

# 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.

①

2. Protein unfolds at  $T = 65^\circ\text{C}$  with  $\Delta H^\circ = 80 \text{ kcal/mole}$   
 What is  $\Delta G^\circ$  at  $25^\circ\text{C}$ ? At the transition temp  $T^*$ ,  $\Delta H^\circ = T^* \Delta S^\circ$

$$\text{so } \Delta S^\circ = \Delta H^\circ / T^* = \frac{80 \text{ kcal/mole}}{(273 + 65) \text{ K}} = 0.24 \frac{\text{kcal}}{\text{mole} \cdot \text{K}}$$

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

$$= 80 \text{ kcal/mole} \left[ 1 - \frac{298}{338} \right] = 90.5 \text{ kcal/mole.}$$

Unfolded state has heat capacity  $\Gamma = 9 \text{ cal/}^\circ\text{C}$  higher than folded state.

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

heat capacity  
differenc.

$$\text{so } \frac{\partial^2 \Delta G^\circ}{\partial T^2} = -\Gamma/T \text{ or } \frac{\partial \Delta G^\circ}{\partial T} = -\Gamma \log T + a$$

$$\text{and } \Delta G^\circ = \Gamma(T - T \log T) + aT + b.$$

To evaluate the constants of integration we note that

$\Delta G^\circ = 0$  at  $T = 65^\circ\text{C}$ , the unfolding temperature.

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

$$-R \log T^* + a = -\Delta H^\circ / T^* \Rightarrow a = -\Delta H^\circ / T^* + R \log T^* \quad (2)$$

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

$$\Rightarrow b = \Delta H^\circ - RT^* \text{ so}$$

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

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

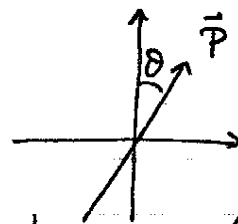
Now put in the numbers:

$$\Delta G^\circ = 9(25 - 65) - 9 \cdot (25 + 273) \log \left( \frac{25 + 273}{65 + 273} \right) + 8 \times 10^4 \cdot \left( 1 - \frac{25 + 273}{65 + 273} \right) = -360 + -338 + 70.5 \times 10^3$$

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

4. Linear potential gradient  $\Rightarrow$  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.  $\Rightarrow$  fix the azimuthal angle

$$P(\theta) d\theta = A e d\theta = A e d\theta$$

$\uparrow$  Normalization

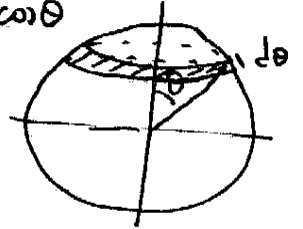
$$A^{-1} = \int_0^{2\pi} e^{\beta p E \cos \theta} d\theta \Rightarrow A^{-1} = 2\pi I_0(\beta p E) \quad (3)$$

↑ modified Bessel function of the 1<sup>st</sup> kind.

$$P(\theta) = \frac{1}{2\pi I_0(\beta p E)} e^{\beta p E \cos \theta}$$

Now let the dipole point anywhere on the unit sphere.

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



and normalization requires

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

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

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

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

$$P(\theta) = \frac{1}{4\pi} \frac{\beta p E}{\sinh(\beta p E)} e^{\beta p E \cos \theta}$$

Notice that if we take

$$E \rightarrow 0 \text{ we get } P_{3D}(\theta) = 1/4\pi$$

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

Now we have three channels  $\Rightarrow 8 = 2^3$  states of the system. ④

$$\frac{[000]}{[ccc]} = e^{-3x} ; x = (\Delta G_{vi} + \alpha V) / RT \text{ extending the argument}$$

in Eq. 1.30 (p. 20) of Jackson.

Similarly each 0 costs one factor of  $e^{-x}$  relative to [ccc]

$$\frac{[00c]}{[ccc]} = e^{-2x} ; \frac{[occ]}{[ccc]} = e^{-x}$$

$$P_0 = \frac{[000]}{[ccc] + [000] + 3[occ] + 3[cco]}$$

↙ permutations of the channels. ↘

Now

$$\frac{[occ]}{[000]} = \frac{[occ]}{[ccc]} \cdot \frac{[ccc]}{[000]} = e^{-x} \cdot e^{3x} = e^{2x} \text{ and etc.}$$

$$P_0 = \frac{1}{e^{3x} + 1 + 3e^{2x} + 3e^x} = \frac{1}{(1 + e^x)^3} \text{ as expected.}$$

If you want, you can put in the interaction term and reproduce Eq. 1.34, or, more accurately it's analog.

$$11. Z = \int \frac{dx dp}{h} e^{-\beta \left[ \frac{p^2}{2m} + \frac{1}{2} \phi(x-x_0)^2 \right]}$$

The partition function  
 $\beta = 1/k_B T$

Our friend, the Gaussian integral:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\pi/\alpha}$$

$$\Omega = \sqrt{\frac{\pi}{\beta/2mh^2}} \sqrt{\frac{\pi}{\beta/2\varphi}} = \frac{\sqrt{2\pi mk_B T}}{h} \cdot \pi^{1/2} \sqrt{\frac{2k_B T}{\varphi}} \quad (5)$$

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

$$\Omega = (2\pi)^{1/2} \sqrt{\frac{k_B T}{\varphi}} \frac{1}{\lambda} \quad \text{dimensions} \quad \left[ \frac{k_B T}{\varphi} \right] = \frac{E}{E/L^2} \quad \text{so } \Omega$$

is dimensionless as expected.

$$G = -k_B T \log \Omega = \boxed{G = -\frac{k_B T}{2} \log \left( \frac{2\pi k_B T}{\lambda^2 \varphi} \right)} \quad \text{Free energy.}$$

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

$$dF = -SdT - pdv$$

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

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

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

so

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

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

Jackson Chapter Two.

6

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

Eq. 2.4  $G = \frac{q^2}{2\epsilon r}$

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

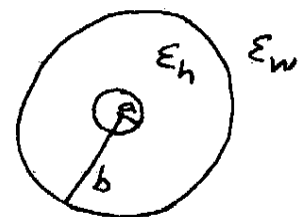
$$E = \frac{q}{\epsilon r^2}$$

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

The total energy is:

$$G = \frac{q^2}{8\pi \epsilon} \int_r^\infty r^2 dr \cdot 4\pi \frac{1}{r^4} = \frac{q^2}{2\epsilon} \int_r^\infty \frac{dr}{r^2} = \frac{q^2}{2\epsilon} \left( -\frac{1}{r} \right) \Big|_r^\infty = \frac{q^2}{2\epsilon r}$$

Eq. 2.7  $G = \frac{q^2}{2\epsilon_h} \left( \frac{1}{a} - \frac{1}{b} \right) + \frac{q^2}{2\epsilon_w b}$



As we worked out in class:

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

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

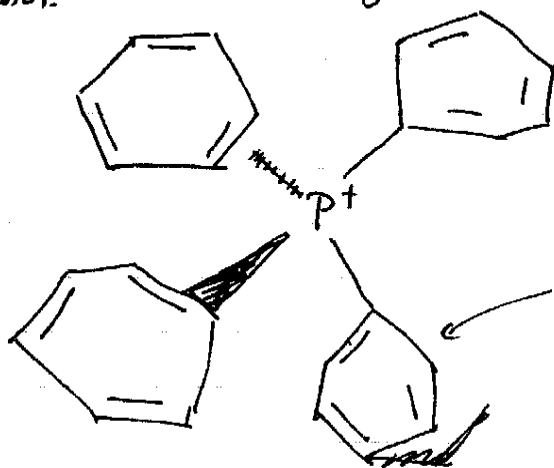
$$\text{Inside: } U_{in} = \int_a^b r^2 dr \frac{4\pi q^2}{8\pi r^4 \epsilon_h} = \frac{1}{2\epsilon_h} \left( \frac{1}{a} - \frac{1}{b} \right)$$

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

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

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  $\sim 4 \text{ \AA}$ .

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

$$\Delta G \approx \frac{(4.8 \times 10^{-10} \text{ emu})^2}{2(4 \times 10^{-9} \text{ cm})} \left( \frac{1}{80} - \frac{1}{2} \right) = -2.8 \times 10^{-12} \text{ erg.}$$

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

What is  $\Delta G$  in  $k_B T$ ? (at room temp.)



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

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J} = 10^{-3} \text{ kg (10}^{-2} \text{ m)}^2/\text{s}^2 = 10^{-7} \text{ J}$$

$$\Delta G = -2.8 \times 10^{-21} \text{ J} = -0.7 k_B T$$

Born Energy difference.

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