

Lecture: P1_Wk1_L5

Inter-Molecular Forces: Keesom Force

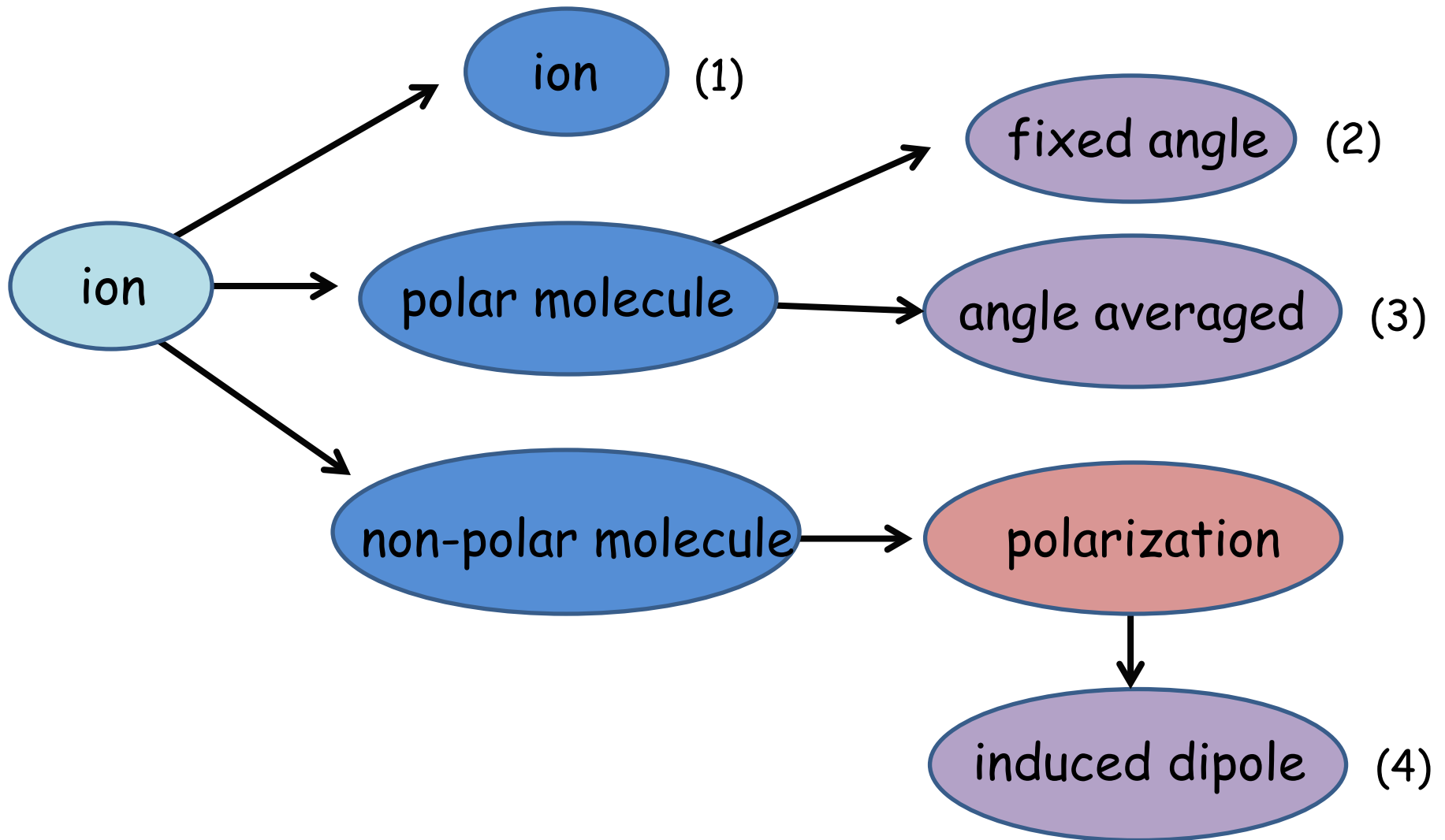
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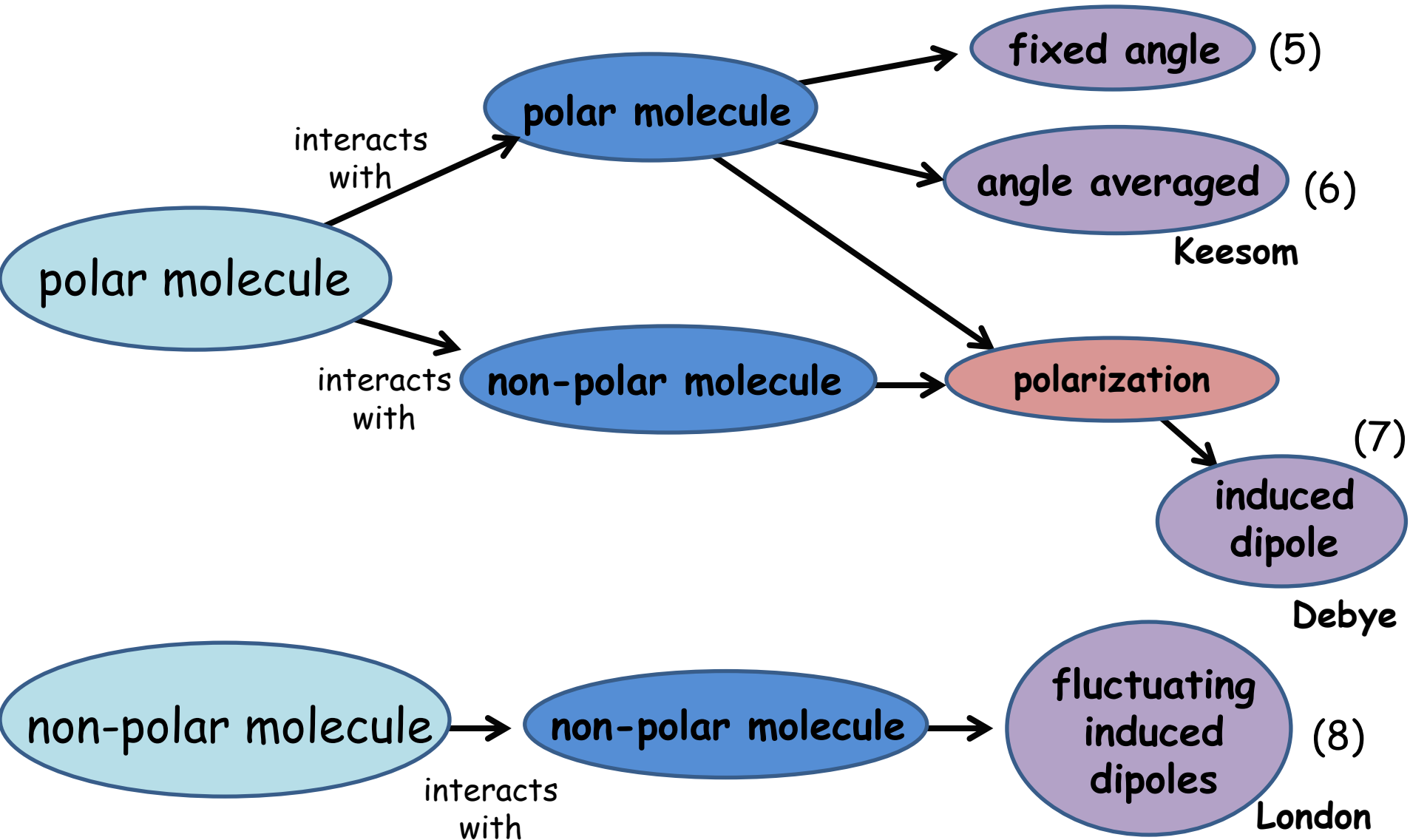
Purdue University

2012

Last Lecture: Electrostatic Intermolecular Interactions



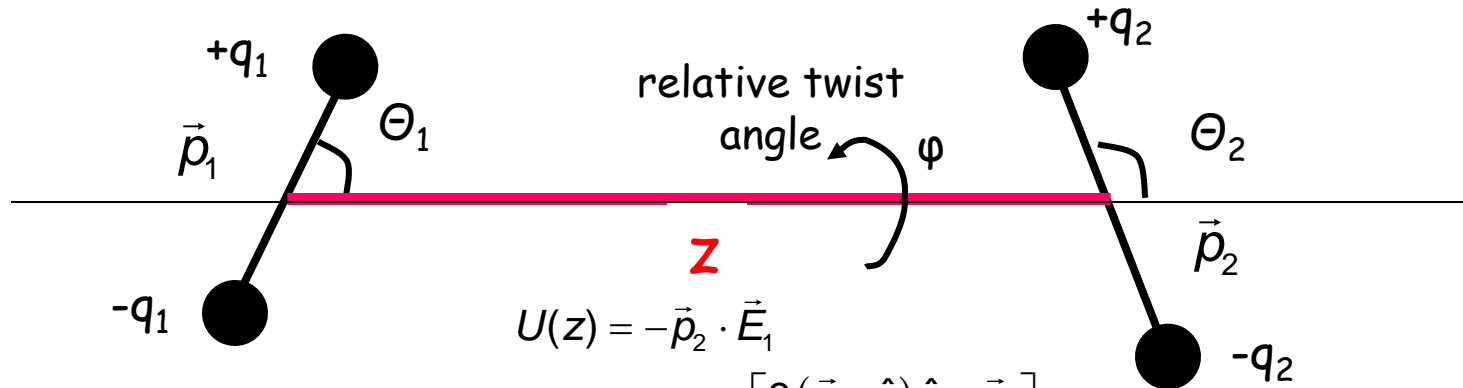
This Lecture: Electrostatic Intermolecular Interactions



Keesom:Debye:London \approx 100:10:1

5. Interaction between polar molecules: fixed orientation

already four parameters: separation distance (z) + 3 angles ($\Theta_1, \Theta_2, \varphi$)



$$U(z) = -\vec{p}_2 \cdot \vec{E}_1$$

$$\vec{E}_1 = \vec{E}_{1, \text{dipole}} = \frac{1}{4\pi\kappa\epsilon_0} \frac{[3(\vec{p}_1 \cdot \hat{z})\hat{z} - \vec{p}_1]}{z^3}$$

$$\therefore U(z) = \frac{\vec{p}_1 \cdot \vec{p}_2}{z^3} - 3 \frac{(\vec{p}_1 \cdot \hat{z})(\vec{p}_2 \cdot \hat{z})}{z^3}$$

or

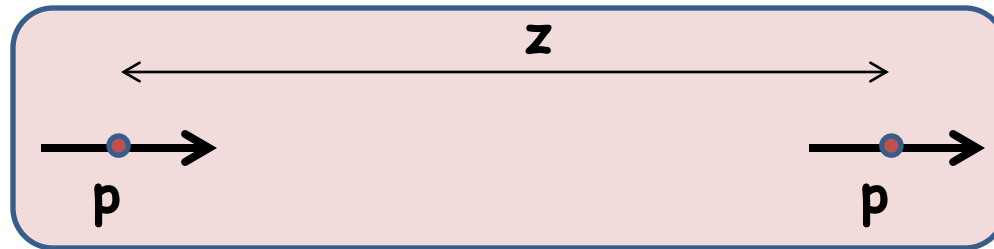
$$U(\theta_1, \theta_2, \varphi, z) = - \frac{p_1 p_2 [2 \cos(\theta_1) \cos(\theta_2) - \sin(\theta_1) \sin(\theta_2) \cos(\varphi)]}{4\pi\kappa\epsilon_0} \frac{1}{z^3}$$

$$= \frac{p_1 p_2}{4\pi\kappa\epsilon_0} \frac{1}{z^3} \cdot f(\theta_1, \theta_2, \varphi); \quad -2 \leq f(\theta_1, \theta_2, \varphi) < 2$$

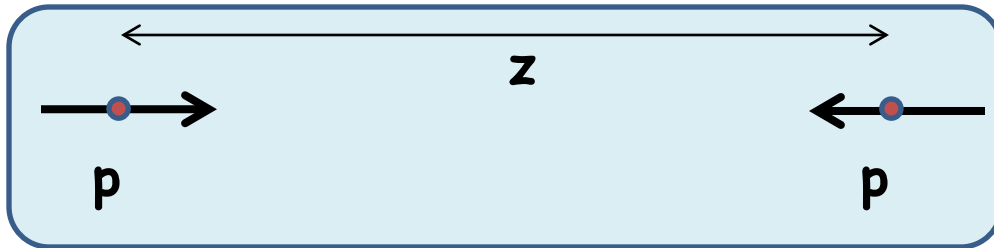
lowest energy when $\theta_1 = \theta_2 = 0 \Rightarrow U(0, 0, \varphi, z) = - \frac{2p_1 p_2}{4\pi\kappa\epsilon_0} \frac{1}{z^3}$

Dipole-Dipole Interactions

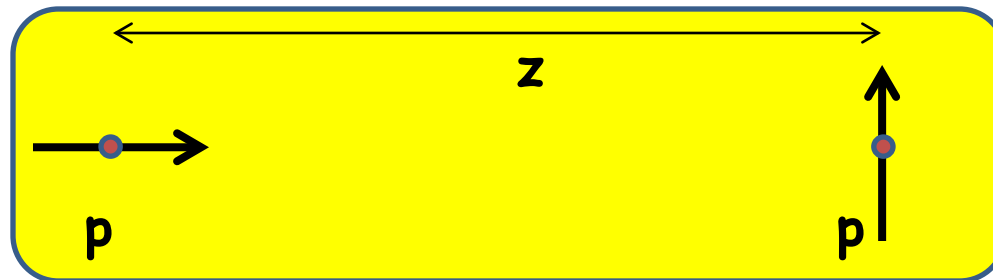
The magnitude and sign of the dipole-dipole energy depends strongly on orientation



$U(z)$ is minimum

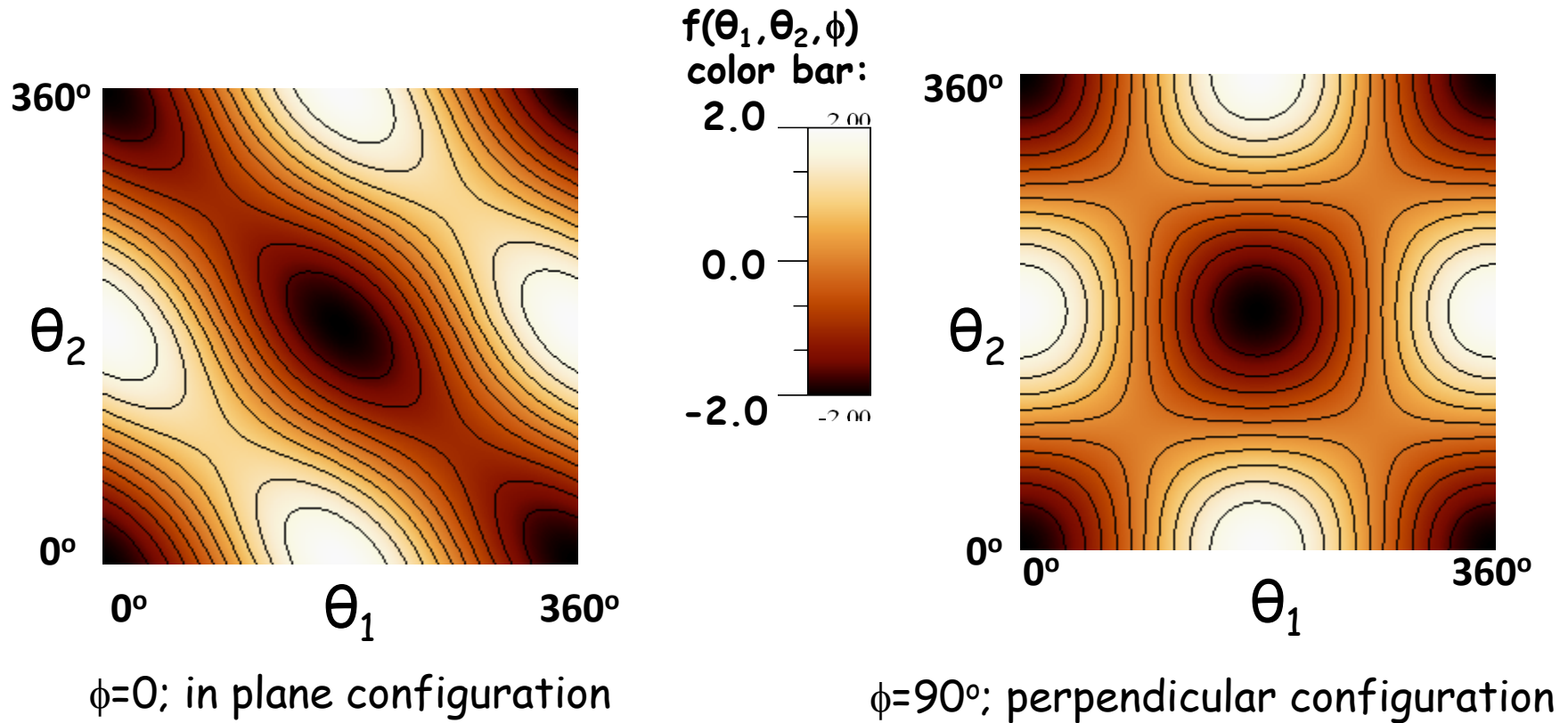


$U(z)$ is maximum



$U(z)$ is zero

Representative plots of $f(\theta_1, \theta_2, \phi)$

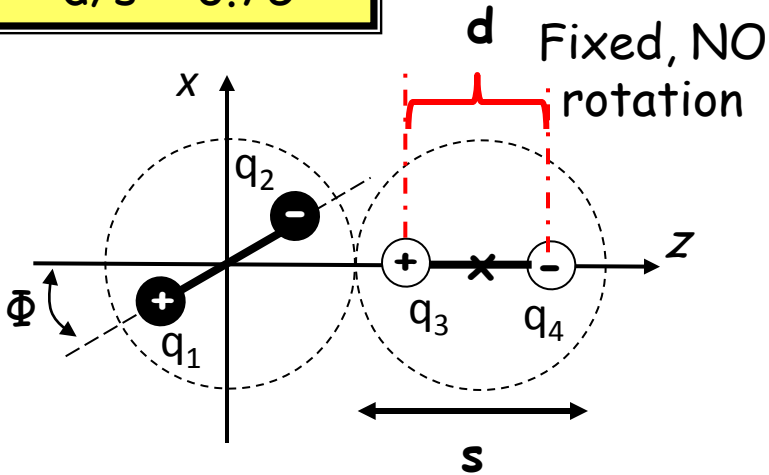


$$U(\theta_1, \theta_2, \varphi, z) = \frac{\rho_1 \rho_2}{4\pi\kappa\epsilon_0} \frac{1}{z^3} f(\theta_1, \theta_2, \varphi)$$

$$f(\theta_1, \theta_2, \varphi) = -[2\cos(\theta_1)\cos(\theta_2) - \sin(\theta_1)\sin(\theta_2)\cos(\varphi)]$$

Interaction potential energy between in-plane ($\phi=0^\circ$) permanent dipoles

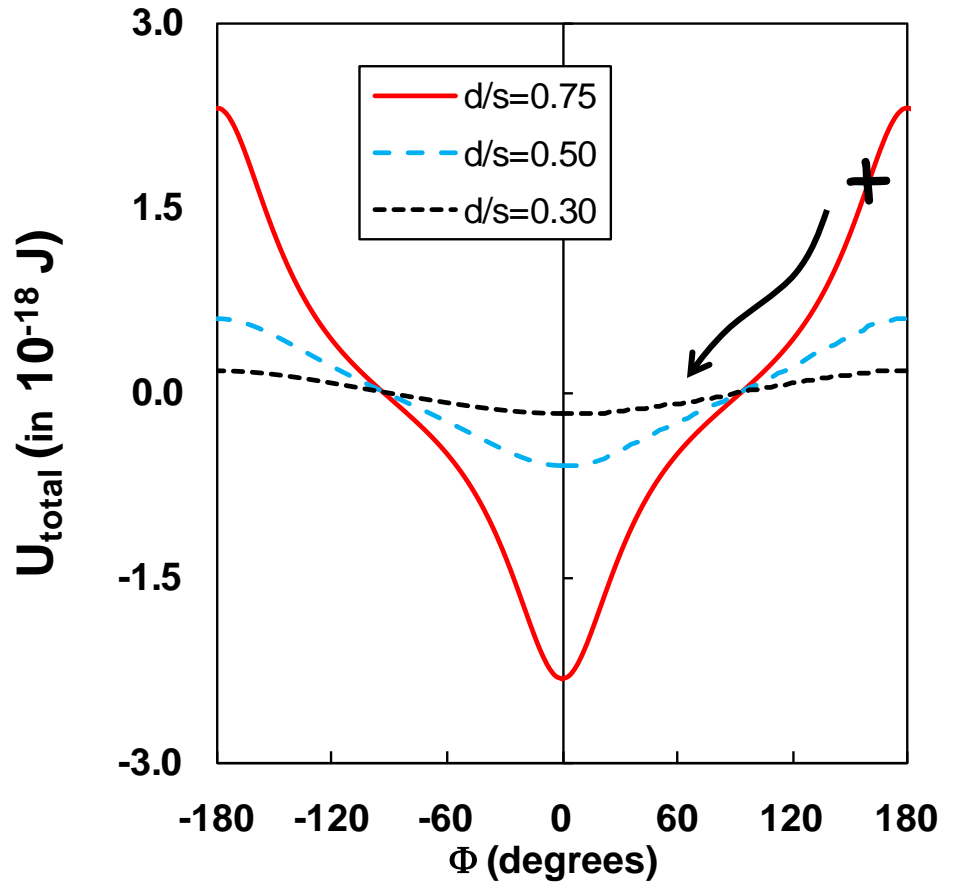
diagram for $d/s \approx 0.75$



Symbol	Actual Charge
q_1	$+q$
q_2	$-q$
q_3	$+q$
q_4	$-q$

Note: $|p_1| = |p_2|$

$|q| = 1 \times 10^{-18} \text{ C}; s = 10 \text{ nm}$



6. Interaction between polar molecules: angle averaged

dipole-dipole interaction must be properly angle-averaged by allowing the orientation of dipoles p_1 and p_2 to fluctuate. Must calculate

$$\langle U(z) \rangle \equiv \left\langle U(z, \theta_1, \theta_2, \phi) e^{-U(z, \theta_1, \theta_2, \phi) / k_B T} \right\rangle$$

$$\text{where } U(z, \theta_1, \theta_2, \phi) = -\frac{p_1 p_2 [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]}{4 \pi \kappa \epsilon_0} \frac{1}{z^3}$$

here $\langle \dots \rangle$ represents the proper thermal average over all angles

The complete derivation is given in Appendix A :

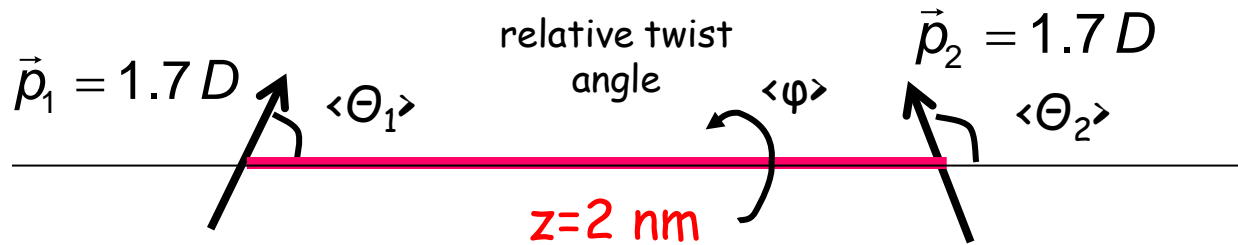
$$U_{\text{Keesom}}(z) = -\frac{2}{3} \frac{1}{k_B T} \left(\frac{p_1 p_2}{4 \pi \kappa \epsilon_0} \right)^2 \frac{1}{z^6} = -\frac{C_K}{z^6}$$

(also known as the Keesom interaction; W.H. Keesom, *Physik. Z.* **22**, 129 (1921) and **22**, 643 (1921))

The Keesom interaction between two ethanol molecules

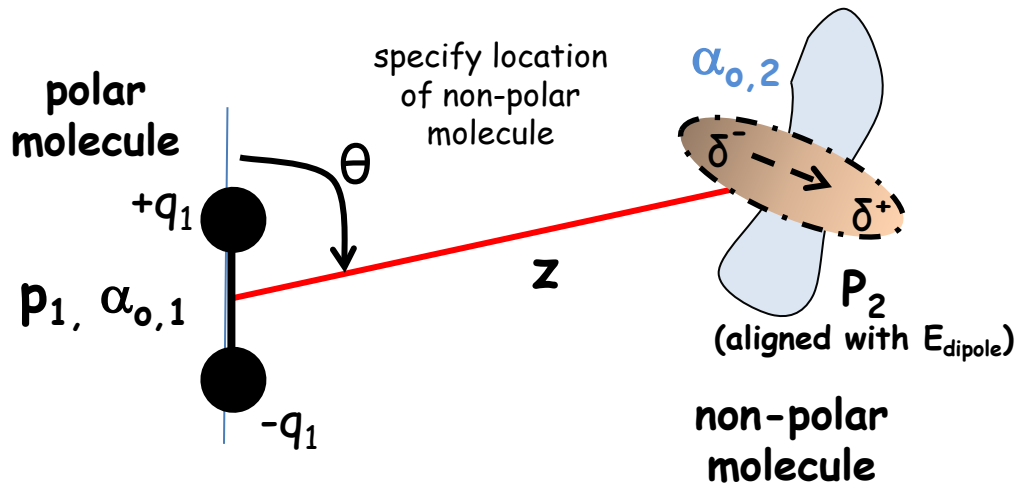
from P1_Wk1_L3

Material	Chemical Formula	κ , dielectric constant ¹	p , dipole moment (in Debye) ^{2,3}	$\alpha_0/4\pi\epsilon_0$ polarizability volume (in 10^{-30} m^3)
Ethanol	$(\text{CH}_3)\text{CH}_2\text{OH}$	24	1.7	5.1



$$\begin{aligned}
 U_{\text{Keesom}}(z) &= -\frac{2}{3} \frac{1}{k_B T} \left(\frac{p_1 p_2}{4\pi\kappa\epsilon_0} \right)^2 \frac{1}{z^6} = -\frac{2}{3} \frac{1}{(1.38 \times 10^{-23} \text{ J/K})(300\text{K})} \frac{1}{4\pi \cdot (24) \cdot 8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2} \left(\left((1.7 \text{ D}) \cdot \left(\frac{3.33 \times 10^{-30} \text{ Cm}}{1 \text{ D}} \right) \right) \right)^2 \frac{1}{(2 \times 10^{-9} \text{ m})^6} \\
 &= -\frac{2}{3} \left(\frac{1}{1.24 \times 10^{-20} \text{ J}} \right) \left(\frac{(5.66 \times 10^{-30})^2}{2.67 \times 10^{-9}} \text{ Nm}^4 \right)^2 \frac{1}{6.40 \times 10^{-53} \text{ m}^6} = -(5.38 \times 10^{19}) \cdot (1.44 \times 10^{-100}) \cdot (1.56 \times 10^{52}) \text{ J} \\
 &= -12.08 \times 10^{-29} \text{ J} \cdot \left(\frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} \right) = -7.55 \times 10^{-10} \text{ eV}
 \end{aligned}$$

7. Interaction potential energy between a polar and non-polar molecule



When a polar molecule is in close proximity to a non-polar molecule, the polarizing electric field is generated by the fixed dipole (p_1) of the polar molecule. This induces a dipole in the electron cloud of the non-polar molecule. The resulting interaction energy is called the Debye interaction energy.

$$\vec{E}_{dipole\ 1}(z, \theta) = \frac{|\vec{p}_1|}{4\pi\kappa\epsilon_0} \frac{1}{z^3} \left[2 \cos \theta \hat{z} + \sin \theta \hat{\theta} \right]$$

$$|\vec{E}_{dipole\ 1}(z, \theta)| = \frac{|\vec{p}_1|}{4\pi\kappa\epsilon_0} \frac{1}{z^3} \left[4 \cos^2 \theta + \sin^2 \theta \right]^{1/2}$$

$$= \frac{|\vec{p}_1|}{4\pi\kappa\epsilon_0} \frac{1}{z^3} \left[3 \cos^2 \theta + 1 \right]^{1/2}$$

$$U_{Debye}(z) = -2 \cdot \frac{p_1^2 \alpha_{o,2}}{(4\pi\kappa\epsilon_0)^2} \frac{1}{z^6}$$

The induced dipole moment is a function of E

$$\vec{p}_{induced}(E) = \alpha_{o,2} \vec{E}$$

In this case, E is due to a dipole

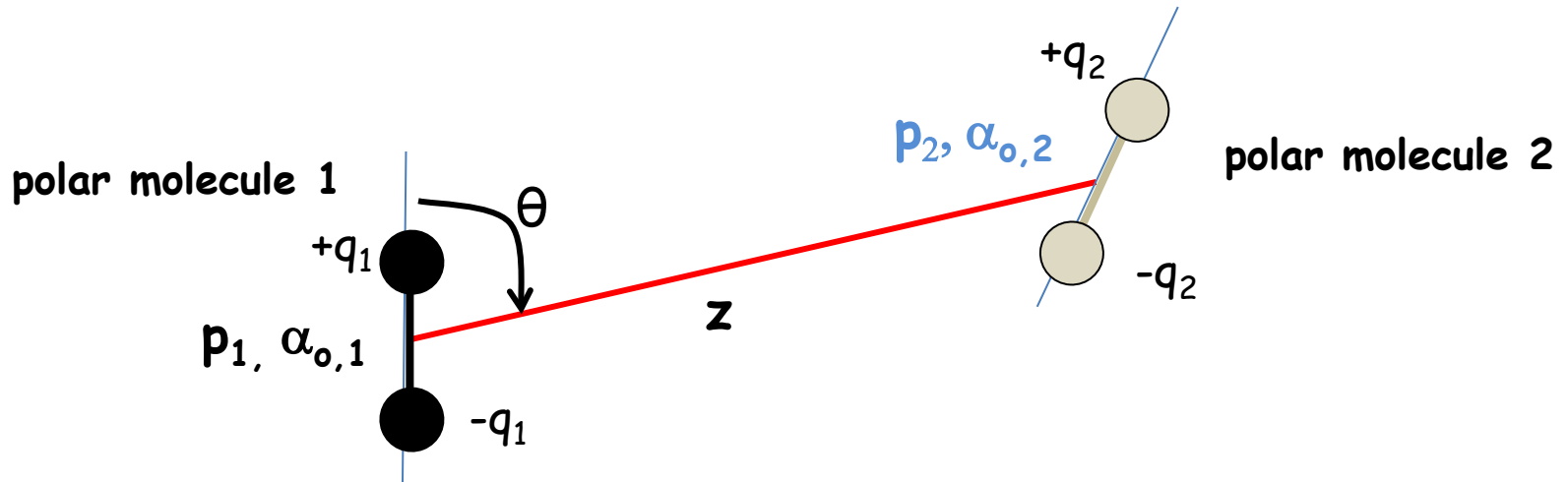
$$U_{Debye}(z, \theta) = -\vec{p}_{induced}(E) \cdot \vec{E} = (\alpha_{o,2} E_{dipole}^2)$$

$$= -\alpha_{o,2} \left(\frac{|\vec{p}_1| [3 \cos^2 \theta + 1]^{1/2}}{4\pi\kappa\epsilon_o z^3} \right)^2 = -\frac{p_1^2 \alpha_{o,2} [3 \cos^2 \theta + 1]}{(4\pi\kappa\epsilon_o)^2 z^6}$$

if an angle average over θ is performed, $\langle \cos^2 \theta \rangle = \frac{1}{3}$ (See Appendix 1, P1_Wk1_L4)

$$U_{Debye}(z) = -2 \cdot \frac{p_1^2 \alpha_{o,2}}{(4\pi\kappa\epsilon_o)^2} \frac{1}{z^6}$$

If the non-polar molecule is replaced by a polar one, then the second molecule could induce a dipole in the first:



The net effect is additive, so we must have

$$U_{Debye}(z) = -\frac{p_1^2 \alpha_{o,2} + p_2^2 \alpha_{o,1}}{(4\pi\kappa\epsilon_0)^2} \frac{1}{z^6}$$

If the two polar molecules are identical, then

$$U_{Debye}(z) = -\frac{2p^2 \alpha_o}{(4\pi\kappa\epsilon_0)^2} \frac{1}{z^6}$$

Appendix A: Derivation of the angle-averaged Keesom interaction

The derivation of the angle-averaged Keesom interaction is usually not given in most textbooks. Rather, the final result is often written down after some statement like "After a lengthy calculation, we find....."

In what follows the derivation is given using the same logic followed when discussing the ion-dipole interaction in the previous lecture (C1_Wk1_L3).

The starting point is the dipole-dipole interaction energy for two dipoles p_1 and p_2 separated by a distance z

$$U(z, \theta_1, \theta_2, \phi) = -\frac{p_1 p_2 [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]}{4\pi\kappa\epsilon_0} \frac{1}{z^3}$$

At first, you might be tempted to perform a straightforward angle average of $U(z, \theta_1, \theta_2, \phi)$ as follows:

$$U(z, \theta_1, \dots) = -\frac{\rho_1 \rho_2 [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]}{4\pi\kappa\epsilon_0} \frac{1}{z^3}$$

$$\text{Let } U(z, \theta_1, \dots) = U_o(z) [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi] = U_o(z) f(\Omega)$$

$$\text{where } U_o(z) \equiv \frac{\rho_1 \rho_2}{4\pi\kappa\epsilon_0} \frac{1}{z^3} \quad \text{and} \quad f(\Omega) = -2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi$$

$$\langle U(z) \rangle \equiv \frac{\int_0^{2\pi} d\phi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} U(z, \theta_1, \dots) \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2}{\int_0^{2\pi} d\phi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2} = U_o(z) \frac{\int_0^{2\pi} d\phi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} f(\Omega) \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2}{\int_0^{2\pi} d\phi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2} = U_o(z) \frac{I_A}{I_B}$$

$$\begin{aligned} I_A &= \int_{\phi=0}^{2\pi} \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [-2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 d\phi \\ &= -2 \left[\int_{\phi=0}^{2\pi} d\phi \int_{\theta_1=0}^{\pi} \sin \theta_1 \cos \theta_1 d\theta_1 \right] \left[\int_{\theta_2=0}^{\pi} \sin \theta_2 \cos \theta_2 d\theta_2 \right] + \left[\int_{\phi=0}^{2\pi} \cos \phi d\phi \right] \left[\int_{\theta_1=0}^{\pi} \sin^2 \theta_1 d\theta_1 \right] \left[\int_{\theta_2=0}^{\pi} \sin^2 \theta_2 d\theta_2 \right] = 0 \end{aligned}$$

$$I_B = \int_0^{2\pi} d\phi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 = 8\pi$$

$$\therefore \langle U(z) \rangle = U_o(z) \cdot \frac{I_A}{I_B} = 0$$

The result is zero because the angle average is performed for a "free" dipole in which all angles are equally likely. Instead, a weighted angle average must be calculated that preferentially weights those angles having lowest energy. This involves a correct treatment of the Boltzmann weighting factor and requires some understanding of statistical thermodynamics.

Weighting the angles using the Boltzmann factor gives

$$\langle U(z) \rangle \equiv \left\langle U(z, \theta_1, \dots) e^{-U(z, \theta_1, \dots)/k_B T} \right\rangle \equiv \frac{\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} U(z, \theta_1, \dots) e^{-U(z, \theta_1, \dots)/k_B T} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2}{\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} e^{-U(z, \theta_1, \dots)/k_B T} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2}$$

let $\beta = -\frac{U_o(z)}{k_B T}$, then

$$\left\langle U(z, \theta_1, \dots) e^{-U(z, \theta_1, \dots)/k_B T} \right\rangle = U_o(z) \frac{\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} f(\Omega) e^{\beta f(\Omega)} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2}{\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} e^{\beta f(\Omega)} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2}$$

Evaluating such a quantity is simplified by recognizing that the numerator and denominator are related by a derivative. Using the well known properties of the natural logarithm:

$$\left\langle U(z, \theta_1, \dots) e^{-U(z, \theta_1, \dots)/k_B T} \right\rangle = U_o(z) \frac{d}{d\beta} \ln \left(\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} e^{\beta f(\Omega)} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \right)$$

$$\text{since } \frac{d}{d\beta} \ln \left(\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} e^{\beta f(\Omega)} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \right)$$

$$= \frac{1}{\left(\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} e^{\beta f(\Omega)} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \right)} \times \left(\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} f(\Omega) e^{\beta f(\Omega)} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \right)$$

This means we must evaluate the integral $\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} e^{\beta f(\Omega)} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2$

if $\beta f(\Omega) \ll 1$, we can write

$$\begin{aligned} \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} e^{\beta f(\Omega)} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 &\approx \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \left[1 + \beta f(\Omega) + \frac{\beta^2}{2} f^2(\Omega) + \dots \right] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\ &= \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [1] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\ &\quad + \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [\beta f(\Omega)] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\ &\quad + \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} \left[\frac{\beta^2}{2} f^2(\Omega) \right] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 + \dots \\ &= I_1 + I_2 + I_3 + \dots \end{aligned}$$

$$I_1 = I_B = 8\pi \quad I_2 = 0$$

$$\begin{aligned} I_3 &= \frac{\beta^2}{2} \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [-2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi]^2 \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\ &= \frac{\beta^2}{2} \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [4 \cos^2 \theta_1 \cos^2 \theta_2] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\ &\quad + \frac{\beta^2}{2} \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [-4 \cos \theta_1 \cos \theta_2 \sin \theta_1 \sin \theta_2 \cos \phi] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\ &\quad + \frac{\beta^2}{2} \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [\sin^2 \theta_1 \sin^2 \theta_2 \cos^2 \phi] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\ &= I_a + I_b + I_c \end{aligned}$$

$$\begin{aligned}
I_a &= 4 \cdot \frac{\beta^2}{2} \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [\cos^2 \theta_1 \cos^2 \theta_2] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\
&= 4 \cdot \frac{\beta^2}{2} [2\pi] \left[-\frac{1}{3} \cos^3 \theta_1 \right]_{\theta_1=0}^{\theta_1=\pi} \left[-\frac{1}{3} \cos^3 \theta_2 \right]_{\theta_2=0}^{\theta_2=\pi} = 4 \cdot \frac{\beta^2}{2} [2\pi] \cdot \left[-\frac{1}{3} \cdot [(-1)^3 - (1)^3] \right]^2 = 4\pi \beta^2 \cdot \frac{4}{9} = \frac{16}{9} \pi \beta^2
\end{aligned}$$

$$\begin{aligned}
I_b &= -4 \cdot \frac{\beta^2}{2} \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [\cos \theta_1 \cos \theta_2 \sin \theta_1 \sin \theta_2 \cos \phi] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\
&= -4 \cdot \frac{\beta^2}{2} \int_0^{2\pi} \cos \varphi d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [\cos \theta_1 \sin^2 \theta_1 \cos \theta_2 \sin^2 \theta_2] d\theta_1 d\theta_2 \\
&= -4 \cdot \frac{\beta^2}{2} [\sin \varphi]_{\varphi=0}^{\varphi=2\pi} \left[\frac{1}{3} \sin^3 \theta_1 \right]_{\theta_1=0}^{\theta_1=\pi} \left[\frac{1}{3} \sin^3 \theta_2 \right]_{\theta_2=0}^{\theta_2=\pi} = 0
\end{aligned}$$

$$\begin{aligned}
I_c &= \frac{\beta^2}{2} \int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [\sin^2 \theta_1 \sin^2 \theta_2 \cos^2 \phi] \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \\
&= \frac{\beta^2}{2} \int_0^{2\pi} \cos^2 \phi d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} [\sin^3 \theta_1 \sin^3 \theta_2] d\theta_1 d\theta_2 \\
&= \frac{\beta^2}{2} \left[\frac{1}{2} (\varphi + \sin \varphi \cos \varphi) \right]_{\varphi=0}^{\varphi=2\pi} \left[\frac{1}{12} (\cos 3\theta_1 - 9 \cos \theta_1) \right]_{\theta_1=0}^{\theta_1=\pi} \left[\frac{1}{12} (\cos 3\theta_2 - 9 \cos \theta_2) \right]_{\theta_2=0}^{\theta_2=\pi} \\
&= \frac{\beta^2}{2} [\pi] \cdot \left[\frac{1}{12} [-1 - 9(-1) - (1 - 9(1))] \right]^2 = \frac{1}{2} \pi \beta^2 \left[\frac{8}{12} + \frac{8}{12} \right]^2 = \frac{1}{2} \pi \beta^2 \left[\frac{4}{3} \right]^2 = \frac{8}{9} \pi \beta^2
\end{aligned}$$

$$I_3 = I_a + I_b + I_c = \frac{16}{9} \pi \beta^2 + 0 + \frac{8}{9} \pi \beta^2 = \frac{24}{9} \pi \beta^2 = \frac{8}{3} \pi \beta^2$$

$$\text{So } I_1 + I_2 + I_3 + \dots = 8\pi \cdot \left(1 + \frac{\beta^2}{3} + \dots \right)$$

$$\begin{aligned} \langle U(z) \rangle &\equiv \left\langle U(z, \theta) e^{-U(z, \theta) / k_B T} \right\rangle = U_o(z) \frac{d}{d\beta} \ln \left(\int_0^{2\pi} d\varphi \int_{\theta_1=0}^{\pi} \int_{\theta_2=0}^{\pi} e^{\beta f(\Omega)} \sin \theta_1 d\theta_1 \sin \theta_2 d\theta_2 \right) \\ &= U_o(z) \frac{d}{d\beta} \ln(I_1 + I_2 + I_3 + \dots) \\ &= U_o(z) \frac{d}{d\beta} \ln \left(8\pi \left(1 + \frac{\beta^2}{3} + \dots \right) \right) = U_o(z) \frac{d}{d\beta} \left[\ln(8\pi) + \ln \left(1 + \frac{\beta^2}{3} + \dots \right) \right] \\ &= 0 + U_o(z) \frac{1}{1 + \frac{\beta^2}{3}} \cdot \frac{2\beta}{3} \\ &\approx U_o(z) \frac{2\beta}{3} \end{aligned}$$

now since $\beta = -\frac{U_o(z)}{k_B T}$ and $U_o(z) \equiv \frac{\rho_1 \rho_2}{4\pi\kappa\epsilon_0} \frac{1}{z^3}$,

we finally obtain

$$\begin{aligned}\langle U(z) \rangle &\equiv \left\langle U(z, \theta_1, \dots) e^{-U(z, \theta_1, \dots)/k_B T} \right\rangle = U_o(z) \frac{2\beta}{3} \\ &= \left(\frac{\rho_1 \rho_2}{4\pi\kappa\epsilon_0} \frac{1}{z^3} \right) \cdot \frac{2}{3} \cdot \left(-\frac{1}{k_B T} \cdot \frac{\rho_1 \rho_2}{4\pi\kappa\epsilon_0} \frac{1}{z^3} \right) \\ &= -\frac{2}{3k_B T} \left(\frac{\rho_1 \rho_2}{4\pi\kappa\epsilon_0} \right)^2 \frac{1}{z^6}\end{aligned}$$