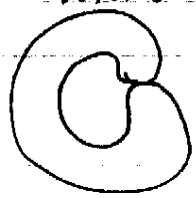
Chapter One: Global Transitions in proteins

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

Global State One
many microstates
phonons etc.

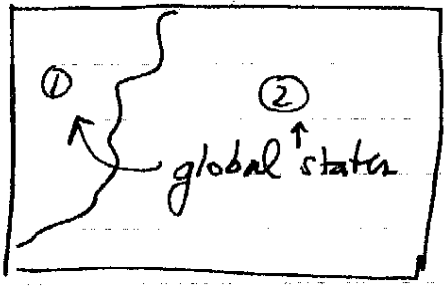


Global state Two

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 relate Fs in terms of chemical potential*

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



all states.

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

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

e.g. denatured protein  "native state" A

 "denatured state" B

* assume P fixed and no volume change.

$A \rightleftharpoons B$

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"

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

In equilibrium $\Delta G = 0 \Rightarrow$

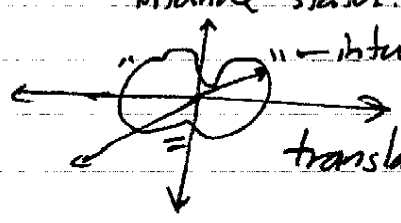
$$\Delta G^\circ = -RT \log\left(\frac{[B]}{[A]}\right) \text{ or}$$

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

Do you remember how this works?

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

$e^{-G_A^\circ/k_BT}$: internal states. $\left(V/\lambda^3\right)$: translational degrees of freedom.



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

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

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

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

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

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

Now if we have a mole proteins in global state A

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

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

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

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

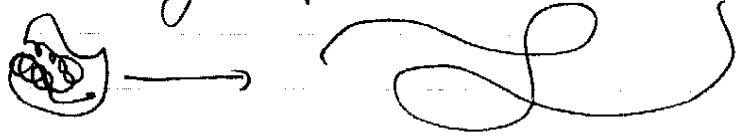
$N_A\tilde{G}_A^{\circ} = G_A^{\circ} - RT\log\left(\frac{N_A\lambda^3 e}{\tilde{V}}\right)$ so

$$\boxed{G_A = G_A^{\circ} + RT\log\left([A]\right)}$$

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ ; \quad \Delta H^\circ = H^\circ_{\text{unfolded}} - H^\circ_{\text{folded}}$$

related to the change in the number of internal contacts in the protein

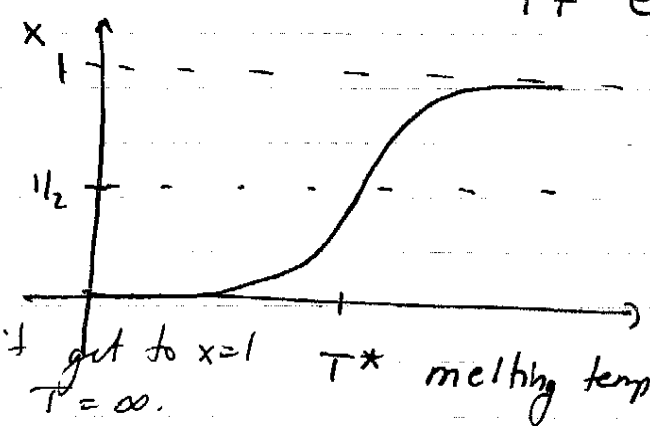
the unfolding should increase the entropy of the protein.

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 →

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



explain the residual gap as in why you can't get to x=1 at $T = \infty$.

$\Delta H^\circ > 0$ since unfolded protein is at higher enthalpy w/ fewer "native contacts"

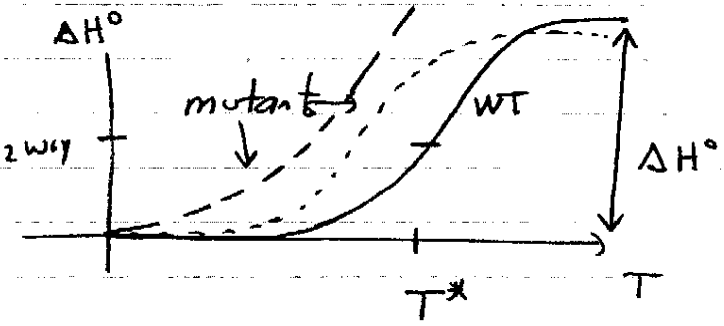
$\Delta S^\circ > 0$ as discussed above.

1.4 Lysozyme unfolding

ΔH° heat absorbed by the protein (at constant pressure) in denaturing.

Scanning calorimetry:

WT = "wild type"



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

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

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

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

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 p. 2 we see that $-\frac{\Delta G^\circ}{RT} = \log\left(\frac{[B]}{[A]}\right)$ so

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

van't Hoff Equation.

We will call this measure of ΔH° $\boxed{\Delta H^\circ_{VH}}$ ← definition.

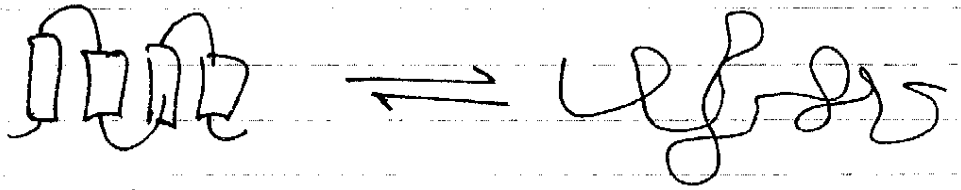
The slope of $\log([B]/[A])$ vs. temp tells us the enthalpy change.

16G $\frac{\partial x}{\partial T} = \frac{-1}{(1+[A]/[B])^2}\frac{\partial}{\partial T}\left(\frac{[A]}{[B]}\right) = -x^2 \frac{\partial [A]}{\partial B}\frac{\partial}{\partial T}\left(\frac{[A]}{[B]}\right)$

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.

$$\Delta H^\circ_{VH} = n\,\Delta H^\circ$$

$A_n \rightleftharpoons B_n$ all or nothing denaturation ↑ for one subunit.

In general $1 < \frac{\Delta H^\circ_{VH}}{\Delta H^\circ} < n$ if there is less than perfect cooperativity. For small proteins ($< 1.5 \times 10^6$ Da) one finds highly cooperative denaturation.

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

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

1 kcal/mol $\cong$ 1.7 $k_B T$ at 300K.

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

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

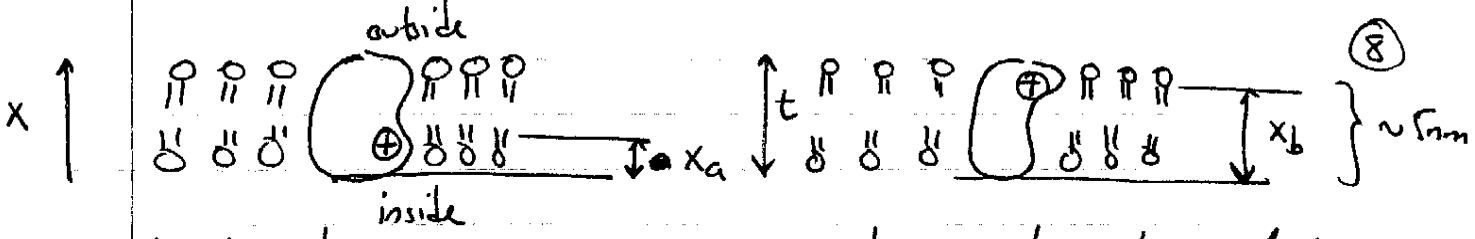
So a protein of mass 14 kDa = 1.4×10^4 Da (like Lysozyme) has about

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

making it up.

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

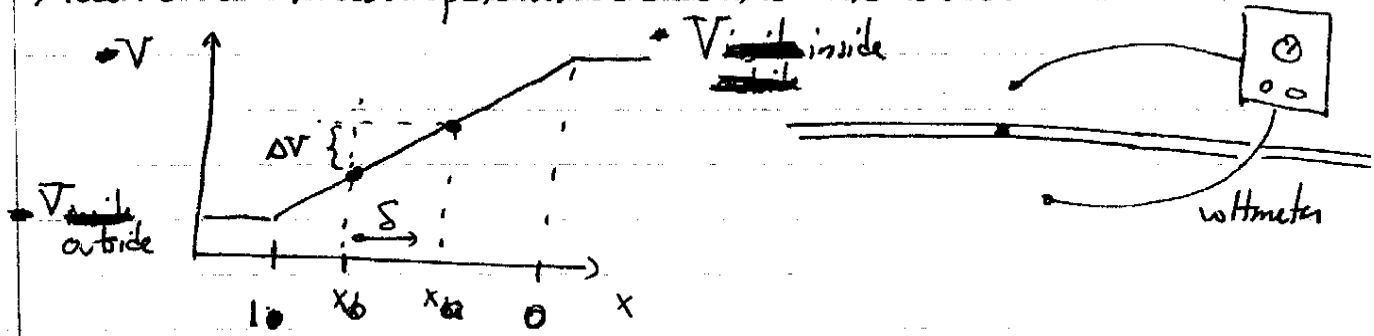
1.8 Voltage induced transitions.



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.

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

ΔG°_{vi}: 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

$$C \rightleftharpoons O \Rightarrow \frac{[O]}{[C]} = e^{-\Delta G^\circ_{vi}/RT - \alpha V/RT}$$

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

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

We can define V_0 and V_s so that

Channel Open probability

$$\boxed{P_o = \left[1 + e^{(V_\bullet - V_0)/V_s}\right]^{-1}};$$

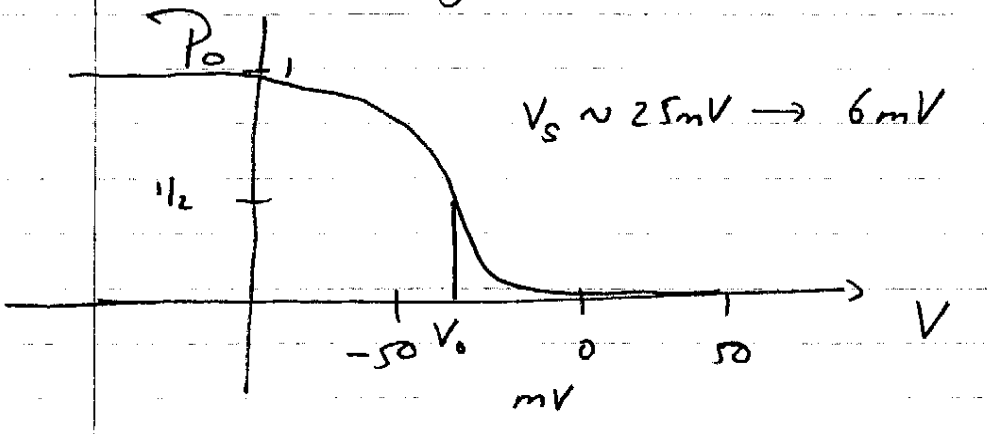
$V_s = RT/\alpha$ controls the steepness of the transition.

$V_0 = -(\Delta G^\circ_{vi}/RT)\, V_s = -\Delta G^\circ_{vi}/\alpha$ is the midpoint voltage where 1/2 the channels should be open.

Recall α a charge that moves so $\frac{k_B T}{e} \sim 25\,mV$ at room temperature. $\longrightarrow$ e is electronic charge

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

Ans. Cooperativity! Multiple charges move together.



Imagine perfect cooperativity between two charge-moving gates.

current | No current

O | O || C O O C C C

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

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

Steeper by squaring the function above.

Now consider enhancing the cooperativity by including an interaction energy Δ

OPEN | CLOSED

Again we have four states: O O || C O O C C C

of which only one is a functional open channel.

The open channel probability is:

$$P_o = \frac{[OO]}{[OO] + [OC] + [CO] + [CC]}$$

Now $\frac{[OO]}{[CC]} = e^{-2(\Delta G^\circ_{vi} + \alpha V)/RT}$ as before.

But $\frac{[CO]}{[CC]} = \frac{[OC]}{[CC]} = e^{-(\Delta G^\circ_{vi} + \Delta + \alpha V)/RT}$ ← interaction energy.

and then:

$$P_o^{-1} = 1 + 2\frac{[OC]}{[OO]} + e^{2(\Delta G^\circ_{vi} + \alpha V)/RT}$$

and $\frac{[OC]}{[OO]} = \frac{[OC]}{[CC]} \times \frac{[CC]}{[OO]} = \exp\left\{-\frac{(\Delta G^\circ_{vi} + \Delta + \alpha V)}{RT} + \frac{2(\Delta G^\circ_{vi} + \alpha V)}{RT}\right\} = \exp\left\{(\Delta G^\circ_{vi} + \alpha V - \Delta)/RT\right\}$

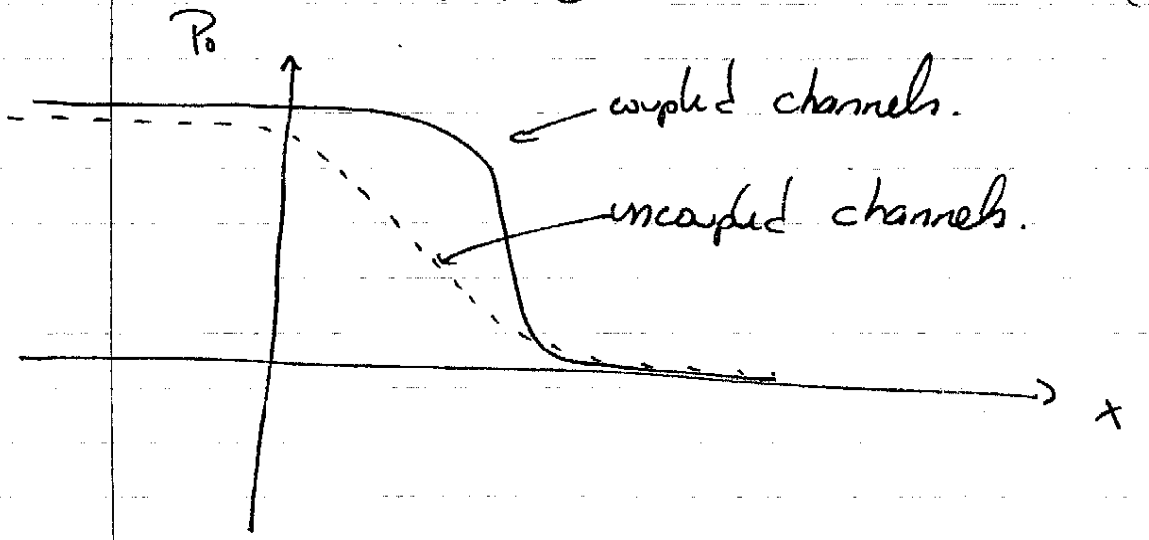
and we get the open channel probability to be:

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

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

"half open" configurations and we get

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

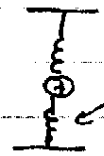


1.12 Compliance of the global state.

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

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

↖ spring constant



$$x' = x - x_0$$

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

~~$\left.\frac{\partial U}{\partial x}\right|_{x=x_0} = 0$~~

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

Check by expanding the square

$$U(x') = qVx_0 + \tfrac{1}{2}\varphi x'^2 + \frac{qV}{\varphi}x'\varphi + \frac{1}{2}\frac{(qV)^2}{\varphi} - \frac{1}{2}\frac{(qV)^2}{\varphi}$$

combine

cancel.

Of course the bottom of the harmonic well is just

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

In thermal equilibrium the mean energy of this system is $\langle U \rangle = qV x_0 - \frac{(qV)^2}{\varphi} + \frac{1}{2} k_B T$

↖ equipartition theorem.

applied to the one quadratic degree of freedom in the Hamiltonian.

Now if the <u>spring constant</u> changes from global state to the other we get a new shift in free energy associated with φ_b and φ_a

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

↑ the scaled change in x_0

and the energy probability takes the form:

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

↑ Generally this term is small for voltage activated channels.

Why bother then? There may be important entropic contributions in other forms of protein allatery — 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 φ? $\quad \langle \frac{1}{2} \varphi_b x^2 \rangle = k_B T/2$

and typical distancements are on the order of 5Å

$\Rightarrow \varphi_b \sim \frac{k_B T}{25 Å^2}$ but we have a nondimensionalized distance $\Rightarrow x \cong 5Å/50Å \sim .1$ $\varphi_b \sim k_B T/10^{-2}$

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

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

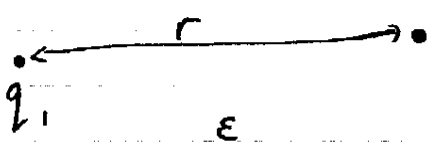
$$\frac{qV}{2\varphi} \approx \frac{qV}{2 \cdot k_B T} 10^{-2} = \frac{V}{2 \cdot 25mV} 10^{-2} \cong V/(5\,\text{Volts})$$

↑ At room temperature

Now membrane potentials are in the range of $\sim 100mV$ 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.

Coulomb interactions



Point out $S = -\frac{\partial G}{\partial T} = \frac{G}{\varepsilon}\frac{\partial \varepsilon}{\partial T}$

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

ε ↖ dielectric constant $TS \approx 1.4\,G$ at $T = 300\,K$.

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

$$F = \frac{q_1 q_2}{\varepsilon r^2} \quad \text{instead of} \quad F = \frac{1}{4\pi\varepsilon_0 \varepsilon}\frac{q_1 q_2}{r^2}$$

"Normal" SI units

and Gauss's Law reads $\vec{\nabla}\cdot\vec{E} = \frac{4\pi\rho}{\varepsilon}$ instead of $\vec{\nabla}\cdot\vec{E} = \rho/\varepsilon_0$

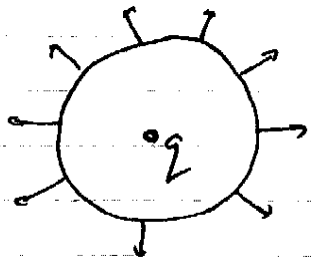
The dielectric constant of water $\varepsilon \cong 80$ and of oil $\varepsilon \cong 2$. Both are dimensionless.

The large value of ε 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.

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



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

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

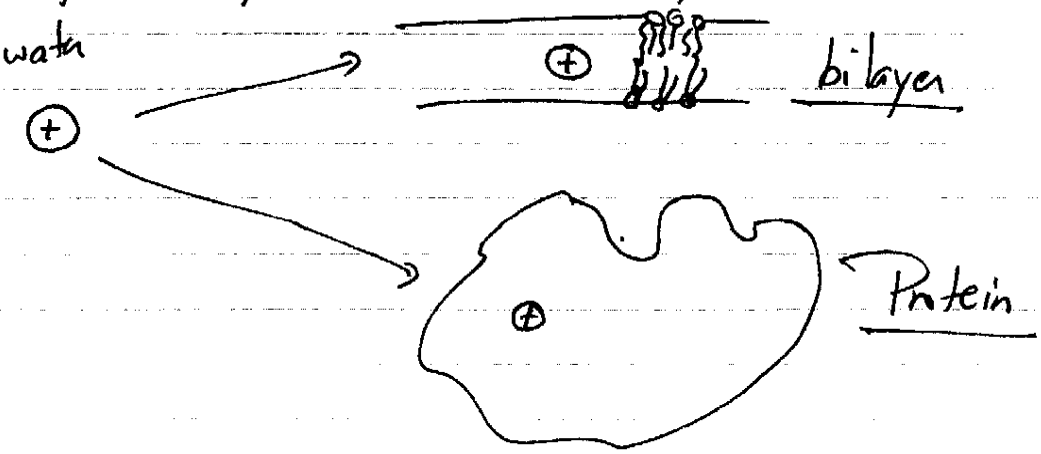
$\vec{E} \rightarrow$ $\quad \leftarrow d\vec{s}$ and $ds = -dr$ $\quad \leftarrow \infty$ Note: three minus signs.

$$\delta W = -\delta q \int_{\infty}^{a} \frac{q}{\varepsilon r^2} dr = \frac{\delta q q}{\varepsilon} \int_{a}^{\infty} \frac{dr}{r^2} = -\frac{q \delta q}{\varepsilon r}\Big|_{a}^{\infty} = \frac{q \delta q}{\varepsilon a}$$

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

$$\boxed{W = \frac{q^2}{2\varepsilon a}}$$ 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 bilayers ⇒ approximate this first by treating it as an infinite expanse of oil.

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

Take the ion radius as ~1Å and see what we get

$$\Delta W = \frac{(5\times10^{-10}\ esu)^2}{2\ 10^{-8}\ cm}\left(\frac{1}{\varepsilon_{oil}} - \frac{1}{\varepsilon_{water}}\right) \cong 12\times10^{-12}\left(\frac{\varepsilon_{water}-\varepsilon_{oil}}{\varepsilon_{oil}\,\varepsilon_{water}}\right) erg.$$

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

$$\Delta W = 1.2\times10^{-19}\ J\left(\quad\right) = 29 k_B T\left(\frac{80-2}{160}\right)$$

Using $k_B T = 4.1\times10^{-21}\ J$;

$$\Delta W_{transfer} \cong 15 k_B T$$!

at room temp

The "Boltzmann weight" to insert an ion from water to oil is thus about

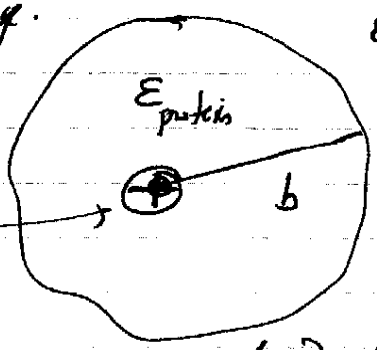
$$\sim e^{-15} \cong 10^{-5}$$

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 ~8nm with one

buried charge.



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

$\vec{D} = \varepsilon \vec{E}$ 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 boundy.

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

$\vec{E}_{in} = \dfrac{q\hat{r}}{r^2 \varepsilon_p}$; $\vec{E}_{out} = \dfrac{q\hat{r}}{r^2 \varepsilon_w}$

ε_p protein and ε_w water dielectric constants.

Just for fun let's compute U_{in} from the volume integral of the electric field's energy density:

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

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

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

For the outside take $\varepsilon_p \to \varepsilon_w$ $a \to b$ and $b \to \infty$

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

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

or

$$U = \frac{q^2}{2\varepsilon_p}\frac{1}{a} + \frac{q^2}{2\varepsilon b}\left(\frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_p}\right)$$

↑ our old answer

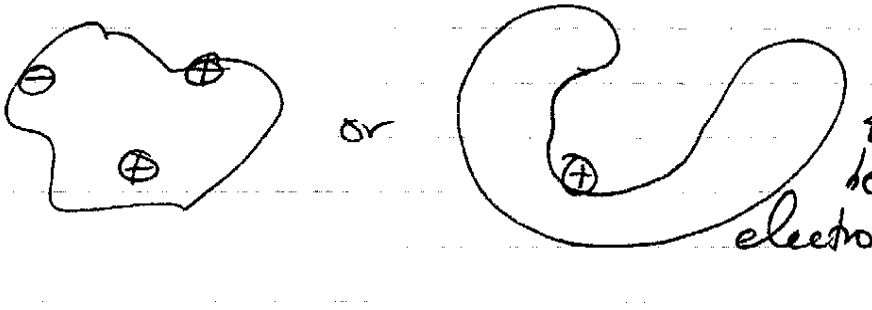
↑ a negative correction since we now have a finite size protein.

How big is our correction for finite size?

$$\frac{|U_{correction}|}{U_{old}} = \left|\frac{a\varepsilon_p}{b}\left(\frac{1}{\varepsilon_w} - \frac{1}{\varepsilon_p}\right)\right| = \frac{a}{b}\frac{|\varepsilon_p - \varepsilon_w|}{\varepsilon_w}$$

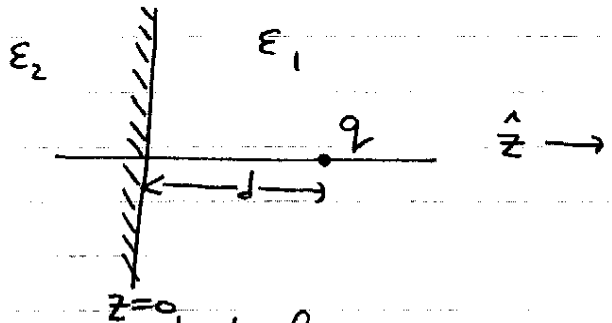
This is roughly $\left(\frac{10^{-1}\,nm}{10\,nm}\right)\left(\frac{78}{80}\right) \sim 1\%$ ... Old first guess was pretty good.

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

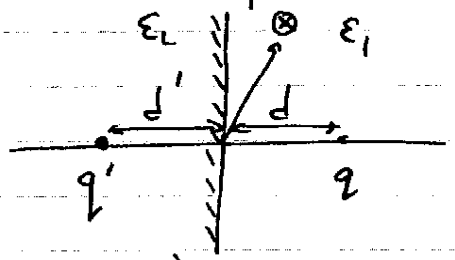


Otherwise, the folded state would be highly unfavorable electrostatically.

What about a dielectric slab?

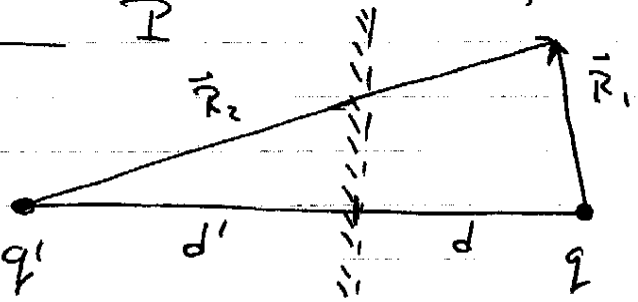


We can look for an image charge solution



$P = (\vec{x}_\perp, z)$

What is the electric potential at point P



for $z>0$ (in the ε_1 side)

$$\Phi_1 = \frac{1}{\varepsilon_1}\left(\frac{q}{R_1} + \frac{q'}{R_2}\right)$$

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 $\Phi_2 = \frac{1}{\varepsilon_2}\frac{q''}{R_3}$ some other charge in place of q. or at least on the line

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

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

and $\frac{\partial}{\partial x}\frac{1}{R_1}\Big|_{z=0} = \frac{\partial}{\partial x}\frac{1}{\sqrt{x^2+y^2+(d-z)^2}}\Big|_{z=0}$ ($x^2+y^2 = x_\perp^2$)

$= -\frac{1}{2}(\quad)^{-3/2} 2x$

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

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

so continuity of E_x and $E_y \Rightarrow$

$$+\frac{1}{\varepsilon_1}\left[\frac{x\,q}{(x_\perp^2+d^2)^{3/2}} + \frac{x\,q'}{(x_\perp^2+d'^2)^{3/2}}\right] = \frac{1}{\varepsilon_2}\frac{q''\,x}{(x_\perp^2+d'^2)^{3/2}}$$

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

Then we need $\boxed{\frac{1}{\varepsilon_1}(q+q') = \frac{1}{\varepsilon_2}q''}$ ← One equation for two unknowns. Fortunately we have the continuity of D_z:

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

because we had $(z+d)$

so we get

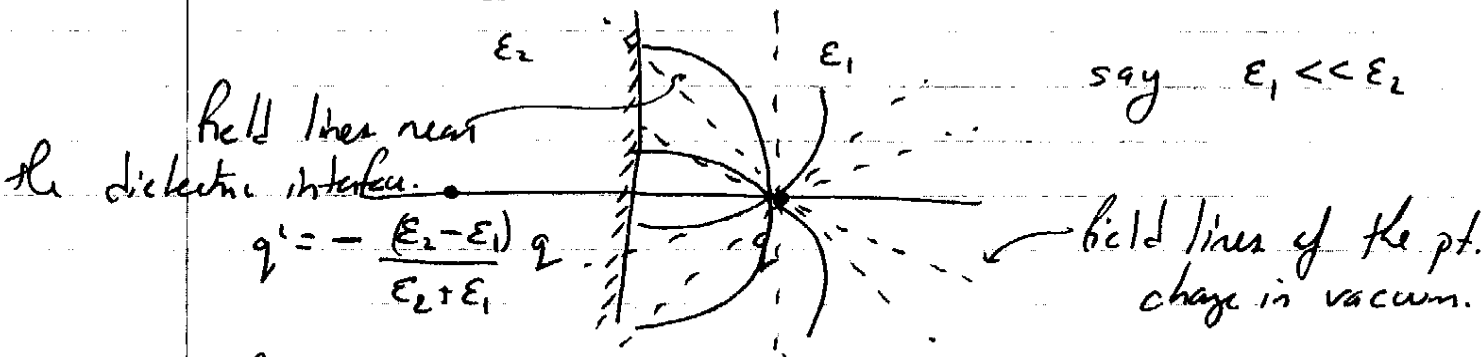
$$\frac{\varepsilon_1}{\varepsilon_1}\left[\frac{q\,d}{(x_\perp^2+d^2)^{3/2}} - \frac{q'd}{(x_\perp^2+d^2)^{3/2}}\right] = \frac{\varepsilon_2}{\varepsilon_2}\frac{d\,q''}{(x_\perp^2+d^2)^{3/2}}$$

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

Solving these two equations we get $q' = \left(\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_2+\varepsilon_1}\right)q$

$$q'' = \left(\frac{2\varepsilon_2}{\varepsilon_2+\varepsilon_1}\right)q$$

So the field inside the ε_1 dielectric is the same as for



if $\varepsilon_2 \to \infty$ (like a metal) we get $q' = -q$ a dipole (distributed) asymmetrically placed across the interface between the two materials.

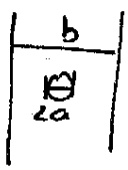
What is the energy of the charge q near a dielectric.

$$U = \frac{q^2}{2\varepsilon_1 a} + \frac{qq'}{\varepsilon_1(2d)} = \frac{q^2}{2\varepsilon_1 a} - q^2\frac{(\varepsilon_2-\varepsilon_1)}{\varepsilon_1(\varepsilon_2+\varepsilon_1)2d}$$

self energy of the charge — energy of charge q in field of image charge q'

We can write this for an oil/water interface as

$$U = \frac{q^2}{2\varepsilon_1 a}\left[1 - \frac{a}{d}\frac{(\varepsilon_2-\varepsilon_1)}{\varepsilon_2+\varepsilon_1}\right]$$



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