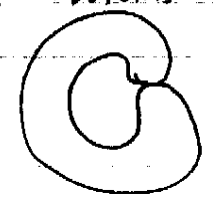


# Chapter One: Global Transitions in proteins

1.1 Defining a global state: Proteins as computers with a one bit memory.



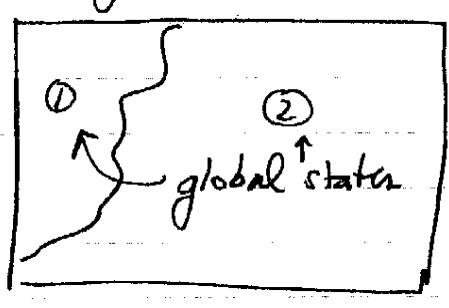
Global State One  
many microstates  
phosors etc.

Global state Two

We can compare the free energies of these global states

$G = -k_B T \log Z_\alpha$  ← Note funny notation for free energy from Jackson? Actually No: we can redo this in terms of chemical potential\*

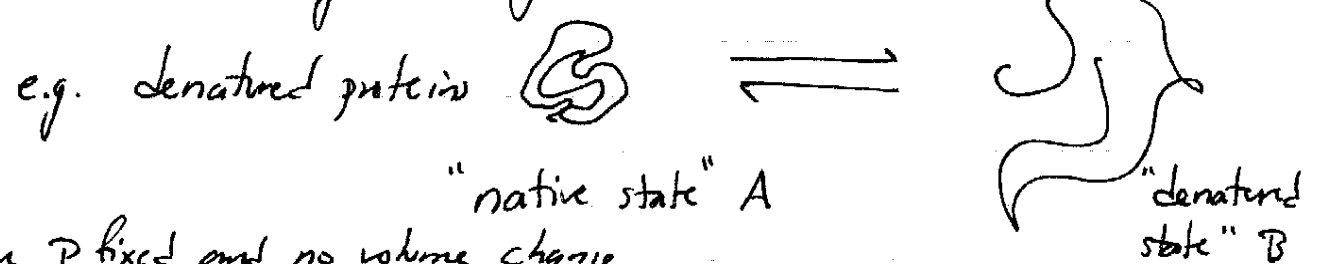
where  $Z_\alpha$  is a sum over only those microstates consistent with the global state  $\alpha = 1, 2$ .



all states.

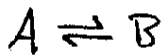
$$Z_\alpha = \sum_{i=1}^{N_\alpha} e^{-\epsilon_i/k_B T}$$

1.2 From this it is a simple matter to predict the equilibrium concentrations of these global states.



\* assume P fixed and no volume change.

②



molar free energy in solution:  $G_a = G_a^\circ + RT \log [A]$

$$G_b = G_b^\circ + RT \log [B]$$

$[x]$  = "concentration of x";  $R = N_A k_B$  "Gas Constant"

$$\Delta G = G_b - G_a = \Delta G^\circ + RT \log \left( \frac{[B]}{[A]} \right); \Delta G^\circ = G_b^\circ - G_a^\circ$$

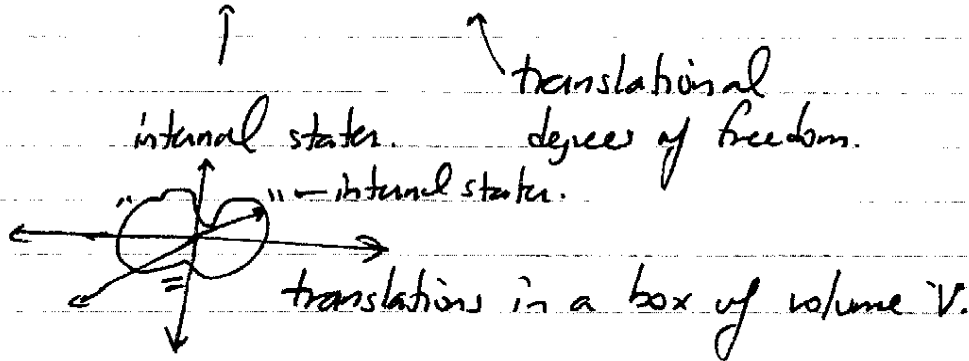
In equilibrium  $\Delta G = 0 \Rightarrow$

$$\Delta G^\circ = -RT \log \left( \frac{[B]}{[A]} \right) \text{ or}$$

$$\frac{[B]}{[A]} = \exp \left\{ -\Delta G^\circ / RT \right\} = K_{eq} \leftarrow \text{"Equilibrium Constant"}$$

Do you remember how this works?

$$Z_A = e^{-G_A / k_B T} (V / \lambda^3) \quad \text{Partition sum for one protein.}$$



Now for  $N$  of ~~more~~ them:  $\frac{1}{N!} Z_A^N$

$$\text{Compute the free energy: } G_A = -k_B T \log \left( \frac{Z_A^N}{N!} \right)$$

Stirling's Approx:  $\log N! = N \log N - N$

$$G_A = N \tilde{G}_A^{\circ} - k_B T N \log \left( \frac{V}{\lambda^3} \right) - k_B T [N \log N - N]$$

$$G_A = N \tilde{G}_A^{\circ} + k_B T N \log \left[ \frac{N \lambda^3}{V} \right] + k_B T N$$

$$G_A = N \tilde{G}_A^{\circ} + N k_B T \log \left[ \frac{N \lambda^3 e}{V} \right]$$

Now if we have a mole proteins in global state A

$$G_A = N_A \tilde{G}_A^{\circ} + R T \log \left( \frac{N_A \lambda^3 e}{V} \right)$$

And we define  $G_A^{\circ}$  to be the free energy at precisely one mole per liter then  $\tilde{V} = 1 \text{ liter}$

$$G_A = N_A \tilde{G}_A^{\circ} + R T \log \left( \frac{N_A \lambda^3 e}{\tilde{V}} \right) + R T \log \left( \frac{[A]}{1} \right)$$

where  $[A] = N/V$  and 1 comes from  $N_A/\tilde{V}$

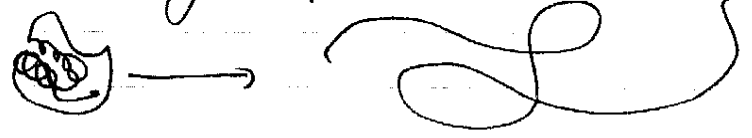
$$N_A \tilde{G}_A^{\circ} = \cancel{N_A} G_A^{\circ} - R T \log \left( \frac{N_A \lambda^3 e}{\tilde{V}} \right) \text{ so}$$

$G_A = G_A^{\circ} + R T \log ([A])$

 molar free energy of A at concentration [A].

### 1.3 Global transition induced by temperature

or  
Cooking an egg.



Divide the free energy into enthalpy and entropy

$G = E + pV - TS = H - TS$  and if  $T$  is fixed at the melting temperature or some one... fixed temp. start here

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ; \quad \Delta H^\circ = H_{un\ folded}^\circ - H_{folded}^\circ$$

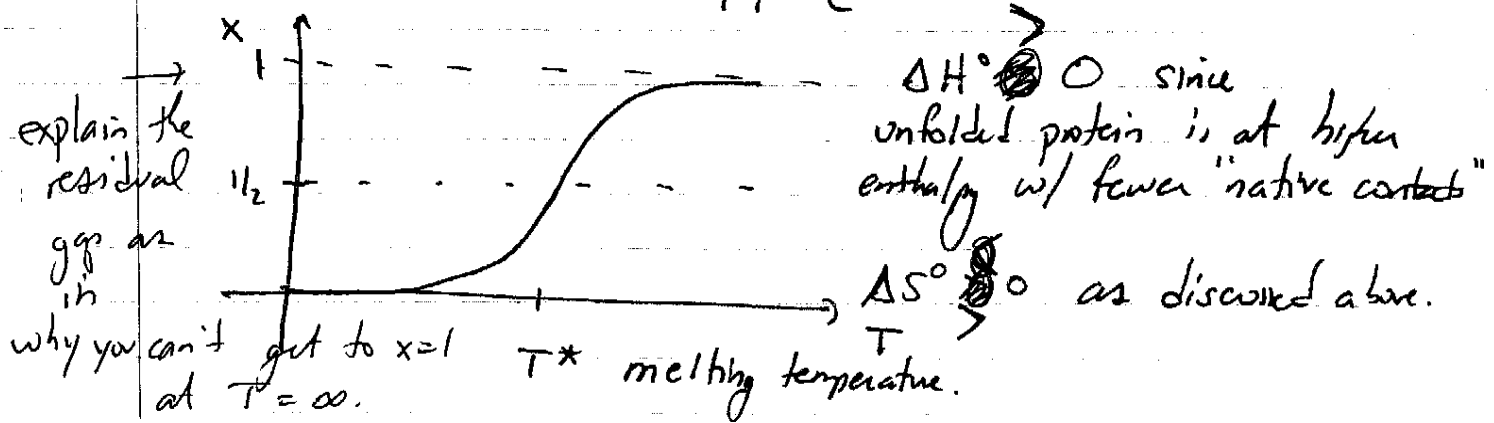
related to the change in the number of internal contacts in the protein.   
 the unfolding should increase the entropy of the protein.

Recall:  $\frac{[B]}{[A]} = e^{-(\Delta H^\circ + T \Delta S^\circ)/RT}$  below  $T^*$   $[B] < [A]$   
above  $T^*$   $[B] > [A]$

let  $x =$  fraction of unfolded protein:  $x = \frac{[B]}{[A] + [B]}$

corrected  
on 4/2/12

$$x = \frac{1}{1 + [A]/[B]} = \frac{1}{1 + e^{(\Delta H^\circ - \Delta S^\circ T)/RT}} = \frac{1}{1 + e^{\frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}}}$$



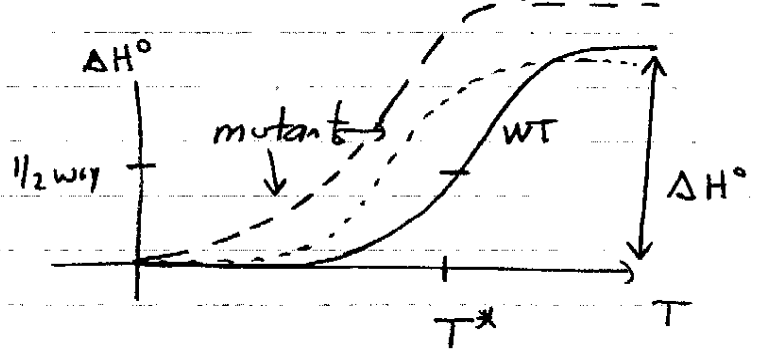
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### 1.4 Lysozyme unfolding

$\Delta H^\circ$  heat absorbed by the protein (at constant pressure) in denaturing.

Scanning calorimetry:

WT = "wild type"



at the melting point  $T^*$   $x = 1/2$

$$\Rightarrow \boxed{\Delta H^\circ / T^* = \Delta S^\circ} \text{ since } \Delta G^\circ = 0 \text{ there.}$$

### 1.5 Steepness and enthalpy

What determines the slope of these calorimetry curves?

Recall  $dG = dE - d(TS) + d(pV)$   
 $= Tds - pdv - Tds - SdT + pdv + vdp$   
 $= -SdT + vdp$

$$\Rightarrow \left. \frac{\partial G}{\partial T} \right|_P = -S$$

or as Jackson writes  $\frac{\partial G^\circ}{\partial T} = -S^\circ$ . Subtracting one free energy (and entropy) from another

$$\frac{\partial \Delta G^\circ}{\partial T} = -\Delta S^\circ \text{ but } \Delta S^\circ = \frac{\Delta G^\circ - \Delta H^\circ}{-T} \text{ see p.4}$$

$$\frac{\partial \Delta G^\circ}{\partial T} = \frac{\Delta G^\circ}{T} - \Delta H^\circ; \quad \Delta G^\circ = T \frac{\partial \Delta G^\circ}{\partial T} + \Delta H^\circ$$

6

Collecting terms:  $\frac{1}{T} \frac{\partial \Delta G^\circ}{\partial T} - \frac{\Delta G^\circ}{T^2} = -\Delta H^\circ / T^2$   
and dividing by  $T^2$

$$\frac{\partial}{\partial T} \left( \frac{\Delta G^\circ}{T} \right) = -\frac{\Delta H^\circ}{T^2}$$

From 7.2 we see that  $-\frac{\Delta G^\circ}{RT} = \log \left( \frac{[B]}{[A]} \right)$  so

$$\frac{\partial}{\partial T} \log \left( \frac{[B]}{[A]} \right) = \frac{\Delta H^\circ}{RT^2}$$

van't Hoff Equation.  
We will call this measure of  $\Delta H^\circ$   
 $\Delta H_{VH}^\circ$  ← definition.

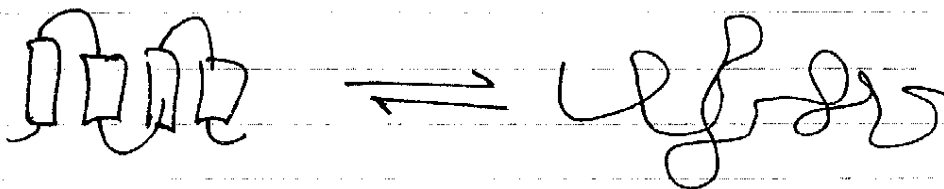
The slope of  $\log([B]/[A])$  vs. temp tells us the enthalpy change.

Note  $\frac{\partial x}{\partial T} = \frac{-1}{(1 + [A]/[B])^2} \frac{\partial}{\partial T} \left( \frac{[A]}{[B]} \right) = -x^2 \frac{\partial}{\partial T} \left( \frac{[A]}{[B]} \right)$

so steep  $\log([B]/[A]) \Rightarrow$  steep  $x$  vs  $T$  as well.

### 1.6 Cooperativity and thermal transitions.

What if the protein doesn't fall apart all at once?



n subunits.

$A_n$

all or nothing denaturation

$B_n$

$$\Delta H_{VH}^\circ = n \Delta H^\circ$$

↑  
for one subunit.

In general  $\frac{1}{n} < \frac{\Delta H_{\text{int}}}{\Delta H^{\circ}} < n$  if there is less than perfect <sup>⑦</sup>

cooperativity. For small proteins ( $< 1.5 \times 10^6$  Da) one finds highly cooperative denaturation.

A word about units: Chemists use  $\text{kcal/mol} = 6.9 \times 10^{-21} \text{ J/molecule}$

The most useful energy scale for us is to compare things to thermal energy  $k_B T$  at room temperature.

$$1 \text{ kcal/mol} \approx 1.7 k_B T \text{ at } 300 \text{ K.}$$

Da = atomic mass unit  $\Rightarrow$   $^{12}\text{C}$  has 12 Da mass.  
 $1 \text{ Da} \approx 1.7 \times 10^{-27} \text{ Kg.}$

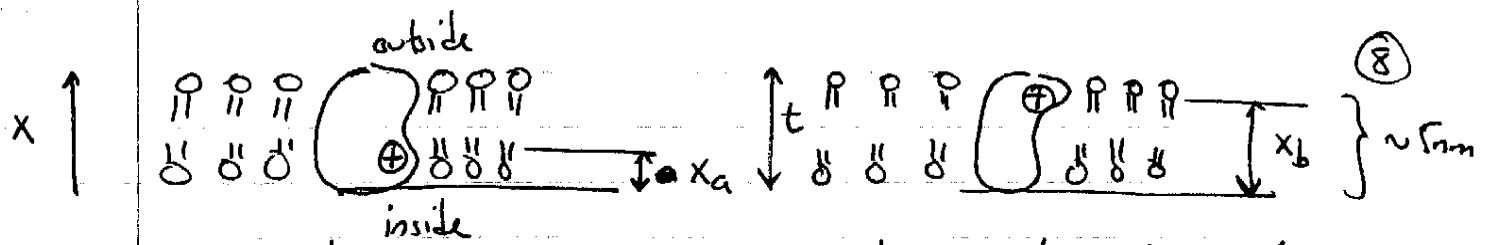
The amino acids, which are the chemical subunits of proteins have masses in the range of  $\sim 100 - \sim 200$  Da

So a protein of mass 14 kDa =  $1.4 \times 10^4$  Da (like Lysozyme) has about

$$\frac{1.4 \times 10^4 \text{ Da}}{10^2 \text{ Da}} \sim 10^2 \text{ amino acids making it up.}$$

We will look at cooperativity in more detail in terms of voltage activated proteins. First we consider transitions due to voltage.

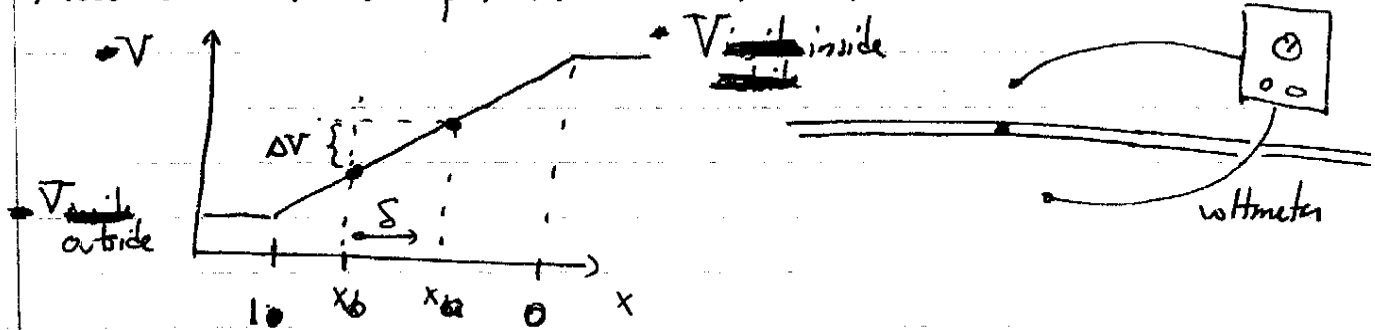
1.8 Voltage induced transitions.



lipid bilayer  
(cell membrane)

$\bar{x}$  = distance / membrane thickness

Assume a linear potential across the membrane



Potential energy of the charge  $q$ :  $qV$ . Take the total potential difference across the membrane to be  $\mathcal{V}$ , then when the charge is at  $x$  its potential relative to being on the inner surface of the membrane is:

$$q \frac{\mathcal{V}}{t} x = q \mathcal{V} \bar{x}$$

↑

membrane thickness

The potential energy change in moving from  $x_a$  to  $x_b$  is

$$q \mathcal{V} \frac{(x_b - x_a)}{t} = q \mathcal{V} \delta$$

We add this energy to the free energy of the protein:

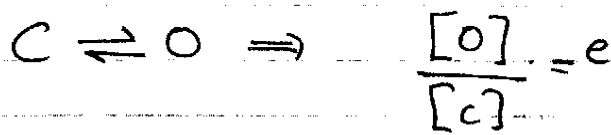


sum on multiple moving charges.

$$\Delta G^\circ = \Delta G_{vi}^\circ + \sum_{i=1}^m q \delta_i \mathcal{V} = \Delta G_{vi}^\circ + \alpha \mathcal{V} \quad (9)$$

↑  
voltage independent part
↑  
 $\sum_{i=1}^m q \delta_i$  for one mole of channels.

Consider the chemical equilibrium between the open O and closed C states of the channel protein



probability of channel opening. voltage  $V > 0$  suppresses the

open probability:  $P_o = \frac{[O]}{[C] + [O]} = \frac{1}{1 + e^{(\Delta G_{vi}^\circ + \alpha V)/RT}}$

We can define  $V_o$  and  $V_s$  so that

Channel  
Open probability

$$P_o = \left[ 1 + e^{(V_o - V)/V_s} \right]^{-1}$$

$V_s = RT/\alpha$  controls the steepness of the transition.  
 $V_o = -(\Delta G_{vi}^\circ/RT) V_s = -\Delta G_{vi}^\circ/\alpha$  is the midpoint

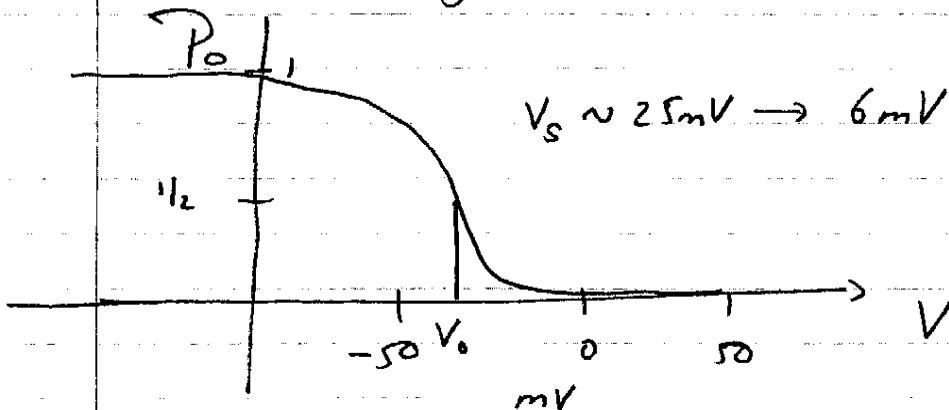
voltage where  $1/2$  the channels should be open.

Recall  $\alpha$  a charge that moves so  $k_B T \sim 25 mV$  at room temperature.  
 one electronic charge  $\rightarrow e$

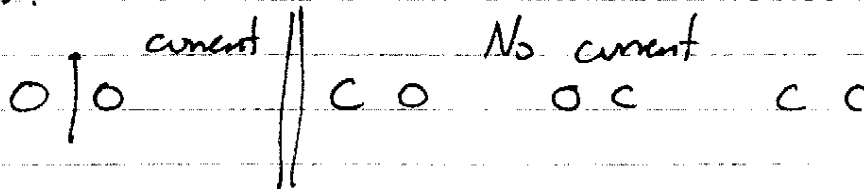
room temperature.

But in some (many channels) the transition is sharper than this. How is that possible? (10)

Ans. Cooperativity! Multiple charges move together.



Imagine perfect cooperativity between two charge-moving gates.



If each opening/closing event is independent but we need both to get a functional open gate then

$$P_0 = \frac{1}{[1 + e^{(V-V_0)/V_s}]^2}$$

Steeper by squaring the function above.

Now consider enhancing the cooperativity by including an interaction energy  $\Delta$ .

Again we have four states: o o // c o o c c c

OPEN      CLOSED

of which only one is a functional open channel.

The open channel probability is:

(11)

$$P_o = \frac{[00]}{[00] + [0c] + [c0] + [cc]}$$

Now  $\frac{[00]}{[cc]} = e^{-2(\Delta G_{vi}^{\circ} + \alpha V)/RT}$  as before.

But  $\frac{[c0]}{[cc]} = \frac{[0c]}{[cc]} = e^{-(\Delta G_{vi}^{\circ} + \Delta + \alpha V)/RT}$  interaction energy.

and then:

$$P_o^{-1} = 1 + 2 \frac{[0c]}{[00]} + e^{2(\Delta G_{vi}^{\circ} + \alpha V)/RT}$$

$$\text{and } \frac{[0c]}{[00]} = \frac{[0c]}{[cc]} \times \frac{[cc]}{[00]} = \exp\left\{-\frac{(\Delta G_{vi}^{\circ} + \Delta + \alpha V)}{RT}\right\} +$$

$$2 \frac{(\Delta G_{vi}^{\circ} + \alpha V)}{RT}\left\} = \exp\left\{\frac{(\Delta G_{vi}^{\circ} + \alpha V - \Delta)}{RT}\right\}$$

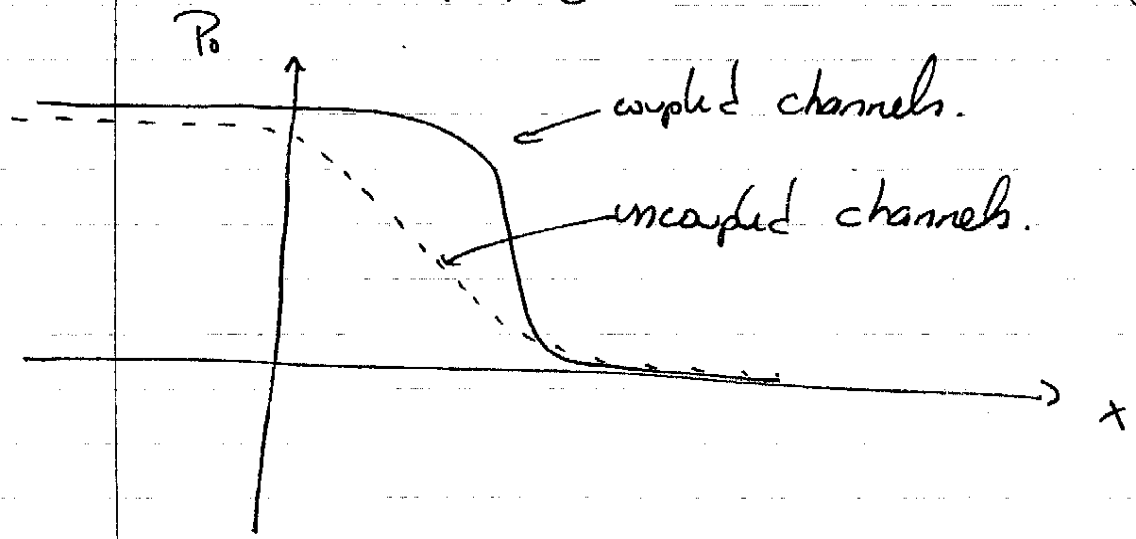
and we get the open channel probability to be:

$$P_o = \frac{1}{1 + 2e^{(\Delta G_{vi}^{\circ} + \alpha V)/RT - \Delta/RT} + e^{2(\Delta G_{vi}^{\circ} + \alpha V)/RT}}$$

If  $\Delta \gg RT$  then we completely suppress the

"half open" configurations and we get

$$P_0 = \frac{1}{1 + e^{2x}} \text{ instead of } P_0 = \frac{1}{(1 + e^x)^2}$$



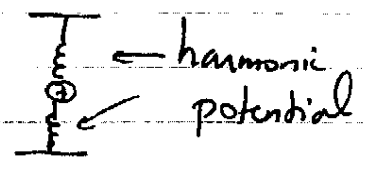
### 1.12 Compliance of the global state.

Fluctuations in a global state shift their free energies. Consider a simple model to account for this.

$$U(x) = qVx + \frac{1}{2} \phi (x - x_0)^2$$

$$x' = x - x_0$$

↖ spring constant



$$U(x') = qV(x_0 + x') + \frac{1}{2} \phi x'^2$$

~~xxxxxxxx~~

We can write this as: 
$$U(x') = qVx_0 + \frac{1}{2} \phi \left(x' + \frac{qV}{\phi}\right)^2 - \frac{1}{2} \frac{(qV)^2}{\phi}$$

Check by expanding the square

$$U(x') = \underbrace{qVx_0 + \frac{qV}{\phi} x' \phi + \frac{1}{2} \frac{(qV)^2}{\phi}}_{\text{combine}} - \frac{1}{2} \frac{(qV)^2}{\phi} \leftarrow \text{cancel}$$

Of course the bottom of the harmonic well is just

$$\frac{\partial U}{\partial x'} = 0 \Rightarrow qV + \frac{1}{2} \cdot 2 \phi x' = 0 \Rightarrow x' = -qV/\phi \text{ as we see from completing the square.}$$

In thermal equilibrium the mean energy of this system

$$\text{is } \langle U \rangle = qVx_0 - \frac{(qV)^2}{\phi} + \frac{1}{2} k_B T$$

applied to the one quadratic degree of freedom is the equipartition theorem. Hamiltonian.

Now if the spring constant changes from global state to the other we get a new shift in free energy associated with  $\phi_b$  and  $\phi_a$

$$\Delta G^\circ = \Delta G_i^\circ + qV\delta - \frac{1}{2} (qV)^2 \left( \frac{1}{\phi_b} - \frac{1}{\phi_a} \right)$$

↑  
the scaled change in  $x_0$

and the opening probability takes the form:

$$P_o = \frac{1}{1 + e^{\{\Delta G_i^\circ + qV\delta - \frac{1}{2} (qV)^2 [\frac{1}{\phi_b} - \frac{1}{\phi_a}]\} / RT}}$$

for voltage activated channels. Generally this term is small

Why bother then? There may be important entropic contributions in other forms of protein allostery - see T.B. McLeish and collaborators.

Before we think about that, let's be sure we see why we expect this term to be

How big is  $\phi$ ?  $\langle \frac{1}{2} \phi_b x^2 \rangle = k_B T / 2$

and typical distances are on the order of 5 Å

$\Rightarrow \phi_b \sim \frac{k_B T}{25 \text{ \AA}^2}$  but we have a nondimensionalized distance  $\Rightarrow x \approx 5 \text{ \AA} / 50 \text{ \AA} \sim .1$   $\phi_b \sim k_B T / 10^{-2}$

Now  $qV\delta - \frac{1}{2}(qV)^2/\phi = qV(\delta - \frac{qV}{2\phi})$

take  $q \approx e$  or just a few electronic charges then

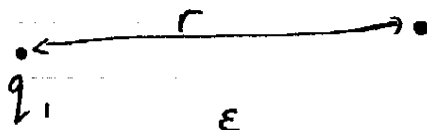
$\frac{qV}{2\phi} \approx \frac{qV}{2 \cdot k_B T} 10^{-2} = \frac{V}{2 \cdot 25 \text{ mV}} 10^{-2} \approx V / (5 \text{ Volts})$

At room temperature

Now membrane potentials are in the range of  $\sim 100 \text{ mV}$  so the correction term here is on the scale of  $10^{-1}$ . Not terribly small but clearly subdominant.

Chapter Two: The fundamental forces holding biological molecules together. (15)  
Coulomb interactions

$$U = \frac{q_1 q_2}{\epsilon r}$$



Point out

$$S = - \frac{\partial G}{\partial T} = G \frac{\partial \epsilon}{\partial T}$$

dielectric constant  $T_S \approx 1.4 G$  at  $T=300K$ .

Note electron charge is  $4.8 \times 10^{-10}$  esu. Our book likes to use these cgs units. In other words Coulomb's law now reads.

$$F = \frac{q_1 q_2}{\epsilon r^2} \text{ instead of } F = \frac{1}{4\pi\epsilon_0 \epsilon} \frac{q_1 q_2}{r^2}$$

"Normal" SI units

and Gauss's Law reads  $\vec{\nabla} \cdot \vec{E} = \frac{4\pi\rho}{\epsilon}$  instead of  $\vec{\nabla} \cdot \vec{E} = \rho/\epsilon_0$

The dielectric constant of water  $\epsilon \approx 80$  and of oil  $\epsilon \approx 2$ . Both are dimensionless.

The large value of  $\epsilon$  in water is due to its large permanent dipole moment



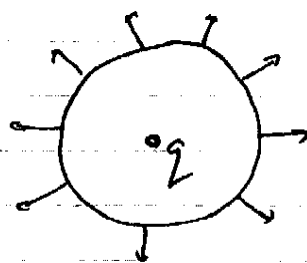
## 2.2 Electrostatic Self-Energy

The work to charge up a sphere of radius  $a$  is the work done against the field.



$4\pi r^2 \cdot \vec{E} = \frac{q}{\epsilon} \text{ Gauss's Law}$

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



Work to bring in charge  $\delta q$ :  $\delta W = - \int_a^\infty \vec{E} \cdot d\vec{s} \delta q$

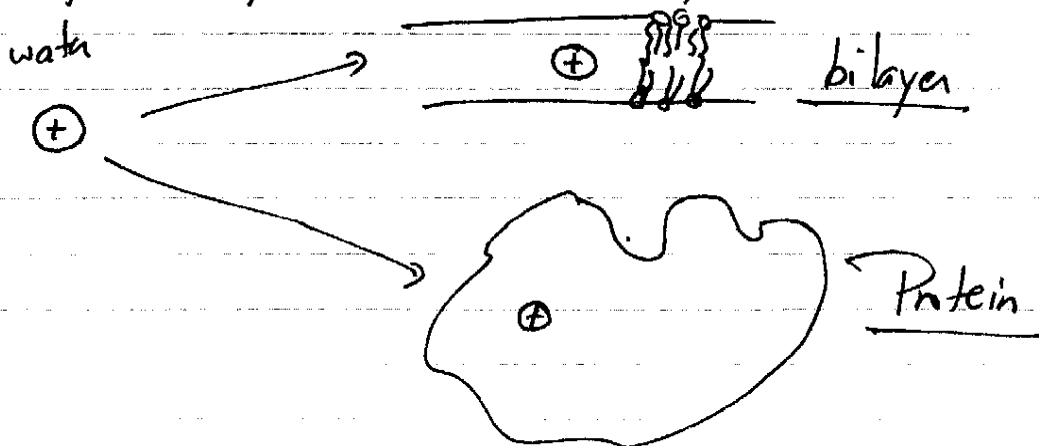
$\vec{E} \parallel d\vec{s}$  and  $ds = -dr$  Note: three minus signs.

$$\delta W = -\delta q \int_a^\infty \frac{q}{\epsilon r^2} dr = \frac{\delta q q}{\epsilon} \int_a^\infty \frac{dr}{r^2} = -\frac{q \delta q}{\epsilon r} \Big|_a^\infty = \frac{q \delta q}{\epsilon a}$$

Total work to charge the sphere:  $W = \frac{1}{2} q^2 \frac{1}{\epsilon a}$

$W = \frac{q^2}{2\epsilon a}$  Self-energy of the charge.

How hard is it to transfer an ion from water into a lipid bilayer? or into a protein?





what to bilayer  $\Rightarrow$  approximate his best by treating it as an infinite expanse of oil. (17)

$$\Delta W = \frac{q^2}{2a} \left( \frac{1}{\epsilon_{oil}} - \frac{1}{\epsilon_{water}} \right)$$

Take the ion radius as  $\sim 1 \text{ \AA}$  and see what we get

$$\Delta W = \frac{(5 \times 10^{-10} \text{ esu})^2}{2 \cdot 10^{-8} \text{ cm}} \left( \frac{1}{\epsilon_{oil}} - \frac{1}{\epsilon_{water}} \right) \approx 12 \times 10^{-12} \left( \frac{\epsilon_{water} - \epsilon_{oil}}{\epsilon_{oil} \epsilon_{water}} \right) \text{ erg.}$$

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

$$\Delta W = 1.2 \times 10^{-19} \text{ J} \left( \frac{80 - 2}{160} \right) = ~~1.2 \times 10^{-19}~~ 29 k_B T$$

using  $k_B T = 4.1 \times 10^{-21} \text{ J};$

at room temp

$$\Delta W_{\text{transfer}} \approx 15 k_B T \quad \blacktriangle$$

The "Boltzmann weight" to insert an ion from water to oil is  $\sim e^{-15}$  about  $\sim 10^{-5}$ . It is hard to make

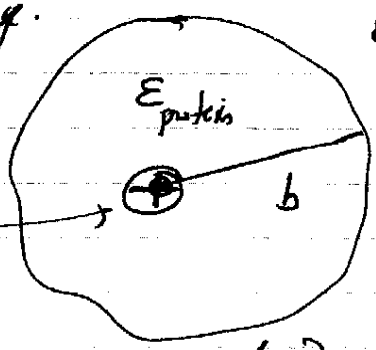
an ion go into a membrane or the oily inside of a protein.

Maybe things get better if we make the oily volume smaller?  
 for example, consider a protein of size  $\sim 8 \text{ nm}$  with one

buried charge.

$\epsilon_{water}$ .

charge at the center of the "protein"



take a spherical cow protein.

How can we solve this? Answer: Recall our electrostatics!

$\vec{D} = \epsilon \vec{E}$  and  $\vec{D} \cdot \hat{n}$  is continuous across the boundary\*  
 $\vec{E} \times \hat{n}$  is continuous across the boundary.

\* we assume no "free charge" at the boundary.

$\vec{D} = \frac{q \hat{r}}{r^2}$  inside and out so

$\vec{E}_{in} = \frac{q \hat{r}}{r^2 \epsilon_p}$  ;  $\vec{E}_{out} = \frac{q \hat{r}}{r^2 \epsilon_w}$

protein and water dielectric constants.

Just for fun let's compute this from the volume integral of the electric field's energy density:

$u = \frac{1}{8\pi} \epsilon |\vec{E}|^2 = \frac{1}{8\pi} \frac{q^2}{r^4 \epsilon}$

Now inside we have  $U_{inside} = \int_a^b r^2 dr 4\pi \frac{1}{8\pi} \frac{q^2}{r^4 \epsilon_p} = \frac{1}{2} \frac{q^2}{\epsilon_p} \int_a^b \frac{dr}{r^2}$

$U_{inside} = \frac{q^2}{2\epsilon_p} \left( \frac{1}{a} - \frac{1}{b} \right)$

For the outside take  $\epsilon_p \rightarrow \epsilon_w$   $a \rightarrow b$  and  $b \rightarrow \infty$  (17)

$$U_{\text{outside}} = \frac{q^2}{2\epsilon_w b}$$

Combining them we get 
$$U = \frac{q^2}{2} \left[ \frac{b-a}{ab\epsilon_p} + \frac{1}{\epsilon_w b} \right]$$

or 
$$U = \frac{q^2}{2\epsilon_p} \frac{1}{a} + \frac{q^2}{2\epsilon_w b} \left( \frac{1}{\epsilon_w} - \frac{1}{\epsilon_p} \right)$$

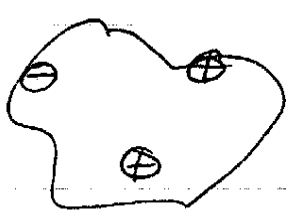
our old answer ↖ a negative correction since we now have a finite size protein.

How big is our correction for finite size?

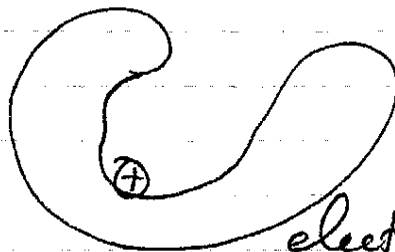
$$\frac{|U_{\text{correction}}|}{U_{\text{old}}} = \left| \frac{a\epsilon_p}{b} \left( \frac{1}{\epsilon_w} - \frac{1}{\epsilon_p} \right) \right| = \frac{a}{b} \frac{|\epsilon_p - \epsilon_w|}{\epsilon_w}$$

This is roughly  $\left( \frac{10^{-1} \text{ nm}}{10 \text{ nm}} \right) \left( \frac{78}{80} \right) \sim 1\%$ . Old first guess was pretty good.

We can conclude that charged groups in proteins are either at the surface or in "pockets" of internal water

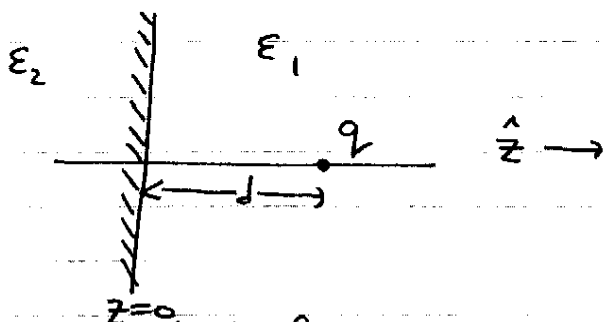


or

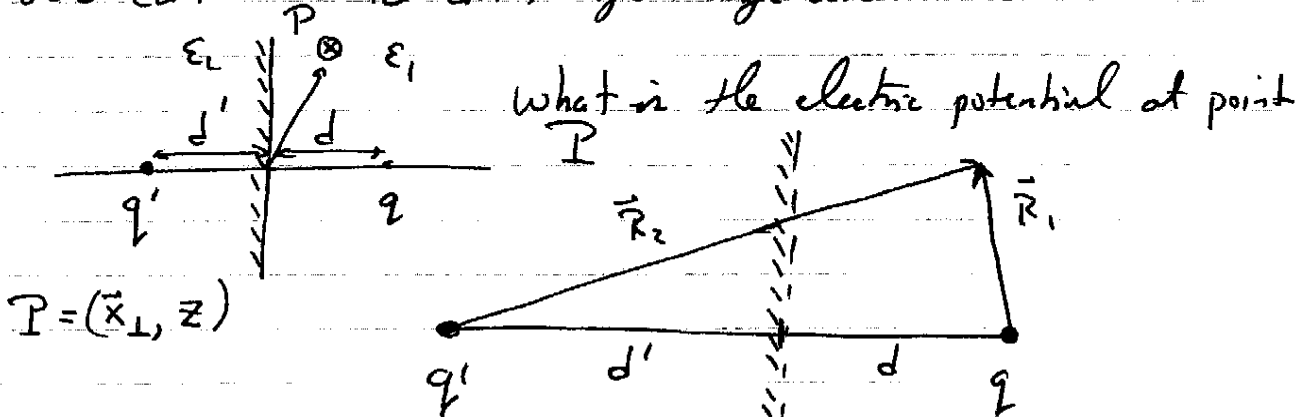


Otherwise, the folded state would be highly unfavorable electrostatically.

What about a dielectric slab?



We can look for an image charge solution



$P = (x_{\perp}, z)$

for  $z > 0$   
(in the  $\epsilon_1$  side)

$$\Phi_1 = \frac{1}{\epsilon_1} \left( \frac{q}{R_1} + \frac{q'}{R_2} \right) \quad \text{where } R_1 = \sqrt{x_{\perp}^2 + (d-z)^2}$$

$$R_2 = \sqrt{x_{\perp}^2 + (d'+z)^2}$$

We also need to propose a solution inside the other dielectric. Here we can't have any charges.

Try  $\Phi_2 = \frac{1}{\epsilon_2} \frac{q''}{R_3}$  some other charge in place of  $q$ .  
or at least on the line  $z=0$

$$R_3 = \sqrt{x_{\perp}^2 + (d''+z)^2}$$

Now  $E_x$  and  $E_y$  are continuous across the  $z=0$  plane

$$\text{and } \left. \frac{\partial}{\partial x} \frac{1}{R_1} \right|_{z=0} = \left. \frac{\partial}{\partial x} \frac{1}{\sqrt{x_{\perp}^2 + y^2 + (d-z)^2}} \right|_{z=0} = -\frac{1}{2} \left( \right)^{-3/2} 2x$$

$$= \frac{-x}{(x_{\perp}^2 + d^2)^{3/2}}$$

While  $\left. \frac{\partial}{\partial x} \frac{1}{R_2} \right|_{z=0} = - \frac{x}{(x_1^2 + d^2)^{3/2}}$

so continuity of  $E_x$  and  $E_y \Rightarrow$

$$+ \frac{1}{\epsilon_1} \left[ \frac{x q}{(x_1^2 + d^2)^{3/2}} + \frac{x q'}{(x_1^2 + d'^2)^{3/2}} \right] = \frac{1}{\epsilon_2} \frac{q'' x}{(x_1^2 + d^2)^{3/2}}$$

If we want a solution for all  $x, y$  we better take  $d = d' = d''$

Then we need  $\boxed{\frac{1}{\epsilon_1} (q + q') = \frac{1}{\epsilon_2} q''}$  ← One equation for

two unknowns. Fortunately we have the continuity of  $D_z$ :

$$\left. \frac{\partial}{\partial z} \frac{1}{R_1} \right|_{z=0} = - \frac{1}{2} \binom{-3/2}{(-1)} 2(d-z)^{\binom{-1}{-3/2}} = \frac{d}{(x_1^2 + d^2)^{3/2}}$$

because we had  $(z+d)$

so we get

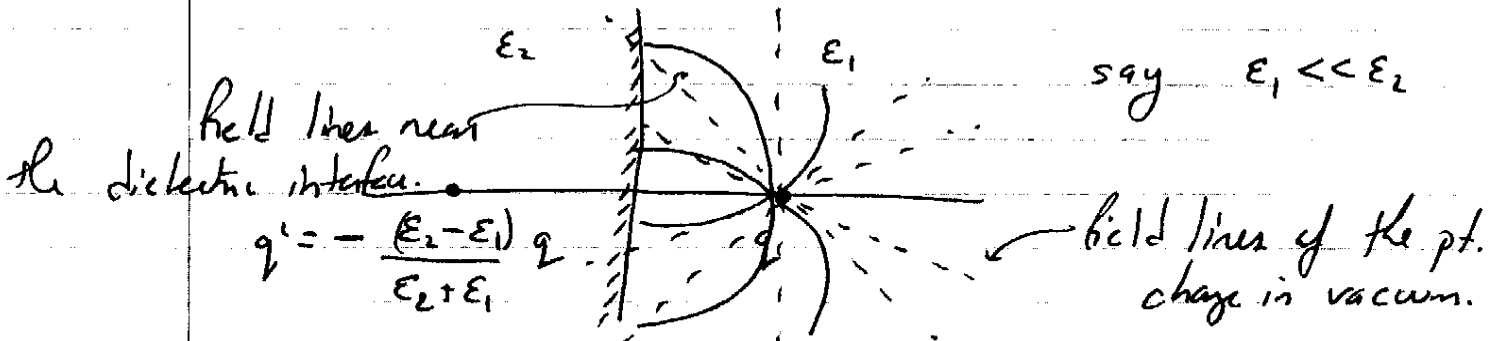
$$\frac{\epsilon_1}{\epsilon_1} \left[ \frac{q d}{(x_1^2 + d^2)^{3/2}} + \frac{q' d}{(x_1^2 + d^2)^{3/2}} \right] = \frac{\epsilon_2}{\epsilon_2} \frac{d q''}{(x_1^2 + d^2)^{3/2}}$$

or  $\boxed{q - q' = q''}$

Solving these two equations we get  $q' = \left( \frac{\epsilon_1 - \epsilon_2}{\epsilon_2 + \epsilon_1} \right) q$

$$q'' = \left( \frac{2\epsilon_2}{\epsilon_2 + \epsilon_1} \right) q$$

So the field inside the  $\epsilon_1$  dielectric is the same as for



if  $\epsilon_2 \rightarrow \infty$  (like a metal) we get  $q' = -q$  a dipole (distributed) symmetrically placed across the interface between the two materials.

What is the energy of the charge  $q$  near a dielectric.

$$U = \frac{q^2}{2\epsilon_1 a} + \frac{qq'}{\epsilon_1 (2d)} = \frac{q^2}{2\epsilon_1 a} - \frac{q^2 (\epsilon_2 - \epsilon_1)}{\epsilon_1 (\epsilon_2 + \epsilon_1) 2d}$$

self energy of the charge  $q$   $\leftarrow$  energy of charge  $q$  in field of image charge  $q'$

We can write this for an oil/water interface as

$$U = \frac{q^2}{2\epsilon_1 a} \left[ 1 - \frac{a}{d} \frac{(\epsilon_2 - \epsilon_1)}{\epsilon_2 + \epsilon_1} \right] \left| \frac{b}{2a} \right|$$

If we have two interfaces, as in a slab, one gets a more complicated answer since one needs an infinite series of image charges...

A. Parsegian (1969) 
$$U = \frac{q^2}{2\epsilon_1 a} \left[ 1 - \frac{a}{b} \log \left( \frac{2\epsilon_w}{\epsilon_w + \epsilon_1} \right) \right]$$