Counterions form a <u>diffuse charge layer</u> around macroions and other microscopic charged bodies. The surface of the macroion and the diffuse charged layer forms an <u>electric double layer</u>. Thus the <u>effective range</u> of the electric field of a macroion in a saline solution is about the width of this double layer — about 1 nm.

Gauss's law says that the electric field $\mathcal{E}(x)$ near a negatively charged sheet is proportional to the surface charge density $-\sigma_q$

$$\mathcal{E} = -\frac{\sigma_q}{\epsilon} . \qquad (7.18)$$

This field points to the surface.

Farther from the surface, the cations with charge density ρ reduce the field

$$\mathcal{E}(x + \tfrac{1}{2}dx) - \mathcal{E}(x - \tfrac{1}{2}dx) = dx\ \rho/\epsilon$$

so that

$$\frac{d\mathcal{E}}{dx} = \frac{\rho}{\epsilon} \quad \text{in bulk.} \qquad (7.20)$$

The Bjerrum length scale ℓ is

$$\ell = \frac{e^2}{4\pi\epsilon kT}. \qquad (7.21)$$

Here

$$\frac{e^2}{4\pi\epsilon\ell} = kT$$

so ℓ is the distance at which two electrons would have electrostatic potential energy kT in an ϵ dielectric.

In water, with $\epsilon = 80\epsilon_0$,

$$l_B = 0.71 \text{ nm}.$$

Define the dimensionless potential $\bar{V}$

as
$$\bar{V}(x) = \frac{e}{kT} V(x) . \qquad (7.22)$$

Now by (7.20),

$$\frac{d^2\bar{V}(x)}{dx^2} = \frac{e}{kT}\frac{d^2V}{dx^2} = -\frac{e}{kT}\frac{d\mathcal{E}}{dx} = -\frac{e}{kT}\frac{\rho}{\epsilon}$$

where $\rho = e\,c(x)$ and $c(x)$ is

the concentration of ions. So

$$\frac{d^2\bar{V}(x)}{dx^2} = -\frac{e^2}{kT\epsilon}c(x)$$

$$= -4\pi l_B c_0 e^{-eV/kT}$$

$$= -4\pi l c_0 e^{-\bar{V}} \qquad (7.23)$$

which is the Poisson-Boltzmann equation.

This equation has many solutions.

We need boundary conditions, like

$$\mathcal{E} = -\frac{dV}{dx} = -\frac{\sigma}{\epsilon} \text{ at surface or}$$

$$\frac{d\bar{V}}{dx} = -\frac{e}{kT}\mathcal{E} = \frac{e\sigma}{kT\epsilon} = 4\pi l \frac{\sigma}{e} \quad (7.24)$$

for $x > 0$ and $\sigma_q > 0$.

Note that if $f(x) = \ln x^n$, then

$$\frac{df}{dx} = \frac{1}{x^n} n x^{n-1} = \frac{n}{x}$$

and
$$e^f = e^{\ln x^n} = x^n.$$

So, $\ln x^n$ is a possible guess as a solution of the P-B equation (7.23).

We try
$$\bar{V}(x) = B \ln\left(1 + \frac{x}{x_0}\right).$$

We get

$$\frac{d\bar{V}}{dx} = \frac{B}{1+\frac{x}{x_0}}\,\frac{1}{x_0} = \frac{B}{x+x_0}$$

and

$$\frac{d^2\bar{V}}{dx^2} = -\frac{B}{(x+x_0)^2} = -4\pi l C_0\, e^{-B\ln\left(1+\frac{x}{x_0}\right)}$$

$$= -\frac{4\pi l C_0}{\left(1+\frac{x}{x_0}\right)^B},$$

So $B = 2$ and

$$\frac{1}{(x+x_0)^2} = \frac{2\pi l C_0 x_0^2}{(x+x_0)^2}.$$

So

$$x_0 = \frac{1}{\sqrt{2\pi l C_0}}.$$

Now we apply the boundary condition

(7.24)
$$\frac{d\bar{V}}{dx} = 4\pi l\,\frac{\sigma}{e}.$$

We get

$$\frac{d\bar{V}}{dx} = \frac{2}{x + x_0} = 4\pi l \frac{\sigma}{e} \quad \text{as } x \to 0.$$

So

$$\frac{1}{x_0} = 2\pi l \frac{\sigma}{e}.$$

So we fix c_0 by

$$x_0^{-1} = \sqrt{2\pi l c_0} = 2\pi l \frac{\sigma}{e} \quad \text{or}$$

$$2\pi l c_0 = 4\pi^2 l^2 \frac{\sigma^2}{e^2}$$

$$c_0 = 2\pi l \frac{\sigma^2}{e^2}$$

and $\quad x_0 = (2\pi l \sigma / e)^{-1}$.

Finally then,

$$\bar{V}(x) = 2 \ln\left(1 + \frac{x}{x_0}\right)$$

or

$$V(x) = 2\frac{kT}{e} \ln\left(1 + \frac{2\pi l \sigma x}{e}\right) \quad (7.25)$$

The cation concentration $c(x)$

is then

$$c(x) = c_0 \, e^{-\bar{V}(x)}$$

$$= 2\pi l \frac{\sigma^2}{e^2} \, e^{-2\ln\left(1 + \frac{x}{x_0}\right)}$$

$$= \frac{2\pi l (\sigma/e)^2}{\left(1 + \frac{x}{x_0}\right)^2}$$

$$= \frac{2\pi l (\sigma/e)^2}{\left(1 + \frac{2\pi l \sigma x}{e}\right)^2} .$$

$\int_0^\infty c(x)\, dx = \frac{\sigma_q}{e}$, so the system

is neutral. This is the <u>Gouy-Chapman</u>

<u>layer</u> of width

$$x_0 = (2\pi l \sigma/e)^{-1} .$$

Two sheets of area A and charges q and $-q$ separated by a distance x_0 is a <u>parallel-plate capacitor</u>. It has energy

$$E = \frac{q^2}{2C}$$

where C is its <u>capacitance</u>

$$C = \frac{\epsilon A}{x_0} \qquad (7.26)$$

in which ϵ is the dielectric constant of the medium between the plates.

Now $q = \sigma A$. The energy per unit area is

$$\frac{E}{A} = \frac{(\sigma A)^2}{(2\epsilon A/x_0)}\frac{1}{A} = \frac{\sigma^2 x^0}{2\epsilon} = \frac{\sigma^2}{2\epsilon}\frac{1}{2\pi \ell(\sigma/e)}$$

$$= \frac{\sigma e}{4\pi\epsilon e^2} 4\pi\epsilon k T = kT(\sigma/e) \qquad (7.27)$$

or about kT per counterion.

If σ is one charge per phospholipid, then $|\sigma/e| \approx 0.7\,\mathrm{nm}^{-2}$. So a sphere of radius $10\mu m$ has

$$E \simeq 4\pi (10\mu m)^2 \frac{0.7}{(nm)^2} kT$$

$$\approx 4\pi\, 0.7 \times 10^8 kT \approx 10^9 kT$$

which is big.

Real cells are bags of saline in saline. Salt shrinks x_0.

Real solutions have coions as well as counterions. We add a constant to $V(x)$ so that $V(x) \to 0$ as $x \to \infty$.

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

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

$$\frac{d^2\bar{V}}{dx^2} = -\frac{1}{2}\lambda^{-2}\left(e^{-\bar{V}} - e^{\bar{V}}\right) \tag{7.34}$$

where $\bar{V} = eV/kT$ and λ is the Debye length

$$\lambda = \frac{1}{\sqrt{8\pi \ell C_\infty}}. \tag{7.35}$$

The solution is

$$\bar{V}(x) = -2 \ln \frac{1 + e^{-(x+\bar{x})/\lambda}}{1 - e^{-(x+\bar{x})/\lambda}} \tag{7.36}$$

in which the constant $\bar{x}$ is given by the surface boundary condition

$$e^{\bar{x}/\lambda} = \frac{e}{2\pi \ell \lambda \sigma}\left(1 + \sqrt{1 + (2\pi \ell \lambda \sigma/e)^2}\right). \tag{7.37}$$

Now $e^{\epsilon} = 1+\epsilon$ so $\ln 1+\epsilon \doteq \epsilon$

So as $x \to \infty$,

$$\bar{V}(x) \to -2 \ln \frac{1+\epsilon}{1-\epsilon} = -2 \ln (1+\epsilon)^2$$

$$= -2 \ln 1 + 2\epsilon = -4\epsilon$$

where

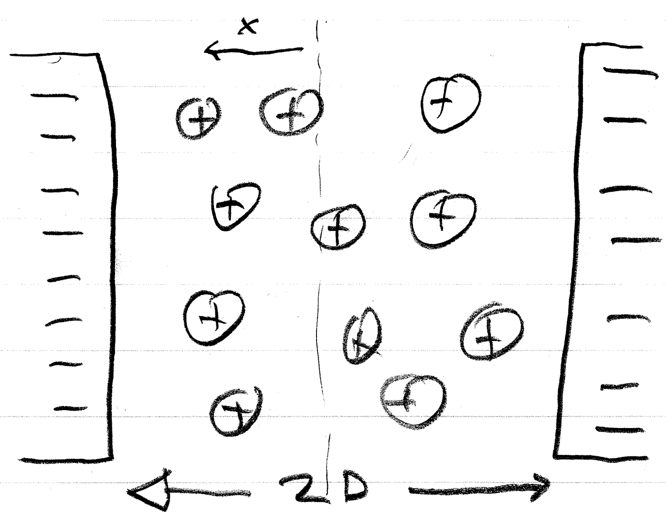
$$\epsilon = e^{-(x+\bar{x})/\lambda},$$

That is,

$$\bar{V}(x) = -4 e^{-\bar{x}/\lambda} e^{-x/\lambda}. \qquad (7.38)$$

So electric fields are screened at λ.

Meanwhile, back in section 7.4.4:



Each surface has charge density $-\sigma$.

Add a constant to $V(x)$ so that $V(0) = 0$.

We try a symmetrical potential

$$\bar{V}(x) = A \ln \cos(\beta x)$$

where A and β are unknown constants. We need

$$\frac{d^2\bar{V}}{dx^2} = -4\pi l C_0 e^{-\bar{V}}.$$

$$\frac{d\bar{V}}{dx} = \frac{A}{\cos\beta x}(-\sin\beta x)\beta = -A\beta\tan\beta x$$

$$\frac{d^2\bar{V}}{dx^2} = -A\beta\left(\beta\frac{\cos\beta x}{\cos\beta x} + \frac{\sin^2\beta x}{\cos^2\beta x}\beta\right)$$

$$= -A\beta^2(1+\tan^2\beta x) = -A\beta^2\left(\frac{1}{\cos^2\beta x}\right)$$

$$= -4\pi l C_0 e^{-A\ln\cos\beta x} = -\frac{4\pi l C_0}{\cos^A\beta x}$$

So $A = 2$ and $\beta^2 = 2\pi l C_0$.

And Eq. (7.24) gives

$$\frac{d\bar{V}}{dx} = 4\pi l \frac{\sigma}{\epsilon} \qquad \text{at} \quad x = -D .$$

So

$$-A\beta \tan(-\beta D) = 4\pi l \frac{\sigma}{e} = 2\beta \tan \beta D \tag{7.29}$$

$$+2\sqrt{2\pi l C_0}\, \tan \sqrt{2\pi e C_0}\, D = 4\pi l \frac{\sigma}{e}$$

or

$$\sqrt{C_0}\, \tan \sqrt{2\pi l C_0}\, D = \sqrt{2\pi l}\, \frac{\sigma}{e} .$$

This is a transcendental equation for $\hat{C}_0 = C(0)$ in terms of $l = l_B = \frac{e^2}{4\pi\epsilon k T}$ and D, which is half the separation, and σ, which is the absolute value of the surface charge density $-\sigma$, and e, which is the absolute value of the charge of the electron. One may solve this equation numerically.

But if $\beta D = \sqrt{2\pi \ell c_0}\, D \ll 1$, then $\tan \beta D \simeq \beta D$ and we have

$$\sqrt{c_0}\,\sqrt{2\pi \ell c_0}\; D = \sqrt{2\pi \ell}\;\frac{\sigma}{e} \qquad \text{or}$$

$$c_0 D = \frac{\sigma}{e} \qquad \text{or}$$

$$c_0 = \frac{\sigma}{e D}$$

as the charge density at $x = 0$. Then the total charge/area of the counterions is

$$2\,D c_+ = e\,2\,D\,c_0 = e\,2\,D\frac{\sigma}{eD} = 2\sigma$$

which just balances the negative charge density the two surfaces -2σ. So the system is neutral as it should be.

In any case, the concentration of counterions is

$$C_+(x) = c_0 e^{-\bar{V}} = c_0 e^{-2 \ln \cos \beta x}$$

$$= \frac{c_0}{\cos^2 \beta x} \qquad (7.30)$$

which has its minimum at $x = 0$

$$c_+(0) = c_0.$$

Far from the negatively charged surfaces, there are no counterions, so

$$C_+(x) \to 0 \quad \text{as} \quad x \to \pm \infty.$$

The pressure p on the surfaces is thus

$$p = \frac{f}{A} = c_0 k T \qquad (7.31)$$

and it shoves the surfaces apart.

$\boxed{7G}$ As $\sigma \to 0$, Eq. (7.29) becomes

$$0 \simeq 4\pi \ell \frac{\sigma}{e} = 2\beta \tan D\beta = 2 D \beta^2$$

and so

$$\beta = \sqrt{2\pi \ell \sigma/(eD)} \quad .$$

In this case

$$\beta D = \sqrt{2\pi e \sigma D/e}$$

and so if

$$\frac{\sigma D \ell}{e} << 1$$

then

$$\beta D << 1$$

which means that the counterion density

$$c_+(x) = \frac{c_0}{\cos^2 \beta(x)}$$

is nearly equal to c_0 throughout the gap

$$-D < x < D.$$

In this case

$$\beta = \sqrt{2\pi \ell c_0} = \sqrt{2\pi e \sigma/(eD)}$$

so that

$$c_0 = \frac{\sigma}{eD} = \frac{2\sigma A}{e2DA} = \frac{Q}{eV} ,$$

Once again, the system is neutral.