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Derivation of the Langevin Poisson-Boltzmann equation for point-like ions using the functional density theory

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Abstract. The Langevin Poisson-Boltzmann equation for point-like ions describing an electrolyte solution in contact with a planar charged surface is derived within the functional density theory. In the model, the water molecules are considered as the Langevin dipoles. It is shown that due to the increased orientational ordering of the water dipoles, the dielectric permittivity of the electrolyte close to the charged surface is decreased.

Key words: Langevin Poisson-Boltzmann equation, point-like ions, orientational ordering of water, dielectric permittivity, functional density theory

1 INTRODUCTION

The contact between a negatively charged surface and an electrolyte solution results in rearrangement of the ion distribution and formation of the so-called electrical double layer (EDL) takes place [1], [2], [3], [4]. Most of the models, describing this phenomenon [1], [5], [6], [7], [8] assume constant dielectric permittivity throughout the system. But actually, close to the charged surface, the water dipoles are oriented thus leading to a varying dielectric permittivity [8].

In this paper, the Langevin Poisson-Boltzmann mean-field equation for the point-like ions is derived within the functional density theory, where the orientational ordering of water molecules is taken into account. In the model, the dielectric permittivity is consistently related to distribution of the involved ions and the electric field strength. The water molecules are considered as the Langevin dipoles [9], [10], [11] which is a very rough treatment of the dielectric properties of the solvent. The finite volume of ions and water [7], [11] in the electrolyte solution (i.e. the excluded volume effect) is not taken into account. The volume density of water is therefore constant in the whole electrolyte solution [12].

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2 THEORY

We consider a planar charged surface in contact with a water solution of monovalent ions (counterions and coions). The planar charged surface bears a charge with surface charge density σ. The Langevin dipole describes the water molecule with a non-zero dipole moment (**p**). A self-consistent statistical mechanical description of the orientational ordering of the water Langevin dipoles is presented. Using the calculus of variation, the ion number density profiles and average orientation of the water dipoles corresponding to the minimum free energy are calculated. The free energy of system F is written as :

$$\begin{aligned} \frac{F}{kT} &= \frac{1}{8\pi l_B}\int \Big(\Psi'\Big)^2\, dV \\ &+ \int \Big[n_+(x)\ln\frac{n_+(x)}{n_0} - (n_+(x)-n_0) \\ &+ n_-(x)\ln\frac{n_-(x)}{n_0} - (n_-(x)-n_0)\Big]\, dV \\ &+ \int n_w \Big\langle \mathcal{P}(x,\omega)\ln\mathcal{P}(x,\omega)\Big\rangle_\omega\, dV \\ &+ \int \Big[\eta(x)\Big(\Big\langle \mathcal{P}(x,\omega)\Big\rangle_\omega - 1\Big)\Big]\, dV, \end{aligned} \tag{1}$$

where averaging over all angles Ω is defined as:

$$\Big\langle F(x)\Big\rangle_\omega = \frac{1}{4\pi}\int F(x,\omega)\; d\Omega \quad , \tag{2}$$

ω is is the angle between the dipole moment vector **p** and the vector $\mathbf{n} = \nabla\phi/|\nabla\phi|$, $\phi(x)$ is the electrostatic potential, $d\Omega = 2\pi \sin\omega \; d\omega$ is an element of a solid angle, n_w is the constant number density of the Langevin dipoles, $n_+(x)$ and $n_-(x)$ are the number densities of counterions and coions, respectively,

$$\Psi(x) = e_0 \phi(x)/\mathrm{kT} \quad , \tag{3}$$

is the reduced electrostatic potential, Ψ' is the first derivative of Ψ with respect to x, e_0 is the elementary charge, kT is the thermal energy, n_0 is the bulk number density of positively and negatively charged monovalent ions in the electrolyte solution, $\mathrm{dV} = \mathrm{Adx}$ is the volume element with thickness dx, where A is the area of the charged surface. The Bjerrum length $l_B = e_0^2/4\pi\varepsilon_0 kT$, where ε_0 is the permittivity of the free space. The first term in Eq.(1) corresponds to the energy of the electrostatic field. The second and the third line in Eq.(1) account for the mixing free energy contribution of the positive and negative salt ions. We assumed $\phi(x \to \infty) = 0$. The fourth line Eq.(1) accounts for the orientational contribution of the Langevin dipoles to the free energy. $\mathcal{P}(x, \omega)$ is the probability that the Langevin dipole located at x is oriented for angle ω with respect to the normal to the charged surface. The last line is the local constraint for orientation of the Langevin dipoles (valid at any position x):

$$\Big\langle \mathcal{P}(x, \omega) \Big\rangle_{\omega} = 1 \quad , \tag{4}$$

where $\eta(x)$ is the local Lagrange multiplier.

The results of the variation in the above free energy gives :

$$n_+(x) = \; n_0 \, \exp(-\Psi) \quad , \tag{5}$$

$$n_-(x) = \; n_0 \, \exp(\Psi) \quad , \tag{6}$$

$$\mathcal{P}(x, \omega) = \Lambda(x) \exp(-p_0 |\Psi'| \cos(\omega)/e_0) \quad , \tag{7}$$

where $\Lambda(x)$ is the constant for given x.

The charges of counterions, coions and water molecules (Langevin dipoles) contribute to the average microscopic volume charge density:

$$\varrho(x) = e_0 \left(n_+(x) - n_-(x)\right) - \frac{\mathrm{d}P}{\mathrm{d}x} \quad . \tag{8}$$

Polarization P is given by

$$P(x) = n_{0w} \, \Big\langle \mathbf{p}(x, \omega) \Big\rangle_B \quad , \tag{9}$$

where $\mathbf{p}$ is the water (Langevin) dipole moment and $\Big\langle \mathbf{p}(x, \omega) \Big\rangle_B$ is its average over the angle distribution in thermal equilibrium. In our case of negatively charged planar surface ($\sigma < 0$) the projection of the polarization vector $\mathbf{P}$ points in the direction opposite to the direction of x-axis. Hence $P(x)$ is considered negative. According to Eq.(7) the values of $\Big\langle \mathbf{p}(x, \omega) \Big\rangle_B$ can be calculated as follows :

$$\Big\langle \mathbf{p}(x, \omega) \Big\rangle_B = \frac{\int_0^{\pi} p_0 \cos\omega \; \mathcal{P}(x, \omega) \; 2\pi \sin\omega \; d\omega}{\int_0^{\pi} \mathcal{P}(x, \omega) \; 2\pi \sin\omega \; d\omega} =$$

$$= -p_0 \; \mathcal{L}\left(\frac{p_0 |\Psi'|}{e_0}\right) \quad . \tag{10}$$

A function $\mathcal{L}(u) = (\coth(u) - 1/u)$ is the Langevin function. Langevin function $\mathcal{L}(p_0|\Psi'|/e_0)$ describes the average magnitude of the Langevin dipole moments at given x. In our derivation we assumed an azimuthal symmetry and negative surface charge density σ.

Inserting the Boltzmann distribution functions of ions (Eqs.(5) and (6)) and expression for polarization (Eqs.(9) and (10)) into Eq.(8), we get the expression for the volume charge density in an electrolyte solution:

$$\begin{aligned} \varrho(x) &= -2 \, e_0 \, n_0 \sinh\Psi \; + \\ &+ \; n_{0w} \, p_0 \; \frac{\mathrm{d}}{\mathrm{d}x} \Big[\mathcal{L}(p_0 |\Psi'|/e_0) \Big] \quad . \end{aligned} \tag{11}$$

Inserting the above expression for volume charge density $\varrho(x)$ (Eq.(11)) into the Poisson equation

$$\Psi'' = -4\pi \, l_B \varrho / e_0 \quad , \tag{12}$$

we get the Langevin Poisson-Boltzmann equation for the point-like ions :

$$\begin{aligned} \Psi'' &= 4\pi l_B \Big(2 \, n_0 \sinh\Psi \; - \\ &- \; n_{0w} \, \frac{p_0}{e_0} \, \frac{\mathrm{d}}{\mathrm{d}x} \Big[\mathcal{L}(p_0 |\Psi'|/e_0) \Big] \Big) \quad , \end{aligned} \tag{13}$$

where Ψ'' is the second derivative of Ψ with respect to x. The Langevin Poisson-Boltzmann differential equation (13) is subject to two boundary conditions. The first boundary condition is obtained by integrating the differential equation (13) :

$$\begin{aligned} \Psi'(x = 0) &= -\frac{4\pi l_B}{e_0} \Big[\; \sigma \; + \\ &+ \; n_{0w} \, p_0 \; \mathcal{L}(p_0 |\Psi'|/e_0) \Big|_{x=0} \Big] \quad . \end{aligned} \tag{14}$$

The condition requiring electro-neutrality of the whole system was taken into account in derivation of Eq.(14). The second boundary condition is :

$$\Psi'(x \to \infty) = 0 \quad . \tag{15}$$

Based on Eqs.(9)-(10), we can express the effective permittivity of electrolyte solution (ε_{eff}) in contact with the planar charged surface as :

$$\varepsilon_{eff} \; = 1 + \frac{|P|}{\varepsilon_0 E} \; = \; 1 + \; n_{0w} \, \frac{p_0}{\varepsilon_0} \; \frac{\mathcal{L}(p_0 E/kT)}{E} \quad , \tag{16}$$

where $E = |\phi'| = \phi'$ (since $\sigma < 0$) is the magnitude of the electric field strength.

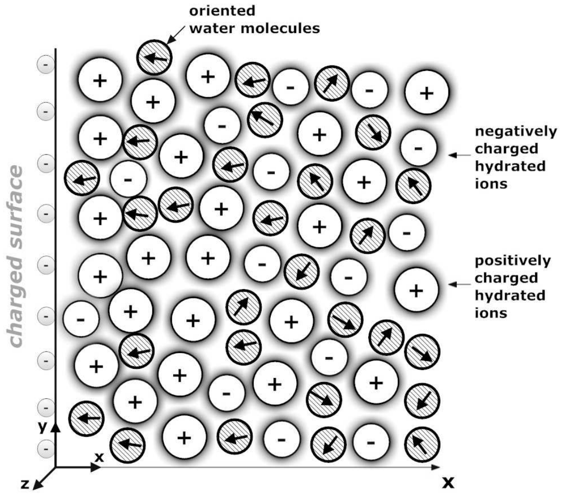

Figure 1. A schematic figure of the electrical double layer near a negatively charged planar surface. The water molecules in the vicinity of the charged surface are predominantly oriented towards the surface.

3 RESULTS AND CONCLUSION

Eq.(16) describes the dependence of effective permittivity ε_{eff} on the magnitude of electric field strength E, calculated within the presented Langevin Poisson-Boltzmann theory, which takes into account the orientational ordering of water molecules (or water clusters) near a charged surface (Fig.1) by considering them as the Langevin dipoles. The finite size of ions is not taken into account in Eq.(16).

For $p_0E/kT < 1$ we can expand the Langevin function in Eq.(16) into a Taylor series up to the cubic term: $\mathcal{L}(x) \approx x/3 - x^3/45$ to get:

$$\varepsilon_{eff} \cong 1 + \frac{n_{0w}{p_0}^2}{3\varepsilon_0 kT} - \frac{n_{0w}p_0^2}{45\varepsilon_0 kT}\,(p_0E/kT)^2 \ . \tag{17}$$

It can be seen in Eq.(17) that ε_{eff} decreases with the increasing magnitude of electric field strength E. Since the value of E increases towards the charged surface (see for example [5]), ε_{eff} decreases towards the charged surface. It can therefore be concluded that due to the preferential orientation of water dipoles in the close vicinity of the charged surface, the effective permittivity of electrolyte ε_{eff} near the charged surface is reduced relative to its bulk value as shown also in Fig.2.

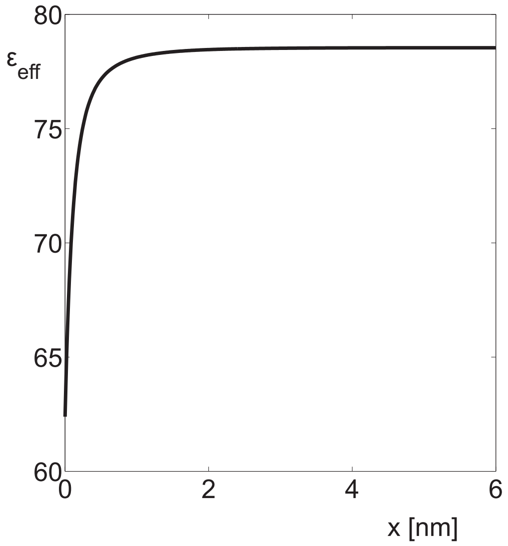

Figure 2. Effective dielectric permittivity ε_{eff} as a function of the distance from the charged surface x within the presented Langevin PB theory for point-like ions. Eqs.(13)-(15) were solved numerically using Finite Element Method within the program package Comsol Multiphysics 3.5a Software. Dipole moment of water $p_0 = 4.794D$, bulk concentration of salt $n_0/N_A = 0.15\,\mathrm{mol/l}$, bulk concentration of water $n_{0w}/N_A = 55\,\mathrm{mol/l}$, surface charge density $\sigma = -0.3\,\mathrm{As/m^2}$.

Recently, a similar Langevin PB equation for the point-like ions (as given in Eq.(13) was derived starting from a partition function of the system [13]. The Langevin PB equation for the point-like ions, given in Abrashkin et al. [13] can be derived also in a somewhat different way by assuming the Boltzmann distribution function also for the water (Langevin) dipoles [14]. The expression for ε_{eff} from [13] can be expanded into series to get:

$$\varepsilon_{eff} \cong 1 + \frac{n_{0w}{p_0}^2}{3\varepsilon_0 kT} + \frac{n_{0w}p_0^2}{30\varepsilon_0 kT}\,(p_0E/kT)^2 \ . \tag{18}$$

It can be seen in Eq.(18) that ε_{eff} increases with the increasing magnitude of electric field strength E. Since the magnitude of the electric field strength in the electrolyte solution increases towards the charged membrane surface, Eq.(18) predicts the incorrect increase of ε_{eff} in the vicinity of the charged membrane surface. This is a consequence of the accumulated water dipoles near the charged surface (due to the assumed Boltzmann distribution for water molecules) (see also [15]) which prevails over the decrease of ε_{eff} due to an increased orientational ordering of water molecules in a strong electric field as predicted by Eqs. (16) and (17).

To conclude, in this work, the PB theory for the point-like ions was modified by introducing the orientational ordering of water molecules. The corresponding Langevin Poisson-Boltzmann equation was derived. The water dipoles are described as the Langevin dipoles with a given dipole moment. It is shown that the effective dielectric permittivity of the electrolyte solution decreases with the increasing magnitude of the electric field strength. Due to the increased magnitude of the electric field in the vicinity of the charged surface in contact with the electrolyte solution, the effective permittivity of electrolyte solution in the region near the charged surface is decreased. The predicted decrease in the permittivity relative to its bulk value is the consequence of the orientational ordering of the water dipoles in the vicinity of the charged surface. It has recently been shown, that for finite sized ions the drop in the number density of water near a charged surface results in an additional decrease of permittivity [11], [14].

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