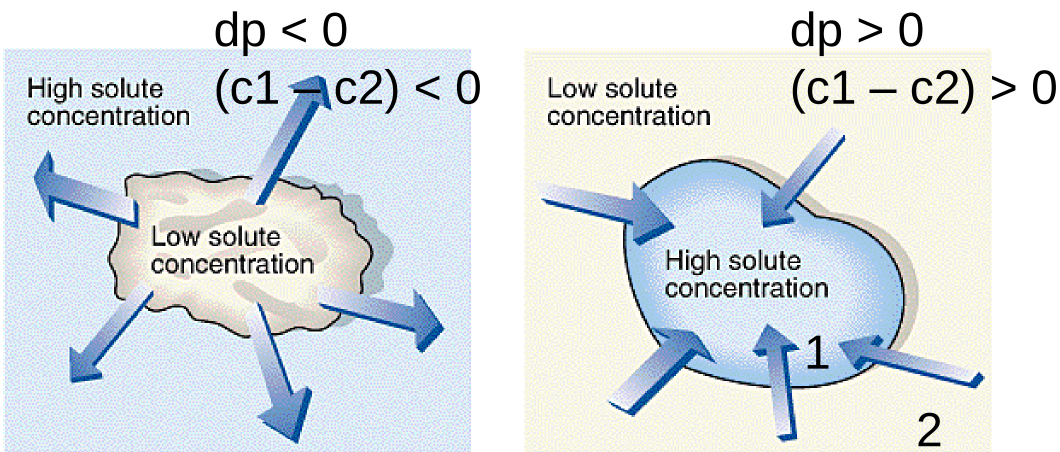
Topic 10: Physics of charged solutions
(chapter 9 in book)

Overview

- Concentration difference across cell → osmotic pressure
- Most biomolecules have charge
- The solution inside and outside cells is full of charged ions
- How do all the charges interact?
- The mobile ions generate a screening field for the charges on biomolecules

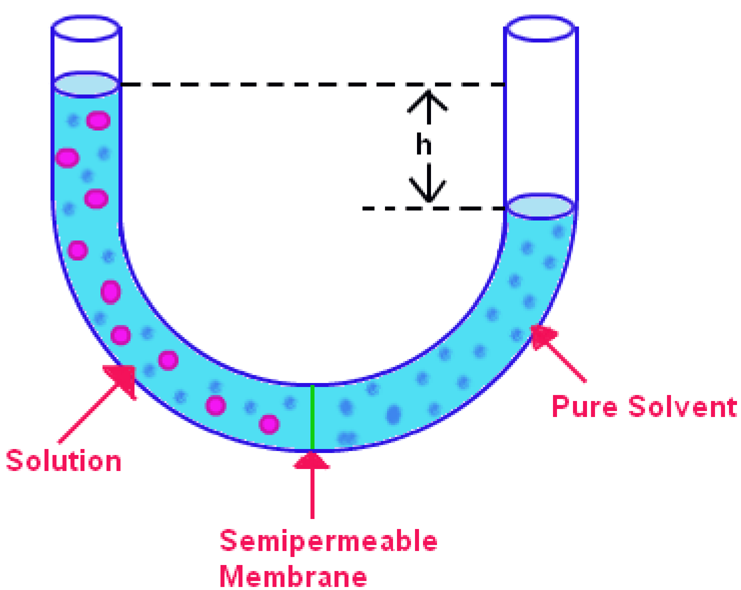
Osmotic pressure:



(a) (b)

Recall, that when there are concentration differences there is a flow,

$$j = -D\frac{dc}{dx}$$



When there is a semi-permeable membrane, some molecules (like water) can go across, but others can not (maintaining the concentration difference).

If there is a concentration difference the resulting osmotic pressure is,

$$\boxed{\Delta p = \Delta c\, k_B T}$$

just like ideal gas pressure → dilute solutions

Is osmotic pressure significant?

Are the osmotic pressures exerted on cells of concern?

Expt: If you put cells into pure water, they explode (lyse) because of all the water that rushes into the cells

Numbers:

$$\boxed{\Delta p = \Delta c \, k_B T}$$

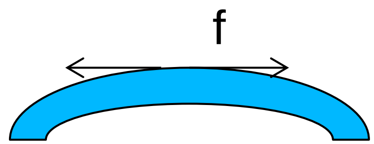
A typical cell contains 1.2 x 10^{-4} M of protein that can't flow across membrane

What's the pressure?

$$p = (1.2 \times 10^{-4})\,(1.38 \times 10^{23})\,(293)/(1 \times 10^{-3}) = 300 \text{ Pa}$$

Is 300 Pa significant for a cell?

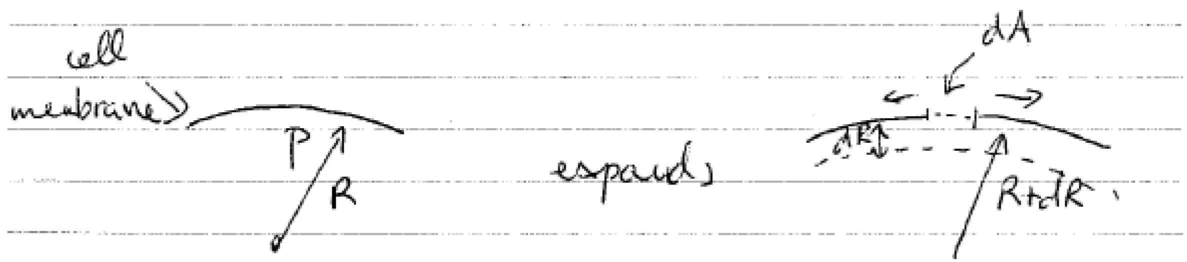
Surface tension redux:



Surface tension is the force / length experienced by membrane when it is stretched

$$\Sigma = f/L$$

Osmotic pressure stretches the membrane:



Pressure does work *p dV* that works against work of membrane = $\Sigma\, dA$. Equilibrium gave Laplace-Young relation → $\Sigma = Rp/2$

For our cell, with R = 10 μm and p = 300 Pa, Σ = 1.5 pN/nm

Is this big??? Tension to rupture most cells is measured to be 3 pN/nm

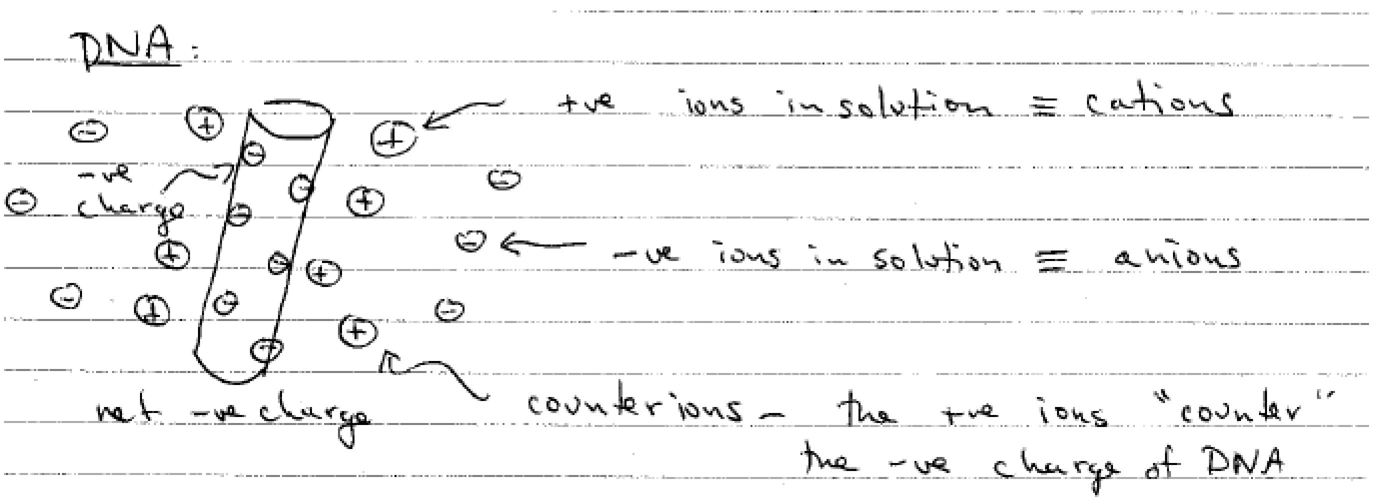
For cells in pure water, [Na] = 1 M inside, [Na] = 0 outside → p = kiloPa

→ will rupture the cell.

We'll see that balancing osmotic pressures is very important for charge balance in nerve cells

Charge objects in solution:

Most biological molecules have charge. What implications does this have?



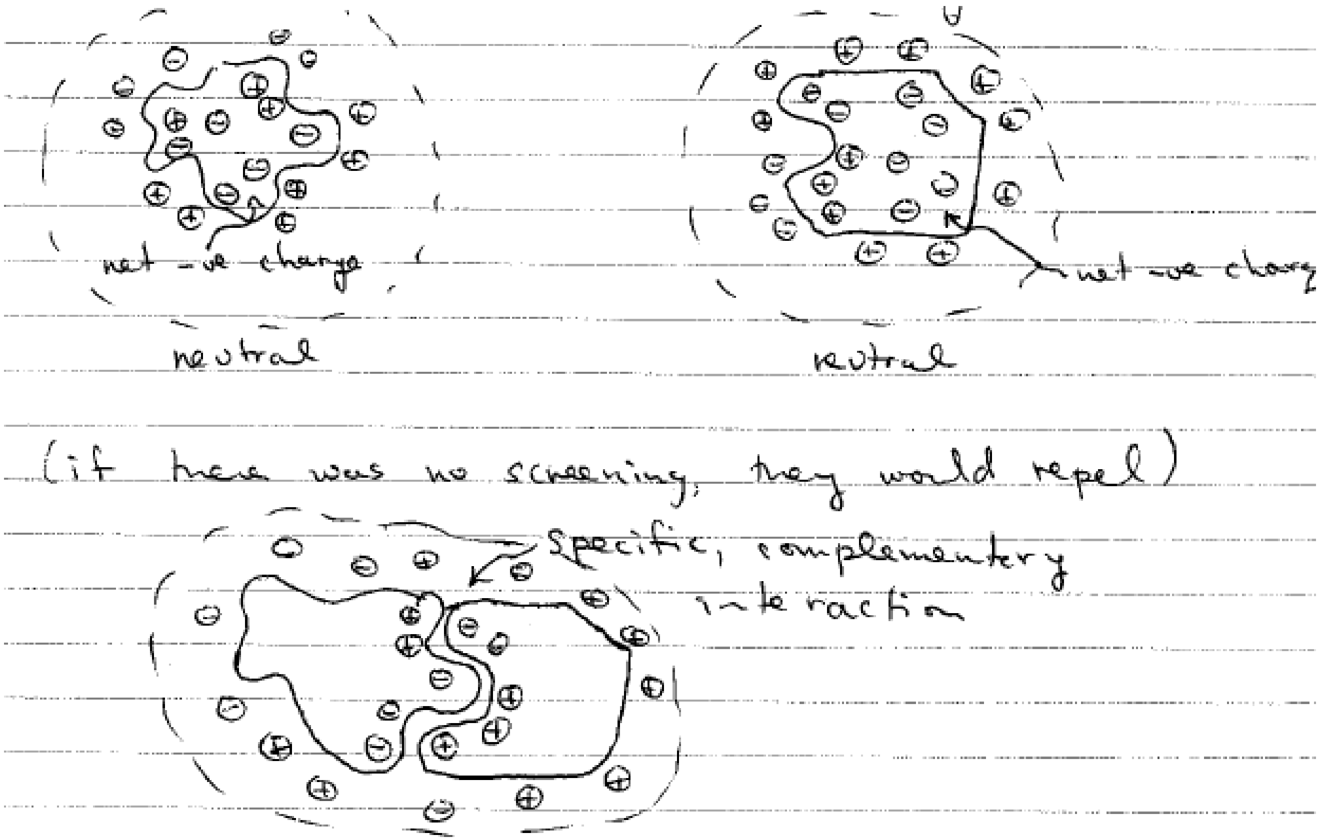
Some intuition: let's consider the energetics of the charged ions that are attracted to the DNA

There is a concentration difference → particles would like to diffuse away and increase the entropy of the solution

But in so doing, they lose electrostatic energy due to interaction with DNA

So there is a tug of war between diffusing away and attraction to DNA
→ leads to an equilibrium charge distribution

Why screening is important?



Counterions form a cloud around charged object → beyond a certain distance the object appears to have no charge = Screening

This prevents all the oppositely charged objects from forming one big aggregate in cell

Specificity: since the interactions are now all short range, only complimentary portions of interacting proteins will interact

Physics of screening: Water is a dielectric

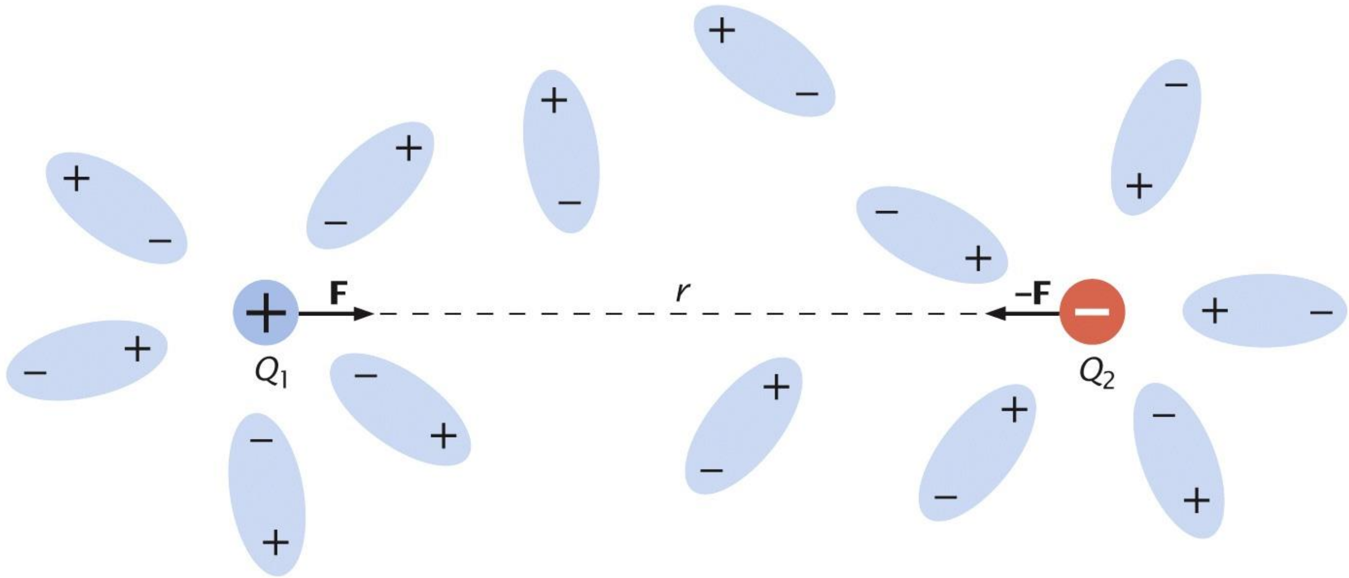


Figure 9.4 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

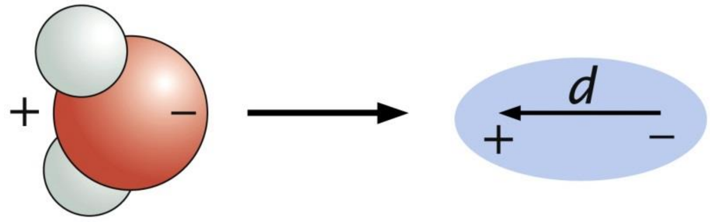


Figure 9.5 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Water is a polarizable molecule. Presence of charge in H20 polarizes the H20 that generates dipoles that help to reduce the strength of the electrostatic forces

Dielectric constant of water: $\epsilon = 80\ \epsilon_o$ where ϵ_o is the permitivity of free space

So as we'll see H20 reduces electrostatic forces by 80

Screening due to mobile ions: counterion fields

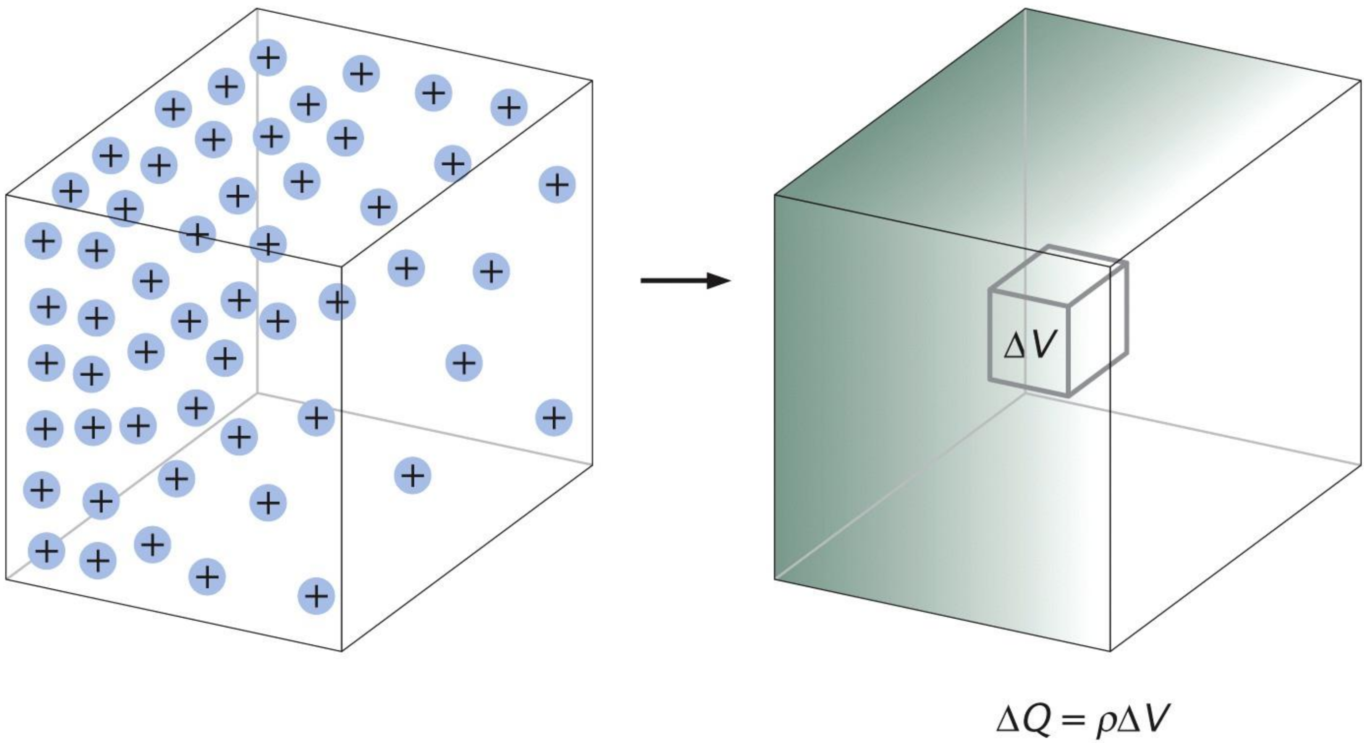


Figure 9.6 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

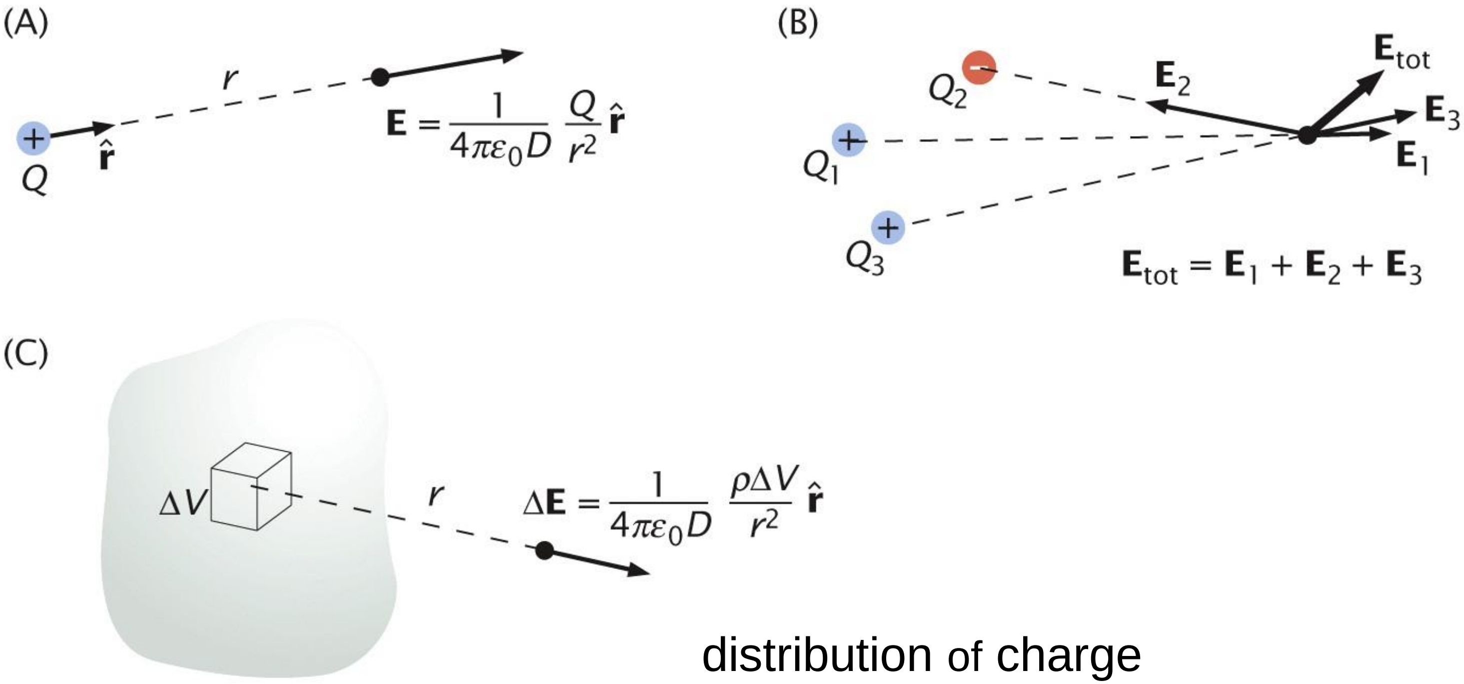
The mobile ions in solution set up concentration differences in the presence of other charged objects.

These concentration differences of charged ions set up counteracting electric fields that effectively screen the charges of the objects in solution

Electrostatic forces exist between charged particles – like charge repel, opposite attract

We define an electric field as the force per unit positive charge: **F** = q **E**

point particle



distribution of charge

Figure 9.7 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Review of Electrostatics:

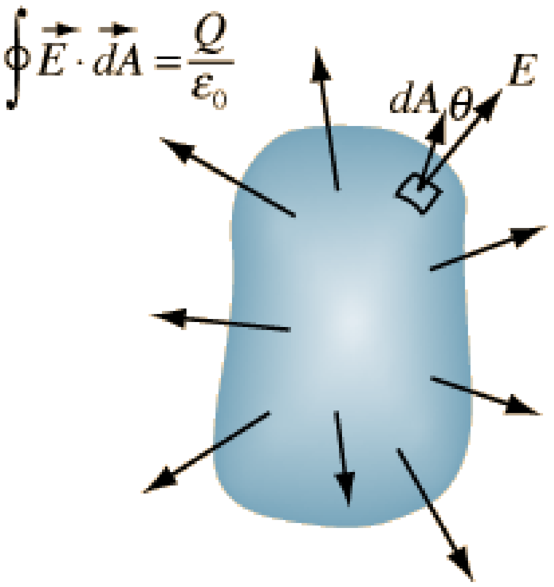
Force: $\boldsymbol{F} = q\,\boldsymbol{E}$

Electric field: $\boldsymbol{E} = \frac{1}{4\pi\epsilon_o D}\frac{Q}{r^2}\hat{r}$

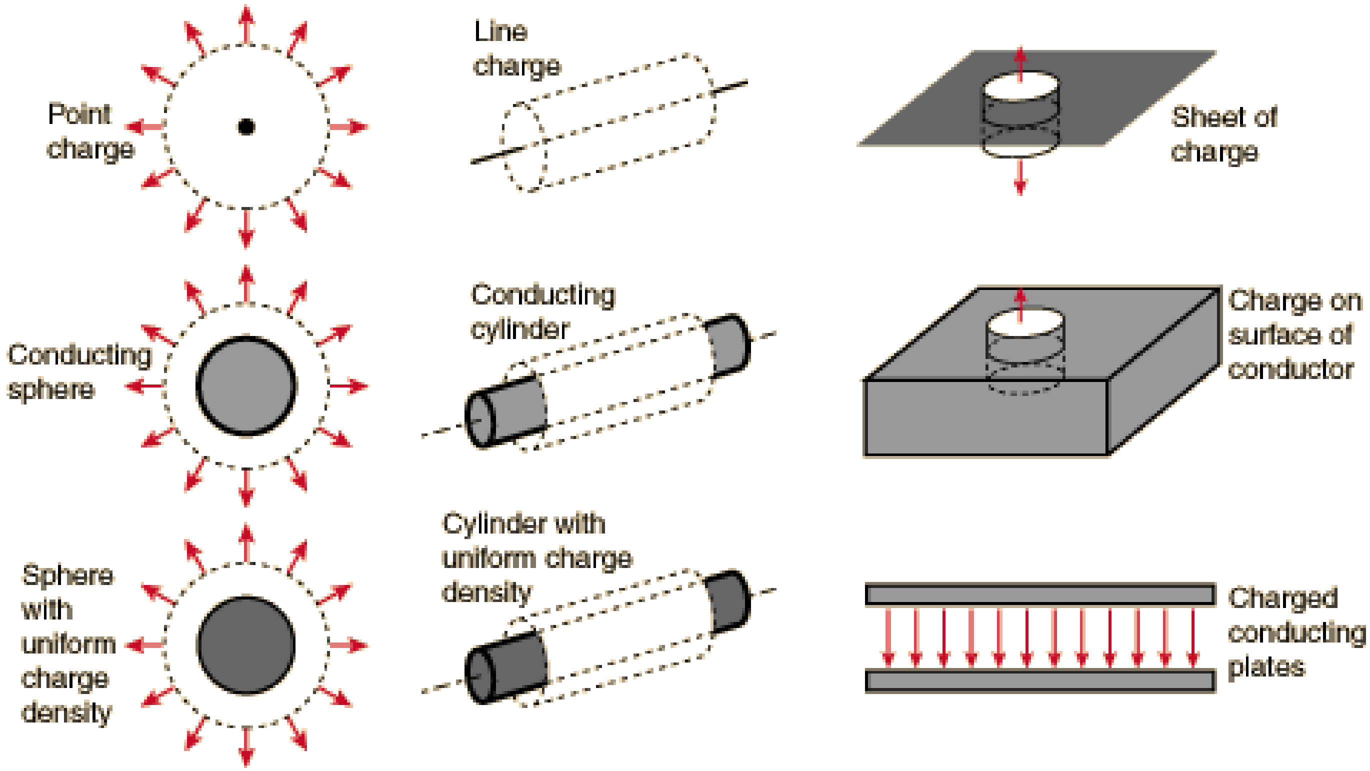
Potential energy: $E = -\frac{dV}{dx}$ and V $= \frac{1}{4\pi\epsilon_o D}\frac{Q}{r}$

Gauss's Law: Calculate electric field by using geometry

in words: (Electric field) x (enclosing area) = (charge enclosed)/($\epsilon_o D$)



Gass's Law applications:



Choose an enclosing volume that has the same symmetry

Take into account in which direction both the electric field and area point

Poisson Boltzmann Equation:

Want to find an equation for the potential due to the mobile charges.

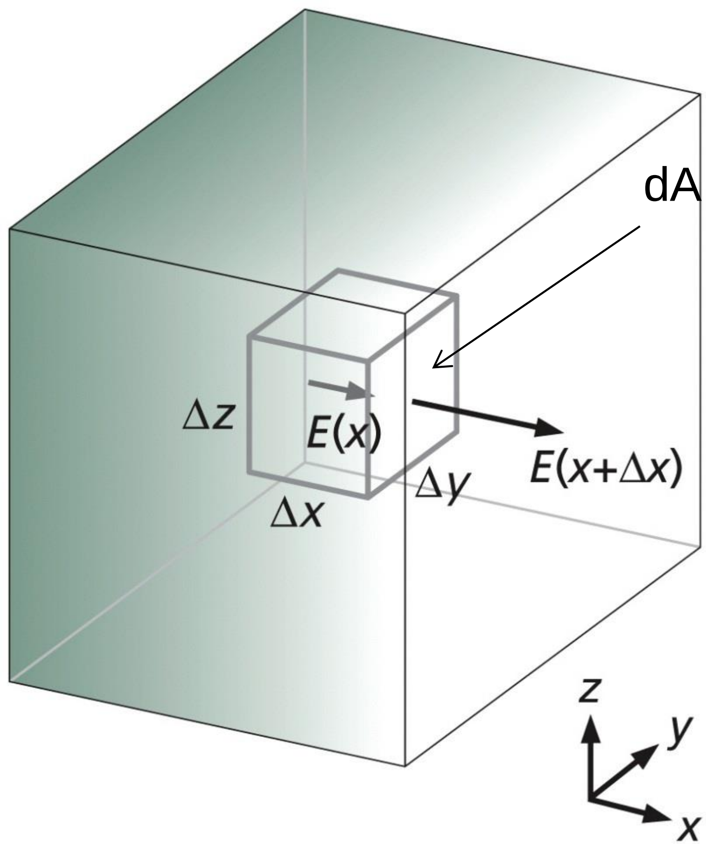


Figure 9.9 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Consider the electric field due to concentration difference in x-direction

Use Gauss's Law:

$$\big(E(x+dx) - E(x)\big)dA = \rho(x)dAdx/\epsilon$$

so

$$\frac{dE}{dx} = \frac{\rho(x)}{\epsilon} \text{ where } \epsilon = 80\,\epsilon_o \quad (1)$$

Now, the ions are mobile so will come to equilibrium distribution due to their energy as a function of position

The electrostatic energy, $G(x) = q\,V(x)$

where q = Z e is charge on ion

From Boltzmann, at equilibrium the charge distribution is $\frac{\rho(x)}{\rho(0)} = \exp\left(-\frac{q\,V(x)}{k_B T}\right)$ (2)

Poisson-Boltzmann Continued:

But recall that we can write the electric field in terms of the potential,

$$E = -dV(x)/dx \qquad (3)$$

So putting (1), (2) and (3) together we arrive at

$$\frac{d^2V(x)}{dx^2} = -\frac{\rho(0)}{\epsilon}\exp(-\frac{Z\,e\,V(x)}{k_BT})$$

Define: $\bar{V}(x) = \frac{e\,V(x)}{kT}$

and

$$\boxed{l_B \equiv \frac{e^2}{4\pi\epsilon kT}} \equiv \text{Bjerrum length}$$

$\equiv$ distance we can push two like charge particles together with k_BT of energy

so

$$\boxed{\frac{d^2\bar{V}}{dx^2} = -4\pi\, l_B\, \rho_0 e^{-\bar{V}}}$$

Poisson-Boltzmann Continued:

$$\boxed{\frac{d^2\bar{V}}{dx^2} = -4\pi\, \ell_B\, \rho_0 e^{-\bar{V}}}$$

This is a non-linear differential equation that is also in general hard to solve.

Method: Find V(x) and then find the counterion distribution, $\rho(x) = \rho(0)\exp(-eV(x)\beta)$

…. now we'll look at an application of the P-B equation for a practical biological example

Debye Screening

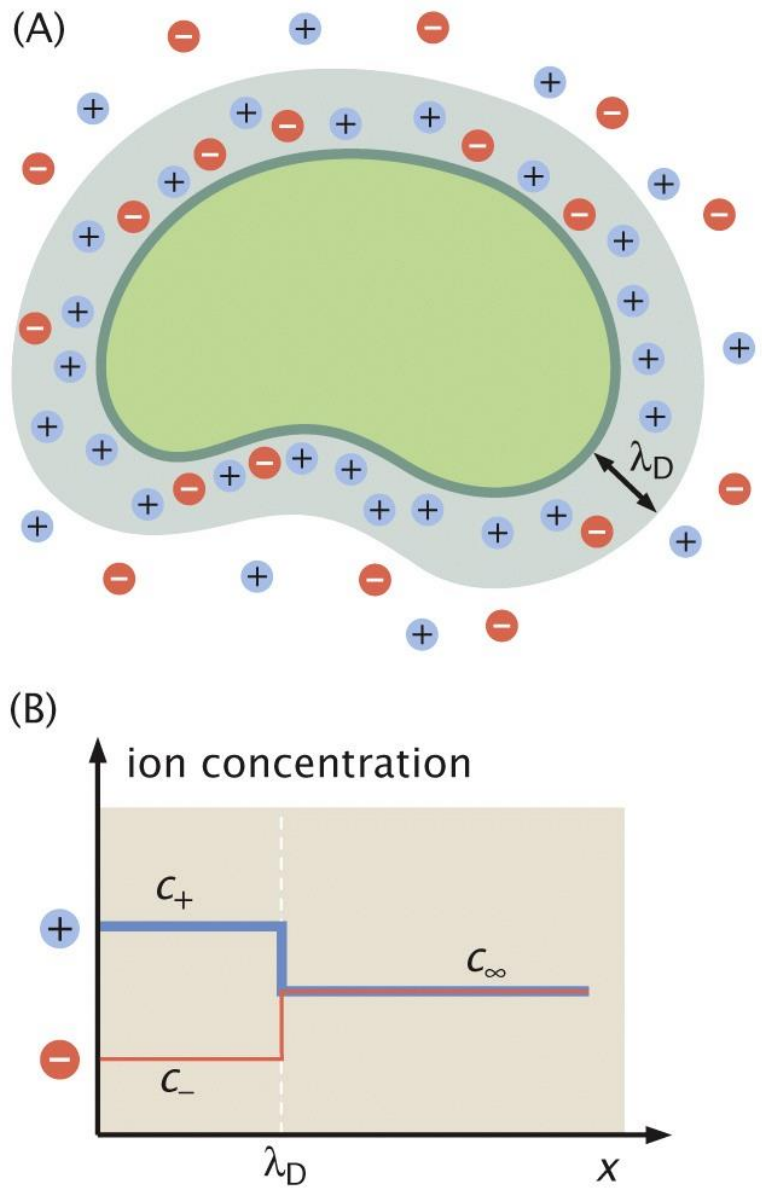


Figure 9.16 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Imagine a salt solution (i.e. NaCl)

There are an equal number of +ve and -ve charges in the solution way out at infinity

What is the screening length of cloud?

Debye screening calculation:

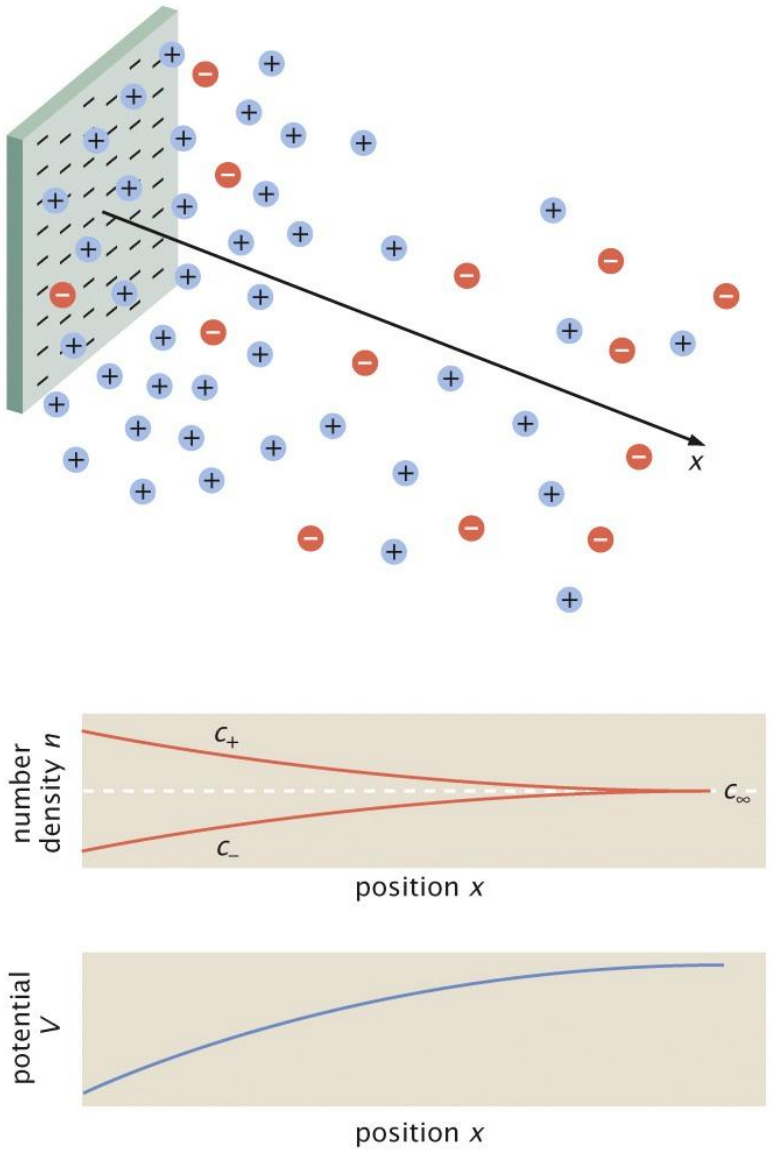


Figure 9.18 Physical Biology of the Cell, 2ed. (© Garland Science 2013)

Imagine a charged surface that has charge per unit area, σ

Solve for the distribution of counterions:

$$c_+ = c_\infty e^{-eV(x)/kT} \qquad c_- = c_\infty e^{+eV(x)/kT}$$

$$\rho(x) = e\,c_+(x) - e\,c_-(x)$$

P-B $$\frac{d^2V}{dx^2} = \frac{e c_\infty}{\varepsilon}\left(e^{eV(x)/kT} - e^{-eV(x)/kT}\right)$$

Now we make assumption that V(x) is small for all x and expand the RHS using

$$\exp\left(\frac{eV(x)}{kT}\right) \approx 1 + eV(x)/kT$$

Debye screening calculation:

The linearized P-B equation is then:

$$\rightarrow \quad \frac{d^2V}{dx^2} = \frac{2e^2c_\infty}{\varepsilon k_BT} V(x) = \frac{V(x)}{\lambda_D^2}$$

where

$$\lambda_D = \sqrt{\frac{\varepsilon k_BT}{2e^2c_\infty}} \equiv \text{Debye-length}$$

For c_∞ ~ 200 mM, and with the dielectric constant of water of $\epsilon = 80\epsilon_o$ at room temperature the Debye length is $\lambda_D \sim 0.7$ nm.

So anything beyond ~ 1 nm is effectively screened by the cloud of counterions.

Rule of thumb formula, at room temperature in water, $\lambda_D = 0.304/\sqrt{C}$ where C is the concentration of the electrolyte expressed in Molar

Solution to linearized P-B equation:

Now

$$V(x) = A e^{-x/\lambda_D} + B e^{+x/\lambda_D}$$

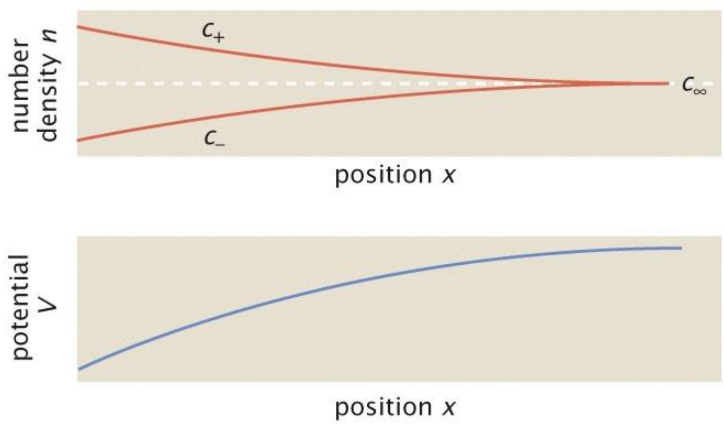
B.C. $\quad V(\infty) = 0 \quad \rightarrow \quad B = 0$

@ $x = 0$, $\quad E(0) = \dfrac{\sigma}{\varepsilon} = -\dfrac{dV}{dx}\Big|_{x=0}$

$$\Rightarrow \quad A = \frac{\sigma \lambda_D}{\varepsilon}$$

so

$$V(x) = \frac{\sigma \lambda_D}{\varepsilon} e^{-x/\lambda_D} \quad \leftarrow \text{screened potential}$$



so for $x > \lambda_D$, charge is effectively screened and $V = 0$.

Conclusions:

- Water is the aether of life – all reactions happen in it
- Membranes generate barriers that maintain concentration differences
- Concentration differences lead to osmotic pressure 100 mM ~ 2 atm of pressure
- Counterions screen charge objects making them look effectively neutral
- For typical concentrations of ions in cells this screening length ~ 1 nm
- Poisson-Boltzmann equation allows us to calculate the distribution of mobile ions
- Screening leads to specificity
- Screening helps pack highly charged objects within a small volume

… how do concentration differences and charge lead to membrane potentials?