Excluded volume effect and orientational ordering near charged surface in solution of ions and Langevin dipoles

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ABSTRACT

The influence of a finite volume of ions and orientational ordering of water Langevin dipoles on the dielectric permittivity profile in the vicinity of charged surface is studied theoretically via a numerical solution of the modified Poisson–Boltzmann equation. It is shown that the dielectric permittivity profile close to the charged surface is mainly determined by two mechanisms; specifically, the depletion of dipoles at the charged surface due to accumulated counterions and the increased orientational ordering of the water dipoles.

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1. Introduction

The distribution of the ions in the electrolyte solution close to the charged surface is determined mainly by competition between electrostatic and van der Waals interactions, configurational and rotational entropy of particles as well as by steric effects [1–8]. Due to the attractive electrostatic forces between charged surface and ions in the solution, the counterions are accumulated close to the charged membrane surface. In addition, the water molecules in electrolyte solution can better organize their hydrogen bonding network without ions, therefore it is favourable that the ions breaking the water hydrogen bonding network are moved from the bulk toward the charged surface [9].

Within standard Poisson–Boltzmann (PB) theory [1,10] the ions are considered as point-like, therefore the number density of counterions at charged surface may exceed the upper value corresponding to their close packing. Different attempts have been made to incorporate steric effects into modified PB theory in order to prevent the prediction of unrealistically high number densities of counterions close to the charged surface.

The first attempt to include finite size of ions in modified PB theory was made by Freise [11] who introduced the excluded volume effect by a pressure-dependent potential, while Wicke and Eigen [12] used a thermodynamic approach. More recently, the finite size of particles has been incorporated into the PB theory, based on a lattice statistics model [3,13–15], by using other functional density approaches [16–18] and by considering the ions and solvent molecules as hard spheres [4,5]. Also Monte Carlo simulations are widely used in order to describe the finite-sized counterions [5,19,20].

In addition to excluded volume effect, the standard PB theory also doesn't consider the solvent structure. Therefore the PB theory has been upgraded by the hydration model, where the interplay between solvent polarization and diffuse double layer takes place [21–23]. The study of the orientational ordering of dipoles at the charged surface has shown that the dipoles predominantly orient perpendicular to the charged surface [24]. The spatial decay of the solvent polarization for increasing distance from the charged surface was predicted [21]. Recently Abrashkin et al. [25] introduced Langevin dipoles into PB theory to study the polarization of the solvent close to the charged surface. Mengistu et al. [26] incorporated a solvent of interacting Langevin dipoles into the PB theory. This approach allows for a surface-induced structural perturbation of the solvent.

The ions may change the dielectric permittivity of electrolyte water solution [9,25]. Therefore in this work the modified PB equation was solved numerically where the finite volumes of the ions were taken into account. Dipolar nature of water molecules is introduced by Langevin dipoles. It is shown that the dielectric permittivity profile close to the charged surface is mainly determined by two mechanisms, i.e. the depletion of dipoles at the charged surface due to accumulation of counterions and decreased orientational ordering of dipoles as the function of the increased distance from the charged surface. The spatial dependence of dielectric permittivity as a function of electric potential and electric field strength is given analytically.

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2. Theory

We consider a charged surface in contact with a solution of monovalent ions (counterions and coions) and Langevin dipoles of finite size. The counterions are accumulated near the charged surface and coions are depleted from this region, thereby creating a diffuse electric double layer [1]. We assume that the surface is uniformly charged with surface charge density σ. The lattice with an adjustable lattice site is introduced in order to describe the system of water and salt ions. All lattice sites are occupied by ions or water.

Free energy of the above defined system (F), measured in units of thermal energy kT, can be written as

$$
\frac{F}{kT} = \frac{1}{8\pi l_B} \int (\nabla\Psi)^2 dV
$$
$$
+ \int \left[n_+(\mathbf{r}) \ln \frac{n_+(\mathbf{r})}{n_0} + n_-(r) \ln \frac{n_-(\mathbf{r})}{n_0} \right] dV
$$
$$
+ \int \left\langle n(\mathbf{r},\omega) \ln \frac{n(\mathbf{r},\omega)}{n_{0w}} \right\rangle dV
$$
$$
+ \lambda \int [n_s - \langle n(\mathbf{r},\omega)\rangle - n_+(\mathbf{r}) - n_-(\mathbf{r})] dV, \tag{1}
$$

where the first term corresponds to electrostatic field energy. Here $\Psi(x) = e_0\phi(x)/kT$, where e_0 is the elementary charge and $\phi(x)$ electrostatic potential. The Bjerrum length $l_B = e_0^2/4\pi\epsilon_0 kT$, where ε_0 is the permittivity of the free space. The second and the third line account for contributions of translational entropy of the ions and orientational entropy of water Langevin dipoles, where $n(\mathbf{r},\omega) = n_w(\mathbf{r})P(\mathbf{r},\omega)$. Here $n_w(\mathbf{r})$ is the number density of water, $P(\mathbf{r},\omega)$ is probability that Langevin dipoles located at $\mathbf{r}$ are oriented for the angle ω with respect to the normal to the charged surface, n_{0w} is bulk number density of water, n_+ and n_- are the number densities of positively and negatively charged ions, respectively, while n_0 is the bulk number density of positively and negatively charged ions, where we assume $\phi(x\rightarrow\infty) = 0$. The last line in Eq. (1) is the constraint due to finite size of particles, n_s being the number density of lattice sites: $n_s = 1/a^3$, where a is the width of the single lattice site. The number density of water $n_w(\mathbf{r})$ in Eq. (1) can be expressed as $n_w(\mathbf{r}) = \langle n(\mathbf{r},\omega)\rangle$, where the averaging over all angles ω (projections) is defined as:

$$
\langle F(\mathbf{r})\rangle = \frac{1}{4\pi} \int F(\mathbf{r},\omega) d\Omega. \tag{2}
$$

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

$$
\varrho(\mathbf{r}) = e_0(n_+(\mathbf{r}) - n_-(\mathbf{r})) - \nabla \cdot \mathbf{P}, \tag{3}
$$

where the polarization is given by $\mathbf{P} = \langle \mathbf{p}\, n(\mathbf{r},\omega)\rangle$, $\mathbf{p}$ is the dipole moment.

The free energy $F = F(n_+, n_-, n)$ fully specifies the system. In thermal equilibrium F adopts minimum with respect to the functions $n_+(\mathbf{r})$, $n_-(\mathbf{r})$ and $n(\mathbf{r},\omega)$. The result of the variational procedure is:

$$
n_+(\mathbf{r}) = n_0 e^{-\Psi + \lambda}, \tag{4}
$$

$$
n_-(\mathbf{r}) = n_0 e^{\Psi + \lambda}, \tag{5}
$$

$$
n(\mathbf{r},\omega) = n_{0w} e^{-\mathbf{p}\cdot\nabla\Psi/e_0 + \lambda}. \tag{6}
$$

Inserting Eqs. (4)–(6) into the constraint (last line of Eq. (1)) we can calculate the parameter λ

$$
e^{\lambda} = \frac{n_s}{2n_0\cosh\Psi + \frac{e_0 n_{0w}}{p_0|\nabla\Psi|}\sinh\frac{p_0|\nabla\Psi|}{e_0}}, \tag{7}
$$

where we took into account

$$
\left\langle e^{-\mathbf{p}\cdot\nabla\Psi/e_0} \right\rangle = \frac{e_0}{p_0|\nabla\Psi|}\sinh\frac{p_0|\nabla\Psi|}{e_0}. \tag{8}
$$

Note that due to the term e^{λ} (Eq. (7)) Eqs. (4)–(6) are not Boltzmann distribution functions. Inserting the distribution functions (4)–(6) into the average microscopic volume charge density $\varrho(\mathbf{r})$ (Eq. (3)) we get the following expression:

$$
\varrho = -2e_0 n_0 e^{\lambda} \sinh\Psi - n_{0w}\nabla\left\langle \mathbf{p}\, e^{-\mathbf{p}\cdot\nabla\Psi/e_0} e^{\lambda} \right\rangle, \tag{9}
$$

where the last term is:

$$
\left\langle \mathbf{p}\, e^{-\mathbf{p}\cdot\nabla\Psi/e_0} \right\rangle = -p_0 \frac{\nabla\Psi}{|\nabla\Psi|} \cdot \mathcal{F}\left(\frac{p_0|\nabla\Psi|}{e_0}\right). \tag{10}
$$

The function $\mathcal{F}(u)$ is defined as:

$$
\mathcal{F}(u) = \mathcal{L}(u)\, \frac{\sinh u}{u}, \tag{11}
$$

where $\mathcal{L}(u) = \coth(u) - 1/u$ is Langevin function. The function $\mathcal{L}(p_0|\nabla\Psi|/e_0)$ describes the average magnitude of dipole moments at given $\mathbf{r}$.

Inserting the volume charge density (Eq. (9)) into Poisson equation $\Delta\Psi = -4\pi l_B \varrho/e_0$ we get [25]

$$
\Delta\Psi = 8\pi l_B n_0 n_s \frac{\sinh\Psi}{\mathcal{H}} - 4\pi l_B n_{0w} n_s \frac{p_0}{e_0}\nabla\left[\frac{\nabla\Psi}{|\nabla\Psi|}\frac{\mathcal{F}(p_0|\nabla\Psi|/e_0)}{\mathcal{H}}\right], \tag{12}
$$

where the function H, related to the finite size of ions, is given by

$$
\mathcal{H} = 2n_0\cosh\Psi + \frac{e_0 n_{0w}}{p_0|\nabla\Psi|}\sinh\frac{p_0|\nabla\Psi|}{e_0}. \tag{13}
$$

Differential Eq. (12) has two boundary conditions. The first boundary condition is obtained by integrating differential Eq. (12):

$$
\nabla\Psi|_S = -4\pi l_B \frac{\sigma}{e_0}\mathbf{n} - 4\pi l_B n_s n_{0w}\frac{p_0}{e_0}\left[\frac{\nabla\Psi}{|\nabla\Psi|}\frac{\mathcal{F}(p_0|\nabla\Psi|/e_0)}{\mathcal{H}}\right]_S, \tag{14}
$$

where the condition of electro-neutrality of the whole system was taken into account. The second boundary condition is $\nabla\Psi|_\infty = 0$.

In the case of one large planar surface differential Eq. (12) reduces to

$$
\Psi'' = 4\pi l_B n_s \left(\frac{2n_0\sinh\Psi}{\mathcal{H}} - n_{0w}\frac{p_0}{e_0}\frac{d}{dx}\left[\frac{\mathcal{F}(p_0|\Psi'|/e_0)}{\mathcal{H}}\right]\right), \tag{15}
$$

with boundary conditions

$$
\Psi'(x=0) = 4\pi \frac{l_B}{e_0}\left[-\sigma - n_s n_{0w} p_0 \frac{\mathcal{F}(p_0|\Psi'|/e_0)}{\mathcal{H}}\bigg|_{x=0}\right] \tag{16}
$$

and

$$
\Psi'(x\rightarrow\infty) = 0. \tag{17}
$$

In the limit of $p_0 \rightarrow 0$ the differential Eq. (15) transforms to [3]

$$
\Psi'' = 8\pi l_B n_0 n_s \frac{\sinh\Psi}{n_{0w} + 2n_0\cosh\Psi}, \tag{18}
$$

with boundary conditions $\Psi'(x=0) = -4\pi l_B\sigma/e_0$ and $\Psi'(x\rightarrow\infty) = 0$.

The effective dielectric permittivity is defined as:

$$
\epsilon_{eff} = 1 + \frac{P}{\epsilon_0 E}, \tag{19}
$$

where the polarization is calculated via the expression $\mathbf{P} = <\mathbf{p} \, n(\mathbf{r},\omega)>$:

$$\mathbf{P} = -p_0 n_{0w} n_s \frac{\nabla\Psi}{|\nabla\Psi|} \cdot \frac{\mathcal{F}\left(\frac{p_0|\nabla\Psi|}{e_0}\right)}{\mathcal{H}}. \tag{20}$$

Inserting Eq. (20) into Eq. (19) and taking into account the definition $\mathbf{E} = -\nabla\Psi$ we can calculate the effective dielectric permittivity:

$$\epsilon_{eff} = 1 + n_{0w} n_s 4\pi l_B \frac{p_0}{e_0} \cdot \frac{\mathcal{F}\left(\frac{p_0|\nabla\Psi|}{e_0}\right)}{|\nabla\Psi| \cdot \mathcal{H}}. \tag{21}$$

In the case of charged planar surface Eq. (21) reads:

$$\epsilon_{eff}(x) = 1 + n_{0w} n_s 4\pi l_B \frac{p_0}{e_0} \cdot \frac{\mathcal{F}\left(\frac{p_0|\Psi'|}{e_0}\right)}{|\Psi'|\mathcal{H}}. \tag{22}$$

In the approximation of small electrostatic energy and small energy of dipoles in electric field compared to thermal energy, i.e. $|\Psi| < 1$ and $p_0|\Psi'|/e_0 < 1$, we can expand Eq. (15) in Taylor series up to third order to get:

$$\Psi'' = \frac{2\Psi + 2\left(-\frac{n_0}{n_s} + \frac{1}{6}\right)\Psi^3 + \frac{n_{0w}}{3n_s}\left(\frac{p_0}{e_0}\right)^2 \Psi\Psi'^2}{\frac{1}{4\pi l_B n_0} + \frac{n_{0w}}{3n_0}\left(\frac{p_0}{e_0}\right)^2 - \frac{n_{0w}}{3n_s}\left(\frac{p_0}{e_0}\right)^2\Psi^2 + \frac{n_{0w}}{n_0}\left(-\frac{n_{0w}}{6n_s} + \frac{1}{10}\right)\left(\frac{p_0}{e_0}\right)^4\Psi'^2}. \tag{23}$$

The boundary condition (16) expanded up to third order is:

$$\Psi'(0) = \frac{-\frac{\sigma}{e_0}}{\left[\frac{1}{4\pi l_B} + \frac{n_{0w}}{3}\left(\frac{p_0}{e_0}\right)^2\left\{1 - \frac{n_0}{n_s}[\Psi(0)]^2 + \left(\frac{p_0}{e_0}\right)^2\left(-\frac{n_{0w}}{6n_s} + \frac{1}{10}\right)[\Psi'(0)]^2\right\}\right]}, \tag{24}$$

while the effective dielectric permittivity can be expressed as:

$$\epsilon_{eff}(x) = \left(1 + \frac{4\pi l_B}{3}n_{0w}\left(\frac{p_0}{e_0}\right)^2\left[1 - \frac{n_0}{n_s}\Psi^2 + \left(-\frac{n_{0w}}{6n_s} + \frac{1}{10}\right)\left(\frac{p_0}{e_0}\right)^2\Psi'^2\right]\right). \tag{25}$$

In the limit of very small $|\Psi|$ and $|\Psi'|$ Eq. (25) transforms into $\epsilon_{eff} = 1 + n_{0w}p_0^2/3\epsilon_0 kT$. In the following Eqs. (23)–(25) were used to calculate the spatial profile of the effective dielectric permittivity.

3. Results and discussion

Fig. 1 shows the number densities of counterions and water molecules as a function of the distance from the charged surface. The number density of counterions ($n_+(x)$) decreases with increasing distance from the charged surface, while the number density of water ($n_w(x) = n_s - n_+(x) - n_-(x)$) increases with increasing distance from the charged surface and reaches a plateau value far away from the charged surface. Near the charged surface the number density of coions is very small compared to the number density of counterions.

The spatial variation of effective dielectric permittivity, calculated according to Eq. (25), is shown in Fig. 2. In calculations the dipole moment p_0 was chosen as 5 Debyes (D) in order to reach the effective dielectric permittivity 78 of pure water far away from the charged surface. The bulk concentration (n_{0w}/N_A) was chosen 55 mol/l, where N_A is Avogadro number. The results are obtained from the approximative differential Eq. (23) derived by expansion of exact differential
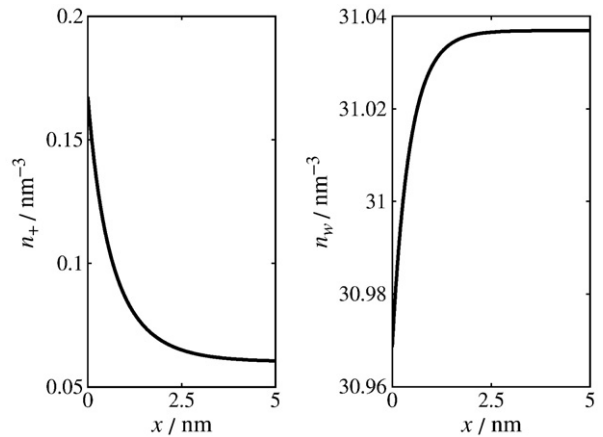

Fig. 1. Number densities of counterions n_+ (left figure) and water n_w (right figure) as a function of the distance from the charged planar surface. Dipole moment of water $p_0 = 5$ D, bulk concentration of salt $n_0/N_A = 0.1$ mol/l, bulk concentration of water $n_{0w}/N_A = 55$ mol/l, surface charge density $\sigma = -0.02$ C/m^2. The width of a single lattice site is $a = 0.318$ nm.
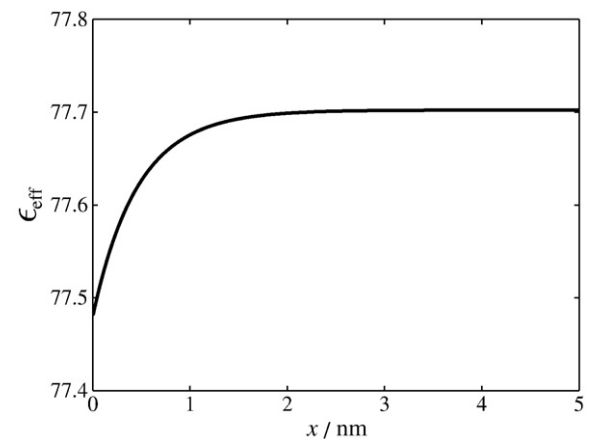

Fig. 2. Effective dielectric permittivity close to charged planar surface. Dipole moment of water $p_0 = 5$ D, bulk concentration of salt is $n_0/N_A = 0.1$ mol/l, bulk concentration of water $n_{0w}/N_A = 55$ mol/l, surface charge density $\sigma = -0.02$ C/m^2. The width of a single lattice site is $a = 0.318$ nm.

Eq. (15) in Taylor series up to third order. As we can see in Fig. 2 the predicted effective dielectric permittivity (ϵ_{eff}) profile only slightly changes in the vicinity of the charged surface. Nevertheless, a clear tendency of decreasing $\epsilon_{eff}(x)$ in the direction towards the charged surface can be observed in Fig. 2.

Fig. 3 shows average cosine of the angle ω between the Langevin dipole vector and the axis perpendicular to the charged surface

$$\overline{\cos\omega} = \frac{\left\langle \cos\omega \, e^{-p_0\Psi'/e_0} \right\rangle}{\left\langle e^{-p_0\Psi'/e_0} \right\rangle} = -\mathcal{L}(p_0\Psi'/e_0) \tag{26}$$

as a function of the distance from the charged surface for two different surface charge densities and bulk ion number density. As shown in Eq. (26) $\overline{\cos\omega}$ is given as a negative value of Langevin function. Fig. 3 shows that the dipole moment vectors at the charged surface are predominantly oriented towards the surface. Far away from the charged surface all orientations of dipoles are equally probable, therefore $\overline{\cos\omega} = 0$ (see Fig. 3).

The calculated decrease of the effective dielectric permittivity close to the charged surface (Fig. 2) is a consequence of increased orientational ordering of the dipoles (Fig. 3) and the depletion of water dipoles near the charged surface due to accumulated counterions (Fig. 1).
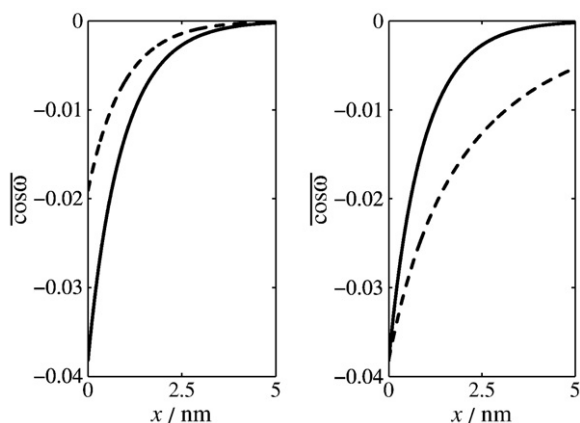
Fig. 3. Average cosine of angle of Langevin dipoles as s function of the distance from the charged planar surface. Left figure: $n_0/N_A = 0.1$ mol/l, surface charge densities are $\sigma = -0.02$ C/m^2 (full line) and $\sigma = -0.01$ C/m^2 (dashed line). Right figure: $\sigma = -0.02$ C/m^2, bulk ion concentrations are $n_0/N_A = 0.1$ mol/l (full line), $n_0/N_A = 0.01$ mol/l (dashed line). The width of a single lattice site is $a = 0.318$ nm.

The surface charge density $\sigma = -0.02$ C/m^2 in Fig. 2 is in the range of values typical for biological membrane surface ($|\sigma| \leq 0.05$ C/m^2) [1,27,28] and too small to induce significant decrease of permittivity in the vicinity of the charged surface. However, the surface charge densities of the model membranes [27] or the surface charge densities of titanium surfaces may be much higher [29], i.e. up to $\sigma \approx -0.5$ C/m^2 or even higher if the external potential is applied [30]. In the case of high magnitudes of σ the depletion of water (see Fig. 4) and water orientational ordering are much stronger and consequently the decrease of the effective dielectric permittivity close to the charged surface is very large.

In the present theoretical study we have analysed the electrical properties of monovalent salt water solution in contact with charged surface by solving numerically the modified Poisson–Boltzmann equation where the finite volumes of ions were taken into account. Our mean field approach involves a number of approximations, as for example we didn't take into account the image forces [37]. Also we neglected the short-range attractive van der Waals forces, long [38] and short-range attractive or oscillatory hydration forces [2]. The oscillatory behavior of water polarization near the charged surface is mainly the consequence of direct interactions between water dipoles [9] which are in our mean field theory, similarly as all other direct particle–particle interactions (ion–ion and ion–dipole), not taken into account. In the case of charged biological and model membranes the membrane surface is not smooth [39], therefore water molecules in
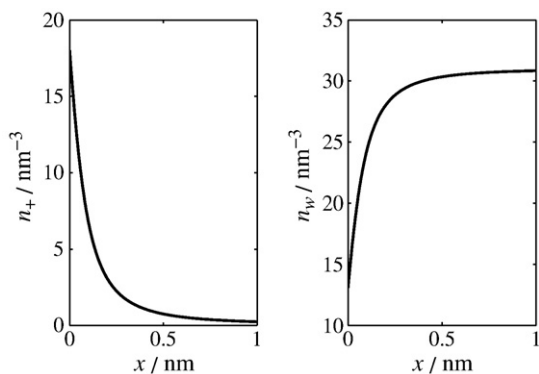
the close vicinity of charged membrane are not organized in perfect successive layers which smooth out the polarization oscillations [40].

To conclude, in this work, the PB theory was improved by introducing the orientational ordering of water dipoles and excluded volume effect through the lattice statistics model. The lattice sites are occupied by ions or water. The water dipoles are described as Langevin dipoles with given dipole moment. Using the calculus of variation, the ion and water number density profiles were calculated. The differential equation for electrostatic potential was expanded in Taylor series up to third order in electrostatic potential and then solved numerically.

Based on Eqs. (4)–(7) it can be concluded for sufficient large surface charge density and lattice constant close to the charged surface nearly all lattice sites are occupied by counterions (see also Fig. (4)), i.e. the plateau of counterion number density close to the charged surface may be observed. The counterion number density in plateau reaches the value close to $1/a^3$. On the other hand the number density of water near the charged surface may approach to zero. Quite the opposite effect is observed far away from the charged surface, where the number density of water reaches plateau.

In the present theory, two effects contribute to the spatial variation of effective dielectric permittivity. First is related to the decrease of the number density of water near the charged surface. The drop of the number density of water results in the decrease of the effective dielectric permittivity. The second is connected to relatively high electric field at charged surface and consequent strong polarization of water in the first layers at the charged surface. Far from the charged surface the number density of water dominate and the effective dielectric permittivity converge to the effective dielectric permittivity of pure water.

Electric double layer theory has different applications in theoretical description of physical properties of biologically important systems as for example in the description of electrostatic properties of biological membranes. Electrostatic properties of biological membranes are among essential functional properties of the membranes [1] which determine the binding of charged ligands to the membrane surface, the interactions of vesicles with the membrane (exocytosis and vesiculation) and transmembrane transport of charged molecules [1,27,31]. Electrostatic interactions are also important for the successful integration of bone metal implants. The negatively charged surface of the metal (titanium) implant attracts cations and repels anions, and consequently an electric double layer is formed [32,33]. Many studies in the past have shown that the negative surface potential of metal implants promotes osteoblast adhesion and consequently the new bone formation [34,35]. Electrostatic interactions, described within the electric double layer theory, are therefore considered as predictors for osteoblast attachment to biomaterials [36]. As shown in the past the properties of electric double layer in biological systems may be strongly influenced by water ordering in the region of electric double layer [2,27,30] which was also the subject of the present work.

Fig. 4. Number densities of counterions n_+ (left figure) and water n_w (right figure) as a function of the distance from the charged planar surface determined by solving Eq. (18) for $p_0 = 0$. Bulk concentration of ions $n_0/N_A = 0.1$ mol/l, bulk concentration of water $n_{0w}/N_A = 55$ mol/l, surface charge density $\sigma = -0.4$ C/m^2. The width of a single lattice site is $a = 0.318$ nm.

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