Physical Properties of Water Near a Highly Charged Surface due to Saturation and Excluded Volume Effect. A Mini Review[*]

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Abstract. Langevin Poisson-Boltzmann model for point-like ions presenting an electrolyte solution in contact with a planar charged surface is described using the functional density theory. In the model, the water molecules are considered as point-like Langevin dipoles. It is shown that due to the increased orientational ordering of water dipoles, dielectric permittivity of the electrolyte solution close to the charged surface is decreased. In the second part, a modification of Langevin Poisson-Boltzmann model is presented by considering also the finite size of the involved molecules, the cavity and reaction fields. A comparison between the theoretical predictions of the Langevin Poisson-Boltzmann model and the modified model of the electrolyte permittivity shows that consideration of finite size of molecules as well as the cavity field makes the reduction of permittivity of the electrolyte solution near the charged surface even stronger. The depletion of water molecules due to accumulation of counterions (excluded volume effect) has stronger influence on the predicted decrease of the relative permittivity of an electrolyte solution near the highly charged surface.

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 [1–7]. The study of the electric double layer has begun in 1879 by Hermann von Helmholtz [8], but today it still remains a scientific challenge. Helmholtz treated the double layer as a simple capacitor,

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[*]In memory of Assoc. Prof. Dr. Marin D. Mitov (1951-2011), one of the founders of the world-wide recognized method for the measurement of the bending rigidity of lipid membranes by means of analysis of the thermally induced shape fluctuations of quasi-spherical lipid vesicles.

assuming that the surface charge density is neutralized by the counterions located at a distance equal to their hydrated radius. Gouy [9] and Chapman [10] 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 [1,7,9,10], the ions in electrolyte solution are treated as dimensionless and uniform permittivity of the electrolyte solution is assumed.

The classical PB theory did not consider the solvent structure and thus the PB theory has been upgraded by hydration models, where interplay between solvent polarization and the diffuse double layer has taken place [7, 14–17]. Study of the orientational ordering of water dipoles at the charged surface has shown that dipoles on average are oriented perpendicularly to the charged surface [7, 17]. Recently, Langevin dipoles were introduced into PB theory to study the polarization of the solvent and the space dependency of permittivity close to the charged membrane surface [18,19]. The spatial decay of solvent polarization for increasing distance from the charged membrane surface was predicted [7,19,20].

Most of the models, describing EDL [1, 2, 11–13] 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 [2].

In this paper, first the Langevin Poisson-Boltzmann mean-field model [7, 19, 21] for 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 the distribution of the involved ions and the electric field strength. The water molecules are considered as Langevin dipoles [17, 22, 23] which is a very rough treatment of the dielectric properties of the solvent. The finite volume of ions and water [13, 17] 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 [24]. In the second part, a modification of the Langevin Poisson-Boltzmann model containing the finite size of molecules, the cavity and reaction fields [6, 25, 26] is presented.

2 Configurational Entropy of Electrolyte Solution

We consider the configurational entropy of an electrolyte solution composed of counterions and coions [7, 25]. Following the classical well-known approach, the finite sizes of ions (macroions) are considered within the lattice model [7, 25, 27]. The system is divided into cells of equal volume ΔV. In the particular cell chosen, there are N_+ counterions and N_- coions. The number of spatial arrangements of non-interacting counterions and coions in a small cell with M

lattice sites is [27]

$$W = \frac{M(M-1)(M-2)\cdots(M-(N-1))}{N_+! \, N_-!} \, , \tag{1}$$

and can be rewritten into

$$W = \frac{M!}{N_+! \, N_-! \, (M-N)!} \, , \tag{2}$$

where

$$N = N_+ + N_- \, . \tag{3}$$

The configurational (translational) entropy of the mixed system of the single cell S_{cell} is [27]

$$S_{\text{cell}} = k \ln W. \tag{4}$$

Using the Stirling's approximation for large N_i: $\ln N_i! \simeq N_i \ln N_i - N_i$, $i = \{+, -\}$, the expression for $\ln W$ transforms into

$$\ln W = -N_+ \ln\left(\frac{N_+}{M}\right) - N_- \ln\left(\frac{N_-}{M}\right) - (M-N)\ln\left(1 - \frac{N}{M}\right). \tag{5}$$

To take into account the excluded volume effect we assume that each lattice site with volume v_0 can be occupied only by one ion. The volume of the cell with M sites is given by $\Delta V = M v_0$. The number density of counterions is defined as $n_+ = N_+/\Delta V$, while the number density of coions is $n_- = N_-/\Delta V$. The configurational entropy of the whole system is obtained by integration over all cells of the system

$$S = \int S_{\text{cell}} \frac{dV}{\Delta V} \, , \tag{6}$$

where S_{cell} is given by Eq. (4). We insert Eq. (5) into Eq. (4) to get

$$\begin{aligned} S = -\, k \int [&n_+ \ln(n_+ v_0) + n_- \ln(n_- v_0) \\ &+ \frac{1}{v_0}\left(1 - n_+ v_0 - n_- v_0\right) \ln\left(1 - n_+ v_0 - n_- v_0\right)] \, dV. \end{aligned} \tag{7}$$

Equation (7) takes into account the finite size of ions. In the following the entropic part of the free energy $\tilde{F}_{\text{ent}} = -T S$ is calculated from Eq. (7). We need to subtract the reference free energy F_{ref} [24]). The difference between the entropic part of the free energy $\tilde{F}_{\text{ent}}$ and the reference entropic part of the free energy F_{ref} is :

$$\begin{aligned} \tilde{F}_{\text{ent}} - F_{\text{ref}} = &kT \int dV \left[\sum_{i=+,-} n_i \ln(n_i v_0) - 2 n_0 \ln(n_0 v_0) \right] \\ &+ kT \int dV \frac{1}{v_0}\left(1 - n_+ v_0 - n_- v_0\right) \ln\left(1 - n_+ v_0 - n_- v_0\right) \\ &- kT \int dV \frac{1}{v_0}\left(1 - 2 n_0 v_0\right) \ln\left(1 - 2 n_0 v_0\right) \, , \end{aligned} \tag{8}$$

where n_0 is the bulk number density of ions. Assuming

$$\int dV \left[2n_0 - \sum_{i=+,-} n_i \right] = 0, \tag{9}$$

and taking into account the relations $\ln(n_0 v_0) = \text{const.}$ and $\ln(1 - 2n_0 v_0) = \text{const.}$ we obtain

$$F_{\text{ent}} = \tilde{F}_{\text{ent}} - F_{\text{ref}} = kT \int dV \sum_{i=+,-} n_i \ln \left(\frac{n_i}{n_0} \right)$$
$$+ kT \int dV \left(\frac{1}{v_0} - n_+ - n_- \right) \ln \left(\frac{v_0^{-1} - n_+ - n_-}{v_0^{-1} - 2 n_0} \right). \tag{10}$$

The number density of lattice sites $n_{\text{s}} = 1/v_0 = 1/a^3$, where we define a as a lattice constant (width of a single lattice site). All lattice sites are occupied by either solvent molecules or macroions, therefore

$$n_{\text{s}} = n_w + \sum_{j=+,-} n_j \ , \tag{11}$$

where n_w is the number density of lattice sites occupied by solvent (water). By taking into account Eq. (11), we may rewrite Eq. (10) in the form

$$F_{\text{ent}} = kT \int \left[n_+ \ln \frac{n_+}{n_0} + n_- \ln \frac{n_-}{n_0} + n_w \ln \frac{n_w}{n_{0w}} \right] dV \ , \tag{12}$$

where $n_w = n_{\text{s}} - n_+ - n_-$ and $n_{0w} = n_{\text{s}} - 2n_0$ is the bulk number density of water. If we assume that $n_+ \ll 1$, $n_- \ll 1$, everywhere in the solution, as well as $n_0 \ll 1$, we can expand the third term in Eq. (12) up to quadratic terms [7] to get (see for example [24])

$$F_{\text{ent}} = kT \int \left[n_+ \ln \left(\frac{n_+}{n_0} \right) + n_- \ln \left(\frac{n_-}{n_0} \right) - (n_+ + n_-) + 2n_0 \right] dV \ . \tag{13}$$

Equation (13) describes the configurational entropy of the electrolyte solution where the excluded volume is not taken into account.

3 Langevin Poisson-Boltzmann Model

We consider a planar charged surface in contact with a water solution of mono-valent ions (counterions and coions) [19,21]. The planar charged surface bears a charge with a 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 water Langevin dipoles is presented [21]. 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 [21]. The free energy of system F is written as

$$
\begin{aligned}
\frac{F}{kT} &= \frac{1}{8\pi l_B} \int \left(\Psi'\right)^2 dV + \int \left[n_+(x) \ln \frac{n_+(x)}{n_0} - (n_+(x) - n_0) \right. \\
&\quad + \left. n_-(x) \ln \frac{n_-(x)}{n_0} - (n_-(x) - n_0) \right] dV \\
&\quad + \int n_w \left\langle \mathcal{P}(x,\omega) \ln \mathcal{P}(x,\omega) \right\rangle_\omega dV \\
&\quad + \int \left[\eta(x) \left(\left\langle \mathcal{P}(x,\omega) \right\rangle_\omega - 1 \right) \right] dV \;,
\end{aligned}
\tag{14}
$$

where averaging over all angles Ω is defined as

$$
\left\langle F(x) \right\rangle_\omega = \frac{1}{4\pi} \int F(x,\omega)\, d\Omega.
\tag{15}
$$

Here ω is the angle between the dipole moment vector $\mathbf{p}$ and the vector $\mathbf{n} = \nabla\phi/|\nabla\phi|$, $d\Omega = 2\pi \sin\omega\, d\omega$ is an element of a solid angle, n_w is the constant number density of the water Langevin dipoles, $n_+(x)$ and $n_-(x)$ are the number densities of counterions and coions, respectively, $\Psi(x) = e_0\phi(x)/kT$, is the reduced electrostatic potential, $\phi(x)$ is the electrostatic potential, Ψ' is the first derivative of Ψ with respect to x, e_0 is the elementary charge, kT is the thermal energy, $dV = Adx$ 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. (14) corresponds to the energy of the electrostatic field. The second and third line in Eq. (14) account for the mixing (configurational) free energy contribution of the positive and negative salt ions (see Section 2). We assumed $\phi(x \to \infty) = 0$. The fourth line of Eq. (14) accounts for the orientational contribution of the Langevin dipoles to the free energy. $\mathcal{P}(x,\omega)$ is the probability that the water 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 water Langevin dipoles (valid at any position x) [21]

$$
\left\langle \mathcal{P}(x,\omega) \right\rangle_\omega = 1 \;,
\tag{16}
$$

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

The results of the variation in the above free energy gives [19, 21]

$$
n_+(x) = n_0 \exp(-\Psi) \;,
\tag{17}
$$

$$
n_-(x) = n_0 \exp(\Psi) \;,
\tag{18}
$$

$$
\mathcal{P}(x,\omega) = \Lambda(x) \exp(-p_0 |\Psi'| \cos(\omega)/e_0) \;,
\tag{19}
$$

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

The charges of counterions, coions and water molecules contribute to the average microscopic volume charge density

$$\varrho(x) = e_0 \left(n_+(x) - n_-(x) \right) - \frac{dP}{dx} \ . \tag{20}$$

Polarization P is given by

$$P(x) = n_{0w} \left\langle \mathbf{p}(x, \omega) \right\rangle_B \ , \tag{21}$$

where $\mathbf{p}$ is the water (Langevin) dipole moment, angle ω describes the orientation of the dipole moment vector with respect to vector $\nabla\phi/|\nabla\phi|$ and $\left\langle \mathbf{p}(x, \omega) \right\rangle_B$ 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.(19) the values of $\left\langle \mathbf{p}(x, \omega) \right\rangle_B$ can be calculated as follows [19, 21]:

$$\left\langle \mathbf{p}(x, \omega) \right\rangle_B = \frac{\int\limits_0^\pi p_0 \cos\omega \ \mathcal{P}(x, \omega) \ 2\pi \sin\omega \ d\omega}{\int\limits_0^\pi \mathcal{P}(x, \omega) \ 2\pi \sin\omega \ d\omega} = -p_0 \ \mathcal{L} \left(\frac{p_0 |\Psi'|}{e_0} \right) \ . \tag{22}$$

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. (17) and (18)) and the expression for polarization (Eqs. (21) and (22)) into Eq. (20), we get the expression for the volume charge density in an electrolyte solution [19, 21]

$$\varrho(x) = -2 \, e_0 \, n_0 \sinh\Psi \ + \ n_{0w} \, p_0 \ \frac{d}{dx} \Big[\mathcal{L}(p_0|\Psi'|/e_0) \Big] \ . \tag{23}$$

Inserting the above expression for volume charge density $\varrho(x)$ (Eq.(23)) into the Poisson's equation

$$\Psi'' = -4\pi \, l_B \varrho/e_0 \ , \tag{24}$$

we get the Langevin Poisson-Boltzmann (LPB) equation for point-like ions [19, 21]

$$\Psi'' = 4\pi l_B \left(2 \, n_0 \sinh\Psi - \ n_{0w} \frac{p_0}{e_0} \frac{d}{dx} \Big[\mathcal{L}(p_0|\Psi'|/e_0) \Big] \right) \ , \tag{25}$$

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where Ψ'' is the second derivative of Ψ with respect to x. The Langevin Poisson-Boltzmann differential equation (25) is subject to two boundary conditions. The first boundary condition is obtained by integrating the differential equation (25) [19, 21]

$$\Psi'(x=0) = -\frac{4\pi l_B}{e_0} \left[\sigma + \; n_{0w} \, p_0 \; \mathcal{L}(p_0 |\Psi'|/e_0) \Big|_{x=0} \right] \; . \tag{26}$$

The condition requiring electro-neutrality of the whole system was taken into account in derivation of Eq.(26). The second boundary condition is

$$\Psi(x \to \infty) = 0 \; . \tag{27}$$

Based on Eqs. (21)-(22), we can express the relative permittivity of the electrolyte solution (ε_r) in contact with a planar charged surface as [19, 21]

$$\varepsilon_r(x) \; = 1 + \frac{|P|}{\varepsilon_0 E} \; = \; 1 + \; n_{0w} \, \frac{p_0}{\varepsilon_0} \, \frac{\mathcal{L}(p_0 E \beta)}{E} \; , \tag{28}$$

where $\beta = 1/kT$ and $E = |\phi'| = \phi'$ (since $\sigma < 0$) is the magnitude of the electric field strength.

Equations (25)-(27) can be written in a more elegant form as [19]:

$$\nabla \cdot [\varepsilon_0 \varepsilon_r(x) \nabla \phi(x)] = -\rho_{\text{free}}(x) \; , \tag{29}$$

where $\rho_{free}(x)$ is the macroscopic (net) volume charge density of coions and counterions (see also Eqs. (17) and (18))

$$\rho_{free}(x) = - \, e_0 \, n_+(x) - \, e_0 \, n_-(x) \; = \; - \, 2 \, e_0 \, n_0 \, \sinh\left(e_0 \phi \beta\right) \; , \tag{30}$$

and $\varepsilon_r(x)$ is the relative permittivity of the electrolyte solution defined by Eq. (28). The boundary condition at the charged surface (Eq. (26)) reads

$$\nabla \phi \, (x=0) = -\frac{\sigma \, \mathbf{n}}{\varepsilon_0 \, \varepsilon_r(x=0)} \; , \tag{31}$$

where $\varepsilon_r(x)$ is again defined by Eq. (28). The second boundary condition is

$$\phi \, (x \to \infty) \; = 0 \; . \tag{32}$$

Equation (28) describes dependence of the relative permittivity ε_r on the magnitude of electric field strength E, calculated within the presented Langevin Poisson-Boltzmann theory. This theory takes into account the orientational ordering of water molecules (or water clusters) near a charged surface (Figure 1) by considering them as Langevin dipoles but without their finite size.

For $p_0 E/kT < 1$ we can expand the Langevin function in Eq.(28) into a Taylor series up to the cubic term: $\mathcal{L}(x) \approx x/3 - x^3/45$ to get [19, 21]

$$\varepsilon_r(x) \cong 1 + \frac{n_{0w} p_0{}^2 \beta}{3\varepsilon_0} - \frac{n_{0w} p_0^2 \beta}{45\varepsilon_0} \left(p_0 E \beta\right)^2 \; . \tag{33}$$
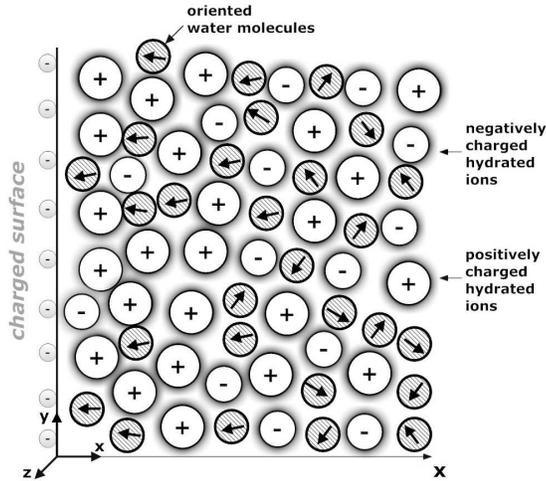
Figure 1. A schematic figure of the electrical double layer near a negatively charged planar surface. The water molecules in the vicinity of the charged surface are predominantly oriented towards the surface.

It can be seen in Eq.(33) that $\varepsilon_r(x)$ decreases with increasing magnitude of the electric field strength E. Since the value of E increases towards the charged
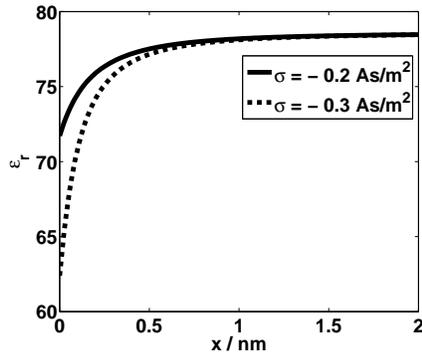

Figure 2. Relative dielectric permittivity ε_r as a function of the distance from the charged surface x within the presented Langevin PB theory for point-like ions. Eqs. (25)-(27) were solved numerically using finite element method within the program package Comsol Multiphysics 3.5a Software as described in [19]. Dipole moment of water $p_0 = 4.79D$, 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 $\sigma = -0.2\,\mathrm{As/m^2}$ (fulline) and $\sigma = -0.3\,\mathrm{As/m^2}$ (dashed line).

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surface (see for example [1, 7, 25]), $\varepsilon_r(x)$ 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 relative permittivity of electrolyte $\varepsilon_r(x)$ near the charged surface is reduced relative to its bulk value as shown also in Figure 2.

4   Gongadze-Iglič Model

In order to develop an integrating framework to clarify the factors influencing the relative permittivity, we recently update the LPB model by taking into account the finite size of the molecules as well as the cavity field [25, 26].

The effective dipole moment of the water molecule should be known before a satisfactory statistical mechanical study of water and aqueous solutions is possible [28]. 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 (*i.e.*, the dipole moment is further increased) and orientationally perturbed by the electric field of the surrounding water molecules [28]. Accordingly, in the above described treatment of water ordering close to the saturation limit at high electric field within the LPB model, the effective dipole moment of water $p_0 = 4.79\,D$ is larger than the dipole moment of an isolated water molecule ($p_0 = 1.85\,D$). However, it is also larger than the dipole moment of a water molecule in clusters ($p_0 = 2.7\,D$) and the dipole moment of an average water molecule in the bulk ($p_0 = 2.4 - 2.6\,D$) [29] since the cavity and reaction fields as well as structural correlations between water dipoles [30, 31], were not explicitly taken into account in the LPB model.

In the past treatment of the cavity and reaction fields and the structural correlations between water dipoles in the Onsager [32], Kirkwood [33] and Fröhlich models [30] were limited to the case of small electric field strengths. Generalization of the Kirkwood-Onsager-Fröhlich theory in the saturation regime was performed by Booth [34]. However, Booth's model does not consider the excluded volume effect in an electrolyte solution near a charged surface. Therefore in this section first the LPB model [19] is generalized to take into account the cavity and reaction fields (but not the structural correlations between water dipoles), as well as the finite size of ions [25, 26] in the saturation regime important in consideration of 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 embedded in the center of the sphere with a volume equal to the average volume of a water molecule in the electrolyte solution (Figure 3). 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
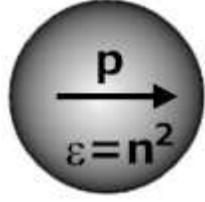
Figure 3. In the model a single water molecule is considered as a sphere with permittivity n^2 and point-like rigid (permanent) dipole with dipole moment **p** at the center of the sphere. Here n is the optical refractive index of water.

of the electrolyte solution (ε_r) can be then expressed as

$$\varepsilon_r(\mathbf{r}) = n^2 + \frac{|\mathbf{P}|}{\varepsilon_0 E}, \tag{34}$$

where **P** is the polarization vector due to a net orientation of permanent point-like water dipoles having dipole moment **p**. The external dipole moment ($\mathbf{p}_e$) of a point-like dipole at the center of the sphere with permittivity n^2 can be then expressed in the form [30]

$$\mathbf{p}_e = \frac{3}{2 + n^2} \mathbf{p} \ , \tag{35}$$

whence

$$\mathbf{p} = \frac{2 + n^2}{3} \mathbf{p}_e \ . \tag{36}$$

In our analysis the short range interactions between dipoles are neglected. The local electric field strength at the center of the sphere at the location of the permanent (rigid) point-like dipole (Figure 3) is [30]

$$\mathbf{E}_c = \frac{3\,\varepsilon_r}{2\,\varepsilon_r + n^2} \mathbf{E} + \tilde{g}\mathbf{p} \ , \tag{37}$$

where the first term represents the field inside a spherical cavity with dielectric permittivity n^2 embedded in the medium with permittivity ε_r and the second term $\tilde{g}\mathbf{p}$ is the reaction-field acting on **p** (due to the dipole moment **p** of the point-like dipole itself). In the following, Eq. (37) is simplified in the form (strictly valid for $\varepsilon_r \gg n^2$ only) :

$$\mathbf{E}_c = \frac{3}{2} \mathbf{E} + \tilde{g}\mathbf{p} \ . \tag{38}$$

For $\varepsilon_r \gg n^2$ the value of $\tilde{g} \cong 1/n^2 r_0^3$, where r_0 is the radius of molecule [34]. The energy of the point-like dipole **p** in the local field $\mathbf{E}_c$ may be then written as

$$W_i = -\mathbf{p} \cdot \mathbf{E}_c = -\mathbf{p} \cdot \left(\frac{3}{2} \mathbf{E} + g\,\mathbf{p} \right) = \gamma p_0 E \cos(\omega) - g p_0^2 \ , \qquad (39)$$

where p_0 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

$$\gamma = \frac{3}{2} \left(\frac{2+n^2}{3} \right), \quad g = \left(\frac{2+n^2}{3} \right)^2 \tilde{g}. \qquad (40)$$

Polarization $P(x)$

$$P(x) = n_w(x) \langle \mathbf{p}(x,\omega) \rangle_B , \qquad (41)$$

is given by [26]

$$P(x) = n_w(x) \left(\frac{2+n^2}{3} \right) p_0 \langle \cos(\omega) \rangle_B = -n_w(x) \left(\frac{2+n^2}{3} \right) p_0 \mathcal{L}(\gamma p_0 E \beta), \quad (42)$$

where

$$\langle \cos \omega \rangle_B = \frac{\int\limits_0^\pi \cos\omega \exp(-\gamma p_0 E \beta \cos(\omega) + \beta g p_0^2) \mathrm{d}\Omega}{\int\limits_0^\pi \exp(-\gamma p_0 E \beta \cos(\omega) + \beta g p_0^2) \mathrm{d}\Omega} = -\mathcal{L}(\gamma p_0 E \beta), \quad (43)$$

and $d\Omega = 2\pi \sin\omega \, d\omega$ is an element of solid angle. Since $\sigma < 0$, the projection of 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.

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 the single lattice site in the bulk solution is occupied by one of the three kind of particles in electrolyte solution (counterions, coions and water molecules) [6, 7, 25]

$$n_+(x \to \infty) = n_-(x \to \infty) = n_s \frac{n_0}{n_0 + n_0 + n_{0w}} , \qquad (44)$$

$$n_w(x \to \infty) = n_s \frac{n_{0w}}{n_0 + n_0 + n_{0w}} , \qquad (45)$$

where n_s is the number density of lattice sites as defined above. In the vicinity of a charged surface the number densities of ions and water molecules are 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 [25, 26]

$$n_+(x) = n_s \frac{n_0 e^{-e_0 \phi \beta}}{n_0 e^{e_0 \phi \beta} + n_0 e^{-e_0 \phi \beta} + n_{0w} \langle e^{-\gamma p_0 E \beta \cos(\omega) + \beta g p_0^2} \rangle_\omega} \qquad (46)$$

$$n_-(x) = n_s \frac{n_0 e^{e_0\phi\beta}}{n_0 e^{e_0\phi\beta} + n_0 e^{-e_0\phi\beta} + n_{0w}\langle e^{-\gamma p_0 E\beta \cos(\omega)+\beta g p_0^2}\rangle_\omega} \qquad (47)$$

$$n_w(x) = n_s \frac{n_{0w}\langle e^{-\gamma p_0 E\beta \cos(\omega)+\beta g p^2}\rangle_\omega}{n_0 e^{e_0\phi\beta} + n_0 e^{-e_0\phi\beta} + n_{0w}\langle e^{-\gamma p_0 E\beta \cos(\omega)+\beta g p_0^2}\rangle_\omega}, \qquad (48)$$

where

$$\langle e^{-\gamma p_0 E\beta \cos(\omega)+\beta g p_0^2}\rangle_\omega = \frac{2\pi \int\limits_\pi^0 d(\cos\omega) e^{-\gamma p_0 E\beta \cos(\omega)+\beta g p_0^2}}{4\pi} =$$
$$= \frac{\sinh(\gamma p_0 E\beta)}{\gamma p_0 E\beta} \exp(\beta g p_0^2) \qquad (49)$$

is the dipole Boltzmann factor after rotational averaging over all possible angles ω. Equations (46)-(48) can be rewritten as [25, 26]

$$n_+(x) = n_0 e^{-e_0\phi\beta} \frac{n_s}{\mathcal{D}(\phi, E)}, \qquad (50)$$

$$n_-(x) = n_0 e^{e_0\phi\beta} \frac{n_s}{\mathcal{D}(\phi, E)}, \qquad (51)$$

$$n_w(x) = \frac{n_{0w} n_s}{\mathcal{D}(\phi, E)} \frac{\sinh(\gamma p_0 E\beta)}{\gamma p_0 E\beta} \exp(\beta g p_0^2). \qquad (52)$$

where

$$\mathcal{D}(\phi, E) = 2n_0 \cosh(e_0\phi\beta) + \frac{n_{0w}}{\gamma p_0 E\beta} \sinh(\gamma p_0 E\beta) \exp(\beta g p_0^2). \qquad (53)$$

Combining Eqs. (42) and (52) gives the polarization in the form

$$P(x) = -\left(\frac{2+n^2}{3}\right) \frac{p_0 n_{0w} n_s}{\mathcal{D}(\phi, E)} \frac{\sinh(\gamma p_0 E\beta)}{\gamma p_0 E\beta} \exp(\beta g p_0^2)\mathcal{L}(\gamma p_0 E\beta). \qquad (54)$$

Using the definition of the function $\mathcal{F}(u)$

$$\mathcal{F}(u) = \mathcal{L}(u) \frac{\sinh u}{u}. \qquad (55)$$

Equation (54) transforms into

$$P = -p_0 n_{0w} n_s \left(\frac{2+n^2}{3}\right) \frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}(\phi, E)} \exp(\beta g p_0^2). \qquad (56)$$

Combining Eqs. (34) and (56) yields the relative (effective) permittivity

$$\varepsilon_r(x) = n^2 + n_{0w} n_s \frac{p_0}{\varepsilon_0}\left(\frac{2+n^2}{3}\right) \frac{\mathcal{F}(\gamma p_0 E\beta)}{\mathcal{D}(\phi, E)E} \exp(\beta g p_0^2). \qquad (57)$$

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Using the above expression for $\varepsilon_r(x)$, we can then write the Poisson equation in the form [25, 26]

$$\nabla \cdot [\varepsilon_0 \varepsilon_r(x) \nabla \phi(x)] = -\rho_{\text{free}}(x) , \qquad (58)$$

where $\rho_{\text{free}}(x)$ is the macroscopic (net) volume charge density of coions and counterions (see also Eqs. (50) and (51)) [25, 26] :

$$\rho_{\text{free}}(x) = e_0 n_+(x) - e_0\, n_-(x) = -2e_0 n_s n_0\, \frac{\sinh\left(e_0\phi\beta\right)}{\mathcal{D}(\phi, E)} . \qquad (59)$$

The boundary conditions are [25, 26]

$$\nabla\phi\,(x = 0) = -\frac{\sigma\, \mathbf{n}}{\varepsilon_0\, \varepsilon_r(x = 0)} , \qquad (60)$$

$$\phi\,(x \to \infty) = 0 . \qquad (61)$$

In the approximation of $g = 0$ and a small electrostatic energy and a small energy of dipoles in the electric field compared to thermal energy, i.e. small $e_0\phi\beta$ and small $\gamma p_0 E\beta$, the relative permittivity within the presented model (Eq. (57)) can be expanded into a Taylor series (assuming $n_s \approx n_{0w}$) to get [25, 26]

$$\varepsilon_r(x) \cong\ n^2 + \frac{3}{2}\left(\frac{2 + n^2}{3}\right)^2 \frac{n_{0w} p_0{}^2\beta}{3\varepsilon_0} - \frac{27}{8}\left(\frac{2 + n^2}{3}\right)^4 \frac{n_{0w} p_0^2\beta}{45\varepsilon_0}(p_0 E\beta)^2 - $$
$$- \frac{3}{2}\left(\frac{2 + n^2}{3}\right)^2 \frac{n_0 p_0^2\beta}{3\varepsilon_0}(e_0\phi\beta)^2. \qquad (62)$$

In the limit of vanishing electric field strength ($E \longrightarrow 0$) and zero potential ($\phi \longrightarrow 0$), the above equations give the Onsager expression for permittivity

$$\varepsilon_r \cong\ n^2 + \left(\frac{2 + n^2}{3}\right)^2 \frac{n_{0w} p_0{}^2\beta}{2\, \varepsilon_0} . \qquad (63)$$

In the above derived expression for the relative (effective) permitivitty (Eq. (57)), the value of the dipole moment $p_0 = 3.1\ D$ predicts a bulk permittivity $\varepsilon_r = 78.5$. This value of p_0 is considerably smaller than the corresponding value in the LPB model ($p_0 = 4.79\ D$) (see Figure 2) which does not take into account the cavity field.

The value $p_0 = 3.1\ D$ (Figure 4) is also close to the experimental values of the effective dipole moment of water molecules in clusters ($p_0 = 2.7\ D$) and in bulk solution ($p_0 = 2.4 - 2.6\ D$) [29].

Figure 4 shows the calculated spatial dependence of the relative number density of counterions (n_+/n_s), water dipoles (n_w/n_s) and $\varepsilon_r(x)$ within modified LPB model (Gongadze-Iglič model) in planar geometry for two values of the
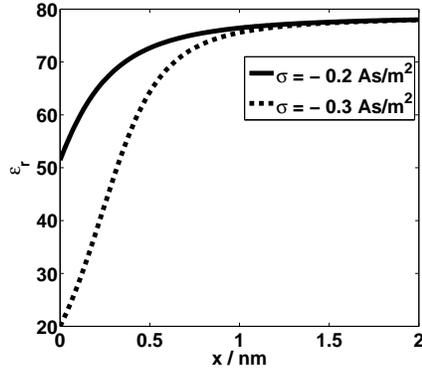
Figure 4. The relative permittivity ε_r (Eq. (57)) as a function of distance from a planar charged surface x (adapted from [25, 26]). Two values of surface charge density were considered: $\sigma = -0.2$ As/m^2 (full line) and $\sigma = -0.3$ As/m^2 (dashed line). Eq. (58) was solved numerically taking into account the boundary conditions (60) and (61) as described in [25, 26]. Values of parameters assumed: dipole moment of water $p_0 = 3.1\ D$, bulk concentration of salt $n_0/N_A = 0.15$ mol/l, optical refractive index $n = 1.33$, $g = 0$, bulk concentration of water $n_{ow}/N_A = 55$ mol/l, where N_A is the Avogadro number.

surface charge density σ. The decrease of $\varepsilon_r(x)$ towards the charged surface is pronounced with increasing σ and is a consequence of the increased depletion of water molecules near the charged surface (due to excluded volume effect as a consequence of counterions accumulation near the charged surface) and increased orientational ordering of water dipoles (saturation effect). Comparison between the predictions of the LPB model (Figure 2) and the GI model shows the stronger decrease of relative permittivity of the electrolyte solution near the highly charged surface stronger in GI model, mainly due to depletion of water molecules in the vicinity of charged surface.

In order to differentiate between the influence of the finite size of ions and the influence of cavity field and reaction field on the relative permittivity near the charged surface, the equations of the above described GI model are written in the limit of $g \to 0$, $\gamma \to 1$ and $n \to 1$ [19, 20, 25] to get

$$\nabla \cdot [\varepsilon_0 \varepsilon_r(x) \nabla \phi(x)] = -\rho_{\text{free}}(x) \ , \tag{64}$$

where $\rho_{\text{free}}(x)$ is the macroscopic (net) volume charge density of coions and counterions

$$\rho_{\text{free}}(x) = -2e_0 n_s n_0 \frac{\sinh(e_0 \phi \beta)}{\mathcal{H}(\phi, E)} \ , \tag{65}$$

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while $\varepsilon_r(x)$ is the relative permittivity

$$\varepsilon_r(x) = 1 + n_{0w} n_s \frac{p_0}{\varepsilon_0} \frac{\mathcal{F}(p_0 E \beta)}{E \, \mathcal{H}(\phi, E)} \ , \tag{66}$$

where

$$\mathcal{H}(\phi, E) = 2n_0 \cosh\left(e_0 \phi \beta\right) + \frac{n_{0w}}{p_0 E \beta} \sinh\left(p_0 E \beta\right) . \tag{67}$$

The corresponding boundary conditions are

$$\nabla \phi(x = 0) = -\frac{\sigma \mathbf{n}}{\varepsilon_0 \varepsilon_r(x = 0)} \ , \tag{68}$$

$$\phi(x \to \infty) = 0 . \tag{69}$$

Figure 5 shows the calculated spatial dependence of $\varepsilon_r(x)$ for two values of the surface charge density σ in the limit of $g \to 0$, $\gamma \to 1$ and $n \to 1$. Comparison between the space dependency of the relative permittivity within the strict GI model for $g = 0$ (Figure 4) and within its limit model for $g \to 0$, $\gamma \to 1$ and $n \to 1$ (Figure 5) shows that consideration of the cavity field makes the reduction of permittivity of the electrolyte solution near the charged surface stronger. More important, in the limit of $g \to 0$, $\gamma \to 1$ and $n \to 1$ again the value $p_0 = 4.79\, D$ (similarly as in LPB model) should be used in order to get $\varepsilon_r(x \to \infty) = 78.5$ which shows the superiority of GI model over the GI limit model for $\gamma \to 1$ and $n \to 1$ (also called Langevin-Bikerman model, see [19, 25]).
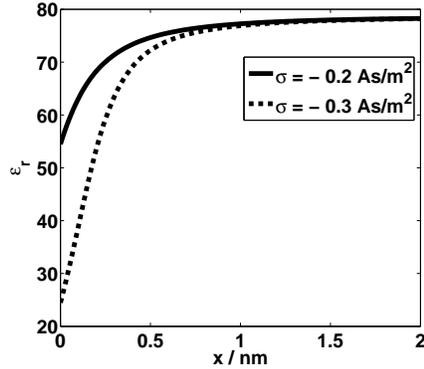

Figure 5. Relative permittivity ε_r (calculated by using Eq. (66)) as a function of the distance from the charged planar surface x. Two values of surface charge density were considered: $\sigma = -0.2$ As/m^2 (full line) and $\sigma = -0.3$ As/m^2 (dashed line). Eq. (64) was solved numerically taking into account the boundary conditions (68) and (69) as described in [19, 20, 25]. The dipole moment of water $p_0 = 4.79\, D$, bulk concentration of salt $n_0/N_A = 0.15$ mo/l, bulk concentration of water $n_{ow}/N_A = 55$ mol/l, where N_A is the Avogadro number.

5   Conclusions

To conclude, in this review paper, the PB theory for point-like ions modified by introducing the orientational ordering of water molecules was described. The corresponding Langevin Poisson-Boltzmann (LPB) equation [19, 21] was presented. It is shown that the relative permittivity of the electrolyte solution decreases with the increasing magnitude of the electric field strength [17, 18]. Due to the increased magnitude of the electric field in the vicinity of the charged surface in contact with the electrolyte solution, the relative permittivity of electrolyte solution in the region near the charged surface is decreased [19, 21] (Figure 2). 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 further been shown that considering the cavity field of a single water molecule and the finite sized ions within GI model results in additional decrease of permittivity near the charged surface [17, 18, 25] (Figure 4). The corresponding analytical expression for the spatial dependence of the relative permittivity of the electrolyte solution near the charged surface in GI model is given [6, 25, 26].

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