Oscillatory and Monotonic Polarization. The Polarization Contribution to the Hydration Force

Marian Manciu and Eli Ruckenstein*

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

The propagation of polarization in water, in the vicinity of a planar surface containing dipoles, is considered to be a consequence of the nonuniformity of the dielectric constant near the dipoles. Discrete finite difference equations have been derived by assuming a layered icelike structure. These equations predicted a polarization that oscillates with the distance from the surface. When the polarizing surface was considered rough or fluctuating, the oscillations were smoothed out and a monotonically decaying average polarization was obtained. Assuming that there are local icelike structures around any of the water molecules, a second-order differential equation for the polarization and expressions for its decay length were derived.

I. Introduction

The direct measurement of the interaction force between two mica surfaces[1] indicated a large repulsion at relatively short distances, which could not be accounted for by the DLVO theory. This force was associated with the structuring of water in the vicinity of the surface.[2] Theoretical work and computer simulations[3–5] indicated that, in the vicinity of a planar surface, the density of the liquid oscillates with the distance, with a periodicity of the order of molecular size. This reveals that, near the surface, the liquid is ordered in quasi-discrete layers. When two planar surfaces approach each other at sufficiently short distances, the molecules of the liquid reorder in discrete layers, generating an oscillatory force.[6]

When the surfaces were not rigid, as in the case of lipid bilayers, the oscillations of the force were smoothed out and the interactions became monotonic. The short-range repulsion between neutral[7] or weakly charged[8] bilayers, often called hydration force, was exhaustively investigated experimentally and was found to have an exponential decay, with a decay length between 1.5 and 3 Å, while the preexponential factor varied by more than an order of magnitude.

A phenomenological treatment of the hydration repulsion, based on a Landau expansion of the free energy density, was proposed by Marcelya and Radic.[9] They showed that, if the free energy density is a function of an "order parameter" that varies continuously from the surface, and if only the quadratic terms in this parameter and its derivative are nonnegligible, an exponential decay

of the repulsion could be obtained for not too short distances. They also suggested that the correlation (decay) length of the order parameter should be of the order of the molecular size. However, the microscopic origin of the order parameter, and more importantly, the dependence of the free energy density on the order parameter, remained obscure.

The interaction was later associated with the propagation of the polarization in water, and two models were proposed. Schiby and Ruckenstein[10] suggested that the polarization propagates because of interaction at the molecular level (mutual orientation of neighboring dipoles); we will return later to this model. Gruen and Marcelja[11] introduced a continuum model, in which equations for both the polarization and the electric field, considered independent quantities, were derived via the minimization of the total free energy of the system. The spatial variation of the polarization was considered dependent on the concentration of the Bjerrum defects, which constitute the source of the polarization field, while the spatial variation of the electric field was considered dependent on the concentration of ions, which constitute the source of the electric field. They showed that the polarization varies smoothly from the interface and that the electrostatic double-layer repulsion is enhanced by a contribution due to the surface polarization. At low separation distances, the effect of polarization becomes dominant and the repulsion decays exponentially, with a decay length inversely proportional to the square root of the concentration of the Bjerrum defects.

A simplified version of the theory was presented by Cevc and Marsh.[12] They started from the Marcelja–Radic phenomenological treatment, assumed that the polarization constitutes the order parameter, and used the Gruen–Marcelja model to explain the various contributions to the free energy density.

The subsequent molecular dynamics simulations[13,14] indicated that the polarization in water does not vary smoothly near the surface, but oscillates, and hence is not

* Corresponding author. E-mail address: feaeliru@acsu.buffalo.edu. Phone: (716) 645-2911/2214. Fax: (716) 645-3822.
(1) Horn, R. G.; Israelachvili, J. N. *J. Chem. Phys.* **1981**, *75*, 1400.
(2) Derjaguin, B. V.; Churaev, N. V. *J. Colloid Interface Sci.* **1974**, *49*, 249.
(3) Nicholson, D.; Parsonage, N. G. *Computer Simulation and the Statistical Mechanics of Adsorption;* Academic Press: New York, 1982.
(4) Ciccotti, G.; Frenkel, D.; MacDonald, I. R. *Simulation of Liquids and Solids;* North-Holland: Amsterdam, 1987.
(5) Evans, R.; Parry, A. O. *J. Phys.: Condens. Matter* **1990**, *2*, SA15–SA32.
(6) Israelachvili, J. N. *Intermolecular and Surface Forces;* Academic Press: New York, 1992.
(7) Rand, R. P.; Parsegian, V. A. *Biochim. Biophys. Acta* **1989**, *988*, 351.
(8) Cowley, A. C.; Fuller, N. L.; Rand, R. P.; Parsegian, V. A. *Biochemistry* **1978**, *17*, 3163.
(9) Marcelja, S.; Radic, N. *Chem. Phys. Lett.* **1976**, *42*, 129.

(10) Schiby, D.; Ruckenstein, E. *Chem. Phys. Lett.* **1983**, *95*, 435.
(11) Gruen, D. W. R.; Marcelja, S. *Faraday Trans. 2* **1983**, 211 and 225.
(12) Cevc, G.; Marsh, D. *Biophys. J.* **1985**, *47*, 21.
(13) Kjellander, R.; Marcelja, S. *Chem. Scr.* **1985**, *25*, 73; *Chem. Phys. Lett.* **1985**, *120*, 393.
(14) Berkowitz, M. L.; Raghavan, K. *Langmuir* **1991**, *7*, 1042.

accurately described by the Gruen−Marcelja theory.[11] It was therefore concluded that the polarization is not a suitable order parameter. It was also noted[15] that the exponential decay of the hydration force in the Gruen−Marcelja model was a consequence of an inconsistent choice for the functional form of the "non-local dielectric function".

The molecular dynamics simulation indicated that, unlike polarization (which oscillates), the disruption of hydrogen bonding varies smoothly in the vicinity of the surface and constitutes therefore a better choice as an order parameter. There were a number of computational approaches[13,14,16] and lattice model calculations[17] which related the hydration force to the disruption of the hydrogen bonding networks when two surfaces approach each other.

An essentially different point of view was suggested by Israelachvili and Wennerstrom, who consider that any interaction that may arise from water structuring effects should be either oscillatory or attractive but not repulsive, and hence that the microscopic origin of the hydration repulsion should be sought elsewhere than in hydrogen bonding or polarizability.[18] They proposed that the protrusion of the molecules belonging to the lipid bilayers could explain the hydration repulsion.[19] It was however argued that the interactions due to protrusion are much smaller than the experimentally measured hydration repulsion,[20] and experiment[21] indicated that the polymerization of the bilayers does not modify the hydration repulsion.

Another mechanism for the hydration repulsion between lipid bilayers was more recently proposed by Marcelja.[22] It is based on the fact that in water the ions are hydrated and hence occupy a larger volume. The volume exclusion effects of the ions are important corrections to the Poisson−Boltzmann equation and modify substantially the double-layer interaction at low separation distances. The same conclusion was reached earlier by Ruckenstein and Schiby,[23] and there is little doubt that the hydration of individual ions modifies the double-layer interaction, providing an excess repulsion force.[23] However, while the hydration of ions affects the double-layer interactions, the hydration repulsion is strong even in the absence of an electrolyte, or double-layer repulsion.

One can therefore conclude that there is no commonly accepted explanation for the microscopic origin of the hydration repulsion. The main purpose of this paper is to show that a suitable model for the polarization of water layers, based on the earlier work of Schiby and Ruckenstein,[10] is compatible with both simulations and experiments on hydration repulsion.

The treatment of polarization based on the assumption that water has a uniform dielectric constant involves a fundamental difficulty. Indeed, a uniform, continuous distribution of dipoles on a planar surface does not generate a field in a homogeneous medium and hence is not able to polarize the water. If the dipoles are distributed in the sites of a 2D planar square lattice, the field is

oscillating above the lattice, with an amplitude decaying exponentially with the normal distance from the lattice. Hence, the average field is vanishing, and the polarization does not propagate in water. In the model of Gruen and Marcelja the spatial variation of polarization was associated with the existence of the Bjerrum defects. Consequently, the absence of such defects implies that the decay length is infinite and the polarization is constant in the medium, instead of being zero, as expected on the above grounds. Cevc and Marsh suggested that the polarization of water near the interface is proportional to the normal component of the dipolar density,[12] which is a plausible assumption. However, the proportionality constant was provided without explanation, and it is not clear why the surface dipoles polarize the continuous medium.

While one cannot rule out that there are contributions of different origins to the hydration repulsion, the polarization contribution might be the dominant one, at least for not too small separations, and this can explain, as shown later in the paper, the quadratic dependence, determined experimentally by Simon and McIntosh,[24] of the hydration repulsion on the surface dipolar potential.

The model proposed in the present paper for the polarization is based on a simple idea. In a real medium, the interactions between remote dipoles are screened by the intervening solvent molecules and hence are decreased by a factor equal to the inverse of the dielectric constant of the medium. On the other hand, the interactions between adjacent dipoles are much less screened and hence are more important. In a medium with homogeneous dielectric properties, a planar layer of dipoles produces a vanishing average electric field above it. However, because the medium is not homogeneous at the molecular level, the field of a nearby dipole is screened less and an electric field is generated above the plane.

To calculate the net field in water, when the dielectric constant is inhomogeneous, one should know the distribution of molecules around a given site. In the following, we will consider that a water molecule belongs locally to an icelike structure. This was suggested by Nemethy and Scheraga,[25] who treated the bulk water as an aggregate of icelike clusters of various sizes. In the vicinity of a surface, it is reasonable to assume that the clusters (which have a layered structure) are aligned by the surface. The alignment is expected to gradually decrease away from the surface.

It will be shown that local inhomogeneities in the dielectric constant of the medium are responsible for the propagation of polarization inside the medium. A discrete representation of the water layers leads to equations with finite differences whose solution allows one to relate the total electrostatic energy (due to polarization) to the density and location of the dipole moments on the surface. We will show that a long-range order in the water structure, normal to the interface, can lead to oscillations of the polarization and that in this case the repulsive force cannot be approximated by an exponentially decaying function. However, the roughness or the undulations of the polarizing surface can smooth out the oscillations and lead to an exponentially decaying repulsion.

II. Hydration Interaction

II.1. Net Field above a Plane of Dipoles. In a homogeneous dielectric described by a constant ϵ, the field

(15) Attard, P.; Wei, D. Q.; Patey, G. N. *Chem. Phys. Lett.* **1990**, *172*, 69.
(16) Besseling, N. A. M. *Langmuir* **1997**, *13*, 2113.
(17) Attard, P.; Batchelor, M. T. *Chem. Phys. Lett.* **1988**, *149*, 206.
(18) Israelachvili, J. N.; Wennerstrom, H. *Nature* **1996**, *379*, 219.
(19) Israelachvili, J. N.; Wennerstrom, H. *Langmuir* **1990**, *6*, 873.
(20) Parsegian, V. A.; Rand, R. P. *Langmuir* **1991**, *7*, 1299.
(21) Binder, H.; Dietrich, U.; Schalke, M.; Pfeiffer, H. *Langmuir* **1999**, *15*, 4857.
(22) Marcelja, S. *Nature* **1997**, *385*, 689.
(23) Ruckenstein, E.; Schiby, D. *Langmuir* **1985**, *1*, 612.

(24) Simon, S. A.; McIntosh, T. J. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 9263.
(25) Nemethy, G.; Scheraga, H. A. *J. Chem. Phys.* **1962**, *36*, 3382.

generated by an infinite planar, uniform distribution of dipoles vanishes. The dipole distribution can be thought of as two planar surface charge distributions, of equal magnitude and opposite sign, separated by the infinitesimal distance δ ($\delta \to 0$ while the surface dipole density $\delta\sigma =$ constant, where σ is the surface density of the charges on the two planes). Both planar charge densities generate constant electric fields, which cancel in the region outside the planes.

The field, normal to the surface, generated by the surface dipoles assumed to be distributed on the sites of a square lattice can be calculated as follows. The field along the z direction, normal to the surface, generated by the positive charges is given by[6]

$$E_z^+ = \frac{\sigma}{2\epsilon\epsilon_0}\left(1 + 2\left(\cos\frac{2\pi x}{d} + \cos\frac{2\pi y}{d}\right)\exp\left(-\frac{2\pi z}{d}\right) + ...\right)$$
(1a)

where ϵ is the dielectric constant, ϵ_0 is the permittivity constant, x and y are the coordinates in the plane of the surface, and the charges are located at the positions $(x, y, z) = (nd, md, 0)$ with n and m integers and d the length of the unit cell of the lattice. The field generated by the negative charges located at $(x, y, z) = (nd, md, -\delta)$ is given by

$$E_z^- = -\frac{\sigma}{2\epsilon\epsilon_0}\left(1 + 2\left(\cos\frac{2\pi x}{d} + \cos\frac{2\pi y}{d}\right)\right.$$
$$\left.\exp\left(-\frac{2\pi(z+\delta)}{d}\right) + ...\right)$$ (1b)

Hence, for the total field generated by the dipoles normal to the surface one obtains

$$E_z^d = E_z^+ + E_z^- =$$
$$\frac{2\pi\sigma\delta}{\epsilon\epsilon_0 d}\left(\cos\frac{2\pi x}{d} + \cos\frac{2\pi y}{d}\right)\exp\left(-\frac{2\pi z}{d}\right)$$ (2)

where the terms of higher order in δ were neglected. The field generated by the surface dipoles, averaged on a planar surface equal to a unit cell of the lattice, vanishes.

However, the medium is not homogeneous at molecular distances, and this can be taken into account by assuming that the field caused by the nearest dipole is screened by a different dielectric constant, $\epsilon_1 < \epsilon$. If one denotes by $E_{z,i}^d$ the field along the z direction, generated in a vacuum by the dipole i of the surface, the field above the lattice is given by

$$E_z^d = \frac{1}{\epsilon_1}E_{z,\text{nearest}}^d + \frac{1}{\epsilon}\sum_{\text{all others}}E_{z,i}^d =$$
$$\left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon}\right)E_{z,\text{nearest}}^d + \frac{1}{\epsilon}\sum_{\text{all}}E_{z,i}^d =$$
$$\frac{(\epsilon - \epsilon_1)}{\epsilon\epsilon_1}E_{z,\text{nearest}}^d \equiv \frac{1}{\epsilon'}E_{z,\text{nearest}}^d$$ (3)

where the sum of the fields generated by all the dipoles in a medium of constant ϵ vanishes on average. Therefore, the net contribution to the field can be calculated by considering only the nearest dipole in a medium with an effective dielectric constant ϵ'.[26] A correction to eq 3 could

be obtained if the dependence of ϵ on distance would be known.

While the effective dielectric constant ϵ' is expected to be small near the surface dipoles, it is expected to acquire the bulk value after a few molecular distances. When calculating the net field generated by the surface dipoles in water, it will be assumed that effective dielectric constants can be used only for the interactions with the water molecules close to the surface (the first water layer). The interactions with more distant water molecules will be considered as in a continuum medium; hence, the net field will vanish on average.

To calculate the net field produced by a surface dipole, we will assume that one dipole of the surface polarizes the water molecules of the first layer located nearby above it. For the sake of simplicity, the area polarized by one dipole will be consider circular of radius R and equal to the area corresponding to a surface dipole (the inverse of the number of dipoles per unit area). The surface dipole $\vec{p}$ has the components p_{xy} in the plane and p_z normal to the surface. Because of symmetry, the field produced by p_{xy} vanishes, and so does the electric field parallel to the surface. The electric field, normal to the surface, generated by a dipole in a medium with an effective constant ϵ', at a point whose position vector makes an angle θ with the z direction, is given by

$$E_z^d = \frac{p_z}{4\pi\epsilon'\epsilon_0\varsigma^3}(3\cos^2\theta - 1)$$ (4)

where $\varsigma = \Delta'/\cos\theta$, Δ' being the distance between the center of the dipole and the center of the first water layer. For the average field produced by a surface dipole one obtains[26]

$$\bar{E} = \frac{1}{\pi R^2}\int_0^R \frac{2\pi\rho\, d\rho}{4\pi\epsilon'\epsilon_0(\Delta'^2 + \rho^2)^{3/2}}\left\{p_z\left(3\frac{\Delta'^2}{(\Delta'^2 + \rho^2)} - 1\right)\right\} =$$
$$\frac{p_z}{\epsilon'}\frac{1}{2\pi\epsilon_0(R^2 + \Delta'^2)^{3/2}}$$ (5)

II.2. Polarization of an Ordered, Icelike Water Structure. While the water molecules in the vicinity of the surface are polarized by the dipoles of the surface and by the neighboring water molecules, the other water molecules are polarized only by the field generated by the neighboring water molecules. To calculate this field, the structure of water between the external surfaces must be known.

Here we will assume that icelike clusters which, as suggested by Nemethy and Scheraga,[25] constitute the liquid water are aligned by the external surfaces and hence that a layered, icelike structure is formed between the surfaces. The water layers, parallel to the surface, are made of out-of-plane hexagonal rings of water molecules. Each layer is composed of two planar sublayers; a water molecule from a sublayer has three hydrogen bonds with three molecules of the other sublayer of the same layer, and one with a molecule belonging to a sublayer of one of the adjacent layers (a schematic picture is presented in Figure 1). All the molecules of a sublayer are assumed to have the same average dipole moment, and the local field, normal to the surface, acting on a site of a sublayer (I or II) of a layer j, can be formally written as

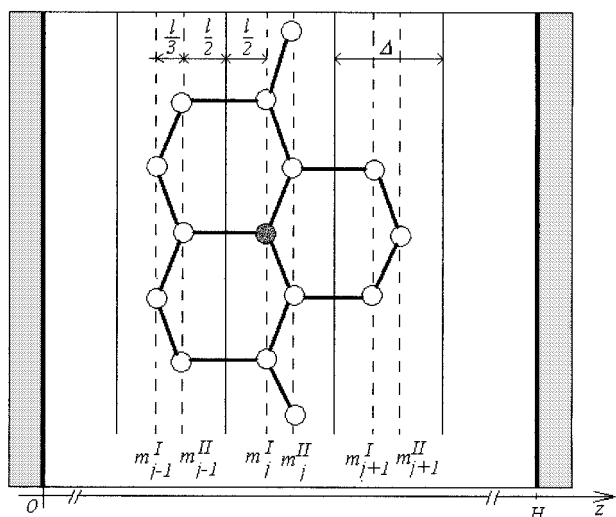(26) Manciu, M.; Ruckenstein, E. *Langmuir* **2001**, *17*, 7061.

Figure 1. Sketch of an icelike cluster around a selected water molecule. In this structure, a molecule from a sublayer (dotted lines) of one layer (delimited with full lines) is connected via hydrogen bonds with three molecules of the other sublayer of the same layer (only two bonds are drawn in the picture; it should be noted that the molecules drawn are not in the same plane) and with one water molecule from an adjacent layer. The first four neighbors are located at the vertexes of a tetrahedron. The projection of the position of the water molecules from one layer in the plane of the surface (denoted in the text as xy) is a hexagonal network. Each icelike cluster involves 26 molecules around the selected molecule (marked); they are located in three water layers: a central and the two adjacent ones.

$$E_j^I = D_0^{I,I}m_j^I + D_0^{II,I}m_j^{II} + D_{-1}^{I,I}m_{j-1}^I +$$
$$D_{-1}^{II,I}m_{j-1}^{II} + D_{+1}^{I,I}m_{j+1}^I + D_{+1}^{II,I}m_{j+1}^{II} + \dots \quad (6a)$$

$$E_j^{II} = D_0^{I,II}m_j^I + D_0^{II,II}m_j^{II} + D_{-1}^{I,II}m_{j-1}^I +$$
$$D_{-1}^{II,II}m_{j-1}^{II} + D_{+1}^{I,II}m_{j+1}^I + D_{+1}^{II,II}m_{j+1}^{II} + \dots \quad (6b)$$

where m_j^α is the average dipole moment of a molecule from the sublayer α (α = I or II) of layer j and the interaction coefficients $D_{\pm k}^{\alpha,\beta}$ account for the contribution of the dipoles of the sublayer α of layer $j \pm k$ to the local field at a site of the sublayer β (α, β = I or II) of layer j. The estimation of the coefficients D on the basis of the icelike model used is provided in Appendix A. It will be assumed that only the molecules within a radius $2l$ from the given site (where l is the distance between adjacent molecules) generate a nonnegligible field at a given site and hence that $k = -1, 0,$ and 1.

The average polarization of a molecule is proportional to the local field:

$$m_j^\alpha = \gamma E_j^\alpha \quad (7)$$

where the proportionality constant is the molecular polarizability.

Equations 6 and 7 constitute a system of $(2N - 4)$ linear equations with constant coefficients for the average polarizations m_j^α, where N is the number of water layers. The other four equations are provided by the boundary conditions. Seeking solutions of the form[27]

$$m_j^I = Ar^j \quad \text{and} \quad m_j^{II} = \bar{A}r^j \quad (8)$$

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

where A, $\bar{A}$, and r are constants, eqs 6 and 7 lead to ($j = 2, \dots, N - 1$)

$$\left(D_{-1}^{I,I} + \left(D_0^{I,I} - \frac{1}{\gamma}\right)r + D_{+1}^{I,I}r^2\right)m_{j-1}^I +$$
$$(D_{-1}^{II,I} + D_0^{II,I}r + D_{+1}^{II,I}r^2)m_{j-1}^{II} = 0 \quad (9a)$$

$$(D_{-1}^{I,II} + D_0^{I,II}r + D_{+1}^{I,II}r^2)m_{j-1}^I +$$
$$\left(D_{-1}^{II,II} + \left(D_0^{II,II} - \frac{1}{\gamma}\right)r + D_{+1}^{II,II}r^2\right)m_{j-1}^{II} = 0 \quad (9b)$$

The corresponding characteristic equation, which provides the values of r, has the form

$$\left(D_{-1}^{I,I} + \left(D_0^{I,I} - \frac{1}{\gamma}\right)r + D_{+1}^{I,I}r^2\right)$$
$$\left(D_{-1}^{II,II} + \left(D_0^{II,II} - \frac{1}{\gamma}\right)r + D_{+1}^{II,II}r^2\right) -$$
$$(D_{-1}^{II,I} + D_0^{II,I}r + D_{+1}^{II,I}r^2)(D_{-1}^{I,II} + D_0^{I,II}r +$$
$$D_{+1}^{I,II}r^2) = 0 \quad (9c)$$

The general solution of the system in eqs 9a,b is

$$m_j^I = A_1 r_1^j + A_2 r_2^j + A_3 r_3^j + A_4 r_4^j \quad (10a)$$

$$m_j^{II} = \bar{A}_1 r_1^j + \bar{A}_2 r_2^j + \bar{A}_3 r_3^j + \bar{A}_4 r_4^j \quad (10b)$$

where the constants A_k ($k = 1, \dots, 4$) have to be determined using the four boundary conditions given below. The relation between the constants A_k and their conjugate $\bar{A}_k$ is obtained by substituting eq 8 in eq 9a or b:

$$\bar{A}_k = -A_k \frac{D_{-1}^{I,I} + \left(D_0^{I,I} - \frac{1}{\gamma}\right)r_k + D_{+1}^{I,I}r_k^2}{D_{-1}^{II,I} + D_0^{II,I}r_k + D_{+1}^{II,I}r_k^2} = \eta_k A_k \quad (11)$$

The boundary conditions should take into account the effect of both the field produced by the surface dipoles and the field produced by the molecules of the first two layers.

$$m_1^I = \gamma(\bar{E}_I + D_0^{I,I}m_1^I + D_0^{II,I}m_1^{II} + D_{+1}^{I,I}m_2^I +$$
$$D_{+1}^{II,I}m_2^{II}) \quad (12a)$$

$$m_1^{II} = \gamma(\bar{E}_{II} + D_0^{I,II}m_1^I + D_0^{II,II}m_1^{II} + D_{+1}^{I,II}m_2^I +$$
$$D_{+1}^{II,II}m_2^{II}) \quad (12b)$$

$$m_N^I = \gamma(-\bar{E}_{II} + D_{-1}^{I,I}m_{N-1}^I + D_{-1}^{II,I}m_{N-1}^{II} +$$
$$D_0^{I,I}m_N^I + D_0^{II,I}m_N^{II}) \quad (12c)$$

$$m_N^{II} = \gamma(-\bar{E}_I + D_{-1}^{I,II}m_{N-1}^I + D_{-1}^{II,II}m_{N-1}^{II} +$$
$$D_0^{I,II}m_N^I + D_0^{II,II}m_N^{II}) \quad (12d)$$

The fields generated by the surface dipoles on the sublayers of the first layer, $\bar{E}_I$ and $\bar{E}_{II}$, are calculated using eq 5, for the corresponding distances from the center of the surface dipole to the centers of the sublayers, Δ_I' and Δ_{II}', respectively. The field in the first sublayer of the first water layer, generated by the surface dipoles, is calculated by considering an effective dielectric constant $\epsilon' < \epsilon$, while, for the field generated in the second sublayer of the same layer, a dielectric constant $\xi\epsilon'$ is employed ($\xi > 1$) to account for the dependence of the screening on the distance.

Since the interaction coefficients D are invariant to the transformation I → II, $k \to -k$, and, additionally, $D_{-1}^{I,I} = D_{+1}^{I,I}$ (see Appendix A), the characteristic equation is invariant to the transformation $r \to 1/r$, which can be directly verified by substitution in eq 9c. Therefore, the solutions of the characteristic equation come in pairs,

$$r_1 = \rho_1, \quad r_2 = \frac{1}{\rho_1}, \quad r_3 = \rho_2, \quad r_4 = \frac{1}{\rho_2}$$

Because for identical surfaces the polarization should be antisymmetric with respect to the middle distance between the two, one can write

$$m_j^I = -m_{N+1-j}^{II} \quad \text{for} \quad j = 1, N$$

Using eqs 10 and 11, the latter equation leads to

$$A_1 \rho_1^{j} + A_2 \rho_1^{-j} + A_3 \rho_2^{j} + A_4 \rho_2^{-j} =$$
$$-(\eta_1 A_1 \rho_1^{N+1-j} + \eta_2 A_2 \rho_1^{-(N+1-j)} + \eta_3 A_3 \rho_2^{N+1-j} +$$
$$\eta_4 A_4 \rho_2^{-(N+1-j)}) \quad (13)$$

which can be rearranged as

$$(A_1 \rho_1^{n} + \eta_2 A_2 \rho_1^{-n})\rho_1^{-k} + (A_2 \rho_1^{-n} + \eta_1 A_1 \rho_1^{n})\rho_1^{k} +$$
$$(A_3 \rho_2^{n} + \eta_4 A_4 \rho_2^{-n})\rho_2^{-k} + (A_4 \rho_2^{-n} + \eta_3 A_3 \rho_2^{n})\rho_2^{k} = 0$$
$$(14)$$

where $n = (N + 1)/2$ and $k = (N + 1 - 2j)/2$. Since, for a given value of N, the equations should be valid for any value of j, the coefficients in parentheses should vanish. The four equations thus obtained reduce to two equations, because $\eta_1\eta_2 = \eta_3\eta_4 \equiv 1$, and the constants A_2 and A_4 can be expressed in terms of A_1 and A_3, respectively. Consequently, the general solution has the form

$$m_j^I = A_1(\rho_1^{j} - \eta_1\rho_1^{N+1-j}) + A_3(\rho_2^{j} - \eta_3\rho_2^{N+1-j}) \quad (15a)$$

$$m_j^{II} = \eta_1 A_1(\rho_1^{j} - \eta_2\rho_1^{N+1-j}) + \eta_3 A_3(\rho_2^{j} - \eta_4\rho_2^{N+1-j}) \quad (15b)$$

For illustration purposes we will present a numerical example.

The interaction coefficients D are evaluated in Appendix A, selecting for the effective dielectric constant for the interaction between neighboring water molecules $\epsilon'' = 1$. This constitutes a lower bound for ϵ''. For the molecular polarizability, we will employ an expression[26] based on the hypothesis of hindered molecular rotations introduced by Debye. This provides a lower bound for γ, which is given by[26]

$$\gamma =$$
$$\frac{\epsilon_0 v}{\frac{\epsilon + 2}{3(\epsilon - 1)} + \epsilon_0 v(D_{-1}^{I,I} + D_{-1}^{II,I} + D_0^{I,I} + D_0^{II,I} + D_{+1}^{I,I} + D_{+1}^{II,I})}$$
$$(16)$$

where ϵ is the dielectric constant of water, ϵ_0 is the permittivity constant, and v is the volume occupied by a water molecule.

The Onsager theory for the molecular polarizability[28] implies that the water molecules can rotate freely in the liquid water and that their permanent dipole moments are higher in the liquid than in the vapor phase (because

of their interaction with a strongly polarizable medium, the liquid water). The value predicted for the molecular polarizability is about four times larger than that provided by eq 16; however, this does not affect the qualitative features of the discussion which follows.

For an icelike structure, the distance between the centers of two adjacent molecules is $l = 2.76$ Å and $v = (8/3\sqrt{3})l^3 = 32.37$ Å³. Using $\epsilon = 80$, the characteristic equation acquires the form

$$r^4 + 0.575r^3 - 25.78r^2 + 0.575r + 1 = 0 \quad (17)$$

The solutions r_k are

$$r_1 = \rho_a, \quad r_2 = \frac{1}{\rho_a}, \quad r_3 = -\rho_b, \quad r_4 = -\frac{1}{\rho_b} \quad (18)$$

with $\rho_a = 4.783$ and $\rho_b = 5.381$. Consequently, the general antisymmetric solutions are

$$m_j^I = A_1(\rho_a^{j} - \eta_1\rho_a^{N+1-j}) +$$
$$A_3(-1)^{j}(\rho_b^{j} - \eta_3(-1)^{N+1}\rho_b^{N+1-j}) \quad (19a)$$

$$m_j^{II} = \eta_1 A_1(\rho_a^{j} - \eta_2\rho_a^{N+1-j}) +$$
$$\eta_3 A_3(-1)^{j}(\rho_b^{j} - \eta_4(-1)^{N+1}\rho_b^{N+1-j}) \quad (19b)$$

which depend on two constants, A_1 and A_3 to be determined from the boundary conditions, eqs 12a and 12b. (The other two boundary conditions, eqs 12c and 12d, are equivalent to eqs 12b and 12a, respectively.)

The above equations are defined only for integer values of j; however, since both ρ_a and ρ_b are real and positive, the above equations can be analytically extended to noninteger values of j. A continuous function of z, which provides the same values as eqs 19 at the discrete positions of the sublayers and interpolates between them can be obtained using the equality

$$\rho^{j} = \exp(\ln(\rho^{j})) = \exp(j \ln(\rho)) = \exp\left(\frac{z}{\Delta} \ln \rho\right) = \exp\left(\frac{z}{\lambda}\right)$$

where $\Delta = {}^{4}/_{3}l$ is the distance between the centers of two adjacent water layers. In what follows, we will define the origin of z at one of the interfaces, located at the external boundary of the first water layer. The first sublayer of the first water layer is located at the distance $z = {}^{1}/_{2}l = {}^{3}/_{8}\Delta$ and corresponds to $j = 1$ in eq 19a. Hence, in eq 19a, $j = z/\Delta + {}^{5}/_{8}$ and $N + 1 - j = (H - z)/\Delta + {}^{3}/_{8}$, where $H = N\Delta$ is the separation distance between the two surfaces. From eqs 19, one obtains

$$m^I(z) =$$
$$A_1\left(\exp\left(\frac{5\Delta}{8\lambda_a}\right)\exp\left(\frac{z}{\lambda_a}\right) - \eta_1\exp\left(\frac{3\Delta}{8\lambda_a}\right)\exp\left(\frac{H-z}{\lambda_a}\right)\right) +$$
$$A_3\cos\left(\pi\left(\frac{z}{\Delta} + \frac{5}{8}\right)\right)\left(\exp\left(\frac{5\Delta}{8\lambda_b}\right)\exp\left(\frac{z}{\lambda_b}\right) -$$
$$(-1)^{N+1}\eta_3\left(\frac{3\Delta}{8\lambda_b}\right)\exp\left(\frac{H-z}{\lambda_b}\right)\right) \quad (20a)$$

and

$$m^{II}(z) = -m^I(H - z) \quad (20b)$$

where $\lambda_a = \Delta/\ln \rho_a = 2.35$ Å and $\lambda_b = \Delta/\ln \rho_b = 2.18$ Å are the decay lengths of the amplitudes of the monotonic and oscillatory terms, respectively.
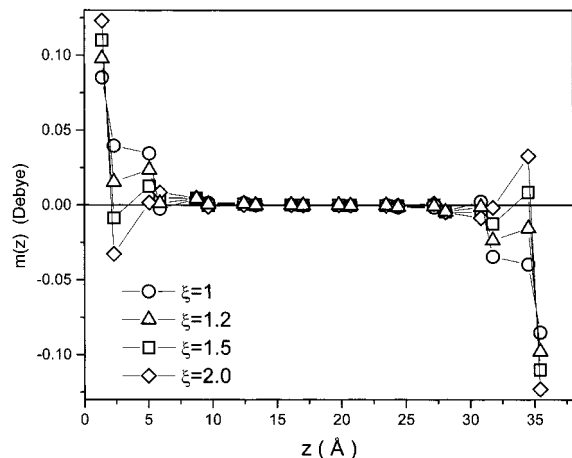
(28) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 261.

Figure 2. Dipole moment as a function of the distance from one surface, calculated in the discrete approach for $N = 10$ and various values of ξ. The values of the other parameters are $l = 2.76$ Å, $(p_z/\epsilon') = 1.0$ D, $\epsilon'' = 1$, $\epsilon = 80$, $\pi R^2 = 50$ Å^2, $\Delta'_\mathrm{I} = 2.88$ Å, and $\Delta'_\mathrm{II} = 3.8$ Å.

The numerical solutions for $N = 10$, $p_z/\epsilon' = 1.0$ D, $A = \pi R^2 = 50$ Å^2, $\Delta'_\mathrm{I} = 2.88$ Å, and $\Delta'_\mathrm{II} = 3.8$ Å are presented in Figure 2, for various values for ξ. The contributions of the monotonic and oscillatory parts of the polarizations depend strongly on the boundary conditions, which basically means the values of $\bar{E}_\mathrm{I}$ and $\bar{E}_\mathrm{II}$. Both the monotonic and oscillatory parts decay from the surface, but with different decay lengths.

The oscillations of the polarization are a consequence of the particular geometry of the system. The field generated by the average dipole moment of one sublayer tends to align in the same direction as the dipole moments of the molecules of the adjacent layers, but in the opposite direction as the dipole moments of the molecules of the other sublayer of the same layer. If the difference between $\bar{E}_\mathrm{I}$ and $\bar{E}_\mathrm{II}$ is large enough, this will produce a polarization which oscillates with the distance from the surface. The magnitude of the oscillations, which are attenuated with the distance, depends on the ratio $\bar{E}_\mathrm{II}/\bar{E}_\mathrm{I}$ and on the strength of the electrostatic interaction between adjacent layers. The total free energy per unit area, due to the polarization of the water molecules, can be calculated using the expression

$$F(N) = -\frac{N_\mathrm{w}}{2}\sum_{j=1}^{N}(m_j^\mathrm{I}E_j^\mathrm{I} + m_j^\mathrm{II}E_j^\mathrm{II}) =$$
$$-\frac{N_\mathrm{w}}{2\gamma}\sum_{j=1}^{N}((m_j^\mathrm{I})^2 + (m_j^\mathrm{II})^2) \quad (21)$$

where N_w is the number of water molecules in a sublayer, per unit area, and the factor $^1\!/_2$ avoids double counting. The above expression can be computed only for integer values of N, that is, an integer number of water layers. The interaction free energy $F_\mathrm{int}(N)$, obtained by subtracting the free energy $F(N\to\infty)$, is represented in Figure 3 for various values of ξ. For higher values of ξ, the electrostatic interaction might become attractive for odd values of N (i.e. $F(N) < F(\infty)$).

II.3. Effect of Partial Disorder. The oscillations of the polarization are a consequence of the long-range order along the direction normal to the surface. For planar surfaces, some disorder is, however, induced by the gradual decrease of the cluster alignment away from the surface.
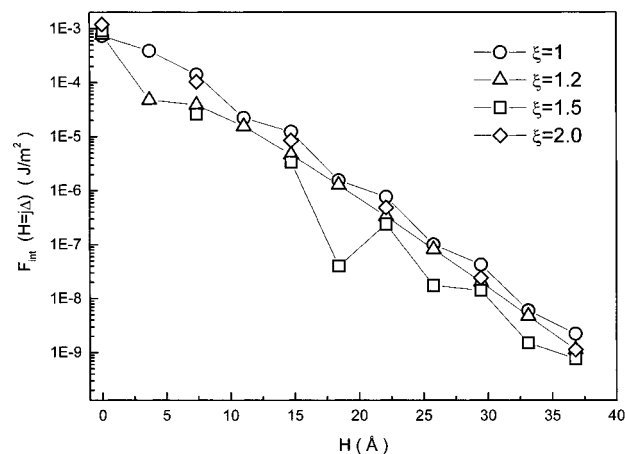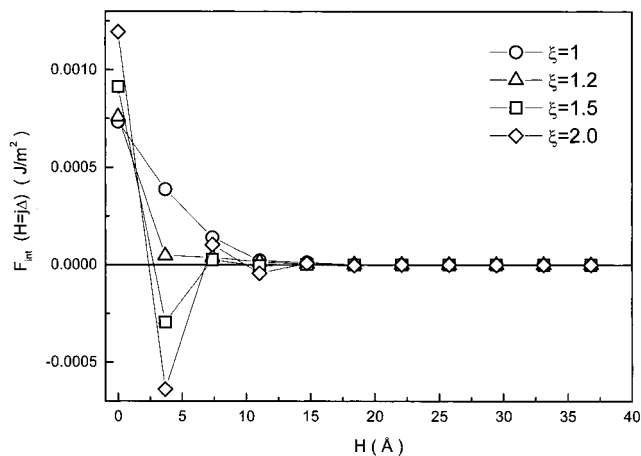

Figure 3. Interaction free energy in the discrete approach as a function of the separation distance between surfaces, calculated in the discrete model for various values of ξ: **(a, top)** linear scale (which shows better the oscillatory behavior near the surface; **(b, bottom)** logarithmic scale (which better reveals the behavior at large distances).

In addition, if the surfaces are not planar, but are sufficiently rough or fluctuating, the average polarization is no longer defined only for discrete values of z (the positions of the water sublayers with respect to one planar surface) but becomes a continuous function of distance, $m(z)$. The system with rough or undulating surfaces will be approximated here by a statistical ensemble of systems with planar surfaces in which the water molecules are organized in long-range icelike structures. Assuming that in the statistical ensemble the surfaces are distributed Gaussian with the root-mean-square fluctuation σ, the average m at a position z from the average surface is obtained from

$$m(z) = \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty}\exp\left(-\frac{s^2}{2\sigma^2}\right)m(z-s)\,\mathrm{d}s =$$
$$\frac{1}{\sqrt{2\pi}\sigma}\sum_{\alpha=\mathrm{I,II}}\sum_{j=1,N}m_j^\alpha\exp\left(-\frac{(z-z_j^\alpha)^2}{2\sigma^2}\right) \quad (22)$$

where z_j^α is the position of the sublayer α of the layer j.

During the fluctuations, the number N of layers changes. However, the values of m_j^α in the layers near the surfaces are almost independent of N, for large N. Figure 4a presents the dependence of m on z for various values of
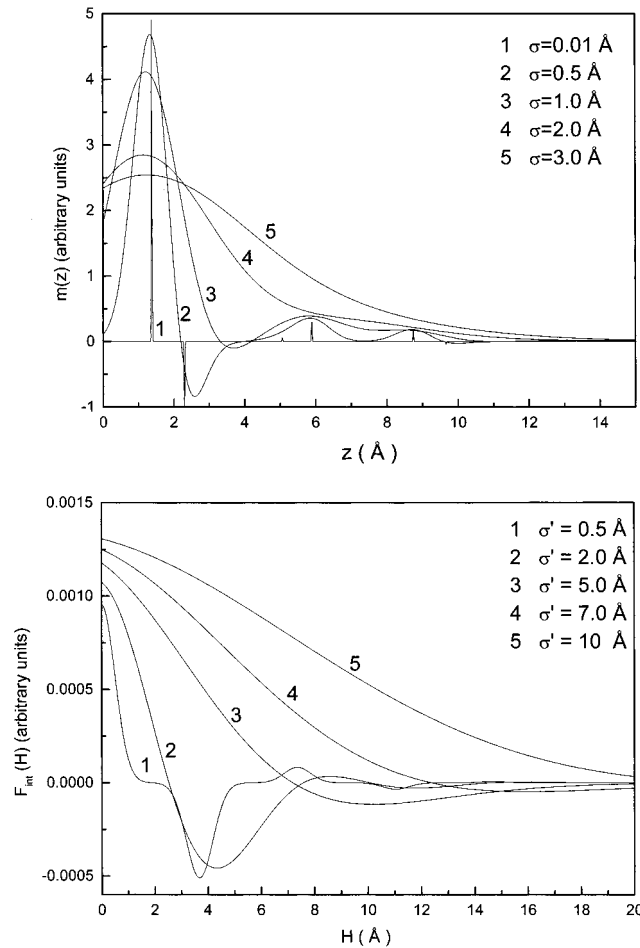
Figure 4. (a, top) Average polarization m as a function of the distance from one surface (the other surface is located at a large separation distance), for a rough or fluctuating surface, calculated using eq 22 for $\xi = 2$ and various values of σ. The functions are multiplied with arbitrary factors for easier comparison of their shapes. (The factors have the following values: (1) 1; (2) 50; (3) 100; (4) 150; (5) 200.) (b, bottom) Interaction free energy as a function of separation distance, for a rough or fluctuating surface, calculated using eq 23 for $\xi = 2$ and various values of σ'. The functions are multiplied with arbitrary factors for easier comparison of their shapes. (The factors have the following values: (1) 1; (2) 5; (3) 20; (4) 35; (5) 50.)

the root-mean-square fluctuation and a large value of N ($N = 20$). For $\sigma \rightarrow 0$, the average dipole moment is nonvanishing only around $z = z_j^\alpha$, while, for $\sigma > 5$ Å, the average dipole moment becomes a smooth, monotonically decreasing function of the distance from the surface. Such a behavior was observed in computer simulations. Molecular dynamics studies of water between rigid surfaces[13,14] indicated that the polarization is oscillating in the vicinity of the surface, with a spatial period of the order of molecular size. However, when the dynamic restrictions on bilayers' headgroups were removed, the polarization became a smooth function of z, monotonically decaying.[29]

A similar procedure can be used to calculate the interaction free energy between two undulating (or rough) surfaces. Assuming that the separation distance between surfaces is normally distributed around H with a dispersion σ', the interaction free energy is given by

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

$$F_{\text{int}}(H) = \frac{1}{\sqrt{2\pi}\sigma'}\sum_{j=0}^{\infty}(F(H_j) - F(\infty))\exp\left(-\frac{(H - H_j)^2}{2\sigma'^2}\right) \tag{23}$$

where $H_j = j\Delta$ is the distance between surfaces in each of the elements of the statistical ensemble. The interaction free energy for various values of σ' is presented in Figure 4b.

II.4. Monotonic Polarization. Let us assume that it is possible to define an average m as a monotonic function of distance to the average surface and that locally an icelike order is preserved in each of the clusters with radius $2l$, l being the distance between the centers of two adjacent water molecule, containing 26 water molecules around a selected water molecule (see Figure 1). If the cluster is aligned with its layers parallel to the external surface, and its center is located at the position z (measured from one of the surfaces), the distance between the centers of two adjacent water layers is $\Delta = {}^4/_3 l$, the positions of the sublayers of the central layer are $z \pm {}^1/_6 l$, and the positions of the other sublayers are $z \pm {}^7/_6 l$ and $z \pm {}^3/_2 l$, respectively. The equations which describe the polarizations of the two sublayers of the central layer are

$$m\left(z - \frac{l}{6}\right) = \gamma\left(D_{-1}^{\text{I,I}}m\left(z - \frac{3l}{2}\right) + D_{-1}^{\text{II,I}}m\left(z - \frac{7l}{6}\right) + D_0^{\text{I,I}}m\left(z - \frac{l}{6}\right) + D_0^{\text{II,I}}m\left(z + \frac{l}{6}\right) + D_{+1}^{\text{I,I}}m\left(z + \frac{7l}{6}\right) + D_{+1}^{\text{II,I}}m\left(z + \frac{3l}{2}\right)\right)$$

$$m\left(z + \frac{l}{6}\right) = \gamma\left(D_{+1}^{\text{II,I}}m\left(z - \frac{3l}{2}\right) + D_{+1}^{\text{I,I}}m\left(z - \frac{7l}{6}\right) + D_0^{\text{II,I}}m\left(z - \frac{l}{6}\right) + D_0^{\text{I,I}}m\left(z + \frac{l}{6}\right) + D_{-1}^{\text{II,I}}m\left(z + \frac{7l}{6}\right) + D_{-1}^{\text{I,I}}m\left(z + \frac{3l}{2}\right)\right) \tag{24a,b}$$

where because of the symmetry of the system to the transformation I ↔ II, $k \leftrightarrow -k$ only six of the interaction coefficients D were used (see Appendix A). When the cluster is not perfectly aligned parallel to the surface but makes a small angle α, the coefficients of interactions are slightly modified (see Appendix B). If the distribution of the tilt angles and their dependence on z would be known, it could be included in the calculations which follow. However, as shown later, the tilting of the local clusters by as much as 20° changes the decay length less than 10%. In addition, the tilting is expected to be lower near the surface. For these reasons, the solution with a constant decay length probably constitutes a good approximation.

We will employ the procedure used by Schiby and Ruckenstein[10] and will expand m around z. Adding the two eqs 24, one obtains (neglecting the terms of order 4 and higher)

$$2m(z) + \frac{\partial^2 m(z)}{\partial z^2}\frac{l^2}{36} =$$
$$\gamma\left\{(D_{-1}^{\text{I,I}} + D_{+1}^{\text{II,I}})\left(2m(z) + \frac{\partial^2 m(z)}{\partial z^2}\frac{9l^2}{4}\right) + \right.$$
$$(D_0^{\text{I,I}} + D_0^{\text{II,I}})\left(2m(z) + \frac{\partial^2 m(z)}{\partial z^2}\frac{l^2}{36}\right) +$$
$$\left.(D_{+1}^{\text{I,I}} + D_{-1}^{\text{II,I}})\left(2m(z) + \frac{\partial^2 m(z)}{\partial z^2}\frac{49l^2}{36}\right)\right\} \tag{25}$$

which can be rewritten as

$$\frac{\partial^2 m(z)}{\partial z^2} - \frac{1}{\lambda_1^2} m(z) = 0 \qquad (26)$$

with λ_1 given by

$$\lambda_1 = l$$

$$\sqrt{\frac{\frac{9}{4}(D_{-1}^{I,I} + D_{+1}^{II,I}) + \frac{49}{36}(D_{-1}^{II,I} + D_{+1}^{I,I}) + \frac{1}{36}\left(D_0^{I,I} + D_0^{II,I} - \frac{1}{\gamma}\right)}{2\left(\frac{1}{\gamma} - (D_{-1}^{I,I} + D_{-1}^{II,I} + D_0^{I,I} + D_0^{II,I} + D_{+1}^{I,I} + D_{+1}^{II,I})\right)}} \qquad (27)$$

A simpler procedure[26] is to consider that the average dipole moment of the water molecules of one layer is obtained by averaging over the two sublayers, $m_j = (m_j^I + m_j^{II})/2$. In this case, the quantities representing the interaction coefficients with the same (C_0) and adjacent (C_{+1} and C_{-1}) layers are given by

$$C_0 = D_0^{I,I} + D_0^{II,I},$$
$$C_1 = C_{-1} = C_{+1} = \frac{1}{2}(D_{-1}^{I,I} + D_{-1}^{II,I} + D_{+1}^{I,I} + D_{+1}^{II,I}) \qquad (28)$$

The average dipole moment is related in this case to the average dipole moment of the molecules from the same and adjacent layers via

$$m(z) = \gamma(C_{-1}m(z - \Delta) + C_0 m(z) + C_1 m(z + \Delta)) \quad (29)$$

where $\Delta = 4l/3$ is the distance between adjacent layers. After a Taylor expansion and neglecting the terms of order 4 and higher, a differential equation of the same type as eq 26 is obtained, but with a decay length λ_2 given by[26]

$$\lambda_2 = \frac{4l}{3}\sqrt{\frac{C_1}{\frac{1}{\gamma} - (C_0 + 2C_1)}} \qquad (30)$$

The solution of eq 26 for two planar, parallel interfaces at a distance H apart, if the average dipole moment of the first water layers (located at $z = \pm\Delta/2$) is $\pm m_1$ (hence, for the boundary condition $m(z=\Delta/2) = m_1$, $m(z=H-\Delta/2) = -m_1$) has the form

$$m(z) = -m_1 \frac{\sinh\left(\frac{2z - H}{2\lambda}\right)}{\sinh\left(\frac{H - \Delta}{2\lambda}\right)} \qquad (31)$$

where λ can be λ_1 or λ_2.

The value of m_1 is related to the local field, which can be obtained by adding to the field generated by the surface dipoles, $\bar{E}$, the field generated by the molecules of the first two layers from the surface

$$m_1 = \gamma E_e = \gamma(\bar{E} + C_0 m_1 + C_1 m_2) \qquad (32)$$

Using eq 31 for $m_2 = m(3\Delta/2)$, one obtains

$$m_1 = \frac{\gamma \bar{E}}{\left(1 - \gamma C_0 - \gamma C_1 \frac{\sinh\left(\frac{H - 3\Delta}{2\lambda}\right)}{\sinh\left(\frac{H - \Delta}{2\lambda}\right)}\right)} \qquad (33)$$

The total electrostatic free energy per unit area, between the two parallel plates, due to the orientation of dipoles $m(z)$ in the local field $E = m(z)/\gamma$ is given by[26]

$$F(H) = -\frac{1}{2S}\sum_{\text{all molecules}}\frac{(m(z))^2}{\gamma} =$$

$$-\frac{1}{2S}\int_{\text{volume}}\frac{(m(z))^2}{\gamma V}\,dV = -\frac{1}{2\gamma v}\int_0^H (m(z))^2\,dz =$$

$$\frac{\gamma \bar{E}^2}{\left(1 - \gamma\left(C_0 + C_1\frac{\sinh\left(\frac{H - 3\Delta}{2\lambda}\right)}{\sinh\left(\frac{H - \Delta}{2\lambda}\right)}\right)\right)^2}\frac{H - \lambda\sinh\left(\frac{H}{\lambda}\right)}{4v\sinh^2\left(\frac{H - \Delta}{2\lambda}\right)} \qquad (34)$$

where $V = SH$ is the volume occupied by the water molecules and S is the area of the planar interfaces. The interaction free energy is obtained by subtracting $F(H\rightarrow\infty)$ from $F(H)$.

Because $\bar{E}$ is proportional to p_s/ϵ', the free energy is proportional to $(p_s/\epsilon')^2$. This result is in agreement with the experiments of Simon and McIntosh[24] and consistent with the theory of Schiby and Ruckenstein.[10]

To verify the accuracy of the continuum approximation, we compared the average dipole moments along the z axis calculated using both the discrete and continuous procedures for integer values of N.

The general solution of the finite differences equation (eq 29) is given by

$$m_j = A_1 r_1^j + A_2 r_2^j \qquad (35)$$

where r_1 and r_2 are the solutions of the characteristic equation

$$r^2 + \frac{C_0 - \frac{1}{\gamma}}{C_1}r + 1 = 0 \qquad (36)$$

and the constants A_k are obtained from the boundary conditions. For the conditions specified in section II.2, $C_0 < 0$ and $-(C_0 - 1/\gamma) > 2C_1$. Consequently, both solutions of the characteristic equation are real and positive:

$$r_1 = \rho, \quad r_2 = \frac{1}{\rho}, \quad \rho = \frac{1 - \gamma C_0}{2\gamma C_1} + \sqrt{\left(\frac{1 - \gamma C_0}{2\gamma C_1}\right)^2 - 1} \qquad (37)$$

For a system with identical surfaces, the average dipole moment should be antisymmetric with respect to the middle distance; hence, $m_j = -m_{N+1-j}$, $j = 1, N$:

$$A_1\rho^j + A_2\rho^{-j} = -(A_1\rho^{N+1-j} + A_2\rho^{-(N+1-j)}) \qquad (38)$$

which can be rearranged as

$$(A_1\rho^{(N+1)/2} + A_2\rho^{-(N+1)/2})(\rho^{(N+1-2j)/2} + \rho^{-(N+1-2j)/2}) = 0 \qquad (39)$$

and can be satisfied for any j (and a given N) only if $A_2 = -A_1\rho^{N+1}$. The corresponding (discrete) solution is

$$m_j = A_1(\rho^j - \rho^{N+1-j}) \qquad (40)$$

Table 1

	$\alpha = 0°$	$\alpha = 5°$	$\alpha = 10°$	$\alpha = 15°$	$\alpha = 20°$
$4\pi\epsilon_0\epsilon'' \beta D_{-1}^{I,I}$	0.688 92	0.681 07	0.657 76	0.619 70	0.568 04
$4\pi\epsilon_0\epsilon'' \beta D_{-1}^{II,I}$	1.844 62	1.823 61	1.761 19	1.659 28	1.520 95
$4\pi\epsilon_0\epsilon'' \beta D_0^{I,I}$	−1.377 84	−1.362 14	−1.315 52	−1.239 39	−1.136 07
$4\pi\epsilon_0\epsilon'' \beta D_0^{II,I}$	−2.388 44	−2.361 22	−2.280 41	−2.148 44	−1.969 35
$4\pi\epsilon_0\epsilon'' \beta D_{+1}^{I,I}$	0.688 92	0.681 07	0.657 76	0.619 70	0.568 04
$4\pi\epsilon_0\epsilon'' \beta D_{+1}^{II,I}$	0.432 00	0.427 08	0.412 46	0.388 59	0.356 20
$4\pi\epsilon_0\epsilon'' \beta C_0$	−3.766 28	−3.723 36	−3.595 93	−3.387 84	−3.105 42
$4\pi\epsilon_0\epsilon'' \beta C_1$	1.827 23	1.806 41	1.744 58	1.643 63	1.506 61
λ_1 (Å)	2.770 4	2.755 0	2.708 6	2.630 8	2.520 8
λ_2 (Å)	2.964 9	2.948 6	2.899 6	2.817 5	2.701 6
λ_3 (Å)	3.137 7	3.122 2	3.075 7	2.997 8	2.888 1

Since z is measured from the external boundary of the first water layer, the center of the first water layer is located at $z = \Delta/2$ and corresponds to $j = 1$. Therefore $j = z/\Delta + 1/2$ and $N + 1 - j = (H - z)/\Delta + \frac{1}{2}$, where $H = N\Delta$ is the distance between surfaces. The analytical extension for $m(z)$ (the continuous expression which provides the exact values at the discrete points and interpolates between them) is thus given by

$$m(z) = 2A_1 \exp\left(\frac{H+\Delta}{2\lambda_3}\right) \sinh\left(\frac{2z-H}{2\lambda_3}\right)$$

where A_1 is obtained from the boundary condition $m(z=\Delta/2) = m_1$; hence,

$$m(z) = -m_1 \frac{\sinh\left(\dfrac{2z-H}{2\lambda_3}\right)}{\sinh\left(\dfrac{H-\Delta}{2\lambda_3}\right)} \tag{41}$$

This solution is of the same type as eq 31, but with a decay length λ_3 given by

$$\lambda_3 = \frac{\Delta}{\ln\rho} = \Delta\left(\ln\left(\frac{1-\gamma C_0}{2\gamma C_1} + \sqrt{\left(\frac{1-\gamma C_0}{2\gamma C_1}\right)^2 - 1}\right)\right)^{-1} \tag{42}$$

Figure 5a presents the values of $m(z)$ calculated with the discrete and continuous approaches for $N = 10$. The interaction free energies derived by the two approaches are compared in Figure 5b; the agreement is very good for distances larger than about the thicknesses of two water layers (7.36 Å). However, when the separation distance between surfaces becomes comparable to the molecular size, one expects the free energy associated with the restructuring of water to become dominant. Therefore, in this region neither the discrete nor its continuum approximation is likely to represent an accurate description of the hydration interaction.

Let us now consider that the layers of the local clusters make an angle α with the surface. In this case, $\cos^2 \theta$ in eq A.1 of Appendix A should be replaced by (Appendix B, eq B.7)

$$\cos^2 \theta' = \cos^2 \theta \cos^2 \alpha + \frac{\sin^2 \theta \sin^2 \alpha}{2} \tag{B.7}$$

Assuming that the average dipole moment remains constant in a layer regardless of the tilt angle, one obtains for the interaction coefficients the values listed in Table 1. Additionally, we computed the decay lengths for the parameter values given in section II.4: λ_1 from the continuous approximation, eq 27; λ_2 from the continuous approximation which treats the polarization of one layer as an average over its two sublayers, eq 30; and λ_3 from
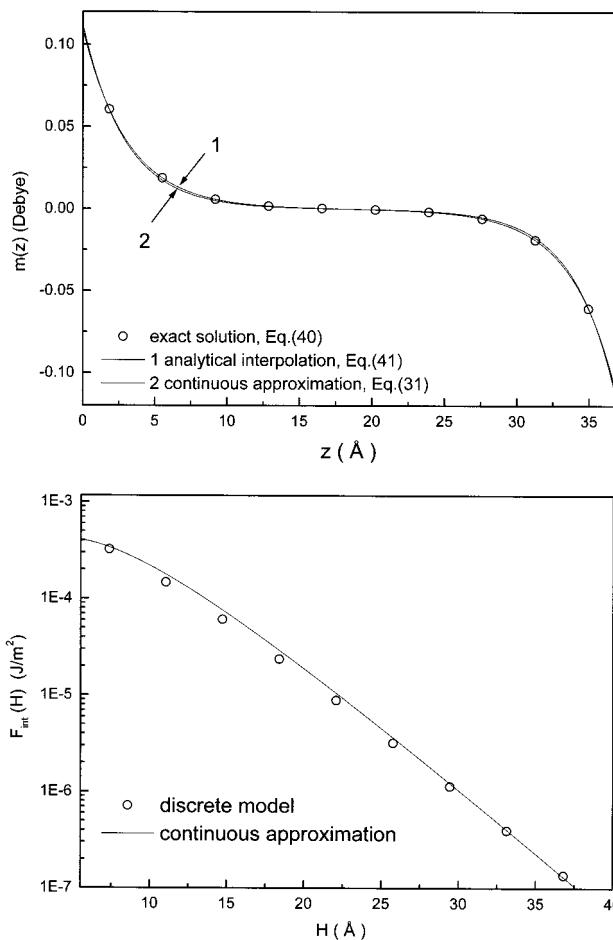

Figure 5. (a, top) Polarization as a function of the distance from one surface. The solution of the discrete approach (eq 40, circles) and its analytical interpolation (eq 41, line 1) are compared to the solution obtained via the continuous approximation (eq 31, line 2). (b, bottom) Interaction energy, as a function of separation distance, for the discrete approach and for the continuous approximation.

the analytical extension of the solution of finite difference equation, eq 42.

As already noted, if the average tilting angle, α, remains below 20°, the interaction coefficients and the decay lengths are only slightly modified.

III. Summary and Conclusions

We followed the model introduced by Schiby and Ruckenstein.[10] Arguments are brought that the local inhomogeneities of the dielectric constant are responsible for the propagation of polarization in water, in the vicinity of a planar surface which has a dipole moment density. If the water has a long-range icelike order along the direction normal to the surface, the system of finite

difference equations, corresponding to the layered structure, leads to discrete solutions, which can oscillate with the distance. However, if some disorder is present, due, for instance, to the roughness or fluctuations of the surfaces, the average polarization becomes a monotonically decaying function of the average distance from the surface. A continuous equation is derived for $m(z)$, and expressions are obtained for the decay length.

Appendix A. Evaluation of the Coefficients $D_k^{\alpha,\beta}$

The coefficients $D_{\pm k}^{\alpha,\beta}$ account for the contributions of the dipoles of the sublayer α of layer $j \pm k$ to the local field at a site of the sublayer β (α, β = I or II) of layer j. While the field produced by remote dipoles can be treated as screened by a medium with a large dielectric constant ($\epsilon \cong 80$), the screening of the neighboring dipoles is much weaker. As noted in section II.1, the net contribution to the local field generated by a layer of dipoles is due to the neighboring dipoles, whose interactions take place in a medium with an effective dielectric constant smaller than ϵ. It is assumed that only the dipoles located within a radius $2l$ (where l denotes the distance between the centers of two adjacent water molecules) from the given site contribute to the local field and that the effective dielectric constant for them has a value ϵ'', smaller than ϵ. The electric field along z, caused by a neighboring molecule having an average dipole moment m along the z direction, is given by

$$E_z = \frac{m(3\cos^2\theta - 1)}{4\pi\epsilon''\epsilon_0\varsigma^3} \tag{A.1}$$

where ς is the distance between a neighboring molecule and the selected site and θ is the angle between $\vec{\varsigma}$ and z. We will consider that the cluster of radius $2l$ has an icelike structure with the layers perpendicular to z (the effect of a tilting angle is evaluated in Appendix B). In an ice-I structure of perfect tetrahedrons, the distances between the sublayers of the same layer is $l/3$ and the distance between adjacent layers is $4l/3$. The edges of the tetrahedron formed by the four first neighbors of a water molecule have the length $l(\sqrt{8/3})$, while the planar projection of the tilted hexagonal lattice has the side $l(\sqrt{8/9})$. The volume occupied in this structure by a water molecule is $v = [8/(3\sqrt{3})]l^3$.

Because the system is invariant at the transformation I → II, $+k \rightarrow -k$ (see Figure 1), only six interaction coefficients should be computed:

$$D_{-1}^{I,I} = D_{+1}^{II,II} = \frac{1}{4\pi\epsilon''\epsilon_0 l^3} 3\frac{3\left(\sqrt{\frac{2}{3}}\right)^2 - 1}{\left(\sqrt{\frac{8}{3}}\right)^3} = \frac{0.6889}{4\pi\epsilon''\epsilon_0 l^3} \tag{A.2a}$$

$$D_{-1}^{II,I} = D_{+1}^{I,II} =$$
$$\frac{1}{4\pi\epsilon''\epsilon_0 l^3}\left(2 + 6\frac{3\left(\sqrt{\frac{3}{11}}\right)^2 - 1}{\left(\sqrt{\frac{11}{3}}\right)^3}\right) = \frac{1.8446}{4\pi\epsilon''\epsilon_0 l^3} \tag{A.2b}$$

$$D_0^{I,I} = D_0^{II,II} = \frac{1}{4\pi\epsilon_0\epsilon'' l^3}\left(6\frac{(-1)}{\left(\sqrt{\frac{8}{3}}\right)^3}\right) = -\frac{1.3778}{4\pi\epsilon_0\epsilon'' l^3} \tag{A.2c}$$

$$D_0^{II,I} = D_0^{I,II} =$$
$$\frac{1}{4\pi\epsilon_0\epsilon'' l^3}\left(3\frac{3\left(\frac{1}{3}\right)^2 - 1}{1} + 3\frac{3\left(\frac{1}{\sqrt{33}}\right)^2 - 1}{\left(\sqrt{\frac{11}{3}}\right)^3}\right) = -\frac{2.3884}{4\pi\epsilon_0\epsilon'' l^3} \tag{A.2d}$$

$$D_{+1}^{I,I} = D_{-1}^{II,II} = \frac{1}{4\pi\epsilon''\epsilon_0 l^3} 3\frac{3\left(\sqrt{\frac{2}{3}}\right)^2 - 1}{\left(\sqrt{\frac{8}{3}}\right)^3} = \frac{0.6889}{4\pi\epsilon''\epsilon_0 l^3} \tag{A.2e}$$

$$D_{+1}^{II,I} = D_{-1}^{I,II} = \frac{1}{4\pi\epsilon''\epsilon_0 l^3}\frac{2}{\left(\frac{5}{3}\right)^3} = \frac{0.432}{4\pi\epsilon''\epsilon_0 l^3} \tag{A.2f}$$

The averaged coefficients of interaction C between layers are obtained from

$$C_0 = D_0^{I,I} + D_0^{II,I} = -\frac{3.76628}{4\pi\epsilon''\epsilon_0 l^3} \tag{A.3a}$$

$$C_1 = C_{-1} = \frac{1}{2}(D_{-1}^{I,I} + D_{-1}^{II,I} + D_{+1}^{I,I} + D_{+1}^{II,I}) = \frac{1.82723}{4\pi\epsilon''\epsilon_0 l^3} \tag{A.3b}$$

Appendix B. Effect of a Tilt Angle of the Cluster

The coefficients $D_k^{\alpha,\beta}$ were calculated in Appendix A by assuming that the layers of the cluster are perpendicular to z. When the cluster is tilted, the angles between z and the direction to the neighboring molecules is modified. To calculate the new angle, let us consider that the neighboring molecule, located at the point (x_1, y_1, z_1) is rotated with an angle α (the tilt angle) around an axis in the xy plane, which makes the angle φ with the x axis. The final coordinate z_3 of the molecule after rotation can be obtained by first calculating the coordinates (x_2, y_2, z_2) in a system $x'y'z$ whose axis x', located in the xy plane, makes the angle φ with x

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = \begin{pmatrix} \cos\varphi & \sin\varphi & 0 \\ -\sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} \tag{B.1}$$

and then rotating the molecule around the x' axis with an angle α:

$$\begin{pmatrix} x_3 \\ y_3 \\ z_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & -\sin\alpha \\ 0 & \sin\alpha & \cos\alpha \end{pmatrix}\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} \tag{B.2}$$

From eqs B.1 and B.2 one obtains

$$z_3 = z_1\cos\alpha - x_1\sin\alpha\sin\varphi + y_1\sin\alpha\cos\varphi \tag{B.3}$$

The angles between the axis z and the direction of the molecule, θ and θ', before and after rotation are given by

$$\cos^2\theta = \frac{z_1^2}{x_1^2 + y_1^2 + z_1^2} \quad \text{and} \quad \cos^2\theta' = \frac{z_3^2}{x_3^2 + y_3^2 + z_3^2} \tag{B.4}$$

Since the distance is not modified by rotation, $x_1^2 + y_1^2 + z_1^2 = x_3^2 + y_3^2 + z_3^2$, and from eqs B.3 and B.4 one obtains

$$\cos^2\theta' = \frac{(z_1\cos\alpha - x_1\sin\alpha\sin\varphi + y_1\sin\alpha\cos\varphi)^2}{x_1^2 + y_1^2 + z_1^2} \tag{B.5}$$

Averaging over the angle φ

$$\frac{1}{2\pi}\int_{\varphi=0}^{2\pi}(z_1\cos\alpha - x_1\sin\alpha\sin\varphi +$$
$$y_1\sin\alpha\cos\varphi)^2\,d\varphi =$$
$$z_1^2\cos^2\alpha + (x_1^2 + y_2^2)\frac{\sin^2\alpha}{2} \tag{B.6}$$

one obtains from eq B.5 the result

$$\langle\cos^2\theta'\rangle = \cos^2\theta\cos^2\alpha + \frac{\sin^2\theta\sin^2\alpha}{2} \tag{B.7}$$

where $\langle\,\rangle$ denotes the average over the angle φ.