - sum of diagonal elements. (considering off-diagonal elements relatively small)

$$\alpha_{ii} = \frac{\vec{\mu}_i \xrightarrow{E_i} - \vec{\mu}_i \xrightarrow{E_i=0}}{E_i}$$

$$\alpha_{ij} = \frac{\vec{\mu}_j \xrightarrow{E_i} - \vec{\mu}_j \xrightarrow{E_i=0}}{E_i}$$

$$\vec{\mu}_i \xrightarrow{E_i} = \vec{\mu}_i \xrightarrow{E_i=0} + \alpha_{ii} E_i \quad \text{and} \quad \vec{\mu}_j \xrightarrow{E_i} = \vec{\mu}_j \xrightarrow{E_i=0} + \alpha_{ij} E_i$$

Test case using Anthracene: Calculate  $\mu_{\text{ind}}$  by applying  $E_x, E_y, E_z$

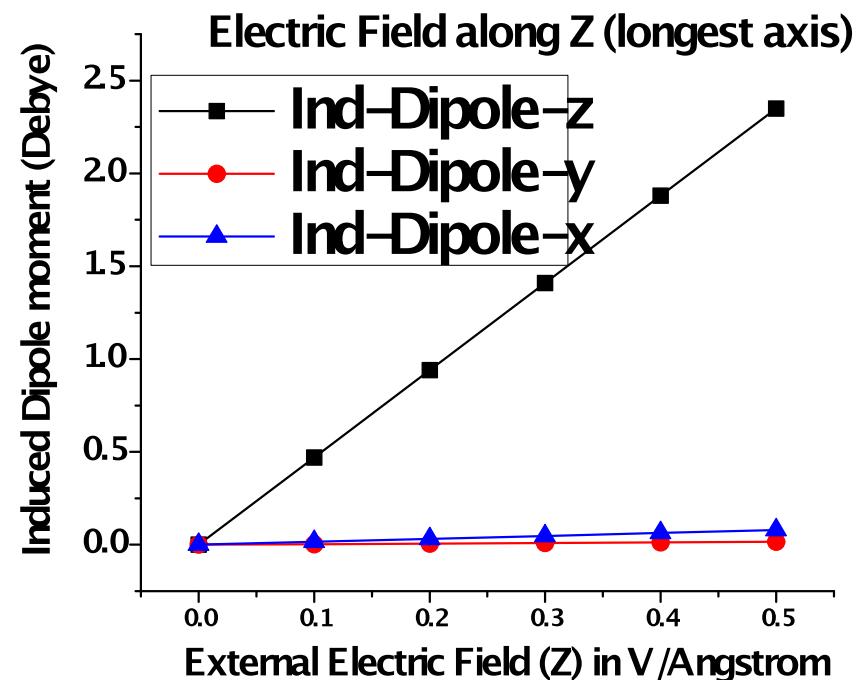
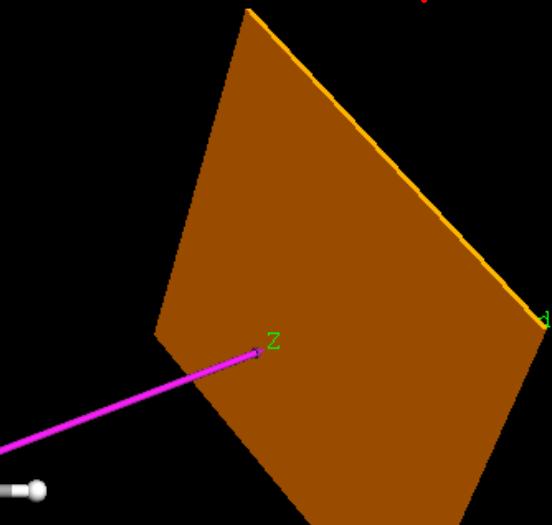
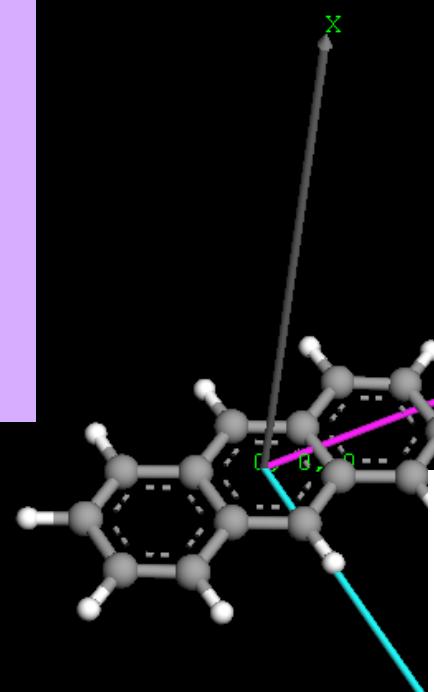


# Apply $E_z$ : Calculate $\mu_{Iz}$ , $\mu_{Iy}$ , $\mu_{Ix}$

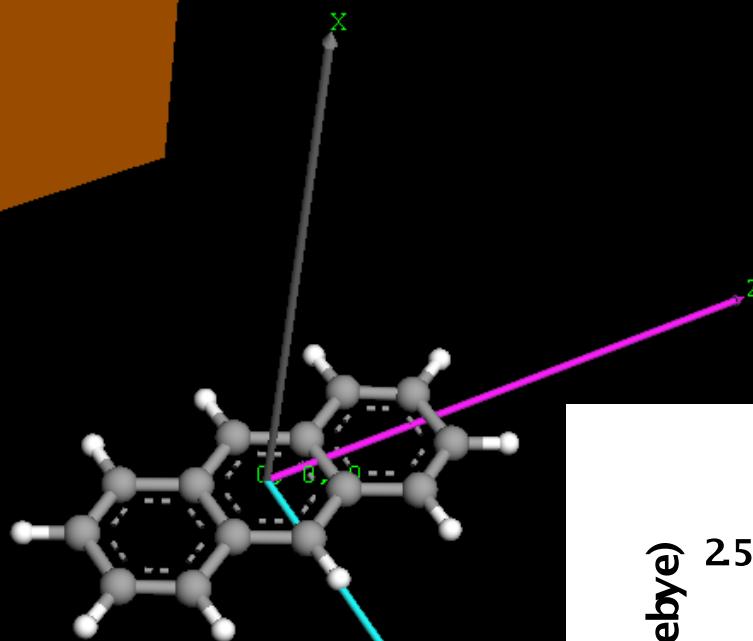
$$\overset{\rightarrow}{\mu_i} = \alpha_{ii} \overset{\rightarrow}{E_i}$$

$$\overset{\rightarrow}{\mu_j} = \alpha_{ij} \overset{\rightarrow}{E_i}$$

$$\alpha_{yz}, \alpha_{xz} \ll \alpha_{zz}$$

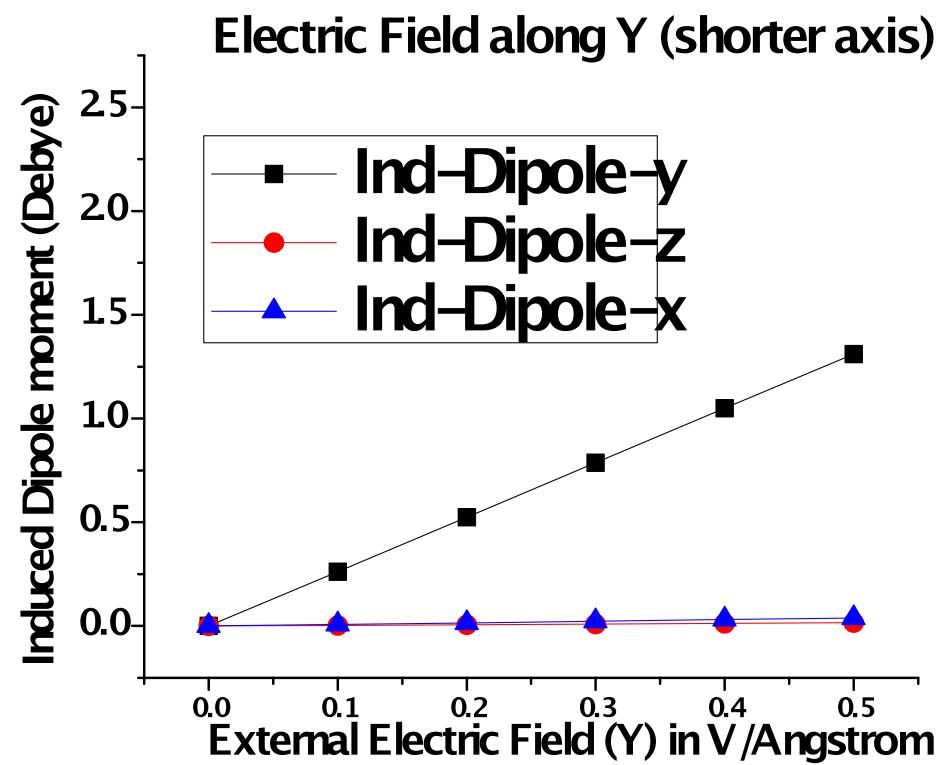


Apply  $E_y$ : Calculate  $\mu_{Iz}$ ,  $\mu_{Iy}$ ,  $\mu_{Ix}$

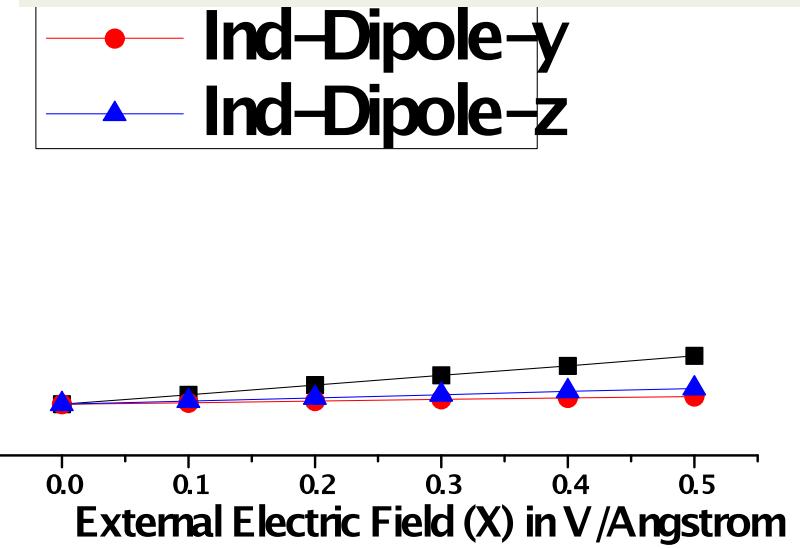
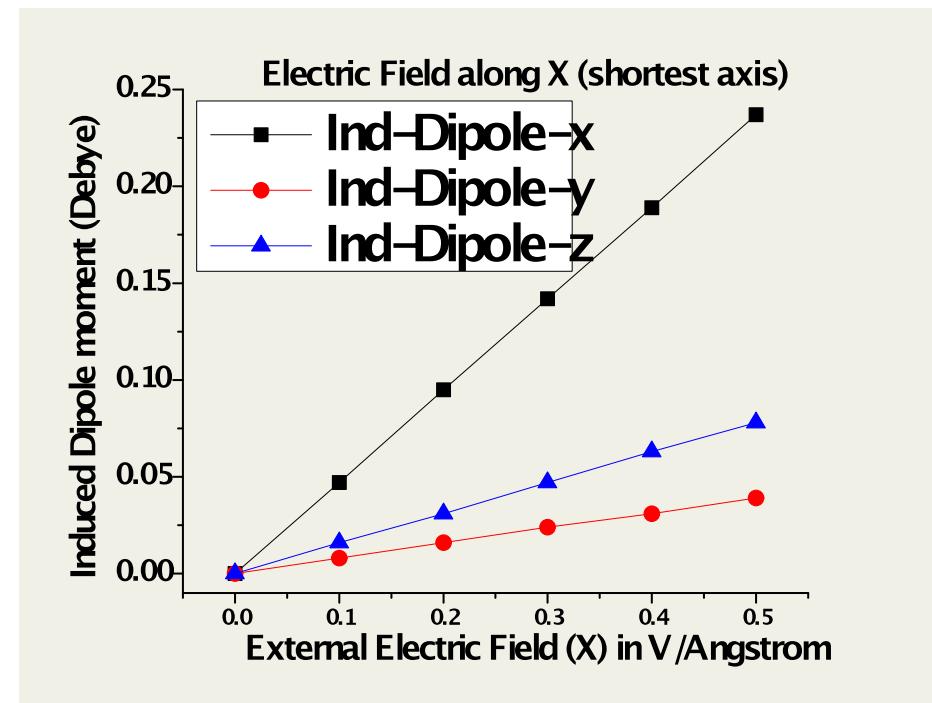
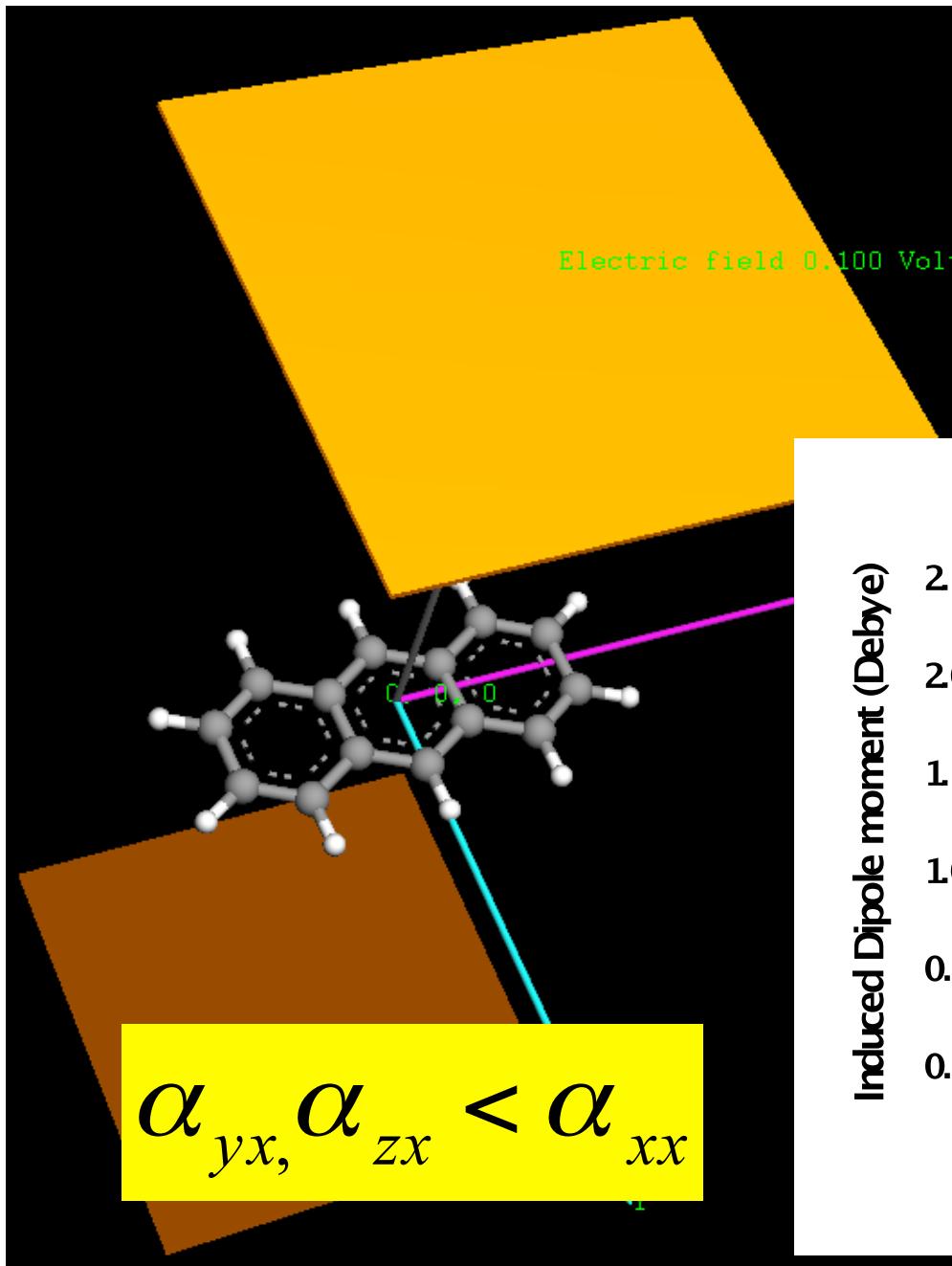


$$\alpha_{xy}, \alpha_{zy} \ll \alpha_{yy}$$

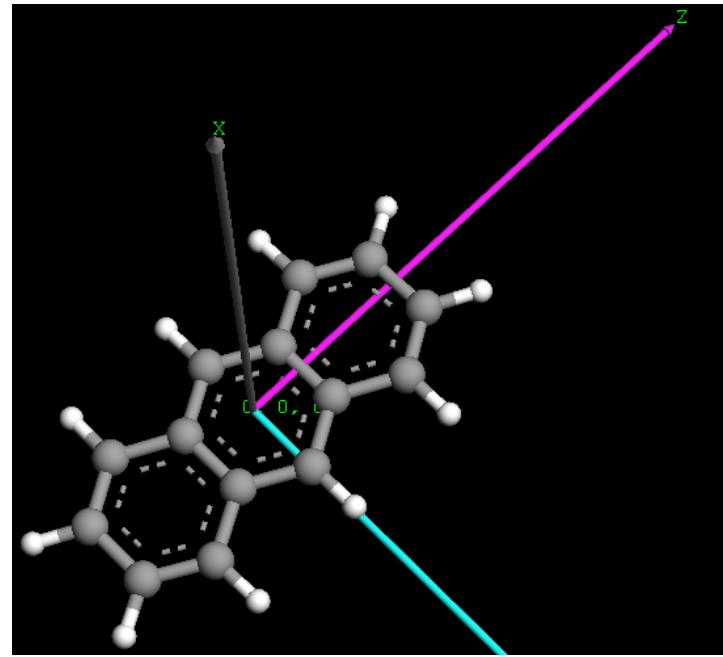
$$\stackrel{\rightarrow}{\mu}_i = \alpha_{ii} \stackrel{\rightarrow}{E}_i ; \quad \stackrel{\rightarrow}{\mu}_j = \alpha_{ij} \stackrel{\rightarrow}{E}_i$$



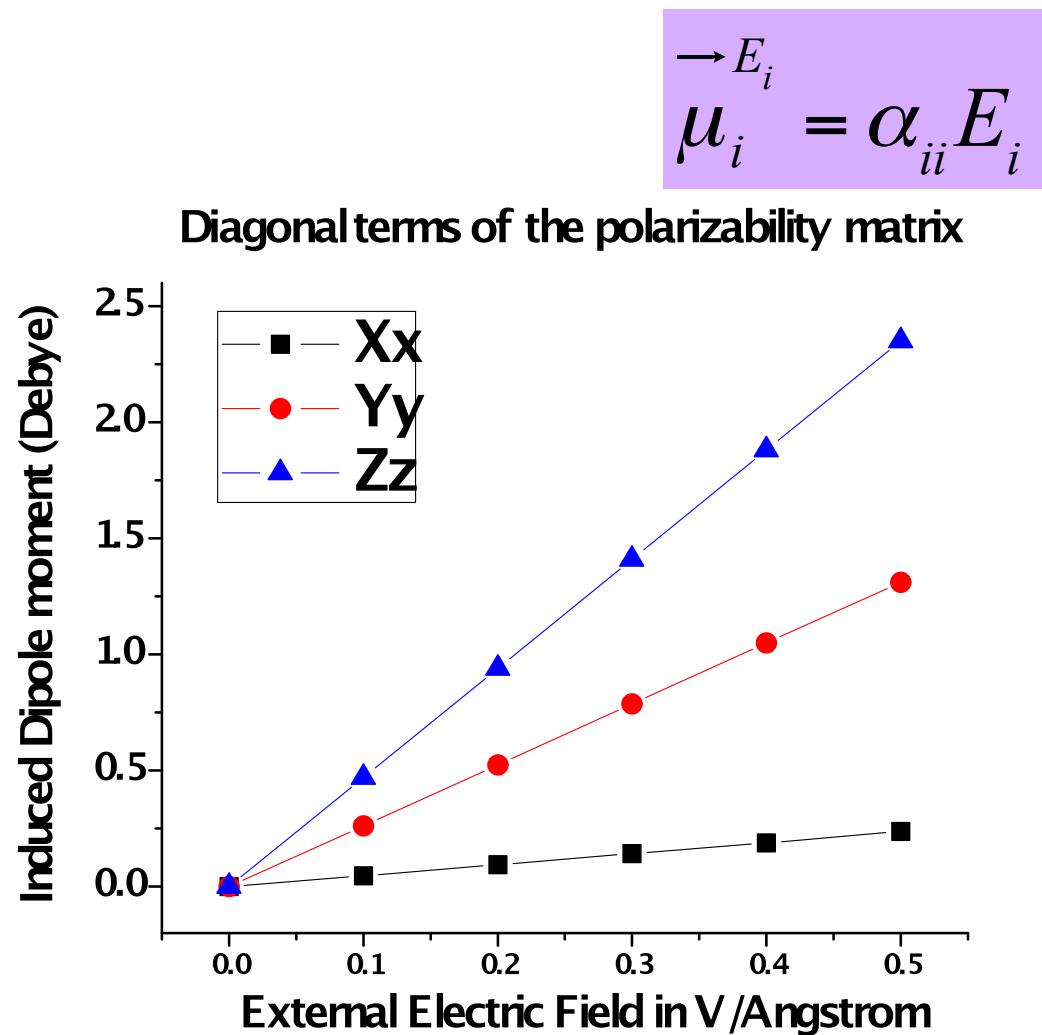
# Apply $E_x$ : Calculate $\mu_{Ix}$ , $\mu_{Iy}$ , $\mu_{Iz}$



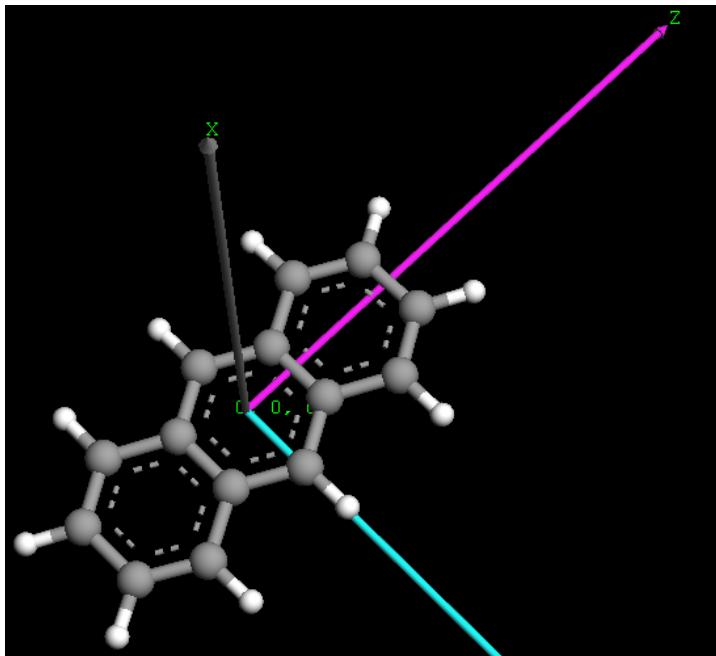
# Diagonal elements of polarizability: $\alpha_{ii}$



$$\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$


$$\alpha_{zz} > \alpha_{yy} > \alpha_{xx}$$

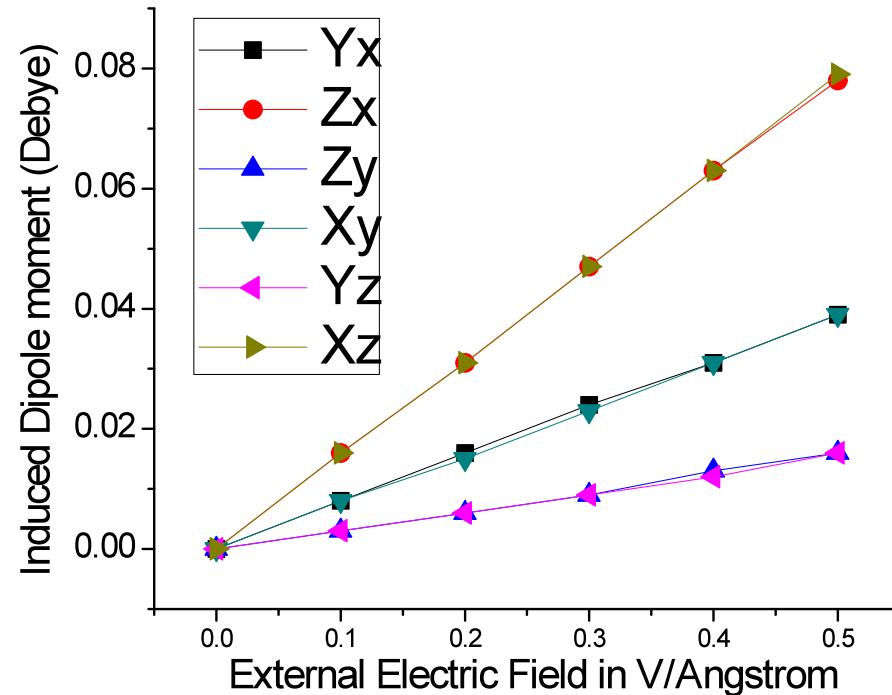
# Off-Diagonal elements ( $\alpha_{ij}$ ) are small



$$\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

$$\vec{\mu}_j = \alpha_{ij} E_i$$

Off-diagonal terms of the polarizability matrix



$$\alpha_{xy} = \alpha_{yx}; \alpha_{xz} = \alpha_{zx}; \alpha_{yz} = \alpha_{zy}$$

## CH107 Tutorial 6 (on Intermolecular forces)

1. Provide three evidences which point to the existence of intermolecular forces for atoms and molecules with no permanent dipole moment.
2. Estimate the ratio of the electric dipole moments of ortho and meta disubstituted chlorobenzene.
3. Show that for an ion-dipole interaction, the interaction potential is expressed as

$$V(r, \theta)_{\text{ion-dipole}} = \vec{\mu}_i \cdot \vec{E} = \frac{\vec{\mu}_i \cdot q_i \cos\theta}{r^2}$$