

Physics 187  
 Homework #2  
 Due Monday 16, 2012

Jackson Chapter Two:

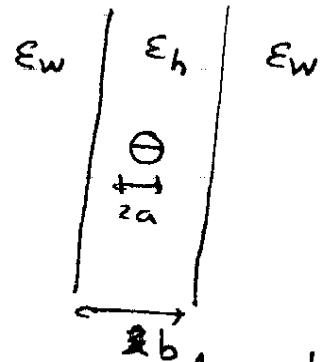
7, 11

Jackson Chapter Three:

1, 3

5. In chapter two we read that A. Parsegian computed the Born energy of a charge of radius  $a$  in a membrane of thickness  $b$ . As he

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



Hint: You will need an infinite series of image charges and then sum the series of contributions to the electrostatic energy coming from each charge. You may be able to get the sum by thinking about the Taylor series for  $\log x$  about  $x=1$ .

## Homework #2 Solutions

①


Jackson 2: 7, 11

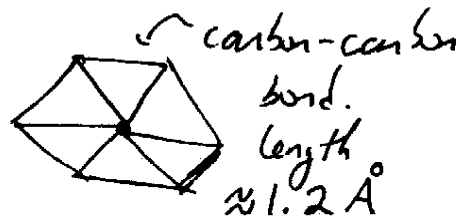
Jackson 3: 1, 3

Parsegian calculation.

1. Hydrophobic free energy of transferring tetraphenylphosphonium from oil to water.

What is the area of a benzene ring?

Area of one triangle   $A = \frac{1}{2} l \frac{\sqrt{3}}{2} l = \frac{\sqrt{3}}{4} l^2$



Area of the hexagon =  $6A = \frac{3\sqrt{3}}{2} l^2 \times 2$  both sides exposed to water.

Total area of hydrophobic surfaces of the molecule  $4 \times 3\sqrt{3} l^2$

We get  $12\sqrt{3} (1.2 \text{ \AA})^2 \times \frac{18 \text{ cal}}{\text{Å}^2} = .374 \text{ kcal/mole.}$

Combine this with problem 5 from last homework we get

$$\Delta G_{\text{transfer}} = -.7 RT + .6 RT \approx -.1 RT$$

from oil to water ↑ (at room temp) ↑ hydrophobic cost  
cost of screening the charge.

2. 11. from Jackson Chapter 2.

(2)

$$U(x) = U_0 + \bar{x}^T A \bar{x}$$

Diagonalize the symmetric (real) matrix  $A$  by an orthogonal similarity transformation  $(\theta^T = \theta^{-1})$

$\exists \theta$  such that  $\theta^T A \theta = D \leftarrow$  diagonal  $n \times n$  matrix.

$$D = \begin{pmatrix} \lambda_1 & & 0 \\ & \ddots & \\ 0 & & \lambda_n \end{pmatrix} \leftarrow \text{eigenvalues of } A \text{ along the diagonal.}$$

Introduce new variables in the partition function integral

$$Z = \int \prod_{i=1}^N dx_i e^{-\beta U(x)}$$

$\vec{\xi} = \theta^{-1} \bar{x}$  then  $U(\bar{x})$  becomes.

$$U = U_0 + (\theta \vec{\xi})^T A (\theta \vec{\xi}) = \vec{\xi}^T \theta^T A \theta \vec{\xi} + U_0$$

$U = U_0 + \vec{\xi}^T D \vec{\xi}$  and the Jacobian of the transformation

is one since  $\det(\theta) = \det(\theta^{-1}) = 1$ .

$$\Rightarrow Z = e^{-\beta U_0} \int \prod_{i=1}^N d\xi_i e^{-\beta \sum_{i=1}^N \lambda_i \xi_i^2}$$

$$Z = e^{-\beta U_0} \prod_{i=1}^N \int d\xi_i e^{-\beta \lambda_i \xi_i^2} = e^{-\beta U_0} \prod_{i=1}^N \sqrt{\frac{\pi}{\beta \lambda_i}}$$

Note that  $\det A = \det(\Theta^{-1} A \Theta) = \det(D) = \prod_{i=1}^N \lambda_i$  ③

$$\Rightarrow Z = e^{-\beta U_0} \prod_{i=1}^N \frac{1}{\sqrt{\pi \lambda_i}} (k_B T \pi)^{N/2}$$

$$Z = \frac{e^{-\beta U_0} (k_B T \pi)^{N/2}}{(\det A)^{1/2}}$$

The free energy  $F = -k_B T \log Z$  can be written as follows.

$$F = -k_B T \left[ -\beta U_0 + \frac{1}{2} \sum_{i=1}^N \log \left( \frac{\pi k_B T}{\lambda_i} \right) \right]$$

$$F = U_0 + \frac{1}{2} k_B T \sum_{i=1}^N \log \left( \frac{\lambda_i}{k_B T \pi} \right) = U_0 + \frac{1}{2} k_B T \sum_{i=1}^N \log \left( \frac{\lambda_i}{\pi k_B T} \right)$$

eigenvalues.  
↓

in terms of  $A$

$$-k_B T \log Z = U_0 - \frac{1}{2} k_B T \log (\pi k_B T / \det A) = F.$$

We can simplify this by noting:  $\text{Tr} A = \log(\det(e^A))$

which is easy to check if  $A$  is diagonal.

$$e^A = \begin{pmatrix} e^{\lambda_1} & & 0 \\ & \ddots & \\ 0 & & e^{\lambda_N} \end{pmatrix} \Rightarrow \det(e^A) = e^{\sum \lambda_i} \Rightarrow$$

$$\log(\det(e^{\sum \lambda_i})) = \sum \lambda_i = \text{Tr} A.$$

Now we can write  $\det A = e^{\text{Tr} A}$  in the last expression. You can compare that to our previous result.

3. Show that Jackson Eqs. 3.4a and 3.4b are consistent with Eq. 3.1 ④

(3.1) is  $\frac{P_g}{P_t} = e^{-\Delta E/k_B T}$  energy difference between g and t states.

left or right

(3.4a, 3.4b) are:  $P_t = \frac{W_t}{W_t + 2W_g} = \frac{1}{1 + 2 \times (.43)} = 0.54$

$P_g = \frac{2W_g}{W_t + 2W_g} = \frac{2(.43)}{1 + 2(.43)} = 0.46.$

We have a free state system  $\begin{array}{c} g-L \quad g-R \\ \hline t \quad \hline \end{array}$   $\Delta E = .5$  kcal/mol  $\uparrow E$

The Boltzmann weights are

$W_t = e^{-0/RT} = 1$ ,  $W_{gR} = W_{gL} = e^{-.5/RT} \approx 0.43$

$Z = W_t + W_{gR} + W_{gL} = W_t + 2W_g$

$P_t = \frac{W_t}{Z}$ ,  $P_g = \frac{W_{gR} + W_{gL}}{Z}$  and we get Eqs. 3.4a, 3.4b.

4. Calculate the prob. of finding  $n$ -pentane w/ no gauche bonds and only one gauche bond. ⑤

The partition sum is  $Z = \sum_{i=1}^N e^{-\Delta E_i / RT}$  for a chain of  $N$  bonds.

Again there are three states per bond and all bonds are treated as independent:

$$Z = (W_t + 2W_g)^N$$

$\uparrow$                        $\uparrow$   
 trans                  two different gauche states with the same energy. These are called degenerate.

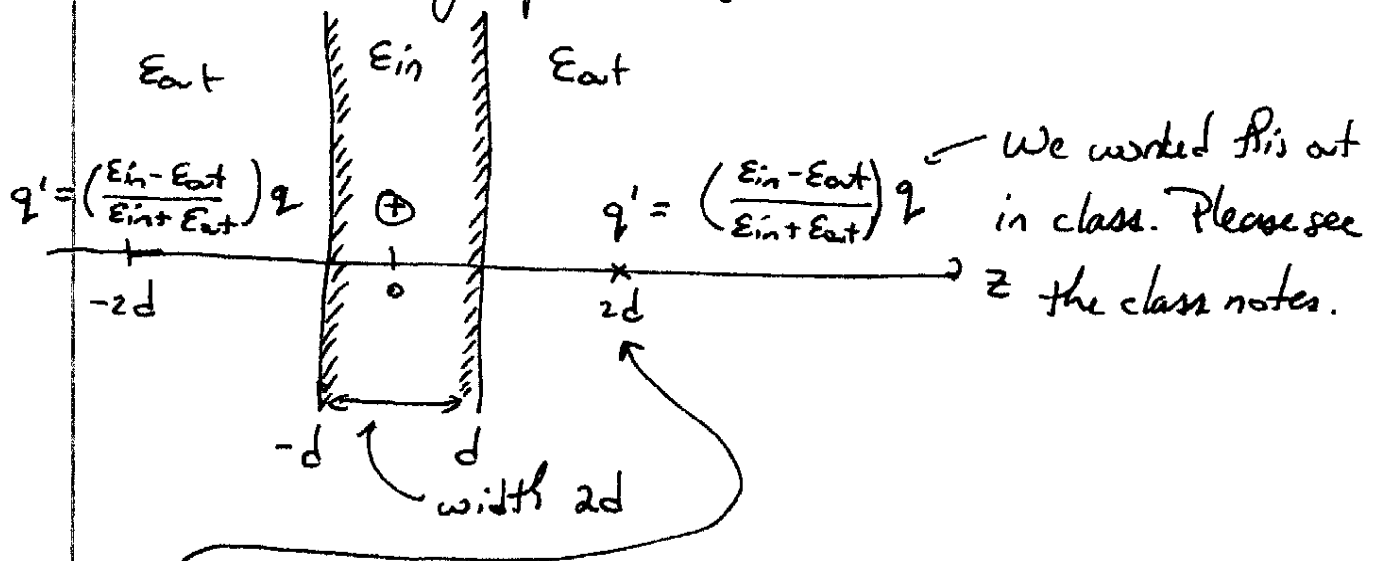
Prob of all trans bonds, i.e. no ~~gauche~~ gauche bonds.

$$P_{\text{all trans}} = \frac{W_t^N}{Z} = \frac{1}{(1 + 2e^{-\Delta E/RT})^N} \quad \text{using the results from the previous problem.}$$

$$P_{\text{one gauche}} = \frac{2N W_t^{N-1} W_g}{Z} = \frac{2N e^{-\Delta E/RT}}{(1 + 2e^{-\Delta E/RT})^N}$$

$N$  places to put the gauche bond and 2 types of gauche bonds are possible

## 5. Self-energy of a charge in a lipid bilayer. (6)



This image charge at  $z=2d$  fixes the b.c. at  $z=d$ . Now, note that it messes up the b.c. at  $z=-d$ . So we need another image charge  $3d$  to the left of the  $z=-d$  boundary.

Continuing we get a sequence of image charges at  $z = \pm 2d, \pm 4d, \pm 6d, \dots$

Sum the interaction energies between the image charges and the center charge, which is the real one:

$$U = \sum_{n=1}^{\infty} \frac{q q'_n}{2nd\epsilon_h}; \quad q'_n = \alpha^n q \quad \text{where } \alpha = \left( \frac{\epsilon_{in} - \epsilon_{out}}{\epsilon_{in} + \epsilon_{out}} \right)$$

$$U = \frac{q^2}{2d\epsilon_h} \sum_{n=1}^{\infty} \frac{\alpha^n}{n}; \quad \text{Note } \log(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} + \dots$$

$$U = -\frac{q^2}{2d\epsilon_h} \log(1-\alpha)$$

$$1-\alpha = \frac{\epsilon_{in} + \epsilon_{out} - \epsilon_{in} + \epsilon_{out}}{\epsilon_{in} + \epsilon_{out}}$$

$$U = -\frac{q^2}{2d\epsilon_h} \log\left(\frac{2\epsilon_{out}}{\epsilon_{in} + \epsilon_{out}}\right)$$

$$= \frac{2\epsilon_{out}}{\epsilon_{in} + \epsilon_{out}}$$

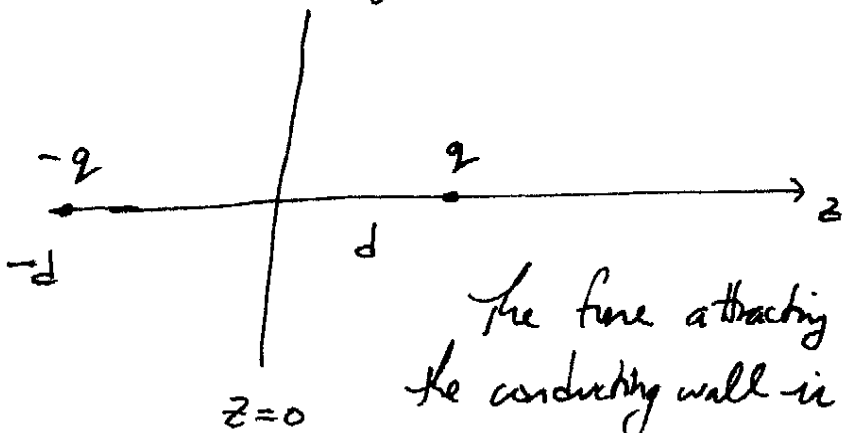
We need to multiply  $\rho_{\text{bs}}$  by two for the two sides and add the Born self-energy of the charge in  $\epsilon_{\text{in}}$

$$U = \frac{q^2}{2\epsilon_{\text{in}} a} - \frac{q^2}{d\epsilon_{\text{in}}} \log\left(\frac{2\epsilon_{\text{out}}}{\epsilon_{\text{in}} + \epsilon_{\text{out}}}\right)$$

Note: my calculation is a factor of two larger than that quoted in A. Parsegian. Recall that our membrane is 2d wide.

We stumbled upon the "famous factor of two puzzle" - see H. Wu et al. Eur. J. Phys. 21, 413-419 (2000).

Consider a conducting wall



The force attracting the real charge to the conducting wall is  $\vec{F} = -\frac{q^2}{(2d)^2} \hat{z}$

The potential energy of the charge is then in our units!

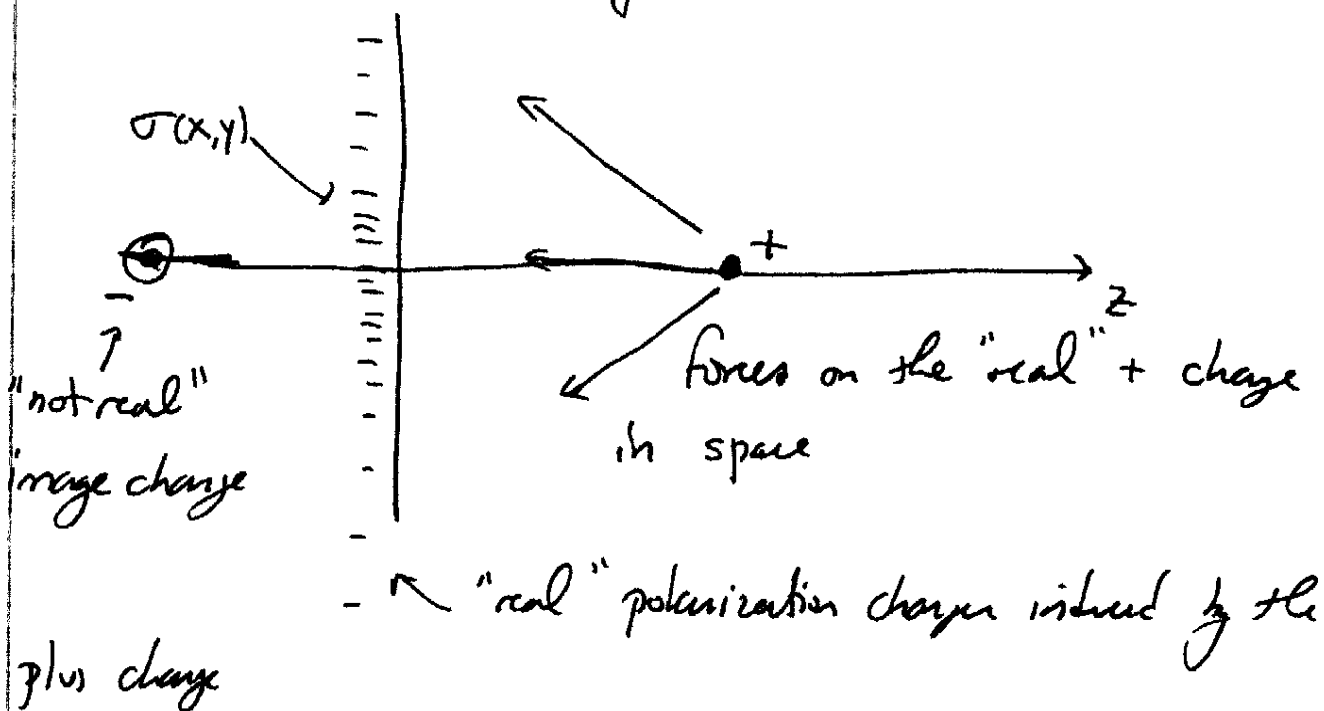
$$\vec{F} = -\vec{\nabla} U \Rightarrow U = -\frac{q^2}{2 \cdot 2d} \text{ why?}$$

$$U(z) = \frac{-q^2}{2d} \frac{1}{z} \Rightarrow F_z = -\partial_z U = -\frac{q^2}{2d} \frac{1}{z^2} \Big|_{z=d} = \frac{-q^2}{2d^2}$$



So  $U = \frac{1}{2} \cdot \frac{-q^2}{2d}$  ← we need a factor of  $1/2$ . ⑧

How do we know we are right? Well in the real world the charge  $q$  is attracted to the polarization charges that it induces on the surface of the conductor.



We can calculate the surface charge density from the normal ( $\hat{z}$ ) component of the  $\vec{E}$ -field.

$$V(\vec{x}) = q \left( \frac{1}{r_+} - \frac{1}{r_-} \right); \quad r_+ = \sqrt{x^2 + y^2 + (z-d)^2} \text{ real charge.}$$

$$r_- = \sqrt{x^2 + y^2 + (z+d)^2} \text{ image charge.}$$

$$\left. E_z \right|_{z=0} = - \left. \frac{\partial V}{\partial z} \right|_{z=0} = \frac{-2dq}{R^3}; \quad R = \sqrt{x^2 + y^2 + d^2}$$

$$\sigma = \frac{1}{4\pi} E_z = -aq / 2\pi R^3.$$

↑ because of our units. Gauss's Law is funny.