Poisson–Boltzmann Equation

Ye Mei[*]

State Key Laboratory of Precision Spectroscopy,

School of Physics and Materials Science,

East China Normal University, Shanghai 200062, China

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Abstract

In this handout, I will go through the Debye-Hückel Theory and Poisson–Boltzmann Equation.

[*]Electronic address: `ymei@phy.ecnu.edu.cn`; URL: `http://faculty.ecnu.edu.cn/s/960/main.jspy`

I. THEORY

The Debye–Hückel theory, the theory for the Poisson-Boltzmann equation in solution chemistry, was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes and plasmas. It is a linearized Poisson-Boltzmann model, which valids only when some preconditions are satisfied.

1. Strong electrolyte. The solute is completely dissociated.

2. Ions are spherical and are not polarizable.

3. The solvent plays no role other than providing a medium of constant relative permittivity (dielectric constant).

4. There is no electrostriction.

5. Individual ions surrounding a "central" ion can be represented by a statistically averaged cloud of continuous charge density, with a minimum distance of closest approach.

With these assumptions, each cation is surrounded by an isotropic cloud of ions, and each ion is surrounded an isotropic cloud of cations. The density of the surrounding charges are determined by means of a Boltzmann distribution, where the interaction is only the electrostatic interaction, as

$$n_i' = n_i \exp\left(\frac{-z_i e \psi_j(r)}{kT}\right). \tag{1}$$

We take this equation into the Poisson equation and find

$$\nabla^2 \psi_j(r) = -\frac{1}{\epsilon} \sum_i \left\{ n_i z_i e \cdot \exp\left(\frac{-z_i e \psi_j(r)}{kT}\right) \right\} \tag{2}$$

Next we expand this exponential term as a truncated Taylor series to first order. The zeroth order term vanishes because the solution is electrically neutral. With only the first order term, we find

$$\nabla^2 \psi_j(r) = \kappa^2 \psi_j(r) \quad with \quad \kappa^2 = \frac{e^2}{\epsilon kT} \sum_i n_i z_i^2. \tag{3}$$