

The internal and external dipole moment of a water molecule and orientational ordering of water dipoles in an electric double layer

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Abstract. The modelling of the electric double layer (EDL) in lattice statistics requires an understanding of the orientational ordering of water molecules in an ion solution and their contribution to the total free energy. Since water is a polar molecule with its own dipole moment, its total dipole moment arises from the internal and external contributions, the latter modified by the cavity field of neighbouring molecules. In the present paper, we first model a single water molecule as a rigid sphere with a point-like dipole at its center inserted into a continuum with a different dielectric permittivity. The internal and external dipole moment are derived in spherical coordinates. We also derive the energy of such a sphere in an electric field, bearing in mind the modified Langevin-Poisson-Boltzmann's (MLPB) equation used to predict the space-dependent relative permittivity in EDL for the case of point-like molecules.

Keywords: electric double layer, water molecule, dielectric properties, cavity field, orientational ordering of water dipoles

Notranji in zunanji električni dipolni moment molekule vode in orientacijsko urejanje vodnih molekul v električni dvojni plasti

Proučevanje električnega dvojnega sloja v modelu mrežne statistične mehanike zahteva razumevanje orientacij vodnih molekul v ionski raztopini in njihov energijski prispevek k prosti energiji. Voda sestoji iz polarnih molekul, celotni električni dipolni moment molekule pa je vsota notranjih in zunanjih prispevkov, kjer so zadnji posledica polarizacije okoliških molekul. V pričujočem članku najprej obravnavamo molekulo vode kot kroglo s točkastim električnim dipolom v njenem središču, vstavljeno v kontinuum z različno dielektrično konstanto. Notranji in zunanji električni dipolni moment izpeljemo v sferičnih koordinatah. Prav tako izpeljemo energijo vodne molekule v zunanjem električnem polju. Na koncu izpeljemo tudi modificirani Langevin-Poisson-Boltzmannov model (MLPB) električne dvojne plasti za točkaste molekule.

1 INTRODUCTION

At the interface between a charged surface and neighbouring electrolyte, the electric double layer (EDL)

plays a crucial role (1–11). The properties of EDL may be strongly dependent on the spatial and orientational ordering of water molecules in this region (12–14). It has been shown that close to the charged surface, orientational ordering and depletion of water molecules may result in a strong decrease in the local permittivity of the electrolyte solution (5; 7; 8; 13; 15; 16).

Considering the orientational ordering of water and finite size of molecules, Outhwaite and collaborators developed a modified Poisson-Boltzmann's (PB) theory of EDL composed of a mixture of hard spheres with point-like dipoles and finite-sized ions (15; 19). Later, Szalai et al. (20) published a mean spherical approximation-based theory (21) that can reproduce simulation results for the electric field dependence of the dielectric permittivity of a dipolar fluid in a saturation regime. In addition, the problem was recently considered also within a lattice statistics model (13; 14).

The dipole moment of an isolated water molecule is around 1.85 D (Debye is $3.336 \cdot 10^{-30}$ Cm). In a solution, on the other hand, the dipole moment of a single water molecule differs from that of an isolated one since each

water molecule is also polarized by the electric field of the neighbouring water molecules, creating an effective value of the dipole moment around 2.4 D - 2.6 D (23; 24). The effect of a polarising environment can be reproduced in the most simple way by introduction of the cavity field (25–27).

By considering the cavity field at the centre of the water molecule (27; 28) and also the electronic polarizability of a water molecule (16; 27; 28), taken into account by portraying a single water molecule as a dielectric sphere with a point-like rigid dipole at its center, the magnitude of the external water dipole moment around 3 D was used within the mean-field lattice statistics approach (14; 16; 27). Neglecting the cavity field and electronic polarizability contribution within a similar lattice statistics, the theoretical models lead to much higher predicted values of the water external dipole moments (around 5 D) (17; 18). In the present paper we examine the derivation of the effective permittivity of a sphere placed in a homogenous electric field and inspect its spatial dependence in ionic solutions. The latter is achieved by dual means: by examination of a relative permittivity of water dipoles and by variational minimization of the Helmholtz's free energy of a point-like ionic solution.

2 THE ENERGY OF AN INTERNAL POINT-LIKE DIPOLE IN A LOCAL FIELD

Using the Laplace's equation, we can find the electric field configuration when a dielectric sphere is placed in a homogenous electric field. Such a uniform field can be attained by a parallel-plate capacitor if the linear dimensions of the plates are large enough with respect to the separation of the plates. Even for large separations between the plates, the field in the inner parts and away from the edges of the plates will be homogenous to a high degree of accuracy. If the size of the plates is increased to infinity and at the same time the distance between them is also increased to infinity for a constant surface charge density on the plates, a uniform electric field is created in the entire space. In this space we place a dielectric sphere. It is clear that as a result of polarization, the field strength near the sphere will change while it will remain unchanged at infinity. Let us determine the electric field strength in the entire space including the region inside the dielectric sphere.

We assume that a sphere of radius R consists of dielectric with permittivity ε_w , while the surrounding space is filled with a dielectric with permittivity ε_r (Fig. 1). In this part, we assume that ε_r is constant through the space, since we are dealing with a single water molecule. Later on, when we will be considering the EDL, we will see that the permittivity has a spatial dependency. We assume that homogenous field \mathbf{E} is directed along the x -axis.

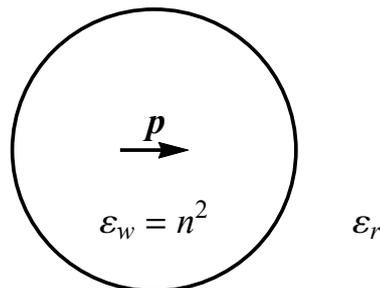


Figure 1. Model of the water molecule consists of a sphere with permittivity $\varepsilon_w = n^2$ and permanent internal point-like dipole \mathbf{p} at the center.

For a homogenous dielectric with permittivity ε_r , the Poisson equation states that

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon_0 \varepsilon_r}, \quad (1)$$

where ϕ is the electric potential and ρ the charge density. Eq. (1) assumes a constant value of permittivity ε_r . In spherical coordinates, the Poisson equation can be written as follows:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial \phi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2 \phi}{\partial \alpha^2} = -\frac{\rho}{\varepsilon_0 \varepsilon_r}, \quad (2)$$

where r is the radial distance, α is the azimuthal angle and θ is the zenith angle. There are no free charges considered in this chapter ($\rho = 0$), and $\partial \phi / \partial \alpha = 0$ on account of the axial symmetry. Hence the problem is reduced to the solution of the Laplace's equation

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \phi}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial \phi}{\partial \theta} \right) = 0. \quad (3)$$

The following conditions must be obeyed:

- 1) potential ϕ is continuous and finite everywhere;
- 2) the normal components of electric displacement field vector \mathbf{D} are continuous on the surface of the sphere;
- 3) the tangential components of vector $\mathbf{E} = -\nabla \phi$ are continuous on the surface of the sphere.

The quantities corresponding to the inner region of the sphere are denoted by subscript 1, while those corresponding to the space outside the sphere are denoted by subscript 2. The general solution of Eq. (3) is given by

$$\phi_1 = A_1 r \cos(\theta) + A_2 r^{-2} \cos(\theta), \quad (4)$$

$$\phi_2 = -E r \cos(\theta) + B_2 r^{-2} \cos(\theta), \quad (5)$$

where A_1 , A_2 and B_2 are constants, and E is the absolute value of the strength of the uniform electric field at infinity.

Since ϕ_1 and ϕ_2 satisfy Eq. (3), they represent the correct electric potential if they satisfy all the conditions

of the problem. Potential ϕ_1 corresponds to the inner region of the sphere, while ϕ_2 corresponds to the space outside it. It can be seen from Eq. (4) that $\phi_1 \rightarrow \infty$ as $r \rightarrow 0$. To avoid the singularity, we set $A_2 = 0$. The continuity equation for ϕ at the boundary has the form

$$A_1 R \cos(\theta) = -ER \cos(\theta) + B_2 R^{-2} \cos(\theta), \quad (6)$$

which simplifies to

$$A_1 = B_2 R^{-3} - E. \quad (7)$$

The tangential component of electric field vector \mathbf{E} on the surface of the sphere is

$$E_t = E_\theta = - \left[\frac{1}{r} \frac{\partial \phi}{\partial \theta} \right]_{r=R}. \quad (8)$$

Condition $E_{1\theta} = E_{2\theta}$ is satisfied if Eq. (6) is valid, i.e. A_1 and B_2 are connected through the relation in Eq. (7).

The normal components of the electric field vector are given by

$$E_{1n} = - \frac{\partial \phi_1}{\partial r} \Big|_{r=R} = -A_1 \cos(\theta), \quad (9)$$

$$E_{2n} = - \frac{\partial \phi_2}{\partial r} \Big|_{r=R} = E \cos(\theta) + 2B_2 R^{-3} \cos(\theta). \quad (10)$$

Here, the electric field components are equal to $E_{1n} = E_{1r}$ and $E_{2n} = E_{2r}$. We change the subscript from n to r to denote the usage of spherical coordinates. Furthermore, it follows from condition $\varepsilon_w E_{1r} = \varepsilon_r E_{2r}$ that

$$A_1 = - \frac{\varepsilon_r}{\varepsilon_w} (E + 2B_2 R^{-3}). \quad (11)$$

The solutions of the system of Eqs. (7) and (11) are

$$A_1 = - \frac{3\varepsilon_r}{\varepsilon_w + 2\varepsilon_r} E, \quad (12)$$

$$B_2 = \frac{\varepsilon_w - \varepsilon_r}{\varepsilon_w + 2\varepsilon_r} R^3 E. \quad (13)$$

The potentials inside and outside the sphere are then

$$\phi_1 = - \frac{3\varepsilon_r}{\varepsilon_w + 2\varepsilon_r} Er \cos(\theta), \quad (14)$$

$$\phi_2 = - \left(1 - \frac{R^3}{r^3} \frac{\varepsilon_w - \varepsilon_r}{\varepsilon_w + 2\varepsilon_r} \right) Er \cos(\theta). \quad (15)$$

The field inside the sphere is constant and parallel to the x -axis:

$$E_{1x} = E_c = - \frac{\partial \phi_1}{\partial x} = - \frac{\partial \phi_1}{\partial (r \cos(\theta))} = \frac{3\varepsilon_r}{\varepsilon_w + 2\varepsilon_r} E. \quad (16)$$

We call field E_c the local cavity field, while the outside field is labeled by E . The local field is the sum of the external field and the field created by the bound charges appearing on the surface of the sphere. If the dielectric constant of sphere ε_w is in the range of optical frequencies, then it is equal to the square of the refractive index of the cavity (n^2). The permittivity of the electronic induced moment of the water molecule at

optical frequencies of the external field can therefore be written as:

$$\varepsilon_w = n^2. \quad (17)$$

Furthermore, when the medium surrounding the cavity has a dielectric constant much larger than the square of the refractive index, $\varepsilon_r \gg n^2$, an approximation may be used (16):

$$E_c \approx \frac{3}{2} E \rightarrow \mathbf{E}_c \approx \frac{3}{2} \mathbf{E}. \quad (18)$$

It has to be noted that so far we have neglected the reaction field, i.e. the field due to the point-like dipole in the center of the cavity. This reaction field is directly proportional to the strength of dipole $\mathbf{E}_{react} \propto \mathbf{p}$. Let us calculate this external dipole moment of a single water molecule. First, we must derive the electric potential of a dipole centered inside a sphere with permittivity $\varepsilon_w = n^2$.

The conditions of finite and continuous potential are the same as in the previous derivation. At the surface of the sphere, the potential inside (ϕ_1) must be equal to the potential outside of the sphere (ϕ_2):

$$\phi_1|_R = \phi_2|_R. \quad (19)$$

If the sphere is surrounded by a medium with permittivity ε_r , the normal derivatives of the electric field must also be continuous at the surface, therefore

$$\varepsilon_w \frac{\partial \phi_1}{\partial r} \Big|_{r=R} = \varepsilon_r \frac{\partial \phi_2}{\partial r} \Big|_{r=R}. \quad (20)$$

The absence of an external field imposes $\phi \rightarrow 0$ as $r \rightarrow \infty$. Similarly, the potential must behave like that of an ideal dipole in the limit $r \rightarrow 0$. These conditions must be obeyed solving the Laplace equation Eq. (3). The general form of the solution is

$$\phi(r, \theta) = \sum_{l=0}^{\infty} \left(A_l r^l + \frac{B_l}{r^{l+1}} \right) P_l(\cos(\theta)). \quad (21)$$

Here, P_l are the Legendre's polynomials of order l . Inside the sphere, we have

$$\phi_1(r, \theta) = \frac{p \cos(\theta)}{4\pi\varepsilon_w r^2} + \sum_{l=0}^{\infty} A_l r^l P_l(\cos(\theta)), \quad (22)$$

and outside, it follows

$$\phi_2(r, \theta) = \sum_{l=0}^{\infty} \left(\frac{B_l}{r^{l+1}} \right) P_l(\cos(\theta)). \quad (23)$$

Applying continuity condition Eq. (19) and equating coefficients of P_l , we get

$$\frac{p}{4\pi\varepsilon_w R^2} + A_1 R = \frac{B_1}{R^2}, \quad (l=1) \quad (24)$$

$$A_l R^l = \frac{B_l}{R^{l+1}}, \quad (l \neq 1). \quad (25)$$

We can therefore express B_l in terms of A_l :

$$B_1 = \frac{p}{4\pi\varepsilon_w} + A_1 R^3, \quad (l=1) \quad (26)$$

$$B_l = R^{2l+1} A_l, \quad (l \neq 1). \quad (27)$$

Using the condition defined by Eq. (20) and equating the coefficients as before, we get

$$-\frac{p}{2\pi R^3} + \varepsilon_w A_1 = -\varepsilon_r \frac{2B_1}{R^3}, \quad (l=1) \quad (28)$$

$$\varepsilon_w A_l l R^{l-1} = -\varepsilon_r \frac{(l+1)B_l}{R^{l+2}}, \quad (l \neq 1). \quad (29)$$

Substituting for B_l (Eq. (27)) into the right-hand side of Eq. (29) gives

$$\varepsilon_w A_l l R^{2l+1} = -\varepsilon_r (l+1) A_l R^{2l+1}. \quad (30)$$

The only way this can be satisfied is if $A_l = 0$ for $l \neq 1$, so we get $A_l = B_l = 0$ for $l \neq 1$. For the $l = 1$ case, Eq. (26) and Eq. (28) yield

$$A_1 = \frac{p}{2\pi R^3 \varepsilon_w} \left(\frac{\varepsilon_f - 1}{\varepsilon_f + 2} \right), \quad (31)$$

$$B_1 = \frac{1}{4\pi \varepsilon_r} \left(\frac{3p}{\varepsilon_f + 2} \right). \quad (32)$$

Here, $\varepsilon_f = \varepsilon_w / \varepsilon_r$ marks the ratio between the permittivities. The potentials are

$$\phi_1(r, \theta) = \frac{p \cos(\theta)}{4\pi \varepsilon_w r^2} \left[1 + 2 \frac{r^3}{R^3} \left(\frac{\varepsilon_f - 1}{\varepsilon_f + 2} \right) \right], \quad (33)$$

$$\phi_2(r, \theta) = \frac{\cos(\theta)}{4\pi \varepsilon_r r^2} \left(\frac{3p}{\varepsilon_f + 2} \right). \quad (34)$$

The denominator of Eq. (34) includes product $\varepsilon_r \varepsilon_f = \varepsilon_w = n^2$, so based on Eq. (34), we can define external dipole moment \mathbf{p}_e in the vector form as (16)

$$\mathbf{p}_e = \frac{3}{n^2 + 2} \mathbf{p}. \quad (35)$$

The energy of an internal point-like dipole in a local field is

$$W_e = -\mathbf{p} \cdot \mathbf{E}_c. \quad (36)$$

Substituting from Eq. (18), we can express the dipole energy as (16)

$$W_e = -\frac{3}{2} \left(\frac{2+n^2}{3} \right) p_0 E \cos(\theta), \quad (37)$$

$$W_e = \gamma p_0 E \cos(\omega), \quad (38)$$

where p_0 is the magnitude of vector \mathbf{p}_e and angle ω is supplementary to θ , as shown in Fig. 2. Constant γ equals (16)

$$\gamma = \frac{3}{2} \left(\frac{2+n^2}{3} \right). \quad (39)$$

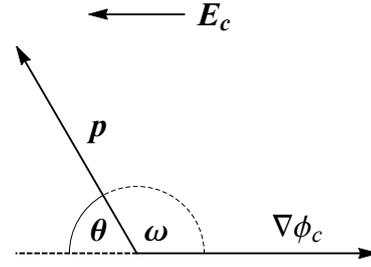


Figure 2. Relation between angles θ and ω . The water internal dipole moment is marked by \mathbf{p} , the local cavity field is given by \mathbf{E}_c and points in the opposite direction of the potential gradient by $\nabla\phi_c$.

3 SPACE-DEPENDENT DIELECTRIC PERMITTIVITY IN THE ELECTRIC DOUBLE LAYER

In general, the relative permittivity is given as

$$\varepsilon_r = 1 + \frac{P}{\varepsilon_0 E_c}, \quad (40)$$

where P is the polarization of water dipoles. The total polarization is given by:

$$P = P_{elect} + |P_{orient}|, \quad (41)$$

where P_{elect} is the electronic polarization and P_{orient} is the orientational polarization. Considering equations Eq. (40) and Eq. (41), the permittivity can be written as

$$\varepsilon_r = 1 + \frac{P_{elect}}{\varepsilon_0 E_c} + \frac{|P_{orient}|}{\varepsilon_0 E_c}. \quad (42)$$

Electronic polarization is connected to the refractive index as $n^2 = 1 + P_{elect} / \varepsilon_0 E_c$, which yields

$$\varepsilon_r = n^2 + \frac{|P_{orient}|}{\varepsilon_0 E_c}. \quad (43)$$

In this formulation, the electronic polarization contribution is described by refractive index n . In our case of a negatively charged planar surface ($\sigma < 0$), the projection of polarization vector \mathbf{P}_{orient} points in the direction opposite to the direction of the x -axis, so the \mathbf{P}_{orient} is considered to have magnitude which points in a negative direction. So far we have assumed that ε_r is a constant quantity, but this is not the case with the electric double layer, where the ordering of water molecules directly affects the spatial dependence of the dielectric permittivity. Orientational polarization P_{orient} is now (29; 31):

$$P_{orient}(x) = n_w(x) p_0 \left(\frac{2+n^2}{3} \right) \langle \cos(\omega) \rangle_\omega, \quad (44)$$

where in this paper we assume $n_w(x) = n_w$ is the constant (bulk) number density of water in the solution

and p_0 is the magnitude of the vector defined in Eq. (35):

$$p_0 = |\mathbf{p}_e|. \quad (45)$$

Factor $\langle \cos \omega \rangle_\omega$ is the ensemble average of the orientation of water molecules over the solid angle, defined as

$$\langle \cos(\omega) \rangle_\omega = \frac{\int \cos(\omega) \exp(-\beta\gamma p_0 E \cos(\omega)) d\Omega}{\int \exp(-\beta\gamma p_0 E \cos(\omega)) d\Omega}, \quad (46)$$

where ω is the angle between the dipoles and potential gradient, as shown in Figure 2. Boltzmann's factor β equals $\beta = 1/kT$, where kT is the thermal energy. The element of solid angle $d\Omega$ is

$$d\Omega = 2\pi \sin(\omega) d\omega. \quad (47)$$

Eq. (47) assumes rotational symmetry with respect to the azimuthal axis of rotation. After integrating, Eq. (46) simplifies to (16):

$$\langle \cos(\omega) \rangle_\omega = -\mathcal{L}(\beta\gamma p_0 E), \quad (48)$$

where \mathcal{L} is the Langevin's function defined as

$$\mathcal{L}(u) = \coth(u) - \frac{1}{u}. \quad (49)$$

The orientational polarization thus becomes (16):

$$P_{orient}(x) = -n_w p_0 \left(\frac{2+n^2}{3} \right) \mathcal{L}(\beta\gamma p_0 E). \quad (50)$$

Considering Eq. (43), the dielectric permittivity is now in general spatially dependent (16):

$$\varepsilon_r(x) = n^2 + \frac{n_w p_0}{\varepsilon_0} \left(\frac{2+n^2}{3} \right) \frac{\mathcal{L}(\beta\gamma p_0 E(x))}{E_c(x)}. \quad (51)$$

In the approximation of a small electrostatic energy and small energy of dipoles compared to the thermal energy, the relative permittivity may be expanded using the Taylor's series. For small x , the Langevin's function is well approximated by

$$\mathcal{L}(u) \approx \frac{u}{3} - \frac{u^3}{45}. \quad (52)$$

In the limit of vanishing the electric field strength ($E \rightarrow 0$) and zero potential ($\phi \rightarrow 0$), the above equation gives the Onsager's expression for the bulk permittivity (16; 25; 29; 31):

$$\varepsilon_r \approx n^2 + \left(\frac{2+n^2}{3} \right)^2 \frac{n_w p_0^2 \beta}{2\varepsilon_0}. \quad (53)$$

Using Eq. (51) for space-dependent relative permittivity $\varepsilon_r(x)$, the Modified Langevin-Poisson-Boltzmann's (MLPB) equation (29; 31) used in calculating the ion concentrations in the EDL becomes

$$\frac{d}{dx} \left[\varepsilon_0 \varepsilon_r(x) \frac{d\phi_c}{dx} \right] = 2e_0 n_0 \sinh(e_0 \phi_c \beta), \quad (54)$$

where e_0 is the elementary charge. The macroscopic (net) volume charge density of coions and counterions is written in the form:

$$\rho_{free}(x) = e_0 n_+(x) - e_0 n_-(x) = -2e_0 n_0 \sinh(e_0 \phi_c \beta). \quad (55)$$

Here, $n_+(x)$ and $n_-(x)$ are the number densities of counterions and coions and n_0 is the bulk number density of counterions and coions in the electrolyte solution. The boundary conditions for the MLPB equation are:

$$\frac{d\phi_c}{dx}(x=0) = \frac{\sigma}{\varepsilon_0 \varepsilon_r(x=0)}, \quad (56)$$

and

$$\frac{d\phi_c}{dx}(x=\infty) = 0. \quad (57)$$

The spatial dependence of permittivity $\varepsilon_r(x)$ is plotted in Fig. 3 for $T = 298$ K, $n_w = 55$ mol/l and $p_0 = 3.1$ Debye (29).

4 MINIMIZATION OF THE FREE ENERGY

The same result for the spatial dependence of solution permittivity ε_r as described by Eq. (51) can be obtained also by using the minimization of the Helmholtz's free energy. Our model considers the electrolyte solution as consisting of a mixture of point-like ions in a water solution, where the water molecules are considered as the Langevin's dipoles. It is assumed that the ions and water molecules create an average electric field within electrolyte $E_c(x)$. We can write the Helmholtz's free energy of the system F as

$$\begin{aligned} F = & \frac{n^2 \varepsilon_0}{2} \int E_c^2(x) dV + kT \left[\int \left(n_+(x) \ln \frac{n_+(x)}{n_0} - \right. \right. \\ & \left. \left. - (n_+ - n_0) \right) dV + \int \left(n_-(x) \ln \frac{n_-(x)}{n_0} - \right. \right. \\ & \left. \left. - (n_- - n_0) \right) dV + \int (\lambda_+ n_+ + \lambda_- n_-) dV + \right. \\ & \left. + \int n_w \langle \mathcal{P}(x, \omega) \ln \mathcal{P}(x, \omega) \rangle_\omega dV + \right. \\ & \left. + \int n_w \eta(x) (\langle \mathcal{P}(x, \omega) \rangle_\omega - 1) dV \right]. \end{aligned} \quad (58)$$

The thermal energy is given by kT . The first term in the above equation is the energy from mean local electric field E_c . The second and third term account for the mixing entropy free energy contribution of point-like counterions and coions. The fourth term gives the constraint of a constant number of particles in the system, where λ_+ and λ_- are the global Lagrange's multipliers for counterions and coions. The fifth term is the free energy that corresponds to orientational entropy of the Langevin's dipoles, while the last term gives the local constraint for orientation of dipoles. $\mathcal{P}(x, \omega)$ is the probability that the Langevin's dipole located at x is oriented at angle ω with respect to the normal to

the charged surface (Fig. 2). The brackets denote the average:

$$\langle \mathcal{F}(x, \omega) \rangle_\omega = \frac{1}{4\pi} \int_0^\pi \mathcal{F}(x, \omega) d\Omega. \quad (59)$$

Here, ω is the angle between internal dipole moment vector \mathbf{p} and $\mathbf{n}_\phi = \nabla\phi/|\nabla\phi|$ (see Fig. 2), while $d\Omega$ marks the element of the solid angle as defined in Eq. (47). We perform a variation on Helmholtz free energy F Eq. (58), so that $\delta F = 0$ (see Appendix A). If we express the local field as local potential $E_c(x) = -\phi'_c(x)$ and perform a variation on the electrostatic term, we obtain

$$\delta \left(\frac{\varepsilon_0 n^2}{2} \int \phi_c'^2 dV \right) = \frac{\varepsilon_0 n^2}{2} \int 2\phi_c' \delta(\phi_c') dV. \quad (60)$$

We can rearrange this term if we consider the rules of differentiating a function product

$$\begin{aligned} (\phi_c \delta \phi_c')' &= \phi_c' \delta \phi_c' + \phi_c \delta \phi_c'', \\ \phi_c' \delta \phi_c' &= (\phi_c \delta \phi_c')' - \phi_c \delta \phi_c''. \end{aligned} \quad (61)$$

The integral in Eq. (60) thus yields

$$\int \phi_c' \delta(\phi_c') dV = \underbrace{\phi_c \delta \phi_c' \Big|_0^\infty}_{=0} - \int \phi_c \delta(\phi_c'') dV, \quad (62)$$

where the first term on the right-hand side equals 0 at infinity, since we pose that the electric potential there is constant and equal to 0. Taking into account the Poisson's law

$$\phi_c''(x) = -\frac{\rho(x)}{\varepsilon_0 n^2}, \quad (63)$$

we can transform the variation by ϕ_c'' to the variation by average microscopic volume charge density $\rho(x)$, which is the sum of the contributions of the local net ion charges and the dipole moments, represented by polarization \mathbf{P}_{orient} (16; 45).

$$\rho(x) = e_0(n_+ - n_-) - \nabla \cdot \mathbf{P}_{orient}, \quad (64)$$

Performing the variation on this charge distribution gives

$$\delta\rho(x) = e_0[\delta n_+(x) - \delta n_-(x)] - \delta(\nabla \cdot \mathbf{P}_{orient}), \quad (65)$$

simplifying the electrostatic energy term to the integral

$$\int \phi_c \delta\rho dV = \int \phi_c (e_0[\delta n_+ - \delta n_-] - \delta(\nabla \cdot \mathbf{P}_{orient})) dV. \quad (66)$$

The variation of the mixing entropy of ions and their constraints of Eq. (58) gives

$$\begin{aligned} \delta F_{mix,c}^{+,-} &= kT \int dV \left[\delta n_+ \left(\ln \frac{n_+}{n_0} + \lambda_+ \right) + \right. \\ &\quad \left. + \delta n_- \left(\ln \frac{n_-}{n_0} + \lambda_- \right) \right]. \end{aligned} \quad (67)$$

For the subscript and superscript nomenclature, see Appendix A. Combining positive ion differentials δn_+

from the electrostatic terms, mixing terms and constraints, we arrive at the variational integral

$$\begin{aligned} \delta F_{el,mix,c}^+ &= \int dV \delta n_+(x) \left[kT \left(\ln \frac{n_+(x)}{n_0} + \lambda_+ \right) + \right. \\ &\quad \left. + \phi_c e_0 \right] = 0. \end{aligned} \quad (68)$$

Since the integrand has to be zero (see Appendix A), we arrive at the expression for the distribution of positively charged ions $n_+(x)$. The derivation for negatively charged ions is practically identical. Both distributions are

$$n_+(x) = n_0 \exp \left(-\beta e_0 \phi_c - \lambda_+ \right), \quad (69)$$

$$n_-(x) = n_0 \exp \left(\beta e_0 \phi_c - \lambda_- \right). \quad (70)$$

Here, $\beta = 1/kT$. The boundary conditions state that $\phi_c(x \rightarrow \infty) = 0$ and $n_{+,-}(x \rightarrow \infty) = n_0$, which renders $\lambda_+ = \lambda_- = 0$. We may now turn our attention to the variation of the dipole orientation. Water molecules polarization \mathbf{P}_{orient} is given by

$$\mathbf{P}_{orient}(x) = n_w \langle \mathcal{P}(x, \omega) \rangle_\omega p \mathbf{n}_\phi, \quad (71)$$

where $p = |\mathbf{p}|$ is the internal point-like dipole magnitude, n_w is the concentration of water molecules in the bulk of the solution and $\langle \mathcal{P}(x, \omega) \rangle_\omega$ is defined by Eq. (59). As mentioned earlier (after Eq. (43)), \mathbf{P}_{orient} points in the direction opposite to the direction of the x -axis for $\sigma < 0$, hence $\mathbf{P}_{orient}(x)$ is considered negative. We may transform the polarization part of the integral in Eq. (66) so that

$$- \int \phi_c \delta(\nabla \cdot \mathbf{P}_{orient}) dV = \int (\nabla \phi_c) (\delta \mathbf{P}_{orient}) dV. \quad (72)$$

Considering Eq. (71), we may write

$$\delta \mathbf{P}_{orient} = \langle n_w \mathbf{p} \delta \mathcal{P}(x, \omega) \rangle_\omega. \quad (73)$$

The variation of the free energy of the Langevin's dipoles in Eq. (58) gives

$$\delta F_{mix}^{\mathcal{P}} = kT n_w \int dV \left[\langle \delta \mathcal{P}(x, \omega) \ln \mathcal{P}(x, \omega) + \delta \mathcal{P}(x, \omega) \rangle_\omega \right], \quad (74)$$

while the variation of the local constraint for orientation of the Langevin's dipoles yields

$$\begin{aligned} \delta F_c^{\mathcal{P},\eta} &= kT n_w \int dV \left[\delta \eta(x) \langle \mathcal{P}(x, \omega) \rangle_\omega + \right. \\ &\quad \left. + \eta(x) \langle \delta \mathcal{P}(x, \omega) \rangle_\omega - \delta \eta(x) \right]. \end{aligned} \quad (75)$$

Combining Eqs. (72-75) and varying by $\mathcal{P}(x, \omega)$, we arrive at the equation (see Appendix A):

$$\begin{aligned} \delta F_{el,mix,c}^{\mathcal{P}} &= \int dV \left[\langle n_w \delta \mathcal{P}(x, \omega) \left(\nabla \phi_c \cdot \mathbf{p} + \right. \right. \\ &\quad \left. \left. + \frac{\ln \mathcal{P}(x, \omega) + \eta(x) + 1}{\beta} \right) \rangle_\omega \right] = 0. \end{aligned} \quad (76)$$

The variation requires the integrand to be zero, which gives us the Lagrange's equation for the dipole orientation. After substituting the gradient of the local potential field with the local electric field (considering $|\mathbf{E}_c| = |\nabla\phi_c|$) and evaluating the dot product $\nabla\phi_c \cdot \mathbf{p} = E_cp \cos(\omega)$ (see Fig. 2), the equation reads

$$E_cp \cos(\omega) + kT \left(\ln \mathcal{P}(x, \omega) + \eta(x) + 1 \right) = 0. \quad (77)$$

Solving for $\mathcal{P}(x, \omega)$ gives

$$\mathcal{P}(x, \omega) = \Lambda(x) \exp \left(-\beta E_cp \cos(\omega) \right), \quad (78)$$

where $\Lambda(x) = \exp(-\eta(x) - 1)$. Substituting local electric field \mathbf{E}_c by electric field \mathbf{E} (Eq. (18)) and dipole moment \mathbf{p} by \mathbf{p}_e (Eq. (35)) gives

$$\mathcal{P}(x, \omega) = \Lambda(x) \exp \left(-\beta \frac{3E}{2} \left(\frac{2+n^2}{3} \right) p_0 \cos(\omega) \right), \quad (79)$$

where p_0 is the magnitude of \mathbf{p}_e . The final result is expressed using constant γ defined in Eq. (39):

$$\mathcal{P}(x, \omega) = \Lambda(x) \exp \left(-\beta \gamma E p_0 \cos(\omega) \right). \quad (80)$$

We can now evaluate the average internal dipole moment by integrating by mean orientations,

$$\begin{aligned} p \langle \cos(\omega) \rangle_\omega &= p_0 \left(\frac{2+n^2}{3} \right) \langle \cos(\omega) \rangle_\omega \\ &= \frac{\int_0^\pi \left(\frac{2+n^2}{3} \right) p_0 \cos(\omega) \exp(-\beta \gamma E p_0 \cos(\omega)) d\Omega}{\int_0^\pi \exp(-\beta \gamma E p_0 \cos(\omega)) d\Omega} \\ &= -p_0 \left(\frac{2+n^2}{3} \right) \mathcal{L}(\beta \gamma E p_0). \end{aligned} \quad (81)$$

Here, \mathcal{L} represents the Langevin's function. In our derivation we assume an azimuthal symmetry. Inserting the Boltzmann's distribution functions of ions (Eqs. (69), (70)) and the expression for polarization (Eq. (81)),

$$\begin{aligned} P_{orient}(x) &= n_w p \langle \cos(\omega) \rangle_\omega \\ &= -n_w p_0 \left(\frac{2+n^2}{3} \right) \mathcal{L}(\beta \gamma E p_0) \end{aligned} \quad (82)$$

into Eq. (64), we get the expression for the average microscopic volume charge density in an electrolyte solution:

$$\begin{aligned} \rho(x) &= -2e_0 n_0 \sinh(\beta e_0 \phi_c(x)) + \\ &+ n_w p_0 \left(\frac{2+n^2}{3} \right) \frac{d}{dx} \left(\mathcal{L}(\beta \gamma E p_0) \right). \end{aligned} \quad (83)$$

Inserting the above expression for average microscopic volume charge density $\rho(x)$ into the Poisson's equation,

$$\phi_c''(x) = -\frac{\rho(x)}{n^2 \varepsilon_0}, \quad (84)$$

we get

$$\begin{aligned} \phi_c''(x) &= \frac{1}{n^2 \varepsilon_0} \left[2e_0 n_0 \sinh(\beta e_0 \phi_c(x)) - \right. \\ &\left. - n_w p_0 \left(\frac{2+n^2}{3} \right) \frac{d}{dx} \left(\mathcal{L}(\beta \gamma E p_0) \right) \right], \end{aligned} \quad (85)$$

where $\phi_c''(x)$ is the second derivative of the electric potential $\phi_c(x)$ with respect to x . As mentioned, this Langevin's PB differential equation is subject to two boundary conditions. The first boundary condition arises from the electro-neutrality of the system. If we integrate Eq. (85) once over the whole system, we get (see Appendix B),

$$\begin{aligned} \phi_c'(x=0) &= -\frac{1}{n^2 \varepsilon_0} \left[\sigma + n_w p_0 \left(\frac{2+n^2}{3} \right) \cdot \right. \\ &\left. \cdot \mathcal{L}(\beta \gamma p_0 E|_{x=0}) \right]. \end{aligned} \quad (86)$$

Here we also consider the second boundary condition, which states that the electric potential far away from the charged surface is constant $\phi_c'(x \rightarrow \infty) = 0$, rendering $\mathcal{L}(\beta \gamma p_0 E|_{x \rightarrow \infty}) = 0$. Based on Eq. (82) and Eq. (43), we can express the effective permittivity of the electrolyte solution (ε_r) in contact with the planar charged membrane surface as

$$\begin{aligned} \varepsilon_r &= n^2 + \frac{|P_{orient}|}{\varepsilon_0 E_c} \\ &= n^2 + n_w \frac{p_0}{\varepsilon_0} \left(\frac{2+n^2}{3} \right) \frac{\mathcal{L}(\beta \gamma E p_0)}{E_c}. \end{aligned} \quad (87)$$

Eq. (85) can be rewritten in a more general form as:

$$\begin{aligned} \nabla \cdot \left[\varepsilon_0 n^2 \nabla \phi_c(\mathbf{r}) \right] + n_w p_0 \left(\frac{2+n^2}{3} \right) \nabla \cdot \left(\mathbf{n}_\phi \mathcal{L}(\beta \gamma E p_0) \right) \\ = 2e_0 n_0 \sinh(\beta e_0 \phi_c(\mathbf{r})), \end{aligned} \quad (88)$$

where $\mathbf{n}_\phi = \nabla \phi_c / |\nabla \phi_c| = \nabla \phi_c / E_c$. It follows from Eq. (88) that

$$\begin{aligned} \nabla \cdot \left[\varepsilon_0 \left(n^2 + \frac{n_w p_0}{\varepsilon_0} \left(\frac{2+n^2}{3} \right) \frac{\mathcal{L}(\beta \gamma E p_0)}{E_c} \right) \nabla \phi_c(\mathbf{r}) \right] \\ = 2e_0 n_0 \sinh(\beta e_0 \phi_c(\mathbf{r})). \end{aligned} \quad (89)$$

Eq. (89) can finally be rewritten in the form

$$\nabla \cdot [\varepsilon_0 \varepsilon_r(\mathbf{r}) \nabla \phi_c(\mathbf{r})] = -\rho_{free}(\mathbf{r}), \quad (90)$$

where $\rho_{free}(\mathbf{r})$ is the macroscopic (net) volume charge density of coions and counterions, while $\varepsilon_r(\mathbf{r})$ is defined by Eq. (87). A more general version of the boundary condition (Eq. (86)) is

$$\begin{aligned} \nabla \phi_c(\mathbf{r} = \mathbf{r}_{surf}) &= -\frac{1}{n^2 \varepsilon_0} \left[\sigma \mathbf{n}_\phi + \mathbf{n}_\phi n_w p_0 \left(\frac{2+n^2}{3} \right) \cdot \right. \\ &\left. \cdot \mathcal{L}(\beta \gamma p_0 E(\mathbf{r})|_{\mathbf{r}=surf}) \right]. \end{aligned} \quad (91)$$

Rearranging, it follows that

$$\nabla\phi_c(\mathbf{r} = \mathbf{r}_{surf}) \left[1 + \frac{\mathbf{n}_\phi}{|\nabla\phi_c(\mathbf{r} = \mathbf{r}_{surf})|} \frac{n_w p_0}{n^2 \varepsilon_0} \left(\frac{2 + n^2}{3} \right) \cdot \mathcal{L}(\beta\gamma p_0 E(\mathbf{r})|_{\mathbf{r}=\mathbf{r}_{surf}}) \right] = -\frac{\sigma}{n^2 \varepsilon_0} \mathbf{n}_\phi. \quad (92)$$

Evaluating the second expression on the left-hand side of Eq. (92) gives

$$\frac{\mathbf{n}_\phi}{|\nabla\phi_c(\mathbf{r} = \mathbf{r}_{surf})|} = \frac{\nabla\phi_c(\mathbf{r} = \mathbf{r}_{surf})}{|\nabla\phi_c(\mathbf{r} = \mathbf{r}_{surf})|} \frac{1}{|\nabla\phi_c(\mathbf{r} = \mathbf{r}_{surf})|} = \frac{1}{E_c(\mathbf{r} = \mathbf{r}_{surf})}. \quad (93)$$

Combining this simplification with Eq. (82), Eq. (92) becomes

$$\nabla\phi_c(\mathbf{r} = \mathbf{r}_{surf}) \varepsilon_r(\mathbf{r} = \mathbf{r}_{surf}) = -\frac{\sigma \mathbf{n}_\phi}{\varepsilon_0}. \quad (94)$$

Here we also take into account the expression for ε_r (Eq. (87)). We see that the term inside the square brackets on the left-hand side of Eq. (92) is precisely the definition of the relative permittivity on the surface of charged membrane $\varepsilon_r(\mathbf{r} = \mathbf{r}_{surf})$ (Eq. (87)), yielding the general result

$$\nabla\phi_c(\mathbf{r} = \mathbf{r}_{surf}) = -\frac{\sigma \mathbf{n}_\phi}{\varepsilon_0 \varepsilon_r(\mathbf{r} = \mathbf{r}_{surf})}. \quad (95)$$

5 DISCUSSION

In the past, treatments of cavity and reaction fields and the structural correlations between water dipoles in the Onsager's (25), Kirkwood's (26) and Fröhlich's (27) models were limited to cases of relatively small electric field strengths, far away from the saturation limit of polarization and orientational ordering of water molecules. High magnitudes of the electric field strength in a saturation regime were later taken into account in (16; 20; 28; 32) and other similar works. Besides the saturation in polarization/water dipole orientation at high magnitudes of the electric field strength (13; 16; 28; 32), the important thing to consider in the EDL studies is also the saturation in the counterion concentration near the charged surface due to the finite size of ions (steric interactions), first considered in the Wicke-Eigen's model (also called the Bikerman's model) and their modifications (3; 6; 33–38).

Generalization of the Kirkwood-Onsager-Fröhlich's theory with the intention of taking into account the saturation of polarization at high magnitudes of the electric field strength was first performed by Booth (28). The generalization of the Kirkwood-Onsager-Fröhlich's theory in the saturation regime in the EDL theory (16; 29; 32) was recently discussed in (40).

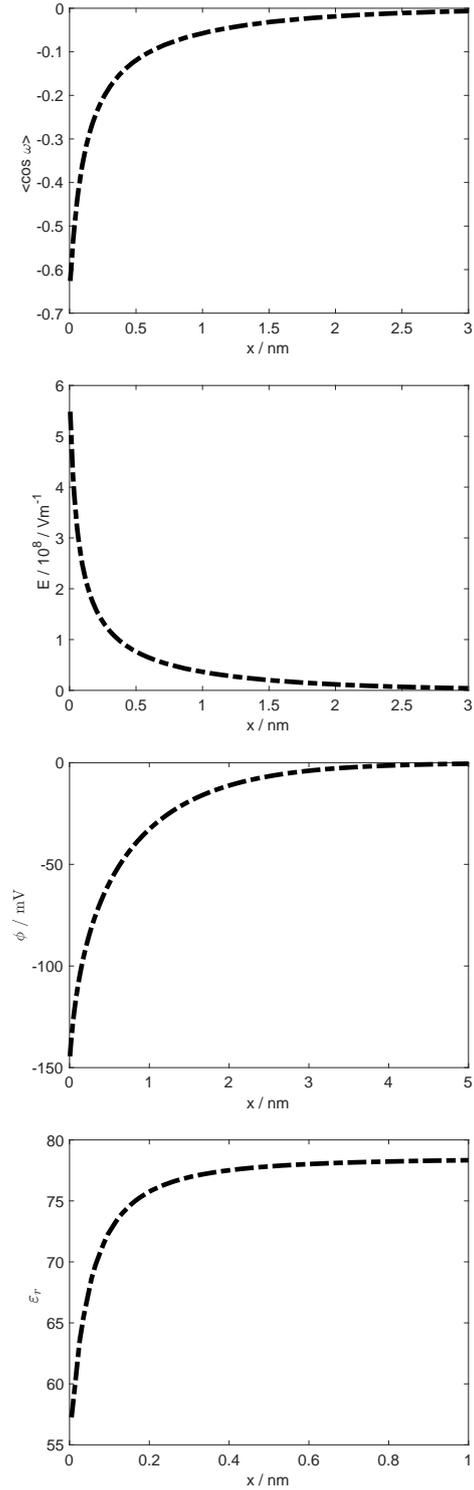


Figure 3. Average orientation ($\langle \cos(\omega) \rangle_\omega$), electric field magnitude (E), potential magnitude (ϕ) and relative permittivity (ε_r) in the electric double layer as a function of the distance from a negatively charged surface $x = 0$ calculated within the MLPB model. The bulk concentration of counterions and coions $n_0 = 0.1 \text{ mol/l}$ and $\sigma = -0.3 \text{ As/m}^2$.

Recently Lopez-Garcia et al. (40) applied the 19th century Maxwell's mixture formula (39) describing the ions as dielectric spheres within an oversimplified macroscopic thermodynamic phenomenological model with many free model parameters to fit the experimentally estimated dependence of the differential capacitance on the electric potential drop. One among many totally unjustified and oversimplified assumptions in (40) is the assumption of a surface charge density-independent relative permittivity in the inner (Stern) layer which is clearly not the case. Due to orientational ordering of water dipoles, the relative permittivity of the Stern's layer depends on the electric field strength, i.e. on the surface charge density (σ) of the electrode (41; 42). Fitting the model curves with many free model parameters to the experimental points (40) cannot prove that the inner (Stern) layer capacitance and permittivity are σ -independent.

The decrease in the relative permittivity close to the charged surface (electrode) is obviously partially the consequence of orientational ordering of water dipoles close to the saturation regime or in the saturation regime as shown theoretically in (10; 13; 15–17; 19–21; 32; 36; 41), a fact totally neglected in (40). Simulations of EDL clearly showed that orientational ordering of water molecules in an electrolyte solution is increased in the direction towards the charged (electrode) surface, including the Stern's and diffuse layers (43), amounting to a decrease in the relative permittivity in this direction, which is in accordance with theoretical predictions (see (29) and references therein). Therefore, the phenomenological approach in (40), with the σ -independent permittivity in the inner (Stern) layer and assumed decrease in the electrolyte solution permittivity in a diffuse layer due to the presence of the dielectric spherical ions with the assumed lower relative permittivity than that of the bulk water cannot contribute to a better understanding of the physics of the electric double layer, since the basic physical mechanism of the decrease in the relative permittivity, i.e. the orientational ordering of water molecules in Stern and diffuse layer, is totally neglected.

Lopez-Garcia et al. (40) claimed that close to the electrode, almost all water molecules belong to water shells around the ions while the free water molecules are excluded. This is certainly not true, namely the results of simulations clearly predicted the increased water ordering in the direction towards the charged surface (including the region close to the charged surface) (43) even for high salt concentrations, in agreement with our theoretical predictions (compare Fig.6 in (43) and Fig.4 in (29)). For example, for the surface charge density magnitude 0.16 As/m^2 there is practically no difference in orientational ordering and space distribution of water dipoles close to the charged surface between water with

and without NaCl (of concentration 500 mmol/l) (43). In general, for the magnitudes of the surface charge density up to around 0.3 As/m^2 , where the mean-field approach can still be justified, there is only a weak quantitative influence of salt on the profile of orientational ordering of water dipoles in Stern and diffuse layers, but no qualitative influence (43). Note that the multi-layering of water predicted in simulations (43) cannot be predicted within our mean-field approach (16; 32) as well also not in (40). In (40) it is also claimed that in model (32), the space occupied by the ions behaves just as a vacuum which is not true since the model assumes that the permittivity of hydrated ions is equal to n^2 (considered also in (16; 32) and other works), where n is the refractive index of water (see also (27; 28)). This means that it assumes that the electronic polarizability of hydrated ions is equal to electronic polarizability of water (16; 32). This is obviously a very rough approximation, but certainly in (32), the space occupied by ions is not considered a vacuum.

In (40), it is further argued that in (32) the magnitude of the external dipole moment is 3.1 D rather than 'generally accepted' 1.85 D (similarly as in Fig. 3) and that this is done in order to recover the water permittivity when the ionic concentrations vanish. Value 3.1 D is certainly not selected in order to recover the water permittivity when the ionic concentrations vanish, but rather in order to get the bulk permittivity around 78.5 for the vanishing electric field in the bulk solution which can be clearly understood from the expansion of the permittivity as a function of the magnitude of the electric field strength and electric potential (see for example the similar expansion of the permittivity given in (16)). The authors of (40) also overlook that in (32) and other similar works there is no referencing to the Onsager's model, using instead the generalized Kirkwood-Onsager-Fröhlich's theory which can also be used in the saturation regime of the water dipole orientational ordering and polarization.

The dipole moment of a water molecule in liquid water differs from that of an isolated water molecule because each molecule is further polarized by the electric field of its neighbours which can be taken into account by means of the cavity and reaction fields (13; 16; 27; 28) and correlations between water dipoles (27; 28; 44). The magnitude of the external dipole moment of an isolated water molecule is indeed around 1.85 D which is a smaller value than the dipole moment of a water molecule in clusters ($p_0 = 2.7 \text{ D}$), and the average dipole moment of a water molecule in the bulk solution ($p_0 = 2.4\text{--}2.6 \text{ D}$) (24). The value 3.1 D in (32) is considerably smaller than the corresponding value 4.79 D used in models (17) and (18), which both did not take into account the cavity field and the electronic polarizability of water molecules (27) as it was later

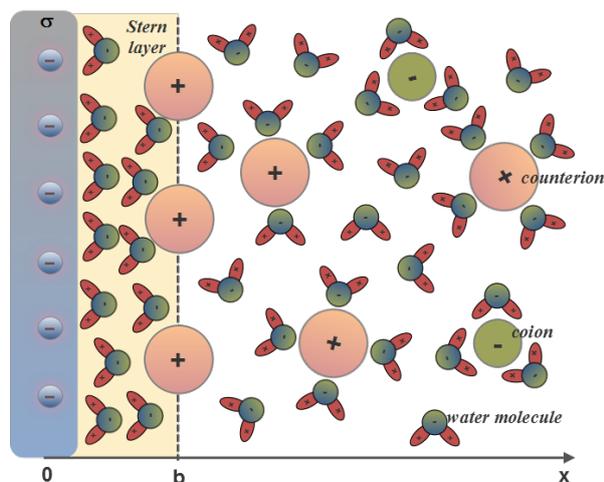


Figure 4. Schematic figure of the electric double layer showing cations, anions and water molecules in contact with a negatively charged planar surface. Distance b denotes the distance of the closest approach (also called the outer Helmholtz's plane), approximately equal to the hydration radius of the counterions (cations in our case) (41).

considered in (16; 29; 32). Including the structural correlations between water dipoles (direct interactions term) (28) would further decrease the magnitude of the external dipole moment to the value around 2.0 D as shown in Fig.8 in (14). However, the Booth's model does not consider the excluded volume effect and non-homogeneous distribution of water molecules as it is the case in the electric double layer close to the charged surface (16; 32). Therefore Booth's model, which considers the direct interactions and structural correlations between water molecules (28), can be applied in a simple way only in the Langevin Poisson-Boltzmann's model for the point-like molecules (13; 14; 29), but not also in (16; 32), where the finite size of molecules in an electrolyte solution is taken into account.

In (40), the authors also argued that in (32) the same value of the magnitude of the external dipole moment of water molecules (i.e. 3.1 D) was used for all values of the electric field, including the strong electric field in the saturation regime. As it is explained above, a somewhat larger value of p_0 determined experimentally in water clusters is mainly the consequence of neglect of the direct interactions between water dipoles (28) which are however not crucially dependent on the electric field. The polarization in (32) depends on the electric field strength due to the electronic polarizability term (see the first term in the expression for the relative permittivity (Eq. 41) and due to the orientational ordering term (see the second term in Eq. 41).

Note that in the case of considering the space-dependent number density of water molecules $n_w(x)$ in Eq. (44), the Eq. (53) for bulk permittivity would transform into (32)

$$\varepsilon_r = n^2 + \left(\frac{2 + n^2}{3} \right)^2 \frac{[n_s - (\alpha_+ + \alpha_-)n_0]p_0^2\beta}{2\varepsilon_0}, \quad (96)$$

where we took into account that in the bulk of the solution (32):

$$n_w(x \rightarrow \infty) = n_s - \alpha_+ n_0 - \alpha_- n_0. \quad (97)$$

Here, n_s is the number density of lattice sites in the EDL model which takes into account the finite size of molecules and α_+ and α_- are the numbers of lattice sites occupied by a single positive and a single negative hydrated ion, respectively (32). We assume that a single water molecule occupies just one lattice site, therefore $n_s/N_A = 55$ mol/l. Eq. (96) predicts the linear decrement of the relative permittivity in bulk solution with salt concentration. Experiments show linear decrement from $\varepsilon_r \approx 78.5$ at zero NaCl concentration to $\varepsilon_r \approx 58$ at 2 mol/l NaCl concentration (46), corresponding to $(\alpha_+ + \alpha_-) \approx 7.5$ in Eq. (96).

6 CONCLUSION

In the present paper we present a thorough derivation of the relation between the external and internal dipole moment of a water molecule. In the model, the water molecule is considered as a rigid sphere with internal point-like dipole \mathbf{p} inserted into a homogenous electric field. We see that the external dipole moment depends on the local field arising from the contribution of the point-like dipole at the center of the sphere, since the net charge is accumulated at the interface of two dielectrics with differing permittivities, and the outside cavity field arising from the contributions of other water molecules surrounding the sphere. We calculate the energy of such a dielectric sphere (with a point-like dipole in the centre) in an electric field. Furthermore, considering orientational ordering of water molecules in the electric double layer, we derive the spatial dependency of the relative permittivity within the MLPB model. At small values of the electrostatic field, we see that such an approximation limits to the Onsager's expression for the bulk permittivity. As shown in (43), an addition of NaCl even at high concentrations (0.5 M) affects the spatial and orientational arrangement adopted by the water molecules only for very high magnitudes of surface charge density σ . Lower magnitudes of the surface charge densities, which still allow for the mean-field approach, barely affect the ordering of the water layers, as already mentioned above. A stronger salt effect on the orientation angle of the water molecules is predicted for higher magnitudes of the surface charge density (43), however, the average orientation angle of

the water dipoles profile is not qualitatively changed after the addition of NaCl even at a concentration of 0.5 M for low enough surface charge densities (43). For example, for the surface charge density 0.16 As/m², there is only a very small quantitative difference in the water average orientation profile between the two cases with and without NaCl (43). Even at the magnitude of the surface charge density 0.48 As/m², the shape of the average orientation angle profile is not changed substantially after the addition of NaCl, but only decreased in values (43). Based on these results, we conclude that considering the orientational ordering of water dipoles in Stern and diffuse layers (10; 13; 15–17; 19–21; 29; 32; 36; 41) is essential to realistically capture the basic physical properties of EDL and cannot be neglected as it is done in some oversimplified 19th century based macroscopic phenomenological models of EDL (40), where the statistical physics orientational ordering of water dipoles in EDL is not taken into account.

APPENDIX APPENDIX A

Helmholtz's free energy F , defined in Eq. (58), is defined as a sum of independent contributions, labelled as

$$F = F_{el}^{+, -, \mathcal{P}} + F_{mix}^{+, -} + F_{mix}^{\mathcal{P}} + F_c^{+, -} + F_c^{\mathcal{P}, \eta}. \quad (98)$$

First term $F_{el}^{+, -, \mathcal{P}}$ accounts for the electrostatic contributions of coions and counterions and the Langevin's dipoles polarization contribution, the second term $F_{mix}^{+, -}$ for the mixing entropy free energy contributions of coions and counterions, the third term $F_{mix}^{\mathcal{P}}$ for the orientational entropy of the Langevin's dipoles, while the fourth and fifth terms $F_c^{+, -}$ and $F_c^{\mathcal{P}}$ contain constraints of the system, the former ensuring a constant number of ions and the latter the local constraint for the orientation of the Langevin's dipoles. For the sake of a compact nomenclature, we write multiple superscripts to indicate independent sums of specific contributions, so that, for example, the electrostatic contribution expands into three independent integrals

$$F_{el}^{+, -, \mathcal{P}} = F_{el}^+ + F_{el}^- + F_{el}^{\mathcal{P}}. \quad (99)$$

Likewise holds for multiple subscripts. A compact expression including all three integrals for counterions would read

$$F_{el, mix, c}^+ = F_{el}^+ + F_{mix}^+ + F_c^+. \quad (100)$$

Since the variation of the total Helmholtz's free energy must be zero, it follows that the sum of the variations must be equal to zero. Using the new compact nomenclature for factoring out common terms, the variation of

Eq. (98) can be rewritten

$$\delta F = \delta F_{el, mix, c}^+ + \delta F_{el, mix, c}^- + \delta F_{el, mix, c}^{\mathcal{P}} + \delta F_c^\eta = 0. \quad (101)$$

We see that the total variation becomes the sum of variations of four independent functions: the number density of counterions ($\delta n_+(x)$, corresponding to $\delta F_{el, mix, c}^+$), the number density of coions ($\delta n_-(x)$, corresponding to $\delta F_{el, mix, c}^-$), the probability of the Langevin's dipoles orientation ($\delta \mathcal{P}(x, \omega)$, corresponding to $\delta F_{el, mix, c}^{\mathcal{P}}$) and the local constraint of the Langevin's dipoles orientation function ($\delta \eta(x)$, corresponding to δF_c^η). Bearing in mind the derivations from the body of the text (Eqs. (60-75)), Eq. (101) expands into

$$\begin{aligned} \delta F = & \underbrace{\int dV \delta n_+(x) \left[kT \left(\ln \frac{n_+(x)}{n_0} + \lambda_+ \right) + \phi_c e_0 \right]}_{\delta F_{el, mix, c}^+} + \\ & + \underbrace{\int dV \delta n_-(x) \left[kT \left(\ln \frac{n_-(x)}{n_0} + \lambda_- \right) - \phi_c e_0 \right]}_{\delta F_{el, mix, c}^-} + \\ & + \underbrace{\int dV n_w \langle \delta \mathcal{P}(x, \omega) \left(\nabla \phi_c \cdot \mathbf{p} + \frac{\ln \mathcal{P}(x, \omega) + \eta(x) + 1}{\beta} \right) \rangle_\omega}_{\delta F_{el, mix, c}^{\mathcal{P}}} + \\ & + \underbrace{kT \int dV n_w \delta \eta(x) \left(\langle \mathcal{P}(x, \omega) \rangle_\omega - 1 \right)}_{\delta F_c^\eta} = 0. \end{aligned} \quad (102)$$

The expressions multiplied by $\delta n_+(x)$, $\delta n_-(x)$, $\delta \mathcal{P}(x, \omega)$ and $\delta \eta(x)$ must therefore equal zero, resulting in a system of equations

$$kT \left(\ln \frac{n_+(x)}{n_0} + \lambda_+ \right) + \phi_c e_0 = 0, \quad (103)$$

$$kT \left(\ln \frac{n_-(x)}{n_0} + \lambda_- \right) - \phi_c e_0 = 0, \quad (104)$$

$$E_c p \cos \omega + \frac{\ln \mathcal{P}(x, \omega) + \eta(x) + 1}{\beta} = 0, \quad (105)$$

$$\langle \mathcal{P}(x, \omega) \rangle_\omega - 1 = 0. \quad (106)$$

Here, we take into account the Boltzmann's factor $\beta = 1/kT$ and the dot product $\nabla \phi_c \cdot \mathbf{p} = E_c p \cos(\omega)$.

APPENDIX B

The electroneutrality of the system supposes that the total net charge of the system is zero, hence

$$\int \rho_{free}(\mathbf{r}) dV - \sigma S = 0, \quad (107)$$

where σ is the negative membrane surface charge density, S is the total membrane surface area and $\rho_{free}(\mathbf{r})$ is the macroscopic (net) volume charge density of coions and counterions. Since the macroscopic volume charge

density is only dependent on x (Eq. (83)) and the differential $dV = S dx$, Eq. (107) may be rewritten

$$\int_0^{\infty} 2e_0 n_0 \sinh(\beta e_0 \phi_c(x)) dx = -\sigma. \quad (108)$$

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