

1 Ions in solutions. (Suggested reading: Piazza)

The study of ionic systems, mostly solutions of ions in water, are a quite difficult topics. There are two main difficulties arising from charged systems. The first is the difficulty of handling a long range interaction. The second is the variability of the number of charged particles in the system, controlled by the association/dissociation processes which can take place in solution. If we put a protein, a DNA molecule or a colloidal particles in water, depending on the temperature and the solution salt concentration, will dissociate and free counter-ions, assuming a net charge to minimize the system free energy.

We start by considering the case of a pure ionic solution of so-called strong salts, the ones that in water completely dissociate (weak salts are instead sensitive to the total concentration). Consider a system made of several species of charged particles in a volume V and let N_j and q_j be respectively the total number of particles of type j and q_j their electric charge. The total number of particles is N and the total charge is zero. Charge unbalance, over large distances requires too much energy for the system to stand it (there is energy in the electric field !). Thus

$$\sum_j N_j q_j = 0 \quad \sum_j N_j = N$$

The energy of a probe point-like particle of charge q located at the origin is

$$U = q\phi(0)$$

where $\phi(0)$ is the potential generated by all charges in the system (except the probe particle). Then

$$\phi(0) = \sum_i' \frac{q_i}{4\pi\epsilon r_i}$$

where the prime indicate that the charge in the origin has to be excluded in the sum and r_i is the distance from the origin of the unknown position of particle i .

Differently from all the electrostatic problems you have encountered in fresh-men courses, in which the position of the charges was given, here we need to evaluate $\phi(0)$ without a priori knowing the detailed positions of the charges q_i , which are determined by the electrostatic potential itself. Since we assume that the charges are point-like, however, we may neglect their discrete nature and try to describe the charge distribution around q as a "charged fluid" characterized by a charge density $\rho(r)$ that we expect to depend on the distance r from the probe charge. This continuum approach allows us to use the standard macroscopic Maxwell's equations ruling the distribution of the electrostatic field in the presence of a distributed charge. In particular, the value of the electrostatic potential $\phi(r)$ generated by all the charges (including q) is fixed by the Poisson equation.

$$\nabla^2\phi(r) = -\frac{\rho(r)}{\epsilon} \tag{1}$$

[Remember that the Poisson equation is nothing more than the Gauss theorem together with the definition of the electric field as gradient of the electric potential,

$$\nabla \cdot \mathbf{E} = \frac{\rho(r)}{\epsilon} \quad \text{and} \quad \mathbf{E} = -\nabla\phi(r) \rightarrow -\nabla \cdot \nabla\phi(r) = \frac{\rho(r)}{\epsilon} \quad]$$

Apparently, this is not a great step forward: $\phi(r)$ and $\rho(r)$ are strongly intertwined (they mutually determine each other), hence Eq. ?? must be solved by iterative methods. Yet, for a system in thermal equilibrium, $\rho(r)$ can be obtained by a simple, although approximate, reasoning. For $r \rightarrow \infty$ we expect the coordination effect induced by the probe particles to vanish, which implies that $\phi(r) \rightarrow 0$, and that the number densities of all types of charges take their average value $\bar{n} = N_j/V$. At finite r , it seems reasonable to assume that the number density $n_j(r)$ changes with respect to \bar{n}_j by the Boltzmann factor of the electrostatic energy $q\phi(r)$ that a charge q_j possesses in r . Hence, we tentatively write for the number density of species j

$$n_j(r) = \bar{n}_j e^{-\beta q_j \phi(r)},$$

so that the total charge density of the coordinated ions is

$$\rho(r) = \sum_j q_j n_j(r) = \frac{1}{V} \sum_j q_j N_j e^{-\beta q_j \phi(r)} \quad (2)$$

Note that assuming the Boltzmann distribution is equivalent to assume constant chemical potential (in the ideal gas approximation) for the ions. Indeed

$$\ln n_j(r) = \ln \bar{n}_j - \beta q_j \phi(r) \quad \rightarrow \quad \ln n_j(r) + \beta q_j \phi(r) = \ln \bar{n}_j$$

Note also that Eq. ?? is valid only for $r \neq 0$: in fact, in the origin we also have the contribution of the fixed probe charge, which can be represented as a charge density $q\delta(r)$, where $\delta(r)$ is the Dirac delta. Substituting Eq. ?? in Eq. ?? we obtain

$$\nabla^2 \phi(r) = -\frac{1}{\epsilon V} \sum_j q_j N_j e^{-\beta q_j \phi(r)} \quad (3)$$

Having been obtained from the Poisson equation using a Boltzmann distribution for the charge density, this Poisson-Boltzmann(PB) equation jointly celebrates the names of two giants of science who, however, neither wrote it, nor of course collaborated.

In principle, Eq.?? is a closed equation for $\phi(r)$. However, it is highly nonlinear, and can be solved analytically only in a simple 1-dimensional planar geometry. Analytical results in the spherical geometry we are considering can be obtained only if the PB equation is suitably linearized: when and how this can be done is discussed in the following section. Before that, however, it is important to point out that at least two approximations have

implicitly been used to obtain Eq. Eq.???. First, by equating the ion distribution to a charged fluid, we have neglected that ions are not point-like, but actually have a finite size. You can easily guess that excluded volume effects may then limit the amount of charge that accumulates around the probe charge. The second approximation is subtler, but more important. To obtain Eq. ?? we have basically assumed that the probability $P(r)$ of a charge q_j to be in r increases (or decreases) with respect to $P(r = \infty)$ by the Boltzmann factor of the energy gain (or cost) required to bring q_j from infinity to r . If $\phi(r)$ were an external fixed potential, this would be correct. However, we did not take into account that, when q_j is moved from infinity to r , the electrostatic potential it generates modifies, in turn, the charge distribution around r .

1.1 The Debye-Hückel equation

In physics, a big help often comes from identifying a length, time, or energy scale, which is somehow intrinsic to the investigated problem. This is for instance the case of the heat capacity of solids, where the characteristic energy scale of vibrations ω_D allows us, when compared to the thermal energy $k_B T$, to state the temperature conditions in which the classical equipartition theorem holds. For a charged fluid, an additional energy scale besides $k_B T$ is provided by the electrostatic interaction energy between two unit charges. Comparing these two quantities, we can introduce an intrinsic length scale,

$$l_B = \frac{e^2}{4\pi\epsilon k_B T} \quad (4)$$

which is the distance at which two unit charges interact with an electrostatic energy equal to the thermal energy. This typical distance is called the Bjerrum length, since it was originally introduced by the Danish chemist Niels Bjerrum to account for ion pairing in solutions. Yet, in the context of plasma physics, it is rather known as the Landau length, because it has been independently introduced by Lev Davidovich Landau to discuss collisions in dilute plasmas.

For electrolytes in water ($\epsilon_r = 80$) we have $l_B \approx 7\text{\AA}$. The Bjerrum length provides us with the condition for the linearization of the PB equation. In fact, this is possible when $q_j \phi \ll k_B T$ for all values of j , so that all the exponential functions $e^{-\beta \phi q_j}$ can be expanded at first order. This condition is equivalent to stating that the kinetic energy of the ions is much larger than their electrostatic potential energy. Calling $d = (V/N)^{1/3}$ the average distance between two arbitrary charges, and taking into account that the all charges q_j typically have a magnitude of the order of the electron charge e , it is easy to see that this implies $d \gg l_B$. If this condition is verified, expanding Eq. ?? at first order we obtain

$$\rho(r) \approx \frac{1}{V} \sum_j N_j q_j (1 - \beta q_j \phi(r)) = -\frac{1}{V} \sum_j N_j q_j^2 \beta \phi(r) \quad (5)$$

where the last equality comes from the charge neutrality condition. Substituting this linearized charge density in the PB equation, we obtain the Debye-Hückel (DH) equation where

$$\nabla^2\phi(r) - \frac{1}{\lambda_{DH}^2}\phi(r) = 0 \quad \text{where} \quad \lambda_{DH} = \sqrt{\frac{\epsilon V k_B T}{\sum_j N_j q_j^2}} \quad (6)$$

is called the Debye-Hückel length. Writing $q_j = z_j e$, where z_j is the valency (with sign) of the type- j ions, λ_{DH} can also be related to the Bjerrum length as

$$\lambda_{DH} = \left(4\pi l_B \sum_j \bar{n}_j z_j^2 \right)^{-1/2}$$

Note also that in the DH approximation, since from Gauss $\nabla^2 \phi(r) = -\frac{\rho(r)}{\epsilon}$ there is a proportionality between charge density and potential:

$$\nabla^2 \phi(r) = \frac{1}{\lambda_{DH}^2} \phi(r) \quad \rightarrow \quad \rho(r) = -\frac{\epsilon}{\lambda_{DH}^2} \phi(r).$$

For electrolyte solutions, it is customary to use ion concentrations c_j , measured in moles per liter. Since

$$c \text{ mol/liter} = N_A c \text{ particelle/liter} = 10^3 c N_A \text{ particle/m}^3$$

($1l = 10^{-3}m^3$, $n/N_A \rightarrow c$), and to introduce the solution *ionic strength*,

$$I = \frac{1}{2} \sum_j c_j z_j^2 = \frac{1}{2} \left(\sum_j \bar{n}_j z_j^2 \right) \times 10^3 N_A$$

Then, λ_{DH} can also be written as ($\sqrt{\frac{1}{8 \cdot 3.14 \cdot 0.7 \cdot 10^{-9} \cdot 6.023 \cdot 10^{23} \cdot 10^3}} = 0.3 \cdot 10^{-9}$)

$$\lambda_{DH} = (8\pi \times 10^3 N_A l_B I)^{-1/2} \approx 0.3 I^{-1/2} \text{ nm}$$

To get an idea of the order of magnitude of the DH length in aqueous solutions, we can observe that, for $I = 100mM = 0.1M$, one obtains $\lambda = 0.3/\sqrt{0.1} \approx 1 \text{ nm}$: for other DH values of I , λ_{DH} is simply obtained dividing the last figure by $\sqrt{I[mM]}/100$.

1.2 Debye-Hückel potential and charge distribution (spherical coordinates)

Because of isotropy, $\phi(r)$ depends only on the radial coordinate, hence the DH equation is readily solved in spherical coordinates, where it reads

$$\frac{1}{r} \frac{d^2}{dr^2} [r\phi(r)] = \frac{1}{\lambda_{DH}^2} \phi(r)$$

which is valid for $r \neq 0$. This equation is readily solved by introducing $u(r) = r\phi(r)$. The general solution for the potential is

$$\phi(r) = \frac{A}{r} e^{-r/\lambda_{DH}} + \frac{B}{r} e^{r/\lambda_{DH}}$$

Requiring $\phi(r)$ to vanish for $r \rightarrow \infty$ implies $B = 0$. The other boundary condition we must impose is that, for $r \rightarrow 0$, $\phi(r)$ coincides with the potential generated by the probe charge (which, remember, we assume to be point-like). Since $\nabla^2 \frac{1}{r} = -4\pi\delta(r)$, and since from the Gauss theorem $\nabla^2\phi(r) = -\frac{\rho(r)}{\epsilon} = -\frac{q\delta(r)}{\epsilon}$ we have

$$\nabla^2\phi(r) = \nabla^2\frac{A}{r} = -4\pi A\delta(r) = -\frac{q\delta(r)}{\epsilon} \quad \rightarrow \quad A = \frac{q}{4\pi\epsilon}$$

$$\phi(r) = \frac{q}{4\pi\epsilon r} e^{-r/\lambda_{DH}}$$

where $\kappa = 1/\lambda_{DH}$ is usually called the screening parameter. Therefore, the net effect of charge coordination is that of turning the Coulomb interaction into a *screened* potential that, decaying exponentially over the characteristic length λ_{DH} , is short-ranged. To find the charge density around the probe charge, we just have to observe that (in the DH approximation) the relation between $\rho(r)$ and $\phi(r)$ gives

$$\rho(r) = -\frac{\epsilon\phi(r)}{\lambda_{DH}^2} = -\epsilon\kappa^2\phi(r)$$

For a point-like charge at the origin, therefore,

$$\rho(r) = -\frac{q\kappa^2}{4\pi r} e^{-\kappa r}$$

The total charge coordinated to q is found by integrating $\rho(r)$ from 0^+ to ∞ (and substituting $t = \kappa r$):

$$\int_{0^+}^{\infty} -\frac{q\kappa^2}{4\pi r} e^{-\kappa r} 4\pi r^2 dr = -q \int_{0^+}^{\infty} t e^{-t} dt = -q$$

which confirms that the net charge accumulating around q fully screens the probe charge, consistently with the charge neutrality condition. In practice, however, the net charge contained in a sphere with a radius of a few DH lengths is already very close to $-q$.

1.3 A colloidal particle in solutions (microions)

So far, we have regarded ions as point-like, which is fully reasonable for simple (and sufficiently dilute) electrolyte solutions. Currently, however, the DH theory finds its main applications in the investigation of colloidal suspensions and of solutions of biological macromolecules like proteins or nucleic acids. In all these cases, we deal with systems where a large size asymmetry exist between the large macroions and the small released counterions. The other charged species that are usually present, like salts added to modify the thermodynamic properties of the macroion solution, can also be regarded as point-like. It is then interesting to consider as "probe" particle a spherical colloidal particle of radius a and charge Ze , and find the distribution of the small ions (either counterions, or due

to added electrolytes) around it. Imposing boundary conditions to the general solution is slightly more complicated, but we can still analytically solve the problem recalling that, because of charge neutrality, the net charge in the DH cloud must necessarily be $-Ze$. From $\phi(r) = Ar^{-1}e^{-\kappa r}$ we have $\phi(a) = Aa^{-1}e^{-\kappa a}$, and therefore

$$\phi(r) = \phi(a)\frac{a}{r}e^{-\kappa(r-a)}$$

Requiring the net charge coordinated around the macroion to be $-Ze$, and recalling that $\rho(r) = -\epsilon\kappa^2\phi(r)$, we must then have

$$\int_a^\infty dr \rho(r) 4\pi r^2 = -4\pi\epsilon\kappa^2 a\phi(a) \int_a^\infty dr r e^{-\kappa(r-a)} = -Ze$$

Let's evaluate the integral. Substituting $z = r - a$, we find

$$\int_a^\infty dr r e^{-\kappa(r-a)} = \int_0^\infty dz (z+a) e^{-\kappa z} = -\frac{d}{d\kappa} \int_0^\infty dz e^{-\kappa z} + a \int_0^\infty dz e^{-\kappa z} = \kappa^{-2} + \frac{a}{\kappa}$$

Then

$$-4\pi\epsilon\kappa^2 a\phi(a) \left(\kappa^{-2} + \frac{a}{\kappa} \right) = -Ze$$

and we obtain the value of the potential at the particle surface

$$\phi(a) = \frac{Ze}{4\pi\epsilon a(1 + \kappa a)}$$

For $r \geq a$, the DH potential around a charged spherical macroion is then

$$\phi(r) = \frac{Ze}{4\pi\epsilon a(1 + \kappa a)} \frac{e^{-\kappa(r-a)}}{r} \quad (7)$$

Note that, compared to the potential around a point-like particle, the apparent particle charge is reduced with respect to the "bare" charge Ze by a factor of $(1 + \kappa a)^{-1}$. This effective charge depends on $\kappa a = a/\lambda_{DH}$, and can therefore be modified by adding salts or other electrolytes that increase the total amount of ions in solution.

1.4 A single charged plane (only counter ions)

Consider an infinite planar surface separating a dielectric medium (e.g. glass, or polystyrene) extending to the left, from an ionic solution on the right. The surface carries a uniform charge density $\sigma < 0$ (charge per unit area), which will be assumed to be negative. Only the corresponding counterions are present in solution. The corresponding PB equation is then

$$\frac{d^2\phi(z)}{dz^2} = -\frac{q\rho_0}{\epsilon} e^{-\beta q\phi(z)}$$

This differential equations admit as a solution

$$\phi(z) = \frac{2k_B T}{q} \ln a(z+b)$$

with a and b integration constants. Indeed

$$\frac{d\phi(z)}{dz} = \frac{2k_B T}{q} \frac{1}{(z+b)} \quad \frac{d^2\phi(z)}{dz^2} = -\frac{2k_B T}{q} \frac{1}{(z+b)^2}$$

and

$$e^{-\beta q \phi(z)} = e^{-\beta q \frac{2k_B T}{q} \ln a(z+b)} = e^{\ln[a(z+b)]^{-2}} = \frac{1}{[a(z+b)]^2}$$

so that

$$-\frac{2k_B T}{q} \frac{1}{(z+b)^2} = -\frac{q\rho_0}{\epsilon} \frac{1}{[a(z+b)]^2}$$

The constant a is thus

$$a^2 = \frac{q^2 \rho_0}{2k_B T \epsilon}$$

To fix the constant b one can consider

$$-\frac{d\phi(z)}{dz} \Big|_{z=0} = E = \frac{\sigma}{\epsilon}$$

which in this case becomes

$$\frac{d\phi(z)}{dz} \Big|_{z=0} = -\frac{2k_B T}{q} \frac{1}{b}$$

and thus

$$\frac{2k_B T}{q} \frac{1}{b} = \frac{\sigma}{\epsilon} \quad b = \frac{2k_B T}{q} \frac{\epsilon}{\sigma}$$

From the potential, one can also calculate the concentration profile as (to avoid to use the $z = \infty$ condition, where $\rho(\infty) = 0$)

$$\rho(z) = \rho(0) e^{-\beta q (\phi(z) - \phi(0))} = \rho(0) \frac{1}{[a(z+b)]^2} \frac{[ab]^2}{1} = \rho(0) \frac{1}{[(z+b)]^2} \frac{b^2}{1}$$

and $\rho(0)$ can be evaluate by imposing charge neutrality ($\sigma < 0$)

$$\int_0^\infty \rho(z) dz = -\sigma$$

and since

$$\int_0^\infty \frac{1}{[(z+b)]^2} dz = \frac{1}{b}$$

we get

$$\int_0^\infty \rho(z) dz = \rho(0) b^2 \frac{1}{b} = -\sigma$$

or

$$\rho(0) = -\frac{\sigma}{b}$$

and we find a charge density (to be divided by q to obtain the number density)

$$\rho(z) = -\frac{\sigma b}{[(z+b)]^2} = \sigma \frac{2k_B T \epsilon}{q} \frac{1}{\sigma (z+b)^2} = \frac{2k_B T \epsilon}{q} \frac{1}{(z+b)^2} = \frac{q}{2\pi l_B} \frac{1}{(z+b)^2}$$

Note that, both the electric field and the density decay algebraically to zero for $z \rightarrow \infty$.

1.5 A single charged plane - (following Barrat-Hansen)

Consider an infinite planar surface separating a dielectric medium (e.g. glass, or polystyrene) extending to the left, from an ionic solution on the right. The surface carries a uniform charge density σ (charge per unit area), which will be assumed to be negative. For the sake of simplicity, the positive counterions and negative co-ions will be assumed to be monovalent (e.g. Na^+ and Cl^-). The corresponding density profiles $\rho_+(z)$ and $\rho_-(z)$ depend only on z , the coordinate orthogonal to the plane; the microions can not penetrate to the left of the planar surface, so that $\rho_+(z < 0) = 0$.

Due to charge neutrality *in the bulk*, $\rho_+ = \rho_- = \rho_0$. Overall charge neutrality requires:

$$\int_0^\infty \rho_c(z) dz = -\sigma$$

The corresponding PB equation

$$\frac{d^2 \phi(z)}{dz^2} = \frac{q\rho_0}{\epsilon} e^{\beta q \phi(z)} - \frac{q\rho_0}{\epsilon} e^{-\beta q \phi(z)} = \frac{2q\rho_0}{\epsilon} \sinh(\beta q \phi(z))$$

This non-linear second-order differential equation for z must be solved subject to the two boundary conditions:

$$\lim_{z \rightarrow \infty} \frac{d\phi(z)}{dz} = 0$$

indicating that the electric field at infinity must be zero and by the condition that the electric field just after the surface, by the Gauss theorem, has to be σ/ϵ . This can be proved by using a surface extending from plus infinity to 0^- , inside which the total charge is zero, followed by an infinitesimal surface centered on the charged surface, for which

$$-\frac{d\phi(z)}{dz} \Big|_{z=0} = \frac{\sigma}{\epsilon}$$

Note that the 'constant charge' boundary condition is physically reasonable for most colloidal systems. Under some circumstances a 'constant potential' boundary condition, or an intermediate 'self-regulating' boundary condition may be more appropriate.

Exact solution of PB. The PB equation for this problem can be solved. Defining $\Psi(z) = \beta q \phi(z)$ the PB equation can be rewritten as

$$\frac{d^2\Psi(z)}{dz^2} = \frac{1}{\lambda_D^2} \sinh(\Psi(z))$$

where we recall that $\lambda_D^2 = \frac{\epsilon k_T V}{\sum_j N_j q_j^2}$.

The solution can be expressed in term of inverse hyperbolic tangent

$$\phi(z) = \frac{k_B T}{q} \Psi(z) = \frac{4k_B T}{q} \operatorname{arctanh}(ge^{-z/\lambda_D})$$

where the integration constant g can be found by solving for $z = 0$

$$\tanh \frac{q\phi(0)}{4k_B T} = g$$

The resulting concentration profiles

$$\rho_+(z) = \rho_0 e^{-\beta q \phi(z)} = \rho_0 e^{-\Psi(z)} = \rho_0 e^{-4 \operatorname{arctanh}(ge^{-z/\lambda_D})}$$

Remembering that

$$\operatorname{arctanh}(x) = \frac{1}{2} \ln \frac{1+x}{1-x}$$

then

$$e^{-4 \operatorname{arctanh}(x)} = e^{-2 \ln \frac{1+x}{1-x}} = \left(\frac{1-x}{1+x} \right)^2$$

and

$$\rho_+(z) = \rho_0 \left(\frac{1 - ge^{-z/\lambda_D}}{1 + ge^{-z/\lambda_D}} \right)^2$$

The same calculation for $\rho_-(z)$ gives

$$\rho_-(z) = \rho_0 e^{\beta q \phi(z)}$$

Since the only difference with ρ_+ is the sign in front of the exponential, one obtains

$$\rho_-(z) = \rho_0 \left(\frac{1 + ge^{-z/\lambda_D}}{1 - ge^{-z/\lambda_D}} \right)^2$$

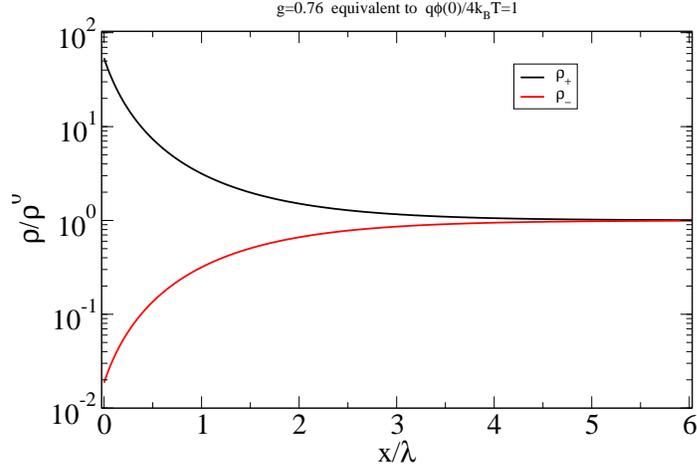


Figure 1: Solution of the PB equation for the plane case

which is the same once g is replaced by $-g$. The solution is graphically shown in Fig. ??.

If we can linearize....

If we go back to the original PB equation and evaluate it for the case in which $\beta q q(z) < 1$, we can expand $\sinh(\Psi(z))$ to the leading order $\Psi(z)$ and obtain

$$\frac{d^2\Psi(z)}{dz^2} = \frac{1}{\lambda_D^2} \Psi(z)$$

The resulting linear differential equation is easily solved with the result

$$\phi(z) = \phi(0)e^{-z/\lambda_D}$$

Again, by using $-d\phi/dz = E = \sigma/\epsilon$,

$$\phi(0)\frac{1}{\lambda_D} = \frac{\sigma}{\epsilon} \quad \rightarrow \quad \phi(z) = \frac{\sigma\lambda_D}{\epsilon} e^{-z/\lambda_D}$$

while the corresponding density profiles reduce to:

$$\rho_{\pm}(z) = \rho_0 \pm \frac{|\sigma|}{2q} e^{-z/\lambda_D}$$

showing that the coion and counterion density profiles decay exponentially towards their bulk value; the width of the electric double-layer varies as $1/\sqrt{\rho_0}$. The exponential decay is reminiscent of the exponential screening of the correlation functions in bulk electrolytes.

Going back to the full solution, we can also there calculate the relation between the surface potential $\phi(0)$ and surface charge σ exploiting the relation $-d\phi/dz = \sigma/\epsilon$.

The derivative of the potential is (recalling that

$$\frac{d \operatorname{arctanh}(x)}{dx} = \frac{1}{1-x^2}$$

and that $2 \sinh(x) \cosh(x) = \sinh(2x)$)

$$\left. \frac{d\phi(z)}{dz} \right|_{z=0} = \frac{4k_B T}{q} \frac{-g}{\lambda_D(1-g^2)} = -\frac{4k_B T}{q} \frac{1}{\lambda_D} \frac{1}{2} \sinh\left(\frac{q\phi(0)}{2k_B T}\right)$$

By equating $-\left. \frac{d\phi(z)}{dz} \right|_{z=0}$ with σ/ϵ one obtains the so-called Grahame's equation:

$$\frac{\sigma}{\epsilon} = \frac{2k_B T}{q} \sqrt{\frac{\sum_i \rho_i q^2}{\epsilon k_B T}} \sinh\left(\frac{q\phi(0)}{2k_B T}\right)$$

or

$$\sigma = \sqrt{4\epsilon k_B T} \sinh\left(\frac{q\phi(0)}{2k_B T}\right) (2\rho_0)^{1/2}$$

If the surface potential is less than about 25 mV at room temperature, the right-hand side may be linearized to yield

$$\sigma = \sqrt{8\rho_0 \epsilon k_B T} \frac{q\phi(0)}{2k_B T} = \sqrt{\frac{8\rho_0 \epsilon k_B T q^2}{4k_B^2 T^2}} \phi(0) = \sqrt{\frac{2\rho_0 q^2}{k_B T \epsilon}} \epsilon \phi(0) = \frac{\epsilon \phi(0)}{\lambda_D}$$

which of course coincide with the result previously derived in the DH approximation.

For a condensator with parallel plates at distance d and surface charge σ , the electric field is $E = \sigma/\epsilon$ and $\Delta V = Ed = \sigma d/\epsilon$. Comparing with the previous expression one sees that for low surface potentials, the electric double-layer behaves as a condenser of width equal to the Debye length.

A trick:

We now note the general relation (note the difference between ρ_{number} and ρ_{charge})

$$\frac{d\rho_{number}}{dz} = \frac{d}{dz} \sum_j \rho_j^\infty e^{-\beta q_j \phi(z)} = - \sum_j \beta q_j \rho_j^\infty e^{-\beta q_j \phi(z)} \frac{d\phi(z)}{dz} = -\beta \rho_{charge}(z) \frac{d\phi(z)}{dz}$$

and by using the Poisson equation $d^2\phi/dz^2 = -\rho_{charge}/\epsilon$

$$\frac{d\rho_{number}}{dz} = \epsilon \beta \frac{d^2\phi(z)}{dz^2} \frac{d\phi(z)}{dz} = \frac{\epsilon \beta}{2} \frac{d}{dz} \left(\frac{d\phi(z)}{dz} \right)^2$$

Using this relation, we can integrate over z and find

$$\rho_{number}(z) - \rho_{number}(\infty) = \frac{\epsilon\beta}{2}E^2(z) \quad \rightarrow \quad \rho_{number}(z) = 2\rho_0 + \frac{\epsilon\beta}{2}E^2(z)$$

Since the microions are non-interacting, the left-hand side is the difference in local osmotic pressure $\Pi = k_B T \rho$, between a point at z and in the bulk; the right-hand side is the electrostatic pressure at z , which vanishes in the bulk. The previous equation thus expresses that a difference in osmotic pressure must be balanced by a difference in electrostatic pressure to ensure mechanical equilibrium.

Now in $z=0$: Going back to the previous expression, evaluated in $z = 0$, one finds

$$\rho_{number}(0) = 2\rho_0 + \frac{\sigma^2\beta}{2\epsilon}$$

The enhancement in density grows quadratically with σ , and becomes quite substantial for high surface charges. In fact at sufficiently high values of σ , the local microion density becomes unphysically large, such that the corresponding packing fraction (calculated with the ionic radii) would exceed close-packing. This breakdown of the PB theory, which systematically overestimates contact densities, can be traced back to the neglect of correlations between microions. This deficiency may be partly remediated by introducing a layer of counterions tightly bound to tile highly charged surface, the so-called Stern layer of "adsorbed" counterions; this reduces the surface charge from its bare value to some effective value σ_{eff} which may be considered as a phenomenological, adjustable parameter. The PB theory sketched above applies then only to the "diffuse" electric double-layer, beyond the Stern layer. We use the word "diffusive" to indicate the charge distribution created by the freely diffusion ions in solutions.

1.6 Two surfaces in water (no electrolyte solution) - Israelevich: Another one-dimension case where the PB can be solved.

In the following sections we shall consider the counterion distribution and force between two similarly charged planar surfaces in a pure liquid such as water, where (apart from H_3O^+ and OH^- ions) **the only ions in the solution are only those that have come off the surfaces**. Such systems occur when, for example, colloidal particles, clay sheets, surfactant micelles or bilayers whose surfaces contain ionizable groups interact in water, and also when thick films of water build up (condense) on an ionizable surface such as glass. But first we must consider some fundamental equations that describe the counterion distribution between two charged surfaces in solution.

When solved, the PB equation gives the potential ϕ , electric field $E = d\phi/dx$, and counterion density ρ , at any point x in the gap between the two surfaces. Let us first determine these values at the surfaces themselves. These quantities are often referred to as the contact values: ϕ_s, E_s, ρ_s , etc.

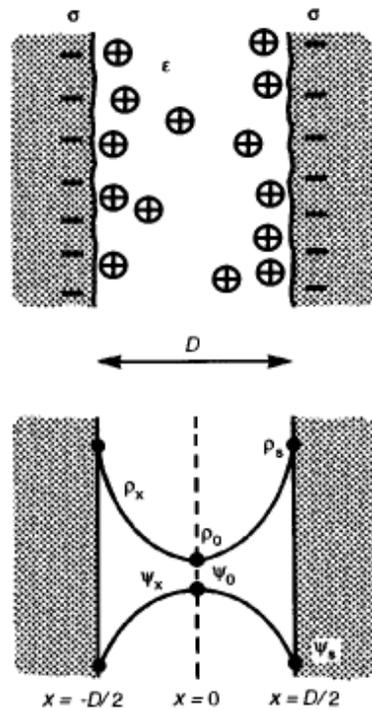


Fig. 12.2. Two negatively charged surfaces of surface charge density σ separated a distance D in water. The only ions in the space between them are the counterions that have dissociated from the surfaces. The counterion density profile ρ_x and electrostatic potential ψ_x are shown schematically in the lower part of the figure. The 'contact' values are ρ_s and ψ_s .

The PB equation is a non-linear second-order differential equation, and to solve for ϕ we need two boundary conditions, which determine the two integration constants. The first boundary condition follows from the symmetry requirement that the field must vanish at the mid-plane, i.e., that $E(0) = -d\phi/dx(0) = 0$. The second boundary condition follows from the requirement of overall electro-neutrality, i.e., that the total charge of the counterions in the gap must be equal (and opposite) to the charge on the surfaces. If σ is the surface charge density on each surface (in Cm^{-2}) and D is the distance between the surfaces, then the condition of electroneutrality implies that

$$\begin{aligned} \sigma &= - \int_0^{D/2} q\rho(x)dx = \text{relating the density to the potential via the Gauss theorem} = \\ &= \epsilon \int_0^{D/2} \frac{d^2\phi}{dx^2} dx = \epsilon \frac{d\phi}{dx} \Big|_0^{D/2} = \epsilon \frac{d\phi}{dx} \Big|_s = -\epsilon E_s \end{aligned}$$

Then the electric field at the surface is related to the surface density by

$$E_s = \frac{\sigma}{\epsilon}$$

(again applying Gauss first to the entire system and then to a tiny volume across the charged surface). This equation gives an important boundary condition relating the surface charge density σ to the electric field E_s at each surface (at $x = \pm D/2$), which we may note is independent of the gap width D .

Turning now to the ionic distribution, we recall that there exists an important general relation between the concentrations of counterions at either surface and at the midplane. Differentiating the Boltzman distribution $\rho(x) = \rho_0 e^{-q\beta\phi(x)}$ and then using the PB we obtain

$$\frac{d\rho}{dx} = -\frac{q\rho_0}{k_B T} e^{-q\phi/k_B T} \left(\frac{d\phi}{dx} \right) = -q\rho_0 e^{-q\phi/k_B T} \left(\frac{d\phi}{dx} \right)$$

recognizing in $q\rho$ the charge density and again using Gauss

$$\frac{d\rho}{dx} = \frac{\epsilon}{k_B T} \left(\frac{d\phi}{dx} \right) \left(\frac{d^2\phi}{dx^2} \right)$$

which can be written as

$$= \frac{\epsilon}{2k_B T} \frac{d}{dx} \left(\frac{d\phi}{dx} \right)^2$$

hence integrating both sides (and remembering that the electric field in 0 is zero)

$$\rho(x) - \rho_0 = \int_0^x d\rho = \frac{\epsilon}{2k_B T} \int_0^x d \left(\frac{d\phi}{dx} \right)^2 = \frac{\epsilon}{2k_B T} \left(\frac{d\phi}{dx} \right)^2 (x) \quad (8)$$

which gives $\rho(x)$ at any point x can be written in terms of ρ_0 at the mid-plane and the electric field $d\phi/dx$ at x . In particular at the surface, $x = D/2$, we obtain the contact value of $\rho(D/2) = \rho_s$. Recalling that

$$\rho_s = \rho_0 + \frac{\sigma^2}{2\epsilon k_B T}$$

This result shows that the concentration of counterions at the surface depends only on the surface charge density σ and the counterion concentration at the midplane. Note that ρ_s never falls below $\frac{\sigma^2}{2\epsilon k_B T}$ even for isolated surfaces, i.e., for two surfaces far apart when $\rho_0 \rightarrow 0$.

The above equations are quite general and are the starting point of all theoretical computations of the ionic distributions near planar charged surfaces, even when the solution contains added electrolyte. To proceed further we consider the specific case of counterions only.

Evaluation of $\rho(x)$. We must now solve the **Poisson Boltzmann** equation. The solution is

$$\phi(x) = \frac{k_B T}{q} \ln(\cos^2 Kx)$$

or

$$e^{-q\phi/k_B T} = \frac{1}{\cos^2 Kx}$$

where K is a constant.

As a proof, consider that

$$\frac{d\phi}{dx} = \frac{k_B T}{ze} \frac{1}{\cos^2 Kx} 2 \cos Kx \sin Kx (-K) = -2K \frac{k_B T}{q} \frac{\sin Kx}{\cos Kx}$$

$$\frac{d^2\phi}{dx^2} = -2K \frac{k_B T}{ze} \frac{K \cos^2 Kx + K \sin^2 Kx}{\cos^2 Kx^2} = -2K^2 \frac{k_B T}{q} \frac{1}{\cos^2 Kx} = -2K^2 \frac{k_B T}{q} e^{-q\phi/k_B T}$$

Comparing with the PB equation

$$\frac{d^2\phi(x)}{dx^2} = \frac{q\rho_0}{\epsilon} e^{-\beta q\phi(x)}$$

one indeed find

$$K^2 = \frac{q^2 \rho_0}{2\epsilon k_B T}$$

With this form for the potential we see that $\phi = 0$ and $d\phi/dx = 0$ at $x = 0$ for all K , as required.

The counterion distribution profile

$$\rho(x) = \rho_0 e^{-q\phi/k_B T} = \frac{\rho_0}{\cos^2 Kx}$$

can be expressed in term of σ and D by evaluating the electric field at the surface and equating it to σ/ϵ as

$$E_s = -\frac{d\phi}{dx_s} = \frac{2Kk_B T}{q} \tan\left(\frac{KD}{2}\right) = \frac{\sigma}{\epsilon}$$

Pressure: Before we proceed to calculate the force or pressure between two surfaces it is instructive to discuss, in qualitative terms, how the counterion distribution, potential field and pressure between two surfaces arise. The first thing to notice is that if there were no ions between two similarly charged surfaces, there would be no electric field in the gap between them. This is because the field emanating from a planar charged surface, $E = \sigma/2\epsilon$, is uniform away from the surface. The two opposing fields emanating from the two plane parallel surfaces therefore cancel out to zero between them. Thus, when the counterions are introduced into the intervening region they do not experience an attractive electrostatic force towards each surface. The reason why the counterions build up at each surface is simply because of their mutual repulsion and is similar to the accumulation of mobile charges on the surface of any charged conductor. The repulsive electrostatic interaction between the counterions and their entropy of mixing alone determine their concentration profile $\rho(x)$, the potential profile $\phi(x)$ and the field $E(x)$ between the surfaces, and we may further note that in all the theoretical derivations so far the only way the surface charge density σ enters into the picture is via the total number of counterions in the gap.

1.6.1 Stern Layer

If the locations of the charged surface groups were not at the physical solid-liquid interface (at $x = \pm D/2$) but at some small distance δ within the surface (Fig. 12.4), the ionic distribution $\rho(x)$, potential $\phi(x)$, field $E(x)$, and the pressure in the medium between $D/2$ and $-D/2$ would not change. But the potential would be different if it were measured at $x = \pm(D/2 + \delta)$. This is the origin of the so called Stern layers which separate the charged plane from the plane from which the ionic atmosphere begins to obey the Poisson-Boltzmann equation. The thickness of the Stern layer δ is of the order of a few \AA and reflects the finite size of the charged surface groups and transiently bound counterions, as illustrated in Fig. 12.4. If the dielectric constant of the Stern layer is uniform and equal to ϵ_δ it can be modelled as a capacitor whence the additional drop in potential across the layer is given by

$$\phi_\delta = \frac{\sigma\delta}{\epsilon_\delta}$$

For example, if $\delta = 0.2$ nm, $\sigma = 0.2$ Cm⁻² and $\epsilon_\delta = 40$, we obtain $\phi_\delta = 130$ mV.

1.6.2 Pressure

We now turn to the origin of the force or pressure between the two surfaces. Contrary to intuition, the origin of the repulsive force between two similarly charged surfaces in a solvent containing counterions and electrolyte ions is entropic (osmotic), not electrostatic. Indeed, the electrostatic contribution to the net force is actually attractive. Consider a surface, initially uncharged, placed in water. When the surface groups dissociate the counterions leave the surface against the attractive Coulombic force pulling them back. What maintains the diffuse double layer is the repulsive osmotic pressure between the counterions which forces them away from the surface and from each other so as to increase their configurational entropy. On bringing two such surfaces together one is therefore forcing the counterions back onto the surfaces against their preferred equilibrium state, i.e., against their osmotic repulsion, but favoured by the electrostatic interaction. The former dominates and the net force is repulsive. To understand why the purely electrostatic part of the interaction is attractive recall that it involves an equal number of positive (counterion) and negative (surface) charges, i.e., the system is overall electrically neutral. The net Coulombic interaction between a system of charges that are overall neutral always favours their association, as we know for the case of ionic crystals (e.g., NaCl) and dipoles.

1.7 Infinte charged cylinder - Barrat-Hansen

Consider now the sheath-like electric double-layer around a uniformly charged cylindrical rod of radius a and length L . This is a model for rod-like colloids, like boehmite, or viruses, like the tobacco mosaic virus (TMV). The aspect ratio L/a of the latter is about 20, and if the main interest is in the immediate vicinity of the rod, end effects are unimportant, and one may usefully consider the simpler case of an infinitely long rod ($L \rightarrow \infty$). Moreover, a charged rod may also serve as a model for stiff polyelectrolytes, i.e. water-soluble polymers made up of ionizable monomers, carrying a line charge, or charge per unit length, ξ .

An important length scale for charged rods or polyelectrolytes is the distance $l = q/\xi$ between successive monovalent charges;

In vacuum, the electrostatic field around an infinite cylindrical rod is radial by symmetry, and its amplitude $E(r)$ follows directly from Gauss' theorem by calculating the flux of the radial field through a coaxial cylinder of radius r ; the result is

$$E(r) = \frac{\xi}{2\pi\epsilon r}$$

and the corresponding electrostatic potential is (where the subscript $_0$ indicates the vacuum condition, reasonably correct very close to the line):

$$\phi_0 = -\frac{\xi}{2\pi\epsilon} \ln r/\lambda$$

where λ here is an arbitrary length determined by the boundary condition imposed on $\phi(r)$.

The radial structure of the double-layer sheath (in italian "guaina") may again be studied within the PB theory. The cylindrical Poisson equation is:

$$\frac{1}{r} \frac{d}{dr} \left[r \frac{d\phi}{dr} \right] = -\frac{q}{\epsilon} \rho_c(r)$$

where $\rho_c(r)$ denotes the radial charge density. Consider first a single charged rod in a monovalent ionic solution. The reduced potential $\psi(r) = \beta q \phi(r)$ satisfies the PB equation:

$$\frac{1}{r} \frac{d}{dr} \left[r \frac{d\psi}{dr} \right] = -\frac{1}{\lambda_D^2} \sinh \psi(r)$$

to be solved subject to boundary conditions similar to to the one seen in the planar case but adapted to the cylindrical geometry. For sufficiently low line charge ξ the reduced potential is small everywhere, so that equation may be linearized by replacing $\sinh \psi$ by ψ . The solution for the electrostatic potential is:

$$\phi(r) = \frac{\xi}{2\pi\epsilon} K_0(r/\lambda_D)$$

where K_0 is a modified Bessel function of the second kind; $\phi(r)$ goes over to $\phi_0(r)$ at short distances, and decays exponentially for $r > \lambda_D$, due to screening.

For sufficiently large line charge, non-linear effects become important and counterion condensation sets in according to a scenario first proposed by Manning. Close to the charged rod, the total electrostatic potential $\phi(r)$ goes over to $\phi_0(r)$, within a constant, so that the distribution of counterions is $\rho(r) = \rho_0 e^{-\psi(r)} \sim r^{-2\Gamma}$, where $\Gamma = l/l_B$ is a dimensionless coupling parameter, equal to the ratio of the Bjerrum length and the distance between the charges along the line.

The total number of counterions, calculated integrating the density, clearly diverges at its lower bound when $\Gamma > 1$, which corresponds to a high line charge. This divergence signals a strong accumulation or 'condensation' of the counterions onto the rod or polyelectrolyte chain. The condensed counterions will partially compensate for the line charge and reduce its effective value until the ratio Γ drops again below 1, and counterion condensation ceases.

The polyelectrolyte and the sheath of condensed counterions is then equivalent to a polyelectrolyte with an average distance between its charged segments equal to l_B . The remaining counterions form the 'diffuse' part of the electric double-layer which, in the presence of salt, extends radially over a distance of the order of λ_{DH} . Counterion condensation has a number of measurable consequences; in polyelectrolyte solutions it leads to a reduction of the osmotic pressure, which is mainly due to the counterions, since the fraction of the latter which are condensed does not contribute to the pressure. The condensed counterions are mobile along the axis of the rod or polyelectrolyte and form a kind of one-dimensional Coulomb gas. The correlated fluctuations of the counterions condensed

on two neighbouring parallel rods lead to an effective attraction between equally charged rods, via a purely classical mechanism reminiscent of the quantum fluctuations of bound electrons which give rise to the van der Waals attraction between molecules.

2 What are we really doing with PB

Let us assume that the system we want to describe is in thermodynamic equilibrium and that we can coarse grain the volume in such a way that in each region of space local equilibrium is reached.

Then, it is natural to write that the free energy of the system can be written as integral over volume of the local free energy density $f(\mathbf{r}) = F/V$, plus the energetic contribution originating by the external field.

$$F[\rho] = \int f(\mathbf{r})d\mathbf{r} - \int \rho(\mathbf{r})\psi(\mathbf{r})d\mathbf{r}$$

The equilibrium $\rho(\mathbf{r})$ is the one that minimize the free energy, satisfying the constraint that the total number of particles remains constant.

Then

$$\frac{\delta [F[\rho] - \mu(\int \rho(\mathbf{r})d\mathbf{r} - N)]}{\delta \rho(\mathbf{r})} = 0$$

which means

$$\left[F[\rho + \delta\rho] - \mu(\int \{\rho(\mathbf{r}) + \delta\rho(\mathbf{r})\}d\mathbf{r} - N) \right] - \left[F[\rho] - \mu(\int \rho(\mathbf{r})d\mathbf{r} - N) \right] = 0$$

$$\delta \int f(\mathbf{r})d\mathbf{r} - \int \delta\rho(\mathbf{r})\psi(\mathbf{r})d\mathbf{r} - \mu \int \delta\rho(\mathbf{r}) = 0$$

If we take the ideal gas expression as

$$\beta f(\mathbf{r}) = \rho(\mathbf{r})[\ln \rho(\mathbf{r})\Lambda^3 - 1]$$

then

$$\begin{aligned} \delta\beta f(\mathbf{r}) &= (\rho(\mathbf{r}) + \delta\rho(\mathbf{r}))[\ln(\rho(\mathbf{r}) + \delta\rho(\mathbf{r}))\Lambda^3 - 1] - \rho(\mathbf{r})[\ln \rho(\mathbf{r})\Lambda^3 - 1] = \\ &= (\rho(\mathbf{r}) + \delta\rho(\mathbf{r}))[\ln\{\rho(\mathbf{r})(1 + \frac{\delta\rho(\mathbf{r})}{\rho(\mathbf{r})}\})\Lambda^3 - 1] - \rho(\mathbf{r})[\ln \rho(\mathbf{r})\Lambda^3 - 1] = \end{aligned}$$

to first order in $\delta\rho(\mathbf{r})$

$$\approx \rho(\mathbf{r})\frac{\delta\rho(\mathbf{r})}{\rho(\mathbf{r})} + \delta\rho(\mathbf{r})(\ln\{\rho(\mathbf{r})\Lambda^3\} - 1) = \delta\rho(\mathbf{r}) \ln\{\rho(\mathbf{r})\Lambda^3\}$$

so that, putting everything together we find that for all possible $\delta\rho(\mathbf{r})$,

$$\int \delta\rho(\mathbf{r}) [k_B T \ln\{\rho(\mathbf{r})\Lambda^3\} - \psi(\mathbf{r}) - \mu] d\mathbf{r} = 0$$

which is equivalent to say (where μ , \mathbf{r} independent, enforces the particle conservation law).

$$[\ln\{\rho(\mathbf{r})\Lambda^3\} - \psi(\mathbf{r}) - \mu] = 0$$

For the case of the electrolytic solutions, one can write expressions like the previous one for each density species and find, identifying $\psi(\mathbf{r})$ with $q\phi(\mathbf{r})$, the PB approximation

$$\rho_{\pm}(\mathbf{r}) = \rho_{\pm}^0 e^{\mp\beta q\phi(\mathbf{r})}$$

where the constant ρ_{\pm}^0 is chosen to satisfy the particle conservation law.