

Water and Aqueous Solutions

6. Electrical Properties of Water and Aqueous Solutions

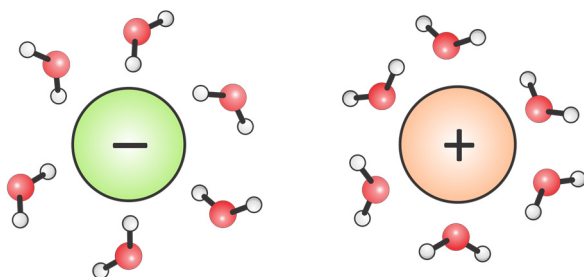
We want to understand the energy and electrical properties and transport of ions and charged molecules in water. These are strong forces. Consider an example of NaCl dissociation in gas phase dissociation energy $\Delta H_{\text{ionization}} \approx 270$ kJ/mol:

$$K_{\text{ionization}}(\text{gas}) = \frac{[\text{Na}^+][\text{Cl}^-]}{[\text{NaCl}]} \approx 10^{-89}$$

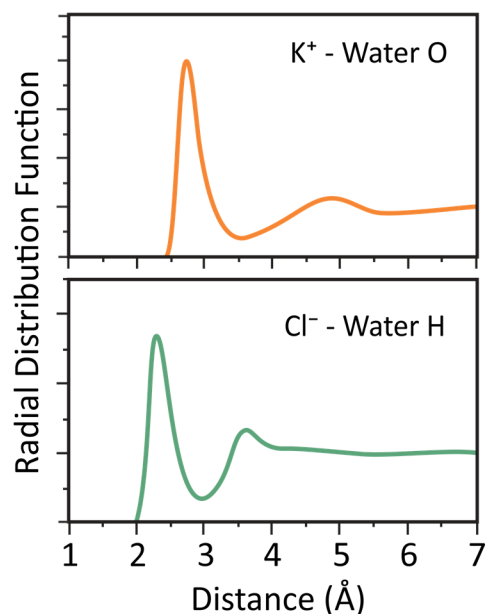
In solution, this process $[\text{NaCl}(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})]$ occurs spontaneously; the solubility product for NaCl is $K_{\text{sp}} = [\text{Na}^+(\text{aq})][\text{Cl}^-(\text{aq})]/[\text{NaCl}(\text{aq})] = 37$. Similarly, water molecules are covalently bonded hydrogen and oxygen atoms, but we know that the internal forces in water can autoionize a water molecule:

$$K_{\text{ionization}}(\text{gas}) = [\text{H}^+][\text{OH}^-] \approx 10^{-75} \text{ and } K_w(\text{H}_2\text{O}) = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

These tremendous differences originate in the huge collective electrostatic forces that are present in water. “Polar solvation” refers to the manner in which water dipoles stabilize charges.

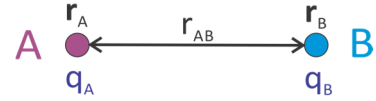


These dipoles are simplifications of the rearrangements of water's structure to accommodate and lower the energy of the ion. It is important to remember that water is a polarizable medium in which hydrogen bonding dramatically modifies the electrostatic properties.



Electrostatics

Let's review a number of results from classical electrostatics. The interactions between charged objects can be formulated using force, the electric field, or the electrostatic potential. The potential is our primary consideration when discussing free energies in thermodynamics and the Hamiltonian in statistical mechanics. Let's describe these, consider the interaction between two ions A and B , separated by a distance r_{AB} , with charges q_A and q_B .



$$\mathbf{r}_{AB} = (\mathbf{r}_A - \mathbf{r}_B)$$

$$r_{AB} = |\mathbf{r}_{AB}|$$

$$\hat{\mathbf{r}}_{AB} = \mathbf{r}_{AB} / r$$

Force and Work

Coulomb's Law gives the force that B exerts on A .

$$\mathbf{f}_{AB} = -\frac{1}{4\pi\epsilon} \frac{q_A q_B}{r_{AB}^2} \hat{\mathbf{r}}_{AB}$$

$\hat{\mathbf{r}}_{AB}$ is a unit vector pointing from \mathbf{r}_B to \mathbf{r}_A . A useful identity to remember for calculations is

$$\frac{e^2}{4\pi\epsilon_0} = 230 \text{ pN nm}^2$$

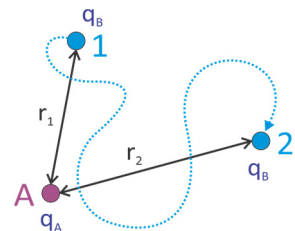
For thermodynamic purposes it is helpful to calculate the reversible work for a process. Electrical work comes from moving charges against a force

$$dw = -\mathbf{f} \cdot d\mathbf{r}$$

As long as q and ϵ are independent of r , and the process is reversible, then work only depends on r , and is independent of path. To move particle B from point 1 at a separation r_0 to point 2 at a separation r requires the following work

$$w_{1 \rightarrow 2} = \frac{1}{4\pi\epsilon} q_A q_B \left(\frac{1}{r_2} - \frac{1}{r_1} \right)$$

and if the path returns to the initial position, $w_{rev} = 0$.



Field, E

The electric field is a vector quantity that describes the action of charges at a point in space. The field from charged particle B at point A is

$$\mathbf{E}_{AB}(\mathbf{r}_A) = -\frac{1}{4\pi\epsilon} \frac{q_B}{r_{AB}^2} \hat{\mathbf{r}}_{AB}$$

\mathbf{E}_{AB} is related to the force that particle B exerts on a charged test particle A with charge q_A through

$$\mathbf{f}_A = q_A \mathbf{E}_{AB}(\mathbf{r}_A)$$

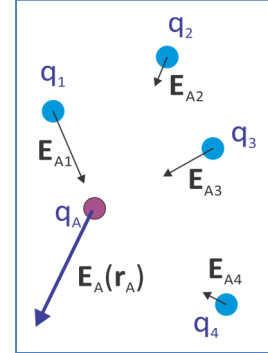
While the force at point A depends on the sign and magnitude of the test charge, the field does not. More generally, the field exerted by multiple charged particles at point \mathbf{r}_A is the vector sum of the field from multiple charges (i):

$$\mathbf{E}(\mathbf{r}_A) = \sum_i \mathbf{E}_{Ai}(\mathbf{r}_A) = -\frac{1}{4\pi\epsilon} \sum_i \frac{q_i}{r_{Ai}^2} \hat{\mathbf{r}}_{Ai}$$

where $r_{Ai} = |\mathbf{r}_A - \mathbf{r}_i|$ and the unit vector $\hat{\mathbf{r}}_{Ai} = (\mathbf{r}_A - \mathbf{r}_i) / r_{Ai}$. Alternatively for a continuum charge density $\rho_q(\mathbf{r})$,

$$\mathbf{E}(\mathbf{r}_A) = -\frac{1}{4\pi\epsilon} \int \rho_q(\mathbf{r}) \frac{(\mathbf{r}_A - \mathbf{r})}{|\mathbf{r}_A - \mathbf{r}|^3} d\mathbf{r}$$

where the integral is over a volume.



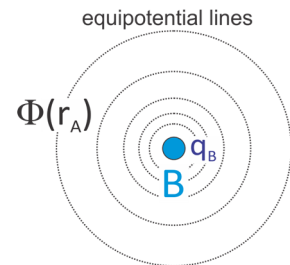
Electrostatic Potential, Φ

For thermodynamics and statistical mechanics, we wish to express electrical interactions in terms of an energy or electrostatic potential. While the force and field are vector quantities, the electrostatic potential Φ is a scalar quantity which is related to the electric field through

$$\mathbf{E} = -\nabla\Phi$$

It has units of energy per unit charge. The electrostatic potential at point \mathbf{r}_A , which results from a point charge at \mathbf{r}_B , is

$$\Phi(r_A) = \frac{1}{4\pi\epsilon} \frac{q_B}{r_{AB}} \quad (1)$$



The electric potential is additive in the contribution from multiple charges:

$$\Phi(r_A) = \frac{1}{4\pi\epsilon} \sum_i \frac{q_i}{r_{Ai}} \quad \text{or} \quad \Phi(r_A) = \frac{1}{4\pi\epsilon} \int \frac{\rho_q(\mathbf{r})}{|\mathbf{r}_A - \mathbf{r}|} d\mathbf{r}$$

The electrostatic energy of a particle A as a result of the potential due to particle B is

$$U_{AB}(r_A) = q_A \Phi(r_A) = \frac{1}{4\pi\epsilon} \frac{q_A q_B}{r_{AB}}$$

Note that $U_{AB} = q_A \Phi(r_A) = q_B \Phi(r_B) = \frac{1}{2} (q_A \Phi(r_A) + q_B \Phi(r_B))$, so we can generalize this to calculate the potential energy stored in a collection of multiple charges as

$$\begin{aligned} U &= \frac{1}{2} \sum_i q_i \Phi(r_{Ai}) \\ &= \frac{1}{2} \int \Phi_A(\mathbf{r}_A) \rho_q(\mathbf{r}_A) d\mathbf{r}_A \end{aligned}$$

Dielectric Constant and Screening

Charge interactions are suppressed in a polarizable medium, which depends on the dielectric constant. The potential energy for interacting charges is long range, scaling as r^{-1} .

$$U(r) = \frac{q_A q_B}{4\pi \epsilon r}$$

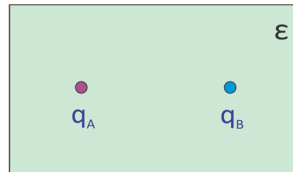
You can think of ϵ as scaling the potential interaction distance $U \propto (\epsilon r)^{-1}$. Here we equate the dielectric constant and the relative permittivity $\epsilon_r = \epsilon/\epsilon_0$, which is a unitless quantity equal to the ratio of the sample permittivity ϵ to the vacuum permittivity ϵ_0 .

The dielectric constant is used to treat the molecular structure and dynamics of the charge environment in a mean sense, to give you a sense of how the polarizable medium screens the interaction of charges. Making use of a dielectric constant implies a separation of the charges of the system into a few important charges and the environment, which encompassed countless countless charges and their associated degrees of freedom.

Two treatments of the electrostatic force that charge b exerts on charge a in a dense medium:

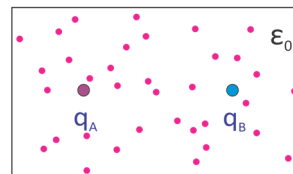
Continuum

$$f_A = \frac{1}{4\pi\epsilon_0} \frac{q_a q_b}{\epsilon_r r^2}$$



Explicit Charges

$$\begin{aligned} f_A &= \frac{1}{4\pi\epsilon_0} \left[\frac{q_a q_b}{r^2} + \sum_{i=1}^N \frac{q_a q_i}{r_{ai}^2} \right] \\ &= \frac{1}{4\pi\epsilon_0} \frac{q_a q_b}{r^2} \left[1 + \sum_{i=1}^N \frac{q_i}{q_b} \frac{r^2}{r_{ai}^2} \right] \end{aligned}$$



i : charged particles of the environment

Free Energy of Ions in Solution

Returning to our continuum model of the solvation free energy, and apply this to solvating an ion. As discussed earlier, ΔG_{sol} will require forming a small cavity in water and turning on the interactions between the ion and water. We can calculate the energy for solvating an ion in a dielectric medium as the reversible work needed to charge the ion from a charge of 0 to its final value q within the dielectric medium:

$$w = \int_0^q \Phi_{\text{ion}} dq \quad (1)$$

As we grow the charge, it will induce a response from the dielectric medium (a polarization) that scales with electrostatic potential: $\Phi = q / 4\pi\epsilon r$. We take the ion to occupy a spherical cavity with radius a . Although we can place a point charge at the center of the sphere, it is more easily solved assuming that the charge q is uniformly distributed over the surface of the sphere. Then the electrostatic potential at the surface of the sphere is $q / 4\pi\epsilon a$ and the resulting work is

$$w = \frac{q^2}{8\pi\epsilon b}$$

In a similar manner, we can calculate the energy it takes to transfer an ion from one medium with ϵ_1 to another with ϵ_2 . We first discharge the ion in medium 1, transfer, and recharge the ion in medium 2. The resulting work, the Born transfer energy, is

$$\Delta w = \frac{q^2}{8\pi a} \left(\frac{1}{\epsilon_2} - \frac{1}{\epsilon_1} \right)$$

If you choose to distribute the charge uniformly through the spherical cavity, the prefactor $q^2/8\pi a$ becomes $3q^2/20\pi a$.

Ion Distributions in Electrolyte Solution

To gain some insight into how ions in aqueous solution at physiological temperatures behave, we begin with the thermodynamics of homogeneous ionic solutions. Let's describe the distribution of ions relative to one another as a function of the concentration and charge of the ions. The free energy for an open system containing charged particles can be written

$$dG = -SdT + Vdp + \sum_{j=1}^{N_{\text{comp}}} \mu_j dN_j + \sum_{i=1}^{N_{\text{charges}}} \Phi(x) dq_i \quad (2)$$

μ_j and N_j are the chemical potential and the number of solutes of type j , in which the solute may or may not be charged and where the contribution of electrostatics is not included. This term primarily reflects the entropy of mixing in electrolyte solutions. The sum i only over charges q_i , under the influence of a spatially varying electrostatic potential. This reflects the enthalpic contribution to the free energy from ionic interactions.

In our case, we will assume that ions are the only solutes present, so that the sum over i and j are the same and this extends over all cations and anions in solution. We can relate the charge and number density through

$$q_i = z_i e N_i$$

where z is the valency of the ion ($\pm 1, 2, \dots$) and e is the fundamental unit of charge. Then expressing dq_i in terms of dN_i , we can write the free energy under constant temperature and pressure conditions as

$$dG|_{T,p} = \sum_i (\mu_i + z_i e \Phi) dN_i = \sum_i \mu'_i dN_i$$

Here μ'_i is known as the electrochemical potential.

To address the concentration dependence of the electrochemical potential, we remember that

$$\mu_i = \mu_i^\circ + k_B T \ln C_i$$

where C_i is the concentration of species i referenced to standard state, $C^\circ = 1\text{M}$. (Technically ionic solutions are not ideal and C_i is more accurately written as an activity.) Equivalently we can relate concentration to the number density of species i relative to standard state. Then the electrochemical potential of species i is

$$\mu'_i(x) = \mu_i^\circ + k_B T \ln C_i(x) + z_i e \Phi(x) \quad (3)$$

Here we write $C(x)$ to emphasize that there may be a spatial concentration profile. At equilibrium, the chemical potential must be the same at all points in space. Therefore, we equate the electrochemical potential at two points:

$$\mu'(x_2) = \mu'(x_1)$$

So from eq. (3)

$$\ln \frac{C(x_2)}{C(x_1)} = \frac{-ze\Delta\Phi}{k_B T} \quad (4)$$

where the potential difference is

$$\Delta\Phi = \Phi(x_2) - \Phi(x_1).$$

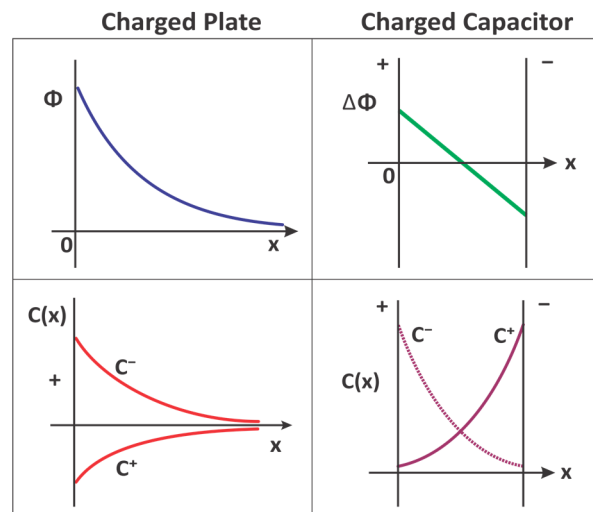
Equation (4) is one version of the Nernst Equation, which describes the interplay of the temperature-dependent entropy of mixing the ions and their electrostatic interactions. Rewriting it to describe $\Delta\Phi$ as a function of concentration is sometimes used to calculate the transmembrane potential as a function of ion concentrations on either side of the membrane.

The Nernst equation predicts Boltzmann statistics for the spatial distribution of charged species, i.e., that concentration gradients around charged objects drop away exponentially in space with the interaction energy

$$\begin{aligned} \Delta U(x) &= ze\Delta\Phi(x) \\ C(x) &= C(x_0)e^{-\Delta U(x)/k_B T} \end{aligned} \quad (5)$$

This principle will hold whether we are discussing the ion concentration profile around a macroscopic object, like a charged plate, or for the average concentration profiles about a single ion. At short distances, oppositely charged particles will have their concentrations enhanced, whereas equally charged objects will be depleted. At short range, the system is dominated by the electrostatic interaction between charges, whereas at long distance, the entropy of mixing dominates.

For the case of charged plates:



Bjerrum Length, ℓ_B

The distance at which electrostatic interaction energy between two charges equals $k_B T$.

$$\text{For } \pm 1 \text{ charges} \quad \ell_B = \frac{1}{4\pi\epsilon} \frac{e^2}{k_B T}$$

At $T = 300 \text{ K}$, $k_B T / e = 25 \text{ mV}$ and

$$\begin{array}{ll} \text{For:} & \epsilon_r = 1 \quad \ell_B = 560 \text{ \AA} \\ & \epsilon_r = 80 \quad \ell_B = 7.0 \text{ \AA} \end{array}$$

For $\ell > \ell_B$ Electrostatic interactions are largely screened, and motion is primarily Brownian

For $\ell < \ell_B$ Attractive and repulsive forces dominate. The Bjerrum length gives ion pairing threshold. For $\ell_B = 7.0 \text{ \AA}$, the ion concentrations are approximately, $6.9 \times 10^{26} \text{ m}^{-3}$ or $\sim 1 \text{ M}$.

Poisson–Boltzmann Equation¹

The Poisson–Boltzmann Equation (PBE) is used to evaluate charge distributions for ions around charged surfaces. It brings together the description of the electrostatic potential around a charged surface with the Boltzmann statistics for the thermal ion distribution. Gauss' equation relates the flux of electric field lines through a closed surface to the charge density within the volume: $\nabla \cdot \bar{E} = \rho / \varepsilon$. The Poisson equation can be obtained by expressing this in terms of the electrostatic potential using $\bar{E} = -\nabla\Phi$

$$-\nabla^2\Phi = \frac{\rho}{\varepsilon} \quad (6)$$

Here ρ is the bulk charge density for a continuous medium.

We seek to describe the charge distribution of ions about charged surfaces of arbitrary geometry. The surface will be described by a surface charge density σ . We will determine $\rho(r)$, which is proportional to the number density or concentration of ions

$$\rho(r) = \sum_i z_i e C_i(r) \quad (7)$$

where the sum is over all ionic species in the solution, and z_i is the ion valency, which may take on positive or negative integer values. Drawing from the Nernst equation, we propose an ion concentration distribution of the Boltzmann form

$$C_i(r) = C_{0,i} e^{-z_i e \Phi(r) / k_B T} \quad (8)$$

Here we have defined the bulk ion concentration as $C_0 = C(r \rightarrow \infty)$, since $\Phi \rightarrow 0$ as $r \rightarrow \infty$. Note that the ionic composition is taken to obey the net charge neutrality condition

$$\sum_i z_i C_{0,i} = 0 \quad (9)$$

The expressions above lead to the general form of the PBE:

$$-\nabla^2\Phi = \frac{e}{\varepsilon} \sum_i z_i C_{0,i} \exp[-z_i e \Phi / k_B T] \quad (10)$$

This is a nonlinear differential equation for the electrostatic potential and can be solved for the charge distribution of ions in solution for various boundary conditions. This can explain the ion distributions in aqueous solution about a charged structure. For instance:

1. M. Daune, *Molecular Biophysics: Structures in Motion*. (Oxford University Press, New York, 1999); M. B. Jackson, *Molecular and Cellular Biophysics*. (Cambridge University Press, Cambridge, 2006).

- Surface (membrane) $\frac{\partial^2 \Phi}{\partial x^2} = \frac{e}{\epsilon} \sum_i z_i C_{0,i} e^{-z_i e \Phi(x)/k_B T}$
- Sphere (protein) $\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial \Phi}{\partial r} = \frac{e}{\epsilon} \sum_i z_i C_{0,i} e^{-z_i e \Phi(r)/k_B T}$
- Cylinder (DNA) $\frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial \Phi}{\partial r} + \frac{\partial^2 \Phi}{\partial z^2} = \frac{e}{\epsilon} \sum_i z_i C_{0,i} e^{-z_i e \Phi(r,z)/k_B T}$

These expressions only vary in the form of the Laplacian ∇^2 . They are solved by considering two boundary conditions: (1) $\Phi(\infty) = 0$ and (2) the surface charge density $\sigma/\epsilon = -\nabla\Phi$. We will examine the resulting ion distributions below.

In computational studies, the interactions of a solute with water and electrolyte solutions are often treated with “implicit solvent”, a continuum approximation. Solving the PBE is one approach to calculating the effect of implicit solvent. The electrostatic free energy is calculated from $\Delta G_{\text{elec}} = \frac{1}{2} \sum_i e z_i \Phi_i$ and the electrostatic potential is determined from the PBE.

As a specific case of the PBE, let’s consider the example of a symmetric electrolyte, obtained from dissolving a salt that has positive and negative ions with equal valence ($z_+ = -z_- = z$), resulting in equal concentration of the cations and anions ($C_{0,+} = C_{0,-} = C_0$), as for instance when dissolving NaCl. Equation (7) is used to describe the interactions of ions with the same charge (co-ions) versus the interaction of ions with opposite charge (counterions). For counterions, z and Φ have opposite signs and the ion concentration should increase locally over the bulk concentration. For co-ions, z and Φ have the same sign and we expect a lowering of the local concentration over bulk. Therefore, we expect the charge distribution to take a form

$$\begin{aligned} \rho &= -zeC_0 \left(e^{ze\Phi/k_B T} - e^{-ze\Phi/k_B T} \right) \\ &= -2zeC_0 \sinh\left(\frac{ze\Phi}{k_B T}\right) \end{aligned} \quad (11)$$

Remember: $2\sinh(x) = e^x - e^{-x}$. Then substituting into eq. (6), we arrive at a common form of the PBE²

$$\nabla^2 \Phi = \frac{2zeC_0}{\epsilon} \sinh\left(\frac{ze\Phi}{k_B T}\right) \quad (12)$$

2. Alternate forms in one dimension:

$$\frac{\partial^2 \Phi}{\partial x^2} = \frac{e}{\epsilon} C_0 2 \sinh\left(\frac{e\Phi}{k_B T}\right) = \frac{k_B T}{e} \frac{1}{\lambda_D^2} \sinh\left(\frac{e\Phi}{k_B T}\right) = \frac{4\pi k_B T}{e} \ell_B C_0 \sinh\left(\frac{e\Phi}{k_B T}\right)$$

Debye–Hückel Theory

Since it is nonlinear, it is not easy to solve the PBE, but for certain types of problems, we can make approximations to help. The Debye–Hückel approximation holds for small electrostatic potential or high temperature conditions such that

$$\frac{ze\Phi}{k_B T} \ll 1$$

This is the regime in which the entropy of mixing dominates the electrostatic interactions between ions. In this limit, we can expand the exponential in eq. (10) as $\exp[-ze\Phi/k_B T] \approx 1 - ze\Phi/k_B T$. The leading term in the resulting sum drops because of the charge neutrality condition, eq. (9). Keeping the second term in the expansion leads to

$$\nabla^2 \Phi = \kappa^2 \Phi \quad (13)$$

where

$$\kappa^2 = \frac{2e^2}{\epsilon k_B T} I$$

and the ionic strength, I , is defined as

$$I = \frac{1}{2} \sum_i C_{0,i} z_i^2$$

Looking at eq. (13), we see that the Debye–Hückel approximation linearizes the PBE. It is known as the Debye–Hückel equation, or the linearized PBE. For the case of the 1:1 electrolyte solution described by eq. , we again obtain eq. (13) using $\sinh(x) \approx x$ as $x \rightarrow \infty$, with

$$\kappa^2 = \frac{2z^2 e^2 C_0}{\epsilon k_B T} = 8\pi z^2 C_0 \ell_B$$

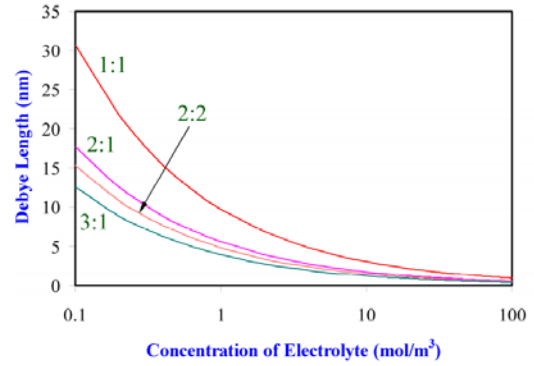
The constant κ has units of inverse distance, and its inverse is known as the Debye length $\lambda_D = \kappa^{-1}$. The Debye length sets the distance scale over which the electrostatic potential decays, i.e., the distance over which charges are screened from one another. For the symmetric electrolytes

$$\lambda_D = \kappa^{-1} = \sqrt{\frac{\epsilon k_B T}{2z^2 e^2 C_0}} \quad (14)$$

As an example: 1:1 electrolytes in H₂O: $\epsilon = 80$; $z_+ = -z_- = 1$; $T = 300$ K leads to

$$\begin{aligned} C_0 = 100 \text{ mM} & \quad \lambda_D = 9.6 \text{ \AA} \\ C_0 = 10 \text{ mM} & \quad \lambda_D = 30.4 \text{ \AA} \\ \lambda_D(\text{\AA}) & \approx 3.04 \cdot [C_0(M)]^{-1/2} \end{aligned}$$

The Debye approximation holds for small electrostatic potentials relative to $k_B T$ ($r > \lambda_D$). For instance, it's ok for ion distribution about large protein or vesicle but not for water in a binding pocket.



The variation of Debye length with concentrations of electrolytes.

Reprinted from P. Ghosh

<http://nptel.ac.in/courses/103103033/module3/lecture3.pdf>.

Ion Distributions Near a Charged Interface

Debye–Hückel Approximation

Describing ions near a negatively charged plane is a way of describing the diffuse layer of cations that forms near the negatively charge interface in lipid bilayers. The simplest approach is to use the Debye–Hückel equation (linearized PBE) in one dimension. x is the distance away from the infinite charged plane with a surface charge density of $\sigma = q/a$.

$$\frac{\partial^2 \Phi(x)}{\partial x^2} = \frac{1}{\lambda_D^2} \Phi(x)$$

Generally, the solution is

$$\Phi(x) = a_1 e^{-x/\lambda_D} + a_2 e^{x/\lambda_D} \quad (15)$$

Apply boundary conditions:

- 1) $\lim_{x \rightarrow \infty} \Phi(x) = 0 \quad \therefore a_2 = 0$
- 2) The electric field for surface with charge density σ (from Gauss' theorem)

$$E = -\left. \frac{\partial \Phi}{\partial x} \right|_{\text{surface}} = \frac{\sigma}{\epsilon} \quad (16)$$

Differentiate eq. (15) and compare with eq. (16):

$$a_1 = \frac{\sigma \lambda_D}{\epsilon}$$

The electrostatic potential decays exponentially away from the surface toward zero.

$$\Phi(x) = \frac{\sigma \lambda_D}{\epsilon} e^{-x/\lambda_D}$$

Nominally, the prefactor would be the “surface potential” at $x = 0$, but the Debye approximation would significantly underestimate this, as we will see later. Substituting Φ into the Poisson equation gives

$$\rho(x) = \frac{-\sigma}{\lambda_D} e^{-x/\lambda_D} \quad (17)$$

Ion distribution density in solution decays exponentially with distance. This description is valid for weak potentials, or $x > \lambda_D$. The potential and charge density are proportional as $\Phi(x) = -\lambda_D^2 \rho(x) / \epsilon$; both decay exponentially on the scale of the Debye length at long range.

Note: Higher ion concentration \rightarrow smaller $\lambda_D \rightarrow$ Double layer less diffuse.

Higher temperature \rightarrow larger $\lambda_D \rightarrow$ Double layer more diffuse.

Note also that the surface charge is balanced by ion distribution in solution:

$$\sigma = -\int_0^{\infty} \rho(x) dx \quad (18)$$

which you can confirm by substituting eq. (17).

Gouy–Chapman Model³

To properly describe the ion behavior for shorter distances ($x < \lambda_D$), one does not need to make the weak-potential approximation and can retain the nonlinear form of the Poisson–Boltzmann equation:

$$\frac{\partial^2 \Phi(x)}{\partial x^2} = \frac{2zeC_0}{\varepsilon} \sinh\left(\frac{ze\Phi(x)}{kT}\right)$$

$$E = -\frac{\partial \Phi}{\partial x} \Big|_{\text{surf}} = \frac{4\pi\ell_B \sigma k_B T}{e^2}$$

In fact, this form does have an analytical solution. It is helpful to define a dimensionless reduced electrostatic potential, expressed in thermal electric units:

$$\tilde{\Phi} = \frac{e}{k_B T} \Phi$$

and a reduced distance which is scaled by the Debye length

$$\tilde{x} = x / \lambda_D$$

Then the PBE for a 1:1 electrolyte takes on a simple form

$$\nabla^2 \tilde{\Phi}(\tilde{x}) = \sinh \tilde{\Phi}(\tilde{x})$$

with the solution:

$$\tilde{\Phi}(\tilde{x}) = 2 \ln \left(\frac{1 + g e^{-\tilde{x}}}{1 - g e^{-\tilde{x}}} \right)$$

Here g is a constant, which we can relate to the surface potential, by setting x to zero.

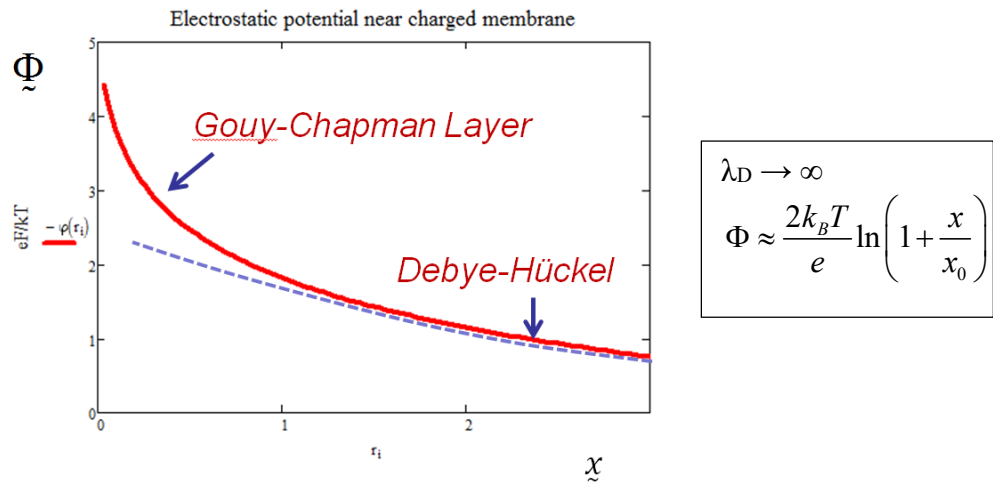
3. H. H. Girault, *Analytical and Physical Electrochemistry*. (CRC Press, New York, 2004).; M. B. Jackson, *Molecular and Cellular Biophysics*. (Cambridge University Press, Cambridge, 2006), Ch. 11.; M. Daune, *Molecular Biophysics: Structures in Motion*. (Oxford University Press, New York, 1999), Ch. 18.; S. McLaughlin, The electrostatic properties of membranes, *Annu. Rev. Biophys. Biophys. Chem.* **18**, 113-136 (1989).

$$\exp(-\Phi(0)/2) = \frac{1-g}{1+g} = -\tanh(\ln(g)/2)$$

$\Phi(0)$ is the scaled surface potential. Using the surface charge density σ we can find:

$$g = -\frac{x_0}{\lambda_D} + \sqrt{1 + \left(\frac{x_0}{\lambda_D}\right)^2} \quad \text{with } x_0 = \frac{e}{2\pi\ell_B\sigma}$$

Then you can get the ion distribution from Poisson equation: $\rho(x) = \varepsilon\nabla^2\Phi(x)$.



The Gouy–Chapman Layer, which is $x < \lambda_D$, has strong enough ionic interactions that you will see an enhancement over Debye–Hückel.

Stern Layer

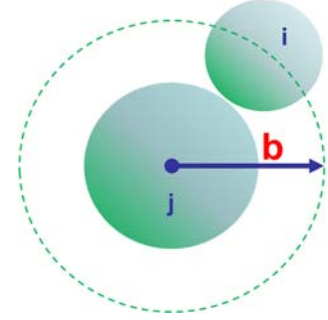
In immediate proximity to a strongly charged surface, one can form a direct contacts layer of counterions on surface: the Stern layer.

The Stern Layer governs the slip plane for diffusion of charged particles. The zeta potential ζ is the potential energy difference between the Stern layer and the electroneutral region of the sample, and governs the electrophoretic mobility of particles. It is calculated from the work required to bring a charge from $x = \infty$ to the surface of the Stern layer.

Ion Distributions Near a Charged Sphere⁴

Now let's look at how ions will distribute themselves around a charged sphere. This sphere could be a protein or another ion. We assume a spherically symmetric charge distribution about ions, and a Boltzmann distribution for the charge distribution for the ions (i) about the sphere (j) of the form

$$\rho(r) = \sum_i e z_i C_{0,i} e^{-z_i e \Phi_j(r) / k_B T} \quad (19)$$



$\Phi_j(r)$ is the electrostatic potential at radius r which results from a point charge $z_j e$ at the center of the sphere. Additionally, we assume that the sphere is a hard wall, and define a radius of closest approach by ions in solution, b . The PBE becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Phi}{dr} \right) = \frac{1}{\epsilon} \sum_i e z_i C_{0,i} e^{-z_i e \Phi(r) / k_B T}$$

To simplify this, we again apply the Debye–Hückel approximation ($ze\Phi \ll k_B T$), expand the exponential in eq. , drop the leading term due to the charge neutrality condition, and obtain

$$\rho(r) = - \sum_i C_{0,i} z_i^2 e^2 \Phi_j(r) / k_B T \quad (20)$$

Then the linearized PBE in the Debye–Hückel approximation is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\Phi}{dr} \right) = \kappa^2 \Phi \quad (21)$$

As before: $\kappa^2 = \lambda_D^{-2} = 2e^2 I / \epsilon k_B T$. Solutions to eq. (21) will take the form:

$$\Phi = A_1 \frac{e^{-\kappa r}}{r} + A_2 \frac{e^{\kappa r}}{r} \quad (22)$$

To solve this use boundary conditions:

- 1) $A_2 = 0$, since $\Phi \rightarrow 0$ at $r = \infty$.
- 2) The field at the surface of a sphere with charge $z_j e$ and radius b is determined from

$$4\pi b^2 E(b) = \frac{z_j e}{\epsilon} \quad (23)$$

4. See M. Daune, *Molecular Biophysics: Structures in Motion*. (Oxford University Press, New York, 1999), Ch. 16.; D. A. McQuarrie, *Statistical Mechanics*. (Harper & Row, New York, 1976), Ch. 15.; Y. Marcus, Ionic radii in aqueous solutions, *Chem. Rev.* **88** (8), 1475-1498 (1988).

Now, using
$$E(b) = -\left. \frac{d\Phi}{dr} \right|_{r=b} \quad (24)$$

Substitute eq. (22) into RHS and eq. (23) into LHS of eq. (24). Solve for A_1 .

$$A_1 = \frac{z_j e e^{\kappa b}}{4\pi\epsilon(1+\kappa b)}$$

So, the electrostatic potential for $r \geq b$ is

$$\Phi(r) = \frac{z_j e}{\underbrace{4\pi\epsilon_0 r}_{\text{vacuum}} \epsilon_r (1+\kappa b)} e^{-\kappa(r-b)} \quad (25)$$

Setting $r = b$ gives us the surface potential of the sphere:

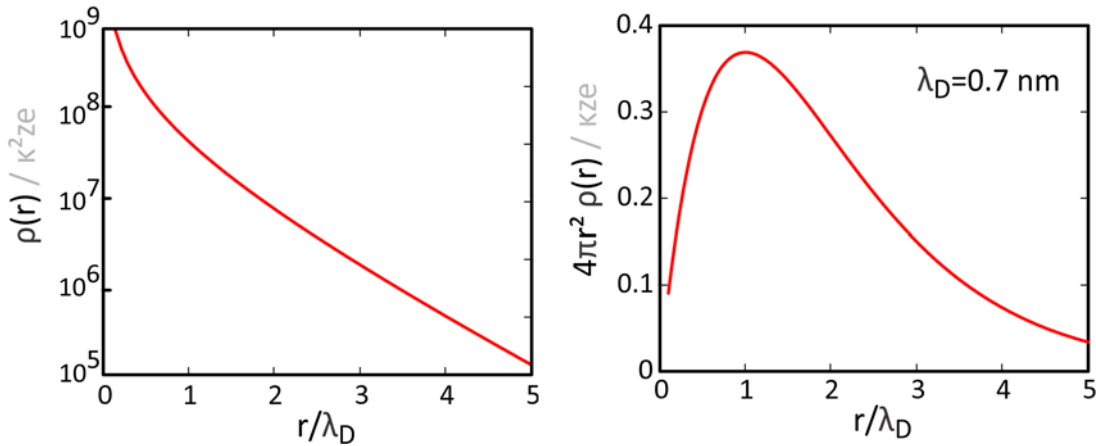
$$\Phi(b) = \frac{z_j e}{4\pi\epsilon b(1+\kappa b)}$$

Note the exponential factor in eq. (25) says that Φ drops faster than r^{-1} as a result of screening. Now substitute eq. (25) into eq. (20) we obtain the charge probability density

$$\rho(r) = \frac{-\kappa^2 z_j e e^{-\kappa(r-b)}}{4\pi r (1+\kappa b)} \quad (26)$$

We see that the charge density about ion drops as $e^{-\kappa(r-b)}/r$, a rapidly decaying function that emphasizes the strong tendency for ions to attract or repel at short range. However, the charge density between r and $r+dr$ is $4\pi r^2 \rho(r)$ and therefore grows linearly with r before decaying exponentially: $r e^{-\kappa(r-b)}$. We plot this function to illustrate the thickness of the “ion cloud” around the sphere, which is peaked at $r = \lambda_D$. Additionally, note, that the charge distribution around that ion is equal and opposite to the charge of the sphere “ j ”.

$$\int_b^\infty \rho(r) 4\pi r^2 dr = -z_j e$$



It is also possible to calculate radial distribution functions for ions in the Debye–Hückel limit.⁵ The radial pair distribution function for ions of type i and j , $g_{ij}(r)$, is related to the potential of mean force W_{ij} as

$$g_{ij}(r) = \exp\left[-W_{ij}(r)/k_B T\right] \quad (27)$$

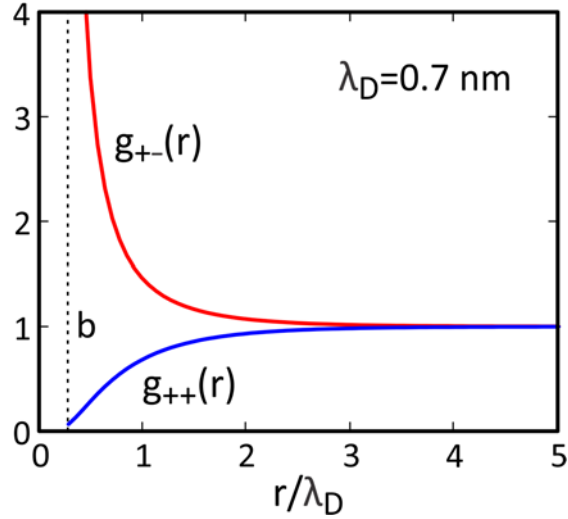
If only considering electrostatic effects, we can approximate W_{ij} as the interaction energy $U_{ij}(r) = z_i z_j \Phi_j(r)$. Using the Debye–Hückel result, eq. (25),

$$U_{ij}(r) = \frac{z_i z_j e^2}{4\pi\epsilon(1+\kappa b)} \frac{e^{-\kappa(r-b)}}{r}$$

Let's look at the form of $g(r)$ for two singly charged ions with $\lambda_D = 0.7$ nm, $\epsilon = 80$, and $T = 300$ K. The Bjerrum length is calculated as $\ell_B = e^2/4\pi\epsilon k_B T = 0.7$ nm. Since the Debye–Hückel holds for $ze\Phi \ll k_B T$, we can expand the exponential in eq. as

$$g_{ij}(r) = 1 - \chi_{ij} + \frac{1}{2} \chi_{ij}^2 + \dots$$

where we define $\chi_{ij} = U_{ij}(r)/k_B T = \ell_B e^{-\kappa(r-b)} r^{-1} (1+\kappa b)^{-1}$. The resulting radial distribution function for co- and counterions calculated for $b = 0.15$ nm are shown below.



5. See D. A. McQuarrie, *Statistical Mechanics*. (Harper & Row, New York, 1976), Ch. 15.

Readings

1. M. Daune, *Molecular Biophysics: Structures in Motion*. (Oxford University Press, New York, 1999), Ch. 16, 18.
2. D. A. McQuarrie, *Statistical Mechanics*. (Harper & Row, New York, 1976), Ch. 15.