Spatial Variation of Permittivity near a Charged Membrane in Contact with Electrolyte Solution

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Contents

Abstract

The interaction between a charged membrane bilayer surface and an electrolyte solution causes the formation of an electrical double layer, which has been a subject of extensive study for more than a century. This chapter provides a statistical mechanical description of orientational ordering of water molecules and of excluded volume effect of ions near the charged membrane surface. The space variation of the permittivity of the electrolyte solution near the charged membrane surface obtained by statistical mechanical model is then included in a phenomenological model for the membrane surface potential for highly charged membranes.

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1. INTRODUCTION

The contact between a negatively charged bilayer membrane surface and an electrolyte solution implies a particular ion distribution and water orientation near the charged surface. In other words, an electrical double layer (EDL) [1–4] is formed.

Within the so-called Poisson–Boltzmann (PB) theory [2,3,5,6], the ions in electrolyte solution are treated as dimensionless, while uniform permittivity of the electrolyte solution is assumed. The Stern model [4] was the first attempt to incorporate finite size of ions in EDL theory by combining the Helmholtz [1] and Gouy–Chapman [2,3] model. Helmholtz treated the double layer mathematically as a simple capacitor, based on a physical model in which a layer of ions with a single layer of solvent around each ion is adsorbed to the surface. Gouy [2] and Chapman [3] 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 (coions) repelled from it. Ions are embedded in a dielectric continuum while the electric potential is subject to the PB differential equation [6–9]. Generally, Stern model [4] consists of an inner Helmholtz plane (coions bound near the surface due to specific adsorption), the so-called outer Helmholtz plane (hydrated counterions at the distance of closest approach), and a diffuse double layer.

Most of the theoretical models describing EDL assume that the permittivity in the whole system is constant. But actually, close to the charged surface, due to accumulation of counterions near the charged surface, the water molecules are partially depleted from this region [8]. The water dipoles show a distinct preferential orientation in the direction perpendicular to the charged surface [10–14]. All these result in a spatial variation of the permittivity near the charged surface [12,13,15]. In this work, we present different models of EDL, which take into account the spatial variation of permittivity. The orientational ordering of water molecules and excluded volume effect near the planar bilayer membrane surface are described within the modified PB theory. The results of this theory are then included in a generalized phenomenological PB model via the space dependency of the permittivity near the charged planar surface.

2. ORIENTATION OF WATER MOLECULES NEAR A CHARGED MEMBRANE SURFACE

The distribution of ions in the electrolyte solution close to the charged membrane surface is described within the PB theory [6,16] by the competition between the electrostatic interactions and the entropy of

the ions in the solution. Due to the electrostatic forces between the charged surface and the ions in the solution, the counterions (the ions with the charge of the opposite sign than the charged surface) are accumulated close to the surface and the coions (the ions with the charge of the same sign than the surface) are depleted from the surface [6]. Near the charged surface, water molecules show a distinct preferential orientation and a strongly reduced permittivity [11]. In this section, the PB theory modified by orientational ordering of water is briefly described. In the model, the finite volumes of ions in the electrolyte solution (i.e., the excluded volume) are not taken into account. Therefore, the predictions of the model are restricted to the cases of low surface charge densities and low bulk ionic strengths when accumulation of the counterions near charged membrane surface is not very pronounced.

We consider a planar charged membrane bilayer surface in contact with solution of ions and water (Langevin) dipoles. The Langevin dipoles describe a water molecule with a nonzero dipole moment ($\mathbf{p}$). The membrane bilayer surface bears charge with surface charge density σ. We assume that counterions and coions are distributed according to the Boltzmann distribution functions [6,11,16]

$$n_+(x) = n_0 e^{-\Psi}, \quad n_-(x) = n_0 e^{\Psi}, \tag{1}$$

while the number density of water molecules ($n_w(x)$) is assumed to be constant everywhere in the electrolyte solution and equal to its bulk value (n_{0w}):

$$n_w(x) = n_{0w}. \tag{2}$$

Here $n_+(x)$ and $n_-(x)$ are the number densities of counterions and coions, respectively and

$$\Psi(x) = e_0 \phi(x)/kT \tag{3}$$

is the reduced electrostatic potential, $\phi(x)$ is the electrostatic potential, e_0 is the elementary charge, kT is the thermal energy, and n_0 is the bulk number density of positively and negatively charged ions in electrolyte solution. The axis x is perpendicular to the membrane surface and points in the direction of bulk solution.

The charges of counterions, coions, and water molecules (Langevin dipoles) contribute to the average microscopic volume charge density:

$$\varrho(x) = e_0(n_+(x) - n_-(x)) - \frac{dP}{dx}. \tag{4}$$

The polarization P is given by

$$P(x) = n_{0w}\langle \mathbf{p}(x, \omega)\rangle_B, \tag{5}$$

where $\mathbf{p}$ is the water (Langevin) dipole moment and $\langle \mathbf{p}(x, \omega)\rangle_B$ is its average over the angle distribution in thermal equilibrium. $P(x)$ is positive if the polarization vector $\mathbf{P}$ points in the direction of x-axis and negative if $\mathbf{P}$ points in the direction pointing from bulk to the charged membrane surface. According to the Boltzmann function law [5], the relative probability of finding the water dipole in an element of the angle $d\Omega = 2\pi \sin \omega \, d\omega$ is proportional to the Boltzmann factor $\exp(-W_d/kT)$, where

$$W_d = -\mathbf{p}{\cdot}E = \mathbf{p}{\cdot}\nabla\phi = (kT/e_0)p_0|\Psi'|\cos(\omega) \tag{6}$$

is the energy of the water (Langevin) dipole $\mathbf{p}$ in the electric field $\mathbf{E} = -\nabla\phi$ and ω is the angle between the dipole moment vector $\mathbf{p}$ and the vector $\nabla\phi$. Hence

$$
\begin{aligned}
\langle \mathbf{p}(x, \omega)\rangle_B &= \frac{\int_0^\pi p_0 \cos \omega \exp\left(-p_0|\Psi'|\cos \omega/e_0\right)2\pi \sin \omega \, d\omega}{\int_0^\pi \exp\left(-p_0|\Psi'|\cos \omega/e_0\right)2\pi \sin \omega \, d\omega} \\
&= \frac{p_0 \int_0^\pi \cos \omega \exp\left(-p_0|\Psi'|\cos \omega/e_0\right)d(\cos \omega)}{\int_0^\pi \exp\left(-p_0|\Psi'|\cos \omega/e_0\right)d(\cos \omega)} \\
&= -p_0\left(\coth\left(\frac{p_0|\Psi'|}{e_0}\right) - \frac{e_0}{p_0|\Psi'|}\right) = -p_0\mathcal{L}\left(\frac{p_0|\Psi'|}{e_0}\right),
\end{aligned}
\tag{7}
$$

where p_0 is the magnitude of the water dipole moment. The function $\mathcal{L}(u) = (\coth(u) - 1/u)$ is the Langevin function. The 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 the azimuthal symmetry. Inserting the ion Boltzmann distribution functions Eq. (1) and expression for polarization (Eq. (5)) into Eq. (4), we get the expression for the volume charge density in electrolyte solution:

$$\varrho(x) = -2e_0n_0 \sinh \Psi + n_{0w}p_0 \frac{d}{dx}\left[\mathcal{L}\left(p_0|\Psi'|/e_0\right)\right]. \tag{8}$$

Inserting the above expression for volume charge density $\varrho(x)$ (Eq. (8)) into Poisson equation

$$\Psi^{''} = -4\pi l_{\mathrm{B}} \varrho / e_0, \tag{9}$$

we get:

$$\Psi^{''} = 4\pi l_{\mathrm{B}} \left(2n_0 \sinh\Psi - n_{0\mathrm{w}} \frac{p_0}{e_0} \frac{\mathrm{d}}{\mathrm{d}x} \left[\mathcal{L}\left(\mathbf{p}_0 |\Psi^{'}|/e_0\right) \right] \right), \tag{10}$$

where l_{B} is the Bjerrum length:

$$l_{\mathrm{B}} = e_0^2 / 4\pi\varepsilon_0 kT \tag{11}$$

and ε_0 the permittivity of the free space. Dipolar PB differential equation (10) is subject to two boundary conditions. The first boundary condition is obtained by integrating the differential equation (10):

$$\Psi^{'}(x=0) = -\frac{4\pi l_{\mathrm{B}}}{e_0} \left[\sigma + n_{0\mathrm{w}} p_0 \mathcal{L}\left(p_0 |\Psi^{'}|/e_0\right)|_{x=0} \right]. \tag{12}$$

The condition requiring electroneutrality of the whole system was taken into account in the derivation of Eq. (12). The second boundary condition is

$$\Psi^{'}(x \to \infty) = 0. \tag{13}$$

Based on Eqs. (5)–(7), we can express the relative permittivity of the electrolyte solution ($\varepsilon = \varepsilon_{\mathrm{r}}$) in contact with the planar charged membrane bilayer surface as [17]

$$\varepsilon = 1 + \frac{1}{\varepsilon_0} \frac{\mathrm{d}|P|}{\mathrm{d}E} = 1 + n_{0\mathrm{w}} \frac{p_0}{\varepsilon_0} \frac{\mathrm{d}(\mathcal{L}(p_0 E/kT))}{\mathrm{d}E}. \tag{14}$$

while the corresponding effective permittivity ($\varepsilon_{\mathrm{eff}}$) can be defined as

$$\varepsilon_{\mathrm{eff}} = 1 + \frac{|P|}{\varepsilon_0 E} = 1 + n_{0\mathrm{w}} \frac{p_0}{\varepsilon_0} \frac{\mathcal{L}(p_0 E/kT)}{E}, \tag{15}$$

where $E = |\phi^{'}|$ is the magnitude of electric field strength.

Figure 1 shows the dependence of the effective permittivity $\varepsilon_{\mathrm{eff}}$ on the magnitude of the electric field strength E calculated within the PB theory (Eq. (15) which takes into account the orientational ordering of water molecules by considering them as Langevin dipoles. The excluded volume
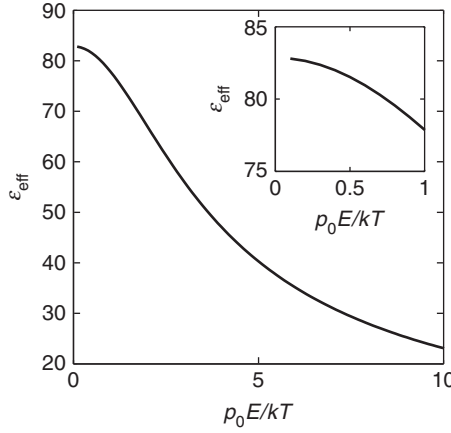
Figure 1 Calculated effective permittivity (see Eq. (15) as a function of the magnitude of electric field strength $E = |\phi'|$. The dipole moment of the water Langevin dipoles $p_0 = 5D$, bulk concentration of water dipoles is $n_{0w}/N_A = 55$ mol/l, the Bjerrum length $l_B = 54.6$ nm.

principle is not taken into account. It can be seen in Fig. 1 that ε_{eff} decreases with increasing magnitude of electric field strength E. Since the value of E decreases with increasing distance from the membrane charge surface (see, e.g., [6]), ε_{eff} increases with the increasing distance from the charged surface. In accordance with the results of other authors, it can be concluded that due to the distinct preferential orientation of water dipoles in the close vicinity of the charged membrane surface, the effective permittivity ε_{eff} near the membrane surface is reduced relative to its bulk value (see, e.g., [11]).

If the Boltzmann distribution function is assumed also for water (Langevin) dipoles:

$$n_+(x) = n_0 e^{-\Psi}, \tag{16}$$

$$n_-(x) = n_0 e^{\Psi}, \tag{17}$$

$$n_w(x) = n_{0w} \left\langle e^{-p_0|\Psi'|\cos\omega/e_0} \right\rangle_\omega, \tag{18}$$

where

$$\left\langle e^{-p_0|\Psi'|\cos\omega/e_0} \right\rangle_\omega = \frac{2\pi \int\limits_\pi^0 d(\cos\omega) e^{-p_0|\Psi'|\cos\omega/e_0}}{4\pi} = \frac{e_0}{p_0|\Psi'|}\sinh\frac{p_0|\Psi'|}{e_0}, \tag{19}$$

a similar procedure as described above leads to the extension of the PB equation in the form [18]

$$\Psi'' = 4\pi l_B \left(2n_0 \sinh\Psi - n_{0w} \frac{p_0}{e_0} \frac{\mathrm{d}}{\mathrm{d}x} \left[\mathcal{F}\left(p_0 |\Psi'|/e_0\right) \right] \right), \qquad (20)$$

where the function $\mathcal{F}$ is defined as

$$\mathcal{F}(u) = \mathcal{L}(u) \frac{\sinh u}{u}. \qquad (21)$$

The corresponding effective permittivity (ε_{eff}) can be defined as [18]

$$\varepsilon_{\text{eff}} = 1 + n_{0w} \frac{p_0}{\varepsilon_0} \frac{\mathcal{F}(p_0 E/kT)}{E}. \qquad (22)$$

Figure 2 shows the dependence of the effective permittivity ε_{eff} on the magnitude of electric field strength $E = |\phi'|$ calculated within the dipolar PB theory which takes into account the Boltzmann distribution for water molecules (Eqs. (18) and (19)) as well as the orientational ordering of water molecules by considering them as Langevin dipoles (Eq. (22)). It can be seen in Fig. 2 that according to Eq. (22), the effective permittivity ε_{eff} increases as a function of increasing E. Since the magnitude of electric field strength
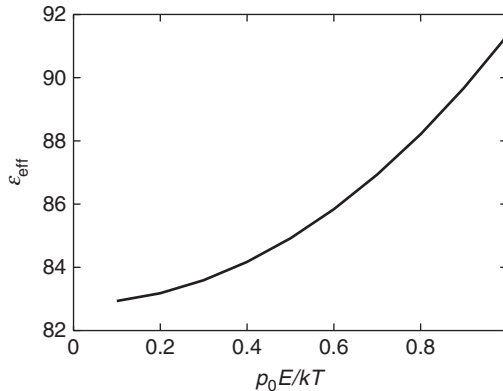

Figure 2 Calculated effective permittivity Eq. (22) as a function of the magnitude of electric field strength $E = |\phi'|$ assuming the Boltzmann space distribution of water dipoles (Eqs. (18) and (19)). Dipole moment of water (Langevin) dipoles is $p_0 = 5D$, bulk concentration of water is dipoles $n_{0w}/N_A = 55$ mol/l, Bjerrum length is $l_B = 54.6$ nm.

in electrolyte solution increases towards the charged membrane surface, Eq. (22) predicts the increase of ε_{eff} in the vicinity of the charged membrane surface [18]. This is a consequence of the accumulation of water dipoles near the charged surface (due to Boltzmann distribution for water molecules) which prevails over the decrease of ε_{eff} due to an increased orientational ordering of water molecules in a strong electric field as shown in Fig. 1. Neglecting the final volumes of ions and water molecules is thus reflected in the predicted unrealistic increase of ε_{eff} near the charged membrane surface [12,18,22].

In Section 3 we first describe the PB theory modified by the excluded volume principle, that is, the finite volumes of ions are taken into account within a simple lattice statistics [8]. In the model, each site of the lattice (of the width a_s) is occupied by one and only one of the three kinds of molecules. The ordering of water molecules in electric field is not taken into account.

Finally, in Section 4 the excluded volume and orientation of water dipoles are considered within same modified PB theory. The predicted decrease of effective permittivity ε_{eff} near the charged membrane surface relative to its bulk value is the consequence of two effects, that is, the depletion of water molecules near the charged membrane surface on the account of accumulation of counterions, and a pronounced orientational ordering of water dipoles in the strong electric field in the vicinity of the charged membrane surface [12].

3. EXCLUDED VOLUME EFFECT

A number of different attempts have been made to incorporate excluded volume effect (i.e., the finite volumes of ions) into the PB equation. Freise [19] introduced the excluded volume effect by a pressure-dependent potential, while Wicke and Eigen [20] used a thermodynamic approach, multiplying the numerical density of ions by a factor containing the number of the vacant sites. The fluctuation potential [16] due to the self-atmosphere of ion and the ion–ion exclusion volume term were taken into account in the modified PB equation [21–23]. More recently, the finite size of ions has been incorporated into the EDL theory in a different way [24,25], among others by using lattice statistics model [8,26], leading to the PB equation modified by the excluded volume effect in the form [8,27] (for monovalent coions and counterions)

$$\frac{d^2\Psi(x)}{dx^2} = \frac{2e_0^2 n_s n_0}{kT\varepsilon\varepsilon_0 n_{0w}} \frac{\sinh(\Psi(x))}{1 + \frac{2n_0}{n_{0w}}\cosh(\Psi(x))}, \tag{23}$$

where ε is the permittivity of electrolyte solution, ε_0 the permittivity of the free space, and n_s is the number density of lattice sites: $n_s = 1/\, a_s^{\,3}$, where a_s is the width of the single lattice site. The x-axis is perpendicular to the membrane surface and points to the bulk solution. The bulk number density of water n_{0w} is connected to number density of lattice sites n_s and ion bulk number density n_0 as $n_{w0} = n_s - 2n_0$.

The two boundary conditions are

$$\frac{d\Psi(x)}{dx}\bigg|_{x \to \infty} = 0, \quad \frac{d\Psi(x)}{dx}\bigg|_{x = 0} = -\frac{\sigma e_0}{kT\varepsilon\varepsilon_0}, \qquad (24)$$

σ is the surface charge density of the bilayer membrane surface. The first boundary condition states that the electric field is zero, far away from the charged surface, while the second boundary condition demands the electroneutrality of the whole system.

The corresponding ion distribution functions are [8,27]

$$n_j(x) = \frac{n_s(n_0/n_{0w}) \exp(-j\Psi(x))}{1 + \frac{2n_0}{n_{0w}} \cosh(j\Psi(x))}), \quad j = +, -, \qquad (25)$$

where $j = +$ for cations and $j = -$ for anions. The above described equations of the PB theory modified by the excluded volume effect assumes that the center of ions can approach to the $x = 0$ plane. The number density of water (Langevin) dipoles n_w can be then calculated from the known n_+ and n_- as

$$n_w(x) = n_s - n_+(x) - n(x). \qquad (26)$$

Figure 3 shows that for higher values of the surface charge density ($|\sigma|$), the counterion number density n_+ increases. For very high $|\sigma|$ the counterion number density n_+ may saturate close to the charged surface to its close packing value, while the classical PB theory predicts unreasonable high values beyond the close-packing value (see also [8,27]). The PB theory modified by the excluded volume effect given by Eq. (25) thus predicts the saturation of the counterions near the charged surface for ions of finite size [8,27,28].

Due to accumulation of counterions near the charged membrane surface (Fig. 3, left panel), the number density of water molecules in this region may be reduced substantially (Fig. 3, right panel). Even not considered in a self-consistent way (i.e., within the above described PB theory modified by excluded volume the permittivity is a constant), the space dependency of the permittivity of the electrolyte solution in contact with a charged membrane surface may be estimated (Fig. 4) by adopting the assumption
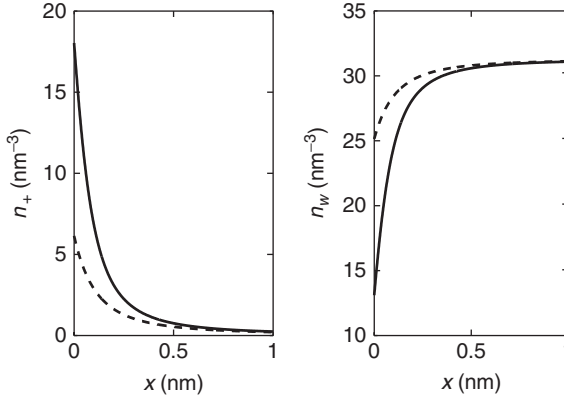
Figure 3   The number density of counter-ions (n_+) as a function of the distance from the planar charged membrane surface (x) for two values of surface charge density σ: -0.2 As/m^2 (dashed line) and -0.4 As/m^2 (full line)(left figure) and the corresponding number density of Langevin dipoles $n_w = (n_s - n_+ - n_-)$ (right figure). The model parameters are: lattice constant $a_s = 0.318$ nm, $\varepsilon = 78.5$, $T = 310$ K, bulk salt concentration $n_0/N_A = 0.1$ mol/l, where N_A is Avogadro number.
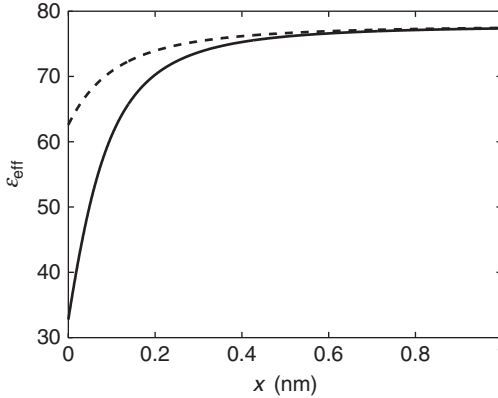

Figure 4   The effective permittivity $\varepsilon_{eff}(x) = 78.5\, n_w(x)/n_{0w}$ of the electrolyte solution calculated for the number densities of counter-ions given in Fig. 3.

that the permittivity is proportional to the relative density of water molecules (Langevin dipoles):

$$\varepsilon_{eff}(x) = 78.5\,\frac{n_w(x)}{n_{0w}}. \tag{27}$$

In the previous two sections, the orientation of water dipoles and the finite size of ions in electrolyte solution were treated separately by two models.

In the second section (Section 2), we considered the orientation of point-like water molecules, while in the third section (Section 3), the finite volume of ions and water molecules was taken into account. In the next section (Section 4), the orientational ordering of water molecules and excluded volume effect near the planar bilayer membrane surface are considered simultaneously by modification of PB equation.

4. EXCLUDED VOLUME EFFECT AND ORIENTATION OF WATER MOLECULES

4.1. Modified Poisson–Boltzmann Equation

As before (see Section 2), we consider a planar charged membrane bilayer surface in contact with a solution of ions and Langevin dipoles of finite size. The Langevin dipoles describe water molecules with nonzero dipole moments ($\mathbf{p}$). The membrane bilayer surface is charged with surface charge density σ. The lattice with an adjustable lattice site is introduced in order to describe the system of Langevin dipoles and salt ions. All lattice sites are occupied by ions or Langevin dipoles. For the sake of simplicity, we assume that the volume of each ion and the volume of a single Langevin dipole are equal. The free energy of the system F, measured in units of thermal energy kT, can be written as [12]

$$
\begin{aligned}
\frac{F}{kT} = {} & \frac{1}{8\pi l_{\mathrm{B}}} \int \left(\Psi'\right)^2 \mathrm{d}V \\
& + \int \left[n_+(x) \ln \frac{n_+(x)}{n_0} + n_-(x) \ln \frac{n_-(x)}{n_0} + n_{\mathrm{w}}(x) \ln \frac{n_{\mathrm{w}}(x)}{n_{0\mathrm{w}}} \right] \mathrm{d}V \\
& + \int n_{\mathrm{w}}(x) \langle \mathscr{P}(\omega) \ln \mathscr{P}(\omega) \rangle_\omega \mathrm{d}V \\
& + \lambda \int [n_{\mathrm{s}} - n_{\mathrm{w}}(x) - n_+(x) - n_-(x)] \mathrm{d}V,
\end{aligned}
\tag{28}
$$

where the averaging over all angles ω is defined as

$$
\langle F(x) \rangle_\omega = \frac{1}{4\pi} \int F(x, \omega) \mathrm{d}\Omega.
\tag{29}
$$

The first term in Eq. (28) corresponds to the energy of the electrostatic field. Here $\Psi(x)$ is the reduced potential, $\mathrm{d}V = A\,\mathrm{d}x$ is the volume element with thickness $\mathrm{d}x$, where A is the membrane area. The second line in Eq. (28) accounts for the mixing free energy contribution of the positive and negative salt ions, n_+ and n_- are the number densities of positively and negatively charged ions, respectively, n_{w} is the number density of Langevin

dipoles, n_0 is the bulk number density of positively and negatively charged ions, while n_{0w} is the bulk number density of Langevin dipoles. We assume $\phi(x \to \infty) = 0$. The third line in Eq. (28) accounts for the orientational contribution of Langevin dipoles to the free energy. $\mathscr{P}(x)$ is the probability that the Langevin dipole located at x is oriented for an angle ω with respect to the normal to the charged membrane bilayer surface. The last line in Eq. (28) is constraint due to finite size of particles, imposing the condition that each site of the lattice is occupied by only one particle (coion, counter-ion, or Langevin water dipole), n_s is the number density of lattice sites: $n_s = 1/a_s^3$ and where a_s is the width of the single lattice site. At any position x, we require the normalization condition

$$\langle \mathscr{P}(x, \omega) \rangle_\omega = 1 \qquad (30)$$

to be fulfilled. The above expression for the free energy can be rewritten in the form:

$$
\begin{aligned}
\frac{F}{kT} = {} & \frac{1}{8\pi l_B} \int \left(\Psi' \right)^2 dV \\
& + \int \left[n_+(x) \ln \frac{n_+(x)}{n_0} + n_-(x) \ln \frac{n(x)}{n_0} \right] dV \\
& + \int \left\langle n(x, \omega) \ln \frac{n(x, \omega)}{n_{0w}} \right\rangle_\omega dV \\
& + \lambda \int \left[n_s - \langle n(x, \omega) \rangle_\omega - n_+(x) - n_-(x) \right] dV,
\end{aligned}
\qquad (31)
$$

where the Langevin dipole distribution function is defined as

$$n(x, \omega) = n_w(x)\mathscr{P}(x, \omega). \qquad (32)$$

By averaging over all angles ω in Eq. (32), the number density of Langevin dipoles is obtained:

$$\langle n(x, \omega) \rangle_\omega = \langle n_w(x)\mathscr{P}(x, \omega) \rangle_\omega = n_w(x)\langle \mathscr{P}(x, \omega) \rangle_\omega = n_w(x), \qquad (33)$$

where we took into account Eq. (30).

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

$$\varrho(x) = e_0(n_+(x) - n_-(x)) - \frac{dP}{dx}. \qquad (34)$$

The polarization P is given by

$$P(x) = n_{\mathrm{w}}(x)\langle \mathbf{p}(x, \omega)\rangle_{\mathrm{B}}, \tag{35}$$

where $\langle \mathbf{p}(x, \omega)\rangle_{\mathrm{B}}$ is the average value of the Langevin dipole moments $\mathbf{p}$ at coordinate x (see Eq. (7)). $P(x)$ is positive if the polarization vector $\mathbf{P}$ points in the direction of x-axis and negative if $\mathbf{P}$ points in direction from the bulk to the charged membrane surface. The rotational averaging is performed over all values of ω. The Langevin function $\mathcal{L}(p_0|\Psi'|/e_0)$ describes the average magnitude of Langevin dipole moments at given x.

The free energy $F = F(n_+, n_-, n(x, \omega))$ fully specifies the system. In thermal equilibrium, F adopts minimum with respect to the functions $n_+(x)$, $n_-(x)$, and $n(x, \omega)$. The results of the variational procedure are

$$n_+(x) = n_0 e^{-\Psi+\lambda}, \tag{36}$$

$$n_-(x) = n_0 e^{\Psi+\lambda}, \tag{37}$$

$$n(x, \omega) = n_{0\mathrm{w}} e^{\left(-\mathbf{p}_0|\Psi'|\cos\omega/e_0\right)+\lambda}. \tag{38}$$

Inserting Eqs. (36)–(38) into the constraint (the last line of Eq. (31))

$$n_s = n_+(x) + n(x) + \langle n(x, \omega)\rangle_\omega, \tag{39}$$

yields

$$n_{\mathrm{s}} = n_0 e^{-\Psi+\lambda} + n_0 e^{\Psi+\lambda} + n_{0\mathrm{w}} e^\lambda \left\langle e^{-p_0|\Psi'|\cos\omega/e_0}\right\rangle_\omega, \tag{40}$$

from where we calculate the parameter λ:

$$e^\lambda = \frac{n_{\mathrm{s}}}{\mathcal{H}}, \tag{41}$$

where the function $\mathcal{H}$ is related to the finite particle size:

$$\mathcal{H} = 2n_0 \cosh\Psi + \frac{e_0 n_{0\mathrm{w}}}{p_0|\Psi'|} \sinh\frac{p_0|\Psi'|}{e_0}. \tag{42}$$

In the above derivation of λ, we took into account (see Eq. (19))

$$\left\langle e^{-p_0|\Psi'|\cos\omega/e_0}\right\rangle_\omega = \frac{e_0}{p_0|\Psi'|} \sinh\frac{p_0|\Psi'|}{e_0}. \tag{43}$$

Using Eqs. (33) and (38), we get the following expression for the number density of Langevin dipoles $n_d(x)$:

$$n_w(x) = \langle n(x, \omega) \rangle_\omega = n_{0w} e^\lambda \left\langle e^{-p_0|\Psi'| \cos \omega/e_0} \right\rangle_\omega. \tag{44}$$

Taking into account Eqs. (41)–(43), it follows from Eq. (44)

$$n_w(x) = \frac{n_{0w} n_s}{\mathcal{H}} \frac{e_0}{p_0|\Psi'|} \sinh \frac{p_0|\Psi'|}{e_0}. \tag{45}$$

Combining Eqs. (35), (7), and (45) yields polarization:

$$P = -p_0 n_{0w} n_s \frac{\mathcal{F}\left(\frac{p_0|\Psi'|}{e_0}\right)}{\mathcal{H}(\Psi, |\Psi'|)}, \tag{46}$$

where the function $\mathcal{F}(u)$ is defined by Eq. (21). Based on Eq. (46), we can express the permittivity of the electrolyte solution (ε) in contact with the planar charged membrane bilayer surface as

$$\varepsilon = 1 + \frac{1}{\varepsilon_0} \frac{d|P|}{dE} = 1 + n_{0w} n_s \frac{p_0}{\varepsilon_0} \frac{d(\mathcal{F}/\mathcal{H})}{dE}, \tag{47}$$

while the corresponding effective permittivity (ε_{eff}) is

$$\varepsilon_{\text{eff}} = 1 + \frac{|P|}{\varepsilon_0 E} = 1 + n_{0w} n_s \frac{p_0}{\varepsilon_0} \frac{\mathcal{F}/\mathcal{H}}{E}, \tag{48}$$

where $E = |\phi'|$ is the magnitude of the electric field strength.

Inserting the Fermi–Dirac-like distribution functions Eqs. (36), (37), and expression for polarization (Eq. (46)) into Eq. (34), we get the expression for the volume charge density in electrolyte solution

$$\varrho = -2e_0 n_0 n_s \frac{\sinh \Psi}{\mathcal{H}} + n_{0w} p_0 n_s \frac{d}{dx} \left[\frac{\mathcal{F}\left(p_0|\Psi'|/e_0\right)}{\mathcal{H}} \right], \tag{49}$$

where we took into account also the equation for the parameter λ Eq. (41). Inserting the volume charge density (49) into Poisson equation

$$\Psi'' = -4\pi l_B \varrho/e_0, \tag{50}$$

we get [12]

$$\Psi'' = 4\pi l_B n_s \left(2n_0 \frac{\sinh\Psi}{\mathcal{H}} - n_{0w} \frac{p_0}{e_0} \frac{d}{dx}\left[\frac{\mathcal{F}\left(p_0|\Psi'|/e_0\right)}{\mathcal{H}}\right]\right). \quad (51)$$

The differential equation (51) has two boundary conditions. The first boundary condition is obtained by integration of the differential equation (51):

$$\Psi'(x=0) = -4\pi \frac{l_B}{e_0}\left[\sigma + n_s n_{0w} p_0 \frac{\mathcal{F}\left(p_0|\Psi'|/e_0\right)}{\mathcal{H}}\Big|_{x=0}\right]. \quad (52)$$

The condition of electroneutrality of the whole system was taken into account. The second boundary condition is

$$\Psi'(x \to \infty) = 0. \quad (53)$$

4.2. Linearized Modified Poisson–Boltzmann Equation

In the approximation of small electrostatic energy and small energy of dipoles in electric field compared to thermal energy, that is, small Ψ and small $p_0|\Psi'|/e_0$, Eq. (51) can be expanded in Taylor series up to third order to get [12]

$$\Psi'' = \frac{2\Psi + 2\left(-\frac{n_0}{n_s} + \frac{1}{6}\right)\Psi^3 + \frac{n_{0w}}{3n_s}\left(\frac{p_0}{e_0}\right)^2 \Psi\Psi'^2}{\frac{1}{4\pi l_B n_0} + \frac{n_{0w}}{3n_0}\left(\frac{p_0}{e_0}\right)^2 - \frac{n_{0w}}{3n_s}\left(\frac{p_0}{e_0}\right)^2 \Psi^2 + \frac{n_{0w}}{n_0}\left(-\frac{n_{0w}}{6n_s} + \frac{1}{10}\right)\left(\frac{p_0}{e_0}\right)^4 \Psi'^2}. \quad (54)$$

The corresponding boundary condition (52) expanded up to third order is

$$\Psi'(0) = \frac{-\sigma/e_0}{\left[\frac{1}{4\pi l_B} + \frac{n_{0w}}{3}\left(\frac{p_0}{e_0}\right)^2\left(1 - \frac{n_0}{n_s}[\Psi(0)]^2 + \mathcal{B}\right)\right]}, \quad (55)$$

where

$$\mathcal{B} = \left(\frac{p_0}{e_0}\right)^2\left(-\frac{n_{0w}}{6n_s} + \frac{1}{10}\right)\left[\Psi'(0)\right]^2, \quad (56)$$

while the effective permittivity (Eq. (48)) can be expressed as

$$\varepsilon_{\text{eff}}(x) = \left(1 + \frac{4\pi l_{\text{B}}}{3} n_{0\text{w}} \left(\frac{p_0}{e_0}\right)^2 \left(1 - \frac{n_0}{n_s} \Psi^2 + \left(-\frac{n_{0\text{w}}}{6n_s} + \frac{1}{10}\right) \left(\frac{p_0}{e_0}\right)^2 \Psi'^2\right)\right).$$

(57)

In the limit of very small Ψ and very small $p_0|\Psi'|/e_0$, Eq. (57) transforms into the well-known expression

$$\varepsilon_{\text{eff}}(x) = 1 + \frac{n_{0\text{w}} p_0^2}{3\varepsilon_0 kT}.$$

(58)

Hereafter, Eqs. (54)–(57) are used to calculate the spatial profile of permittivity of the medium.

Figure 5 shows the spatial variation of permittivity, calculated according to Eq. (57). The dipole moment of a single water (Langevin) dipole was chosen to be 5 Debyes (D) in order to reach the permittivity of pure water 78.5 far away from the charged membrane surface. The bulk water dipole concentration ($n_{0\text{w}}/N_{\text{A}}$) was chosen 55 mol/l, where N_{A} is Avogadro number.

Figure 6 shows the number densities of counterions ($n+$) and water (Langevin) dipoles (n_{w}) as functions of the distance from the charged membrane surface. The results are given for two different bulk concentrations of the involved ions. The number density of counterions decreases
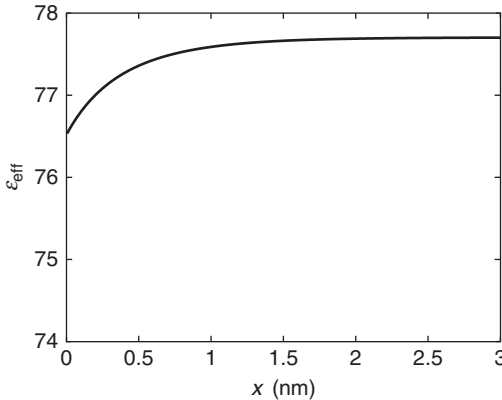

Figure 5 Calculated permittivity close to charged bilayer membrane surface. The dipole moment of water dipoles $p_0 = 5D$, the bulk concentration of water dipoles $n_{0w}/N_{\text{A}} = 55$ mol/l, surface charge density $\sigma = -0.05$ As/m^2, the width of a single lattice site $a_s = 0.318$ nm, the bulk concentration of ions is $n_0/N_{\text{A}} = 0.1$ mol/l (adapted from [29]).
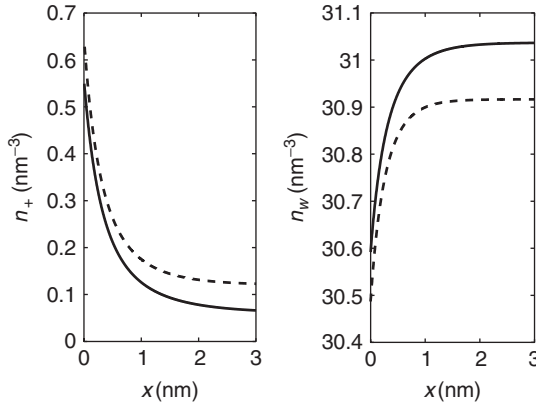
Figure 6 Number densities of counterions ($n+$) and Langevin dipoles (n_w) as functions of the distance from the charged bilayer membrane surface. The bulk concentration of ions: full line $n_0/N_A = 0.1$ mol/l and dashed line $n_0/N_A = 0.2$ mol/l. Model parameters: dipole moment of water $p_0 = 5D$, bulk concentration of Langevin dipoles $n_{0w}/N_A = 55$ mol/l, membrane surface charge density $\sigma = -0.05$ As/m^2. The width of a single lattice site $a_s = 0.318$ nm.

with increasing distance from the charged membrane surface. The number density of Langevin dipoles (i.e., water molecules) increases with increasing distance from the charged membrane surface and reaches a plateau value far away from the charged surface. The depletion of water molecules near the charged membrane surface also helps that water molecules can better organize their hydrogen bonding network without ions; therefore it is favorable that ions which disrupt the water–hydrogen-bonded water network are moved from the bulk towards the charged membrane surface [13]. Near the charged membrane surface, the number density of coions is negligible when compared with the number density of counterions. The thickness of EDL increases with decreasing bulk concentration of ions.

The average cosine of the angle ω between the dipole vector of Langevin dipoles and the axis perpendicular to the metal surface is given by equation

$$\langle \cos\omega \rangle_{\mathrm{B}} = \frac{\left\langle \cos\omega e^{-p_0|\Psi'|\cos\omega/e_0} \right\rangle_\omega}{\left\langle e^{-p_0|\Psi'|\cos\omega/e_0} \right\rangle_\omega} = -\mathcal{L}(p_0|\Psi'|/e_0), \qquad (59)$$

where $\langle \dots \rangle_{\mathrm{B}}$ means the averaging over all angles ω weighted by Boltzmann factor (see Eq. (7)). The average cosine $\langle \cos\omega \rangle_{\mathrm{B}}$ as a function of the distance from the charged surface for different surface charge densities and bulk counterion number densities, is shown in Fig. 7. Figure 7 shows that the Langevin
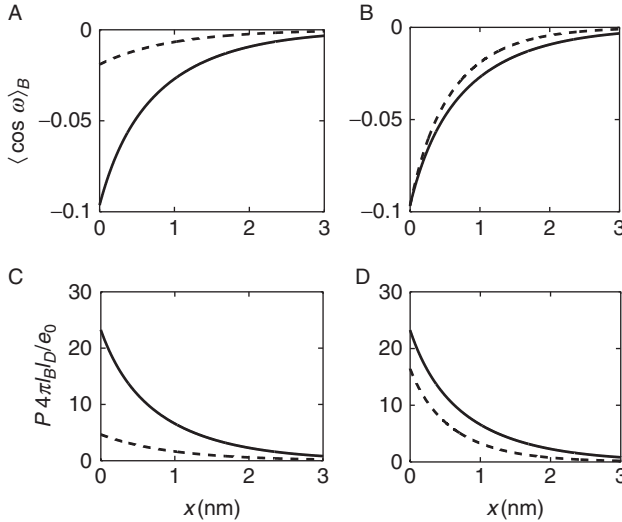
Figure 7   Average cosine of angle of Langevin dipoles (A, B) and polarization (C, D) as functions of the distance from the charged membrane surface. (A) and (C) $n_0/N_A = 0.1$ mol/l, surface charge densities $\sigma = -0.05$ As/m^2 (full line) and $\sigma = -0.01$ As/m^2 (dashed line). Figures B and D: $\sigma = -0.05$ As/m^2, bulk salt concentrations $n_0/N_A = 0.1$ mol/l (full line), $n_0/N_A = 0.2$ mol/l (dashed line). The width of a single lattice site $a_s = 0.318$ nm (adapted from [29])).

dipole moment vectors at the charged membrane surface are predominantly oriented towards the surface. Far away from the charged membrane surface all orientations of dipoles are equally probable; therefore $\langle \cos \omega \rangle_B = 0$ (see Fig. 7). The absolute value of $\langle \cos \omega \rangle_B$ increases with increasing σ corresponding to stronger orientation of Langevin dipoles. Due to stronger screening, the absolute value of $\langle \cos \omega \rangle_B$ is decreasing with increasing n_0.

5. PHENOMENOLOGICAL MODEL OF SPATIAL VARIATION OF PERMITTIVITY AND THE MEMBRANE SURFACE POTENTIAL

We have shown that close to the charged membrane surface the permittivity profile (Fig. 5) is mainly determined by the depletion of water dipoles due to accumulated counterions (Fig. 6) and by orientational ordering of water dipoles (Fig. 7). In this section, the space dependency of permittivity, previously determined only at small Ψ and small $|\Psi'|$ (i.e., at small potential, see Fig. 5), is assumed to be more pronounced. In the phenomenological model presented in this section, we assume a strong

space variation of the permittivity, which corresponds to large magnitude of the surface charge density (see also Fig. 4). Based on the results given in Figs. 4 and 5, the space dependency of the effective permittivity is approximately described by a simple step function. Similarly, as in Section 4, the volume charge density in an electrolyte solution is written as

$$\rho(x) = \sum_i v_i e_0 n_i(x),$$ (60)

where for monovalent ions, the valence v_i is

$$v_+ = 1, \quad v_- = -1.$$ (61)

The ions are assumed to be distributed according to the Boltzmann distribution [5,6]:

$$n_i(x) = n_0 \exp(-v_i e_0 \phi(x)/kT).$$ (62)

According to the schematic on Fig. 8, the permittivity of the electrolyte solution is approximately described by a step function (see Fig. 9):

$$\varepsilon(x) = \begin{cases} \varepsilon_2, & x < a, \\ \varepsilon_1, & x \geq a. \end{cases}$$ (63)

By inserting Eqs. (60)–(63) into Poisson's equation, we obtain the PB differential equation (see also [5,6]) corresponding to two different regions:

$$\frac{d^2\phi}{dx^2} = \begin{cases} \dfrac{2e_0 n_0}{\varepsilon_2 \varepsilon_0} \sinh(e_0 \phi(x)/kT), & 0 \leq x < a, \\ \dfrac{2e_0 n_0}{\varepsilon_1 \varepsilon_0} \sinh(e_0 \phi(x)/kT), & a \leq x < \infty. \end{cases}$$ (64)

The boundary condition at $x = 0$ is consistent with the condition of electroneutrality of the whole system:

$$\frac{d\phi}{dx}\Big|_0 = -\frac{\sigma_{\mathrm{eff}}}{\varepsilon_2 \varepsilon_0}.$$ (65)

The validity of Gauss law at $x = a$, respectively, is fulfilled by the following equation:

$$\varepsilon_2 \frac{d\phi}{dx}\Big|_{a_-} = \varepsilon_1 \frac{d\phi}{dx}\Big|_{a_+}.$$ (66)
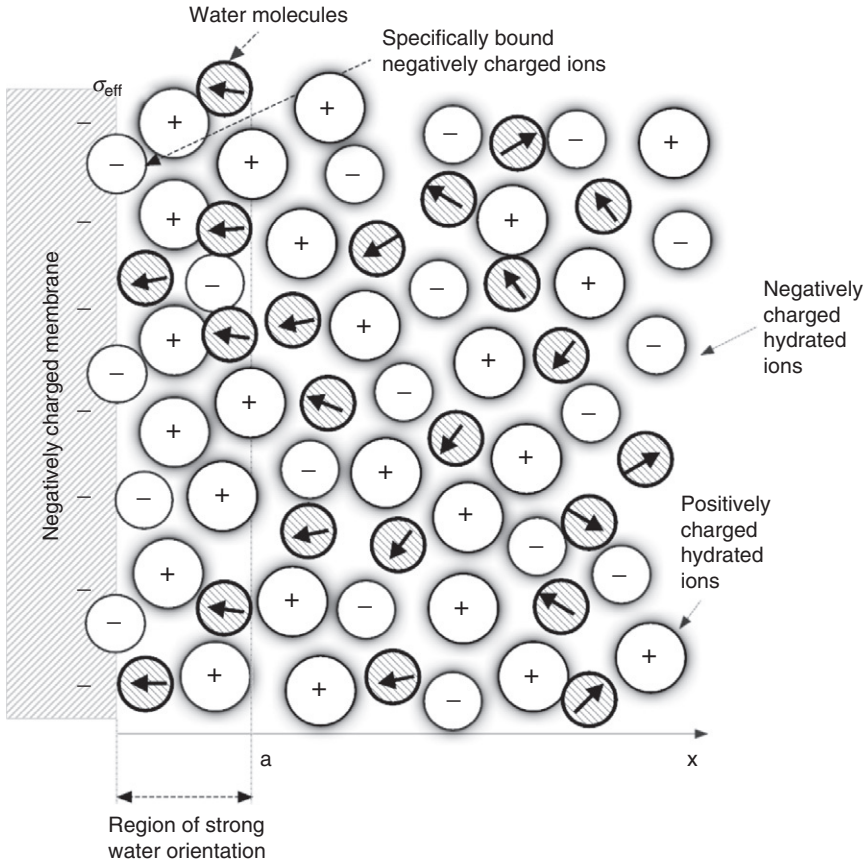
Figure 8   Schematic figure of electrical double layer near the negatively charged planar membrane surface. Here *a* is the region of strong water orientation, where the permittivity substantially differs from the bulk value. The surface charge density σ_{eff} incorporates the negatively charged surface as well as the specifically bound negatively charged ions.

Due to the screening effect of the negatively charged membrane surface caused by the accumulated cations, we assume that far away from the charged metal surface the strength of electric field tends to zero:

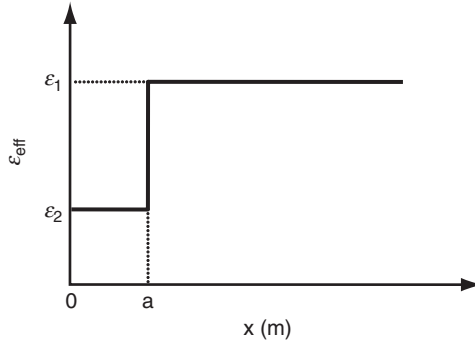$$\frac{\mathrm{d}\phi}{\mathrm{d}x}\bigg|_{\infty} = 0. \tag{67}$$

Figure 9 Model of the space variation of permittivity in electrolyte solution near the charged membrane surface assuming a step function. Here a is the region of strong orientation of water molecules. The value of $\varepsilon_1 \cong 78.5$ corresponds to the bulk value, while ε_2 is in the range of $10 - 60$.

Equations (64) are rewritten in dimensionless form:

$$\frac{d^2\Psi}{d\xi^2} = \begin{cases} 2K\sinh(\Psi), & 0 \leq \xi < 1, \\ 2L\sinh(\Psi), & 1 \leq \xi < \infty, \end{cases} \tag{68}$$

where the reduced potential $\Psi(x) = e_0\,\phi(x)/kT$ is defined as previously (Eq. (3)) and the reduced length is

$$\xi = \frac{x}{a}, \tag{69}$$

while the constants are defined as

$$K = \frac{e_0^2 n_0 a^2}{\varepsilon_2 \varepsilon_0 kT}, \quad L = \frac{e_0^2 n_0 a^2}{\varepsilon_1 \varepsilon_0 kT}. \tag{70}$$

Respectively, the boundary conditions for the dimensionless case are

$$\left.\frac{d\Psi}{d\xi}\right|_0 = -\frac{\sigma_{\text{eff}} a e_0}{\varepsilon_2 \varepsilon_0 kT}, \tag{71}$$

$$\varepsilon_2 \left.\frac{d\Psi}{d\xi}\right|_{-1} = \varepsilon_1 \left.\frac{d\Psi}{d\xi}\right|_{1_+}, \tag{72}$$

$$\left.\frac{d\Psi}{d\xi}\right|_\infty = 0. \tag{73}$$

In addition to Eqs. (71)–(73), we consider also the continuity of the electric potential at $x = a$. Hereafter, we have a closer look at the derivation of the solutions of Eq. (68). Equation (68) is multiplied at both sides by $2\frac{d\Psi}{d\xi}$

$$\frac{d}{d\xi}\left(\frac{d\Psi}{d\xi}\right)^2 = 2\frac{d\Psi}{d\xi}\frac{d^2\Psi}{d\xi^2}. \tag{74}$$

By taking into account the continuity of the electric potential at $x = a$ and after integration we get

$$\int d\left(\frac{d\Psi}{d\xi}\right)^2 = \int 4K\sinh(\Psi)d\Psi, \quad 0 \le \xi < 1, \tag{75}$$

$$\int d\left(\frac{d\Psi}{d\xi}\right)^2 = \int 4L\sinh(\Psi)d\Psi, \quad 1 \le \xi < \infty. \tag{76}$$

These transformations lead to

$$\frac{d\Psi}{d\xi} = \left(\begin{array}{ll} \sqrt{C + 4K\cosh\Psi}, & 0 \le \xi < 1, \\ -\sqrt{8L}\sinh(\Psi/2), & 1 \le \xi < \infty, \end{array} \right. \tag{77}$$

where

$$C = \left(\frac{\sigma_{\text{eff}}e_0 a}{\varepsilon_2\varepsilon_0 kT}\right)^2 - 4K\cosh\Psi(0). \tag{78}$$

Applying the boundary condition (72) and taking into account Eqs. (77) and (78) yields

$$\varepsilon_2\left(\left(\frac{\sigma_{\text{eff}}e_0 a}{\varepsilon_2\varepsilon_0 kT}\right)^2 - 4K[\cosh\Psi(0) - \cosh\Psi(1)]\right)^{1/2} = -\varepsilon_1\sqrt{8L}\sinh(\Psi(1)/2). \tag{79}$$

Now we proceed with the solution of Eq. (77) in the interval $1 \le \xi < \infty$. We first rearrange the corresponding expression from Eq. (77) as

$$d\xi = \frac{-d\Psi}{\sqrt{8L}\sinh\frac{\Psi}{2}}. \tag{80}$$

Integrating Eq. (80)

$$\int_1^\xi d\xi = -\frac{1}{\sqrt{8L}}\int_{\Psi(1)}^{\Psi(\xi)} \frac{d\Psi}{\sinh\frac{\Psi}{2}} \tag{81}$$

gives the following solution:

$$\xi - 1 = \frac{1}{\sqrt{2L}} \ln\left(\frac{\tanh\frac{\Psi(1)}{4}}{\tanh\frac{\Psi}{4}}\right). \tag{82}$$

By transforming Eq. (82), we get the final result for Ψ in the form:

$$\Psi = 4\tanh^{-1}\left(\tanh\frac{\Psi(1)}{4}\exp\left(\sqrt{2L}(1-\xi)\right)\right), \quad 1 \le \xi < \infty. \tag{83}$$

It follows from Eq. (83)

$$\Psi(0) = 4\tanh^{-1}\left(\tanh\frac{\Psi(1)}{4}\exp\left(\sqrt{2L}\right)\right). \tag{84}$$

Eqs. (79) and (84) are two equations for two unknown quantities $\Psi(0)$ and $\Psi(1)$. Eqs. (79) and (84) can be solved numerically to determine the surface electric potential $\phi(0) = \Psi(0)kT/e_0$. Figure 10 shows the electric membrane surface potential $\phi(0)$ as a function of the relative permittivity in the highly ordered region of water molecules (ε_2) (see Fig. 9). It becomes clear that the absolute value of the electric potential increases with the decrease of the permittivity ε_2.

6. Conclusions

Most of the models describing the EDL assume that the permittivity in the whole system is constant [5–7]. The classical PB theory does not consider the solvent structure. Therefore the PB theory has been upgraded by hydration models, where the interplay between solvent polarization and diffuse double layer takes place [10,12,18,22,30,31]. The study of the orientational ordering of dipoles at the charged surface has shown that dipoles predominantly orient perpendicularly to the charged surface [12]. Langevin dipoles were introduced into the PB theory to study the polarization of the solvent and the space dependency of the permittivity close to the charged membrane surface [12,18,29]. The spatial decay of the solvent polarization for increasing distance from the charged membrane surface was predicted [12].

The presence of ions changes the permittivity of the electrolyte solution [12,13,18]. Recently, the modified PB equation, taking into account the finite volumes of ions, was solved numerically in the limit of small electric
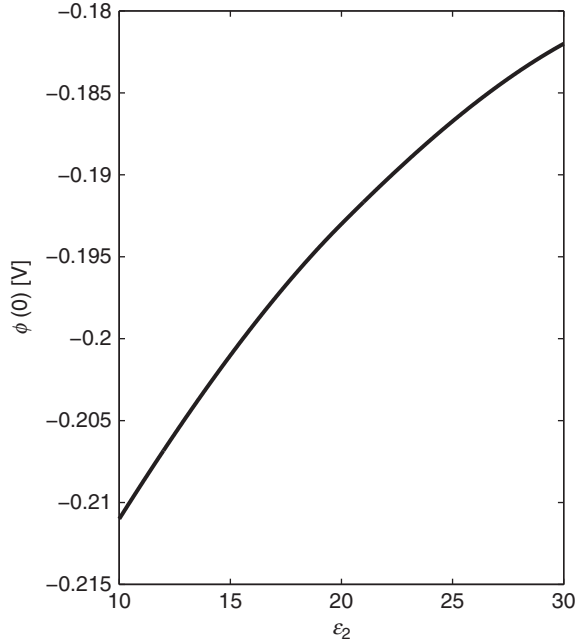
Figure 10 Membrane surface potential $\phi(0)$ as a function of the permittivity in the ordered region of water molecules (ε_2) (see Figs. 8 and 9) for surface charge density: $\sigma_{\text{eff}} = -0.4$ As/m^2, thickness of the ordered water layer $a = 0.2$ nm, bulk salt concentration $n_0/N_A = 0.1$ mol/1, permittivity of the region $x > a$: $\varepsilon_1 = 78.5$.

potential and small electric field, where the dipolar nature of water molecules was introduced by Langevin dipoles [12]. The dependence of the permittivity as a function of the electric potential was given analytically (Eq. (48)), while the spatial dependency of the effective permittivity was calculated numerically in the limit of small electric potential and small electric field (Fig. 5) [12].

In this chapter, the orientational ordering of water dipoles and the excluded volume effect were explicitly taken into account in the described modified PB model in order to estimate the space variation of the permittivity in the vicinity of a charged membrane surface in contact with an electrolyte solution [12,29]. In the limit of small electric potential and small electric field, it was shown that the dipole moment vectors of water molecules at the charged membrane surface are predominantly oriented towards the negatively charged surface, while all orientations of water dipoles far away from the charged membrane surface are equally probable (Fig. 7). It was shown that the permittivity profile close to the charged membrane surface may be significantly influenced by the depletion of water molecules due to accumulation of counterions. Due to strong accumulation

of counterions near the charged membrane surface at higher surface charge densities (Figs. 3 and 6), it can be anticipated that the permittivity near the charged membrane surface may be significantly decreased at high magnitude of the surface charge density of the membrane. Therefore, a simple phenomenological model assuming a step function for the space variation of the permittivity was introduced to study the influence of the space variation of the permittivity on the membrane surface potential at higher magnitudes of surface charge density. Both models (phenomenological and statistical mechanical) complement each other, since the phenomenological model is not so restricted to small magnitudes of the surface charge, making it a good supplement to the statistical mechanical approach. Although for larger surface charge density (as for example in Figs. 3, 4 and 10) the so-called electrostatic coupling parameter [22] is well above 1, we expect that the conclusions based on presented results are qualitatively correct and may help to better understand the combined role of water ordering and finite size of ions in the properties of the electric double layer.

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