



Asymmetric size of ions and orientational ordering of water dipoles in electric double layer model - an analytical mean-field approach



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ABSTRACT

Electric double layer is theoretically described within the mean-field approach by taking into account the orientational ordering of water dipoles and asymmetric size of cations and anions. Analytical expressions for the spatial distribution of ions and water dipoles are derived. The effect of asymmetric ionic size on accumulation of counterions and partial depletion of water molecules near the charged surface, on spatial dependence of relative permittivity and on differential capacitance of electric double layer are presented.

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1. Introduction

Accumulation of counterions and depletion of coions in the vicinity of a charged surface in contact with an electrolyte solution results in a formation of electric double layer (EDL) [1–15]. Helmholtz initiated the investigation of EDL [16,17] followed by Gouy [18] and Chapman [19] who upgraded the model by considering Boltzmann spatial distribution of the counterions and coions in the Poisson's equation [1,20–22]. Later, Debye and Hückel generalized the Gouy-Chapman model [1,20].

Stern [23] was the first to include the finite size of ions in the EDL model by assuming the distance of closest approach of counterions to the charged surface [24,25]. A more sophisticated approach to take into account the finite size of ions in EDL was introduced by Bikerman [2] and followed by further advance studies [8,12,26–36]. EDL models were further improved by considering the orientational ordering of water dipoles resulting in prediction of local decrease of relative permittivity of electrolyte solution in the saturation regime close to the charged surface [37–39,12,14,15,24,40–44].

Recently, a mean-field model of EDL was developed by Gongadze and Igljč [45] (referred as in this paper as GI model) which encapsulates both, the excluded volume effect (finite size of ions) and orientational ordering of water dipoles, considered as point-like dipoles at the centres of the finite sized spheres with

permittivity equal to the square of optical refractive index of water. In the GI model, the different size of positively and negatively charged ions in EDL was not taken into account [45]. Therefore, in this paper the equations of GI model are generalised in order to incorporate the latter feature. The corresponding analytical expressions for ion spatial distribution functions are derived and included respectively into the Poisson's equation. The influence of different size of ions on the ion and water spatial distribution functions, on spatial dependence of relative permittivity and on differential capacitance for negative and positive voltage are presented and discussed.

2. Theory

2.1. Equal size of ions

By assuming that coions, counterions and water molecules occupy a single lattice site, the number density of water molecules (n_{0w}), counterions (n_0) and coions (n_c) in the bulk electrolyte solution is constant. Therefore, the probability that a single lattice site in a bulk solution is occupied by one of the three kinds of particles (positive ions, negative ions and water molecules) in the electrolyte solution is:

$$\mathcal{P}_+(x \rightarrow \infty) = \mathcal{P}_-(x \rightarrow \infty) = \frac{n_0}{n_0 + n_0 + n_{0w}}, \quad (1)$$

$$\mathcal{P}_w(x \rightarrow \infty) = \frac{n_{0w}}{n_0 + n_0 + n_{0w}}, \quad (2)$$

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The corresponding number densities in a bulk solution are:

$$n_+(x \rightarrow \infty) = n_-(x \rightarrow \infty) = n_s \frac{n_0}{n_0 + n_0 + n_{0w}}, \quad (3)$$

$$n_w(x \rightarrow \infty) = n_s \frac{n_{0w}}{n_0 + n_0 + n_{0w}}, \quad (4)$$

where n_s is the number density of lattice sites:

$$n_s = 2n_0 + n_{0w}. \quad (5)$$

In the vicinity of the charged surface, the number density of ions and water molecules is influenced by the charged surface, so the probabilities that a single lattice site is occupied by a particle of one of the three kinds should be corrected by the corresponding Boltzmann factors, leading to ion and water dipole distribution functions in the form [14,45]:

$$n_+(x) = n_s \frac{n_0 e^{-e_0 \phi \beta}}{n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (6)$$

$$n_-(x) = n_s \frac{n_0 e^{e_0 \phi \beta}}{n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (7)$$

$$n_w(x) = n_s \frac{n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}{n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (8)$$

where $\beta = 1/kT$, kT is the thermal energy, k is the Boltzmann constant, T is the absolute temperature, e_0 is the unit charge and ϕ is the electric potential. Further

$$\begin{aligned} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega &= \frac{2\pi \int_{-\pi}^0 d(\cos \omega) e^{-\gamma p_0 E \beta \cos(\omega)}}{4\pi} \\ &= \frac{\sinh(\gamma p_0 E \beta)}{\gamma p_0 E \beta}. \end{aligned} \quad (9)$$

is the water dipole Boltzmann factor after rotational averaging over all possible angles ω [14,45,5]. The angle ω is the angle between the gradient of the electric potential and the vector of the water dipole moment [14,45]. Here p_0 is the magnitude of the external water dipole moment, E is the magnitude of electric field strength. In the model, a single water molecule is considered as a finite sized sphere with permittivity n^2 and a point-like rigid (permanent) dipole/quadrupole at the centre of the sphere, where n is the optical refractive index of water [14,45]. Hence, the cavity field and the electronic polarisability of water molecules are taken into account [46], while the short range interactions between water molecules are neglected. Accordingly, the value of the constant γ is given by [45,14]:

$$\gamma = \frac{3}{2} \left(\frac{2+n^2}{3} \right). \quad (10)$$

2.2. Different size of ions

Consider now a case where negative and positively charged ions occupy more than one lattice site, while a single water molecules still occupy just one lattice site. In the following, α_+ and α_- are the number of lattice sites occupied by a single positive and negative ion, respectively. The probabilities that a single lattice site in the bulk solution is occupied by one of the three kind of particles in electrolyte solution (positive ion, negative ion and water molecule) are then:

$$\mathcal{P}_+(x \rightarrow \infty) = \frac{\alpha_+ n_0}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (11)$$

$$\mathcal{P}_-(x \rightarrow \infty) = \frac{\alpha_- n_0}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (12)$$

$$\mathcal{P}_w(x \rightarrow \infty) = \frac{n_{0w}}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (13)$$

while the corresponding number densities in bulk are

$$n_+(x \rightarrow \infty) = \left(\frac{n_s}{\alpha_+} \right) \frac{\alpha_+ n_0}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (14)$$

$$n_-(x \rightarrow \infty) = \left(\frac{n_s}{\alpha_-} \right) \frac{\alpha_- n_0}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (15)$$

$$n_w(x \rightarrow \infty) = n_s \frac{n_{0w}}{\alpha_+ n_0 + \alpha_- n_0 + n_{0w}}, \quad (16)$$

where n_s is the number density of lattice sites:

$$n_s = \alpha_+ n_0 + \alpha_- n_0 + n_{0w}. \quad (17)$$

Similarly as in [14,45], in the vicinity of the charged surface, the number densities of ions and water molecules are corrected by the corresponding Boltzmann factors:

$$n_+(x) = n_s \frac{n_0 e^{-e_0 \phi \beta}}{\alpha_- n_0 e^{e_0 \phi \beta} + \alpha_+ n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (18)$$

$$n_-(x) = n_s \frac{n_0 e^{e_0 \phi \beta}}{\alpha_- n_0 e^{e_0 \phi \beta} + \alpha_+ n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}, \quad (19)$$

$$n_w(x) = n_s \frac{n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}{\alpha_- n_0 e^{e_0 \phi \beta} + \alpha_+ n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega)} \rangle_\omega}. \quad (20)$$

Taking into account Eq. (9), we can rewrite Eqs. (18)–(20) as:

$$n_+(x) = n_0 e^{-e_0 \phi \beta} \frac{n_s}{\mathcal{D}(\phi, E)}, \quad (21)$$

$$n_-(x) = n_0 e^{e_0 \phi \beta} \frac{n_s}{\mathcal{D}(\phi, E)}, \quad (22)$$

$$n_w(x) = \frac{n_{0w} n_s}{\mathcal{D}(\phi, E)} \frac{\sinh(\gamma p_0 E \beta)}{\gamma p_0 E \beta}. \quad (23)$$

where:

$$\mathcal{D}(\phi, E) = \alpha_- n_0 e^{e_0 \phi \beta} + \alpha_+ n_0 e^{-e_0 \phi \beta} + \frac{n_{0w}}{\gamma p_0 E \beta} \sinh(\gamma p_0 E \beta). \quad (24)$$

The magnitude of the polarisation in the vicinity of the negatively charged surface is given by [14,43,45]:

$$P(x) = n_w(x) \left(\frac{2+n^2}{3} \right) p_0 \mathcal{L}(\gamma p_0 E \beta). \quad (25)$$

Combining Eq. (23) and Eq. (25) gives the polarization in the form:

$$P(x) = p_0 n_{0w} n_s \left(\frac{2+n^2}{3} \right) \frac{\mathcal{F}(\gamma p_0 E \beta)}{\mathcal{D}(\phi, E)}, \quad (26)$$

where the function $\mathcal{F}(u)$ is defined as: $\mathcal{F}(u) = \mathcal{L}(u)(\sinh u/u)$. Combining $\varepsilon_r(x) = n^2 + P/\varepsilon_0 E$ and Eq. (26) yields the relative (effective) permittivity:

$$\varepsilon_r(x) = n^2 + n_{0w} n_s \frac{p_0}{\varepsilon_0} \left(\frac{2+n^2}{3} \right) \frac{\mathcal{F}(\gamma p_0 E \beta)}{\mathcal{D}(\phi, E) E}. \quad (27)$$

In the limit of vanishing electric field strength ($E \rightarrow 0$) and zero potential ($\phi \rightarrow 0$), the above derived expression for relative permittivity (Eq. (27)) gives the Onsager expression for permittivity [47].

Using the above expression for $\varepsilon_r(x)$, we can rewrite the Poisson's equation into the form of:

$$\frac{d}{dx} \left[\varepsilon_0 \varepsilon_r(x) \frac{d\phi}{dx} \right] = 2 e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{\mathcal{D}(\phi, E)}, \quad (28)$$

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