

Polarization of Water near Dipolar Surfaces: A Simple Model for Anomalous Dielectric Behavior

Marian Manciu*

Department of Physics, University of Texas at El Paso, El Paso, Texas 79968

Eli Ruckenstein‡

Department of Chemical and Biological Engineering, State University of New York at Buffalo, Buffalo, New York 14260

Received July 5, 2005. In Final Form: September 17, 2005

A model for the electrostatic interactions in water in the vicinity of a surface is suggested, which accounts, within the Poisson–Boltzmann mean field approach, for the screening of the charges and for the coupling interactions between neighboring dipoles. When the water molecules near a solid surface are assumed to be organized in icelike layers, the polarization is not a continuous function but exists only at the discrete positions of the water molecules. The particular positions of the water molecules in the icelike structure govern the manner in which the average water dipoles align with each other. On the basis of this model, one could explain the nonmonotonic behavior of the polarization and the electrical potential as well as the anomalous dielectric response of water (the nonproportionality of the polarization and the macroscopic electric field), which were obtained recently via molecular dynamics simulations.

1. Introduction

The interactions between charged particles in water is described in the traditional Derjaguin–Landau–Verwey–Overbeek (DLVO) model by a van der Waals attraction between particles, coupled with a double layer repulsion due to the overlapping of the ion clouds formed near charged surfaces.¹ In the traditional approach, the ions are assumed to have Boltzmannian distributions in a mean electric field generated by charges, which in turn obeys the Poisson equation with a uniform dielectric constant (corresponding to bulk water).² These assumptions are oversimplified, and many corrections to the model have been proposed to improve its accuracy (by accounting for image forces, finite sizes of the hydrated ions, ion correlations, dependence of dielectric constant on the field and electrolyte concentration, ion hydration and ion dispersion forces, etc.; for a recent review, see ref 3).

Whereas the corrections to the traditional Poisson–Boltzmann approach could explain many experimental results, there are systems, such as the vesicles formed by neutral lipid bilayers in water, for which an additional force is required to explain their stability.⁴ This force was related to the organization of water in the vicinity of hydrophilic surfaces; therefore it was called “hydration force”.⁵

The first physical models for the hydration force related the interactions to the polarization of water near a surface,

and two different approaches were proposed concomitantly.^{6,7} One of these models⁷ was based on the observation that the exponential decaying force, observed experimentally, is mathematically equivalent to a Landau order-parameter expansion if only the quadratic terms of the expansion are retained.⁸ While the physical grounds for such an expansion remained obscure,⁸ it was later conjectured that the Bjerrum defects might constitute the source of the polarization field in analogy with the ions, which provide the source of the electric field.⁷ The polarization and the electric fields are no longer considered proportional to each other, and coupled equations for them were obtained through a variational procedure. A suitable concentration of Bjerrum defects had to be selected to match the experimental results for the hydration force.⁷

The Gruen–Marcelja model could relate the hydration force to the physical properties of the surfaces by assuming that the polarization of water near the interface is proportional to the surface dipole density.⁹ This assumption led to the conclusion that the hydration force is proportional to the square of the surface dipolar potential of membranes (in agreement with the Schiby–Ruckenstein model),⁶ a result that was confirmed by experiment.¹⁰ However, subsequent molecular dynamics simulations revealed that the polarization of water oscillated in the vicinity of an interface, instead of being monotonic.¹¹ Because the Gruen–Marcelja model was particularly built to explain the exponential decay of the polarization, it was clearly invalidated by the latter simulations. Other conceptual difficulties of this model have been also reported.^{12,13}

* Corresponding author. Phone: (915) 747-7531; fax: (915) 747-5447; e-mail: mmanciu@utep.edu.

‡ Phone: (716) 645-2911/2214; fax: (716) 645-3822; e-mail: feaeliru@acsu.buffalo.edu.

(1) Deryagin, B. V.; Landau, L. *Acta Physicochim. URSS* **1941**, *14*, 633; Verwey, E. J.; Overbeek, J. Th. G. *Theory of Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.

(2) Gouy, G. *J. Phys. Radium* **1910**, *9*, 457; Chapman, D. L. *Philos. Mag.* **1913**, *25*, 475.

(3) Manciu M.; Ruckenstein, E. *Adv. Colloid Interface Science* **2003**, *105*, 63.

(4) Rand, R. P.; Parsegian, V. A. *Biochim. Biophys. Acta* **1989**, *988*, 351.

(5) Derjaguin, B. V.; Churaev, N. V.; Muller, V. M. *Surface Forces*; Plenum Publishing: New York, 1987.

(6) Schiby, D.; Ruckenstein, E. *Chem. Phys. Lett.* **1983**, *95*, 435.

(7) Gruen, D. W. R.; Marcelja, S. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 211.

(8) Marcelja, S.; Radic, N. *Chem. Phys. Lett.* **1976**, *42*, 129.

(9) Cevc, G.; Marsh, D. *Biophys. J.* **1985**, *47*, 21.

(10) Simon, S. A.; McIntosh, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 9263.

(11) Berkowitz, M. L.; Raghavan, K. *Langmuir* **1991**, *7*, 1042.

(12) Attard, P.; Wei, D. Q.; Patey, G. N. *Chem. Phys. Lett.* **1990**, *172*, 69.

Recent molecular dynamics simulations of water between two surfactant (sodium dodecyl sulfate) layers, reported by Faraudo and Bresme,¹⁴ revealed oscillatory behaviors for both the polarization and the electric fields near a surface and that the two fields are not proportional to each other. While the nonmonotonic behavior again invalidated the Gruen–Marcelja model for the polarization, the nonproportionality suggested that a more complex dielectric response of water might be at the origin of the hydration force. The latter conclusion was also supported by recent molecular dynamics simulations of Faraudo and Bresme, who reported interactions between surfactant surfaces with a nonmonotonic dependence on distance.¹⁵

This type of oscillatory hydration was previously observed experimentally in interactions between mica surfaces in water,¹⁶ and has been associated with the layering of water in the vicinity of a surface.^{16,17} The discrete nature of the water molecules, considered hard spheres, was suggested to be responsible for these nonmonotonic interactions;^{18,19} however, the high fluidity of the water confined in molecularly thin films²⁰ seems to be inconsistent with the “crystallization” of water predicted by the hard-sphere model.¹⁸

It is commonly accepted that nonassociative liquids have the tendency to crystallize near surfaces.²¹ Whether or not water is layered near a surface, however, is still under debate. Experiments on phospholipid bilayers involving coherent anti-Stokes Raman scattering (CARS) microscopy²² or electron spin resonance (ESR)²³ indicate that the water is highly ordered in the vicinity of a surface containing strong dipoles, with the permanent dipoles of the water molecules aligned parallel to the surface dipoles. The alignment is so strong that it weakens the hydrogen bonding in water near a strong dipolar interface.²²

Even if one assumes that the water near a surface has the same structure as it does in bulk, the oscillations of the short-range interactions between surfaces could be explained by a nonlocal dielectric constant for water.²⁴ This model assumes that the dielectric displacement field ($D = \epsilon_0 E + P$) at a position r not only depends on the local electric field [$D(r) = \epsilon(r)E(r)$], but also depends on the electric field in the whole space: $D(r) = \int \epsilon(r, r')E(r')dr'$. In this model, the oscillations of the interactions are due to charge overscreening²⁵ and are analogous to the charge density waves in plasmas.²⁴

Whereas in the Henderson and Lozada–Cassou model¹⁸ the oscillatory hydration interactions are not affected much by the electrolyte concentration, in the Cheperanov model²⁴ the electrolyte concentration plays a major role (the oscillations increasing resonantly for concentrations larger than 0.01 M). Both models^{18,24} predict many oscillations in the hydration interactions with a periodicity of ~ 2 Å, which is in excellent agreement with the

experiment for the force between mica surfaces at 10^{-3} M. However, they are inconsistent with the polarization data obtained via molecular dynamics simulations of electrolyte solutions of higher ionic strengths confined between flat surfaces.^{11,14} Because the above models do not relate the magnitude of the hydration force to the physical properties of the surfaces, they cannot explain why in most systems the hydration interactions are monotonic functions of the separation distance (such as for neutral lipid bilayers),⁴ why their magnitude depends on the surface dipole density,^{4,10} and why the hydration decay length itself depends on the nature of the surface (being ~ 2 Å for neutral lipid bilayers, but on the order of 10 Å for the interactions between mica surfaces).²⁶ It was recently shown that all of the above effects could be explained within the framework of Ruckenstein’s model for water polarization.²⁷

Let us now briefly review the basics of the model for water polarization proposed by Schiby and Ruckenstein.⁶ The main idea was that the neighboring dipoles are able to orient each other, a hypothesis that seems to be validated by more recent experiments.^{22,23} A planar surface with a homogeneous, constant surface dipole density cannot generate any electric field in a continuous medium. At any point, the field generated by the neighboring dipoles is exactly compensated by the opposing field of the more remote dipoles. Consequently, in a continuum theory (such as the Gruen–Marcelja model),⁷ the surface dipoles are not able to polarize the nearby water molecules. However, at the molecular level water is hardly a continuum, and the interactions between neighboring dipoles are much stronger than the interactions between remote dipoles, which are screened by the intervening water molecules.¹³ Therefore, one can expect on intuitive grounds that the electrical interactions between neighboring dipoles take place in a medium with a much lower dielectric constant than that of bulk water. Because of the change in dielectric screening with distance, the fields generated by the neighboring and the remote dipoles do not cancel each other any longer, and a net electric field is generated in the medium. This field is able to polarize the neighboring dipoles, which in turn generate electric fields in their vicinity, polarizing their neighboring dipoles and so on, which is in agreement with the recent CARS microscopy results for the orientation of water molecules in the vicinity of a phospholipid bilayer surface.²²

To calculate the dipole correlations, Schiby and Ruckenstein assumed a homogeneous distribution of water molecules, which simplified the calculations considerably and led to an exponential decay of the polarization of water from a dipolar surface. The overlap of the polarized regions, when two surfaces approach one another, increases the free energy of the system, and this generates a repulsion with a roughly exponential behavior, which has a magnitude and a decay length that are very similar to the hydration forces measured in neutral lipid bilayers systems.⁴

The monotonic decay of the polarization in the Schiby–Ruckenstein model (the main critique of the polarization models) is a consequence of the assumption of the homogeneous distribution of water molecules in the vicinity of the surface. However, when the water was assumed to be structured in icelike layers in the vicinity of the surface, the polarization became an oscillatory function of the distance from the interface.¹³ This result was due to the particular locations of the water molecules

(13) Manciu, M.; Ruckenstein, E. *Langmuir* **2001**, *17*, 7582.

(14) Faraudo, J.; Bresme, F. *Phys. Rev. Lett.* **2004**, *92*, 236102.

(15) Faraudo, J.; Bresme, F. *Phys. Rev. Lett.* **2005**, *94*, 077802.

(16) Israelachvili, J. N.; Pashley, R. M. *Nature* **1983**, *306*, 249.

(17) Cleveland, J. P.; Schaeffer, T. E.; Hansma, P. K. *Phys. Rev. B* **1995**, *52*, R8692.

(18) Henderson, D.; Lozada-Cassou, M. *J. Colloid Interface Sci.* **1986**, *114*, 180.

(19) Trokhymchuk, A.; Henderson, D.; Wasan, D. T. *J. Colloid Interface Sci.* **1999**, *210*, 320.

(20) Zhu, Y. X.; Granick, S. *Phys. Rev. Lett.* **2001**, *87*, 096104.

(21) Israelachvili, J. N.; McGuigan, P. M.; Homola, A. M. *Science* **1988**, *240*, 189.

(22) Cheng, J.-X.; Pautot, S.; Weitz, D. A.; Xie, X. S. *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 9826.

(23) Ge, M.; Freed, J. H. *Biophys. J.* **2003**, *85*, 4023.

(24) Cherepanov, D. A. *Phys. Rev. Lett.* **2004**, *93*, 266104.

(25) Kornyshev, A. A.; Leikin, S.; Sutmann, G. *Electrochim. Acta* **1997**, *42*, 849.

(26) Pashely, R. M. *J. Colloid Interface Sci.* **1981**, *83*, 531.

(27) Manciu, M.; Ruckenstein, E. *Adv. Colloid Interface Sci.* **2004**, *112*, 109.

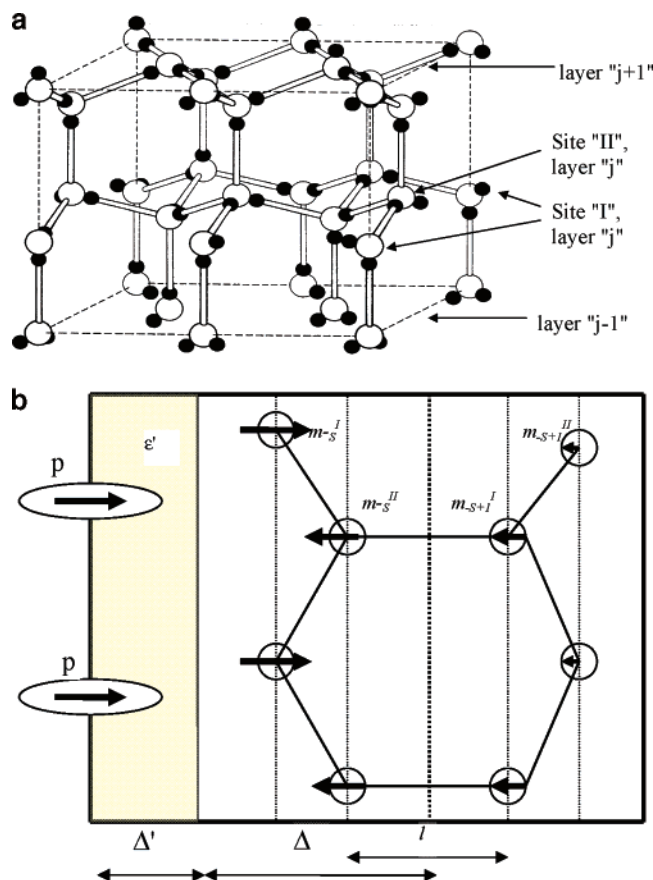


Figure 1. (a) The structure of ice-I. Each water molecule is connected by hydrogen bonding with three water molecules from sites of different kind of the same layer and one water molecule from one of the adjacent layers. The two different sites I and II of the same layer are marked on the Figure. (b) A schematic model: the dipoles p of the surface groups are embedded in a medium of dielectric constant ϵ' , formed by the bound water molecules. The centers of the dipoles are at a distance Δ' from the first water layer (of thickness Δ). The polarization of the water molecules is due to the interactions with neighboring dipoles as well as with all the other charges of the system (surface charges and electrolyte ions).

in the icelike structure (see Figure 1a). In each icelike layer, the water molecules can occupy two distinct sites. As it will be shown later, the dipoles generate an electric field in the same direction in neighboring water molecules from adjacent layers; however, they generate a field in the opposite direction in the neighboring water molecules from the same layer, thus polarizing them in opposite directions. Therefore, it is possible for the dipoles of the water molecules belonging to different sites of the same layer to become oriented in antiparallel directions, leading to an oscillatory behavior in the polarization. This picture is the electrostatic equivalent of the antiferromagnetic materials, in which neighboring spins align with each other in opposite directions.

A schematic drawing is presented in Figure 1b in which the surface dipoles p align with the dipoles of the water molecules of sites "I" of the first layer "S" in the same direction, generating the average dipolar moment m_S^I , whereas the average dipole moment m_S^{II} of the water molecules of sites "II" of the same layer are oriented in opposite direction. This picture is supported by the calculations presented in Section 3. It should be noted that molecular dynamics simulations of water between flat surfaces^{11,14,15} showed an oscillatory behavior in the polarization; however, when the dynamic restrictions on

the surface headgroups were removed, the statistical fluctuations of the surfaces render the polarization a monotonic function with the distance from the surface.²⁸ This explains the monotonic decay of the hydration force obtained in most experiments¹³ and justifies the approximation employed in the Schiby–Ruckenstein model.⁶ This "smearing out" of oscillations in disordered systems was suggested by Israelachvili and Pashley¹⁶ and was analyzed more quantitatively elsewhere.¹³ It should also be noted that, if the surface dipoles are strong enough to orient all of the dipoles of the neighboring water molecules parallel to those of the surface by weakening the hydrogen bonding,²² the icelike layering of the water near the interface will be disrupted. Consequently, no oscillations in the polarization would occur.

A simple model that illustrated the behavior of the polarization when the water molecules are organized in water layers between perfectly flat surfaces was previously suggested.¹³ That model took into account the nearest-neighbor dipole interactions, but ignored the surface charges and the electrolyte ions. The model is extended here to cases in which an electrolyte as well as surface charges are also present. It will be shown that a treatment of all electrostatic interactions, in the assumption of an icelike structuring of water near interfaces, can predict an oscillatory behavior for both the polarization and the electric potential as well as a nonproportionality between the polarization and the electric fields.

It will be shown in what follows that the oscillations of the polarization are due to the structuring of water in a particular form, the coupling interactions between neighboring dipoles, the electrolyte concentration, and the boundary conditions (surface charge and surface dipole density).

2. Basic Equations

The average polarization of a water molecule is due to the electric field generated by all of the other charges and dipoles and obeys the Poisson equation, which in the vicinity of a planar surface has the form²⁹

$$\frac{d^2\psi(x)}{dx^2} = -\frac{\sum_i c_i(x)q_i}{\epsilon_0} + \frac{1}{\epsilon_0} \frac{dP(x)}{dx} \quad (1)$$

in which ψ is the electrical "mean field" potential, considered to depend only on the distance x from the planar surface; q_i is the charge of an ion of kind i and concentration $c_i(x)$; $P(x)$ is the polarization of the medium; and ϵ_0 is the vacuum permittivity. The local concentrations of the ions in the "mean" electric field are assumed to have Boltzmannian distributions:

$$c_i = c_E \exp\left(-\frac{q_i\psi(x)}{kT}\right) \quad (2)$$

in which c_E represents the electrolyte concentration in the reservoir far from the plate. By assuming that the polarization is proportional to the macroscopic field, $P = -\epsilon_0(\epsilon - 1)d\psi/dx$, the Poisson–Boltzmann equation is obtained from eqs 1 and 2. However, the Schiby and Ruckenstein model suggested that the neighboring dipoles create a supplementary field, and the average polarization

(28) Perera, L.; Essmann, U.; Berkowitz, M. L. *Prog. Colloid Polym. Sci.* **1997**, 103, 107.

(29) Ruckenstein, E.; Manciu, M. *Langmuir* **2002**, 18, 7584.

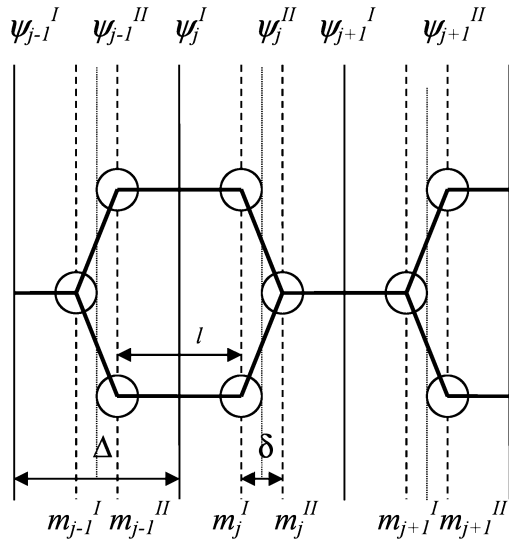


Figure 2. Sketch of the structuring of water in icelike layers in the vicinity of surfaces and the points at which the discrete variables are defined. The water molecules (circles) for the two sites of each icelike layer j have the average polarization m_j^I and m_j^{II} , respectively. The average value of the potential ψ_j^I is defined at the position between two adjacent layers $j-1$ and j , whereas ψ_j^{II} is defined at the middle of layer j .

of a water molecule is proportional to the total field acting at its location.

The molecular field acting at the location of a water molecule is composed of a macroscopic field, $E = -(\mathrm{d}\psi/\mathrm{d}x)$, a local field (the Lorentz field E_L) that occurs because each molecule is surrounded by a dielectric medium (constituted of all the other water molecules), $E_L = P/3\epsilon_0$, plus an additional field, E_P , due to the neighboring dipoles.^{13,27} Assuming that the additional field is generated only by the neighboring molecules from the same and adjacent icelike water layers (see Figure 2), at each of the sites (I or II) of layer “ j ” the field is provided by¹³

$$E_P^{I,j} = D_0^{II,I} m_j^I + D_0^{II,I} m_j^{II} + D_{-1}^{II,I} m_{j-1}^I + D_{-1}^{II,I} m_{j-1}^{II} + D_{+1}^{II,I} m_{j+1}^I + D_{+1}^{II,I} m_{j+1}^{II} \quad (3a)$$

$$E_P^{II,j} = D_0^{I,II} m_j^I + D_0^{I,II} m_j^{II} + D_{-1}^{I,II} m_{j-1}^I + D_{-1}^{I,II} m_{j-1}^{II} + D_{+1}^{I,II} m_{j+1}^I + D_{+1}^{I,II} m_{j+1}^{II} \quad (3b)$$

in which the m 's and the D 's are average dipole moments and coupling coefficients, respectively (m_j^I represents the average dipole moment of a molecule at site I of layer j , and the coupling coefficient $D_0^{I,II}$ represents the ratio between the electric field generated by all of the molecules of sites I of layer j at the positions of sites II of layer j and the average dipole moment of the former molecules, m_j^I).

The molecular polarizability of a water molecule, γ , can be related to macroscopic quantities by taking into account that, in a uniformly polarized medium, the fields generated by the near neighbors cancel each other. Consequently, one obtains²⁹

$$m = \gamma \left(E + \frac{m}{3\epsilon_0 v_0} \right) = P v_0 = \epsilon_0 v_0 (\epsilon - 1) E \quad (4)$$

in which v_0 represent the average volume occupied by a water molecule, which leads to the Claussius–Mossotti equation, $\gamma = 3\epsilon_0 v_0 (\epsilon - 1)/(\epsilon + 2)$. The average dipole

moments of the molecules in the two sites, I and II, of layer j are therefore provided by

$$m_j^I = \gamma \left(E + E_P + \frac{m_j^I}{3\epsilon_0 v_0} \right) = \epsilon_0 v_0 (\epsilon - 1) \left[-\left(\frac{\mathrm{d}\psi}{\mathrm{d}x} \right)_j^I + D_{-1}^{I,I} m_{j-1}^I + D_{-1}^{II,I} m_{j-1}^{II} + D_0^{I,I} m_j^I + D_0^{II,I} m_j^{II} + D_{+1}^{I,I} m_{j+1}^I + D_{+1}^{II,I} m_{j+1}^{II} \right] \quad (5a)$$

$$m_j^{II} = \gamma \left(E + E_P + \frac{m_j^{II}}{3\epsilon_0 v_0} \right) = \epsilon_0 v_0 (\epsilon - 1) \left[-\left(\frac{\mathrm{d}\psi}{\mathrm{d}x} \right)_j^{II} + D_{-1}^{I,II} m_{j-1}^I + D_{-1}^{II,II} m_{j-1}^{II} + D_0^{I,II} m_j^I + D_0^{II,II} m_j^{II} + D_{+1}^{I,II} m_{j+1}^I + D_{+1}^{II,II} m_{j+1}^{II} \right] \quad (5b)$$

in which the derivatives of the potentials of eqs 5a and 5b should be taken at the location of sites I and II, respectively, of layer j .

3. General Behavior of the Solutions of the System

Although the nonlinear system of equations can be solved numerically, here we focus on the linear approximation of the Poisson–Boltzmann equation (which is accurate for small values of the potentials ψ , $q\psi/kT \ll 1$). Because the average polarization of water is $P(x) = m(x)/v_0$, in this approximation eqs 1 and 2 become

$$\frac{\mathrm{d}^2 \psi}{\mathrm{d}x^2} = \frac{\epsilon}{\lambda_{\mathrm{DH}}^2} \psi + \frac{1}{\epsilon_0 v_0} \frac{\mathrm{d}m(x)}{\mathrm{d}x} \quad (6)$$

in which ϵ is the dielectric constant of water, and $\lambda_{\mathrm{DH}} = (\epsilon \epsilon_0 kT/2e^2 c_E)^{1/2}$ is the Debye–Hückel length for a uni-univalent electrolyte of concentration c_E , where e is the elementary charge, k is the Boltzmann constant, and T is the absolute temperature.

The polarizations of the water molecules are discrete quantities, being defined only at the locations of the water molecules (sites I and II in an icelike layer). To combine the discrete eq 5a,b with the continuous Poisson–Boltzmann eq 6, the latter equation must also be discretized. To do this, we define for each layer j the average discrete potentials ψ_j^I and ψ_j^{II} , which are defined at the boundary and the middle of the layer, respectively (see Figure 2). These positions were selected because the potential undergoes a steep change at the crossing of a dipolar surface (at the locations of dipoles m_j^I and m_j^{II}), whereas, in the remainder of the space, it varies slowly (only because of the distribution of electrolyte ions). By integrating eq 6 between site II of layer $j-1$ and site I of layer j , and between site I of layer j and site II of the same layer j one obtains

$$\begin{aligned} \frac{\mathrm{d}\psi}{\mathrm{d}x} \Big|_j^I - \frac{\mathrm{d}\psi}{\mathrm{d}x} \Big|_{j-1}^{II} &\cong \left(\frac{\psi_j^{II} - \psi_j^I}{\Delta/2} \right) - \\ \left(\frac{\psi_j^I - \psi_{j-1}^{II}}{\Delta/2} \right) &\equiv 2 \frac{\psi_j^{II} - 2\psi_j^I + \psi_{j-1}^{II}}{\Delta} = \frac{\epsilon}{\lambda_{\mathrm{DH}}^2} \psi_j^I (\Delta - \delta) + \\ &\quad \frac{1}{\epsilon_0 v_0} (m_j^I - m_{j-1}^{II}); \quad (7a) \end{aligned}$$

$$\frac{d\psi}{dx}\bigg|_j^{\text{II}} - \frac{d\psi}{dx}\bigg|_j^{\text{I}} \cong \left(\frac{\psi_{j+1}^{\text{I}} - \psi_j^{\text{II}}}{\Delta/2} \right) - \left(\frac{\psi_j^{\text{II}} - \psi_j^{\text{I}}}{\Delta/2} \right) \equiv 2 \frac{\psi_{j+1}^{\text{I}} - 2\psi_j^{\text{II}} + \psi_j^{\text{I}}}{\Delta} = \frac{\epsilon}{\lambda_{\text{DH}}} \psi_j^{\text{II}} \delta + \frac{1}{\epsilon_0 v_0} (m_j^{\text{II}} - m_j^{\text{I}}) \quad (7b)$$

in which Δ is the distance between the centers of two adjacent icelike layers, δ is the distance between the sites I and II of the same layer, and $d\psi/dx|_j^{\text{I}}$ represents the derivative of the potential with respect to distance, calculated at site I of layer j , which is approximated using finite differences. The same approximations in eqs 5a and 5b lead to

$$m_j^{\text{I}} = \epsilon_0 v_0 (\epsilon - 1) \left(2 \frac{\psi_j^{\text{I}} - \psi_j^{\text{II}}}{\Delta} + D_{-1}^{\text{II,I}} m_{j-1}^{\text{I}} + D_{-1}^{\text{II,I}} m_{j-1}^{\text{II}} + D_0^{\text{II,I}} m_j^{\text{I}} + D_0^{\text{II,I}} m_j^{\text{II}} + D_{+1}^{\text{II,I}} m_{j+1}^{\text{I}} + D_{+1}^{\text{II,I}} m_{j+1}^{\text{II}} \right) \quad (7c)$$

$$m_j^{\text{II}} = \epsilon_0 v_0 (\epsilon - 1) \left(2 \frac{\psi_j^{\text{II}} - \psi_{j+1}^{\text{I}}}{\Delta} + D_{-1}^{\text{I,II}} m_{j-1}^{\text{I}} + D_{-1}^{\text{I,II}} m_{j-1}^{\text{II}} + D_0^{\text{I,II}} m_j^{\text{I}} + D_0^{\text{I,II}} m_j^{\text{II}} + D_{+1}^{\text{I,II}} m_{j+1}^{\text{I}} + D_{+1}^{\text{I,II}} m_{j+1}^{\text{II}} \right) \quad (7d)$$

Consequently, there are 4 independent variables m_j^{I} , m_j^{II} , ψ_j^{I} , and ψ_j^{II} for each icelike layer j , and a system of 4 linear equations with finite differences (eqs 7a–7d) is obtained. We try solutions of the type³⁰

$$\begin{aligned} \psi_j^{\text{I}} &= ar^j \\ \psi_j^{\text{II}} &= br^j \\ m_j^{\text{I}} &= cr^j \\ m_j^{\text{II}} &= dr^j \end{aligned} \quad (8)$$

which, when introduced in the system of eqs 7a–7d, lead to

$$\left[\frac{4}{\Delta} + \frac{\epsilon}{\lambda_{\text{DH}}^2} (\Delta - \delta) \right] a - \frac{2}{\Delta} \left(1 + \frac{1}{r} \right) b + \frac{1}{\epsilon_0 v_0} c - \frac{1}{\epsilon_0 v_0} \frac{1}{r} d = 0 \quad (9a)$$

$$- \frac{2}{\Delta} (1 + r) a + \left[\frac{4}{\Delta} + \frac{\epsilon}{\lambda_{\text{DH}}^2} (\Delta - \delta) \right] b - \frac{1}{\epsilon_0 v_0} c + \frac{1}{\epsilon_0 v_0} d = 0 \quad (9b)$$

$$m_j^{\text{I}} = \frac{2a}{\Delta} - \frac{2b}{\Delta} + \left[\frac{D_{-1}^{\text{II,I}}}{r} + D_0^{\text{II,I}} + D_{+1}^{\text{II,I}} r - \frac{1}{\epsilon_0 v_0 (\epsilon - 1)} \right] c + \left(\frac{D_{-1}^{\text{II,I}}}{r} + D_0^{\text{II,I}} + D_{+1}^{\text{II,I}} r \right) d = 0 \quad (9c)$$

$$m_j^{\text{II}} = - \frac{2r}{\Delta} a + \frac{2b}{\Delta} + \left(\frac{D_{-1}^{\text{I,II}}}{r} + D_0^{\text{I,II}} + D_{+1}^{\text{I,II}} r \right) c + \left[\frac{D_{-1}^{\text{I,II}}}{r} + D_0^{\text{I,II}} + D_{+1}^{\text{I,II}} r - \frac{1}{\epsilon_0 v_0 (\epsilon - 1)} \right] d = 0 \quad (9d)$$

The linear system of eqs 9a–9d has nontrivial solutions for the constants a , b , c , and d only if its determinant

vanishes. This condition leads to an equation of 6 degrees in r , which provides 6 values for r . The physical symmetry of the system (the invariance at a simultaneous exchange of layers $j-1$ and $j+1$ and of sites I and II) requires that for each solution r_k , its reciprocal $1/r_k$ should also be a solution of the system; hence, only three values of r_k are independent.

There is a simple correspondence between the solutions r_k of a linear system with finite differences and the characteristic lengths of a linear system of differential equations. By denoting $x = j\Delta$ as a continuous position variable, one obtains

$$r_k^j = r_k^{x/\Delta} = \exp\left(\frac{x}{\Delta} \ln r_k\right) = \exp\frac{x}{\lambda_k} \quad (10a)$$

with

$$\lambda_k \equiv \frac{\Delta}{\ln(r_k)} \quad (10b)$$

as a characteristic length associated to the solution r_k . The associate solution $1/r_k$ corresponds to the characteristic length $-\lambda_k$. While a description in terms of characteristic lengths is more appealing intuitively, one should note that those solutions are defined only at the discrete points $x = j\Delta$ (with j integer). Because the determinant of the system (eq 9) vanishes for any r_k , three of the constants for each set of a_k , b_k , c_k , and d_k can be determined as functions of the fourth one. This means that the solution depends on six constants, which have to be determined from the boundary conditions. When the surfaces are identical, the symmetry implies that there are only three independent boundary conditions (For an even number of layers, ψ^{I} is a symmetric function with respect to the middle distance between surfaces and $m_j^{\text{I}} = m_{-j-1}^{\text{II}}$, whereas, for an odd number of layers, ψ^{II} is symmetric with respect to the middle distance and $m_j^{\text{I}} = m_{-j}^{\text{II}}$). Assuming a surface charge density σ and a surface dipole density p_{\perp}/A , in which p_{\perp} is the normal component of the dipole moment of a polar surface group and A is the average area occupied by each dipole located at a distance Δ' from the boundary of the first icelike water layer, the Poisson equation provides the first boundary condition:

$$\frac{d\psi_{-S}^{\text{I}}}{dx} = - \frac{\sigma}{\epsilon_0 \epsilon'} \quad (11a)$$

in which ϵ' is the dielectric constant of the medium formed by the surface polar groups and the disorganized water molecules between them (see Figure 1b). The remaining two boundary conditions are provided by the polarization of the water molecules located on the two sites of the first water layers (denoted by $j = \pm S$):

$$m_{-S}^{\text{I}} = \epsilon_0 v_0 (\epsilon - 1) \left(2 \frac{\psi_{-S}^{\text{I}} - \psi_{-S}^{\text{II}}}{\Delta} + D_0^{\text{II,I}} m_{-S}^{\text{I}} + D_0^{\text{II,I}} m_{-S}^{\text{II}} + D_{+1}^{\text{II,I}} m_{-S+1}^{\text{I}} + D_{+1}^{\text{II,I}} m_{-S+1}^{\text{II}} + E_{-S}^{\text{I}} \right) \quad (11b)$$

(30) Mickens, R. E. *Difference Equations*; Van Nostrand Reinhold Company: New York, 1987.

$$m_{-S}^{\text{II}} = \epsilon_0 v_0 (\epsilon - 1) \left(2 \frac{\psi_{-S}^{\text{II}} - \psi_{-S+1}^{\text{I}}}{\Delta} + D_0^{\text{I,II}} m_{-S}^{\text{I}} + D_0^{\text{II,II}} m_{-S}^{\text{II}} + D_{+1}^{\text{I,II}} m_{-S+1}^{\text{I}} + D_{+1}^{\text{II,II}} m_{-S+1}^{\text{II}} + E_{-S}^{\text{II}} \right) \quad (11c)$$

The main differences between eqs 11a–11c and eqs 5a and 5b exist in the absence of water dipoles in the layer $-S-1$ (because the layer $-S$ is the first icelike layer) and the presence of the fields E_{-S}^{I} and E_{-S}^{II} , generated at sites I and II of layer $-S$, respectively, by the surface dipoles. Because the dielectric constant for the latter interaction, ϵ' , is much smaller than the dielectric constant of bulk water, only the nearest surface dipole has a significant contribution to these fields, which can be approximated by¹³

$$E_{-S}^{\text{I}} = \frac{p_{\perp}}{\epsilon'} \frac{1}{2\pi\epsilon_0 \left[\frac{A}{\pi} + \left(\Delta' + \frac{\Delta - \delta}{2} \right)^2 \right]^{3/2}} \quad (12a)$$

$$E_{-S}^{\text{II}} = \frac{p_{\perp}}{\epsilon'} \frac{1}{2\pi\epsilon_0 \left[\frac{A}{\pi} + \left(\Delta' + \frac{\Delta + \delta}{2} \right)^2 \right]^{3/2}} \quad (12b)$$

The linear system of eqs 9a–9d with finite differences, together with the three boundary conditions (for identical surfaces), can be solved analytically to provide solutions of the type³⁰

$$\begin{aligned} \psi_j^{\text{I}} &= \sum_{k=1}^6 a_k r_k^j \\ \psi_j^{\text{II}} &= \sum_{k=1}^6 b_k r_k^j \\ m_j^{\text{I}} &= \sum_{k=1}^6 c_k r_k^j \\ m_j^{\text{II}} &= \sum_{k=1}^6 d_k r_k^j \end{aligned} \quad (13)$$

In the following section, a model solution of the system is presented for surfaces separated by seven icelike layers (corresponding to a separation distance of ~ 25 Å). This will clarify the general behavior of the system and will demonstrate the nonproportionality between the polarization and the electric field.

4. A Model Solution for Polarization and Electric Potential

In what follows, we examine the general behavior of the solutions of the system of eqs 9a–9d for the boundary conditions given by eqs 11a–11c by assuming perfect icelike layers. It is taken into account that the distance between the centers of two adjacent water molecules is $l = 2.76$ Å, the distance between the centers of two adjacent icelike water layers is $\Delta = 4/3l = 3.68$ Å, the distance between the two distinct sites in the same layer is $\delta = l/3 = 0.92$ Å (see Figure 2), and the volume occupied by a water molecule is $v_0 = 8l^3/3\sqrt{3} = 32.37$ Å³.

A legitimate first question is related to the magnitude of errors generated by the discretization of the Poisson–Boltzmann equation (the replacement of eq 6 by eqs 7a–

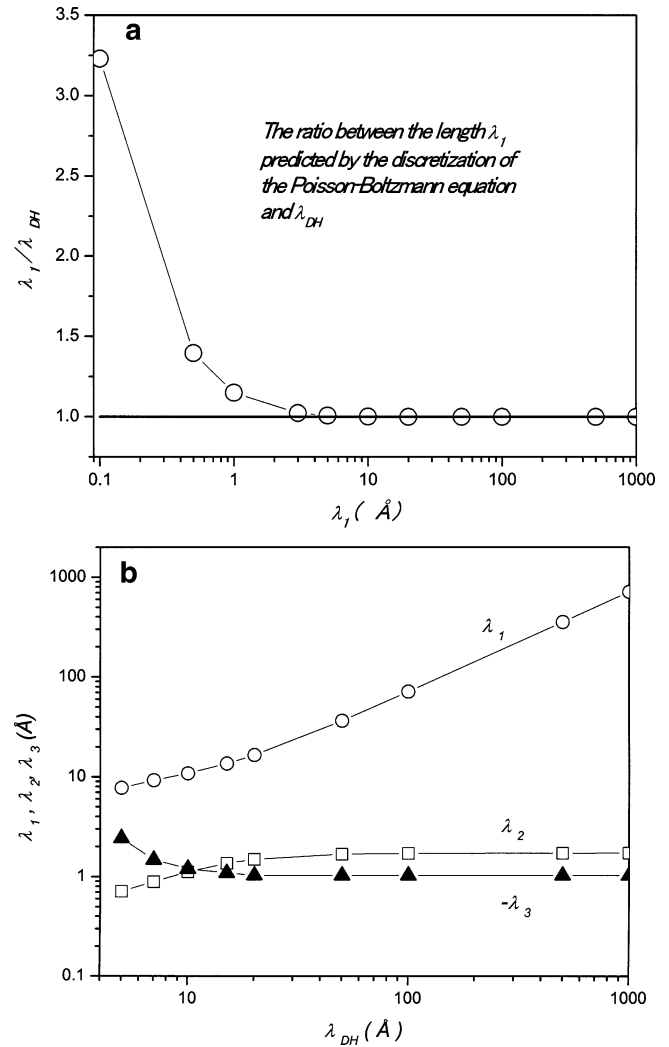


Figure 3. (a) The ratio between the Debye–Hückel length λ_{DH} and the characteristic length of the system (eqs 9a–9d), in the absence of the coupling interactions between dipoles (all D coefficients vanish), as a function of λ_{DH} . The results obtained via the discretization of the Poisson–Boltzmann equation are accurate, except for very small values of λ_{DH} . (b) The characteristic lengths of the linear system with finite differences as a function of the Debye–Hückel length, for the coupling coefficients given by eqs 14a–14f.

7d). Considering that all the coupling coefficients D vanish (therefore, neglecting the coupling between neighboring dipoles), one should recover the traditional Poisson–Boltzmann equation. Indeed, the condition of vanishing of the determinant of the system (eqs 9a–9d) generates in this case only two solutions, r_1 and $1/r_1$, and the corresponding decay lengths (provided by eq 10b) are almost identical to $\pm\lambda_{DH}$, at least for distances larger than Δ (see Figure 3a). To calculate the coupling coefficients D , we employ the approximations used in ref 13, which assume that only the dipoles of the neighboring water molecules, within a distance $2l$ from a particular point, generate a significant electric field at that point and that the fields generated by all the other dipoles are negligible. This means that the field E_p is generated at a site of a water molecule only by the dipoles of its first 26 neighbors, which are located either in the same icelike layer or in one of the adjacent layers. By assuming an effective dielectric constant, $\epsilon'' = 1$, for this interaction, one obtains¹³

$$D_{-1}^{I,I} \equiv D_1^{II,II} \frac{0.689}{4\pi\epsilon_0 l^3} \quad (14a)$$

$$D_{-1}^{II,II} \equiv D_1^{I,I} \frac{0.689}{4\pi\epsilon_0 l^3} \quad (14b)$$

$$D_{-1}^{I,II} = D_1^{II,I} = \frac{0.432}{4\pi\epsilon_0 l^3} \quad (14c)$$

$$D_{-1}^{II,I} = D_1^{I,II} = \frac{1.845}{4\pi\epsilon_0 l^3} \quad (14d)$$

$$D_0^{I,I} = D_0^{II,II} = -\frac{1.378}{4\pi\epsilon_0 l^3} \quad (14e)$$

$$D_0^{I,II} = D_0^{II,I} = -\frac{2.388}{4\pi\epsilon_0 l^3} \quad (14f)$$

The condition of vanishing of the determinant provides three pairs of solutions $r_1, 1/r_1$; $r_2, 1/r_2$; and $r_3, 1/r_3$, with the last one being negative. The 3 decay lengths corresponding to the 6 solutions are plotted in Figure 3b as functions of the decay length λ_{DH} . The length λ_1 is reminiscent of the Debye–Hückel length (at least at low electrolyte concentrations), whereas λ_2 is comparable to the hydration decay length, which was determined experimentally for the interactions between neutral lipid bilayers.⁴ The negative sign of r_3 implies that the terms proportional to r_3^j and $1/r_3^j$ have different signs in adjacent layers; hence, λ_3 corresponds to a decay length of an oscillatory contribution to the polarization and potential (with an oscillation length 2Δ). These types of oscillations are provided by the system of equations with finite differences (eqs 9a–9d) and are generated by the coupling coefficients between neighboring dipoles.

The physical origin of this behavior is related to the particular structure of the icelike layers: the field generated by a dipole \vec{p} , at a distance \vec{r} from the dipole, is given by

$$\vec{E} = \frac{1}{4\pi\epsilon_0\epsilon r^5} [3(\vec{p}\vec{r})\vec{r} - r^2\vec{p}] \quad (15a)$$

Because we are interested only in the polarization along the x axis, the field along this axis, at a position that makes an angle θ with the x axis, becomes

$$E_x = \frac{p_x}{4\pi\epsilon_0\epsilon r^3} (3 \cos^2 \theta - 1) \quad (15b)$$

Consequently, the neighboring water molecules belonging to different layers (with small θ) tend to align with each other in the same direction, whereas the neighboring dipoles from the different sites of the same layer (for which the angle $\theta = \cos^{-1}(1/3) \approx 71^\circ$) tend to align with each other in opposite directions (these interactions dominate the coupling coefficient $D_0^{I,II}$, which is negative). The relatively low magnitude of the decay length of the “oscillatory” part of the polarization and electrical potential indicates that the oscillations are attenuated rapidly with the distance from the surface. In a continuous model, in which the water molecules are not constrained to particular positions corresponding to an icelike structure, the water dipoles tend to align themselves in the same directions. Under these conditions, the oscillations vanish,

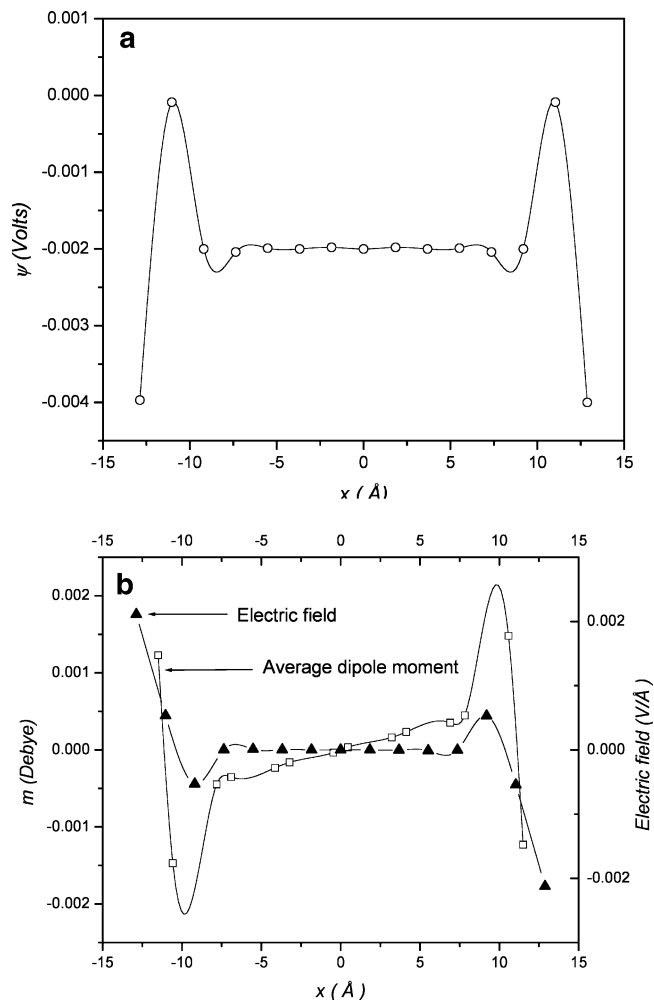


Figure 4. (a) The electric potential (circles) as a function of the distance from the surface for the system described in the text. The continuous line represents a Spline interpolation. (b) The average polarization of a water molecule (squares) as a function of the distance from surface for the system described in text; the macroscopic electric field (triangles) obtained through the numerical derivative of the potential is not proportional to the average polarization.

and only the characteristic lengths λ_1 and λ_2 remain.²⁹ The vanishing of the oscillations of polarization due to structural disorder (the absence of the icelike structuring of water near interfaces) has also been observed in molecular dynamics simulations. In the latter case, when surface disorder was generated by allowing the motion of the surface groups, the polarization decayed monotonically from the surface.²⁸

Let us investigate the electrical potential and the polarization of a typical system. For two surfaces separated by 7 icelike water layers ($S = 3, j = 0$ corresponding to the middle layer), with $\sigma = 1.9 \times 10^{-4}$ C/m², $p_1/\epsilon' = 0.1$ D, $A = 50$ Å² and $\lambda_{DH} = 50$ Å, the solutions of the system (eqs 9a–9d) with boundary conditions given in eqs 11a–11c for the potential and polarization as functions of the distance between surfaces are plotted in Figure 4, panels a and b, respectively. Although the solutions are defined only at particular positions in each layer (dots), for clarity they have been numerically interpolated using splines. Both the electrical potential (Figure 4a, circles) and the polarization (Figure 4b, squares) have an oscillatory behavior with respect to the distance. Furthermore, the numerical derivative of the electrical potential (Figure 4b, triangles) shows that the polarization is not proportional to the macroscopic electric field. The result is

particularly clear in the middle region between the surfaces, where the polarization varies slowly (mainly because of the coupling between dipoles), whereas the electric potential is almost constant (because the electrolyte ions can attenuate the electric field). Near the surfaces, the rapid variation of ψ generates a strong electric field, which has a large contribution to the polarization of the water molecules. Accounting for the facts that, in a real system, the water molecules are not perfectly structured in icelike layers (the consequences of this disorder have been investigated elsewhere),¹³ and that the charges and surface dipoles were selected here to be sufficiently small for the linear approximation to hold, the behavior of the calculated electrical potential and polarization are in excellent qualitative agreement with the results of molecular dynamics simulations (see Figures 1 and 2 of ref 14).

5. Conclusions

It was recently shown via molecular dynamics simulations¹⁴ that, in the close vicinity of a surface, water molecules exhibit an anomalous dielectric response, in which the local polarization is not proportional to the local electric field. The recent findings are also in agreement with earlier molecular dynamics simulations, which showed that the polarization of water oscillates in the vicinity of a dipolar surface,^{11,14} leading therefore to a nonmonotonic hydration force.¹⁵ Previous models for oscillatory hydration forces, based either on volume-excluded effects,^{18,19} or on a nonlocal dielectric constant,²⁴ predicted many oscillations with a periodicity of ~ 2 Å, which is inconsistent with these molecular dynamics simulations,^{11,13,14} in which the polarization exhibits only a few oscillations in the vicinity of the surface, with a larger periodicity.

It is suggested here that this behavior of water in the vicinity of a surface is a result of a coupling between neighboring dipoles when the water is organized in an icelike layer in the vicinity of the surface. This coupling constituted the basis of a model for water polarization, which was proposed earlier to explain the monotonic hydration interactions⁶ (either in the absence of water structuring, or when statistical disorder has been taken into account).^{13,27} The interactions between neighboring dipoles are the most important because they are much

less screened than those between more remote dipoles. Whereas in the latter case, there are many intervening water molecules that screen the interactions, in the former case there are no intervening water molecules. This behavior, due to the discrete (molecular) nature of water, is in sharp contrast with the classical results obtained by treating water as a continuum with a constant bulk dielectric constant. The continuum treatment assumes that a homogeneous surface dipolar density cannot polarize the water, whereas, in this model, the water is polarized by the surface dipoles.^{6,13}

As shown earlier,¹³ if one takes into account the coupling between neighboring dipoles and one also assumes a structuring of the water in icelike layers near the surfaces, one can explain the oscillation of the water polarization in the vicinity of the surfaces. The oscillations are essentially due to the particular positions of water molecules in an icelike structure. Whereas the water molecules from different icelike layers tend to align with each other in the same direction, the water molecules from two sites of the same layer tend to align with each other in opposite directions (other crystalline structures may not necessarily lead to an oscillatory polarization). That model, which involved a vanishing electrolyte concentration, was extended here to the general case that takes into account all of the electrostatic interactions between charges (electrolyte ions and surface charges) and dipoles (water as well as surface dipoles). A general formalism, which employs an analytical solution in the linear approximation, is suggested, and the general behavior of the system is investigated. It was shown that, in the linear approximation, the polarization is a superposition of three exponentially decreasing functions, two of them being monotonic and one oscillating with the periodicity of two icelike water layers (~ 7 Å). The decay lengths of the functions depend on the electrolyte concentration and on the coupling interactions between neighboring dipoles.

A model calculation predicted an anomalous dielectric behavior of water in the vicinity of a surface and an oscillatory dependence on distance of the water polarization and the electric potential in the close vicinity of a surface, which are very similar to the results obtained via molecular dynamics simulations.¹⁴

LA051802G