

# Electrostatic Correlations

## 1. Mean-Field Theory

Continuum models like the Poisson-Nernst-Planck equations are “mean-field approximations” which describe how discrete ions are affected by the mean concentrations  $\bar{c}_i$  and potential  $\bar{\phi}$ . Each ion migrates in the mean electric field, which is produced by the mean charge density, not by the discrete, fluctuating charges in the molecular system. The self-consistent system of PNP equations we have derived thus far is

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

However, discrete ion-ion interactions are a significant component of the excess chemical potential for a charged species in a bulk electrolytic solution. To accurately model such systems, it is important to account for these discrete interactions.

## 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

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

which says that the mean volume per ion must be at least six times larger than a sphere whose radius is the Bjerrum length. Put another way, the “correlation volume” within one Bjerrum length of an ion should contain fewer than  $\sim 6$  neighboring ions for the Debye-Huckel mean-field theory 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 an electrolyte, we have  $g_{ij}(r)$  for different types of ion pairs.  $g_{+-}(r)$  is the counter-ion pair correlation function, and  $g_{--}(r)$  is the co-ion pair correlation.

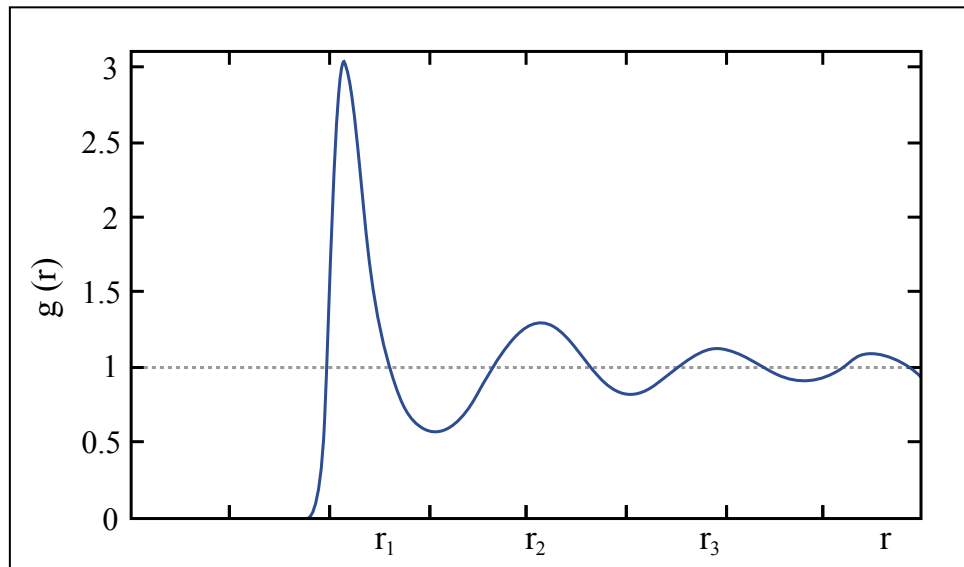


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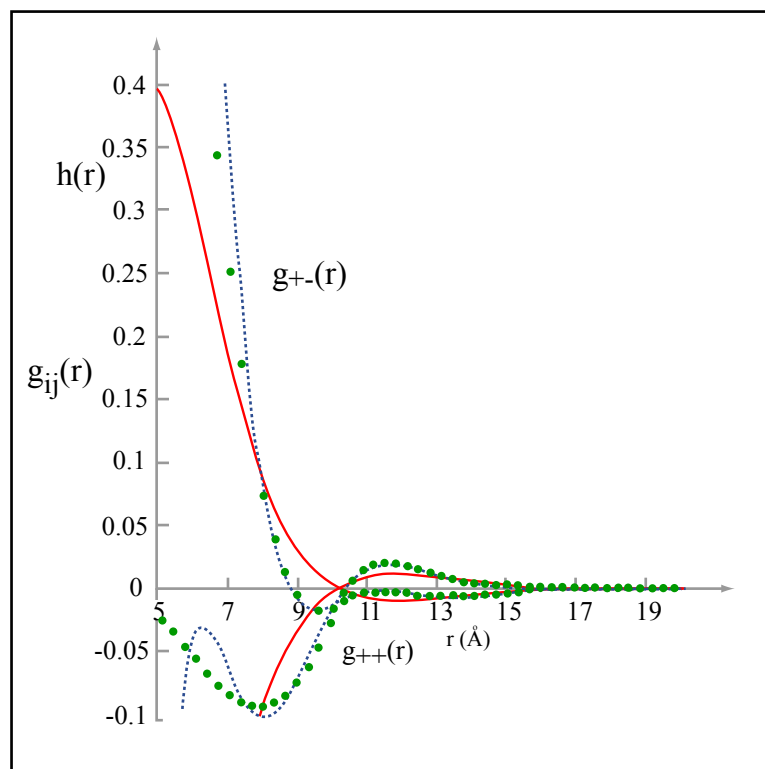
FIG. 1 Typical  $g(r)$  for a liquid. The first neighbor distance is  $r_1$ , the second is  $r_2$ , etc.

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FIG. 3 Total correlation functions for a monovalent binary electrolyte with diameter of the ion =  $5\text{\AA}$ .  $g_{++}(r)$  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.

For pair interactions, the excess chemical potential of species  $i$  is

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

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

#### 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 given by the Debye-Hückel equation for a general dilute electrolyte

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

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

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

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.

$$\begin{aligned} -\epsilon \frac{d\psi}{dr} \Big|_{r=a} &= \frac{z_i e}{4\pi a^2} \\ -\frac{z_i e}{4\pi a^2 \epsilon} &= \frac{d\psi}{dr} \Big|_{r=a} = e^{-a/\lambda_D} A \left( -\frac{1}{a} - \frac{\lambda_D}{a^2} \right) \\ A &= \frac{e^{a/\lambda_D} z_i e}{4\pi \epsilon (a + \lambda_D)} \end{aligned}$$

Incorporating these boundary conditions gives the screened Coulomb potential

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

The pair correlation function then becomes

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

Using this definition 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. Under bulk neutrality conditions, this term is zero but would otherwise diverge. The excess chemical potential simplifies to

$$\mu_i^{ex} = k_B T \ln(\gamma_i) = -\frac{(z_i e)^2}{8\pi \epsilon} \left( \frac{1}{a + \lambda_D} \right)$$

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 given by Debye-Hückel theory 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

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

## 5. Ionic Liquids

Ionic liquids exist both as molten salt (e.g. NaCl at 2000°C) and as room temperature ionic liquids (e.g. large organic or fatty ions). RTILs can withstand up to  $\pm 6$  V, making them good candidates for supercapacitor 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-Hückel 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, 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.

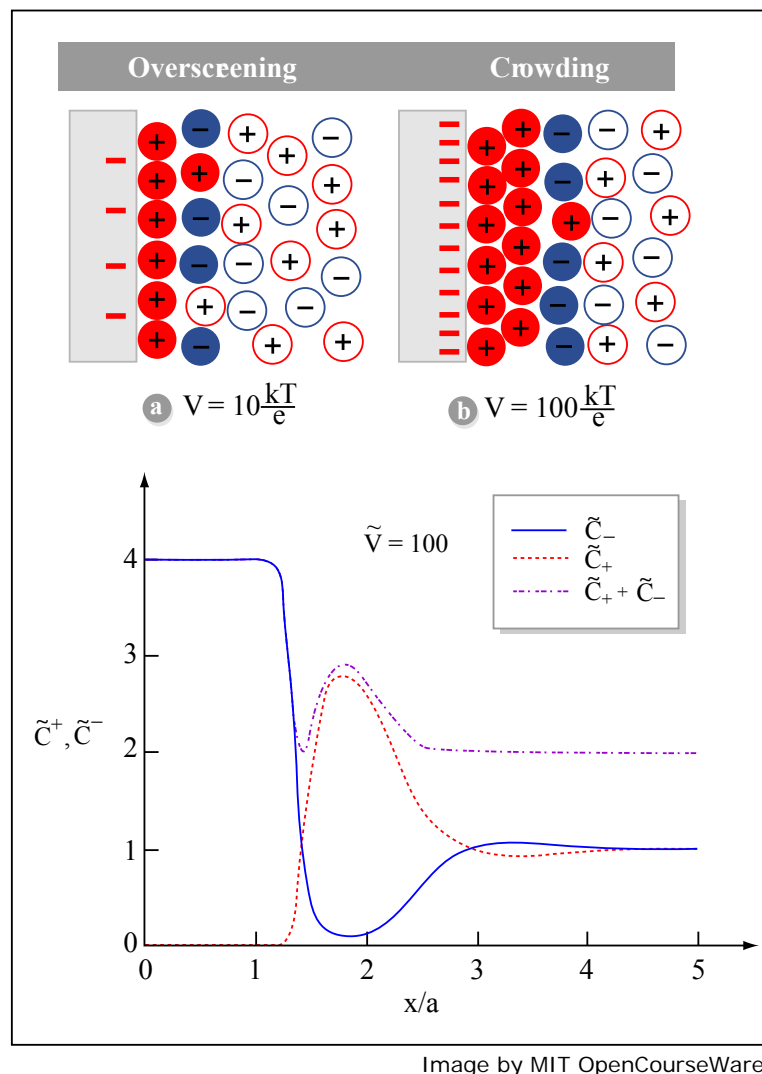


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FIG. 2 TOP: Structure of the ionic-liquid double layer (in color) predicted by the modified Poisson equation (\*), in agreement with molecular dynamics simulations. (a) At a moderate voltage,  $V \approx 10k_B T/e$  (0.26 V), the surface charge is 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.

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

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

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

Source: <http://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems->