Lecture: P1_Wk1_L3

Inter-Molecular Forces: Physical Models

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In this lecture we will review physical models that allow estimates for the strength of inter-molecular interactions.

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Charges in the microscopic world

Charge Distribution	Classical E&M	Real World	Examples	Chemical Formula
point charges	+q or -q	ions	Li^+, Mg^{++}, Cl^-	
permanent dipoles	p= q d	(di)polar molecules	acetone, acetonitrile, ethanol, methanol, Freon-41, water	$(CH_3)_2CO$ CH_3CN C_2H_5OH CH_3OH CH_3F H_2O
induced dipoles	p(t) = q d	non-polar molecules (hydrocarbons) inert atoms	hexane, benzene, toluene He, Ar, Kr, Xe,	C_6H_{14} C_6H_6 C_7H_8 (or $C_6H_5CH_3$)
surface charge distribution	σ	charged objects	metal plate with voltage	
volume charge distribution	ρ	charged objects	charged non-conductors	

Electrostatic Potential Energy

	Mechanics	Electrostatics
Work	$W=\int F dz$	$W=\int q\vec{E}\cdot d\vec{l}$
Potential Energy, U	$U(z)=-W$	$U(r)=-W$

If Force is conservative (not a function of time), then Potential Energy at point P (in 1d) can be defined as:

$$U_P(z) \equiv -\int_{ref}^{P} F(z)d\ z \Rightarrow F(z) = -\frac{\partial U_P(z)}{\partial z}$$

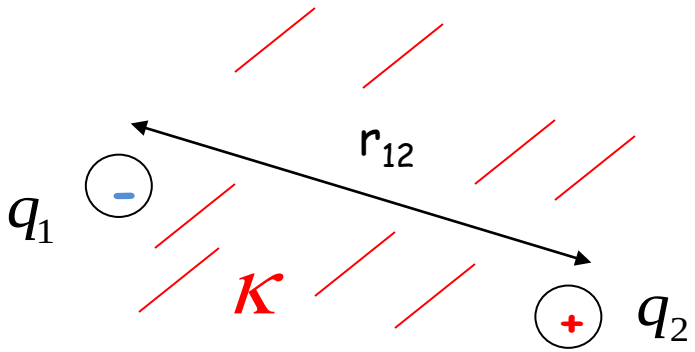
In general, if electric field is conservative (not a function of time), then the force acting on a charge q at an arbitrary point P can be defined as:

$$U_P(\vec{r}) \equiv -\int_{\infty}^{P} q\vec{E}\cdot d\vec{\ell} \Rightarrow \vec{F} = -\vec{\nabla}U_P(\vec{r})$$

$$\vec{F}\ at\ point\ P = -\left.\frac{\partial U(x,y,z)}{\partial x}\right|_P \hat{i} - \left.\frac{\partial U(x,y,z)}{\partial y}\right|_P \hat{j} - \left.\frac{\partial U(x,y,z)}{\partial z}\right|_P \hat{k}$$

Electrostatic Potential Energy - Examples

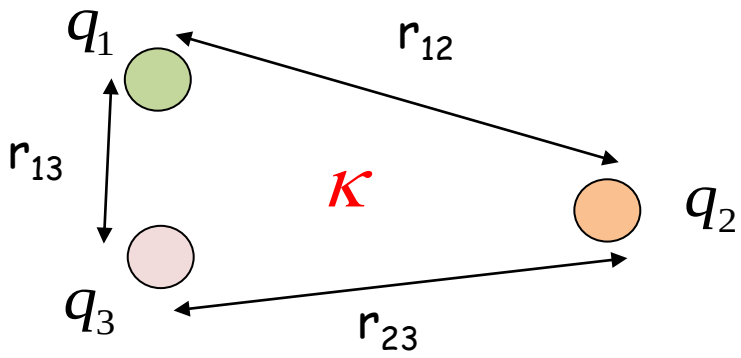
Two point charges embedded in dielectric :



$$U_{electr} = \frac{1}{4\pi\kappa\varepsilon_o}\left[\frac{(-q_1)q_2}{r_{12}}\right] = -\frac{1}{4\pi\kappa\varepsilon_o}\left[\frac{q_1 q_2}{r_{12}}\right]$$

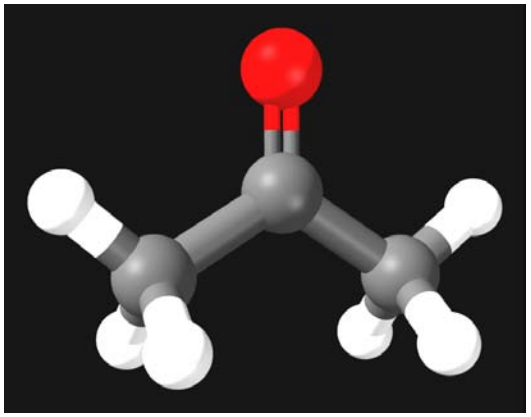
Important : The sign of U_{electr} depends on polarity of charges.

Three point charges in dielectric:

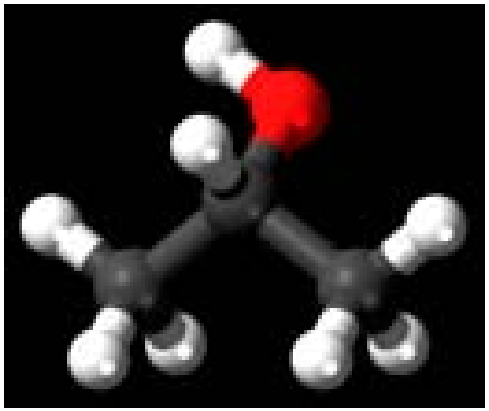


$$U_{electr} = \frac{1}{4\pi\kappa\varepsilon_o}\left[\frac{(q_1)(q_2)}{r_{12}} + \frac{(q_2)(q_3)}{r_{23}} + \frac{(q_1)(q_3)}{r_{13}}\right]$$

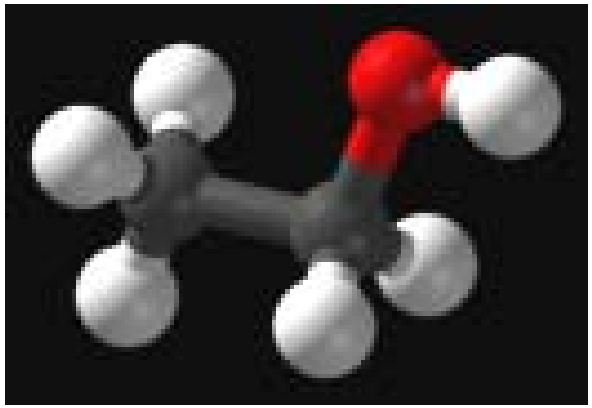
Atomic structure of a few common solvent molecules



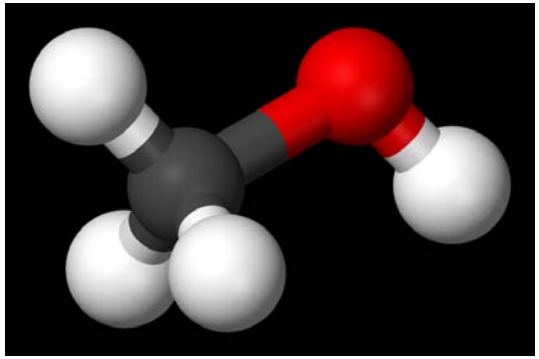
Acetone
$(CH_3)_2CO$



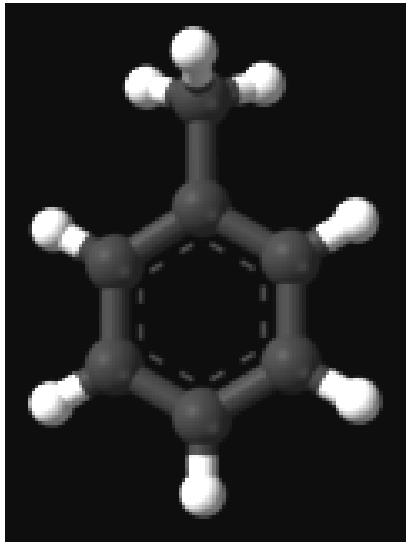
Isopropanol
$(CH_3)_2CHOH$



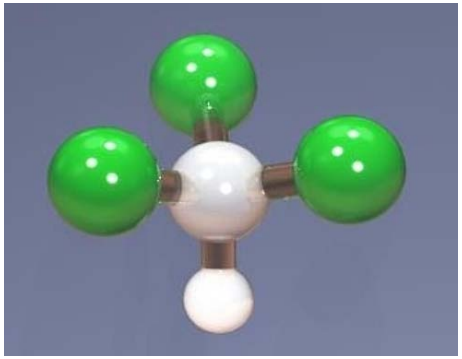
Ethanol
$(CH_3)CH_2OH$



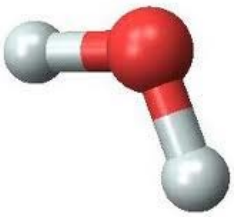
Methanol
CH_3OH



Toluene
$C_6H_5CH_3$



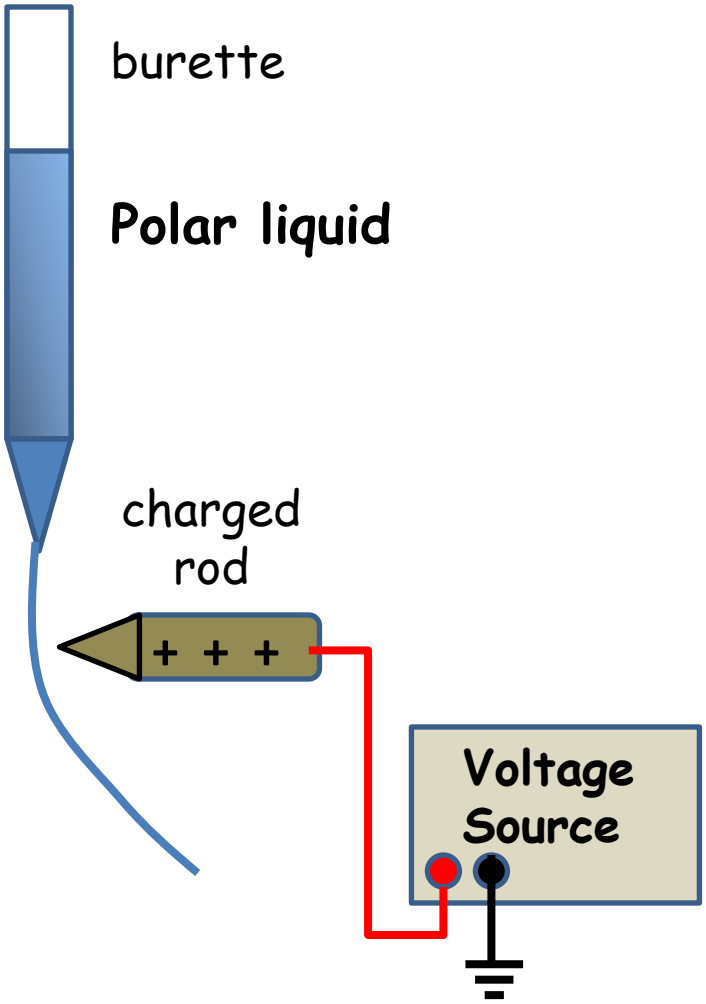
Trichlorofluoromethane
$CC\ell_3F$

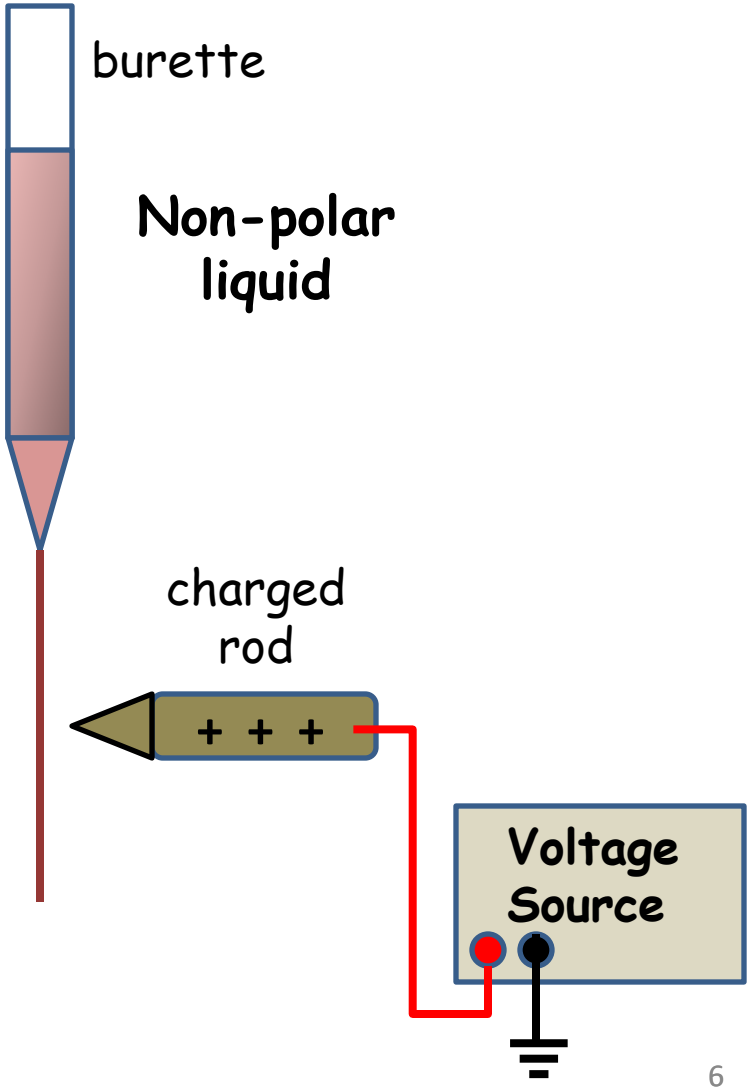


Water
H_2O

Experimental identification of (di)polar and non-(di)polar molecules

(traditional)



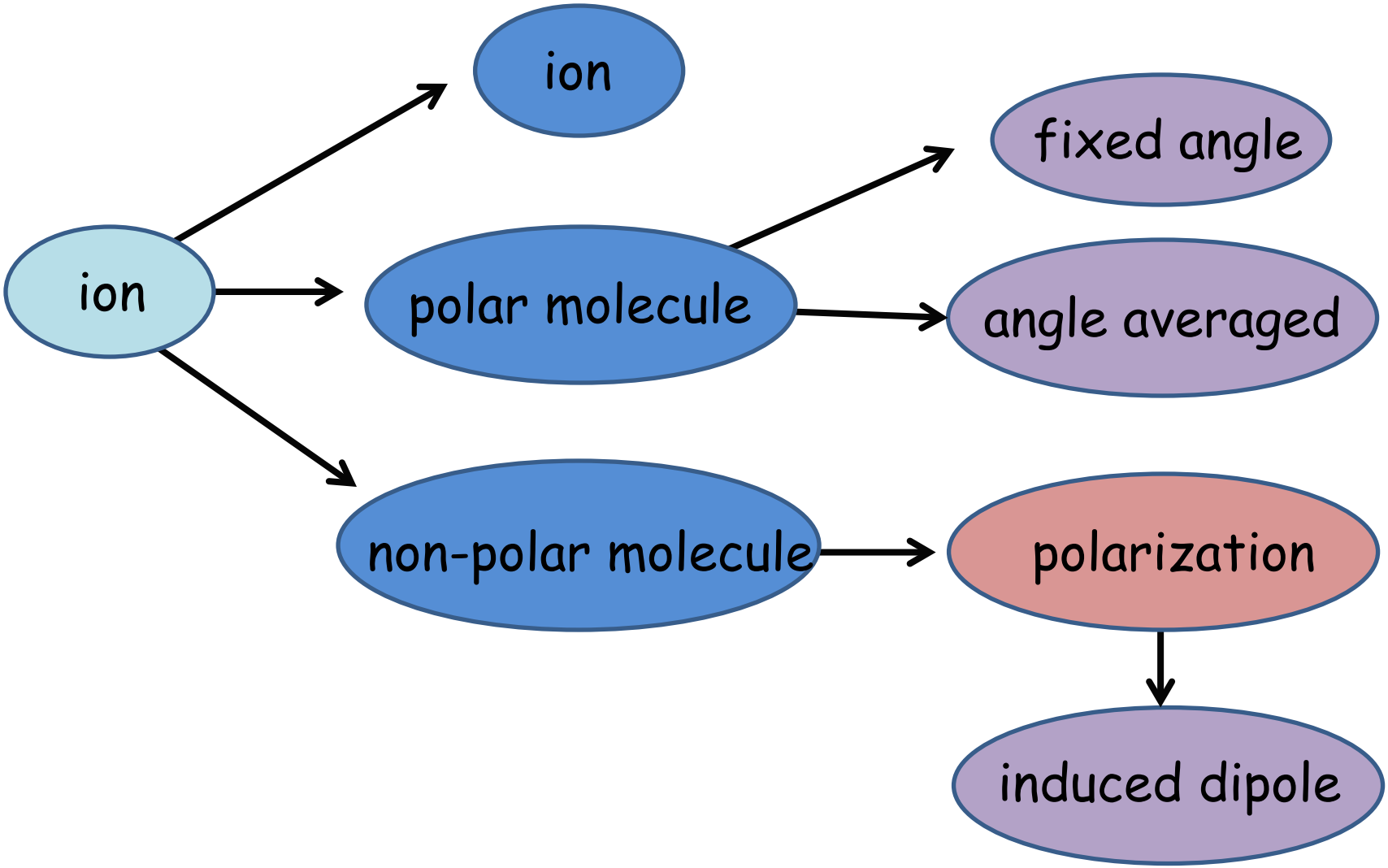


Relevant properties of a few common solvent molecules

Material	Chemical Formula	κ, dielectric constant[1]	p, dipole moment (in Debye)[2,3]	$\alpha_o/4\pi\varepsilon_o$ polarizability volume (in 10^{-30} m^3)
Acetone	$(CH_3)_2CO$	21	2.9	6.3
Isopropanol	$(CH_3)_2CHOH$	18	1.7	6.9
Ethanol	$(CH_3)CH_2OH$	24	1.7	5.1
Methanol	CH_3OH	33	1.7	3.3
Toluene	$C_6H_5CH_3$	2.4	0.4	12.3
Trichlorofluoromethane (CFC-11, Freon-11)	CCl_3F	2.0	0.4[5]	8.5
Water	H_2O	80	1.8	1.5

[1]solvents with κ<15 are generally considered non-polar
[2]dipole moments can be different depending on gas or liquid phase
[3] 1 Debye= 3.33×10^{-30} C·m
Source: http://www.chemspider.com/

Overview: Electrostatic Intermolecular Interactions



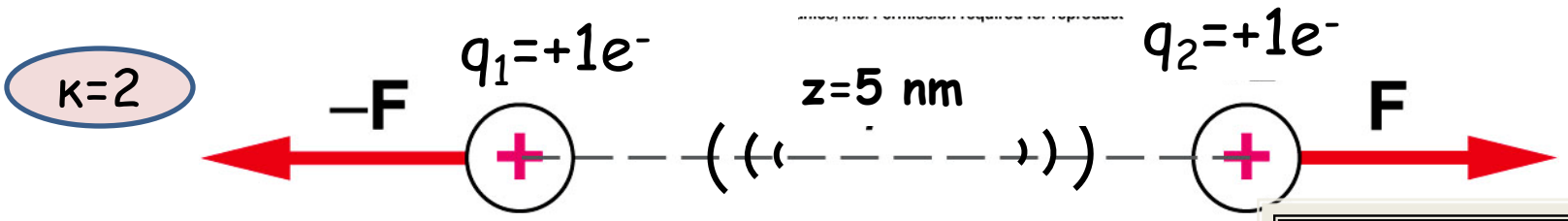
1. Ion-ion interactions

In vacuum, κ=1

$\kappa\,\varepsilon_o \rightarrow \varepsilon_o$

κ (dielectric constant)≥1

Point charges ONLY!



Force is a vector

$$U_{electr}(z) = \frac{1}{4\pi\kappa\varepsilon_o}\frac{q_1 q_2}{z} \quad (in\ Joules)$$

$$= \frac{1}{4\pi(2)} \cdot \frac{1}{8.85\times10^{-12}\ C^2/Nm^2} \cdot \frac{\left(1.6\times10^{-19}C\right)^2}{5\times10^{-9}m}$$

$$= 2.3\times10^{-20}J \cdot \frac{1eV}{1.6\times10^{-19}J} = 0.14eV$$

$$k_B T\big|_{300K} = 1.38\times10^{-23}\,J/K \cdot 300K = 4.1\times10^{-21}J \cdot \frac{1eV}{1.6\times10^{-19}J} = 0.026eV$$

$$|\vec{F}| = -\frac{dU_{electr}}{dz} = \frac{1}{4\pi\kappa\varepsilon_o}\frac{q_1 q_2}{z^2} = \frac{1}{4\pi(2)} \cdot \frac{1}{8.85\times10^{-12}\ C^2/Nm^2} \cdot \frac{\left(1.6\times10^{-19}C\right)^2}{\left(5\times10^{-9}m\right)^2}$$

$$= 4.6\times10^{-12}N = 4.6pN$$

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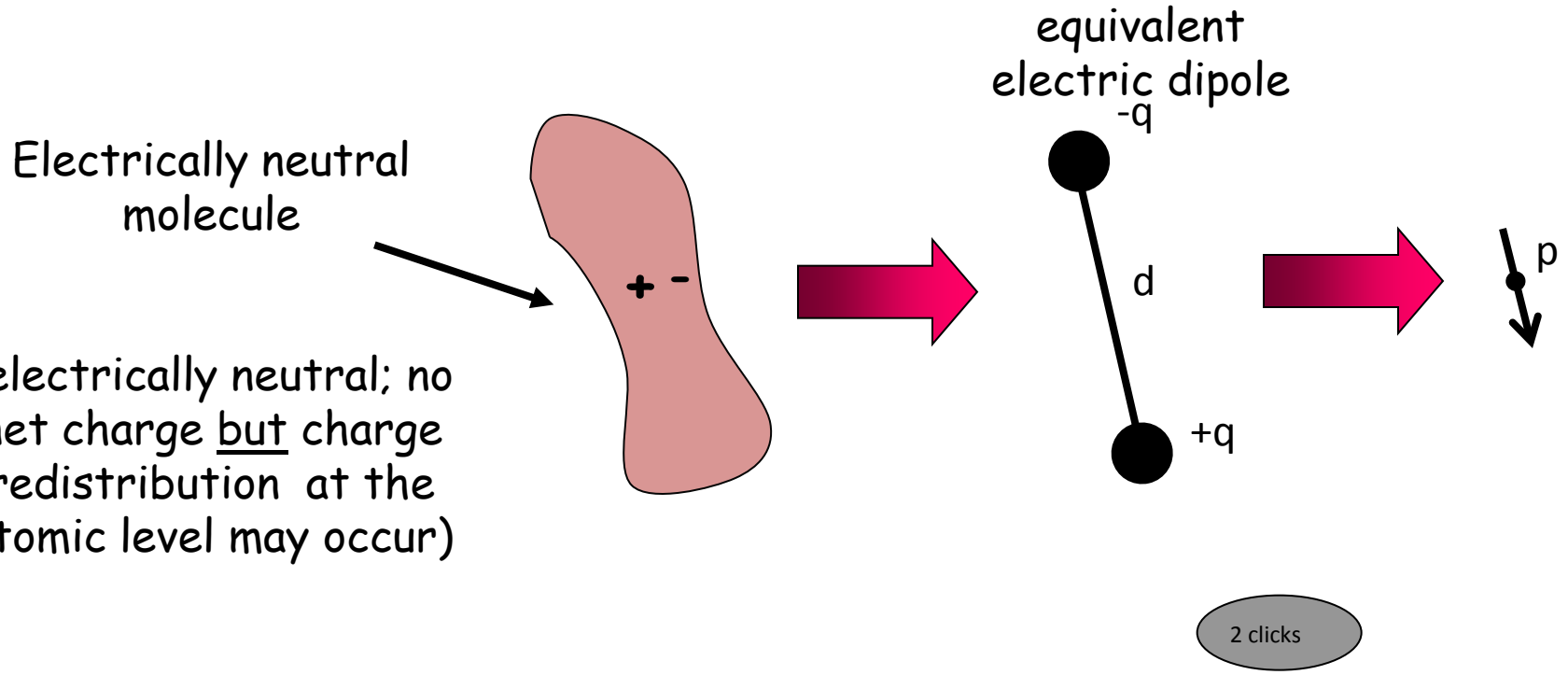
Polar Molecules

Molecules come in all shapes and sizes.

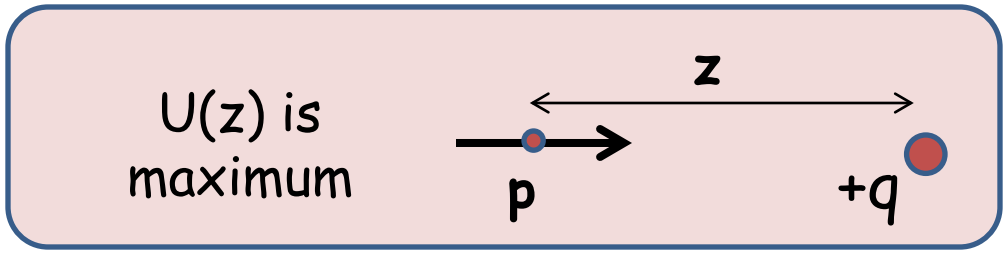
The permanent dipole of a molecule is defined by:
(the magnitude of the charge separated) x (separation distance)

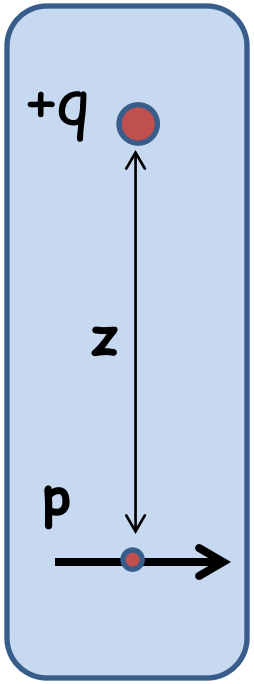
$$|p|=qd$$



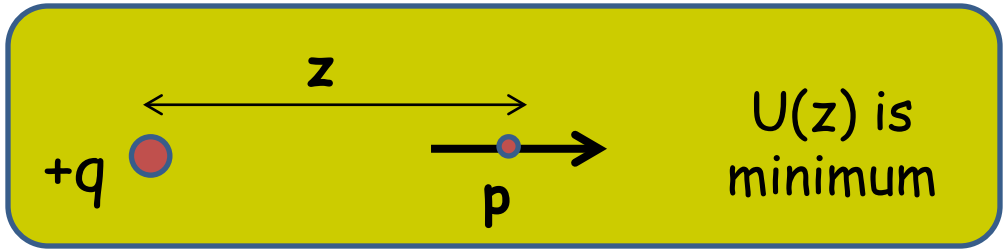
2. Ion -Dipole Interactions

The magnitude and sign of the ion-dipole interaction energy depends strongly on orientation





U(z) is zero



The interaction energy of a point charge Q with a dipole p having a fixed angle θ

$$U_{electr} = \frac{Q}{4\pi\kappa\varepsilon_0}\left(\frac{q}{r_+} + \frac{(-q)}{r_-}\right)$$

$$r_-^2 = \left(x_o + \frac{d}{2}\right)^2 + y_o^2 = \left(x_o^2 + y_o^2\right) + x_o d + \left(\frac{d}{2}\right)^2 \simeq z^2\left(1 + \frac{x_o d}{z^2}\right)$$

$$r_+^2 = \left(x_o - \frac{d}{2}\right)^2 + y_o^2 \simeq z^2\left(1 - \frac{x_o d}{z^2}\right)$$

$$U_{electr} = \frac{Qq}{4\pi\kappa\varepsilon_0}\left[\left(z^2\left(1 - \frac{x_o d}{z^2}\right)\right)^{-1/2} - \left(z^2\left(1 + \frac{x_o d}{z^2}\right)\right)^{-1/2}\right]$$

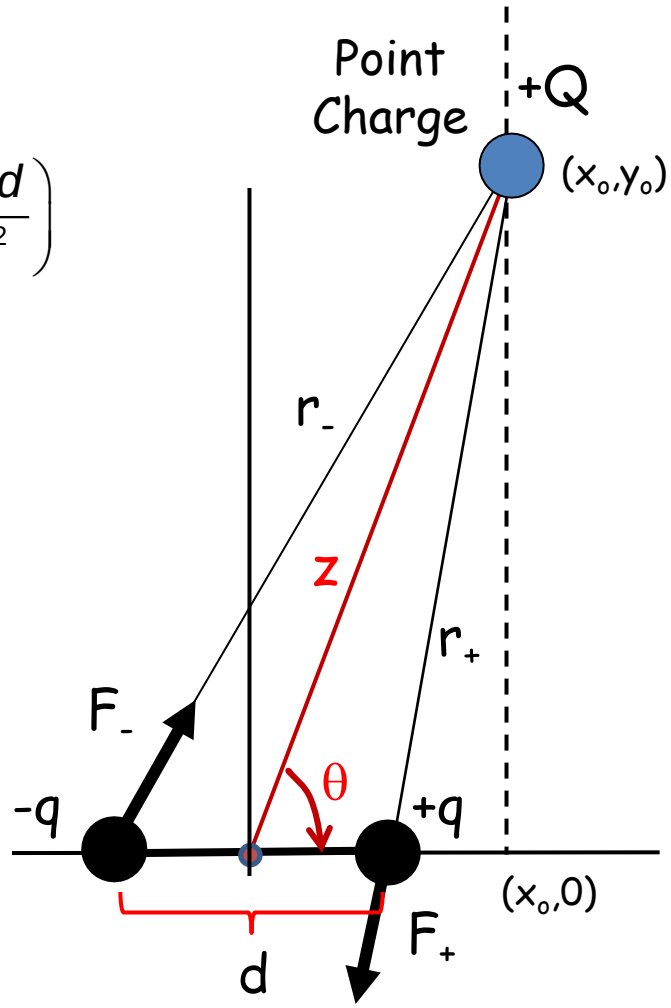
$$= \frac{Qq}{4\pi\kappa\varepsilon_0}\frac{1}{z}\left[\left(1 + \frac{1}{2}\frac{x_o d}{z^2} + \ldots\right) - \left(1 - \frac{1}{2}\frac{x_o d}{z^2} + \ldots\right)\right]$$

$$= \frac{Qq}{4\pi\kappa\varepsilon_0}\frac{1}{z}\frac{x_o d}{z^2} = \frac{Qp}{4\pi\kappa\varepsilon_0}\frac{1}{z^2}\cos\theta$$

$U_{electr} > 0$ *when* $0 \le \theta \le \frac{\pi}{2}$

$U_{electr} < 0$ *when* $\frac{\pi}{2} \le \theta \le \pi$

sign of U_{electr}



$$|\vec{p}| = |q|\,d$$

Ion-Dipole Example

$$U(z) = \frac{Q\,p}{4\pi\kappa\varepsilon_0}\frac{1}{z^2}\cos\theta$$

$$p = 1D = 3.33\times10^{-30} C\cdot m$$

$$z = 5\,nm; \quad Q = +1\left|e^-\right|; \quad \kappa = 2$$

$$U(z) = \frac{1.6\times10^{-19} C\cdot 3.33\times10^{-30} C\cdot m}{4\pi(2)8.85\times10^{-12}\ C^2/Nm^2}\frac{1}{\left(5\times10^{-9} m\right)^2}\cos\theta$$

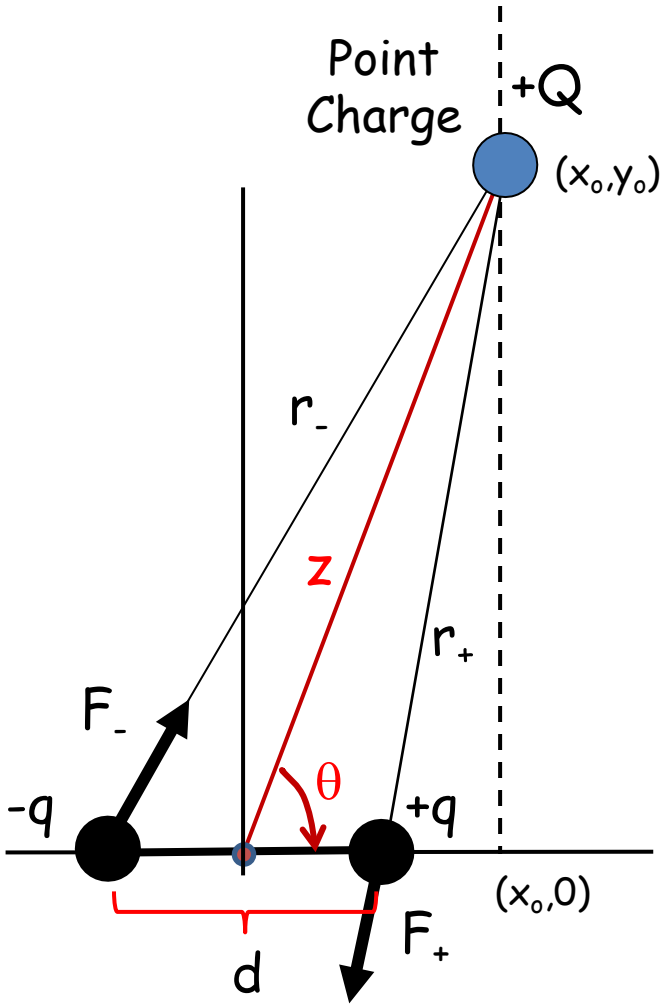
$$= \frac{2.39\times10^{-39}}{25\times10^{-18}}\cos\theta = 9.6\times10^{-23}\cos\theta\,[J]$$

Recall $1ev = 1.6\times10^{-19} J$

$$= 6.0\times10^{-4}\cos\theta\,[eV]$$

magnitude and sign of interaction depends on θ

~200 times weaker than ion-ion interaction



If ion and dipole are not permanently fixed in space, how do we average over angle?