10.40 Thermodynamics **Fall 2003**
Problem Set 7

Problems 10.4 & 10.5 Text

Solution:
<u>10.4</u>

$$<\Phi_{ij}> = \frac{\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} \Phi_{ij} \sin\alpha_i \sin\alpha_j \, d\alpha_i d\alpha_j d\gamma}{\int_0^{\pi}\int_0^{\pi}\int_0^{\pi} \sin\alpha_i \sin\alpha_j \, d\alpha_i d\alpha_j d\gamma} \equiv \frac{I_2}{I_1} \qquad (1)$$

where $\gamma \equiv \gamma_i - \gamma_j$. Now to compute the definite integrals I_1, and I_2 with $d_{m,i} = d_{m,j} = d_m$

$$I_1 = (-\cos\alpha_i \,|_0^{\pi})\,(-\cos\alpha_j \,|_0^{\pi})\,(2\pi - 0) = 2\pi\,(2)(2) = 8\pi \qquad (2)$$

$$I_2 = -\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} \frac{d_m^2}{4\pi\varepsilon_o r^3}\,[2\cos\alpha_i \cos\alpha_j - \sin\alpha_i \sin\alpha_j \cos\gamma]\, \sin\alpha_i \sin\alpha_j \, d\alpha_i \, d\alpha_j \, d\gamma \qquad (3)$$

$$= \frac{-d_m^2}{4\pi\varepsilon_o r^3}\int_0^{2\pi}\int_0^{\pi} \left[\cos^2\alpha_i \cos\alpha_j \sin\alpha_j - \left(\frac{\alpha_i}{2} - \frac{\sin 2\alpha_i}{4}\right)\sin^2\alpha_j \cos\gamma\right]\Bigg|_0^{\pi} d\alpha_j d\gamma$$

$$= \frac{-d_m^2}{4\pi\varepsilon_o r^3}\int_0^{2\pi}\int_0^{\pi} \left[\frac{-\pi}{2}\sin^2\alpha_j \cos\gamma\right] d\alpha_j \, d\gamma = \frac{-d_m^2}{4\pi\varepsilon_o r^3}\int_0^{2\pi} \frac{-\pi}{2}\left[\frac{\alpha_j}{2} - \frac{\sin 2\alpha_j}{4}\right]\Bigg|_0^{\pi} \cos\gamma d\gamma$$

$$I_2 = \frac{-d_m^2}{4\pi\varepsilon_o r^3}\int_0^{2\pi} \frac{-\pi^2}{4}\cos\gamma d\gamma = \frac{d_m^2}{4\pi\varepsilon_o r^3}\sin\gamma\Bigg|_0^{2\pi} = 0 \qquad (4)$$

Now substituting Eqs. (2) and (4) into Eq. (1)

$$<\Phi_{ij}> = I_2/I_1 = 0/8\pi = 0 \qquad (5)$$

With uniform weighting to all orientations, this result is expected.

10.5

Expanding the exponential term in a Taylor series, the Boltzmann-averaged potential energy $<\Phi_{ij}>$ becomes

$$<\Phi_{ij}> = I_4/I_3 \tag{1}$$

where

$$I_3 \equiv \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\left(1 - \frac{\Phi_{ij}}{kT} + \frac{\Phi_{ij}^2}{2(kT)^2} - \dots\right)\sin\alpha_i \sin\alpha_j \, d\,\alpha_i \, d\,\alpha_j \, d\gamma$$

$$I_4 \equiv \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\left(\Phi_{ij} - \frac{\Phi_{ij}^2}{kT} + \frac{\Phi_{ij}^3}{2(kT)^2} - \dots\right)\sin\alpha_i \sin\alpha_j \, d\,\alpha_i \, d\,\alpha_j \, d\gamma$$

where

$$\Phi_{ij} = \frac{-d_{m,i}d_{m,j}}{4\pi\varepsilon_o r^3}\left[2\cos\alpha_i \cos\alpha_j - \sin\alpha_i \sin\alpha_j \cos\gamma\right] \tag{2}$$

If we truncate after the second term in the expansion, then

$$I_3 \approx I_1 - \frac{I_2}{kT} = 8\pi - \frac{0}{kT} = 8\pi \tag{3}$$

where I_1 and I_2 are given in Problem 10.4. Now to evaluate I_4, again truncating after the second did before, then the integration can be done analytically.

$$I_4 \approx \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\left(\Phi_{ij} - \frac{\Phi_{ij}^2}{kT}\right)\sin\alpha_i \sin\alpha_j \, d\alpha_i \, d\alpha_j \, d\gamma \tag{4}$$

$$I_4 \approx I_2 - \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\frac{\Phi_{ij}^2}{kT}\sin\alpha_i \sin\alpha_j \, d\alpha_i \, d\alpha_j \, d\gamma \tag{5}$$

but $I_2 = 0$. Now substituting Eq. (2) into Eq. (5):

$$I_4 = \frac{-d_{m,i}^2 d_{m,j}^2}{(4\pi\varepsilon_o)^2 r^6 kT}\left[I_5 + I_6 + I_7\right] \tag{6}$$

where

$$I_5 = \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} 4\cos^2\alpha_i \cos^2\alpha_j \sin\alpha_i \sin\alpha_j \, d\alpha_i \, d\alpha_j \, d\gamma = \left(\frac{-4}{3}\cos^3\alpha_i\right)\Bigg|_0^{\pi}\left(\frac{-4}{3}\cos^3\alpha_j\right)\Bigg|_0^{\pi}\gamma \quad \Bigg|_0^{2\pi}$$

$$I_5 = \frac{16}{9}\,(2\pi) = \frac{32\pi}{9}$$

$$I_6 = -\int_0^{2\pi}\int_0^{\pi}\int_0^{\pi} 4\cos\alpha_i\,\cos\alpha_j\,\sin^2\alpha_i\,\sin^2\alpha_j\,\cos\gamma\,d\alpha_i\,d\alpha_j\,d\gamma$$

$$I_6 = \left(-\frac{4}{3}\,\frac{\sin^3\alpha_i}{3}\right)\Bigg|_0^{\pi}\int_0^{2\pi}\int_0^{\pi}\sin^2\alpha_j\cos\alpha_j\cos\gamma\,d\alpha_j\,d\gamma = 0$$

$$I_7 = \int_0^{2\pi}\int_0^{\pi}\int_0^{\pi}\sin^3\alpha_i\,\sin^3\alpha_j\,\cos^2\gamma\,d\alpha_i d\alpha_j d\gamma$$

$$I_7 = \left(\frac{\cos^3\alpha_i}{3} - \cos\alpha_i\right)\Bigg|_0^{\pi}\left(\frac{\cos^3\alpha_i}{3} - \cos\alpha_j\right)\Bigg|_0^{\pi}\left(\frac{\gamma}{2} + \frac{\sin^2\gamma}{2}\right)\Bigg|_0^{2\pi}$$

$$I_7 = (4/3)\,(4/3)\,(2\pi/2) = \frac{16\pi}{9}$$

Therefore, substituting into Eq. (6)

$$I_4 = \frac{-d_{m,i}^2 d_{m,j}^2}{(4\pi\varepsilon_o)^2\,r^6 kT}\left[\frac{32\pi}{9} + 0 + \frac{16\pi}{9}\right] = -\frac{48\pi\,d_{m,i}^2\,d_{m,j}^2}{9(4\pi\varepsilon_o)^2\,r^6 kT} \qquad (7)$$

and with Eq. (1):

$$<\Phi_{ij}> \; = \frac{I_4}{I_3} = \frac{-2}{3}\,\frac{d_{m,i}^2 d_{m,j}^2}{(4\pi\varepsilon_o)^2 r^6 kT} \quad \text{QED!} \qquad (8)$$

which is Eq. (10-83).