Physics 187

Homework #1
Due April 9, 2012

Jackson Chapter One

Problems: 2, 4, 7, 11

Jackson Chapter Two:

Problems: 2, 5

Reading: Jackson Chapters one and two. We are starting with a simple analysis of protein conformational transitions and a review of the role of electrostatics.

Homework 1.
Solutions.

2. Protein unfolds at $T = 65°C$ with $\Delta H° = 80\,kcal/mole$

what is $\Delta G°$ at $25°C$? At the transition temp T^*, $\Delta H° = T^* \Delta S°$

so $\Delta S° = \Delta H° / T^* = \dfrac{80\,kcal/mole}{(273+65)k} = 0.24 \dfrac{kcal}{mole \cdot K}$

$$\Rightarrow \boxed{\Delta G° = \Delta H° - T\Delta S° = \Delta H°\left[1 - \frac{T}{T^*}\right]}$$

$$= 80\,kcal/mole\left[1 - \frac{249}{169}\right] = 9.05\,kcal/mole.$$

Unfolded state has heat capacity $\Gamma = 9 cal/°C$ higher than folded state.

$$\frac{\partial \Delta G°}{\partial T} = -\Delta S° \Rightarrow T\frac{\partial^2 \Delta G°}{\partial T^2} = -T\frac{\partial \Delta S°}{\partial T} = -\Gamma$$

heat capacity differen.

so $\dfrac{\partial^2 \Delta G°}{\partial T^2} = -\Gamma/T$ or $\dfrac{\partial \Delta G°}{\partial T} = -\Gamma \log T + a$

and $\Delta G° = \Gamma(T - T\log T) + aT + b.$

To evaluate the constants of integration we note that

$\Delta G° = 0$ at $T^* = 65°C$, the unfolding temperature.

and $\dfrac{\partial \Delta G°}{\partial T} = -\Delta S° = -\Delta H°/T^*$ at that temp.

$$-\Gamma \log T^* + a = -\Delta H^\circ / T^* \Rightarrow a = -\Delta H^\circ/_{T^*} + \Gamma \log T^*$$

$$0 = \Delta G^\circ = \Gamma (T^* - T^* \log T^*) - \Delta H^\circ + \Gamma T^* \log T^* + b$$

$$\Rightarrow \quad b = \Delta H^\circ - \Gamma T^* \quad \text{so}$$

$$\Delta G^\circ = \Gamma (T - T \log T) + \Gamma T \log T^* - \Delta H^\circ \frac{T}{T^*} + \Delta H^\circ - \Gamma T^*$$

$$\boxed{\Delta G^\circ = \Gamma (T - T^*) - \Gamma T \log (T/T^*) + \Delta H^\circ \left(1 - \frac{T}{T^*}\right)}$$

Now put in the numbers:

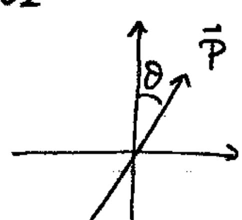
$$\Delta G^\circ = 9(25-65) - 9 \cdot (25+273) \log\left(\frac{25+273}{65+273}\right) + 8 \times 10^4 \cdot$$

$$\cdot \left(1 - \frac{25+273}{65+273}\right) = -360 + -338 + 70.5 \times 10^3$$

$$\Delta G^\circ = 69.8 \text{ kcal/mole.}$$

4. Linear potential gradient $\Longrightarrow$ constant electric field $\vec{E}$
Energy of a dipole in the field is

$$E = -\vec{p} \cdot \vec{E}$$



First, things are stuck in one plane. $\Longrightarrow$ fix the azimuthal angle

$$P(\theta)\, d\theta = A e^{+\vec{p}\cdot\vec{E}\beta} d\theta = A e^{\beta p E \cos\theta} d\theta$$

Normalization

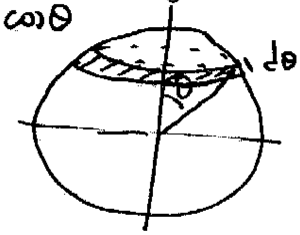
$$A^{-1} = \int_0^{2\pi} e^{\beta p E \cos\theta}\, d\theta \implies A^{-1} = 2\pi\, I_0(\beta p E)$$ 3

modified Bessel function of the 1st kind.

$$\boxed{P_{2D}(\theta) = \frac{1}{2\pi\, I_0(\beta p E)}\, e^{\beta p E \cos\theta}}$$

Now let the dipole point _anywhere_ on the unit sphere.

$$d\theta\, P(\theta) = d\theta\, A \int_0^{2\pi} d\varphi\, \sin\theta\, e^{\beta p E \cos\theta} = 2\pi \sin\theta\, e^{\beta p E \cos\theta} A$$



and normalization requires

$$2\pi A \int_0^{\pi} \sin\theta\, e^{\beta p E \cos\theta}\, d\theta = 1 \implies \frac{1}{2\pi A} = \int_{-1}^{+1} dx\, e^{\beta p E x}$$

$$= \frac{1}{\beta p E}\left(e^{\beta p E} - e^{-\beta p E}\right)$$

$$\frac{1}{2\pi A} = \frac{2}{\beta p E}\sinh(\beta p E) \quad \text{or} \quad A = \frac{\beta p E}{4\pi \sinh(\beta p E)} \quad \text{and}$$

$$\boxed{P_{3D}(\theta) = \frac{1}{4\pi}\, \frac{\beta p E}{\sinh(\beta p E)}\, e^{\beta p E \cos\theta}}$$

Notice that if we take $E \to 0$ we get $P_{3D}(\theta) = 1/4\pi$

7. Now consider three channels instead of two, as in class.

Now we have three channels $\Rightarrow$ $8 = 2^3$ states of the system.

$$\frac{[OOO]}{[CCC]} = e^{-3X} \quad ; \quad X = (\Delta G^\circ_{V_i} + \alpha V)/RT$$ extending the argument in Eq. 130 (p. 20) of Jackson.

Similarly each O costs us one factor of e^{-X} relative to [CCC]

$$\frac{[OOC]}{[CCC]} = e^{-2X} ; \quad \frac{[OCC]}{[CCC]} = e^{-X}$$

$$P_o = \frac{[OOO]}{[CCC] + [OOO] + 3[OCC] + 3[CCO]}$$

permutations of the channels.

Now

$$\frac{[OCC]}{[OOO]} = \frac{[OCC]}{[CCC]} \times \frac{[CCC]}{[OOO]} = e^{-X} \cdot e^{3X} = e^{2X}$$ and etc.

$$P_o = \frac{1}{e^{3X} + 1 + 3e^{2X} + 3e^{X}} = \frac{1}{(1 + e^{X})^3}$$ as expected.

If you want, you can put in the interaction term and reproduce Eq. 1.34, or, more accurately its analogue.

11. $$Z = \int \frac{dx\,dp}{h} e^{-\beta\left[\frac{p^2}{2m} + \frac{1}{2}\varphi(x - x_0)^2\right]}$$ The partition function $\beta = 1/k_BT$

Our friend, the Gaussian integral: $$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\pi/\alpha}$$

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$$Z = \sqrt{\frac{\pi}{\beta/2mh^2}}\sqrt{\frac{\pi}{\frac{\beta}{2}\varphi}} = \frac{\sqrt{2\pi m k_B T}}{\sqrt{h^2}} \cdot \pi^{1/2}\sqrt{\frac{2k_BT}{\varphi}}$$

or $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ Thermal de Broglie wavelength

$$Z = (2\pi)^{1/2}\sqrt{\frac{k_BT}{\varphi}}\,\frac{1}{\lambda}$$ dimensions $\left[\frac{k_BT}{\varphi}\right] = \frac{E}{E/L^2}$ so Z

is dimensionless as expected.

$$G = -k_BT\log Z = \boxed{G = -\frac{k_BT}{2}\log\left(\frac{2\pi k_BT}{\lambda^2\varphi}\right)}$$ Free energy.

entropy $\frac{\partial F}{\partial T} = -S = -\frac{k_B}{2}\log\left(\frac{2\pi k_BT}{\lambda^2\varphi}\right) - \frac{k_BT}{2}\,\frac{\lambda^2\varphi}{2\pi k_BT}\,\frac{2\pi k_B}{\lambda^2\varphi}$

$dF = -SdT - pdV$

$$\Rightarrow \quad S = \frac{1}{2}k_B\log\left(\frac{2\pi k_BT}{\lambda^2\varphi}\right) + \frac{k_BT}{2T} = \frac{1}{2}k_B\log\left(\frac{2\pi k_BT}{\lambda^2\varphi}\right) + \frac{1}{2}k_B$$

$$\boxed{S = \frac{1}{2}k_B\log\left(\frac{2\pi k_BT}{\lambda^2\varphi}e\right)}$$ entropy.

Recall $G = H - TS$ from $H = E + pV$ and $G = E + pV - TS$

so

$$H = G + TS = \frac{1}{2}k_BT\log\left(\frac{2\pi k_BT}{\lambda^2\varphi}\right) + \frac{1}{2}k_BT$$

$$\boxed{H = \frac{1}{2}k_BT\log\left(\frac{2\pi k_BT}{\lambda^2\varphi}e\right)}$$ Enthalpy.

Jackson Chapter Two.

2. $u = \dfrac{\varepsilon E^2}{8\pi}$ Derive Eqs. 2.4 and 2.7

Eq. 2.4 $G = \dfrac{q^2}{2\varepsilon r}$

electric field outside a sphere w/ charge q and radius r (assuming the charge is distributed uniformly on the sphere) in a dielectric ε.

$$E = \frac{q}{\varepsilon r^2}$$

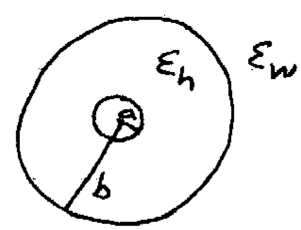
The energy density is: $u = \dfrac{\varepsilon}{8\pi}\dfrac{q^2}{\varepsilon^2 r^4} = \dfrac{q^2}{8\pi\varepsilon}\dfrac{1}{r^4}$

The total energy is:

$$G = \frac{q^2}{8\pi\varepsilon}\int_r^\infty \bar{r}^2 d\bar{r}\, 4\pi \frac{1}{\bar{r}^4} = \frac{q^2}{2\varepsilon}\int_r^\infty \frac{d\bar{r}}{\bar{r}^2} = \frac{q^2}{2\varepsilon}\left(-\frac{1}{\bar{r}}\right)\Big|_r^\infty$$

$$= \frac{q^2}{2\varepsilon r} \checkmark$$

Eq. 2.7 $G = \dfrac{q^2}{2\varepsilon_h}\left(\dfrac{1}{a} - \dfrac{1}{b}\right) + \dfrac{q^2}{2\varepsilon_w b}$



As we worked out in class:

$\vec{E} = \dfrac{q\hat{r}}{r^2\varepsilon_h}$; $a < r < b$ Inside the protein

$\vec{E} = \dfrac{q\hat{r}}{r^2\varepsilon_w}$; $b \leq r$ Outside the protein.

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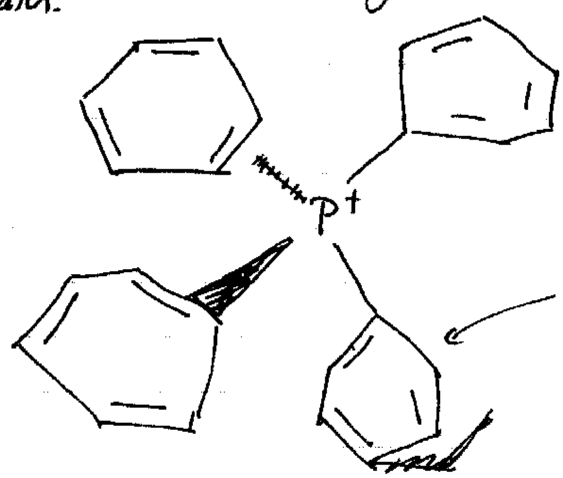
Inside: $U_{in} = \int_a^b r^2 dr \frac{4\pi}{8\pi} \frac{q^2}{r^4 \varepsilon_h} = \frac{1}{2} \frac{q^2}{\varepsilon_h} \left(\frac{1}{a} - \frac{1}{b}\right)$

Outside $U_{out} = \int_b^\infty r^2 dr \frac{1}{2} \frac{q^2}{r^4 \varepsilon_w} = \frac{q^2}{2\varepsilon_w} \frac{1}{b}$

$$G = \frac{q^2}{2\varepsilon_h}\left(\frac{1}{a} - \frac{1}{b}\right) + \frac{q^2}{2\varepsilon_w}\frac{1}{b}$$

5 Calculate energy difference for moving —— from oil to water.



from Wikipedia

charge is (+1e)

benzene rings. about 2 Å across

How big a sphere? radius ~ 4Å.

$$G_{water} - G_{oil} = \frac{(1e)^2}{2r}\left(\frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_{oil}}\right) = \Delta G$$

$$\Delta G \cong \frac{(4.8\times10^{-10}\,esu)^2}{2(4\times10^{-8}\,cm)}\left(\frac{1}{80} - \frac{1}{2}\right) = -2.8\times10^{-12}\,erg.$$

Recall 1esu = $1\sqrt{g\,cm^3}/s$ or $1\ erg^{1/2}\,cm^{1/2}$

What is that in k_BT? (at room temp.)

⑧

$k_B T = 4\,pN\,nm = 4 \times 10^{-21}\,N \cdot m = 4 \times 10^{-21}\,kg\,m^2/s^2$

$1\,erg = 1\,g\,cm^2/s^2 = 10^{-3}\,kg\,(10^{-2}m)^2/s^2 = 10^{-7}\,J$

$\Delta G = -2.8 \times 10^{-21}\,J = -.7\,k_B T$ Born Energy difference.

Not like the small ion from class ~~mainly~~ because we took a much bigger radius.