

# ENTROPY IN BIOLOGY

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## Lecture 4: The Poisson-Boltzmann Equation

Derivation of the Poisson-Boltzmann equation from entropy and electrostatic energy with total volume fraction constrained.

Standard Poisson-Boltzmann equation for dilute solutions

Linearized Poisson-Boltzmann equation

Balance of pressure and electrostatic forces

Example & Homework

## Poisson-Boltzmann Equation

In this derivation of the Poisson-Boltzmann equation, we consider the effects of crowding which are usually neglected

Consider an ideal incompressible ionic solution filling all of space. The solvent, denoted by the index  $i=0$ , is electrically neutral. There are  $n$  ionic solute species in the system, indexed by  $i=1 \dots n$ . Each ion of the  $i^{\text{th}}$  species carries a charge  $qz_i$ , where  $z_i$  is a positive or negative integer, and  $q$  is the elementary charge, i.e., the charge on a proton.

We assume for simplicity that each ion has the same volume as a solute molecule, and we denote that volume by  $v_0$ .

The more general case in which each species has its own volume  $v_i$  can also be considered in much the same way as here, but the algebra gets considerably more complicated.

Let  $c_i(\underline{x})$  be the concentration (number of particles per unit volume) of the  $i^{\text{th}}$  species at the location  $\underline{x} \in \mathbb{R}^3$ . Then the charge density  $\rho(\underline{x})$  is given by

(1) 
$$\rho(\underline{x}) = \rho_b(\underline{x}) + \sum_{i=1}^n q_i z_i c_i(\underline{x}) .$$

In this equation,  $\rho_b(\underline{x})$  is the charge density associated with some fixed background charges. Because these charges are fixed in place, they do not contribute to the entropy of the system, nor do they count when considering the mole fractions of the species  $i=0 \dots n$ .

In effect, the system of background charges is a single molecule, frozen in place, and a count of 1 has a negligible effect on our macroscopic system.

With regard to the background charges, we make the further idealization that they do not occupy any volume, i.e., that their volume fraction is zero.

Finally, we assume that  $\rho_b$  has bounded support, so there are no background charges for  $\|\underline{x}\|$  sufficiently large.

An important constraint on the concentrations  $c_i(\underline{x})$  is that their sum is the total number of particles per unit volume, which is equal to  $1/v_0$ , since each particle has volume  $v_0$ . Thus,

$$(2) \quad \sum_{i=0}^n c_i(\underline{x}) = \frac{1}{v_0} \cdot$$

Note that the sum in (1) is only over solute species, since the solvent is electrically neutral, but the sum in (2) is over all species, including solvent.

The mole fraction of species  $i$  at location  $\underline{x}$  is denoted by  $X_i(\underline{x})$  and is given by

$$(3) \quad X_i(\underline{x}) = \frac{c_i(\underline{x})}{\sum_{j=0}^n c_j(\underline{x})}, \quad i=0 \dots n.$$

Because of (2), this can be written more simply as



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$$(4) \quad \chi_i(\underline{x}) = \frac{1}{\epsilon_0} \rho_i(\underline{x}), \quad i=0 \dots n,$$

From (3), or from (2) & (4), we see immediately that

$$(5) \quad \sum_{i=0}^n \chi_i(\underline{x}) = 1.$$

The electrostatic energy of the whole ionic solution is given by

$$(6) \quad U = \frac{1}{2} \epsilon \int_{\mathbb{R}^3} \|\underline{E}(\underline{x})\|^2 d\underline{x}$$
$$= \frac{1}{2} \epsilon \int_{\mathbb{R}^3} \nabla\phi \cdot \nabla\phi d\underline{x}.$$

Here,  $\underline{E} = -\nabla\phi$  is the electric field,  $\phi$  is the electrostatic potential,  $d\underline{x} = dx_1 dx_2 dx_3$  is the volume element in  $\mathbb{R}^3$ , and  $\epsilon$  is the dielectric constant

of the solution, which we are assuming is independent of the concentrations of the solutes, so that it does not depend on  $\underline{x}$ .

The electrostatic potential  $\phi$  is related to the charge density  $\rho$  by the Poisson equation

$$(7) \quad -\Delta\phi = \frac{\rho}{\epsilon} \quad ,$$

with the boundary condition

$$(8) \quad \phi(\underline{x}) \rightarrow 0 \quad \text{as} \quad \|\underline{x}\| \rightarrow \infty \quad .$$

If the charge density changes by the amount  $\delta\rho(\underline{x})$ , then the change  $\delta\phi(\underline{x})$  in the electrostatic potential will be given by

$$(9) \quad -\Delta(\delta\phi) = \frac{\delta\rho}{\epsilon} \quad ,$$

with

$$(10) \quad \delta\phi(\underline{x}) \rightarrow 0 \quad \text{as} \quad \|\underline{x}\| \rightarrow \infty \quad .$$

To first order in  $\delta\rho$  and  $\delta\phi$ , the resulting change in electrostatic energy can then be evaluated as follows

$$\begin{aligned}
(11) \quad \delta U &= \epsilon \int_{\mathbb{R}^3} \nabla(\delta\phi) \cdot \nabla\phi \, d\underline{x} \\
&= \int_{\mathbb{R}^3} (-\epsilon \Delta(\delta\phi)) \phi \, d\underline{x} \\
&= \int_{\mathbb{R}^3} (\delta\rho) \phi \, d\underline{x} \quad .
\end{aligned}$$

In the first step of (11), the factor  $\frac{1}{2}$  in the definition of  $U$  is canceled because two identical terms appear when we apply  $\delta$  to  $U$ . In the next step, we integrate by parts, making the assumption that

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$$(12) \quad \lim_{r \rightarrow \infty} \int_{\|\underline{x}\|=r} \phi(\underline{x}) \frac{\underline{x}}{\|\underline{x}\|} \cdot \nabla (\delta\phi(\underline{x})) \, da(\underline{x}) = 0 .$$

Although we do not prove it here, this will be true if  $\delta\rho$  has bounded support. Then, in the last step of (11), we use equation (9) to write  $\delta U$  in terms of  $\delta\rho$  and  $\phi$ .

Although the final result of (11) looks like it came from a perturbation in  $\rho$  without a corresponding perturbation in  $\phi$ , this is not the case. The actual formula for  $U$  in terms of  $\rho$  and  $\phi$  is

$$(13) \quad U = \frac{1}{2} \int_{\mathbb{R}^3} \rho \phi \, d\underline{x} ,$$

and by starting from (13), we get

$$(14) \quad \delta U = \frac{1}{2} \int_{\mathbb{R}^3} (\delta\rho) \phi \, d\underline{x} + \frac{1}{2} \int_{\mathbb{R}^3} \rho (\delta\phi) \, d\underline{x} .$$

Comparison with (11) shows that the two terms on the right-hand side of (14) are equal, and that both are included on the last line of (11).

Equation (11) can be rewritten in terms of changes in concentration. From Equation (1), we have

$$(15) \quad \delta p(\underline{x}) = \sum_{i=1}^n \beta z_i \delta c_i(\underline{x}) ,$$

since  $\beta_b(\underline{x})$  is fixed, and therefore not perturbed. By combining (15) and (11), we get the result that

$$(16) \quad \delta U = \int_{\mathbb{R}^3} \sum_{i=1}^n \beta z_i \phi(\underline{x}) \delta c_i(\underline{x}) d\underline{x} .$$

Next, we consider the entropy of the system. Although the total entropy is infinite, there is a finite entropy per unit volume given by

$$(17) \quad \sigma(\underline{x}) = -k \sum_{i=0}^n c_i(\underline{x}) \log X_i(\underline{x})$$

in which  $k$  is Boltzmann's constant

If the concentrations change by  $\delta c_i(\underline{x})$ , then the resulting change  $\delta \sigma(\underline{x})$ , to first order in the  $\delta c_i$ , is given by

$$(18) \quad \delta \sigma(\underline{x}) = -k \sum_{i=0}^n \delta c_i(\underline{x}) \log X_i(\underline{x})$$

$$-k \sum_{i=0}^n c_i(\underline{x}) \frac{\delta X_i(\underline{x})}{X_i(\underline{x})},$$

but the second term on the right-hand side of (18) is zero, since  $c_i(\underline{x})/X_i(\underline{x})$  is independent of  $i$ , see equation (4), and since  $\sum_{l=0}^n \delta X_l = 0$  because of (5).

Thus

$$(19) \quad \delta\sigma(\underline{x}) = -k \sum_{i=0}^n \delta c_i(\underline{x}) \log X_i(\underline{x}),$$

and this can be integrated (for example, if  $\delta c_i(\underline{x})$  has bounded support) to give the change in entropy of the whole system as

$$(20) \quad \delta S = -k \int_{\mathbb{R}^3} \sum_{i=0}^n \delta c_i(\underline{x}) \log X_i(\underline{x}) d\underline{x}.$$

The  $\delta c_i(\underline{x})$  that appear in equation (20) are not all independent because of the constraint (2), which implies that

$$(21) \quad \delta c_0(\underline{x}) = - \sum_{i=1}^n \delta c_i(\underline{x}).$$

Making use of this, we can rewrite equation (20) as follows

$$(22) \quad \delta S = -k \int_{\mathbb{R}^3} \sum_{i=1}^n \delta c_i(\underline{x}) \log \left( \frac{X_i(\underline{x})}{X_0(\underline{x})} \right) d\underline{x}.$$

At equilibrium  $\delta U - T \delta S = 0$ , and from (16) & (22) this gives the result that

$$(23) \quad \int_{\mathbb{R}^3} \sum_{i=1}^n \delta c_i(\underline{x}) \left( \int z_i \phi(\underline{x}) + kT \log \frac{X_i(\underline{x})}{X_0(\underline{x})} \right) d\underline{x} = 0.$$

The  $\delta c_i(\underline{x})$  that appear in (23) are independent of each other, since we have eliminated  $\delta c_0(\underline{x})$ , but each of them obeys the constraint that

$$(24) \quad \int_{\mathbb{R}^3} \delta c_i(\underline{x}) d\underline{x} = 0,$$

since we are considering perturbations that redistribute solute without any solute creation or destruction.



Since the  $dC_j$  are arbitrary except for the restriction (24), the conclusion from (23) is that the coefficient of each of the  $dC_j(x)$  is constant.

We can evaluate this constant by setting  $\|\underline{x}\| = \infty$ , since this gives  $\phi = 0$ .

In this way, we get

$$(25) \quad \sum z_i \phi(x) + kT \log \frac{X_i(x)}{X_0(x)}$$

$$= kT \log \frac{X_i^\infty}{X_0^\infty}, \quad i = 1 \dots n,$$

which can be solved for  $X_i(x)$

$$(26) \quad X_i(x) = X_0(x) \frac{X_i^\infty}{X_0^\infty} \exp\left(-\frac{\sum z_i \phi(x)}{kT}\right),$$

$$i = 1 \dots n.$$

By summing both sides of (26) over  $1 \dots n$ , we get an equation for  $X_0(\underline{x})$ :

$$(27) \quad 1 - X_0(\underline{x}) = X_0(\underline{x}) \sum_{i=1}^n \frac{X_i^{\infty}}{X_0^{\infty}} \exp\left(-\frac{g z_i \phi(\underline{x})}{kT}\right),$$

which has the solution

$$(28) \quad X_0(\underline{x}) = \frac{1}{1 + \sum_{i=1}^n \frac{X_i^{\infty}}{X_0^{\infty}} \exp\left(-\frac{g z_i \phi(\underline{x})}{kT}\right)},$$

and by substituting this back into (26), we get the following formula for  $X_i(\underline{x})$ :

$$(29) \quad X_i(\underline{x}) = \frac{\frac{X_i^{\infty}}{X_0^{\infty}} \exp\left(-\frac{g z_i \phi(\underline{x})}{kT}\right)}{1 + \sum_{j=1}^n \frac{X_j^{\infty}}{X_0^{\infty}} \exp\left(-\frac{g z_j \phi(\underline{x})}{kT}\right)},$$

$$i = 1 \dots n.$$

Equation (29) can be rewritten as follows:

$$(30) \quad X_i(x) = \frac{X_i^\infty \exp\left(-\frac{z_i \phi(x)}{kT}\right)}{X_0^\infty + \sum_{j=1}^n X_j^\infty \exp\left(-\frac{z_j \phi(x)}{kT}\right)}$$

$$= \frac{X_i^\infty \exp\left(-\frac{z_i \phi(x)}{kT}\right)}{1 + \sum_{j=1}^n X_j^\infty \left(\exp\left(-\frac{z_j \phi(x)}{kT}\right) - 1\right)}$$

$i=1 \dots n,$

and this can be rewritten in terms of concentrations by making use of equation (4):

$$(31) \quad c_i(x) = \frac{c_i^\infty \exp\left(-\frac{z_i \phi(x)}{kT}\right)}{1 + v_0 \sum_{j=1}^n c_j^\infty \left(\exp\left(-\frac{z_j \phi(x)}{kT}\right) - 1\right)}$$

$i=1 \dots n,$

The solute concentrations at  $\infty$  are regarded as given, and we assume that they satisfy

$$(32) \quad \sum_{i=1}^n g z_i c_i^{\infty} = 0.$$

Since  $\rho_b$  has bounded support, this implies that  $\rho(\underline{x}) \rightarrow 0$  as  $\|\underline{x}\| \rightarrow \infty$ .

Let

$$(33) \quad Z(\phi) = 1 + v_0 \sum_{j=1}^n c_j^{\infty} \left( \exp\left(-\frac{g z_j \phi}{kT}\right) - 1 \right).$$

Then

$$(34) \quad Z'(\phi) = -\frac{v_0}{kT} \sum_{j=1}^n g z_j c_j^{\infty} \exp\left(-\frac{g z_j \phi}{kT}\right),$$

$$(35) \quad Z''(\phi) = \frac{v_0}{(kT)^2} \sum_{j=1}^n (g z_j)^2 c_j^{\infty} \exp\left(-\frac{g z_j \phi}{kT}\right).$$

Because of (32),  $Z'(0) = 0$ . Also,  $Z(0) = 1$ , and  $Z''(\phi) > 0$  for all real  $\phi$ .

Thus  $Z(\phi)$  is a strictly convex function with its minimum at  $\phi = 0$  where it has the value  $Z = 1$ .

From equation (31), we immediately get a formula for  $p(\underline{x})$ :

$$(36) \quad p(\underline{x}) = p_b(\underline{x}) + \frac{\sum_{i=1}^n g z_i c_i^{\infty} \exp\left(-\frac{g z_i \phi(\underline{x})}{kT}\right)}{1 + v_0 \sum_{j=1}^n c_j^{\infty} \left(\exp\left(-\frac{g z_j \phi(\underline{x})}{kT}\right) - 1\right)}$$

$$= p_b(\underline{x}) - \frac{kT}{v_0} \frac{Z'(\phi(\underline{x}))}{Z(\phi(\underline{x}))}$$

$$= p_b(\underline{x}) - \frac{kT}{v_0} (\log Z)'(\phi(\underline{x}))$$

With  $\rho(\underline{x})$  known in terms of  $\phi(\underline{x})$ , we can finally state the Poisson-Boltzmann equation for  $\phi$ :

$$(37) \quad -\Delta\phi = \frac{1}{\epsilon} \left( \rho_b(\underline{x}) - \frac{kT}{v_0} (\log Z)'(\phi(\underline{x})) \right).$$

with  $Z(\phi)$  given by (33).

This is a non-standard version of the Poisson-Boltzmann equation because it does not assume that the solution is dilute and it incorporates the constraint (2).

To get the dilute-solution limit, we see from (33) that  $Z$  is close to 1 when the solute concentrations are small. Thus, we can replace  $(\log Z)$  by  $Z-1$  in (37). But  $(Z-1)' = Z'$ , which is given by (34). In this way, we get the standard Poisson-Boltzmann equation:

$$(38) \quad -\Delta\phi = \frac{1}{\varepsilon} \left( \rho_b(\underline{x}) + \sum_{i=1}^n qz_i c_i^\infty \exp\left(-\frac{qz_i \phi(\underline{x})}{kT}\right) \right).$$

Another route to (38) is to note that as  $Z \rightarrow 1$ , equation (31) reduces to

$$(39) \quad c_i(\underline{x}) = c_i^\infty \exp\left(-\frac{qz_i \phi(\underline{x})}{kT}\right), \quad i=1, \dots, n,$$

from which (38) follows, since

$$\rho(\underline{x}) = \rho_b(\underline{x}) + \sum_{i=1}^n qz_i c_i(\underline{x}).$$

A further approximation that is often useful is to linearize the Poisson-Boltzmann equation by assuming that

$$(40) \quad \left| \frac{qz_i \phi(\underline{x})}{kT} \right| \ll 1$$

for  $i=1, \dots, n$  and for all  $\underline{x} \in \mathbb{R}^3$ . Then, because of the electroneutrality condition, equation (32), at  $\infty$ , equation (38) becomes

$$(41) \quad -\Delta\phi + \left( \sum_{i=1}^n \frac{(\sum z_i)^2 c_i^\infty}{kT\epsilon} \right) \phi(\underline{x}) = \frac{1}{\epsilon} \rho_b(\underline{x})$$

and equation (39) becomes

$$(42) \quad c_i(\underline{x}) = c_i^\infty \left( 1 - \frac{\sum z_i \phi(\underline{x})}{kT} \right)$$

In this approximation, the concentration of solvent is independent of  $\underline{x}$ , since the electroneutrality condition at  $\infty$  together with (42) imply that

$$(43) \quad \sum_{i=1}^n c_i(\underline{x}) = \sum_{i=1}^n c_i^\infty$$

The constant  $l_D$  defined by

$$(44) \quad l_D = \left( \sum_{i=1}^n \frac{(\sum z_i)^2 c_i^\infty}{kT\epsilon} \right)^{-\frac{1}{2}}$$

has units of length and is called the Debye length.



In an ionic solution, any charges that may be present are screened by counterions and thus have only a short-range influence on the electrical potential. The Debye length is the order of magnitude of the length of this influence. In biological cells, the Debye length is very short — less than the thickness of the cell membrane.

The approximation (40) says nothing about the solution being dilute, so we could have applied it directly to equation (37) instead of (38). We leave it to the reader to verify that the same result is obtained in this way.

Returning now to the exact Poisson-Boltzmann equation (37), it is interesting to consider the force per unit volume  $\underline{f}(\underline{x})$  that is applied by the electric field to the ionic solution. We do not include in  $\underline{f}(\underline{x})$  the force on the background charge, since that force is separately balanced by whatever forces are holding the background charge in place. The force density  $\underline{f}(\underline{x})$  is given by

$$\begin{aligned}
 (45) \quad \underline{f}(\underline{x}) &= - \sum_{i=1}^n f z_i c_i(\underline{x}) \nabla \phi(\underline{x}) \\
 &= \frac{kT}{v_0} (\log Z)'(\phi(\underline{x})) \nabla \phi(\underline{x}) \\
 &= \nabla \left( \frac{kT}{v_0} \log Z(\phi(\underline{x})) \right)
 \end{aligned}$$

It is a very important check on the self-consistency of our theory that this turns out to be a gradient, since the only force available to balance it is a pressure gradient. Indeed, for an incompressible fluid at rest with an applied force per unit volume  $\underline{f}(\underline{x})$  the equation of mechanical equilibrium is

$$(46) \quad 0 = -\nabla p + \underline{f}(\underline{x})$$

Thus, in our case, we get mechanical equilibrium if

$$(47) \quad p(\underline{x}) = \frac{kT}{v_0} \log(Z(\phi(\underline{x})))$$

$$= \frac{kT}{v_0} \log \left( 1 + v_0 \sum_{j=1}^n c_j^{\infty} \left( \exp \left( -\frac{z_j z_j \phi(\underline{x})}{kT} \right) - 1 \right) \right)$$

In (47), we have made  $p(\underline{x})$  unique by imposing the boundary condition that

$$(48) \quad p(\underline{x}) \rightarrow 0 \quad \text{as} \quad \|\underline{x}\| \rightarrow \infty$$

In the dilute-solution limit, (47) becomes simply

$$(49) \quad p(\underline{x}) = \sum_{j=1}^n kT (c_j(\underline{x}) - c_j^{\infty})$$

which is just van't Hoff's law. Note, however, that in the present situation there is no membrane restricting the motion of the ions!

Example :

In this example, we consider the standard (nonlinear) Poisson-Boltzmann equation (38), with solute concentrations given by (39), in a one-dimensional case with

$$(50) \quad n=2, \quad z_1=+1, \quad z_2=-1$$

and with

$$(51) \quad \rho_b(x) = \begin{cases} -\rho^* & , x < 0 \\ 0 & , x > 0 \end{cases}$$

where  $\rho^*$  is a positive constant.

Boundary conditions are specified at  $x=+\infty$  as follows:

$$(52) \quad c_1(+\infty) = c_2(+\infty) = c^*, \quad \phi(+\infty) = 0.$$

The limiting behavior of  $c_1, c_2,$  and  $\phi$  as  $x \rightarrow -\infty$  will be determined below.

The equation that we need to solve is

$$(53) \quad -\frac{d^2\phi}{dx^2} = \frac{1}{\epsilon} \left( \rho_b(x) + q_c^* \left( e^{-\frac{q\phi}{kT}} - e^{\frac{q\phi}{kT}} \right) \right)$$

which can also be written as

$$(54) \quad \frac{d^2\phi}{dx^2} = \frac{1}{\epsilon} \begin{cases} \rho^* + 2q_c^* \sinh \frac{q\phi}{kT}, & x < 0 \\ 2q_c^* \sinh \frac{q\phi}{kT}, & x > 0 \end{cases}$$

As  $x \rightarrow -\infty$ , we require that

$$(55) \quad \frac{d^2\phi}{dx^2} (-\infty) = 0$$

which is the condition of electroneutrality. This gives

$$(56) \quad \rho^* + 2q_c^* \sinh \left( \frac{q\phi(-\infty)}{kT} \right) = 0$$

or

$$(57) \quad \sinh\left(\frac{z\phi(-\infty)}{kT}\right) = \frac{\rho^*}{2\gamma C^*}$$

This determines  $\phi(-\infty)$ . An explicit formula for  $\phi(-\infty)$  can be found by solving a quadratic equation, but we skip this detail and simply regard  $\phi(-\infty)$  as known. Note that

$$(58) \quad \phi(-\infty) < 0$$

With  $\phi(-\infty)$  known, we also have

$$(59) \quad c_1(-\infty) = C^* e^{-\frac{z\phi(-\infty)}{kT}}$$

$$(60) \quad c_2(-\infty) = C^* e^{+\frac{z\phi(-\infty)}{kT}}$$

Each of the two right-hand sides of (54) can be written as the derivative of a function of  $\phi$ :

$$(61) \quad \frac{d^2 \phi}{dx^2} = \begin{cases} \frac{d}{d\phi} \left( \frac{\rho^* \phi}{\epsilon} + \frac{2kTC^*}{\epsilon} \cosh\left(\frac{q\phi}{kT}\right) \right), & x < 0 \\ \frac{d}{d\phi} \left( \frac{2kTC^*}{\epsilon} \cosh\left(\frac{q\phi}{kT}\right) \right), & x > 0 \end{cases}$$

Now multiply both sides of (61) by  $2 \frac{d\phi}{dx}$  and note on the right-hand side that

$$(62) \quad \frac{d\phi}{dx} \frac{d}{d\phi} = \frac{d}{dx}$$

This gives

$$(63) \quad \frac{d}{dx} \left( \frac{d\phi}{dx} \right)^2 = \begin{cases} \frac{d}{dx} \left( \frac{2\rho^* \phi}{\epsilon} + \frac{4kTC^*}{\epsilon} \cosh\left(\frac{q\phi}{kT}\right) \right), & x < 0 \\ \frac{d}{dx} \left( \frac{4kTC^*}{\epsilon} \cosh\left(\frac{q\phi}{kT}\right) \right), & x > 0 \end{cases}$$

Each of the two equations in (63) can be integrated, and we choose the two constants of integration such that

$$(64) \quad \frac{d\phi}{dx} (\pm\infty) = 0 .$$

In this way, we get

$$(65) \quad \left(\frac{d\phi}{dx}\right)^2 = \frac{2\rho^*}{\epsilon} (\phi(x) - \phi(-\infty)) + \frac{4kTc^*}{\epsilon} \left( \cosh\left(\frac{q\phi(x)}{kT}\right) - \cosh\left(\frac{q\phi(-\infty)}{kT}\right) \right),$$

$$x < 0 ,$$

and

$$(66) \quad \left(\frac{d\phi}{dx}\right)^2 = \frac{4kTc^*}{\epsilon} \left( \cosh\left(\frac{q\phi(x)}{kT}\right) - 1 \right)$$

$$x > 0 .$$



Now we impose the conditions that  $\phi$  and  $\frac{d\phi}{dx}$  are continuous at  $x=0$ . This gives an equation for  $\phi(0)$ :

$$(67) \quad 2\rho^* (\phi(0) - \phi(-\infty)) = 4kTc^* \left( \cosh \left( \frac{q\phi(-\infty)}{kT} \right) - 1 \right)$$

or

$$(68) \quad \phi(0) = \phi(-\infty) + \frac{2kTc^*}{\rho^*} \left( \cosh \left( \frac{q\phi(-\infty)}{kT} \right) - 1 \right)$$

Clearly  $\phi(0) > \phi(-\infty)$ , and we claim that  $\phi(0) < 0$ . To see this, note that

$$(69) \quad \cosh \left( \frac{q\phi(-\infty)}{kT} \right) - 1 = 2 \sinh^2 \left( \frac{1}{2} \frac{q\phi(-\infty)}{kT} \right)$$

and therefore, from (68), (69), and (57),

$$(70) \quad \frac{q\phi(0)}{kT} = \frac{q\phi(-\infty)}{kT} + \frac{89C^*}{\rho^*} \sinh^2\left(\frac{1}{2} \frac{q\phi(-\infty)}{kT}\right)$$

$$= \frac{q\phi(-\infty)}{kT} - \frac{4 \sinh^2\left(\frac{1}{2} \frac{q\phi(-\infty)}{kT}\right)}{\sinh\left(\frac{q\phi(-\infty)}{kT}\right)}$$

$$= \frac{q\phi(-\infty)}{kT} - 2 \tanh\left(\frac{1}{2} \frac{q\phi(-\infty)}{kT}\right)$$

$$= 2 \left( \frac{1}{2} \frac{q\phi(-\infty)}{kT} - \tanh\left(\frac{1}{2} \frac{q\phi(-\infty)}{kT}\right) \right)$$

$$< 0$$

since  $\phi(-\infty) < 0$ . Thus  $\phi(0) < 0$ ,  
as claimed.

Since we expect  $\phi(x)$  to be an increasing function for all  $x$ , we take the positive square root on both sides of (65) & (66) to obtain

$$(71) \quad \frac{d\phi}{dx} = \left( \frac{2\rho^*}{\epsilon} (\phi(x) - \phi(-\infty)) + \frac{4kTc^*}{\epsilon} \left( \cosh\left(\frac{q\phi(x)}{kT}\right) - \cosh\left(\frac{q\phi(-\infty)}{kT}\right) \right) \right)^{1/2}$$

$x < 0,$

and

$$(72) \quad \frac{d\phi}{dx} = \left( \frac{4kTc^*}{\epsilon} \left( \cosh\left(\frac{q\phi(x)}{kT}\right) - 1 \right) \right)^{1/2}, \quad x > 0.$$

For both of these ODE, we have the initial condition  $\phi(0)$  as given by (68); and the constant  $\phi(-\infty)$  is given by (57).

HW:

For the cases

$$\frac{\rho^*}{\rho c^*} = 1, 10, 100$$

Solve (71) and (72) numerically,  
and plot

$$\phi(x), c_1(x), c_2(x)$$

Plot  $\phi$  in units of  $\left(\frac{kT}{q}\right)$  and

$c_1, c_2$  in units of  $c^*$ , as functions  
of  $x$  in units of  $l_D$ , see equation (44).