

# Chem 163, Lecture 19

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## 1 Electrostatics in solution

Much of the material we'll cover today is in Chapters 11 and 12 of Israelachvili. It's a really fabulous book, and pretty easy to read. It give a good introduction to the richness of phenomena that occur between bodies immersed in water or electrolyte solutions.

Electrostatics in solution is a complicated beast because entropy makes charges want to move around randomly, but the charges exert long-range forces on each other. Thus each ion feels forces not only from fixed charges, but also fluctuating forces from all the other ions.

## 2 Introduction

Almost everything in a cell is charged: DNA has a formal negative charge of 2 electrons per base pair due to the phosphate groups (we'll see that this isn't strictly accurate in an electrolyte solution).

Proteins have nonuniform distributions of charge due to the different amino acids (even though they are called "amino acids", they should more accurately be called "amino zwitterions" because the amino group acts as a base). In a protein the amino group and the carboxylic acid group are both occupied by the amide bond, and the true charge of the protein is determined by the behavior of the side groups.

For most amino acids the side groups are electrically neutral at neutral pH. Exceptions are: Aspartic Acid (Asp) and Glutamic Acid (Glu) which have negatively charged carboxylate groups on the side-chains; and Lysine (Lys), Arginine (Arg), and Histidine (His) which are positively charged.

Most lipid membranes of cells are made of a mixture of zwitterionic lipids such as phosphatidylcholine (PC), and anionic (negatively charged) lipids such as dioleoyl phosphatidyl serine (DOPS).

In fact, most materials immersed in liquid develop a surface charge. Even glass, which is seemingly inert, becomes negatively charged in water because SiOH groups on the surface are slightly acidic, forming SiO<sup>-</sup> moieties. Most solids are slightly acidic or slightly basic. Also, some solids preferentially adsorb charged species from solution. For instance, a hydrophobic surface will adsorb surfactants from solution, and these surfactants might be anionic or cationic. Even the air-water interface is often charged, either due to the presence of surfactants, or because different ions actually have different affinities for this interface.

The fact that almost everything is charged has important biological implications for the adhesion of cells; the interactions of biomolecules; the properties of DNA; and the conduction of neural impulses. In fact, van der Waals forces are always attractive between like bodies, so were it not for electrostatics all the components in the cell would spontaneously aggregate. These charges are also extremely important technologically: they are used in electrophoresis, in microfluidics, and in purifications.

The plan for today is to discuss the charge and potential distribution around a single charged object. Then we'll discuss the charge-mediated forces between objects. In solutions of multivalent counterions the mean-field description we use will break down, and we'll discuss ways people are trying to go beyond mean-field theory. This is a topic for much current research.

Then we'll discuss what happens when we have external electric fields around charged bodies. That leads to the coupled worlds of electrophoresis and electroosmosis. The behavior of charged bodies in solution is wondrously subtle and is a subject of much active research.

## 2.1 Mean-field approximation

It would be hopelessly complicated to apply Coulomb's law to the motion of every charged particle in a solution, and then to try a Langevin or Smoluchowski approach to the motion of the particles. The only possibility for making progress is to make a mean-field approximation, as follows: we assume that each charge interacts with the average density of surrounding charges, and we ignore the fact that the motion of nearby charges might be correlated. That is, while the real interaction energy between two pieces of solution is:

$$dU = \frac{\langle \rho_1 \rho_2 \rangle}{4\pi\epsilon\epsilon_0 r_{1,2}} dV_1 dV_2, \quad (1)$$

we'll approximate this energy as:

$$dU = \frac{\langle \rho_1 \rangle \langle \rho_2 \rangle}{4\pi\epsilon\epsilon_0 r_{1,2}} dV_1 dV_2. \quad (2)$$

This factorization is tantamount to ignoring fluctuations. We do this at our peril, but we are reasonably safe as long as each charge interacts with a large number of other charges. Then we can assume the fluctuations  $\langle \delta\rho^2 \rangle / \langle \rho^2 \rangle$  are small. There are some famous cases where this mean-field approximation fails spectacularly.

## 3 Charged interfaces

### 3.1 Gouy-Chapman Theory

Consider a planar charged surface immersed in an electrolyte solution. In an inhomogeneous potential the concentration of a mobile charged species  $i$  obeys

$$C_i = C_i^0 \exp\left(\frac{-z_i e \Phi}{k_B T}\right), \quad (3)$$

where  $z_i$  is the valence,  $e$  is the electron charge, and  $\Phi$  is the local potential. The region of inhomogeneous potential is assumed to be connected to a vast reservoir of particles at zero potential and with concentration  $C_i^0$ . It is almost always the case that the enhancement or depletion of ions near an interface leaves the bulk concentration essentially unchanged.

The excess charge density is

$$\rho = \sum_i C_i z_i e. \quad (4)$$

The potential in turn depends on the excess charge density via Poisson's equation. For the planar geometry we are considering here, this becomes

$$\frac{d^2\Phi}{dx^2} = -\frac{1}{\epsilon\epsilon_0}\rho(x). \quad (5)$$

Together Eqs. 3–5 form the coupled Poisson-Boltzmann equation, a nonlinear differential equation:

$$\frac{d^2\Phi}{dx^2} = -\frac{1}{\epsilon\epsilon_0} \sum_i C_i^0 z_i e \exp\left(\frac{-z_i e\Phi}{k_B T}\right). \quad (6)$$

Before we get into the complete solution, let's consider the limiting case where the exponential term is small, i.e. the potential is  $\ll 26$  mV/ $z$  (a frequently violated condition). Then we can linearize the exponent, and we get the equation:

$$\frac{d^2\Phi}{dx^2} = -\frac{e}{\epsilon\epsilon_0} \sum_i C_i^0 z_i \left(1 - \frac{-z_i e\Phi}{k_B T}\right). \quad (7)$$

The first term on the r.h.s. disappears because  $\sum_i C_i^0 z_i = 0$  by electroneutrality of the bulk solution. The  $\Phi$  dependent part of the r.h.s. gives us the equation

$$\frac{d^2\Phi}{dx^2} = \Phi \frac{1}{\epsilon\epsilon_0 k_B T} \sum_i C_i^0 z_i^2 e^2. \quad (8)$$

The solutions to this equation have the form

$$\Phi(x) = Ae^{x/\lambda_D} + Be^{-x/\lambda_D}, \quad (9)$$

where the Debye length is:

$$\lambda_D = \left(\frac{\epsilon\epsilon_0 k_B T}{\sum_i C_i^0 z_i^2 e^2}\right)^{1/2}. \quad (10)$$

For the special case of a 1:1 electrolyte, the Debye length is:

$$\lambda_D = \left(\frac{\epsilon\epsilon_0 k_B T}{2C^0 z^2 e^2}\right)^{1/2}. \quad (11)$$

Table 3.1 gives the Debye lengths (sometimes called the ‘‘Double layer’’ thickness) for various concentrations of monovalent 1:1 electrolytes.

Where does the Debye length come from? Well, there are two fundamental length scales in an ionic solution: the mean spacing between ions (determined by the concentration), and

$C^0$ (Molar)	$\lambda_D$ (nm)
1	0.3
$10^{-1}$	0.96
$10^{-2}$	3.0
$10^{-3}$	9.6
$10^{-4}$	30
$10^{-7}$	960

Table 1: Double layer thicknesses for various concentrations of a 1:1 monovalent electrolyte. The last line corresponds to the case of deionized water, for which  $[\text{H}^+] = [\text{OH}^-] = 10^{-7}$  M.

the Bjerrum length,  $l_B$ , which is the distance at which the interaction energy of two unit charges equals  $k_B T$ :

$$l_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T}. \quad (12)$$

For unit charges in water at room temperature, the Bjerrum length is 0.7 nm.

The Debye length is an amalgamation of these two lengths. Ignoring the numerical factor, which is just a convention, we have:

$$\lambda_D = \left( \frac{1}{4\pi \sum_i C_i^0 l_{B,i}} \right)^{1/2}. \quad (13)$$

You can check the units to see that this works.

For a charged planar interface exposed to a semi-infinite solution in the positive  $\hat{x}$  direction, clearly only the decaying exponential is physical:  $\Phi(x) = Ae^{-x/\lambda_D}$ . Now we need to find the prefactor  $A$ . To do this, we will use the fact that the electric field ( $d\Phi/dx$ ) far from the interface vanishes. If it didn't vanish in the bulk, there would be a net electric current, which would flow until the electric field did vanish. This implies that if the bound surface charge density is  $\sigma$ , the total charge held in the double layer must  $-\sigma$ .

Recall from electrostatics that if you have an isolated surface with charge density  $\sigma$ , the electric field on either side of the surface is:

$$\mathbf{E} = \frac{\sigma}{2\epsilon\epsilon_0} \hat{\mathbf{n}}, \quad (14)$$

where  $\hat{\mathbf{n}}$  is the unit-normal to the surface. This formula is a consequence of Gauss' law. Now we have surface charge  $\sigma$  on our solid, and  $-\sigma$  in the solution, so the total electric field at the surface of the solid is:

$$\mathbf{E}_{\text{tot}} = \frac{\sigma}{\epsilon\epsilon_0} \hat{\mathbf{n}}. \quad (15)$$

This electric field is just  $\frac{d\Phi}{dx}|_{x=0}$ . Plugging in our result from the solution to the linearized P-B equation we get:

$$\frac{A}{\lambda_D} = \frac{\sigma}{\epsilon\epsilon_0}, \quad (16)$$

or

$$\Phi(x) = \frac{\lambda_D \sigma}{\epsilon\epsilon_0} e^{-x/\lambda_D}. \quad (17)$$

The bulk charge density at the interface is:

$$\begin{aligned}\rho(x=0) &= -\epsilon\epsilon_0 \left. \frac{d^2\Phi}{dx^2} \right|_{x=0} \\ &= \frac{-\sigma}{\lambda_D}.\end{aligned}\tag{18}$$

This result makes sense: the screening charge is proportional to the fixed charge  $\sigma$ , spread over sheet of thickness  $\lambda_D$ .

Let's now calculate the concentrations of the two ions at the interface for the case of a simple 1:1 electrolyte. In the linearized limit, the deviations in concentration of the two ions are equal and opposite. Say  $C_+ = C^0 + \Delta C$  and  $C_- = C^0 - \Delta C$ . Then the charge density is just  $\rho = 2ze\Delta C$ , or

$$\Delta C = \frac{-\sigma}{2\lambda_D ze}.\tag{19}$$

The solution to the full nonlinear P-B equation is given by the Gouy-Chapman formula:

$$\frac{\tanh(ze\Phi/4k_B T)}{\tanh(ze\Phi_0/4k_B T)} = e^{-x/\lambda_D},\tag{20}$$

where  $\Phi_0$  is the potential on the surface.

The Gouy-Chapman formula is an implicit solution for the potential. To get the exact potential we need to solve numerically.

For potentials where the nonlinear term in the P-B equation is significant, the Gouy-Chapman theory breaks down anyway because it does not take into account the finite size of the ions. In the Gouy-Chapman theory, ions may approach infinitesimally close to the surface, leading to a divergence in the screening charge at large surface potentials. The Stern theory remedies this defect by setting a finite distance of minimum approach, but we don't need to go into it here.

For a colloidal particle, the above analysis applies provided that the radius  $a \gg \lambda_D$ . Then one can think of the surface as essentially planar. Table 3.1 shows that this condition applies in standard buffers for objects larger than a few nanometers in diameter.

### 3.2 Charge renormalization

The effects of any charge are exponentially screened over a distance of order the Debye length in solution. So electrostatics in solution looks nothing like electrostatics in vacuum, where interactions fall off as  $1/r$ . The potential around a point charge can be shown to fall off as:

$$\Phi(r) \sim \frac{e^{-r/\lambda_D}}{r}.\tag{21}$$

This potential is called a Yukawa potential and has the same functional form as the strong nuclear force that holds the protons and neutrons together in the nucleus. We all know that the electrostatic interaction is mediated by photons, which are massless. In the case of the strong nuclear force, the potential is mediated by pions, which have a mass, and therefore can only propagate a finite distance before they decay. The exponential decay of pions as

they propagate is the cause of the exponentially decaying Yukawa potential in the strong nuclear force.

Anyway, we find that far from a charged surface, the potential decays exponentially with a decay constant  $\lambda_D$ , as

$$\Phi(x) = \Phi_{\text{eff}}^0 e^{-x/\lambda_D}. \quad (22)$$

Here  $\Phi_{\text{eff}}^0$  is the “effective” surface potential which is not equal to the true surface potential, due to the accumulation of ions near the surface. This effect is called “charge renormalization” and also happens in quantum electrodynamics. Due to charge renormalization, highly charged surfaces don’t lead to potentials that are very different from weakly charged surfaces, except very near the surface.

## 4 Ion-mediated forces

Consider two parallel planar surfaces with equal surface charge  $\sigma$ . In the absence of mobile ions, what’s the electric field in the gap? It’s zero! Consider the symmetry of the problem to convince yourself of this.

This means that the potential in the gap is initially constant, so counterions will accumulate in the gap. These ions repel each other, so they tend to accumulate near the charged interfaces (just the way charged particles accumulate near the surface of a conductor). You might be tempted to think that the counterions accumulate near the surface because of their attraction for the surface, but that would be wrong.

Do the two surfaces attract or repel each other? This is a subtle issue. Energetically, you might think that the counterions want to be closer to the surfaces. If you squeeze the surfaces together, the counterions are confined closer to the surfaces, so the electrostatic energy would be lower. But this is wrong! We just said that the surfaces contribute nothing to the electric field in the gap. So every counterion is pulled on equally by both surfaces. On the other hand, by squeezing the surfaces together you’ve increased the concentration of counterions (remember the total number must remain constant and is set by the surface charge density), so the osmotic pressure goes up. You get a net repulsive force for like-charged surfaces.

We’ll use a trick to calculate the pressure between the walls. If this pressure were anywhere inhomogeneous, there would be a flow of solution from the region of higher pressure to the region of lower pressure. So we know the pressure is constant across the gap. We’ll calculate the pressure at the midpoint, since that is the easiest. This pressure is due to the osmotic pressure of the counterions. So if we can find their concentration, we can find their osmotic pressure. Actually, we want the *excess* osmotic pressure above that of the bulk solution. This excess pressure is:

$$P = k_B T \left[ \sum_i C_i - \sum_i C_i^0 \right]. \quad (23)$$

If we assume a symmetric 1:1 electrolyte, then each sum has two terms, one for cations and

one for anions. Let's regroup the terms to have the cations together and the anions together:

$$\begin{aligned} P &= k_B T C^0 [(e^{-e\Phi/k_B T} - 1) + (e^{+e\Phi/k_B T} - 1)] \\ &\approx \frac{e^2 \Phi^2 C^0}{k_B T}. \end{aligned} \quad (24)$$

To get the second line we took a second order Taylor expansion assuming that the potential at the midpoint between the plates was small compared to  $k_B T$ . Since we only went to first order in  $e\Phi_0/k_B T$  in the linearized P-B problem, does Eq. 24 require deviating from the linearized P-B solution? Possibly, depending on how big an approximation the linearized P-B equations make.

Another reasonable approximation is that this potential is the sum of the potentials due to each of the plates in isolation. Using the full nonlinear P-B equations, this assumption yields

$$\Phi(h/2) \approx \frac{8k_B T \gamma}{e} e^{-h/(2\lambda_D)}, \quad (25)$$

where

$$\gamma = \tanh \left[ \frac{ze\Phi_{\text{surf}}}{4k_B T} \right]. \quad (26)$$

The pressure is then:

$$P = 64k_B T C^0 \gamma^2 e^{-h/\lambda_D}. \quad (27)$$

For low surface potential, this simplifies further to:

$$P \approx \frac{2\sigma^2}{\epsilon\epsilon_0} e^{-h/\lambda_D}, \quad (28)$$

which is indeed what we would have gotten from the linearized P-B solution. Note that the surface pressure between two charged plates in vacuum is

$$P_{\text{vac}} = \frac{2\sigma^2}{\epsilon\epsilon_0}, \quad (29)$$

so the Debye screening decreases the pressure proportional to the amount of screening between the plates, as one might expect.

For spheres of radius  $R$ , a similar calculation shows that the force is

$$F \approx \frac{2\pi R \lambda_D \sigma^2}{\epsilon\epsilon_0} e^{-h/\lambda_D}. \quad (30)$$

Comparing the two expressions above, we see that the effective ‘‘contact area’’ over which the pressure is applied to the sphere is the product of the radius and the Debye length. This should remind you of the example we considered earlier of depletion forces, where the *excluded* particles yielded an attractive force given by the product of the osmotic pressure, the radius of the sphere, and the size of the small particles.

## 5 DLVO theory

DLVO stands for: Derjaguin, Landau, Verwey, and Overbeek, four clever fellows who came up with this theory in 1948 (the same year as the Casimir Polder result—after WWII all these people who had been working on weapons or hiding during the war started to think about interesting problems again. There was a huge burst of creative activity immediately following the war.).

Let's now talk qualitatively about the interaction of colloidal particles in water. The dominant forces are usually electrostatics and van der Waals. The electrostatics we just discussed. Let's assume that the separation between the spheres,  $h$  is much less than their radii,  $R$ . Let's further assume that the Debye length is much less than the radii too. Then the non-retarded van der Waals potential is approximately:

$$U_{\text{vdw}} = -\frac{AR}{12h}, \quad (31)$$

where  $A$  is an empirical constant called the Hamaker constant. The total potential is the sum of the van der Waals term and what you get from integrating the double-layer force, to wit:

$$U = -\frac{AR}{12h} + \frac{2\pi R\lambda_D^2\sigma^2}{\epsilon\epsilon_0}e^{-h/\lambda_D}. \quad (32)$$

[DRAW EXAMPLES OF DLVO POTENTIAL]

This potential can have various shapes depending on the relative strengths of the van der Waals and electrostatic contributions. At low salt, electrostatics dominates, so the potential has a long-range repulsion and a short-range attraction. Under such conditions colloidal particles are usually stable in solution—they would like to aggregate, but the rates of aggregation are imperceptibly slow. At intermediate salt concentrations, the potential develops a local minimum at intermediate radii. That is, particles can become bound, but not aggregated. Lowering the salt again will cause the particles to re-separate. This process is called flocculation. At high salt, the dispersion becomes unstable and the particles irreversibly aggregate. This is called coagulation.

There is a critical concentration of ions at which coagulation occurs, creatively called the “critical coagulation concentration” or ccc. The ccc occurs when the potential maximum crosses zero, i.e. when  $U(h) = 0$  and  $dU/dh = 0$ . You can show that this concentration depends on the valence of the charges to the *sixth* power:

$$ccc \propto 1/z^6. \quad (33)$$

This is an amazing result. Particles with valence 2 are 64 times as good at coagulation as are particles of valence 1. Particles of valence 3 are 729 times as good!

While this result is reasonably consistent with experiment, our whole approach runs into trouble when we deal with polyvalent ions. The problem is that our initial assumption, that we can neglect fluctuations, breaks down. Ion-correlation effects can lead to very odd effects, such as the attraction of like-charged bodies in solution (think of the classical analog of the van der Waals force), and may play an important role in the stability of RNA and protein structures. This is a topic of much current research and is something that is very interesting and subtle.



## 5.1 Applications of DLVO

One application of this is in the condensation of DNA. The molecule spermine has 4 amines that can be protonated at physiological pH (it probably has a charge of +3 or +4). This makes it an extremely effective condensing agent. As its name suggests, it is in high concentration in sperm, where a lot of DNA needs to be packed into a small compartment. Other polyvalent cations, such as Cobalt and Ruthenium complexes are also very good at condensing DNA.

Coagulation is a very important process. For instance, when you have a river run into the ocean, you get a mixing of the fresh water from the river with the salt water from the ocean. Rivers typically carry a huge amount of silt and dirt in the form of colloidal particles. When these particles encounter salt water, all of a sudden they aggregate and become heavy enough to fall out of solution. This leads to deposits of mud where the river reaches the ocean. This mud then blocks the path of the river, so the river fans out into the characteristic delta pattern.

Another example of application of the DLVO theory is in the making of cheese and yogurt. Of course this is a very complicated process, and the details depend on whether you are making yogurt, or any of the hundreds of different kinds of cheeses. But the main idea is that bacteria ferment the sugar lactose into lactic acid. The acid lowers the pH and neutralizes the negative surface charge on casein and fat globules. Once these globules have lost their protective electrostatic repulsion they aggregate into a solid.

I hope you can see from the discussion of today and the previous two classes that the forces between bodies in solution can be wonderfully subtle and complex. If you include van der Waals, electrostatic, and depletion forces, it is possible to have effective pair-potentials with several maxima and minima. As you tune the system parameters by changing pH, ionic strength, temperature, surfactants, you can cause particles to transition between many qualitatively different regimes.