Homework 12

Debye-Hückel Theory for Electrolytes[1]

In many experimental situations, one has to deal with solutions with free ions within them. This can happen for example in water with low pH, where the addition of a strong acid (usually HCl) results in the formation of ions of opposite charges (e.g. H^+ and Cl^-), in a way such that the overall electroneutrality of the solution is ensured. Another typical example comes from the addition of salts such as e.g. NaCl, which again "break up" to form both positive (Na^+) and negative (Cl^-) ions.

Driven by thermal fluctuations, such ions wander within the solution, but because of the mutual electrostatic interaction their distributions present strong correlations. In particular, each ion will have on average many neighbor ions of opposite charge and relatively few of the ones with a charge of the same sign. At the simplest level, a typical way to deal with the equilibrium properties of such a system consists in focusing on a particular ion and trying to compute the net electrostatic potential felt by a trial charge because of the action of such ion and of the cloud of ions around it. By fixing the origin at the center of the chosen ion, the potential at position $\vec{r}$ will follow the Poisson equation

$$\nabla^2\phi(\vec{r}) = -\frac{\rho(\vec{r})}{\epsilon\,\epsilon_0}\,, \tag{1}$$

where $\phi(\vec{r})$ is the electrostatic potential, $\rho(\vec{r})$ the charge density, ϵ_0 the permittivity of vacuum and ϵ the electrical permittivity of the solvent, here treated as a continuous object (e.g. for water at room temperature $\epsilon \simeq 78$).

1. Write a formula to express $\rho(\vec{r})$ as a function of the local concentrations $c_i(\vec{r})$ of the various ions whose valences are given by z_i.

On the other hand, since we are interested in the equilibrium properties of the electrolytic solution, we expect the charges to be distributed according to the Boltzmann distribution. Thus, the concentration of ion i around our reference ion will be given by

$$c_i(\vec{r}) = c_{i,\infty}e^{-\frac{z_i e\phi(\vec{r})}{k_B T}}\,, \tag{2}$$

where $c_{i,\infty} \equiv c_i(\infty)$ is the bulk concentration, and corresponds to the actual concentration of i put in the solution by the experimenter.

2. By putting together equations (1) and (2), derive the following self-consistent relation, known as *Poisson-Boltzmann equation*

$$\nabla^2\phi(\vec{r}) = -\sum_i \frac{ez_i}{\epsilon\,\epsilon_0}c_{i,\infty}e^{-\frac{z_i e\phi(\vec{r})}{k_B T}}\,. \tag{3}$$

3. For weak enough fields (corresponding to relatively low concentrations of ions), the rhs of the previous equation can be expanded. Stopping at the linear term, exploiting the net

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[1] M. Daune, "Molecular Biophysics" (1999)

electroneutrality of the solution and assuming the ions to be isotropically distributed around the origin, show that

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\phi}{dr}\right)=\frac{1}{l_D^2}\phi(r) \tag{4}$$

and give an explicit formula for the *Debye length* l_D.

4. Assuming the reference ion to be a uniformly charged hard sphere of radius a and total charge ze, what is the electric field at its surface? Does it depend on the other ions?

5. By solving equation (4) with suitable boundary conditions, show that the potential is given by the *Debye-Hückel formula*

   $$\phi(r)=\frac{ze}{4\pi\epsilon\,\epsilon_0}\frac{e^{-\frac{r-a}{l_D}}}{r\left(1+\frac{a}{l_D}\right)}\,. \tag{5}$$

   According to such a formula, the effect of the counterions is to screen the Coulomb interaction between the reference ion and a trial charge at distance r, according to a Yukawa-like potential.

   Hint: make use of the auxiliary variable $u \equiv r\phi$.

6. Compute the infinitesimal net charge found at distance r from the reference ion and use the result to find a physical interpretation of the Debye length.

Scaling Arguments for the Fluctuations of Ion Density in Electrolytes[2]

In this exercise we propose some simple scaling arguments which shed light on the physical meaning of the Debye length l_D.

1. Compute the *Bjerrum length* l_B, defined as the distance at which the unscreened electrostatic energy of interaction between two elementary charges is equal to k_BT. Show that in a monovalent electrolytic solution (i.e. $z=1$), apart from some universal constants $l_D \sim 1/\sqrt{l_B c}$, where c is the bulk concentration of ions.

2. For the sake of discussion, let us consider the ions of a monovalent electrolytic solution as a non-interacting gas. If we consider a region of size R, compute: i) the average total charge; ii) the typical charge fluctuations; iii) the electrostatic energy stored in this region. How does it behave with R?

3. What happens to the electrostatic energy when $R \sim l_D$?

4. For $R > l_D$, what is the behavior of the fluctuations?

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[2] We acknowledge Prof. M. Rubinstein for this physical argument.