Metal surface in contact with electrolyte solution - influence of spatial variation of dielectric constant

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Abstract. The interaction between a charged metal surface and an electrolyte solution causes the formation of an electrical double layer, which has been a subject of an extensive study for more than a century. The present paper provides a statistical mechanical description of orientational ordering of water molecules and excluded volume effect near charged metal surface. The results of statistical mechanical model are then included in generalized phenomenological Stern model by taking into account the spatial variation of the dielectric constant near the charged surface and the finite size of counterions.

Key words: orientational ordering of water, generalized Stern model, excluded volume effect, dielectric constant

Naelektrena kovinska površina v stiku z elektrolitsko raztopino - vpliv krajevne odvisnoti dielektrične konstante

Povzetek. Električna dvojna plast nastane kot posledica interakcije med naelektreno kovinsko površino in elektrolitsko raztopino. Pričujoči članek podaja statistično mehanski opis vpliva orientacije dipolov vodnih molekulin končnih velikosti molekul na električno dvojno plast. Napovedi statistično-mehanskega modela so v nadaljevanju na fenomenološki način vključene v posplošen Sternov model električne dvojne plasti z upoštevanjem prostorske odvisnosti dielektrične konstatne v bližini naelektrene kovinske površine.

Ključne besede: orientacijsko urejanje vodnih dipolov, Sternov model, končni volumni molekul, dielekrična konstanta

1 Introduction

The contact between a negatively charged metal surface and electrolyte solution results into rearrangement of the ion distribution and water reorientation near the metal surface and the formation of the so-called electrical double layer (EDL). Most of the models describing this phenomenon assume that the dielectric constant in the whole system is constant. But actually close to the charged surface the water dipoles cannot move as freely as away from it and show a distinct preferential orientation in direction of the normal to the charged surface [1, 2, 3]. Also, due to accumulation of counterions near the charged metal surface [4] the water molecules are partially depleted from this region. All these result in spatial variation of dielectric constant near the charged surface [1, 33, 2]. Therefore, here we present a simple model of EDL, which takes into account the spatial variation of the dielectric constant. The orientational ordering of water molecules and the excluded volume effect near the charged metal surface are described within a statistical mechanical approach. The results of the statistical mechanical model are then included in a generalized Stern model via space dependency of the dielectric constant near the charged surface and the distance of closest approach for counterions. A possible application of the predicted results is also described.

2 Theory

2.1 Statistical mechanical description of excluded volume effect and orientation of water molecules near a charged metal surface in contact with an electrolyte solution

We consider a charged metal surface in contact with a solution of ions and the Langevin dipoles of a finite size. The metal surface is charged with surface charge density σ_{eff}. The lattice with an adjustable lattice site is introduced in order to describe the system of the Langevin water dipoles and salt ions. All lattice sites are occupied by ions or dipoles. For the sake of simplicity we assume that the volume of each ion is equal to the volume of a water molecule. Free energy of system F, measured in units of thermal energy kT, can be written as [1]

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

where the first term corresponds to the electrostatic field energy. Here

$$
\Psi(x) = e_0 \phi(x)/kT \ , \qquad (2)
$$

is the reduced potential, where e_0 is the elementary charge and $\phi(x)$ electrostatic potential. The Bjerrum length is equal to $l_B = e_0^2/4\pi\epsilon_0 kT$, where ϵ_0 the permittivity of the free space. The second line accounts for 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, while n_0 is the bulk number density of positively and negatively charged ions, where we assume $\phi(x \to \infty) = 0$. The third line accounts for the orientational and translational entropy contribution of water (Langevin) dipoles to the free energy, where n_{0w} is a bulk number density of dipoles. The dipole distribution function is given by

$$
n(\mathbf{r}, \omega) = n_d(\mathbf{r}) P(\mathbf{r}, \omega) \ , \qquad (3)
$$

where $n_d(\mathbf{r})$ is the number density of water dipoles and $P(\mathbf{r}, \omega)$ is probability that dipoles located at $\mathbf{r}$ are oriented for the angle ω with respect to the normal to the charged metal surface. At any position $\mathbf{r}$ we require the normalization condition $\left\langle P(\mathbf{r}, \omega) \right\rangle = 1$ to be fulfilled, where the averaging over all angles ω is defined as:

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

The last line in Eq.(1) is the constraint due to finite size of particles, n_s being the number density of lattice sites: $n_s = 1/a_s^3$, where a_s is the width of the single lattice site. Averaging over all angles ω in Eq.(3) gives the number density of water dipoles $n_w(\mathbf{r})$

$$
\begin{aligned}
\left\langle n(\mathbf{r}, \omega) \right\rangle &= \left\langle n_d(\mathbf{r}) P(\mathbf{r}, \omega) \right\rangle = \\
&= n_d(\mathbf{r}) \left\langle P(\mathbf{r}, \omega) \right\rangle = n_d(\mathbf{r}) \ . \qquad (5)
\end{aligned}
$$

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

$$
\varrho(\mathbf{r}) = e_0 \left(n_+(\mathbf{r}) - n_-(\mathbf{r}) \right) - \nabla \cdot \mathbf{P} \ , \qquad (6)
$$

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

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 results of the variational procedure are

$$
\begin{aligned}
n_+(\mathbf{r}) &= n_0\, e^{-\Psi + \lambda} \ , & (7) \\
n_-(\mathbf{r}) &= n_0\, e^{\Psi + \lambda} \ , & (8) \\
n(\mathbf{r}, \omega) &= n_{0w}\, e^{-\mathbf{p} \cdot \nabla \Psi / e_0 + \lambda} \ . & (9)
\end{aligned}
$$

Inserting Eqs.(7)-(9) into the constraint (see the last line of Eq.(1)):

$$
n_s = n_+(\mathbf{r}) + n_-(\mathbf{r}) + \left\langle n(\mathbf{r}, \omega) \right\rangle \ , \qquad (10)
$$

we can calculate the parameter λ:

$$
e^\lambda = \frac{n_s}{2 n_0 \cosh \Psi + \frac{e_0 n_{0w}}{p_0 |\nabla \Psi|} \sinh \frac{p_0 |\nabla \Psi|}{e_0}} \ , \qquad (11)
$$

where we take into account:

$$
\begin{aligned}
\left\langle e^{-\mathbf{p} \cdot \nabla \Psi / e_0} \right\rangle &= \qquad (12) \\
&= \frac{\int e^{-\mathbf{p} \cdot \nabla \Psi / e_0} d\Omega}{4\pi} = \\
&= \frac{2\pi \int\limits_{-1}^{1} d(\cos \omega) e^{-p_0 |\nabla \Psi| \cos \omega / e_0}}{4\pi} = \\
&= \frac{e_0}{p_0 |\nabla \Psi|} \sinh \frac{p_0 |\nabla \Psi|}{e_0} \ ,
\end{aligned}
$$

where p_0 is the size of the water dipole moments. In the above derivation we assume the azimuthal symmetry, where ω is the polar angle between the dipole moment and the axis perpendicular to the charged metal surface. Inserting the Boltzmann distribution functions Eqs.(7)-(9) into Eq.(6), we get the following expression for the volume charge density in the electrolyte solution:

$$
\begin{aligned}
\varrho &= -2\, e_0\, n_0\, e^\lambda \sinh \Psi - \qquad (13) \\
&- n_{0w}\, \nabla \cdot \left(e^\lambda \left\langle \mathbf{p}\, e^{-\mathbf{p} \cdot \nabla \Psi / e_0} \right\rangle \right) \ ,
\end{aligned}
$$

where:

$$\frac{\left\langle \mathbf{p}\, e^{-\mathbf{p}\cdot\nabla\Psi/e_0} \right\rangle}{\left\langle e^{-\mathbf{p}\cdot\nabla\Psi/e_0} \right\rangle} =$$

$$= \frac{\int \mathbf{p}\, e^{-\mathbf{p}\cdot\nabla\Psi/e_0}\, d\Omega}{\int e^{-\mathbf{p}\cdot\nabla\Psi/e_0}\, d\Omega} =$$

$$= \frac{p_0 \frac{\nabla\Psi}{|\nabla\Psi|} \int\limits_{-1}^{1} du\, u\, e^{-p_0|\nabla\Psi|u/e_0}}{\int\limits_{-1}^{1} du\, e^{-p_0|\nabla\Psi|u/e_0}} =$$

$$= -p_0 \frac{\nabla\Psi}{|\nabla\Psi|}\left(\coth\left(p_0|\nabla\Psi|/e_0\right) - \frac{e_0}{p_0|\nabla\Psi|}\right) . \quad (14)$$

In the last step of the above derivation we assume the azimuthal symmetry and defined $u = \cos\omega$. Using Eq.(12) it follows from Eq.(14):

$$\left\langle \mathbf{p}\, e^{-\mathbf{p}\cdot\nabla\Psi/e_0} \right\rangle = -p_0 \frac{\nabla\Psi}{|\nabla\Psi|}\cdot\mathcal{F}\left(\frac{p_0|\nabla\Psi|}{e_0}\right) . \quad (15)$$

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

$$\mathcal{F}(u) = \mathcal{L}(u)\,\frac{\sinh u}{u} , \quad (16)$$

where $\mathcal{L}(u) = (\coth(u) - 1/u)$ is the Langevin function. 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 (13) into the Poisson equation $\Delta\Psi = -4\pi\,l_B\varrho/e_0$ we get [1]:

$$\Delta\Psi = 8\pi l_B\, n_0\, n_s\,\frac{\sinh\Psi}{\mathcal{H}} - \quad (17)$$

$$- 4\pi l_B\, n_{0w}\, n_s\,\frac{p_0}{e_0}\,\nabla\cdot\left[\frac{\nabla\Psi}{|\nabla\Psi|}\frac{\mathcal{F}(p_0|\nabla\Psi|/e_0)}{\mathcal{H}}\right] ,$$

where function $\mathcal{H}$, related to the finite particle size, is given by

$$\mathcal{H} = 2n_0\,\cosh\Psi + \frac{e_0\,n_{0w}}{p_0|\nabla\Psi|}\,\sinh\frac{p_0|\nabla\Psi|}{e_0} . \quad (18)$$

The differential equation (17) has two boundary conditions. The first boundary condition is obtained by integrating the differential equation (17) [1]:

$$\nabla\Psi|_S = -4\pi l_B\,\frac{\sigma}{e_0}\,\frac{\nabla\Psi}{|\nabla\Psi|} - \quad (19)$$

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

where $\frac{\nabla\Psi}{|\nabla\Psi|}$ is the vector normal to the surface S. 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 charged metal surface being in contact with the electrolyte solution, the differential equation (Eq.(17)) reduces to [1]:

$$\Psi'' = 4\pi l_B\, n_s\left(2n_0\,\frac{\sinh\Psi}{\mathcal{H}} - \right.$$

$$\left. - n_{0w}\,\frac{p_0}{e_0}\,\frac{d}{dx}\left[\frac{\mathcal{F}(p_0|\Psi'|/e_0)}{\mathcal{H}}\right]\right) , \quad (20)$$

with boundary conditions

$$\Psi'(x = 0) = 4\pi\frac{l_B}{e_0}\left[-\sigma_{eff} - \right.$$

$$\left. - n_s\, n_{0w}\, p_0\,\frac{\mathcal{F}(p_0|\Psi'|/e_0)}{\mathcal{H}}\right|_{x=0}\right] \quad (21)$$

and

$$\Psi'(x \to \infty) = 0 . \quad (22)$$

The polarization (where x-axis is perpendicular to the charged surface) is proportional to the electric field strength

$$\mathbf{P} = \epsilon_0(\epsilon_{eff} - 1)\mathbf{E} , \quad (23)$$

where ϵ_{eff} is the dielectric constant. From Eq. (23) the dielectric constant can be calculated

$$\epsilon_{eff} = 1 + \frac{\mathbf{P}}{\epsilon_0\mathbf{E}} . \quad (24)$$

On the other hand, the polarization can be defined also via the expression for the volume density of dipole moments $\mathbf{P} = \left\langle \mathbf{p}\, n(\mathbf{r},\omega)\right\rangle$, in which we insert Eqs. (11) and (15) to get:

$$\mathbf{P} = -p_0\, n_{0w}\, n_s\,\frac{\nabla\Psi}{|\nabla\Psi|}\cdot\frac{\mathcal{F}\left(\frac{p_0|\nabla\Psi|}{e_0}\right)}{\mathcal{H}} . \quad (25)$$

Inserting Eq.(25) into Eq.(24) and taking into account the definition $\mathbf{E} = -\nabla\phi$, we can calculate the dielectric constant:

$$\epsilon_{eff} = 1 + n_{0w}\, n_s\, 4\pi l_B\,\frac{p_0}{e_0}\cdot\frac{\mathcal{F}\left(\frac{p_0|\nabla\Psi|}{e_0}\right)}{|\nabla\Psi|\cdot\mathcal{H}} . \quad (26)$$

In the case of charged planar metal surface Eq.(26) reads [1]:

$$\epsilon_{eff}(x) = 1 + n_{0w}\, n_s\, 4\pi l_B\,\frac{p_0}{e_0}\cdot\frac{\mathcal{F}\left(\frac{p_0|\Psi'|}{e_0}\right)}{|\Psi'|\cdot\mathcal{H}} \quad (27)$$

In the approximation of small electrostatic energy and small energy of dipoles in the electric field compared to thermal energy, i.e. small Ψ and small $p_0|\Psi'|/e_0$, Eq.(20) can be expanded in the Taylor series up to the third order to get [1]:

$$\Psi'' = \frac{2\Psi + 2(-\frac{n_0}{n_s} + \frac{1}{6})\Psi^3 + \frac{n_{0w}}{3n_s}\left(\frac{p_0}{e_0}\right)^2\Psi\Psi'^2}{A + \frac{n_{0w}}{n_0}\left(-\frac{n_{0w}}{6n_s} + \frac{1}{10}\right)\left(\frac{p_0}{e_0}\right)^4\Psi'^2} \quad (28)$$

where

$$A = \frac{1}{4\pi l_B n_0} + \frac{n_{0w}}{3n_0}(\frac{p_0}{e_0})^2 - \frac{n_{0w}}{3n_s}(\frac{p_0}{e_0})^2 \Psi^2 \ . \qquad (29)$$

The corresponding boundary condition Eq.(21) expanded up to the third order is:

$$\Psi'(0) = \frac{-\frac{\sigma_{eff}}{e_0}}{\left[\frac{1}{4\pi l_B} + \frac{n_{0w}}{3}\left(\frac{p_0}{e_0}\right)^2 \left(1 - \frac{n_0}{n_s}[\Psi(0)]^2 + B\right)\right]}, \qquad (30)$$

where

$$B = \left(\frac{p_0}{e_0}\right)^2 \left(-\frac{n_{0w}}{6n_s} + \frac{1}{10}\right)[\Psi'(0)]^2 \ , \qquad (31)$$

while the dielectric constant can be expressed as [1]:

$$\epsilon_{eff}(x) = \left(1 + \frac{4\pi l_B}{3}n_{0w}\left(\frac{p_0}{e_0}\right)^2 B1\right) \ , \qquad (32)$$

where

$$B1 = 1 - \frac{n_0}{n_s}\Psi^2 + \left(-\frac{n_{0w}}{6n_s} + \frac{1}{10}\right)\left(\frac{p_0}{e_0}\right)^2 \Psi'^2 \ . \qquad (33)$$

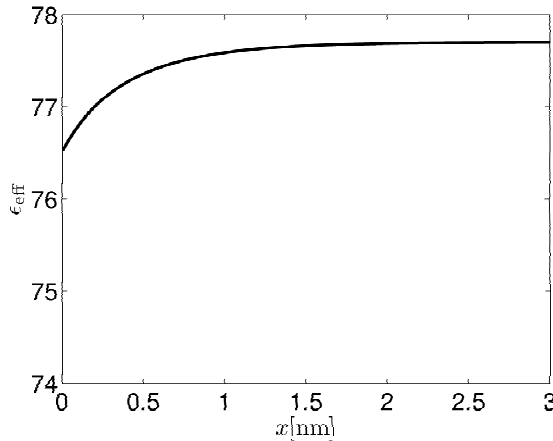Hereafter Eqs.(28)-(32) were used to calculate the spatial profile of the dielectric constant.

Figure 1.   Dielectric constant close to the charged metal surface.   Dipole moment of water $p_0 = 5D$, bulk concentration of water $n_{0w}/N_A = 55\,\mathrm{mol/l}$, surface charge density $\sigma_{eff} = 0.05\,\mathrm{As/m^2}$. The width of a single lattice site $a_s = 0.318$ nm.   Bulk concentration of salt is $n_0/N_A = 0.1\,\mathrm{mol/l}$.

Slika 1.   Krajevna odvisnost dielektrične konstante v bližini naelektrene kovinske plošče. Modelini parametri so: dipolni moment vodnih molekul $p_0 = 5D$, koncetracija vodnih molekul daleč stran od plošče $n_{0w}/N_A = 55\,\mathrm{mol/l}$, površinska gostota naboja na kovinski plošči $\sigma_{eff} = 0.05\,\mathrm{As/m^2}$, širina mrežnega mesta $a = 0.318$ nm. Koncetracija soli daleč stran od plošče $n_0/N_A = 0.1\,\mathrm{mol/l}$ (polna črta). Širina mrežnega mesta $a_s = 0.318$ nm.

Fig.1 shows the spatial variation of dielectric constant, calculated according to Eq.(32). The dipole moment of a single water molecule was chosen to be 5 Debyes (D) in order to reach the dielectric constant of pure water 78.5 far away from the charged metal surface. The bulk water concentration (n_{0w}/N_A) was chosen 55 mol/l, where N_A is Avogadro number.
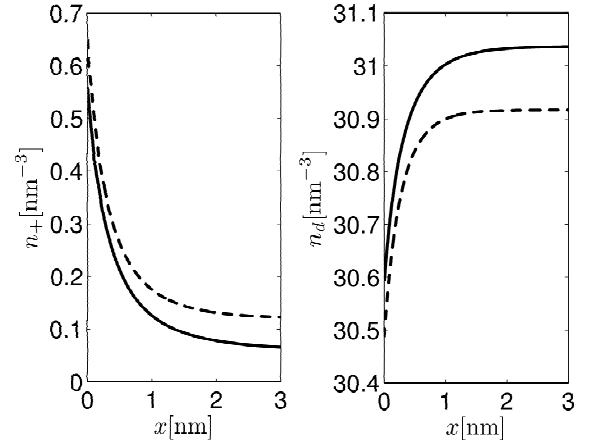

Figure 2.   Number densities of counterions (n_+) and water molecules (n_d) as a function of the distance from the charged metal surface.   Bulk concentration of salt: full line $n_0/N_A = 0.1\,\mathrm{mol/l}$ and dashed line $n_0/N_A = 0.2\,\mathrm{mol/l}$. Model parameters: dipole moment of water $p_0 = 5D$, bulk concentration of water $n_{0w}/N_A = 55\,\mathrm{mol/l}$, metal surface charge density $\sigma_{eff} = 0.05\,\mathrm{As/m^2}$. The width of a single lattice site $a_s = 0.318$ nm.

Slika 2.   Številska gostota protionov (n_+) in vodnih molekul (n_d) kot funkcija razdalje od naelektrene kovinske plošče. Koncetracija soli daleč stran od plošče : $n_0/N_A = 0.1\,\mathrm{mol/l}$ (polna črta) in $n_0/N_A = 0.2\,\mathrm{mol/l}$ (prekinjena črta). Modelni parametri so: električni dipolni moment vodnih molekul $p_0 = 5D$, koncentracija vodnih molekul daleč stran od plošče $n_{0w}/N_A = 55\,\mathrm{mol/l}$, površinska gostota naboja $\sigma_{eff} = 0.4\,\mathrm{As/m^2}$. Širina mrežnega mesta $a_s = 0.318$ nm.

Fig. 2 shows the number densities of counterions and water molecules as a function of the distance from the charged metal surface. The results are given for three different bulk concentrations of salt. The number density of counterions decreases with increasing distance from the charged metal surface. The number density of water molecules increases with the increasing distance from the charged metal surface and reaches a plateau value far away from the charged surface. Near the charged surface, the number density of coions is negligible compared to the number density of counterions. The thickness of EDL increases with the decreasing bulk concentration of salt.

The average cosine of the angle ω between the dipole vector of the Langevin dipoles and the axis perpendicular

to the metal surface is given by equation:

$$\left\langle \cos\omega \right\rangle_B = \frac{\left\langle \cos\omega\, e^{-p_0|\Psi'|\cos\omega/e_0} \right\rangle}{\left\langle e^{-p_0|\Psi'|\cos\omega/e_0} \right\rangle}$$

$$= -\mathcal{L}(p_0|\Psi'|/e_0), \qquad (34)$$

where $\left\langle ... \right\rangle_B$ means the averaging over all angles ω weighted by the Boltzmann factor. The average cosine $\left\langle \cos\omega \right\rangle_B$, as a function of the distance from the charged surface for different surface charge densities and bulk counterion number densities, is shown in Fig. 3. Fig. 3 shows that the dipole moment vectors at the charged metal surface are predominantly oriented towards the surface. Far away from the charged metal surface all orientations of dipoles are equally probable, therefore $< \cos\omega >_B = 0$ (see Fig. 3). The absolute value of $< \cos\omega >_B$ increases with increasing σ_{eff} corresponding to stronger orientation of water dipoles. Due to the stronger screening, the absolute value of $< \cos\omega >_B$ is decreasing with increasing n_0.
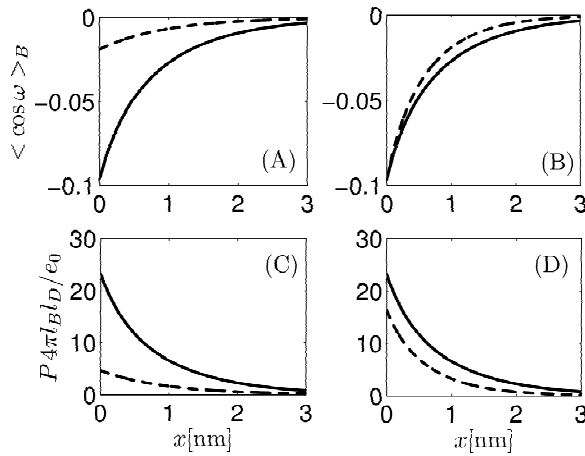

Figure 3. Average cosine of angle of the Langevin dipoles (A,B) and polarization (C,D) as s function of the distance from the charged metal surface. Figures A and C: $n_0/N_A = 0.1\,\text{mol/l}$, surface charge densities from bottom to top are $\sigma_{eff} = 0.05\,\text{As/m}^2$ and $\sigma_{eff} = 0.01\,\text{As/m}^2$. Figures B and D: $\sigma_{eff} = 0.05\,\text{As/m}^2$, bulk salt concentrations from bottom to top follows as $n_0/N_A = 0.1\,\text{mol/l}$, $n_0/N_A = 0.2\,\text{mol/l}$. The width of a single lattice site $a_s = 0.318$ nm (from [1]).
Slika 3. Krajevna odvisnost povprečnega cosinusa nagnjenosti dipolov vodnih molekul in polarizacije v bližini naelektrene kovinske plošče. Sliki A in C: $n_0/N_A = 0.1\,\text{mol/l}$, površinska gostota naboja na kovinski plošči od spodaj navzgor: $\sigma_{eff} = 0.05\,\text{As/m}^2$ in $0.01\,\text{As/m}^2$. Sliki B in D: $\sigma_{eff} = 0.05\,\text{As/m}^2$, Koncetracija soli daleč stran od plošče od spodaj navzgor $n_0/N_A = 0.1\,\text{mol/l}$ in $0.2\,\text{mol/l}$. Širina mrežnega mesta $a_s = 0.318$ nm (iz [1]).

2.2 Generalized Stern model. Influence of spatial variation of dielectric constant

The Stern Model [5] was the first attempt to incorporate steric effects by combining the Helmholtz [8] and Gouy-Chapman [6, 7] 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 at the surface. Gouy [6] and Chapman [7] 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 by it embedded in a dielectric continuum described by the Poisson-Boltzmann (PB) differential equation [9, 10, 4, 11]. In its simple version the Stern Model [5] consists of the inner Helmholtz plane (IHP), where the coions are bound near the surface due to specific adsorption, and the so-called outer Helmholtz plane (OHP) of hydrated counterions at the distance of the closest approach (b), and a diffuse double layer.

In our generalized Stern model the electrolyte solution consists of water molecules, monovalent cations and anions (Fig.4). As mentioned above that the dielectric constant profile close to the charged surface (Fig.1) is mainly determined by two opposing mechanisms: the depletion of water dipoles at the charged surface due to accumulated counterions (Fig.2) and the decrease in orientational ordering of the water dipoles as a function of the increasing distance from the charged membrane surface (Fig.3).

Also water molecules in the electrolyte solution can better organize their hydrogen bonding network without ions, therefore it is favourable that ions which disrupt the hydrogen bonded water network are moved from the bulk towards the charged membrane surface [2]. In accordance with the predictions given in Fig.2 in our generalized Stern model, the dielectric constant of the solution is approximately described by step function (Fig.5). In this way, the orientational ordering of water molecules near the charged metal surface (Figs.3 and 4) is taken into account phenomenologically.

In our generalized Stern model, the hard core interactions between the cations (counterions) and the negatively charged metal surface with effective surface charge density σ_{eff} is taken into account by means of the distance of the closest approach $b < a$ (see Fig.4). In Fig.4 a is defined as the region of strong water orientation, where the dielectric constant substantially differs from the bulk value. The parameter b defines the distance of the closest approach for counterions.

Similarly as in the Stern model [5], the charge density in the different layers can be written as (see Eq.(6))

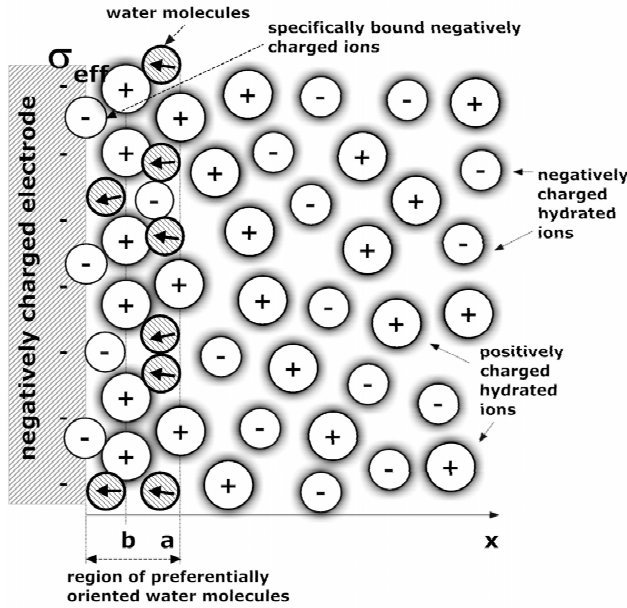$$\varrho(x) = \sum_i \nu_i\, e_0\, n_i(x) \ , \qquad (35)$$

Figure 4. Schematic figure of the generalized Stern model of electric double layer near the negatively charged metal surface, where b is the distance of the closest approach for the counterions and a is the region of strong water orientation. The effective surface charge density σ_{eff} accounts also for specifically bound (adsorbed) negatively charged ions (coions).
Slika 4. Shematični prikaz pospošenega Sternovega modela električne dvojne plasti v bližini naelektrene kovinske plošče, kjer je b razdalja priblžanja centrov kationov, a pa označuje področje močne ureditve vodnih dipolov. Efektivna površinska gostota naboja na kovinski plošči σ_{eff} zajema tudi prispevek specifično vezanih koionov.
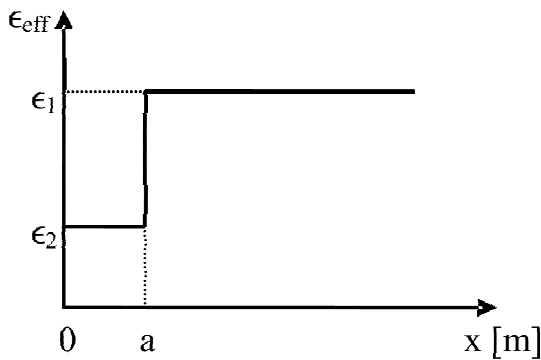

Figure 5. Model of the dielectric constant in electrolyte solution with respect to the distance from the charged surface. The value of $\epsilon_1 \cong 78.5$ corresponds to the bulk value, while ϵ_2, which is in the range of 10 - 60, and a are the model parameters of the generalized Stern model (see Fig.4).
Slika 5. Shematični prikaz krajevne odvisnosti dielektrične konstante elektrolitske raztopine v bližini naelektrene kovinske plošče. Vrednost $\epsilon_1 \cong 78.5$ ustreza vrednosti daleč stran od naelektrene kovinske plošče, ϵ_2 v območju blizu naelektrene kovinske plošče je parameter posplošenega Sternobega modela (glejte sliko 4).

where for monovalent ions, the valence ν_i is

$$\nu_+ = 1 \ , \quad \nu_- = -1 \ . \tag{36}$$

The ions are assumed to be distributed according to the Boltzmann distribution:

$$n_i(x) = n_i(\infty) \cdot \exp(-\nu_i \, e_0 \, \phi(x) \, /kT) \ . \tag{37}$$

According to the results given in Fig. 2 the dielectric constant of the solution is approximately described by the step function (see Fig.5):

$$\epsilon(x) = \begin{cases} \epsilon_2 \ , & x < a \\ \epsilon_1 \ , & x \geq a \end{cases} \tag{38}$$

By inserting Eqs.(35)-(38) into the Poisson equation, we obtain the Poisson-Botzmann (PB) differential equations (see also [9]) corresponding to the three different regions:

$$\frac{d^2\phi}{dx^2} = \begin{cases} \frac{e_0 n_0}{\epsilon_2 \epsilon_0} \cdot \exp(e_0\phi(x)/kT) \ , & 0 \leq x < b \\ \frac{2e_0 n_0}{\epsilon_2 \epsilon_0} \cdot \sinh(e_0\phi(x)/kT) \ , & b \leq x < a \\ \frac{2e_0 n_0}{\epsilon_1 \epsilon_0} \cdot \sinh(e_0\phi(x)/kT) \ , & a \leq x < \infty \end{cases} \tag{39}$$

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

$$\left.\frac{d\phi}{dx}\right|_0 = -\frac{\sigma_{eff}}{\epsilon_2\epsilon_0} \ . \tag{40}$$

The validity of the Gauss's law at x = b and x = a, respectively, is fulfilled by the following equations:

$$\left.\frac{d\phi}{dx}\right|_{b_-} = \left.\frac{d\phi}{dx}\right|_{b_+} \ , \tag{41}$$

$$\epsilon_2 \left.\frac{d\phi}{dx}\right|_{a_-} = \epsilon_1 \left.\frac{d\phi}{dx}\right|_{a_+} \ . \tag{42}$$

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

$$\left.\frac{d\phi}{dx}\right|_\infty = 0 \ . \tag{43}$$

Equations (39) are rewritten in dimensionless form:

$$\frac{d^2\Psi}{d\xi^2} = \begin{cases} K \cdot \exp(\Psi) \ , & 0 \leq \xi < \frac{b}{a} \\ 2K \cdot \sinh(\Psi) \ , & \frac{b}{a} \leq \xi < 1 \\ 2L \cdot \sinh(\Psi) \ , & 1 \leq \xi < \infty \end{cases} \tag{44}$$

where the reduced potential $\Psi(x) = e_0\phi(x)/kT$ (Eq.(2)) and the reduced length:

$$\xi = \frac{x}{a} \ , \tag{45}$$

and the constants are defined as:

$$K = \frac{e_0^2 n_0 a^2}{\epsilon_2 \epsilon_0 kT} \quad , \quad L = \frac{e_0^2 n_0 a^2}{\epsilon_1 \epsilon_0 kT} \quad . \tag{46}$$

Respectively, the boundary conditions for the dimensionless case are

$$\left. \frac{d\Psi}{d\xi} \right|_0 = -\frac{\sigma_{eff} a e_0}{\epsilon_2 \epsilon_0 kT} \quad , \tag{47}$$

$$\left. \frac{d\Psi}{d\xi} \right|_{\frac{b}{a}-} = \left. \frac{d\Psi}{d\xi} \right|_{\frac{b}{a}+} \quad , \tag{48}$$

$$\epsilon_2 \left. \frac{d\Psi}{d\xi} \right|_{1_-} = \epsilon_1 \left. \frac{d\Psi}{d\xi} \right|_{1_+} \quad , \tag{49}$$

$$\left. \frac{d\Psi}{d\xi} \right|_\infty = 0 \quad . \tag{50}$$

In addition to Eqs.(47)-(50) we consider also continuity of the electric potential at x=b and x=a.
Hereafter, we take a closer look at the derivation of the solutions of Eq.(44). Equation (44) is multiplied at both sides by $2\frac{d\Psi}{d\xi}$

$$\frac{d}{d\xi}\left(\frac{d\Psi}{d\xi}\right)^2 = 2\frac{d\Psi}{d\xi}\frac{d^2\Psi}{d\xi^2} \tag{51}$$

by taking into account the continuity of the electric potential at x=b and x=a, and integrated to get respectively:

$$\int d\left(\frac{d\Psi}{d\xi}\right)^2 = \int 2K \exp(\Psi) d\Psi \qquad 0 \le \xi < \frac{b}{a} \tag{52}$$

$$\int d\left(\frac{d\Psi}{d\xi}\right)^2 = \int 4K \sinh(\Psi) d\Psi \qquad \frac{b}{a} \le \xi < 1 \tag{53}$$

$$\int d\left(\frac{d\Psi}{d\xi}\right)^2 = \int 4L \sinh(\Psi) d\Psi \qquad 1 \le \xi < \infty \tag{54}$$

These transformations lead to:

$$\frac{d\Psi}{d\xi} = \begin{cases} \sqrt{C + 2K\exp(\Psi)}, & 0 \le \xi < \frac{b}{a} \\ \sqrt{D + 4K\cosh\Psi}, & \frac{b}{a} \le \xi < 1 \\ -\sqrt{8L}\sinh\left(\frac{\Psi}{2}\right), & 1 \le \xi < \infty \end{cases} \tag{55}$$

where

$$C = \left(\frac{\sigma_{eff} e_0 a}{\epsilon_2 \epsilon_0 kT}\right)^2 - 2K\exp(\Psi(0)) \quad , \tag{56}$$

$$D = C - 2K\exp\left(\Psi\left(-\frac{b}{a}\right)\right) \quad . \tag{57}$$

Now we proceed with the solution of Eq. (55) considered separately in each of the three intervals. In the interval $0 \le \xi < \frac{b}{a}$ we can get an analytical solution of Eq.(55) by rearranging it as:

$$d\xi = \frac{d\Psi}{\sqrt{C + 2K\exp(\Psi)}}. \tag{58}$$

For the sake of simplicity, let u to be equal to

$$u = \sqrt{C + 2K\exp(\Psi)} \tag{59}$$

and we obtain

$$du = \frac{K\exp(\Psi)}{\sqrt{C + 2K\exp(\Psi)}} d\Psi \tag{60}$$

and

$$u^2 - C = 2K\exp(\Psi). \tag{61}$$

Integrating Eq. (58) gives:

$$\begin{aligned} \xi &= \int_{u(0)}^{u(\xi)} \frac{2du}{u^2 - C} \\ &= \begin{cases} \frac{1}{\sqrt{C}} \ln \frac{\sqrt{C}+u(0)}{\sqrt{C}-u(0)} \cdot \frac{\sqrt{C}-u}{\sqrt{C}+u} & C > 0 \\ \frac{2}{\sqrt{|C|}}\left(\arctan\frac{u}{\sqrt{|C|}} - \arctan\frac{u(0)}{\sqrt{|C|}}\right) & C < 0 \end{cases} \end{aligned} \tag{62}$$

In order to obtain $u(\xi)$, we can transform Eq. (62) as:

$$\exp(\sqrt{C}\xi) = \frac{\sqrt{C}+u(0)}{\sqrt{C}-u} \cdot \frac{\sqrt{C}-u}{\sqrt{C}+u} \quad C > 0 \tag{63}$$

And for $C < 0$

$$\sqrt{|C|}\frac{\xi}{2}) = \left(\arctan\frac{u}{\sqrt{|C|}} - \arctan\frac{u(0)}{\sqrt{|C|}}\right) \tag{64}$$

And then u is equal to:

$$u = \begin{cases} \sqrt{C}P & C > 0 \\ \sqrt{|C|}\tan(q1 + \arctan\frac{u(0)}{\sqrt{|C|}}) & C < 0 \end{cases} \tag{65}$$

where

$$P = \frac{(\sqrt{C}+u(0)) - (\sqrt{C}-u(0))\exp(\sqrt{C}\xi)}{(\sqrt{C}-u(0))\exp(\sqrt{C}\xi)} \tag{66}$$

$$q1 = (\sqrt{|C|}\frac{\xi}{2}), \tag{67}$$

Now we refer to Eq. (59) and rewrite Eq. (65) as:

$$\sqrt{C + 2K\exp(\Psi)} = \begin{cases} \sqrt{C}Q & C > 0 \\ \sqrt{|C|}\tan(q1 + q2) & C < 0 \end{cases}$$

where

$$Q = \frac{(\sqrt{C} + \gamma) - (\sqrt{|C|} - \gamma)\exp(\sqrt{C}\xi)}{(\sqrt{|C|} - \gamma)\exp(\sqrt{|C|}\xi)} \quad , \quad (68)$$

$$\gamma = \sqrt{C + 2K\exp(\Psi(0))} \quad , \quad (69)$$

$$q2 = \arctan\frac{\gamma}{\sqrt{|C|}} \quad . \quad (70)$$

Finally, from Eq. (68) we receive Ψ as:

$$\Psi = \left\{ \begin{array}{ll} ln\left[\frac{C}{2K}\left(Q^2 - 1\right)\right] & C > 0 \\ ln\left[\frac{|C|}{2K}\left(\tan^2(q1 + q2) - 1\right)\right] & C < 0 \end{array} \right. \quad (71)$$

In the interval $\frac{b}{a} < \xi < 1$, the corresponding equation from Eq. (55):

$$\frac{d\Psi}{d\xi} = \sqrt{D + 4K\cosh\Psi} \quad (72)$$

is solved numerically.

In the interval $1 \leq \xi < \infty$, we rearrange the corresponding equation from Eq.(55) as:

$$d\xi = \frac{-d\Psi}{\sqrt{8L}\sinh\frac{\Psi}{2}}. \quad (73)$$

Integrating Eq.(73)

$$\int_1^\xi d\xi = -\frac{1}{\sqrt{8L}}\int_{\Psi(1)}^{\Psi(\xi)} \frac{d\Psi}{\sinh\frac{\Psi}{2}} \quad (74)$$

gives the following solution:

$$\xi - 1 = \frac{1}{\sqrt{2L}}\ln\left(\frac{\tanh\frac{\Psi(1)}{4}}{\tanh\frac{\Psi}{4}}\right) \quad . \quad (75)$$

By transforming Eq.(75), we get the final result for Ψ in the form:

$$\Psi = 4\tanh^{-1}\left(\tanh\frac{\Psi(1)}{4}\exp(\sqrt{2L}(1-\xi))\right) \quad . \quad (76)$$

The space dependency of the dielectric constant near a charged metal surface is considered in both models, within the statistical mechanical approach and also within the generalized Stern model, where the space dependency of dielectric constant is approximated by a simple step function. The corresponding parameters ϵ_2 and a (see Fig.5) in the generalized Stern model are determined by
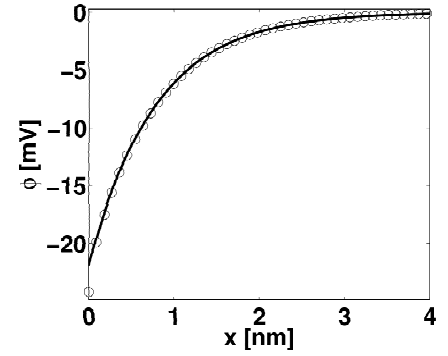

Figure 6. Electric potential ϕ as a function of the distance from the charged surface (x) calculated using the statistical mechanical model (full line) and generalized the Stern model (circles) for $\sigma_{eff} = -0.02\,\mathrm{As/m^2}$, the bulk salt concentration is $n_0/N_A = 0.1\mathrm{mol/l}$. Model parameters within the statistical mechanical description: width of a single lattice site $a_s{=}0.318$ nm, dipole moment of water $p_0 = 5D$. In the generalized Stern model $\epsilon_2 = 30$, $\epsilon_1 = 78.5$, $b = 0.01$ nm and $a = 0.1$ nm.
Slika 6.   Elektrostatski potencial ϕ kot funkcija razdalje od naelektrene kovinske plošče (x) izračunan v okviru statistično mehanskega modela (polna črta) in posplošenega Sternovega modela (krogci) za vrednosti efektivne površinske gostote naboja na kovinski plošči $\sigma_{eff} = -0.02\,\mathrm{As/m^2}$ (spodnja slika). Koncetracija soli daleč stran od kovinske plošče $n_0/N_A = 0.1\mathrm{mol/l}$. Modelni parametri statistično mehanskega modela: širina mrežnega mesta $a_s{=}0.318$ nm, dipolni momemnt vodne molekule $p_0 = 5D$, koncentracija vode daleč stran od kovinske plošče $n_{0w}/N_A = 55\,\mathrm{mol/l}$. Modelni parametri posplošenega Sternovega modela $\epsilon_2 = 30$, $\epsilon_1 = 78.5$, $b = 0.01$ nm in $a = 0.1$ nm.
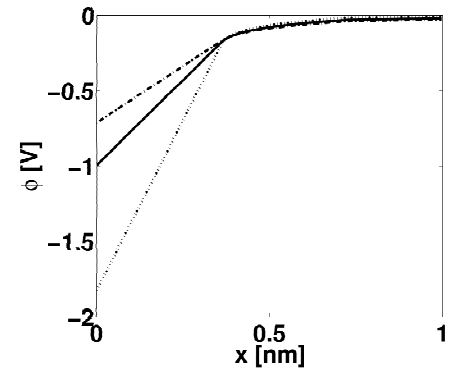

Figure 7. Electric potential ϕ as a function of the distance from the charged surface (x) calculated using the generalized Stern model for $\sigma_{eff} = -0.4\,\mathrm{As/m^2}$ and three values of the dielectric constant ϵ_2 : 10, 20, 30 (see Fig.4). Model parameters are: bulk salt concentration is $n_0/N_A = 0.15\mathrm{mol/l}$, $\epsilon_1 = 78.5$, $b = 0.36$ nm and $a = 0.72$ nm.
Slika 7.   Elektrostatski potencial ϕ kot funkcija razdalje od naelektrene kovinske plošče (x) izračunan v okviru posplošenega Sternovega modela za efektivno površinsko gostoto naboja na kovinski plošči $\sigma_{eff} = -0.4\,\mathrm{As/m^2}$ in tri vrednosti dielektrične konstante ϵ_2 :10, 20, 30 (see Fig.4) . Ostali modelni parametri so: koncetracija soli daleč stran od kovinske plošče $n_0/N_A = 0.15\mathrm{mol/l}$, $\epsilon_1 = 78.5$, $b = 0.36$ nm in $a = 0.72$ nm.

fitting the space dependency of electric potential calcu-

lated by using the statistical mechanical model (Fig.6).

The inference from Fig.6 is that both approaches are in a good agreement, when we choose a small value for the distance of closest approach b. This is justified by the fact that in the statistical mechanical approach the excluded volume effect is taken into account namely by allowing the centers of ions and water molecules to approach x=0 plane. Both models complement each other, since the GS model is not restricted to small values of the surface charge, making it a good supplement to the statistical mechanical approach (see Fig.7).

Fig.7 presents the distribution of the electric potential for values of the dielectric constant of 10, 20 and 30. It becomes clear that the absolute value of the electric potential decreases with the increase in the dielectric constant.

3 Conclusions and Discussion

The presented results might be important for the improvement of the biocompatibility of the implant surfaces. Namely, for the clinical success of an implant, a profound knowledge of the interaction between the biomaterial and the cells is needed [12]. The functional activity of cells in contact with the biomaterial is determined by the material characteristics of the surface as well as the surface topography [13]. As described in this work, the contact between negatively charged metal surface and electrolyte solution results into rearrangement of the ion distribution and water orientational ordering near the metal surface. Thus, the surface electric potential is modified, which may among others assist the protein adhesion and the proliferation of the osteoblasts. Most of the models describing this phenomenon assume that the dielectric constant in the whole system is constant.

Therefore, in this work the orientational ordering of water dipoles and the excluded volume were explicitly taken into account in the statistical mechanical model. It was shown that the dipole moment vectors of water molecules at the charged metal surface are predominantly oriented towards the negatively charged surface while all orientations of water dipoles far away from the charged metal surface are equally probable. Due to accumulation of counterions near the metal surface, we predicted that the dielectric constant is there significantly reduced.

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