Lecture: P1_Wk1_L4

Inter-Molecular Forces: Ion-Dipole Interaction

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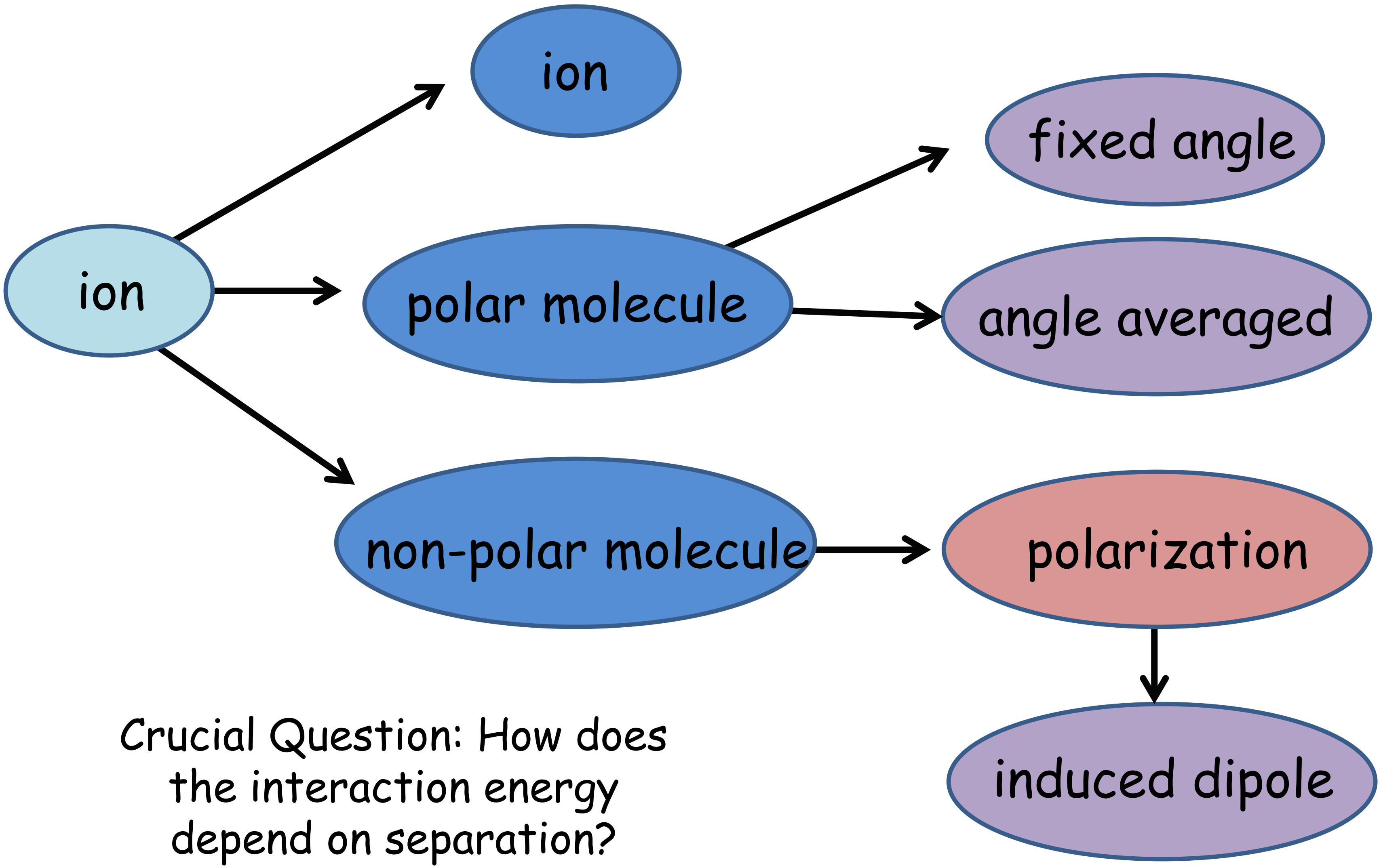
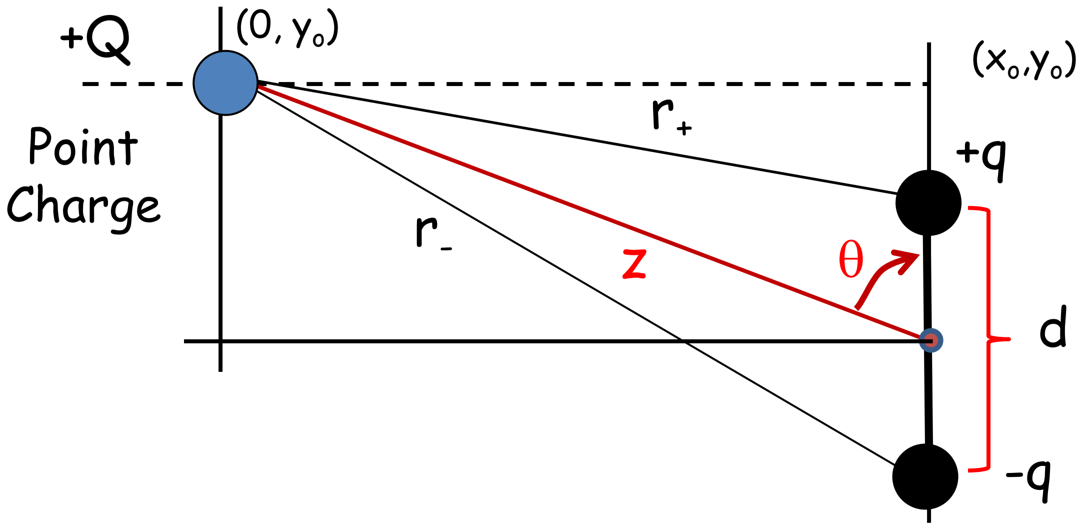
Overview: Electrostatic Intermolecular Interactions



Crucial Question: How does the interaction energy depend on separation?

3. The interaction of a point charge Q with a thermally fluctuating permanent dipole p



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

(from P1_Wk1_L3)

Now, all θ are possible

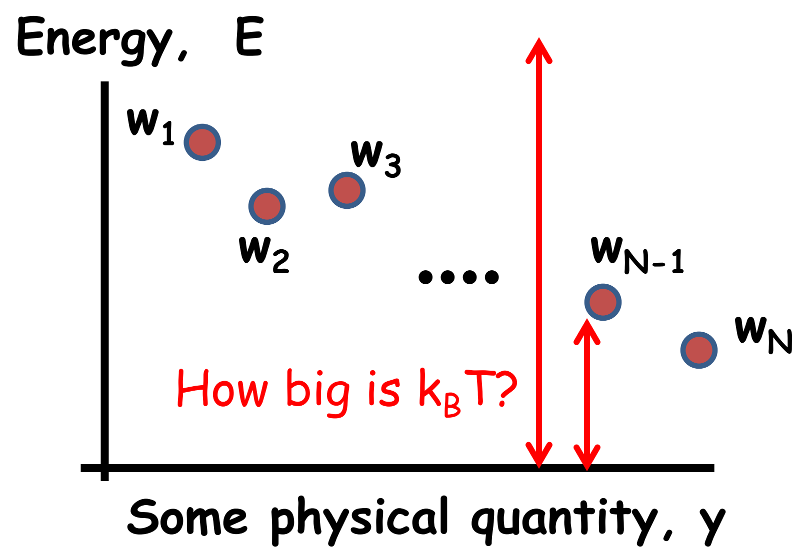
How to properly average over θ?

Use Boltzmann statistics

Quick Review: Calculating Thermodynamic Averages

Question : What is the most likely value you will measure for some quantity "y" in a system that is in thermodynamic equilibrium with a reservoir at temperature T?

Some physical quantity, y	Energy, E	Multiplicity, w
y_1	E_1	w_1
y_2	E_2	w_2
y_3	E_3	w_3
••••	••••	••••
y_{N-1}	E_N	w_N
y_N	E_{N-1}	w_{N-1}



$$\langle y \rangle = \overline{y} = \sum_r y_r P_r$$

P_r = *probability that quantity* y_r *is observed*

P_r = probability of finding a state with energy E_r, degeneracy w_r

$$= \frac{w_r e^{-E_r/k_B T}}{\sum_r w_r e^{-E_r/k_B T}} \text{ when in thermal equilibrium}$$

where $e^{-E_r/k_B T}$ *is the Boltzman factor*

Most probable value of some quantity y with possible values y_r :

$$\langle y \rangle = \bar{y} = \left\langle y e^{-E_r/k_B T} \right\rangle = \frac{\sum_r y_r w_r e^{-E_r/k_B T}}{\sum_r w_r e^{-E_r/k_B T}}$$

Partition function

If varible y is continuous, replace sums by integrals.

Working out the math (see Appendix for details)

$$\langle U(z)\rangle \equiv \left\langle U(z,\theta)e^{-U(z,\theta)/k_BT}\right\rangle = \frac{\int_0^{2\pi} d\varphi \int_0^{\pi} U(z,\theta)e^{-U(z,\theta)/k_BT}\sin\theta\, d\theta}{\int_0^{2\pi} d\varphi \int_0^{\pi} e^{-U(z,\theta)/k_BT}\sin\theta\, d\theta}$$

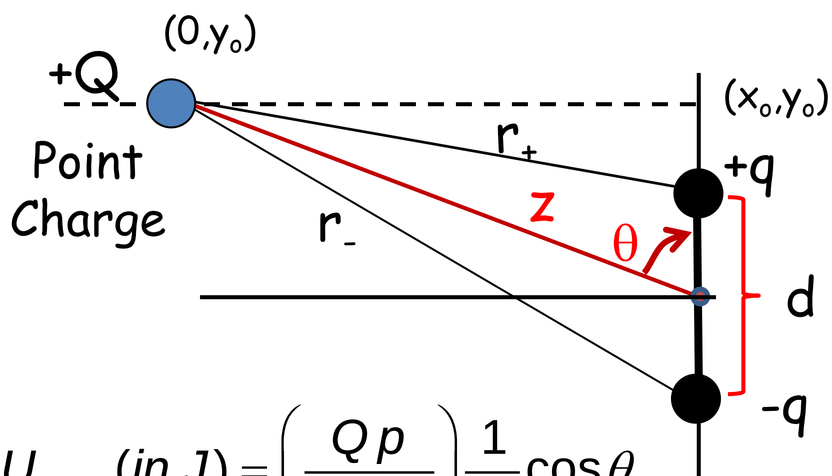
where $U(z,\theta) = \dfrac{Qp}{4\pi\kappa\varepsilon_0}\dfrac{\cos(\theta)}{z^2} = U_o(z)\cos\theta$ **from P1_Wk1_L3**

assume $U(z,\theta)/k_BT << 1;\qquad e^{-U(z,\theta)/k_BT} \simeq 1 - \dfrac{U(z,\theta)}{k_BT} + \ldots;$

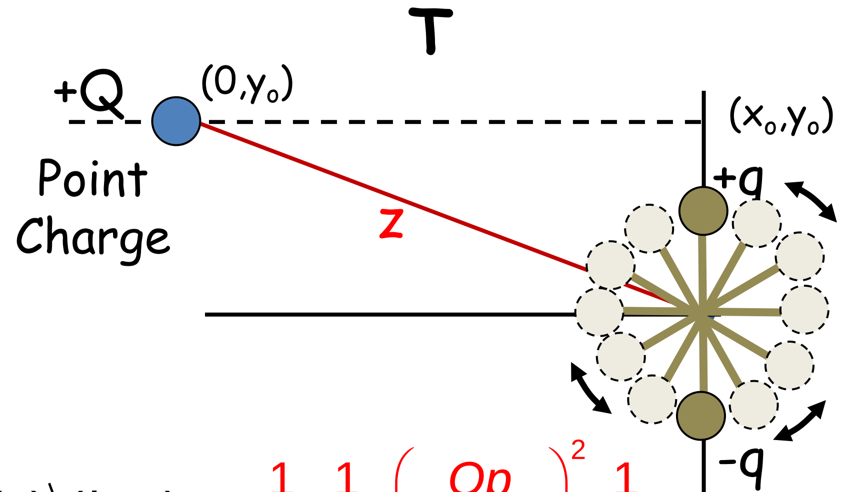
$$\langle U(z)\rangle = -\frac{1}{3}\frac{U_o^2}{k_BT} = -\frac{1}{3}\frac{1}{k_BT}\left(\frac{Qp}{4\pi\kappa\varepsilon_0}\right)^2\frac{1}{z^4}$$

Interaction potential energy between a point charge Q with a <u>thermally fluctuating</u> permanent dipole p

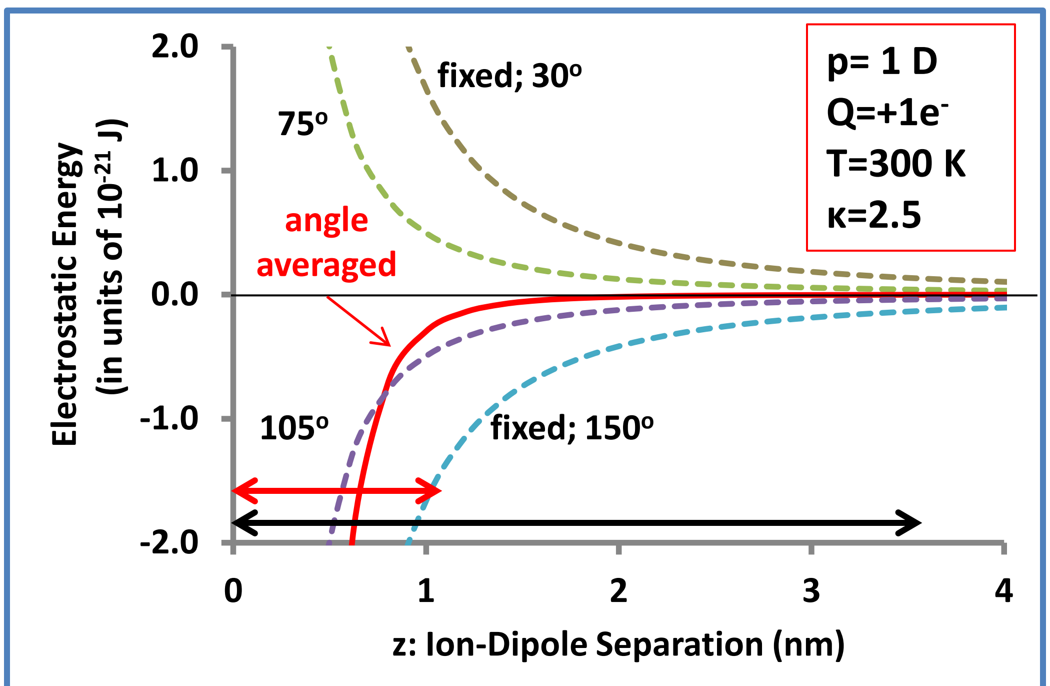
Summarizing the Results



$$U_{electr}(in\ J) = \left(\frac{Q\,p}{4\pi\kappa\varepsilon_0}\right)\frac{1}{z^2}\cos\theta$$



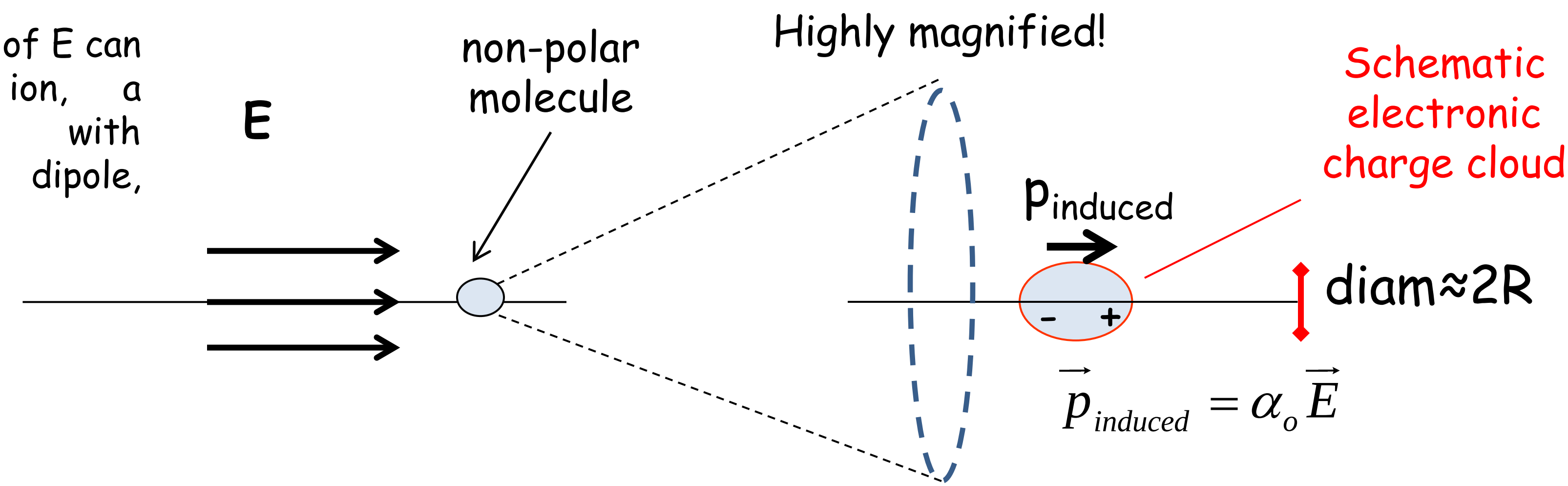
$$\langle U(z)\rangle(in\ J) = -\frac{1}{3}\frac{1}{k_BT}\left(\frac{Qp}{4\pi\kappa\varepsilon_0}\right)^2\frac{1}{z^4}$$



Induction: polarizing a non-polar molecule

Any molecule **not** having an intrinsic dipole moment can be polarized by an external electric field.

The origin of E can be an ion, a molecule with permanent dipole, etc.



$$\vec{p}_{induced} = \alpha_o \vec{E}$$

α_o is called the **electronic** polarizability

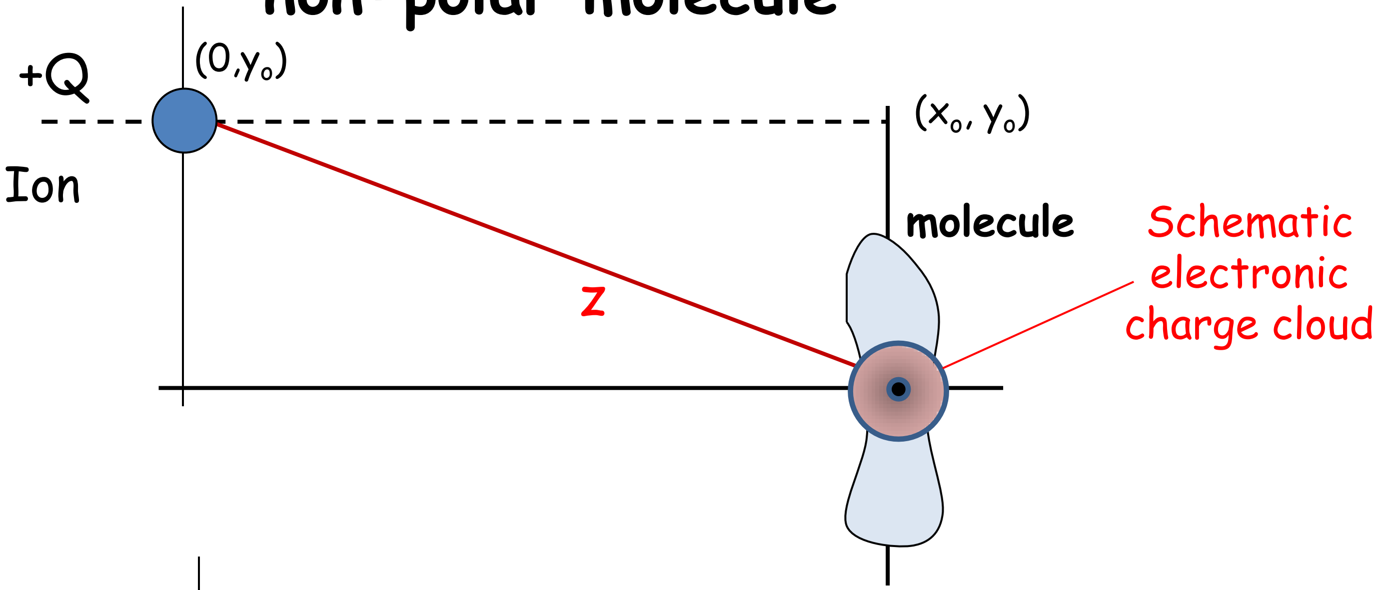
$$\alpha_o \equiv 4\pi\varepsilon_0\alpha \left[units\ C^2m/N\right]; \quad \alpha\left(\text{"electronic polariability volume"}\right) \approx R^3$$

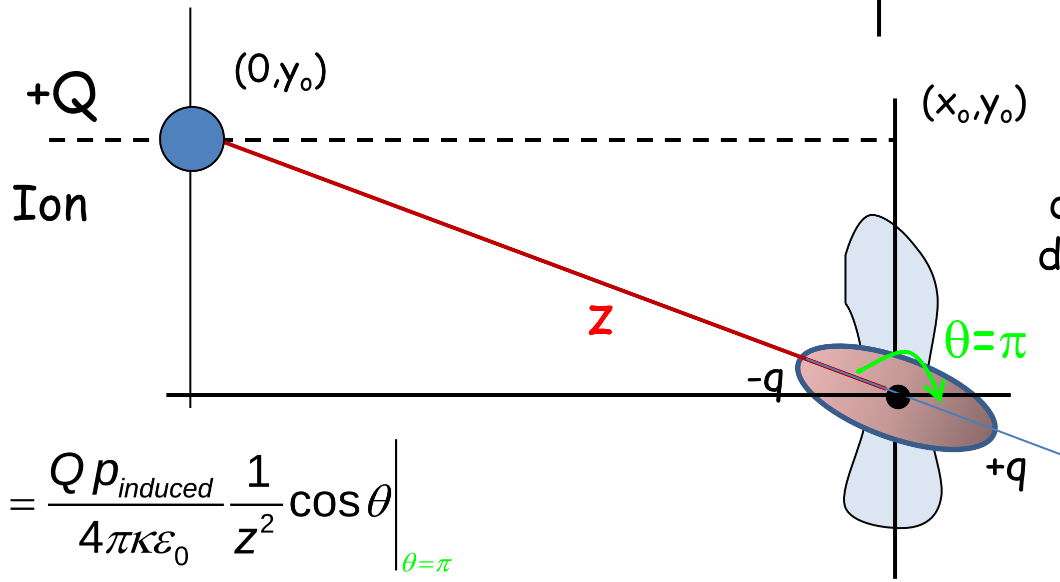
- α has units of m^3.
- to a good approximation, α is proportional to molecule size:

For water, $\alpha = \alpha_o/4\pi\varepsilon_o = 1.48\times10^{-30}\ m^3$

$\rightarrow$ R=0.114 nm – compare to $R_{H_2O} \approx 0.135$ nm

4. The interaction of a point charge Q with a non-polar molecule





Direction of induced dipole is locked by the direction of E from ion.

$$\vec{p}_{induced} = \alpha_o \vec{E} + \ldots$$

$$\alpha_o = 4\pi\varepsilon_o \alpha$$

$$U_{induced}(z) = \frac{Q\,p_{induced}}{4\pi\kappa\varepsilon_0}\frac{1}{z^2}\cos\theta\Big|_{\theta=\pi}$$

$$= -\frac{Q\,p_{induced}}{4\pi\kappa\varepsilon_0}\frac{1}{z^2}$$

Working out the math

$$U_{induced}(z) = -\frac{Q\,p_{induced}}{4\pi\kappa\varepsilon_0}\frac{1}{z^2}$$

$$\left|p_{induced}\right| = \alpha_o E + \ldots; \quad \textit{where } E \textit{ is from point charge}$$

$$E = \frac{1}{4\pi\kappa\varepsilon_o}\frac{Q}{z^2}$$

$$U_{induced}(z) = -\frac{Q\,p_{induced}}{4\pi\kappa\varepsilon_0}\frac{1}{z^2} = -\frac{Q\,\alpha_o E}{4\pi\kappa\varepsilon_0}\frac{1}{z^2}$$

$$= -\frac{Q\,\alpha_o}{4\pi\kappa\varepsilon_0}\frac{1}{4\pi\kappa\varepsilon_o}\frac{Q}{z^2}\frac{1}{z^2} = -\frac{\alpha_o Q^2}{\left(4\pi\kappa\varepsilon_0\right)^2}\frac{1}{z^4}$$

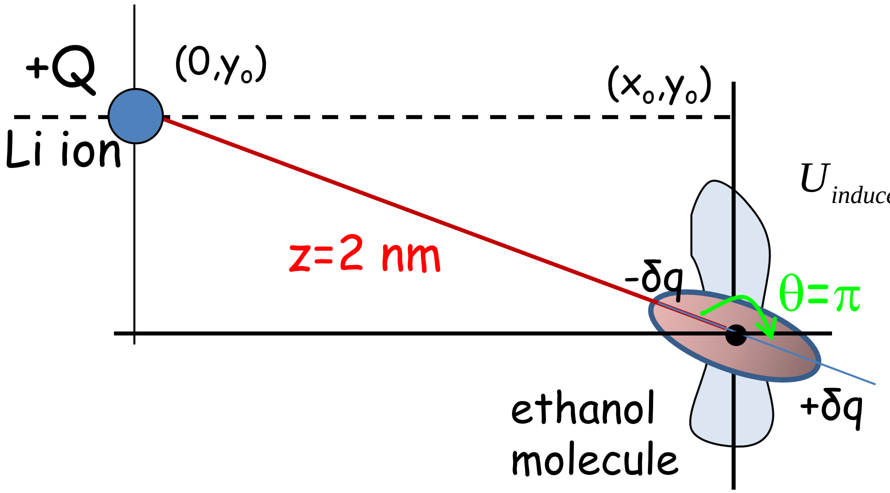
The electrostatic interaction between an ion of charge Q and a molecule with polarizability α_o varies as z^{-4}

Li ion induces dipole in ethanol molecule

from C1_Wk1_L3

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)
Ethanol	$(CH_3)CH_2OH$	24	1.7	5.1

Permanent dipole moment



$$U_{induced}(z) = -\frac{\alpha_o Q^2}{(4\pi\kappa\varepsilon_0)^2}\frac{1}{z^4} = -\frac{4\pi\varepsilon_0\alpha Q^2}{(4\pi\kappa\varepsilon_0)^2}\frac{1}{z^4}$$

$$= -\frac{\alpha Q^2}{(4\pi\varepsilon_0)}\frac{1}{\kappa^2}\frac{1}{z^4}$$

$$= -\frac{(5.1\times10^{-30}\,m^3)(1.6\times10^{-19}\,C)^2}{4\pi\cdot 8.85\times10^{-12}\,C^2/Nm^2}\frac{1}{(24)^2}\frac{1}{(2\times10^{-9}\,m)^4}$$

$$= 1.17\times10^{-57}\cdot 1.74\times10^{-3}\cdot 6.25\times10^{34}\,J$$

$$= 1.27\times10^{-25}\,J\cdot\frac{1eV}{1.6\times10^{-19}\,J} = -7.94\times10^{-7}\,eV$$

$$k_BT\big|_{300K} = 4.1\times10^{-21}\,J\cdot\frac{1eV}{1.6\times10^{-19}\,J}$$

$$= 0.026\,eV$$

Compare to interaction of Li ion with "angle-averaged", permanent dipole interaction energy

(assume T=300K)

$$\langle U(z)\rangle = -\frac{1}{3}\frac{1}{k_BT}\left(\frac{Qp}{4\pi\kappa\varepsilon_0}\right)^2\frac{1}{z^4}$$ (from slide 6, this lecture)

$$= -\frac{1}{3}\frac{1}{\left(1.38\times10^{-23}J/K\right)\left(300K\right)}\left(\frac{1.6\times10^{-19}C\cdot(1.7D)\cdot\left(\frac{3.33\times10^{-30}Cm}{1D}\right)}{4\pi\cdot(24)\cdot8.85\times10^{-12}C^2/Nm^2}\right)^2\frac{1}{\left(2\times10^{-9}m\right)^4}$$

$$= -\left(\frac{1}{1.24\times0^{-20}J}\right)\cdot\left(\frac{9.06\times10^{-49}}{2.67\times10^{-9}}Nm^3\right)^2\cdot6.25\times10^{34}m^{-4}$$

$$= -5.81\times0^{-25}J\cdot\frac{1eV}{1.6\times10^{-19}J} = -3.63\times0^{-6}eV$$

$$\frac{\langle U(z)\rangle}{U_{induced}} = \frac{-3.63\times0^{-6}eV}{-7.94\times10^{-7}eV} = 4.6$$

Up next, what happens if
there are no ions?

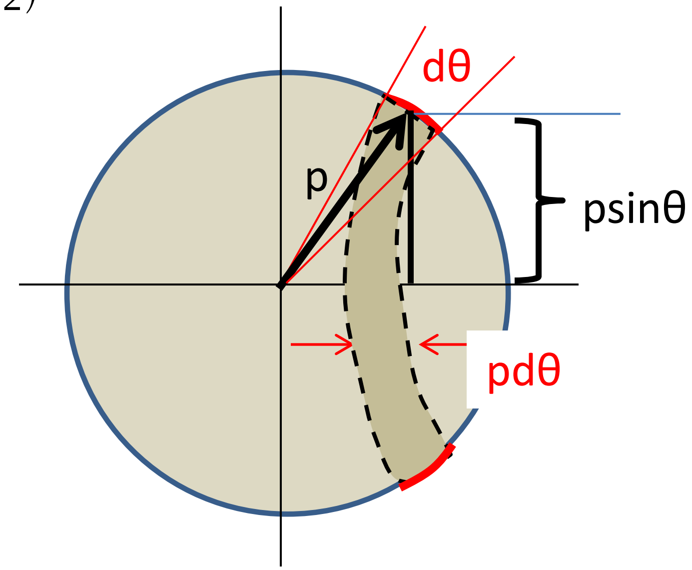
Molecule-molecule
(or atom-atom)
dipolar interactions

Appendix 1: Weighting the angle of the dipole

$$P(\theta) = \text{probability that vector } \vec{p} \text{ lies between } \left(\theta - {}^{d\theta}\!/_{2}\right) \text{ and } \left(\theta + {}^{d\theta}\!/_{2}\right)$$

$$= \frac{\text{area of stripe}}{\text{surface area of sphere}} = \frac{\int_{\varphi=0}^{2\pi} d\varphi \cdot (p\sin\theta)\cdot(p\,d\theta)}{\int_{\varphi=0}^{2\pi} d\varphi \cdot \int_{\theta=0}^{\pi} (p\sin\theta)\cdot(p\,d\theta)}$$

$$= \frac{\sin\theta\,d\theta}{\int_0^{\pi}\sin\theta\,d\theta} = \frac{\sin\theta\,d\theta}{-\cos\theta\big|_0^{\pi}} = \frac{1}{2}\sin\theta\,d\theta$$



$$\text{angle weighted value of some } f(\theta) \equiv \langle f(\theta)\rangle = \frac{1}{2}\int_0^{\pi} f(\theta)\sin\theta\,d\theta$$

Standard results:

$$\langle C\rangle = \frac{C}{2}\int_0^{\pi}\sin\theta\,d\theta = -\frac{C}{2}\cos\theta\Big|_0^{\pi} = C \qquad \langle\cos\theta\rangle = \frac{1}{2}\int_0^{\pi}\cos\theta\sin\theta\,d\theta = 0$$

$$\langle\sin\theta\rangle = \frac{1}{2}\int_0^{\pi}\sin^2\theta\,d\theta = \frac{1}{2}\cdot\frac{(\theta-\sin\theta\cos\theta)}{2}\Big|_0^{\pi} = \frac{\pi}{4}$$

$$\langle\sin^2\theta\rangle = \frac{1}{2}\int_0^{\pi}\sin^3\theta\,d\theta = \frac{1}{2}\frac{(\cos3\theta - 9\cos\theta)}{12}\Big|_0^{\pi} = \frac{1}{2}\frac{(-1)-9(-1)-(1-9)}{12} = \frac{2}{3}$$

$$\langle\cos^2\theta\rangle = \frac{1}{2}\int_0^{\pi}\cos^2\theta\sin\theta\,d\theta = \frac{1}{2}\int_0^{\pi}\cos^2\theta\,d(\cos\theta) = \frac{1}{2}\int_{-1}^{1}x^2dx = \frac{1}{2}\cdot\frac{x^3}{3}\Big|_{-1}^{1} = \frac{1}{3}$$

$$\langle\sin\theta\cos\theta\rangle = \frac{1}{2}\int_0^{\pi}\cos\theta\sin^2\theta\,d\theta = \frac{1}{2}\frac{\sin^3\theta}{3}\Big|_0^{\pi} = 0$$

Appendix 2: Derivation of the angle-averaged point charge-dipole interaction

You might be tempted to just perform the angle average of U(z,θ)

$$\langle U(z)\rangle \equiv \frac{\int_0^{2\pi} d\varphi \int_0^{\pi} U(z,\theta)\sin\theta\, d\theta}{\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta\, d\theta}; \qquad \text{where} \quad U(z,\theta) = \frac{Qp}{4\pi\kappa\varepsilon_0}\frac{\cos(\theta)}{z^2} = U_o(z) f(\theta); \quad f(\theta) = \cos\theta$$

$$\langle U(z)\rangle = \frac{U_o(z)\int_0^{\pi} \cos\theta \sin\theta\, d\theta}{\int_0^{\pi} \sin\theta\, d\theta} = \frac{-\frac{1}{2}\cos^2\theta\Big|_0^{\pi}}{-\cos\theta\Big|_0^{\pi}} = \frac{1}{2}\frac{\left[(-1)^2 - (1)^2\right]}{(-1)-(1)} = 0$$

The result is zero because it calculates the angle average for a free dipole in which all angles are equally likely. Instead, a weighted angle average must be performed that preferentially weights those angles with lowest energy. This requires the Boltzmann weighting factor

$$\langle U(z)\rangle \equiv \left\langle U(z,\theta)\, e^{-U(z,\theta)/k_BT} \right\rangle = \frac{\int_0^{2\pi} d\varphi \int_0^{\pi} U(z,\theta) e^{-U(z,\theta)/k_BT} \sin\theta\, d\theta}{\int_0^{2\pi} d\varphi \int_0^{\pi} e^{-U(z,\theta)/k_BT} \sin\theta\, d\theta}$$

$$= \frac{U_o(z) \int_0^{\pi} f(\theta) e^{-U_o(z) f(\theta)/k_BT} \sin\theta\, d\theta}{\int_0^{\pi} e^{-U_o(z) f(\theta)/k_BT} \sin\theta\, d\theta}$$

$$\textit{define} \quad \beta = -\frac{U_o(z)}{k_BT}, \quad \textit{then} \quad \left\langle U(z,\theta) e^{-U(z,\theta)/k_BT} \right\rangle = U_o(z) \frac{\int_0^{\pi} f(\theta) e^{\beta f(\theta)} \sin\theta\, d\theta}{\int_0^{\pi} e^{\beta\theta} \sin\theta\, d\theta}$$

$$= U_o(z) \frac{d}{d\beta} \ln\left(\int_0^{\pi} e^{\beta f(\theta)} \sin\theta\, d\theta \right)$$

$$\textit{since} \quad \frac{d}{d\beta} \ln\left(\int_0^{\pi} e^{\beta f(\theta)} \sin\theta\, d\theta \right) = \frac{1}{\left(\int_0^{\pi} e^{\beta f(\theta)} \sin\theta\, d\theta \right)} \times \left(\int_0^{\pi} f(\theta) e^{\beta f(\theta)} \sin\theta\, d\theta \right)$$

This means you only need to evaluate the integral $\int_0^{\pi} e^{\beta f(\theta)} \sin\theta\, d\theta$ and then take a derivative *if* $\beta f(\theta) << 1$, *we can write*

$$\int_0^{\pi} e^{\beta f(\theta)} \sin\theta \, d\theta \simeq \int_0^{\pi} \left[1 + \beta f(\theta) + \frac{\beta^2}{2} f^2(\theta) + \ldots \right] \sin\theta \, d\theta$$

$$= \int_0^{\pi} \sin\theta \, d\theta + \beta \int_0^{\pi} f(\theta) \sin\theta \, d\theta + \frac{\beta^2}{2} \int_0^{\pi} f^2(\theta) \sin\theta \, d\theta + \ldots$$

$$= -\cos\theta \Big|_0^{\pi} + 0 + \frac{\beta^2}{2} \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta + \ldots = 2 - \frac{\beta^2}{2} \frac{1}{3} \cos^3\theta \Big|_o^{\pi} = 2 - \frac{\beta^2}{2} \frac{1}{3} \left[(-1)^3 - (1)^3 \right]$$

$$= 2 + \frac{\beta^2}{3}$$

$$\therefore \quad \langle U(z) \rangle \equiv \left\langle U(z,\theta) e^{-U(z,\theta)/k_B T} \right\rangle = U_o(z) \frac{d}{d\beta} \ln\left(\int_0^{\pi} e^{\beta f(\theta)} \sin\theta \, d\theta \right) = U_o(z) \cdot \frac{d}{d\beta} \ln\left(2 + \frac{\beta^2}{3} \right)$$

$$= U_o(z) \cdot \frac{1}{\left(2 + \frac{\beta^2}{3} \right)} \cdot \frac{2\beta}{3} \simeq \frac{\beta}{3} U_o(z);$$

where $\beta \equiv -\dfrac{U_o(z)}{k_B T}$ *and* $U_o(z) = \dfrac{Qp}{4\pi\kappa\varepsilon_0} \dfrac{\cos(\theta)}{z^2}$

$$= -\frac{1}{3} \left(\frac{U_o(z)}{k_B T} \right) \cdot U_o(z) = -\frac{1}{3 k_B T} \frac{(Qp)^2}{(4\pi\kappa\varepsilon_0)^2} \frac{1}{z^4}$$