

# V. Electrostatics

## Lecture 28: Electrostatic Correlations

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### 1. Mean-Field Theory

Until now, we have developed continuum models for the dynamics of electrolytes at the macroscopic scale, much larger than typical length scales for intermolecular forces. In particular, we have used principles of nonequilibrium thermodynamics, to arrive at general models of interfacial voltage (Nernst equation), reaction kinetics (Butler-Volmer equation), and transport (Poisson-Nernst-Planck equations):

$$\begin{cases} \mu_i = k_B T \ln(\gamma_i \bar{c}_i) + z_i e \bar{\phi} \\ F_i = -M_i \bar{c}_i \nabla \mu_i \\ \frac{\partial \bar{c}_i}{\partial t} + \nabla \cdot F_i = 0 \\ -\nabla \cdot (\epsilon \nabla \bar{\phi}) = \bar{\rho} = \sum_i z_i e \bar{c}_i \end{cases}$$

For short-range interactions, such as chemical bonds or collision forces contributing to the diffusivity ( $D_i = M_i / k_B T$ ), this formulation is easily justified, but for long-range interactions, such as the electrostatic Coulomb potential, which decays very slowly with distance (like  $1/r$ ), it can be more problematic.

Continuum models like the Poisson-Nernst-Planck equations are “mean-field approximations” which express the statistically averaged behavior of a large number of discrete ions in terms of only the mean concentrations  $\bar{c}_i$  (number/volume) and a particular definition of the mean potential  $\bar{\phi}$ . Each ion migrates in the mean electric field,  $\bar{E} = -\nabla \bar{\phi}$ , which is self-consistently produced by the mean charge density, not by the discrete, fluctuating charges in the molecular system. Due to the long-range nature of electrostatic forces, however, discrete ion-ion interactions leading to “electrostatic correlations” are important, even in dilute electrolytes.

### 2. Bjerrum length

What is the length scale below which electrostatic correlations are important? In very dense charged systems, it is the ion size, as in solvent free ionic liquids (see below). In typical electrolytes, however, the relevant scale is the Bjerrum length, where the bare Coulomb energy between two elementary charges is balanced by the thermal fluctuation energy:

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

At larger length scales, we may expect that thermal fluctuations are strong enough to justify replacing discrete ion-ion Coulomb forces with a continuum mean-field theory. In water at room temperature, the Bjerrum length is 0.7nm, which is only a few molecular lengths, so it makes sense to try to use mean-field theories based on the continuum PNP equations (such as Gouy-Chapman) to describe the diffuse part of the double layer, at least at low salt concentrations, when the Debye length greatly exceeds the Bjerrum length. Note that these two length scales are related as follows:

$$\lambda_D = \frac{1}{\sqrt{4\pi l_B \sum_i z_i^2 c_0}} = \frac{1}{\sqrt{8\pi l_B I}}$$

where  $I = \frac{1}{2} \sum_i z_i^2 c_0$  is the molar ionic strength, which arises in Debye-Huckel theory, based on linearization of the PNP mean-field theory above for small voltages. (See also below.) The condition  $\lambda_D \gg l_B$ , which is needed to justify a mean-field theory of the diffuse part of the double layer, thus corresponds to an upper bound on the ionic strength:

$$I \ll \frac{1}{6} \cdot \frac{3}{4\pi l_B^3}$$

For a  $z:z$  electrolyte, this implies that the mean volume per ion must be at least  $3z^2$  times larger than the “correlation volume” (inside a sphere whose radius is the Bjerrum length) in order for a mean-field theory of electrostatics to hold.

### 3. Correlation Functions

How can we go beyond mean field theory, if we know the interactions between discrete particles (e.g. Coulomb)? We simply need a statistical description of the liquid that gives us the probabilities of finding different local ionic configurations, whose energies we could in principle calculate. From experiments (e.g. neutron scattering) or simulations (e.g. molecular dynamics, Monte Carlo, etc.), it is possible to measure statistical correlations between discrete particles, related to their interactions. For a given system of ions of species  $i$  and species  $j$ , the number of pairs of said ion, separated by a distance  $r$  to  $r+dr$  is given by

$$n_{ij}(r) = 4\pi r^2 g_{ij}(r) \bar{c}_i \bar{c}_j$$

where  $g_{ij}(r)$  is the pair correlation function ( $g$  is unity in a uniform ideal gas). In a crystal with long-range order,  $g(r)$  has sharp, well-separated peaks located around the discrete mean neighbor separations. In liquid (Fig 1), there is only short range order up to several molecular neighbors, beyond which there is complete mixing  $g=1$ .

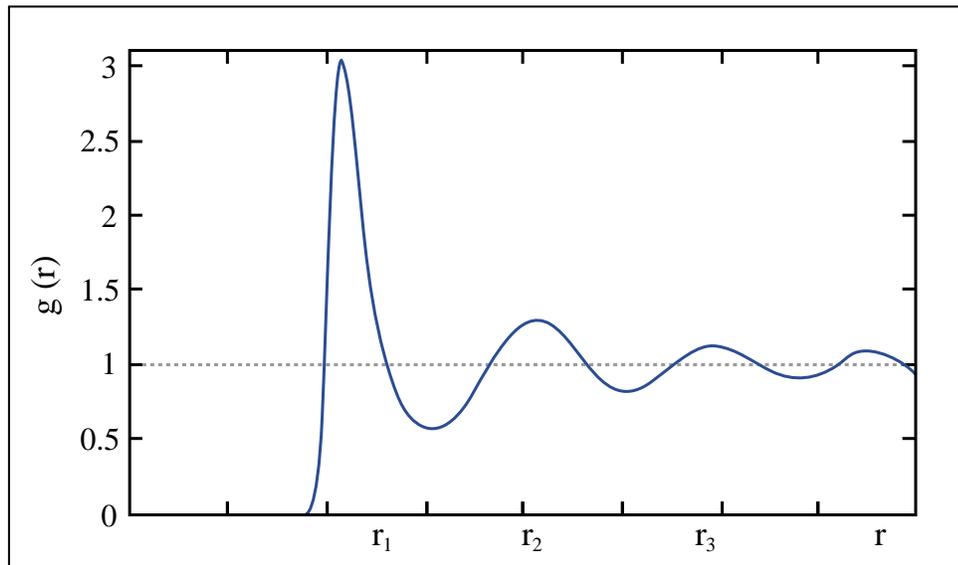


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FIG. 1 Typical  $g(r)$  for a liquid. The first neighbor distance is  $r_1$ , the second is  $r_2$ , etc.

For pairwise interactions, the enthalpic contribution to excess chemical potential (due to internal energy, not entropy) can be expressed as sum over all species of radial integrals over the pair correlation function

$$\mu_i^{ex} = k_B T \ln \gamma_i = \frac{1}{2} \sum_j \int_0^\infty K_{ij}(r) 4\pi r^2 g_{ij}(r) \bar{c}_j dr + \text{many-body terms}$$

where  $K_{ij}(r)$  = pair interaction energy. The factor of  $\frac{1}{2}$  prevents double-counting when evaluating all of the pairwise interactions.

For example, in the case of a single species with only pairwise self-interactions (regular solution model), we have expressed the excess chemical potential as  $\mu^{ex} = -2\Omega c$ , so we can now relate the macroscopic regular solution parameter to the microscopic statistical physics via

$$\Omega = -\int_0^\infty K(r)g(r)\pi r^2 dr$$

From this expression, we can already see the difficulty in describing electrostatic forces in condensed phases, because the slow decay of the Coulomb interaction,  $K \sim 1/r$ , makes the interaction energy infinite, unless there is a sufficiently fast decay of the pair correlation function (faster than  $1/r^2$ ). Of course, the interaction energy must be finite, and indeed, we will show in the next section that the electrostatic pair correlation function decays exponentially, at least in a bulk dilute electrolyte.

In an electrolyte, we have  $g_{ij}(r)$  for different types of ion pairs.  $g_{+}(r)$  is the counter-ion (opposite charge) pair correlation function, and  $g_{-}(r)$  is the co-ion (same charge) pair correlation. As shown in the figure, counterions are generally attracted ( $g_{+} > 1$ ), while co-ions are repelled ( $g_{-} < 1$ ).

<1). The difference between these distributions defines the statistically averaged the “screening cloud” of excess opposite charge around each ion. The long range tail of these correlation functions is dominated by electrostatics and can be modeled by Debye-Huckel theory (below), as a first approximation. However, as shown in Fig 2, there can be an oscillation in the charge density of the screening cloud (crossing of the two correlation functions at 10Å), due to weak “overscreening” by the closest counter-ions. This effect is much stronger in solvent-free ionic liquid, and requires more sophisticated electrostatic models (below).

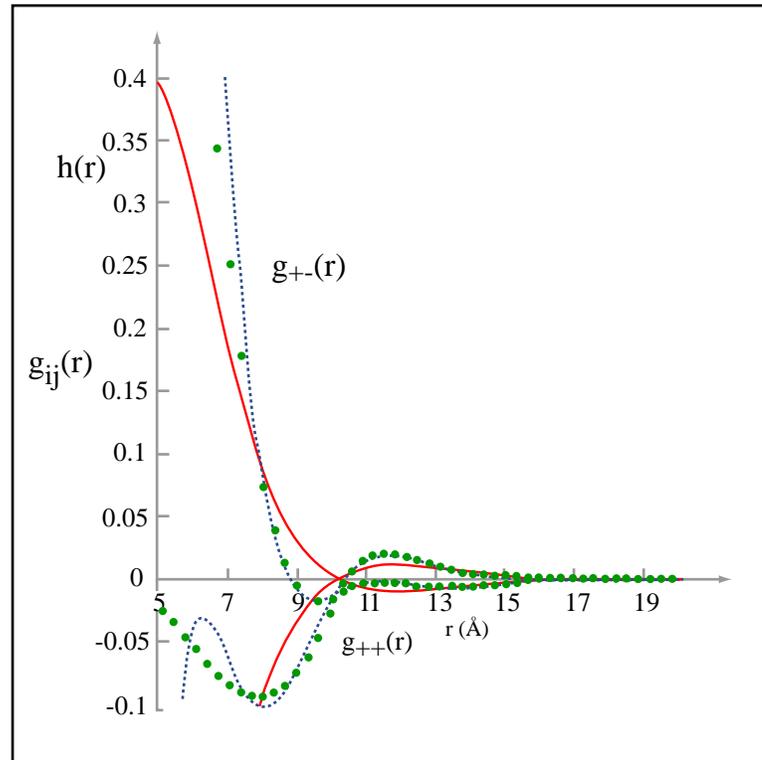


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FIG. 2 Total correlation functions for a monovalent binary electrolyte with diameter of the ion = 5Å.  $g_{++}(r)$  is the pair correlation function for a central atom and a neighboring co-ion and shows repulsion.  $g_{+-}(r)$  is the counter-ion pair correlation function and shows attraction. The solid lines result from asymptotic analysis of the double layer and the dashed lines result from setting the mean force potential equal to the sum of the core and electrostatic asymptotes.

#### 4. Electrostatic Correlations in a Dilute Electrolyte (Debye-Hückel Theory)

The bare coulomb interaction in a dielectric solvent for point charges is given by

$$K_{ij} = \frac{(z_i e)(z_j e)}{4\pi\epsilon r}$$

To calculate ion profiles in the “screening cloud,” the region of excess diffuse charge or diffuse countercharge, of a spherical central ion of species  $I$ , we use the Debye-Hückel approximation

$$c_j(r) = g_{ij}(r) \bar{c}_j = \bar{c}_j e^{-z_j e \psi / k_B T} \approx \bar{c}_j \left( 1 - \frac{z_j e \psi}{k_B T} \right)$$

where  $\psi$  is the perturbation of electrostatic potential in the screening cloud of the central ion and is  $\psi = \phi - \bar{\phi}$ . The fluctuations have energy on the order of  $\sim k_B T$  which is of a small enough magnitude that the linearization in the above equation is valid. The linear response of a screened central ion is then given by the linearized Poisson-Boltzmann equation, or Debye-Hückel equation, for a general dilute electrolyte:

$$\lambda_D^2 \nabla^2 \psi = \psi$$

Over the length scales considered, the potential varies only with distance from the central ion. The potential is thus a function of  $r$  only and the above equation simplifies to

$$\frac{\lambda_D^2}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) = \psi$$

Because the fluctuations in the potential decrease with increasing distance from the central ion ( $\phi \rightarrow \bar{\phi}$  as  $r \rightarrow \infty$ ),  $\psi(\infty) = 0$ . Applying this boundary condition, the solution to the above equation is a modified spherical Bessel function

$$\psi(r) = A \frac{e^{-r/\lambda_D}}{r/\lambda_D}$$

The constant  $A$  can be evaluated using Gauss's law for a point charge. The electric field generated about a point charge is indistinguishable from that at the surface of a spherically symmetric charge distribution of the same total charge.

$$-\epsilon \left. \frac{d\psi}{dr} \right|_{r=a} = \frac{z_i e}{4\pi a^2}, \text{ which implies } A = \frac{e^{a/\lambda_D} z_i e}{4\pi \epsilon (a + \lambda_D)}$$

Incorporating these boundary conditions gives the screened Coulomb potential

$$\psi(r) = \frac{e^{(a-r)/\lambda_D} z_i e}{4\pi \epsilon r (1 + \frac{a}{\lambda_D})}$$

The pair correlation function then becomes

$$g_{ij}(r) = 1 - \frac{(z_i e)(z_j e) e^{(a-r)/\lambda_D}}{4\pi \epsilon k_B T r (1 + \frac{a}{\lambda_D})}$$

This form describes the long-range tail of the correlation functions, which decay exponentially at the scale of the Debye length. Note that in a dilute solution, counter-ions are attracted just as much as co-ions are repelled:

$$\frac{1}{2}(g_{++}(r) + g_{+-}(r)) = 1$$

Using the Debye approximation for the pair correlation function and ignoring many-body terms, the excess chemical potential for species  $i$  is

$$\begin{aligned} \mu_i^{ex} &= \frac{1}{2} \sum_j \int_a^\infty \frac{(z_i e)(z_j e)}{4\pi\epsilon r} \left( 1 - \frac{(z_i e)(z_j e) e^{-(a-r)/\lambda_D}}{4\pi\epsilon k_B T r (1 + a/\lambda_D)} \right) 4\pi r^2 \bar{c}_j dr \\ &= \int_a^\infty \left[ \frac{(z_i e)}{8\pi\epsilon r} \left( \sum_j z_j e c_j \right) - \frac{(z_i e)^2}{8\pi\epsilon} \left( \frac{\sum_j (z_j e)^2 c_j}{\epsilon k_B T} \right) \frac{e^{-(a-r)/\lambda_D}}{(1 + a/\lambda_D)} \right] dr \end{aligned}$$

The first term in the above summation is the product of the bare Coulomb potential and the bulk charge density. Assuming bulk electroneutrality, this term is zero, but would otherwise diverge!

The excess chemical potential simplifies to

$$\mu_i^{ex} = k_B T \ln(\gamma_i) = -\frac{(z_i e)^2}{8\pi\epsilon (a + \lambda_D)}$$

where  $\lambda_D$  is the Debye screening length. The screening length can also be written in terms of the molar ionic strength  $I$

$$\lambda_D = \sqrt{\frac{\epsilon k_B T}{\sum_j (z_j e)^2 c_j}} = \sqrt{\frac{\epsilon k_B T}{2I}}$$

Note that *the excess chemical potential due to Debye-Hückel electrostatic correlations is negative*. The electrostatic interaction between an ion and its oppositely charged screening cloud is attractive, thereby lowering the total electrostatic energy of the system. The excess chemical potential of species  $i$  can be written in terms of its activity coefficient. Using the above expression for the screening length, the Debye-Hückel activity coefficient for dilute electrolytes can be written as

$$\ln(\gamma_i) = \frac{-z_i^2 \alpha \sqrt{I}}{1 + Ba\sqrt{I}}$$

**Simpler derivation:** Although the derivation based on correlation functions above is very general and could be applied to any kind of molecular interactions, there is an easier way to derive the excess chemical potential for purely electrostatic correlations. The screened Coulomb potential at the particle surface is the extra energy gain per charge by adding an ion to the system, relative to its bare Coulomb potential (in the solvent, without any ionic charge relaxation). This immediately leads to the DH formula:

$$\mu_i^{\text{ex}} = \frac{z_i e}{2} \left( \psi(a) - \frac{z_i e}{4\pi\epsilon a} \right) = -\frac{(z_i e)^2}{8\pi\epsilon (a + \lambda_D)}$$

where the  $\frac{1}{2}$  factor again avoids double counting of the pairwise electrostatic forces. This formula also corresponds to the “Gutenberg charging process”, a thought experiment in which we turn on charge relaxation after placing an ion in the solvent.

## 5. Ionic Liquids

Ionic liquids are solvent-free mixtures of ions. Examples include simple molten salts (e.g. NaCl at 2000°C), and as room temperature ionic liquids (e.g. large organic or fatty ions). Some RTILs can withstand up to  $\pm 6$  V, making them good candidates for supercapacitors. They are also widely used as designer solvents. In ionic liquids, there is no solvent, only highly crowded ions, so the Gouy-Chapman-Stern model for dilute electrolytes is not valid. In fact, the Debye-Huckel screening length is smaller than the size of a single ion, and the relevant length scale for electrostatic correlations and double-layer screening is the ion size.

For highly concentrated electrolytic solutions or ionic liquids, the short-range Coulomb correlations are very strong, and generally lead to “overscreening,” whereby an excess of counter-ions are attracted to a central charge, leading to an excess co-ions in the next layer. The end result is  $+ - + - + -$  oscillations in the charge density until electroneutrality is reached. The analog of Debye correlations in the bulk is the formation of strongly correlated “zwitterion” pairs of oppositely charged ions (+-).

Electrostatic correlations can also affect the permittivity of an ionic liquid. In a dilute electrolyte, we can safely use the long-wavelength permittivity of the solvent, which is dominated by the polarization (or alignment) of dipolar solvent molecules in an electric field. In an ionic liquid, however, there is no solvent, and the bulk permittivity is that of the ions themselves, which may be fairly small, if the ions have small dipole moments. However, electrostatic correlations can increase the effective permittivity via the alignment of zwitterion pair dipoles, especially if the electric field varies at the length scale of the ion size. In other words, electrostatic correlations lead to a wave-length dependent permittivity.

To describe these correlation phenomena in ionic liquids, a 4<sup>th</sup> order modified Poisson-Boltzmann equation has recently been proposed [1]:

$$-\epsilon \left( 1 - l_c^2 \nabla^2 \right) \nabla^2 \psi = \rho_{eq}(\psi) \quad (*)$$

where  $l_c$  is an electrostatic correlation length. The fourth derivative term gives rise to the “overscreening” oscillations. This theory is consistent with experiments and simulations using  $\rho_{eq}(\psi)$  for a lattice gas to account for “crowding” due to excluded volume and is convenient for mathematical modeling of RTIL.

#### REFERENCE

1. M. Z. Bazant, B. D. Storey, A. A. Kornyshev. “Double layer in ionic liquids: Overscreening versus crowding”, Phys. Rev. Lett. (2011).

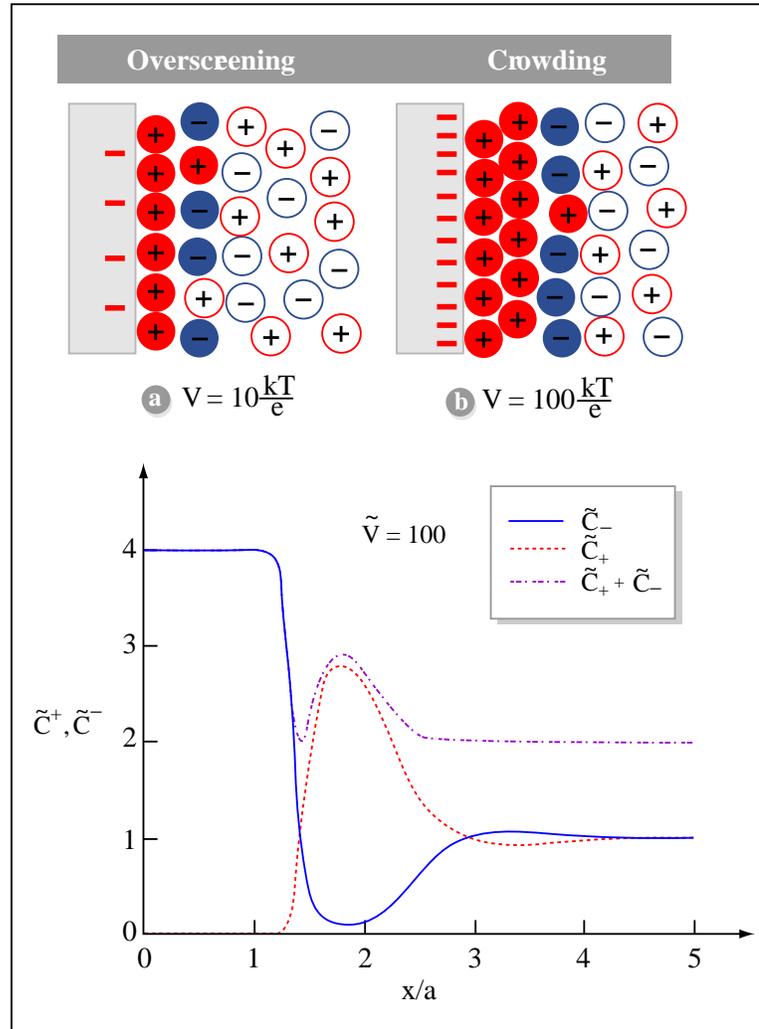


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FIG. 2 TOP: Structure of the ionic-liquid double layer (in color) predicted by the modified Poisson equation (\*), in agreement with molecular dynamics simulations. (a) At a moderate voltage,  $V \approx 10k_B T/e$  (0.26 V), the surface charge is overscreened by a monolayer of counterions, which is corrected by an excess of coions in the second monolayer. (b) At a high voltage,  $V \approx 100k_B T/e$  (2.6 V), the crowding of counterions extends across two monolayers and dominates overscreening, which now leads to a coion excess in the third monolayer. Because of electrostriction, the diffuse double layer (colored ions) is more dense than the quasineutral bulk liquid (white ions). BOTTOM: Ion profiles obtained by solving (\*) at high voltage, showing the structures of the top figure.

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