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On the orientational ordering of water and finite size of molecules in the mean-field description of the electric double layer - a mini review

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Abstract. The distribution of ions in an electrolyte solution close to a charged surface is determined by competition between electrostatic interactions and the entropy of the ions. The diffuse electric double layer (EDL) created influences the overall electrostatic interaction of the charged surface with its environment. Different approaches were introduced through the years to overcome some of the limitations of classical EDL Poisson-Boltzmann models and to better capture the complex phenomena of the EDL. The core of these models is the spatial variation of the relative permittivity, achieved by taking into account the spatial and orientational distribution of water molecules and the excluded volume effect.

1. Introduction

The contact between a charged surface and an electrolyte solution implies a characteristic spatial and orientational distribution of ions and water molecules which is reflected in the formation of the electric double layer (EDL) [1–6]. Study of the electric double layer began in 1879 with Hermann von Helmholtz, but today it still remains a scientific challenge. Helmholtz treated the double layer as a simple capacitor, assuming that the surface charge density is neutralized by the counterions located at a distance equal to their hydrated radius. Gouy [1] and Chapman [1, 2] considered the thermal motion of ions and pictured a diffuse double layer composed of ions of opposite charge (counterions) attracted to the surface, and ions of the same charge (co-ions) repelled from it. Ions are embedded in a dielectric continuum while the electric potential is subject to the Poisson-Boltzmann (PB) differential equation. Within the so-called Poisson-Boltzmann theory [1–3], the ions in an electrolyte solution are treated as dimensionless and a uniform permittivity of the electrolyte solution is assumed. Surfaces are considered to be uniformly charged (see also Refs. [3–8]).

The Stern model [9] was the first attempt to incorporate the finite size of ions in EDL theory by combining the Helmholtz [10] and Gouy-Chapman [1, 2] models. Furthermore, in 1942, Bikermann introduced the first complete modified Poisson-Boltzmann (modified Gouy-Chapman) model with consideration of steric effects in the electrolyte phase [11]. The tendency was continued by Grimley and Mott [12, 13], and Freise [14] who included the excluded volume effect with a pressure-dependent potential. Wicke and Eigen [15] used a thermodynamic

approach, multiplying the numerical density of ions by a factor containing the number of vacant sites. Also more recently, the finite size of particles has been incorporated into the electric double layer theory in different ways [16], for example by using a lattice statistics model [17] or by including surface charge correlations where ions and solvent molecules were treated as hard spheres [5]. The properties of the electric double layer may thus be strongly influenced by the ordering of water molecules [7, 8, 18–22] and their depletion in the region of the electric double layer [23]. Outhwaite developed a modified Poisson-Boltzmann (PB) theory of the electrical double layer composed of a mixture of hard spheres with point dipoles and finite sized ions. The Langevin expression for the permittivity appeared as the first closure, while the second closure led to the Onsager expression for the relative permittivity [18].

It was shown that close to the charged surface, water dipole ordering in the saturation regime and depletion of water molecules may result in a strong local decrease of permittivity [20, 21, 23, 24].

In this work EDL mean-field theories of electrolyte solution in contact with a charged surface are reviewed. It is indicated that consideration of the orientational ordering of water molecules near a highly charged (metal) surface, the finite size of molecules, electronic polarizability and cavity field of water molecules is essential to better describe the physical properties of the EDL at high values of the surface charge density [23].

2. Gongadze-Iglič model

The effective dipole moment of a water molecule should be known before a satisfactory statistical mechanical study of water and aqueous solutions is possible [25–27]. The dipole moment of a water molecule in liquid water differs from that of an isolated water molecule because each water molecule is further polarized and orientationally perturbed by the surrounding water molecules [25–28].

In the past treatment of the cavity and the correlations between water dipoles in the Onsager [29], Kirkwood [30] and Fröhlich models [25] were limited to the case of small electric field strengths. Generalization of the Kirkwood-Onsager-Fröhlich theory in the saturation regime was performed later by Booth [26]. However, Booth's model does *not consider the excluded volume effect* in an electrolyte solution near a charged surface.

In order to develop an integrating framework to clarify the factors influencing the relative permittivity, in this review a generalisation of the Langevin Poisson-Boltzmann (LPB) model [22] is presented. The model takes into account the cavity field [25] (but not the structural correlations between water dipoles), as well as the finite size of ions [8, 23] in the saturation regime (an important consideration for an electrolyte solution in contact with a highly charged surface).

In the model electronic polarization is taken into account by assuming that the point-like rigid (permanent) dipole is embedded in the centre of a sphere with a volume equal to the average volume of a water molecule in the electrolyte solution (figure 1). The permittivity of the sphere is taken to be n^2 , where $n = 1.33$ is the optical refractive index of water. The relative (effective) permittivity of the electrolyte solution (ε_r) is then expressed as:

$$\varepsilon_r(\mathbf{r}) = n^2 + \frac{|\mathbf{P}|}{\varepsilon_0 E}, \quad (1)$$

where \mathbf{P} is the polarization vector due to the net orientation of permanent point-like water dipoles having dipole moment \mathbf{p} . The external dipole moment (\mathbf{p}_e) of a point-like dipole at the center of the sphere with permittivity n^2 can then be expressed in the form [25] $\mathbf{p}_e = 3\mathbf{p}/(2 + n^2)$ whence it follows:

$$\mathbf{p} = \frac{2 + n^2}{3} \mathbf{p}_e \quad . \quad (2)$$

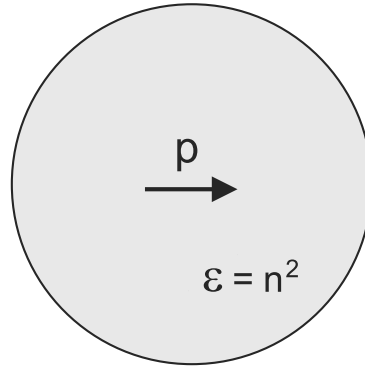


Figure 1. In the model a single water molecule is considered as a sphere with permittivity $n^2 = 1.33^2$ and a point-like rigid (permanent) dipole with dipole moment \mathbf{p} at the centre of the sphere. Here $n = 1.33$ is the optical refractive index of water.

The short range interactions between dipoles are neglected. The local electric field strength at the centre of the sphere at the location of the permanent (rigid) point-like dipole (figure 2) is [25] :

$$\mathbf{E}_c = \frac{3\epsilon_r}{2\epsilon_r + n^2} \mathbf{E} \quad , \quad (3)$$

where the expression represents the field inside a spherical cavity with dielectric permittivity n^2 embedded in a medium with permittivity ϵ_r . In the following, Eq. (3) is simplified to the form (strictly valid for $\epsilon_r \gg n^2$ only): $\mathbf{E}_c = \frac{3}{2} \mathbf{E}$. The energy of the point-like dipole \mathbf{p} in the local field \mathbf{E}_c may then be written as:

$$W_i = -\mathbf{p} \cdot \mathbf{E}_c = \gamma p_o E \cos(\omega) \quad , \quad (4)$$

where p_o is the magnitude of the dipole moment \mathbf{p}_e , ω is the angle between the dipole moment vector \mathbf{p} and the vector $-\mathbf{E}$ and γ is [23]:

$$\gamma = \frac{3}{2} \left(\frac{2 + n^2}{3} \right) \quad . \quad (5)$$

The polarization $P(x) = n_w(x) \langle \mathbf{p}(x, \omega) \rangle_B$ is given by [23]:

$$P(x) = n_w(x) \left(\frac{2 + n^2}{3} \right) p_o \langle \cos(\omega) \rangle_B = -n_w(x) \left(\frac{2 + n^2}{3} \right) p_o \mathcal{L}(\gamma p_o E \beta) \quad , \quad (6)$$

where we took into account the well known result (see for example [25]):

$$\langle \cos(\omega) \rangle_B = \frac{\int_0^\pi \cos \omega \mathcal{P}(x, \omega) 2\pi \sin \omega d\omega}{\int_0^\pi \mathcal{P}(x, \omega) 2\pi \sin \omega d\omega} = -\mathcal{L}(\gamma p_o E \beta) \quad , \quad (7)$$

and $\beta = 1/kT$, where kT is the thermal energy. Since $\sigma < 0$, the projection of the polarization vector \mathbf{P} on the x-axis points in the direction from the bulk to the charged surface and $P(x)$ is considered negative.

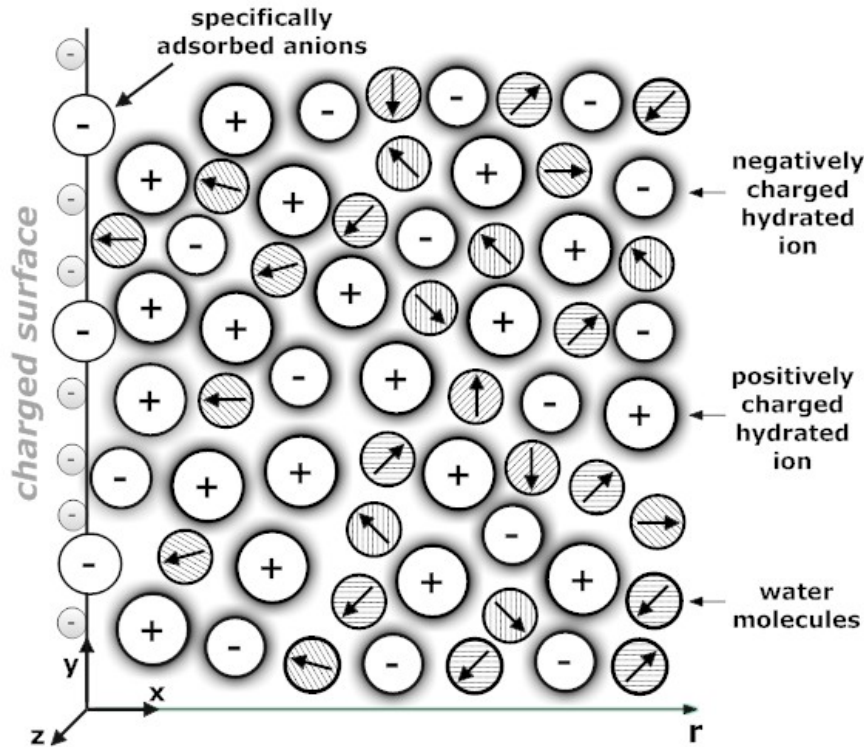


Figure 2. Schematic figure of the EDL near a negatively charged planar metal surface. The water dipoles in the vicinity of the charged surface are partially oriented towards the surface (adapted from [23, 37]).

Since in the bulk solution the number densities of water molecules (n_{0w}), counterions (n_0) and co-ions (n_0) are constant, their number densities can be expressed in a simple way by calculating the corresponding probabilities that a single lattice site in the bulk solution is occupied by one of the three kind of particles in the electrolyte solution (counterions, co-ions and water molecules) [8, 33, 34]. However, in the vicinity of a charged surface the number densities of ions and water molecules are influenced by the charged surface (figure 2), 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 [23]:

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

$$n_-(x) = n_s \frac{n_0 e^{e_0 \phi \beta}}{n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_o E \beta \cos(\omega)} \rangle_\omega}, \quad (9)$$

$$n_w(x) = n_s \frac{n_{0w} \langle e^{-\gamma p_o E \beta \cos(\omega)} \rangle_\omega}{n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_o E \beta \cos(\omega)} \rangle_\omega}, \quad (10)$$

where n_s is the number density of lattice sites as defined above and

$$\langle e^{-\gamma p_o E \beta \cos(\omega)} \rangle_\omega = \frac{2\pi \int_0^\pi d(\cos \omega) e^{-\gamma p_o E \beta \cos(\omega)}}{4\pi} = \frac{\sinh(\gamma p_o E \beta)}{\gamma p_o E \beta}. \quad (11)$$

is the dipole Boltzmann factor after rotational averaging over all possible angles ω . Eqs. (8)-(11) can be rewritten as [23]:

$$n_+(x) = n_0 e^{-e_0\phi\beta} \frac{n_s}{\mathcal{D}(\phi, E)} , \quad (12)$$

$$n_-(x) = n_0 e^{e_0\phi\beta} \frac{n_s}{\mathcal{D}(\phi, E)} , \quad (13)$$

$$n_w(x) = \frac{n_{0w} n_s}{\mathcal{D}(\phi, E)} \frac{\sinh(\gamma p_0 E \beta)}{\gamma p_0 E \beta} . \quad (14)$$

where $\mathcal{D}(\phi, E) = 2n_0 \cosh(e_0\phi\beta) + \frac{n_{0w}}{\gamma p_0 E \beta} \sinh(\gamma p_0 E \beta)$. Combining Eqs. (6) and (14) gives the polarization in the form:

$$P(x) = - \left(\frac{2 + n^2}{3} \right) \frac{p_0 n_{0w} n_s}{\mathcal{D}(\phi, E)} \frac{\mathcal{L}(\gamma p_0 E \beta)}{\gamma p_0 E \beta} \sinh(\gamma p_0 E \beta) . \quad (15)$$

Using the definition of the function $\mathcal{F}(u)$: $\mathcal{F}(u) = \mathcal{L}(u) (\sinh u/u)$ Eq. (15) transforms into:

$$P = - p_0 n_{0w} n_s \left(\frac{2 + n^2}{3} \right) \frac{\mathcal{F}(\gamma p_0 E \beta)}{\mathcal{D}(\phi, E)} . \quad (16)$$

Combining Eqs. (1) and (16) yields the relative (effective) permittivity [23] :

$$\varepsilon_r(x) = n^2 + n_{0w} n_s \frac{p_0}{\varepsilon_0} \left(\frac{2 + n^2}{3} \right) \frac{\mathcal{F}(\gamma p_0 E \beta)}{\mathcal{D}(\phi, E) E} . \quad (17)$$

Using the above expression for $\varepsilon_r(x)$, we can then write the Poisson equation in the form [8, 23]:

$$\nabla \cdot [\varepsilon_0 \varepsilon_r(x) \nabla \phi(x)] = -\rho_{free}(x) , \quad (18)$$

where $\rho_{free}(x)$ is the macroscopic (net) volume charge density of co-ions and counterions (see also Eqs. (12) and (13)) [23] :

$$\rho_{free}(x) = e_0 n_+(x) - e_0 n_-(x) = -2 e_0 n_s n_0 \frac{\sinh(e_0\phi\beta)}{\mathcal{D}(\phi, E)} . \quad (19)$$

The boundary conditions are [23]:

$$\nabla \phi(x=0) = -\frac{\sigma \mathbf{n}}{\varepsilon_0 \varepsilon_r(x=0)} , \quad \phi(x \rightarrow \infty) = 0 . \quad (20)$$

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. (17)) gives the well-known Onsager expression for permittivity:

$$\varepsilon_r \cong n^2 + \left(\frac{2 + n^2}{3} \right)^2 \frac{n_{0w} p_0^2 \beta}{2 \varepsilon_0} . \quad (21)$$

In the above derived expression for the relative (effective) permittivity (Eq. (17)), the value of the dipole moment $p_0 = 3.1 \text{ D}$ (Debye is $3.336 \cdot 10^{-30} \text{ C/m}$) predicts a bulk permittivity $\varepsilon_r = 78.5$. This value is considerably smaller than the corresponding value in previous similar

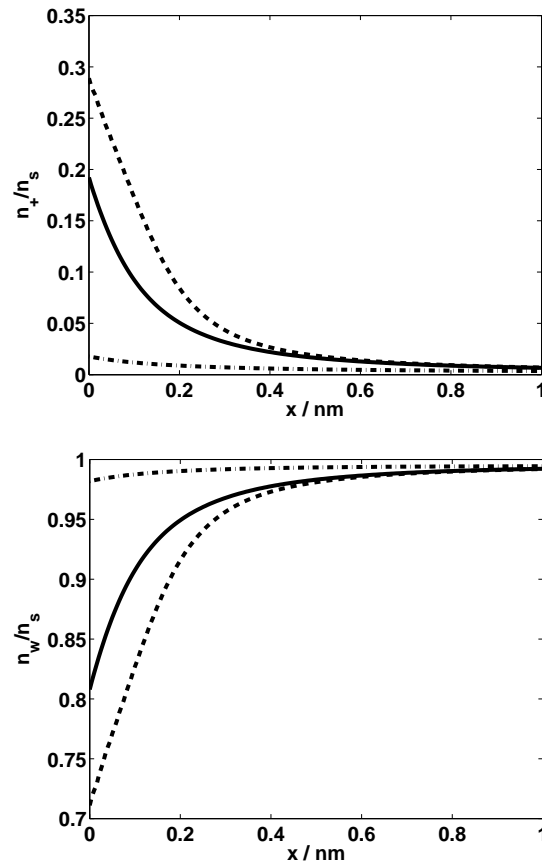


Figure 3. The relative number density of counter ions (n_+/n_s) and water dipoles (n_w/n_s) (calculated using Eqs. (12) and Eq. (14) as a function of distance from a planar charged surface x calculated for three values of surface charge density: $\sigma = -0.1 \text{ As/m}^2$ (dashed-dotted line), $\sigma = -0.2 \text{ As/m}^2$ (full line) and $\sigma = -0.3 \text{ As/m}^2$ (dashed line) (from [23]). Values of parameters assumed: dipole moment of water $p_0 = 3.1 D$, bulk concentration of salt $n_0/N_A = 0.15 \text{ mol/l}$, optical refractive index $n = 1.33$, bulk concentration of water $n_{ow}/N_A = 55 \text{ mol/l}$, where N_A is the Avogadro number.

models ($p_0 = 4.79 D$) [22, 31, 32] which did not take into account the cavity field and electronic polarizability of water molecules.

Figures 3 and 4 show the calculated spatial dependence of the relative number density of counter ions (n_+/n_s), water dipoles (n_w/n_s) and $\varepsilon_r(x)$ within the finite sized Gongadze-Iglič (GI) model in planar geometry for three values of the surface charge density σ .

It can be seen in figure 3 that close to the charged plane there may be a considerable excluded volume effect on the density profile of the counterions and on the solvent molecules. The concentration of counterions there is comparable to the concentration of solvent lattice sites, so that the concentration of solvent lattice sites deviates significantly from its value far from the charged surface.

The ratio between the concentration of the counterions near the charged plane and the bulk counter-ion concentration as a function of the surface charge density σ is higher for dimensionless ions than for ions of finite size. The discrepancy between the results for dimensionless ions and for ions of finite size grows with increasing $|\sigma|$ [35]. The deviation can be attributed to the steric

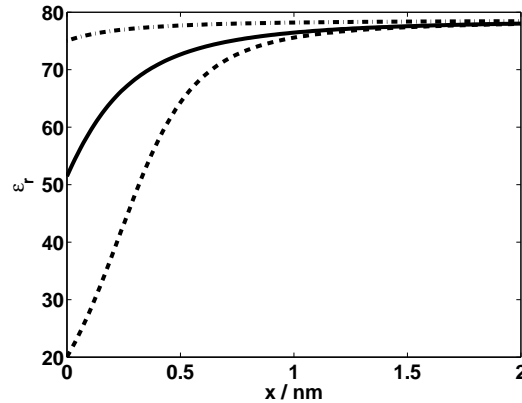


Figure 4. Relative permittivity ε_r (Eq. (17)) as a function of distance from a planar charged surface x (from [23]). Three values of surface charge density were considered: $\sigma = -0.1 \text{ As/m}^2$ (dashed-dotted line), $\sigma = -0.2 \text{ As/m}^2$ (full line) and $\sigma = -0.3 \text{ As/m}^2$ (dashed line). Eq. (18) was solved numerically taking into account the boundary conditions as described in [23]. Values of the model parameters are the same as in the previous figure.

effect of counterions and solvent molecules in the small region in the vicinity of the charged surface. The counter-ion concentration profile shows a rapid decrease for small lattice constant and a plateau region near the charged plane for large lattice constant. For large counterions we can therefore distinguish between two regions within the electric double layer: the saturated layer dominated by steric repulsion and the diffuse layer extending into the solution.

The decrease of $\varepsilon_r(x)$ towards the charged surface is pronounced with increasing σ (figure 4) and is a consequence of the increasing depletion of water molecules near the charged surface (due to the excluded volume effect as a consequence of accumulation of counterions near the charged surface) (figure 4) and increased orientational ordering of water dipoles (saturation effect). Comparison between the predictions of the GI model [23] and the Langevin Poisson-Boltzmann (LPB) model [8, 22] which does not take into account the finite size of molecules (i.e. assumes a constant density of water molecules), shows a stronger decrease of relative permittivity of the electrolyte solution near the highly charged surface stronger in the GI model than in the LPB model, mainly due to depletion of water molecules in the vicinity of the charged surface in the GI model (see figure 3).

3. Langevin-Bikerman model

In order to differentiate between the influence of the finite size of ions and the influence of the cavity field on the relative permittivity near the charged surface, the equations of the above described Gongadze-Iglič (GI) [23] model may be written in the limit of $\gamma \rightarrow 1$ and $n \rightarrow 1$ [8] to get [8, 36] :

$$\nabla \cdot [\varepsilon_0 \varepsilon_r(x) \nabla \phi(x)] = -\rho_{free}(x) \quad , \quad (22)$$

where $\rho_{free}(x)$ is the macroscopic (net) volume charge density of co-ions and counterions in the Langevin-Bikerman (LB) model :

$$\rho_{free}(x) = -2 e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{\mathcal{H}(\phi, E)} \quad , \quad (23)$$

while $\varepsilon_r(x)$ is the relative permittivity in the LB model [31, 32, 36] :

$$\varepsilon_r(x) = 1 + n_{0w}n_s \frac{p_0}{\varepsilon_0} \frac{\mathcal{F}(p_0 E \beta)}{E \mathcal{H}(\phi, E)} , \quad (24)$$

where $\mathcal{H}(\phi, E) = 2n_0 \cosh(e_0 \phi \beta) + \frac{n_{0w}}{p_0 E \beta} \sinh(p_0 E \beta)$.

Comparison between the space dependency of the relative permittivity within the GI model and within its limiting LB model for $\gamma \rightarrow 1$ and $n \rightarrow 1$ shows that consideration of the cavity field and electronic polarizability of water molecules makes the reduction of permittivity of the electrolyte solution near the charged surface stronger in the GI model [37]. More important, in the LB model (i.e. limit of $\gamma \rightarrow 1$ and $n \rightarrow 1$ of the GI model) the value $p_0 = 4.79 D$ [31, 32, 36] (similarly as in the LPB model [8, 22]) should be used in order to get $\varepsilon_r(x \rightarrow \infty) = 78.5$.

4. Bikerman model

In the limit of $p_0 \rightarrow 0$ the particle distribution functions (12)-(14) transform into Fermi-Dirac-like Bikerman distribution functions [11–15, 17, 35, 38, 39] :

$$n_+(x) = \frac{n_0 n_s}{n_{0w}} \frac{e^{-e_0 \phi \beta}}{1 + (2n_0/n_{0w}) \cosh(e_0 \phi \beta)} , \quad (25)$$

$$n_-(x) = \frac{n_0 n_s}{n_{0w}} \frac{e^{e_0 \phi \beta}}{1 + (2n_0/n_{0w}) \cosh(e_0 \phi \beta)} , \quad (26)$$

$$n_w(x) = \frac{n_s}{1 + (2n_0/n_{0w}) \cosh(e_0 \phi \beta)} , \quad (27)$$

while Eq. (18) transforms into the Bikerman equation [11–15, 17, 35, 38, 39] :

$$\nabla \cdot [\varepsilon_0 \varepsilon_r \nabla \phi(x)] = -\rho_{free}(x) \quad (28)$$

where we made the transformation $\varepsilon_0 \rightarrow \varepsilon_r \varepsilon_0$ with $\varepsilon_r = 78.5$, while $\rho_{free}(x)$ is defined by Eq.(23). Eq. (25) predicts a Fermi-Dirac-like distribution for counterions if the lattice constant a is large enough. For higher values of the surface charge density ($|\sigma|$), the counter-ion density saturates close to the charged surface to its close packing value, while the well-known Gouy-Chapman model [1–3] predicts unreasonably high values beyond the close-packing values (see also [11, 17, 35]).

5. Gouy-Chapman model

In the limit of a very dilute solution everywhere in the electrolyte solution:

$$\sum_{j=+,-} n_j(x) \ll n_w(x) , \quad (29)$$

and by taking into account the approximation $n_{0w} \simeq n_s$, we can neglect the second term in the denominator of Eqs. (25) and (26), so the particle distribution function (25) and (26) transform into Boltzmann distribution functions within the Gouy-Chapman model [1–4, 7, 40]:

$$n_+(x) = n_0 e^{-e_0 \phi \beta} , \quad (30)$$

$$n_-(x) = n_0 e^{e_0 \phi \beta} , \quad (31)$$

while the number density of water molecules (Eq.(27)) becomes constant [17, 35] :

$$n_w(x) = n_{0w} . \quad (32)$$

The Bikerman Eq.(28) transforms into the Poisson-Boltzmann equation within the Gouy-Chapman model [1–3]:

$$\nabla \cdot [\varepsilon_0 \varepsilon_r \nabla \phi(x)] = 2e_0 n_0 \sinh(e_0 \phi \beta) . \quad (33)$$

6. Discussion and Conclusions

In theoretical models of the EDL, the effect of a polarizing environment can be captured by introducing the cavity field [25, 29, 30]. In the past, treatments of the cavity field in the Onsager [29], Kirkwood [30] and Fröhlich [25] models were limited to the case of small electric field strengths far away from the saturation limit [41]. Later a generalization in the saturation regime was performed [23, 26, 41].

In this review it was shown that considering the cavity field of a single water molecule and the finite size of the ions result in a more realistic description of the decrease of the permittivity near the charged surface [8, 23]. The corresponding analytical expression for the spatial dependence of relative permittivity of an electrolyte solution near the charged surface is given in [8, 23, 34].

The dipole moment of an isolated water monomer is 1.855 D, while the dipole moment of a water molecule in bulk liquid water [27] is around 2.4 - 2.6 D [28, 42]. By considering the cavity field at the centre of a water molecule and its electronic polarizability [25], a magnitude of the external water dipole moment around 3 D was suggested within the mean-field lattice statistics approach [23] in accordance with predictions of previous theoretical treatments within the lattice model approach [27, 42]. Neglecting the cavity field and the electronic polarizability within lattice statistics theoretical models leads to much higher predicted values of the water external dipole moment around 5 D [22, 31].

To ascertain whether the described Gongadze-Iglič (GI) mean-field model (which includes orientational ordering of water, cavity field, electronic polarizability of water and finite size of molecules) has improved the agreement between theory and experiments with respect to the classical Gouy-Chapman model, one should compare the measured and the predicted values of electric potential and differential capacitance of the EDL in both models. Within the GI model the predicted values of the electric potential at higher surface charge densities σ are substantially more negative than the corresponding values within the Gouy-Chapman model (see Ref. [33] and references therein).

Within the Gouy-Chapman model, we can estimate the electric potential ϕ_0 at the surface (of the electrode for example) by the using Grahame equation [20]:

$$\sigma = \sqrt{8 n_0 \varepsilon_0 \varepsilon_r / \beta} \cdot \sinh \left(\frac{e_0 \beta \phi_0}{2} \right) , \quad (34)$$

where ϕ_0 is the surface potential, i.e. $\phi(x=0)$. The corresponding Gouy-Chapman differential capacitance is [20]:

$$C_{GC} = \frac{d\sigma}{d\phi_0} = \sqrt{2 e_0^2 \beta n_0 \varepsilon_0 \varepsilon_r} \cdot \cosh \left(\frac{e_0 \beta \phi_0}{2} \right) . \quad (35)$$

The Gouy-Chapman model provides relatively good predictions for monovalent salts at concentrations below 0.2 mol/l in aqueous solutions and magnitudes of surface potentials below 50–80 mV [20]. However, by increasing the surface charge density (i.e. increasing the magnitude of ϕ_0) the differential capacitance calculated within the GI model decreases. By applying a voltage of up to 1V, the differential capacitance drops to very small values in accordance with experimental results (see also Refs. [20, 21, 33]). Obviously, the GI model also works efficiently at higher surface charge densities or potentials, where the classical Gouy-Chapman model completely fails as the differential capacitance C_{GC} (unlike the experimental results) strongly and monotonously increases with increasing ϕ_0 .

On the contrary, in the GI model, in accordance with the experimental results [20, 43], the differential capacitance decreases with increasing ϕ_0 after reaching its maximum. The predicted values of differential capacitance at high values of ϕ_0 are much smaller than the corresponding values calculated using the empirical formula for $\varepsilon(x)$ [21]. Moreover, if the Gongadze-Iglič (GI) model is modified by also taking into account the distance of closest approach [8], the predicted values of differential capacitance would closely approach to the experimental values [43].

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