

The quadrupole moment of water molecules and the permittivity of water near a charged surface



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ABSTRACT

The interface electrolyte-charged surface has been captured within the generalized Langevin Poisson–Boltzmann and Langevin–Bikerman models. Here we have modified the latter models to illustrate the importance of the non-zero quadrupole moment of the water molecule within a triangular atomic model. It is shown that the local decrease of relative permittivity of electrolyte solution near the charged surface is further pronounced due to quadrupole moment of the water molecule. The effect is stronger for larger magnitudes of surface charge density.

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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 electric double layer (EDL) [1–9]. The properties of EDL may be strongly influenced by the ordering of water molecules [10–16] and the depletion of water molecules in this region [17]. It has been shown that close to the charged surface water dipole ordering in saturation regime and depletion of water molecules may result in a strong local decrease of permittivity [18,12,13,19,15,17,20–23].

Considering the orientational ordering of water and finite size of molecules, Outhwaite developed a modified Poisson–Boltzmann (PB) theory of the EDL composed of a mixture of hard spheres with point dipoles and finite-sized ions [18,24]. Later, Szalai et al. [25] published a mean spherical approximation [26] based theory that can reproduce simulation results for the electric field dependence of the dielectric permittivity of a dipolar fluid in saturation regime. The problem was recently considered also within lattice statistics model [16,17].

The dipole moment of an isolated water monomer is 1.855 D (Debye is 3.336×10^{-30} C/m). On the other hand, the dipole moment of a water molecule in bulk liquid water differs from that of an isolated water molecule, because each water molecule is also polarized by the electric field of the neighbouring water molecules [27], therefore the corresponding value in the condensed water phase is around 2.4–2.6 D [28,29]. The effect of the polarizing environment can be captured in a most simple way by introducing the cavity field [30–32]. In the past, treatments of the cavity field in the Onsager [30], Kirkwood [31] and Fröhlich [32] models were limited to the case of small electric field strengths, i.e. they were far away from the saturation limit [25]. Later generalization of the Kirkwood–Onsager–Fröhlich theory in the saturation regime was performed [17,25,33] which is also the case of the model presented in this paper.

By considering the cavity field at the centre of a water molecule [32,33] and also the electronic polarizability of a water molecule [17,32,33] (taken into account by picturing the single water molecules as a dielectric sphere and a point-like rigid dipole at the centre of the sphere [32]) the magnitude of external water dipole moment around 3 D was suggested within the mean-field lattice statistics approach [16,17] in accordance with predictions of previous theoretical ice lattice treatments [27,28]. On the other hand, neglecting the cavity field and the electronic polarizability

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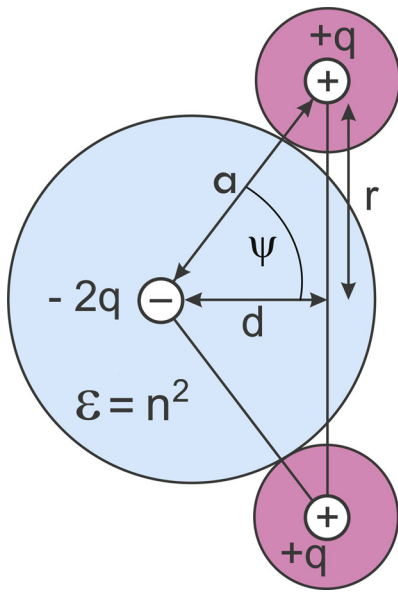


Fig. 1. A schematic figure of charge distribution of single water molecule within triangular atomic model ($+ \equiv +q$ and $- \equiv -q$). In the model a single water molecule is considered as a sphere with permittivity n^2 and point-like rigid (permanent) dipole/quadropole at the center of the sphere. Here n is the optical refractive index of water.

within the similar lattice statistics, the theoretical models lead to much higher predicted value of the water external dipole moments around 5 D [15,34].

In this work, generalization of EDL mean-field theory of electrolyte solution in contact with a charged surface based on lattice statistics is performed. The non-zero value of water quadrupole moment is taken into account while considering orientational ordering of water molecules near the charged surface. The finite volumes of molecules, cavity field and the electronic polarizability are also taken into account.

2. Theory

2.1. Point-like molecules

In the presented model, the charge distribution within a single water molecule is taken into account considering a point-like and rigid (permanent) dipole/quadropole in the centre of a sphere with a volume equal to the average volume of a water molecule in the electrolyte solution (as shown in schematic Fig. 1). The permittivity of the sphere is n^2 , where $n = 1.33$ is the optical refractive index of water. The energy of the point-like dipole/quadropole in the local field $E_c = E(3\epsilon_r/(2\epsilon_r + n^2)) \approx 3E/2$ (assuming $\epsilon_r \gg n^2$) [16,17,30,32,33], i.e. in the field inside a spherical cavity with dielectric permittivity n^2 (at the location of the the point-like dipole/quadropole) embedded in a medium with permittivity ϵ_r , may be written as (see online Supplementary Information):

$$W(\omega) = \gamma p_0 |E| \cos \omega - \gamma q \frac{r^2}{2} \left| \frac{dE}{dx} \right| \sin^2 \omega, \quad (1)$$

where we assume a triangular atomic model of the water molecule (Fig. 1) (see also [35]). Here p_0 is the magnitude of the external water dipole moment $\mathbf{p}_e = (3/(2+n^2))\mathbf{p}$ [32,17], $p = 2qd$ (see Fig. 1), ω is the angle between the dipole moment vector \mathbf{p} and the vector $-\mathbf{E}$, $2r$ is the distance between the positive charges in the triangular atomic model of water (see Fig. 1) and the factor γ is [17]: $\gamma = (3/2)((2+n^2)/3)$. The external water dipole moment \mathbf{p}_e is the (effective) dipole moment of the water sphere with permittivity n^2

and the point-like dipole \mathbf{p} located at its centre [32,30,33,17] (see also Fig. 1).

In the limit of $r \rightarrow 0$ the above expression for the energy of a single water molecule $W(\omega)$ in the external electric field transforms into $W(\omega) \rightarrow \gamma p_0 |E| \cos \omega$ [17]. It can be seen from Eq. (1) that for zero quadrupole term ($\alpha = 0$), the minimum of $W(\omega)$ coincides with $\omega = \pi$, i.e. orientation of the water dipole in the direction of the electric field vector, while for increasing quadrupole contribution (i.e. increasing $\gamma q(r^2/2)|dE/dx|$), the minimum is moving towards $\omega = \pi/2$ as expected (see also Fig. 2 in Ref. [36]).

The relative (effective) permittivity of the electrolyte solution (ϵ_r) is expressed as:

$$\epsilon_r = n^2 + \frac{|\mathbf{P}|}{\epsilon_0 |\mathbf{E}|}, \quad (2)$$

where \mathbf{P} is the polarization vector due to orientation of water dipoles. In Eq. (2) we have neglected the water quadrupole moment in averaged microscopic charge distribution within the single water molecule, i.e. we assumed the validity of relation [37,38] $\rho(x) = \rho_{free}(x) - \nabla \cdot \mathbf{P}$, where $\rho(x)$ is the average microscopic volume charge density and $\rho_{free}(x)$ macroscopic volume charge density equal to the sum of the contributions of the local net ion charges (see also [16,17,32]). The water quadrupole moment is therefore taken into account directly only in the energy of the single water molecules, i.e. in the average orientation of the single water molecule.

The polarization $P(x)$ is then given by [17]:

$$P(x) = n_w(x) \left(\frac{2+n^2}{3} \right) p_0 \langle \cos(\omega) \rangle_B \quad (3)$$

where

$$\langle \cos(\omega) \rangle_B = \frac{\int_0^\pi \cos \omega \exp(-\beta W(\omega)) d\Omega}{\int_0^\pi \exp(-\beta W(\omega)) d\Omega}, \quad (4)$$

$n_w(x)$ is the number density of water molecules, $d\Omega = 2\pi \sin \omega d\omega$ is an element of solid angle and x is the distance from the charged surface in the perpendicular direction. Since the surface charge density $\sigma < 0$, the projection of the polarization vector on the x -axis points in the direction from the bulk to the charged surface and $P(x)$ is considered negative.

Combining Eqs. (1) and (4) and performing the necessary integrations yields:

$$\langle \cos \omega \rangle_B = \frac{e^{-(\Lambda/2\alpha)-\alpha^2} - e^{-(\Lambda/2\alpha)+\alpha^2} - \sqrt{\pi} \beta [\text{erf}((\Lambda/2\alpha) + \alpha) - \text{erf}((\Lambda/2\alpha) - \alpha)]}{\sqrt{\pi} \alpha [\text{erf}((\Lambda/2\alpha) + \alpha) - \text{erf}((\Lambda/2\alpha) - \alpha)]}, \quad (5)$$

where

$$\alpha = \sqrt{\beta \gamma q \frac{r^2}{2} \left| \frac{dE}{dx} \right|}, \quad \Lambda = \gamma p_0 \beta |E| \quad (6)$$

and $\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$ is the error function. In the limit of small α , i.e. large $\Lambda/2\alpha$, the above expression for $\langle \cos \omega \rangle_B$ transforms into:

$$\langle \cos \omega \rangle_B = \frac{-\mathcal{L}(\Lambda)}{[1 + (2\alpha^2/\Lambda)\mathcal{L}(\Lambda)]}, \quad (7)$$

where the expansion $\text{erf}(z) \cong 1 - (1/\sqrt{\pi})(1/z)e^{-z^2}[1 - (1/2)(1/z^2)]$ was used. Here $\mathcal{L}(u) = (\coth(u) - 1/u)$ is the Langevin function.

Fig. 2 shows the dependence of $\langle \cos \omega \rangle_B$ on the parameter $\Lambda = \beta \gamma p_0 |E|$ for different values of α describing the magnitude of quadrupole moment of water molecules. The absolute value of $\langle \cos \omega \rangle_B$ decreases with increasing α since increasing α moves the minimum of the energy of the single water molecule W (Eq. (1))

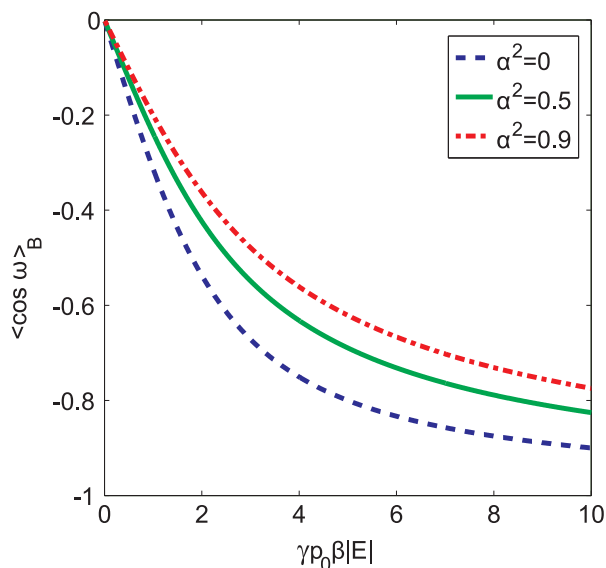


Fig. 2. The average orientation of water molecules characterized by $\langle \cos \omega \rangle_B$ as a function of the magnitude of electric field strength for different values of parameter α (Eq. (6)) describing the quadrupole charge distribution within single water molecule.

towards $\omega = \pi/2$, i.e. away from $\omega = \pi$ which corresponds to zero quadrupole moment of water molecule ($\alpha = 0$). In accordance, in the limit of vanishing quadrupole term ($\alpha = 0$) Eq. (7) recovers the previous result $\langle \cos \omega \rangle_B = -\mathcal{L}(\Lambda)$ [17]. Fig. 2 indicates that the increasing quadrupole of water molecules reduces the orientation of water dipole moment in the direction of the electric field vector. In the limit of a very large quadrupole moment or very large $|dE/dx|$, the orientation of water dipole moment vector would be perpendicular to the electric field vector as predicted for divalent quadrupole particles [39,40].

For the sake of simplicity we first assume that the number density of water molecules is constant everywhere in the solution, i.e. $n_w(x) = n_{0w}$ which coincides with the assumption of point-like ions [6,15]. Using Eq. (7) the polarization can be then written in the form:

$$P(x) = -n_{0w}p_0 \left(\frac{2+n^2}{3} \right) \frac{\mathcal{L}(\Lambda)}{[1+(2\alpha^2/\Lambda)\mathcal{L}(\Lambda)]}, \quad (8)$$

where x is the distance from the charged surface in the perpendicular direction. Since $\sigma < 0$, the projection of the polarization vector on the x -axis points in the direction from the bulk to the charged surface and $P(x)$ is negative. Using Eq. (8) it follows from Eq. (2):

$$\varepsilon_r(x) = n^2 + \frac{n_{0w}p_0}{\varepsilon_0|E|} \left(\frac{2+n^2}{3} \right) \frac{\mathcal{L}(\Lambda)}{[1+(2\alpha^2/\Lambda)\mathcal{L}(\Lambda)]}, \quad (9)$$

or

$$\varepsilon_r(x) = n^2 + \frac{3}{2} \left(\frac{2+n^2}{3} \right)^2 \frac{n_{0w}p_0^2\beta}{\varepsilon_0} \frac{\mathcal{L}(\gamma p_0 \beta |E|)}{\gamma p_0 \beta |E|} \times \frac{1}{[1+2Q|dE/dx|(\mathcal{L}(\gamma p_0 \beta |E|))/(\gamma p_0 \beta |E|)]}, \quad (10)$$

where

$$Q = \beta \gamma q \frac{r^2}{2}. \quad (11)$$

For room temperature, refractive index $n = 1.33$, $r = a \sin \Psi \approx 0.08$ nm (see Fig. 1), where $\Psi \approx 52.5^\circ$ and $a \approx 0.1$ nm

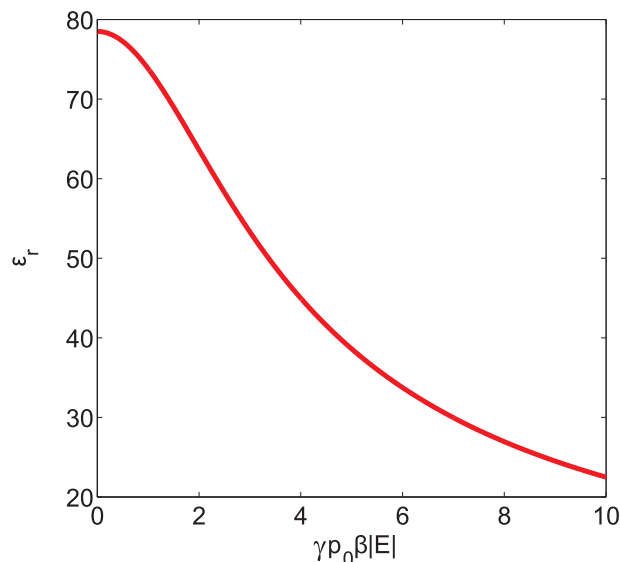


Fig. 3. Calculated relative permittivity ε_r (see Eq. (10)) as a function of the parameter $\gamma p_0 \beta |E|$ for quadrupole parameter $Q = 0$ (for definition see Eq. (10)). Values of other model parameters are: magnitude of the external water dipole moment of the water $p_0 = 3.1$ D, optical refractive index $n = 1.33$, bulk concentration of water $n_{0w}/N_A = 55$ mol/l, where N_A is Avogadro number.

(taken from Ref. [35]), it follows that $Q \approx 2.3 \times 10^{-19}$ m²/V. In the limit of zero quadrupole moment of water (i.e. $Q = 0$), the above Eq. (10) recovers the result of modified Langevin Poisson–Boltzmann model [41,15], where the quadrupole moment of water was not taken into account. In the limit of vanishing $|E|$ and $|dE/dx|$ (or very small $|E|$ and $|dE/dx| = 0$) Eq. (10) yields the Onsager expression for permittivity:

$$\varepsilon_r \approx n^2 + \left(\frac{2+n^2}{3} \right)^2 \frac{n_{0w}p_0^2\beta}{2\varepsilon_0}, \quad (12)$$

where we took into account that for very small or zero $|E|$ the ratio becomes $\mathcal{L}(\beta \gamma p_0 |E|)/\beta \gamma p_0 |E| = 1/3$. The Onsager expression for permittivity [30,32,33] describes the permittivity of electrolyte solution far away from the charged surface (i.e. in the bulk solution) where due to the screening of the electrostatic field the values of $|E|$ and $|dE/dx|$ are zero. At room temperature and bulk number density of water $n_{0w}/N_A = 55$ mol/l. Eq. (12) predicts the bulk value of permittivity ($\varepsilon_r = 78.5$) for $p_0 = 3.1$ D (see also Figs. 3–5).

Fig. 3 shows the dependence of the relative permittivity ε_r (see Eq. (10)) on the parameter $\gamma p_0 \beta |E|$, which is proportional to the magnitude of electric field strength $|E|$, for $Q = 0$. It can be seen in Fig. 3 that ε_r increases with decreasing $|E|$ and attains the value 78.5 at $|E| = 0$. Since the value of $|E|$ decreases with increasing distance from the charged surface (due to screening), the magnitude of ε_r decreases with the increasing distance from the charged surface in accordance with our previous results [15,17].

Using the method presented in [16,17] Poisson equation $\nabla \cdot [\varepsilon_0 \varepsilon_r(x) \nabla \phi(x)] = -\rho_{free}(x)$ in a planar geometry can be written in the form of a modified Langevin Poisson–Boltzmann equation:

$$\frac{d}{dx} \left[\varepsilon_0 \varepsilon_r(x) \frac{d\phi}{dx} \right] = 2e_0 n_0 \sinh(e_0 \phi \beta), \quad (13)$$

where $\phi(x)$ is the electric potential, $\varepsilon_r(x)$ is defined by Eq. (10), $\rho_{free}(x) = e_0 n_+(x) - e_0 n_-(x) = -2e_0 n_0 \sinh(e_0 \phi \beta)$ is the macroscopic (net) volume charge density [15,38] of point-like counterions (+) and coions (−) of electrolyte solution distributed according to Boltzmann distribution functions [6,12]: $n_+(x) = n_0 \exp(-e_0 \phi(x) \beta)$ and $n_-(x) = n_0 \exp(e_0 \phi(x) \beta)$, e_0 is the unit charge and n_0 bulk number

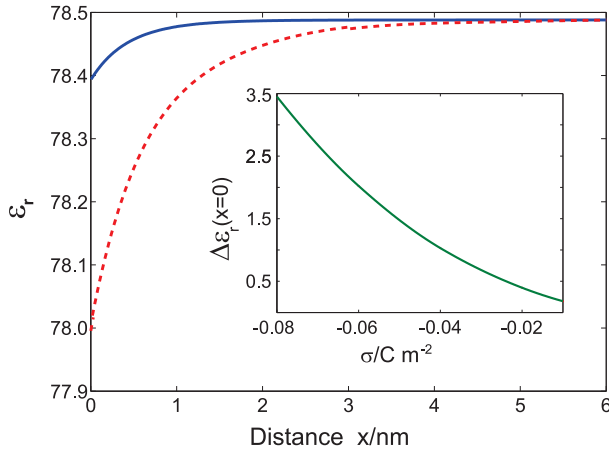


Fig. 4. The space dependence of relative permittivity $\varepsilon_r(x)$ for point-like molecules (Eq. (10)) as a function of distance from a planar charged surface x calculated for two values of the quadrupole parameter Q (Eq. (11)): $0.0 \text{ m}^2/\text{V}$ (full curve) and $2.3 \times 10^{-19} \text{ m}^2/\text{V}$ (dashed curve). Inset show the difference in $\varepsilon_r(x=0)$ for the above two values of Q as a function of surface charge density σ . Values of other model parameters are: surface charge density $\sigma = -0.02 \text{ As/m}^2$, $p_0 = 3.1 \text{ D}$, $n = 1.33$, bulk concentration of salt $n_0/N_A = 0.1 \text{ mol/l}$ and $n_{ow}/N_A = 55 \text{ mol/l}$.

density of coions and counterions. The boundary conditions are (see also [16]):

$$\frac{d\phi}{dx}(x=0) = -\frac{\sigma}{\varepsilon_0 \varepsilon_r(x=0)}, \quad \frac{d\phi}{dx}(x \rightarrow \infty) = 0, \quad \phi(x \rightarrow \infty) = 0. \quad (14)$$

Eq. (13) was solved numerically for a planar geometry using finite element method (FEM) within Comsol Multiphysics 4.3a software program package (COMSOL AB, Stockholm). The boundary conditions (Eqs. (14)) were taken into account. Eq. (13) was solved numerically also in Matlab2012b using standard implemented function for solving boundary value problems (bvp4c) with two boundary conditions (Eqs. (14)). Again the space dependence of $\varepsilon_r(x)$ (Eq. (10)) in Eq. (13) was taken into account in on iteration process outside of bvp4c function.

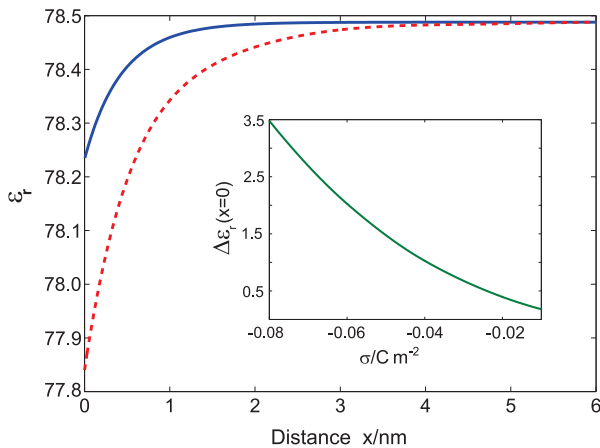


Fig. 5. The space dependence of relative permittivity $\varepsilon_r(x)$ for finite sized molecules (Eq. (28)) as a function of distance from a planar charged surface x calculated for surface charge density $\sigma = -0.02 \text{ As/m}^2$ and two values of quadrupole parameter $Q = 0$ (full curve) and $Q = 2.3 \times 10^{-19} \text{ m}^2/\text{V}$ (dashed curve). Inset show the difference in $\varepsilon_r(x=0)$ for the above two values of Q as a function of surface charge density. Values of other model parameters are: bulk concentration of salt $n_0/N_A = 0.1 \text{ mol/l}$ and $n_{ow}/N_A = 55 \text{ mol/l}$.

2.2. Finite-sized molecules

In the previous section the finite size of molecules is not taken into account. Therefore the equations above are generalized the equations above are generalized to take into account also the finite size of molecules (water and ions). The finite size of molecules were described within lattice statistic model (i.e. modified Langevin–Bikerman model) [17] by assuming that ions and water dipoles are distributed in a lattice, where each lattice site is occupied by only one of the three molecular species (cations, co-ions, water molecules):

$$n_+(x) = n_s \frac{n_0 e^{-e_0 \phi \beta}}{n_0 e^{-e_0 \phi \beta} + n_0 e^{e_0 \phi \beta} + n_{0w} \langle e^{-\beta W(\omega)} \rangle_\omega}, \quad (15)$$

$$n_-(x) = n_s \frac{n_0 e^{e_0 \phi \beta}}{n_0 e^{-e_0 \phi \beta} + n_0 e^{e_0 \phi \beta} + n_{0w} \langle e^{-\beta W(\omega)} \rangle_\omega}, \quad (16)$$

$$n_w(x) = n_s \frac{n_{0w} \langle e^{-\beta W(\omega)} \rangle_\omega}{n_0 e^{-e_0 \phi \beta} + n_0 e^{e_0 \phi \beta} + n_{0w} \langle e^{-\beta W(\omega)} \rangle_\omega}, \quad (17)$$

where n_s being the number density of lattice sites and

$$\begin{aligned} \langle e^{-\beta W(\omega)} \rangle_\omega &= \frac{1}{4\pi} \int_0^\pi 2\pi \sin \omega e^{-\beta \gamma |E| p_0 \cos \omega + \beta \gamma q (r^2/2) |dE/dx| \sin^2 \omega} d\omega \\ &= \frac{\sqrt{\pi} e^{\alpha^2 + (\Lambda^2/4\alpha^2)}}{4\alpha} \left[\operatorname{erf} \left(\frac{\Lambda}{2\alpha} + \alpha \right) - \operatorname{erf} \left(\frac{\Lambda}{2\alpha} - \alpha \right) \right], \end{aligned} \quad (18)$$

is the dipole Boltzmann factor after rotational averaging over all possible angles ω . In the limit of small α , i.e. large $\Lambda/2\alpha$, the above expression transforms into:

$$\langle e^{-\beta W(\omega)} \rangle_\omega = \frac{\sinh(\Lambda)}{\Lambda} \left[1 + 2\alpha^2 \frac{\mathcal{L}(\Lambda)}{\Lambda} \right]. \quad (19)$$

Eqs. (15)–(17) can be rewritten as:

$$n_+(x) = n_0 e^{-e_0 \phi \beta} \frac{n_s}{\mathcal{G}}, \quad (20)$$

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

$$n_w(x) = \frac{n_{0w} n_s}{\mathcal{G}} \frac{\sinh(\Lambda)}{\Lambda} \left[1 + 2\alpha^2 \frac{\mathcal{L}(\Lambda)}{\Lambda} \right], \quad (22)$$

where

$$\mathcal{G} = 2n_0 \cosh(e_0 \phi \beta) + n_{0w} \frac{\sinh(\Lambda)}{\Lambda} \left[1 + 2\alpha^2 \frac{\mathcal{L}(\Lambda)}{\Lambda} \right]. \quad (23)$$

or

$$\mathcal{G} = 2n_0 \cosh(e_0 \phi \beta) + n_{0w} \frac{\sinh(\gamma p_0 \beta |E|)}{\gamma p_0 \beta |E|} \left[1 + 2Q \left| \frac{dE}{dx} \right| \frac{\mathcal{L}(\gamma p_0 \beta |E|)}{\gamma p_0 \beta |E|} \right]. \quad (24)$$

Hence the corresponding macroscopic (net) volume charge density of coions and counterions reads:

$$\rho_{free}(x) = e_0 n_+(x) - e_0 n_-(x) = -2e_0 n_0 n_s \frac{\sinh(e_0 \phi \beta)}{\mathcal{G}}. \quad (25)$$

Combining Eqs. (3), (5), (22) and (24) gives the polarization in the form:

$$P(\omega) = -p_0 n_{0w} n_s \left(\frac{2 + n^2}{3} \right) \frac{\mathcal{F}(\Lambda)}{\mathcal{G}(\phi, \Lambda, \alpha)}, \quad (26)$$

where

$$\mathcal{F}(\Lambda) = \mathcal{L}(\Lambda) \frac{\sinh(\Lambda)}{\Lambda}. \quad (27)$$

Combination of Eq. (26) and Eq. (2) yields the space dependent relative (effective) permittivity $\varepsilon_r(x)$:

$$\varepsilon_r(x) = n^2 + n_{0w}n_s \frac{p_0}{\varepsilon_0} \left(\frac{2+n^2}{3} \right) \frac{\mathcal{F}(\Lambda)}{|E| \mathcal{G}(\phi, \Lambda, \alpha)}. \quad (28)$$

In the limit of zero quadrupole moment of water (i.e. $Q=0$), the above Eq. (28) gives the same result as the modified Langevin–Bikerman model [17], where the quadrupole moment of water was not taken into account. In the limit of vanishing $|E|$ and $|dE/dx|$ Eq. (28) yields the Onsager expression for permittivity (Eq. (12)). Following the previous described method [17] and inserting the above expression for $\varepsilon_r(x)$ (Eq. (28)) and macroscopic volume charge density $\rho_{free}(x)$ (Eq. (25)) in Poisson equation $\nabla \cdot [\varepsilon_0 \varepsilon_r(x) \nabla \phi(x)] = -\rho_{free}(x)$ the corresponding generalized Gongadze–Iglič equation can be written in the form:

$$\frac{d}{dx} \left[\varepsilon_0 \varepsilon_r(x) \frac{d\phi}{dx} \right] = 2e_0 n_0 n_s \frac{\sinh(e_0 \phi \beta)}{\mathcal{G}(\phi, \Lambda, \alpha)}, \quad (29)$$

where $\varepsilon_r(x)$ is defined by Eq. (28). Eq. (29) was solved numerically for a planar geometry using finite element method (FEM) within Comsol Multiphysics 4.3a software program package where the space dependence of ε_r (Eq. (28)) was taken into account in an iterative procedure. The boundary conditions (14) were taken into account, where again $\varepsilon_r(x)$ is defined by Eq. (28).

3. Results

Fig. 4 shows the spatial dependence of $\varepsilon_r(x)$ in a planar geometry for zero and non-zero value of the quadrupole parameter Q (Eq. (11)) calculated within the above presented generalized Langevin Poisson–Boltzmann model for point-like molecules. The predicted decrease of ε_r towards the charged surface is more pronounced for non-zero value of quadrupole parameter Q , which may be explained by reduced polarization with increasing $|dE/dx|$ (close to the charged surface) in the direction towards the charged surface, i.e. weaker orientation of water dipoles in the direction of negative x -axis due increasing $|dE/dx|$ in accordance with the results given in Fig. 2. The effect increases with increasing magnitude of the surface charge density σ . In conclusion, comparison between the predictions of our model for different values of the quadrupole parameter Q shows that the decrease of relative permittivity of the electrolyte solution near the charged surface is strengthened due to quadrupole charge distribution within a water molecule (see also Fig. 1).

Fig. 5 shows the space dependence of relative permittivity $\varepsilon_r(x)$ for finite-sized molecules as a function of the distance from the planar charged surface x for zero and non-zero quadrupole moment. Comparison of Figs. 4 and 5 indicates that for considered values of surface charge density σ the effect of water quadrupole moment on the decrease of $\varepsilon_r(x)$ near the charged surface is the same for point-like and finite-sized ions.

4. Discussion

Electrostatic interactions play an important role in many biologically processes – in binding of proteins to the cell membrane surface, conformational changes of membrane proteins, cell–cell interactions, interaction of cells with the implant surface, transport of ions through the membrane protein channels, binding of RNA molecules and charged peptides and many others [3,5,42–44]. In simulations and theoretical modelling of these processes the electrostatic potential is usually calculated by using the standard

Poisson–Boltzmann (PB) equation. Moreover, this equation is very often considered within Debye–Hückel approximation, i.e. linearized, assuming small values of electric potential. Frequently the PB description is further simplified by assuming constant values of relative permittivity in the whole system or space dependence of permittivity $\varepsilon_r(r)$ is approximated by different constant values in different regions of the Debye–Hückel model [44]. In this work an analytical formula for the spatial dependence of the relative permittivity in an electrolyte solution being in contact with a charged surface is derived which takes into account the dipole and quadrupole moment of water molecule.

The presented analytical expression for space dependent permittivity can be used in different types of simulations by solving the appropriate Poisson equation, i.e. the generalized Langevin Poisson–Boltzmann equation for point-like salt ions (Eq. (13)) or generalized Langevin–Bikerman (Gongadze–Iglič) equation (Eq. (29)) which takes into account the finite size of salt ions and water molecules. Note that RHS of the derived generalized Langevin Poisson–Boltzmann (Eq. (13)) is exactly the same as the RHS of the standard PB equation. This means that the derived space dependent permittivity for point-like ions (Eq. (10)) can be incorporated in already existing computations models, like for example in the recently published model of Do et al., 2013 [44]. Our two analytical expressions for space dependence of permittivity (Eqs. (10) and (28)) are therefore very general and easy to apply in different computational methods to study the electrostatics-driven phenomena in biological systems. The derived expression for space of permittivity takes into account the dipole and quadrupole moment of the water molecule within a triangular atomic model. To our knowledge, this is the first time that the water quadrupole moment is considered within the mean-field description of electric double layer and that the corresponding analytical expressions for spatial dependence of permittivity is derived for point-like molecules and finite-sized molecules in an electrolyte solution.

In the present work the finite size of ions was taken into account within simple lattice statistics mean-field approach. For simplicity reason the centres of the ions of an electrolyte solution are assumed to be completely free to approach to the charged surface located at $x=0$. The opposite limiting case would be to postulate an interfacial region, i.e. the so-called Stern layer [45,46], completely depleted of ions and having the dielectric permittivity much smaller than that of the bulk solution due to strong orientation of water in saturation regime and partially also depletion of water molecules due to excluded volume effect as presented also in this work. The latter can be described in the model by introducing the distance of the closest approach with the centres of (counter) ions in the so-called outer Helmholtz plane [12,16,19,45,47]. The real situation is usually somewhere in between and depends on the magnitude of the surface charge density σ [19]. As shown in this paper the properties of electric double layer depend on the water orientation also at the distances further away from one or two most strongly oriented layers of water molecules at the charged surface. Taking into account also the direct interactions (which is beyond the presented simple mean-field approach) would make the influence of strongly oriented layers of water close to the charged surface even more important. Namely, because the local decrease of permittivity at the charged surface the corresponding image charges repel both the counterions and the coions as recently shown by Nagy et al. [19].

The spatial dependence of permittivity of electrolyte solution in the vicinity of charged surface deserved much attention in scientific literature in the last years [15,17,19–23]. We have shown in this work that close to the charged surface the quadrupole moment of water molecules reduces the orientation of water dipole moment in the direction of the electric field vector. In the limit of very large $|dE/dx|$ the orientation of the water dipole moment vector

would be perpendicular to the electric field vector as predicted for divalent quadrupole particles [39,40]. Since the quadrupole moment decreases the average orientation of the water molecules in the direction perpendicular to the charged surface the relative permittivity of an electrolyte solution near a charged surface is additionally reduced as shown in Figs. 4 and 5 of this work. The effect is stronger for larger magnitudes of the surface charge density. In the range of the values of the surface charge density σ considered in this work, there is practically no difference in the effect of the water quadrupole moment on the permittivity decrease near the charged surface between the generalized Langevin Poisson–Boltzmann and Langevin–Bikerman models (see the insets in Figs. 4 and 5). This is the consequence of small values of $|\sigma|$ where the depletion of water molecules near the charged surface predicted within generalized Langevin–Bikerman model (see also [16,17]) does not have considerable effect on dE/dx and therefore also not on the quadrupole dependent permittivity. Based on the theory and results presented in this work and in [16,17] it can be anticipated that the difference between the predictions of both models would be much larger at higher values of $|\sigma|$.

5. Conclusions

Based on the results presented in this work, it can be concluded that the quadrupole moment of water molecules may have an important influence on the physical properties of electric double layer in an electrolyte solution near a charged surface. The mean-field theoretical method of description of electrolyte solution near a charged surface used in this work adopts several simplifying assumptions and can not be applied for large surface charge densities. To this end, it would be important to further investigate the role of the quadrupole moment of water molecules also at large surface charge densities where the direct interactions between oriented water molecules might play an important role.

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Appendix A. Supplementary Data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2013.07.126>.

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