Hydration forces between silica surfaces: Experimental data and predictions from different theories

J. J. Valle-Delgado
Grupo de Física de Fluidos y Bioceloides, Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

J. A. Molina-Bolívar
Departamento de Física Aplicada II, Escuela Universitaria Politécnica, Universidad de Málaga, 29013 Málaga, Spain

F. Galisteo-González and M. J. Gálvez-Ruiz
Grupo de Física de Fluidos y Bioceloides, Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

A. Feiler
Centre for Surface Biotechnology, Uppsala Biomedical Centre, 751 23 Uppsala, Sweden

M. W. Rutland
Department of Chemistry, Surface Chemistry, Royal Institute of Technology and Institute for Surface Chemistry, 100 44 Stockholm, Sweden

(Received 2 February 2005; accepted 23 May 2005; published online 28 July 2005)

Silica is a very interesting system that has been thoroughly studied in the last decades. One of the most outstanding characteristics of silica suspensions is their stability in solutions at high salt concentrations. In addition to that, measurements of direct-interaction forces between silica surfaces, obtained by different authors by means of surface force apparatus or atomic force microscope (AFM), reveal the existence of a strong repulsive interaction at short distances (below 2 nm) that decays exponentially. These results cannot be explained in terms of the classical Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory, which only considers two types of forces: the electrical double-layer repulsion and the London–van der Waals attraction. Although there is a controversy about the origin of the short-range repulsive force, the existence of a structured layer of water molecules at the silica surface is the most accepted explanation for it. The overlap of structured water layers of different surfaces leads to repulsive forces, which are known as hydration forces. This assumption is based on the very hydrophilic nature of silica. Different theories have been developed in order to reproduce the exponentially decaying behavior (as a function of the separation distance) of the hydration forces. Different mechanisms for the formation of the structured water layer around the silica surfaces are considered by each theory. By the aid of an AFM and the colloid probe technique, the interaction forces between silica surfaces have been measured directly at different pH values and salt concentrations. The results confirm the presence of the short-range repulsion at any experimental condition (even at high salt concentration). A comparison between the experimental data and theoretical fits obtained from different theories has been performed in order to elucidate the nature of this non-DLVO repulsive force. © 2005 American Institute of Physics. [DOI: 10.1063/1.1954747]

I. INTRODUCTION

Chemically, silica is silicon oxide (SiO₂). The smoothness of its surface and its applicability in fields, such as material science, optics, and electronics, has converted silica in a model system, target of numerous studies. Thus, it can be found in the literature different experimental works devoted to the analysis of the interaction between silica surfaces. The interaction forces measured directly by means of surface force apparatus (SFA) or atomic force microscope (AFM) reveal the existence of a strong repulsive interaction at short distances (below 2 nm) that decays exponentially. From the point of view of the theory proposed by Derjaguin and Landau and Verwey and Overbeek (DLVO) theory to explain the interactions and stability of colloidal systems, this short-range repulsion is completely unexpected and could be responsible for the stability of silica suspensions at high electrolyte concentrations. We must remember that the DLVO theory only considers two types of interactions: the attractive van der Waals forces and the electrical double-layer repulsion. The latter depends on the ionic strength in the medium; it is of long range at very low electrolyte concentrations, but it becomes negligible at electrolyte concentrations high enough. Contrary to this tendency, the short-range repulsion between silica surfaces is indepen-
dent of the ionic strength, at least when the salt concentration is not too high. (Yotsumoto and Yoon\textsuperscript{12} found a decrease of the stability of silica suspensions at the isoelectric point when the NaCl concentration is larger than 2 M.)

The origin of the short-range repulsive force between silica surfaces is a very controversial issue. Traditionally, the appearance of this force has been associated with the presence of a structured layer of water molecules at the silica surface. The overlap of these hydrated layers of different silica surfaces gives rise to short-range repulsions which are commonly known as hydration forces. This assumption is supported by the very hydrophilic nature of silica. But the international scientific community is divided since Vigil \textit{et al.}\textsuperscript{13} proposed an alternative explanation for these forces in 1994 (really, this alternative was previously pointed out by other authors\textsuperscript{14}); the short-range repulsion is, in fact, a steric interaction between silica chains or silica gel layers formed on the silica surfaces in aqueous medium.

However, some works that appeared in the literature seem to suggest that hydration forces are responsible for the short-range repulsion observed between silica surfaces. Some of these works were carried out by Grabbe and Horn\textsuperscript{2} (who studied the interactions between silica surfaces subjected to different surface treatments with the aid of a SFA) and by Yoon and Vivek\textsuperscript{15} (who measured and analyzed by means of an AFM the decrease or even the disappearance of the short-range repulsion between silica surfaces in different solutions of alcohols—10% and 20% ethanol and 15% methanol—in water). In both cases, the authors conclude from their results that the short-range repulsion is due to hydration effects, discarding the steric interaction.

Equations (1) and (2) have been successfully used to fit the experimental short-range forces (that exponentially decay on the separation distance) between different surfaces: silica, mica, montmorillonite, lipids bilayers,\text\superscript{1,2,16–19}

\begin{equation}
F_H(x) = C_H \exp \left( -\frac{x}{\lambda} \right),
\end{equation}

\begin{equation}
F_H(x) = C_1 \exp \left( -\frac{x}{\lambda_1} \right) + C_2 \exp \left( -\frac{x}{\lambda_2} \right),
\end{equation}

where \(F_H\) is the short-range force, \(x\) is the separation distance between the surfaces, \(\lambda\) is the decay length, and \(C_H\) is a hydration constant (assuming that the short-range force is due to hydration forces). Equation (2) uses two decay lengths \(\lambda_1\) and \(\lambda_2\) to get a better fit of the experimental results. It is important to emphasize that Eqs. (1) and (2) are empirical relations, which are not supported by any theory.

Different theoretical models have appeared in the literature in the last three decades, which deduce mathematical expressions for the hydration forces. Their short range and their exponential behavior (as a function of the separation distance) are the main characteristics that these theories try to reproduce. Thus, the appearance of hydration forces has been ascribed to different mechanisms according to each theory: polarization effects of surface dipoles or charges on the nearest water molecules, presence of an adsorbed layer of hydrated cations at the interface, image-charge effect due to a great difference between the dielectric constants of water and silica, formation and breakage of hydrogen bonds between water molecules and surface groups,\text\superscript{...} Some of those theoretical models have not been directly used to fit experimental results. Others have been applied to a specific experimental system.

The main purposes of this paper are to present a summary of the different models on hydration forces and to test their validity to reproduce our experimental interaction curves between silica surfaces measured by AFM. In this way, we can throw light on the microscopic origin of the hydration forces in silica systems.

\section{II. MATERIALS AND METHODS}

The force measurements between silica surfaces were performed using a Nanoscope III AFM (Digital Instruments, USA) and the colloid probe technique. The technique used in this study and the operation mode of the AFM are well described in the literature.\text\superscript{1,7,8,20–23} In brief, the colloid probe technique allows the measurement of interactions between a spherical particle mounted on an AFM cantilever and a flat surface placed on the piezoelectric scanner of the AFM. The AFM cantilevers used were standard V-shaped tipless cantilevers whose spring constant (0.12 N/m) was achieved using the resonance method proposed by Cleveland \textit{et al.}\textsuperscript{24} The forces reported are normalized by the radius of the sphere attached to the cantilever.

Silica spheres are nonporous beads with a diameter of 5 \(\mu\text{m}\) [density of 1.96 g/cm\(^3\), refractive index of (589 nm) ~1.37], which were supplied by Bangs Laboratories Inc. (USA). One of these colloidal silica particles was glued to the end of the cantilever using an optical microscope and a micromanipulator arm. Silica planes, with an area around \(1.37 \times 10^2 \text{m}^2\) area. The water contact angle of the silica surfaces was around 21\(^\circ\).

All the interaction experiments were performed in an aqueous medium at different \(pH\) and salt concentrations. All chemicals used were of analytical grade quality. NaCl and CaCl\(_2\) solutions were prepared with double distilled water (Milli-Q System). The \(pH\) was controlled using different buffers (acetate at \(pH\) 5, phosphate at \(pH\) 7, and borate at \(pH\) 9, at constant ionic strength of 2 mM); a dilute HCl solution was used to keep the medium at \(pH\) 3.

\section{III. RESULTS AND DISCUSSION}

Figures 1 and 2 show the force curves between silica surfaces as a function of \(pH\) at different NaCl concentrations. The long-range repulsion observed in Fig. 1 is due to the electrical double-layer interaction. This repulsion diminishes as the \(pH\) decreases (Fig. 1) or the NaCl concentration increases (Fig. 2), in such a way that it becomes negligible at
pH 3 or at 1-M NaCl. The observed behavior as a function of the pH is due to the protonation of the silanol surface groups (responsible for the negative surface charge of the silica) as pH decreases according to the reaction\(^1\),\(^2\),\(^3\) [the isoelectric point of silica is between 2 and 3 (Refs. 8 and 11)]:

\[
\text{Si} - \text{OH} \rightleftharpoons \text{Si} - \text{O}^- + \text{H}^+.
\]

The decrease of the long-range repulsion as the electrolyte concentration increases can be accounted for by the classical DLVO theory; the high concentration of ions in the medium compresses the electrical double layers and yields a negligible double-layer repulsion as compared with the attractive van der Waals forces. The total screening of the double-layer repulsion gives rise to the independence of the interaction curves on the pH.

However, as can be seen in Fig. 1 and 2, a strong repulsion is observed in all the curves at very short separation distances (below 2 nm). This short-range repulsion is especially clear in the cases in which the double-layer repulsion is negligible (pH 3, high NaCl concentration). A small attraction between the silica surfaces at separations around 2 nm can be observed in Fig. 2; this is probably due to the attractive van der Waals forces. The force curves obtained at 0.5-M CaCl\(_2\) are identical to those shown in Fig. 2.

In the following, the characteristic short-range repulsion between silica surfaces shown in the previous figures is analyzed by different theoretical models for the hydration forces.

### A. Marčelja and Radić model

In 1976, with the purpose to explain the first and then recent measurement of hydration forces between phospholipid bilayers performed by LeNeveu et al.,\(^1\),\(^8\) Marčelja and Radić presented a phenomenological model that is considered the first theoretical model for hydration forces.\(^25\)

According to this model, the origin of the hydration forces is associated with a larger order of the water molecules next to the surfaces than in the bulk. On the analogy of the phase transitions, Marčelja and Radić considered that the system could be described in terms of an order parameter \(\eta(z)\) which depends on the distance \(z\) to the surface. This parameter is null where the system is disordered (the bulk) and reaches its maximum value \(\eta_0\) by the surfaces.

Following a formalism similar to the phenomenological theory of Landau for phase transitions,\(^26\) Marčelja and Radić developed the free-energy density \(g(z)\) of the system as a function of the order parameter (Landau expansion),

\[
g(z) = g_0 - a\eta^2(z) + c\left(\frac{d\eta(z)}{dz}\right)^2,\tag{3}
\]

where \(g_0\) is the free-energy density in the bulk and \(c\) is a positive parameter.\(^28\) Since the free energy of the water molecules next to hydrophilic surfaces is lower than in the bulk, the second term in the sum of Eq. (3) must be negative, that is, the parameter \(a\) must be positive.

The real state of the system is obtained by derivation of Eq. (3) with respect to the order parameter. Assuming the boundary condition \(\eta(x/2) = -\eta(-x/2) = \eta_0\) (the surfaces are located in \(z = \pm x/2\)), the interaction potential energy per unit area \(V_\mu\) between two planar surfaces due to the order of the water molecules can be obtained from the excess free energy per unit area,\(^27\)

\[
V_\mu(x) = \Delta G(x) = \int_{-x/2}^{x/2} (g(z) - g_0)dz = \frac{a\eta_0^2x}{\sinh^2(Kx/2)},\tag{4}
\]

where \(K = \sqrt{a/c}\).

According to the Derjaguin approximation, the interaction force \(F\) between a plane and a sphere of radius \(R\) can be calculated from the potential energy per unit area \(V\) between two planar surfaces,\(^28\)

\[
F(x) = 2\pi RV(x).\tag{5}
\]

From Eqs. (4) and (5), the following expression is obtained for the hydration forces in the Marčelja and Radić model:

\[
\frac{F_\mu(x)}{R} = 2\pi a\eta_0^2\frac{x}{\sinh^2(Kx/2)}.\tag{6}
\]

Equation (6) has been used, together with the equations of the DLVO theory, to fit our force curves between silica surfaces,
The Hamaker constant of a system is a measure of the van der Waals attraction. The value of the Hamaker constant for silica in aqueous medium is 10−21 J.28,29 Since the dielectric constant of silica is much lower than that of water, and since silica possesses surface dipoles (the silanol groups), the previous repulsive mechanism could be also present when two silica surfaces interact. But what we present in this section is the image-charge model—related to the Jönsson and Wennerström model—developed eight years ago.

Using Eqs. (6)–(8)—taking $\Psi_S$, $\Psi_P$, $a \sigma_0^2$, and $K$ as the fitting parameters—theoretical force curves similar to that shown in Fig. 3 can be obtained. As can be seen, the Marčelja and Radič model reproduces the short-range repulsion between the silica surfaces successfully. The values of the parameters $a \sigma_0^2$ (related to the intensity of the hydration forces) and $K$ (related to the inverse of the range of such forces) are very similar at high NaCl or CaCl2 concentrations, independent of $\phi$ (results not shown). However, in spite of the apparent success obtained in the fits of the experimental curves, this model has an important limitation: it is a phenomenological theory, that is, there is not a physical interpretation of the order parameter. This means that is difficult to judge if the values of the fitting parameters are acceptable from a physical point of view.

B. Attard and Patey model

In 1983 Jönsson and Wennerström developed a model to try to explain the appearance of hydration forces between phospholipid bilayers.30 Due to the great difference between the dielectric constants of the lipid and aqueous media, the surface dipoles of one of the bilayers can induce polarization charges in the other bilayer. According to Jönsson and Wennerström, the hydration forces are simply the repulsive interaction between the surface dipoles of each bilayer and their respective induced polarization charges. Physically the problem is the same, but the mathematical treatment is simpler, if the polarization charges are substituted for image charges placed inside the lipid region. This model was modified and generalized a little later by Kjellander.31

Since the dielectric constant of silica is much lower than that of water, and since silica possesses surface dipoles (the silanol groups), the previous repulsive mechanism could be also present when two silica surfaces interact. But what we present in this section is the image-charge model—related to the Jönsson and Wennerström model—developed eight years ago.

In 1983 Jönsson and Wennerström developed a model to try to explain the appearance of hydration forces between phospholipid bilayers.30 Due to the great difference between the dielectric constants of the lipid and aqueous media, the surface dipoles of one of the bilayers can induce polarization charges in the other bilayer. According to Jönsson and Wennerström, the hydration forces are simply the repulsive interaction between the surface dipoles of each bilayer and their respective induced polarization charges. Physically the problem is the same, but the mathematical treatment is simpler, if the polarization charges are substituted for image charges placed inside the lipid region. This model was modified and generalized a little later by Kjellander.31

Since the dielectric constant of silica is much lower than that of water, and since silica possesses surface dipoles (the silanol groups), the previous repulsive mechanism could be also present when two silica surfaces interact. But what we present in this section is the image-charge model—related to the Jönsson and Wennerström model—developed eight years ago.

Using Eqs. (6)–(8)—taking $\Psi_S$, $\Psi_P$, $a \sigma_0^2$, and $K$ as the fitting parameters—theoretical force curves similar to that shown in Fig. 3 can be obtained. As can be seen, the Marčelja and Radič model reproduces the short-range repulsion between the silica surfaces successfully. The values of the parameters $a \sigma_0^2$ (related to the intensity of the hydration forces) and $K$ (related to the inverse of the range of such forces) are very similar at high NaCl or CaCl2 concentrations, independent of $\phi$ (results not shown). However, in spite of the apparent success obtained in the fits of the experimental curves, this model has an important limitation: it is a phenomenological theory, that is, there is not a physical interpretation of the order parameter. This means that is difficult to judge if the values of the fitting parameters are acceptable from a physical point of view.

In 1983 Jönsson and Wennerström developed a model to try to explain the appearance of hydration forces between phospholipid bilayers.30 Due to the great difference between the dielectric constants of the lipid and aqueous media, the surface dipoles of one of the bilayers can induce polarization charges in the other bilayer. According to Jönsson and Wennerström, the hydration forces are simply the repulsive interaction between the surface dipoles of each bilayer and their respective induced polarization charges. Physically the problem is the same, but the mathematical treatment is simpler, if the polarization charges are substituted for image charges placed inside the lipid region. This model was modified and generalized a little later by Kjellander.31

Since the dielectric constant of silica is much lower than that of water, and since silica possesses surface dipoles (the silanol groups), the previous repulsive mechanism could be also present when two silica surfaces interact. But what we present in this section is the image-charge model—related to the Jönsson and Wennerström model—developed eight years ago.

In 1983 Jönsson and Wennerström developed a model to try to explain the appearance of hydration forces between phospholipid bilayers.30 Due to the great difference between the dielectric constants of the lipid and aqueous media, the surface dipoles of one of the bilayers can induce polarization charges in the other bilayer. According to Jönsson and Wennerström, the hydration forces are simply the repulsive interaction between the surface dipoles of each bilayer and their respective induced polarization charges. Physically the problem is the same, but the mathematical treatment is simpler, if the polarization charges are substituted for image charges placed inside the lipid region. This model was modified and generalized a little later by Kjellander.31

Since the dielectric constant of silica is much lower than that of water, and since silica possesses surface dipoles (the silanol groups), the previous repulsive mechanism could be also present when two silica surfaces interact. But what we present in this section is the image-charge model—related to the Jönsson and Wennerström model—developed eight years ago.

B. Attard and Patey model

In 1983 Jönsson and Wennerström developed a model to try to explain the appearance of hydration forces between phospholipid bilayers.30 Due to the great difference between the dielectric constants of the lipid and aqueous media, the surface dipoles of one of the bilayers can induce polarization charges in the other bilayer. According to Jönsson and Wennerström, the hydration forces are simply the repulsive interaction between the surface dipoles of each bilayer and their respective induced polarization charges. Physically the problem is the same, but the mathematical treatment is simpler, if the polarization charges are substituted for image charges placed inside the lipid region. This model was modified and generalized a little later by Kjellander.31

Since the dielectric constant of silica is much lower than that of water, and since silica possesses surface dipoles (the silanol groups), the previous repulsive mechanism could be also present when two silica surfaces interact. But what we present in this section is the image-charge model—related to the Jönsson and Wennerström model—developed eight years ago.

In 1983 Jönsson and Wennerström developed a model to try to explain the appearance of hydration forces between phospholipid bilayers.30 Due to the great difference between the dielectric constants of the lipid and aqueous media, the surface dipoles of one of the bilayers can induce polarization charges in the other bilayer. According to Jönsson and Wennerström, the hydration forces are simply the repulsive interaction between the surface dipoles of each bilayer and their respective induced polarization charges. Physically the problem is the same, but the mathematical treatment is simpler, if the polarization charges are substituted for image charges placed inside the lipid region. This model was modified and generalized a little later by Kjellander.31

Since the dielectric constant of silica is much lower than that of water, and since silica possesses surface dipoles (the silanol groups), the previous repulsive mechanism could be also present when two silica surfaces interact. But what we present in this section is the image-charge model—related to the Jönsson and Wennerström model—developed eight years ago.
later by Attard and Patey. These authors analyzed the electrostatic interaction between two planar dipolar lattices through a dielectric continuum. Their model and the final equations are presented in the following.

Consider two dielectric media with relative dielectric constant \( \varepsilon_2 \) separated by a liquid medium whose relative dielectric constant is \( \varepsilon_1 (\varepsilon_1 \gg \varepsilon_2) \). There is a planar dipolar lattice at a distance \( h \) from each interface (see Fig. 4). Two cases can be distinguished: (1) the dipoles are in the liquid medium (\( h > 0 \)) and (2) the dipoles are in the outer dielectric medium (\( h < 0 \)). Considering that the dipoles are arranged in a square lattice with constant \( d \), and applying the Derjaguin approximation given by Eq. (5), simplified expressions are obtained for the short-range repulsion between a plane and a sphere of radius \( R \). Thus, for case 1,

\[
F_{\mu}(x) = \frac{8 \pi^2}{d^3} \frac{1}{\varepsilon_0 \varepsilon_1 (\varepsilon_1 + \varepsilon_2)} \left[ 2m_{\parallel}^2 \left( 1 - \frac{e_1 - e_2}{e_1 + e_2} \right) \right] \exp \left( \frac{4 \pi h}{d} \right) + m_{\parallel}^2 \left[ 1 + \frac{e_1 - e_2}{e_1 + e_2} \exp \left( \frac{4 \pi h}{d} \right) \right] \exp \left( \frac{4 \pi (x - h)}{d} \right),
\]

(9)

and, for case 2,

\[
F_{\mu}(x) = \frac{32 \pi^2}{d^3} \frac{1}{\varepsilon_0 (\varepsilon_1 + \varepsilon_2)} \left( 2m_{\parallel}^2 + m_{\parallel}^2 \right) \exp \left( \frac{4 \pi (x - h)}{d} \right),
\]

(10)

where \( m_{\parallel} \) and \( m_\perp \) are the perpendicular and parallel (to the interfaces) components of the dipolar moment of each surface dipole. On average over all the surface dipoles, \( m_{\parallel} \) can be considered zero.

As can be noted, Eqs. (9) and (10) predict an exponential decay of the hydration forces as a function of the separation distance between the surfaces. The decay length is related to the lattice constant \( d \). It should be taken into account that these equations are valid if the correlations between the dipolar lattices are not important (that is, the direct electrostatic interaction between the dipolar lattices is negligible).

The model developed by Attard and Patey only considers surfaces with dipoles. In the case that surface charge also exists, an additional term must be introduced to take into account the interaction between the charges of one surface and the dipoles of the other. From the electrostatic interaction energy between a charge and a dipole it is possible to deduce the interaction energy per surface unit between two parallel planes due to the interaction between the charges of one plane and the dipoles of the other. The following expression for the corresponding interaction force between a plane and a sphere of radius \( R \) can be reached using Eq. (5) and the equation \( \alpha_0 = \varepsilon_0 \varepsilon_\kappa \varepsilon_0 \), valid for low surface potentials (Debye-Hückel approximation):

\[
F = -\frac{2 \pi R m_{\parallel}}{d^2},
\]

(11)

where \( \varepsilon_0 \) is the surface potential when the surfaces are separated far away. Note that Eq. (11) corresponds to an attractive interaction. It does not depend on the separation distance between the surfaces whenever that distance is so small that dipolar lattice can be considered infinite.

Equations (7)–(11) have been used to fit our experimental force curves between silica surfaces, taking \( \Psi_0 \) (in all the cases \( \Psi_0 = \Psi_0 = \Psi_0 \)), \( d \), \( h \), and \( m_{\parallel} \) as the fitting parameters. At high salt concentrations the double-layer contribution in Eq. (7) is negligible because of the high value of \( \kappa \) (the effect is the same as canceling out that contribution by choosing \( \Psi_0 = 0 \)). The values used for the relative dielectric constants were \( \varepsilon_1 = 78.5 \) (aqueous medium) and \( \varepsilon_2 = 4 \) (silica).

Figure 5 shows an example of the theoretical force curves obtained with the Attard and Patey model. The values of the fitting parameters are presented in Table I. As can be seen, the Attard and Patey model gives theoretical curves that apparently fit the experimental data successfully. And we underline “apparently” because the fitting parameters are not physically acceptable in many cases. The values of \( h > 2 \) nm or positive values of \( h \) in case 2 are nonsensical.

<table>
<thead>
<tr>
<th>( pH )</th>
<th>( 3 )</th>
<th>( 5 )</th>
<th>( 7 )</th>
<th>( 9 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>( \Psi_0 = -10 ) mV</td>
<td>( \Psi_0 = -17 ) mV</td>
<td>( \Psi_0 = -20 ) mV</td>
<td>( \Psi_0 = -20 ) mV</td>
</tr>
<tr>
<td>( d )</td>
<td>3.5 nm</td>
<td>6.6 nm</td>
<td>6.6 nm</td>
<td>6.6 nm</td>
</tr>
<tr>
<td>( h )</td>
<td>2.0 nm</td>
<td>0.1 nm</td>
<td>0.1 nm</td>
<td>0.1 nm</td>
</tr>
<tr>
<td>( m_{\parallel} )</td>
<td>0.1 D</td>
<td>1 D</td>
<td>1 D</td>
<td>1 D</td>
</tr>
<tr>
<td>NaCl</td>
<td>( \Psi_0 = -12 ) mV</td>
<td>( \Psi_0 = -12 ) mV</td>
<td>( \Psi_0 = -17 ) mV</td>
<td>( \Psi_0 = -20 ) mV</td>
</tr>
<tr>
<td>( d )</td>
<td>3.8 nm</td>
<td>3.8 nm</td>
<td>1.9 nm</td>
<td>1.6 nm</td>
</tr>
<tr>
<td>( h )</td>
<td>5.9 nm</td>
<td>5.9 nm</td>
<td>2.0 nm</td>
<td>0.1 nm</td>
</tr>
<tr>
<td>( m_{\parallel} )</td>
<td>0.005 D</td>
<td>0.005 D</td>
<td>0.035 D</td>
<td>1 D</td>
</tr>
<tr>
<td>NaCl</td>
<td>( \Psi_0 = 0 ) mV</td>
<td>( \Psi_0 = 0 ) mV</td>
<td>( \Psi_0 = 0 ) mV</td>
<td>( \Psi_0 = 0 ) mV</td>
</tr>
<tr>
<td>( d )</td>
<td>6.0 nm</td>
<td>6.0 nm</td>
<td>6.0 nm</td>
<td>6.0 nm</td>
</tr>
<tr>
<td>( h )</td>
<td>0.1 nm</td>
<td>0.1 nm</td>
<td>0.1 nm</td>
<td>0.1 nm</td>
</tr>
<tr>
<td>( m_{\parallel} )</td>
<td>1.0 D</td>
<td>1.0 D</td>
<td>1.0 D</td>
<td>1.0 D</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( pH )</th>
<th>( 3 )</th>
<th>( 5 )</th>
<th>( 7 )</th>
<th>( 9 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>( \Psi_0 = -10 ) mV</td>
<td>( \Psi_0 = -17 ) mV</td>
<td>( \Psi_0 = -20 ) mV</td>
<td>( \Psi_0 = -20 ) mV</td>
</tr>
<tr>
<td>( d )</td>
<td>3.8 nm</td>
<td>6.6 nm</td>
<td>6.6 nm</td>
<td>6.6 nm</td>
</tr>
<tr>
<td>( h )</td>
<td>2.7 nm</td>
<td>-0.1 nm</td>
<td>-0.1 nm</td>
<td>-0.1 nm</td>
</tr>
<tr>
<td>( m_{\parallel} )</td>
<td>0.5 D</td>
<td>1 D</td>
<td>1 D</td>
<td>1 D</td>
</tr>
<tr>
<td>NaCl</td>
<td>( \Psi_0 = -12 ) mV</td>
<td>( \Psi_0 = -12 ) mV</td>
<td>( \Psi_0 = -17 ) mV</td>
<td>( \Psi_0 = -20 ) mV</td>
</tr>
<tr>
<td>( d )</td>
<td>3.6 nm</td>
<td>3.6 nm</td>
<td>1.9 nm</td>
<td>6.6 nm</td>
</tr>
<tr>
<td>( h )</td>
<td>4.6 nm</td>
<td>4.6 nm</td>
<td>2.0 nm</td>
<td>-0.1 nm</td>
</tr>
<tr>
<td>( m_{\parallel} )</td>
<td>0.014 D</td>
<td>0.014 D</td>
<td>0.019 D</td>
<td>1 D</td>
</tr>
<tr>
<td>NaCl</td>
<td>( \Psi_0 = 0 ) mV</td>
<td>( \Psi_0 = 0 ) mV</td>
<td>( \Psi_0 = 0 ) mV</td>
<td>( \Psi_0 = 0 ) mV</td>
</tr>
<tr>
<td>( d )</td>
<td>6.4 nm</td>
<td>6.4 nm</td>
<td>6.4 nm</td>
<td>6.4 nm</td>
</tr>
<tr>
<td>( h )</td>
<td>-0.1 nm</td>
<td>-0.1 nm</td>
<td>-0.1 nm</td>
<td>-0.1 nm</td>
</tr>
<tr>
<td>( m_{\parallel} )</td>
<td>150 D</td>
<td>150 D</td>
<td>150 D</td>
<td>150 D</td>
</tr>
</tbody>
</table>

Downloaded 29 Mar 2007 to 150.214.40.140. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp
Also the values of \( m_\perp \) at 1-M NaCl are excessively high. Related to this, Attard and Patey themselves stated that, with the parameter values used by them (\( d=1 \text{ nm}, h=0.1 \text{ nm}, \text{ and } m_\perp=24 \text{ D} \)), the van der Waals attraction was stronger than the repulsion predicted by their model. The only way to overcome the van der Waals interaction is using dipolar moments \( m_\perp \) excessively high. [Different authors conclude that the interaction between surfaces with dipoles through a continuum dielectric medium (continuum electrostatics) is always attractive because of the correlation of the dipoles or because the van der Waals attraction is stronger than the repulsion between surface dipoles and their image charges.]

In spite of Attard and Patey pointed out that their model could be applied to describe the short-range repulsions observed between silica or mica surfaces in aqueous medium, the results presented in this section question the validity of such model, at least in the case of silica.

**C. Paunov, Kaler, Sandler, and Petsev model**

Recently, in 2001, Paunov et al. presented a model to try to justify the appearance of hydration forces in protein suspensions. There are several evidences of the existence of an additional repulsive interaction between proteins at high salt concentrations and \( \text{pH} \) above their isoelectric points. This repulsion is associated with the presence of hydrated ions around the protein surfaces. Thus, Paunov et al. proposed that the hydration forces are due to the overlap of layers of hydrated ions adsorbed on the surfaces. Figure 6 shows a schematic picture of this repulsive mechanism.

It can be proved that the interaction force \( F_H \) between a plane and a sphere of radius \( R \) due to the overlap of the hydrated ion layers (Stern layers) is given, according to the model of Paunov et al., by the following expression:

\[
\frac{F_H(x)}{R} = \begin{cases} 
- \frac{4 \pi \delta_0 kT}{u_w} \left( \phi_S + \ln(1 - \phi_S) \right) \left( \frac{2 \delta_0}{x} - 1 \right), & x_{\text{min}} \leq x \leq 2 \delta_0, \\
0, & x \geq 2 \delta_0,
\end{cases}
\]

where \( u_w \) is the volume occupied by a water molecule (\( u_w = 0.03 \text{ nm}^3 \)), \( \phi_S \) is the volume fraction of hydrated ions in the Stern layer, and \( \delta_0 \) is the diameter of the hydrated ions. Notice that, according to this model, the hydration forces do not appear until the Stern layers come into contact. \( x_{\text{min}} \) is a lower limit to avoid a value too high for the volume fraction of ions in the overlapped Stern layers.

Equations (7), (8), and (12) have been used to fit the experimental force curves between silica surfaces obtained by means of an AFM. But it is necessary to introduce some modifications in Eq. (8): the origin plane for the double-layer repulsion must be displaced to the Stern layer (that is, \( x \) must be replaced by \( x - \delta_0 \)) and the surface potential \( \Psi_0 \) has to be substituted by the diffuse potential \( \Psi_d \). \( \Psi_d \) and \( \phi_d \) have been taken as the fitting parameters; their values are summarized in Table II. Figure 7 shows an example of a fitting curve obtained with this model. The point in which the Stern layers come into contact (\( x=2\delta_0 \)) has been marked by a vertical dotted line. The value used for \( \delta_0 \) was 0.72 nm for Na\(^+\) and 0.82 nm for Ca\(^{2+}\).

<table>
<thead>
<tr>
<th>( \text{pH} )</th>
<th>( \Psi_d = \text{mV} )</th>
<th>( \phi_d = \text{ }}</th>
<th>( \Psi_d = \text{mV} )</th>
<th>( \phi_d = \text{mV} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>0.01-M</td>
<td>( \Psi_d = -8 \text{ mV} )</td>
<td>( \phi_d = 0.001 )</td>
<td>( \Psi_d = -11 \text{ mV} )</td>
</tr>
<tr>
<td></td>
<td>1-M</td>
<td>( \Psi_d = 0 \text{ mV} )</td>
<td>( \phi_d = 0.073 )</td>
<td>( \Psi_d = 0 \text{ mV} )</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>0.01-M</td>
<td>( \Psi_d = -7 \text{ mV} )</td>
<td>( \phi_d = 0.001 )</td>
<td>( \Psi_d = -8 \text{ mV} )</td>
</tr>
<tr>
<td></td>
<td>0.5-M</td>
<td>( \Psi_d = 0 \text{ mV} )</td>
<td>( \phi_d = 0.062 )</td>
<td>( \Psi_d = 0 \text{ mV} )</td>
</tr>
</tbody>
</table>

**FIG. 6. Schematic picture for the origin of the hydration forces according to the model of Paunov et al.**
The adsorption of cations onto the silica surfaces is very small at low salt concentrations, as can be deduced from Table II. The obtained fitting curves can reproduce the experimental results in an acceptable way, although the short-range repulsion is overestimated. The increase in $\phi_2$ at high salt concentrations gives more importance to the repulsion proposed by Paunov et al. However, this repulsion does not come into play until separation distances below $2\delta_0$. Since at high ionic strength the double-layer repulsion becomes negligible (similar effect to choose $\Psi_2=0$), the attractive van der Waals interaction should give rise to a deep attractive minimum before the Stern layers overlap (see Fig. 7). However, the experimental minimum is not so deep, which questions the validity of this model for the case of silica. Moreover, there are experimental evidences that are in disagreement with the model of Paunov et al.: hydration forces between silica surfaces are also present even in distilled water, when the ion concentration is negligible (in this case the repulsive mechanism proposed by Paunov et al. should be negligible too).

D. Ruckenstein and Manciu model

In the last years Ruckenstein and co-workers have published several works presenting a theoretical model for the hydration forces.\textsuperscript{33–46} This model, based on previous works of Schiby and Ruckenstein,\textsuperscript{47,48} states that the short-range repulsive forces have their origin in the polarization of the water molecules by surface dipoles. The polarization induced by these dipoles on the neighboring water molecules propagates towards successive water layers. The overlap of these polarized water layers around different particles or surfaces gives rise to an increase in the free energy of the system; consequently, a short-range repulsive force appears between those particles or surfaces when they approach each other. Actually, and in contrast to other models, the repulsive interaction proposed by Ruckenstein and co-workers is not an independent interaction, but it is coupled with the electrical double-layer repulsion as the authors demonstrated in an extensive theoretical development.\textsuperscript{45,46}

Ruckenstein and Manciu assume that the water molecules near a surface are arranged in layers (parallel to such surface) following the ice structure. In this geometry, the distance between two water molecules joined by a hydrogen bond is $l=0.276$ nm, the distance between two water layers is $\Delta=(4/3)l=0.368$ nm, and the volume occupied by a water molecule is $v_w=8l^3/3\sqrt{3}=0.0324$ nm$^3$.

The total interaction force between a plane and sphere of radius $R$ can be obtained from Eq. (5), where the interaction potential energy can be divided into two components: an attractive component $V_A$ (due to van der Waals forces) and a repulsive component $V_R$ (due to double-layer repulsion coupled with polarization effects).

$$\frac{F(x)}{R} = 2\pi[V_A(x) + V_R(x)],$$

where $V_A$ (van der Waals potential energy per unit area between two plane surfaces) is given by\textsuperscript{28}

$$V_A(x) = -\frac{A}{12\pi x^2}.$$  (14)

The expression for $V_R$ in the case of low surface potentials and at boundary conditions of constant surface charge is presented in the Appendix.

The authors apparently could explain with their model the experimental behavior of protein-latex complexes observed by Molina-Bolivar and Ortega-Vinuesa.\textsuperscript{39,46} Here we are going to test the validity of this model in the case of silica. With that purpose Eqs. (13) and (14), and those that appear in the Appendix have been used to fit our experimental interaction curves between silica surfaces, taking $K$ and $\sigma_0$ (see the Appendix) as the fitting parameters. Figure 8 shows an example of the fitting curve obtained with the Ruckenstein and Manciu model. Table III presents the fitting parameter values.

As can be seen in Fig. 8, the Ruckenstein and Manciu model is not able to explain the presence of a strong repulsion at short distances between silica surfaces. The van der Waals attraction always dominates at distances below 2 nm.
When the appearance of a repulsion is forced (increasing the number of surface dipoles, that is, increasing \( K \)), this appears at larger distances and disappears below 2 nm (just when the experimental repulsion comes into play).

An increase of the silica surface charge as the medium \( p\H \) increases can be observed in Table III. This behavior is according to the deprotonation mechanism of the surface silanol groups, responsible of the negative charge of the silica surfaces. On the other hand, Ruckenstein and Manciu associate the formation of surface dipoles to the adsorption of counterions on the surface-charged groups. Thus, as the electrolyte concentration increases the number of surface dipoles should increase and the surface charge should decrease. This can explain the dependence of the surface charge on the NaCl concentration observed in Table III. However, the behavior of \( K \) as a function of the NaCl concentration observed in Table III is not the expected one: \( K \) should increase as the salt concentration increases due to an augmentation in the number of surface dipoles.

The incoherence of the obtained results together with the unsuccessful fit of the theoretical curves makes clear that the Ruckenstein and Manciu model is not valid to explain the origin of the short-range repulsion between silica surfaces. Other criticisms to this model can also be found in a very recent paper of López-León et al.

### E. Attard and Batchelor model

In 1988, Attard and Batchelor suggested the possibility that the formation and rupture of hydrogen bonds between water molecules had a relevant role in the appearance of repulsive forces between surfaces at short distances.\(^{50}\) It should be taken into account that the formation of a network of hydrogen bonds between the water molecules is responsible of the exceptional properties of water: its liquid state at room temperature in spite of its low molecular weight, its great heat capacity, heat vaporization and melting and boiling points, and its high surface tension are some examples.

According to Attard and Batchelor, the arrangement of the water molecules around the surfaces (by means of dipolar interactions or hydrogen bonds with surface groups) affects the arrangement of the rest of the water molecules. The consequence of this is a decrease in the number of configurations that the water molecules can adopt to satisfy the formation of a tetrahedral network of hydrogen bonds, which can lead to the breaking of part of those bonds. The smaller the separation distance between the surfaces, the more important this effect is, appearing a strong repulsion (hydration forces) at short distances. (The rupture of hydrogen bonds is an energetically unfavorable process and the decrease in the configuration number of the system diminishes its entropy; both effects contribute to the appearance of a repulsive interaction force.)

Experiments carried out in different polar media indicate that the repulsion between phospholipid bilayers by solvation forces is stronger as the solvent molecule capacity to form hydrogen bonds is larger.\(^{51}\) These experimental results and the simulation works of Kjellander and Marčelja\(^{52}\) strengthen the hypothesis of Attard and Batchelor.

The model developed by Attard and Batchelor considers the water molecules distributed in a two-dimensional square lattice.\(^{50}\) This is an important simplification, but the results can be taken as a first approximation for the three-dimensional case. In this model, the water molecules can adopt six different orientations (a six-vertex model), each of them have Boltzmann weight 1. The Boltzmann weight associated with a Bjerrum defect (two neighboring water molecules not joined by a hydrogen bond) is \( w \approx 1 \).

By means of the transfer-matrix method it is possible to deduce an expression for the short-range repulsion between two surfaces in aqueous medium at fixed boundary conditions (which represent the ordering effects of the surfaces).\(^{50}\) Thus, for the case of surfaces that only possess proton donors (such as silanol groups in the silica surfaces) the hydration forces between a plane and a sphere of radius \( R \) are given by

\[
F_{\text{H}}(x) = \frac{4\pi dkT}{R} \frac{1}{v_w} \frac{(1 + w)(1 + 2w)}{(1 - w)^2 \ln \left( \frac{3(1 + w)}{1 - w} \right)} \times \exp \left( -\frac{x}{d} \ln \left( \frac{3(1 + w)}{1 - w} \right) \right),
\]

where, as before, \( v_w \) is the volume occupied by a water molecule and \( d \) is the lattice constant. Typical values assigned to these parameters are \( v_w = 0.03 \, \text{nm}^3 \) and \( d = 0.3 \, \text{nm} \).

As can be observed in Eq. (15), as first approximation the hydration forces exponentially decay as the distance between the surfaces increases. The intensity and the decay length of these forces depend on the concentration of Bjerrum defects (related to \( w \)). Equations (7), (8), and (15) have been employed to fit our experimental data of silica-

---

**Table III.** Values of the parameters obtained in the fits of the experimental interaction curves between silica surfaces according to the Ruckenstein and Manciu model. Equations (13) and (14), and those that appear in the Appendix were used.

<table>
<thead>
<tr>
<th>( pH )</th>
<th>( \sigma_0 )</th>
<th>( K )</th>
<th>( \alpha_x )</th>
<th>( \alpha_y )</th>
<th>( \alpha_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>(-2.25 \times 10^{-3}) C/m(^2)</td>
<td>(-3.65 \times 10^{-3}) C/m(^2)</td>
<td>(-4.39 \times 10^{-3}) C/m(^2)</td>
<td>(-4.52 \times 10^{-3}) C/m(^2)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>(-0.5 \times 10^{-31}) C m</td>
<td>(-2.5 \times 10^{-31}) C m</td>
<td>(-4.4 \times 10^{-31}) C m</td>
<td>(-4.3 \times 10^{-31}) C m</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(-0 ) C/m(^2)</td>
<td>(-1.5 \times 10^{-3}) C/m(^2)</td>
<td>(-2.0 \times 10^{-3}) C/m(^2)</td>
<td>(-2.0 \times 10^{-3}) C/m(^2)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>(-6.5 \times 10^{-3}) C m</td>
<td>(-1.15 \times 10^{-29}) C m</td>
<td>(-1.35 \times 10^{-29}) C m</td>
<td>(-1.48 \times 10^{-29}) C m</td>
<td></td>
</tr>
<tr>
<td>0.01-M</td>
<td>(-0 ) C/m(^2)</td>
<td>(-0 ) C/m(^2)</td>
<td>(-0 ) C/m(^2)</td>
<td>(-0 ) C/m(^2)</td>
<td></td>
</tr>
<tr>
<td>0.1-M</td>
<td>(-0 ) C/m(^2)</td>
<td>(-0 ) C/m(^2)</td>
<td>(-0 ) C/m(^2)</td>
<td>(-0 ) C/m(^2)</td>
<td></td>
</tr>
<tr>
<td>1-M</td>
<td>(-0 ) C/m(^2)</td>
<td>(-0 ) C/m(^2)</td>
<td>(-0 ) C/m(^2)</td>
<td>(-0 ) C/m(^2)</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>(-6.5 \times 10^{-30}) C m</td>
<td>(-6.5 \times 10^{-30}) C m</td>
<td>(-6.5 \times 10^{-30}) C m</td>
<td>(-6.5 \times 10^{-30}) C m</td>
<td></td>
</tr>
</tbody>
</table>

---

\( d = 6.50 \times 10^{-30} \) C m

\( 0 = -2.25 \times 10^{-3} \) C/m\(^2\)

\( 0 = -3.65 \times 10^{-3} \) C/m\(^2\)

\( 0 = -4.39 \times 10^{-3} \) C/m\(^2\)

\( 0 = -4.52 \times 10^{-3} \) C/m\(^2\)

\( K = 0.5 \times 10^{-31} \) C m

\( K = 2.5 \times 10^{-31} \) C m

\( K = 4.4 \times 10^{-31} \) C m

\( K = 4.3 \times 10^{-31} \) C m

\( \alpha_x = 1.15 \times 10^{-3} \) C/m\(^2\)

\( \alpha_y = 2.0 \times 10^{-3} \) C/m\(^2\)

\( \alpha_z = 2.0 \times 10^{-3} \) C/m\(^2\)

\( K = 1.15 \times 10^{-29} \) C m

\( K = 1.35 \times 10^{-29} \) C m

\( K = 1.48 \times 10^{-29} \) C m

\( K = 1.60 \times 10^{-29} \) C m

---

\( \alpha_x = 0 \) C/m\(^2\)

\( \alpha_y = 0 \) C/m\(^2\)

\( \alpha_z = 0 \) C/m\(^2\)

\( K = 6.50 \times 10^{-30} \) C m

\( K = 6.50 \times 10^{-30} \) C m

\( K = 6.50 \times 10^{-30} \) C m

\( K = 6.50 \times 10^{-30} \) C m

---

**Downloaded 29 Mar 2007 to 150.214.40.140. Redistribution subject to AIP license or copyright, see http://jcp.aip.org/jcp/copyright.jsp**
TABLE IV. Values of the parameters obtained in the fits of the experimental interaction curves between silica surfaces according to the Attard and Batchelor model. Equations (7), (8), and (15) were used.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\Psi_0$ (mV)</th>
<th>$w$ (M)</th>
<th>$\Psi_0$ (mV)</th>
<th>$w$ (M)</th>
<th>$\Psi_0$ (mV)</th>
<th>$w$ (M)</th>
<th>$\Psi_0$ (mV)</th>
<th>$w$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$-9$</td>
<td>0.25</td>
<td>$-14$</td>
<td>0.25</td>
<td>$-21$</td>
<td>0.25</td>
<td>$-21$</td>
<td>0.25</td>
</tr>
<tr>
<td>5</td>
<td>$-7$</td>
<td>0.15</td>
<td>$-11$</td>
<td>0.25</td>
<td>$-14$</td>
<td>0.25</td>
<td>$-19$</td>
<td>0.25</td>
</tr>
<tr>
<td>7</td>
<td>$0$</td>
<td>0.10</td>
<td>$0$</td>
<td>0.10</td>
<td>$0$</td>
<td>0.10</td>
<td>$0$</td>
<td>0.10</td>
</tr>
<tr>
<td>9</td>
<td>$-10$</td>
<td>0.25</td>
<td>$-11$</td>
<td>0.25</td>
<td>$-14$</td>
<td>0.25</td>
<td>$-14$</td>
<td>0.25</td>
</tr>
</tbody>
</table>

silica interaction. Only $\Psi_0$ and $w$ have been considered as the fitting parameters. Their values are presented in Table IV.

Figure 9 shows a typical fitting curve obtained with the Attard and Batchelor model. Although there is an overestimation of the intensity of the short-range repulsion, it is surprising that the general tendency of the experimental curves is well reproduced by this approximated (two-dimensional) model: it predicts repulsion where a repulsion is observed experimentally, and it can explain the presence of a small attractive minimum at high salt concentrations. The long-range interaction is well described by the DLVO theory—Eq. (8)—which points out that at large separation distances the medium can be considered as a continuum (the discrete nature of the solvent is not important at large separations).

In Table IV the expected decrease of $\Psi_0$ as the pH diminishes or the electrolyte concentration increases can be observed (in such a way that the double-layer repulsion becomes negligible at very high salt concentrations). $\Psi_0$ also decreases when NaCl is substituted by CaCl$_2$ (a more screening salt). With regards to the parameter $w$, this seems to be independent of the pH and the salt type in the medium. However, it changes with the salt concentration: $w$ takes the value 0.25 at low salt concentrations (which is an acceptable value for bulk water), but this value decreases to 0.10 at high salt concentrations. This means that the concentration of the Bjerrum defects diminishes as the ion number in the solution increases, which is phenomenally difficult to explain in principle.

The overestimation of the intensity of the short-range repulsion by the Attard and Batchelor model may be due to the boundary conditions imposed on the surfaces. It has been implicitly assumed that all water molecules next to the surfaces bind to a surface group. But actually, the silica surfaces might not have enough silanol groups and, therefore, more water molecules are “free” on the surfaces. This would give rise to a repulsion not so strong as predicted by the theoretical model.

Anyway, a generalization of the Attard and Batchelor model could provide better results. Related to this point, Besseling proposed a three-dimensional model to explain the main properties of water that could be considered as such generalization. A detailed description of this model and a comparison with our experimental results will be presented in a coming paper.

F. Other models

In addition to the aforementioned, there are other models that appeared in the literature to explain the existence of hydration forces in different systems. They will be briefly commented in this section.

In the 1980s the nonlocal electrostatic theory reaches a great popularity because it apparently explained the presence and the exponential decay of the short-range repulsion between lipid bilayers. This theory assumes that the electric field generated by the surface dipoles modifies the polarizability of the neighboring water molecules in such a way that the relative dielectric constant of the water near the surfaces decreases until a value $\varepsilon_{\infty} \approx 5$. Far away from the surfaces the relative dielectric constant of the water keeps its characteristic value $\varepsilon_{\infty} \approx 80$. However, soon after Attard et al. revealed the weaknesses of this theory. In particular, the obtaining of a short-range repulsive and exponentially decaying...

---

FIG. 9. Attard and Batchelor model for the hydration forces. The experimental points correspond to the interaction force between silica surfaces in 1-M NaCl at pH 5. The continuous line represents the fitting curve according to Eqs. (7), (8), and (15). The fitting parameters are presented in Table IV.
force crucially depends on the assumed expression for the variation of the relative dielectric constant with the distance to the surface,
\[
\varepsilon_r(q) = \varepsilon_\infty + \frac{\varepsilon_w - \varepsilon_\infty}{1 + \lambda^2 q^2 (\varepsilon_w/\varepsilon_\infty)},
\]
(16)
where \( \lambda \) is the decay length and \( q = 2\pi/z \), being \( z \) as the distance to the surface. Note that \( \varepsilon_r = \varepsilon_w \) near the surfaces \((q \to \infty)\) and \( \varepsilon_r = \varepsilon_w \) in the bulk \((q \to 0)\). Attard et al. proved that Eq. (16) is not applicable to polar molecules like water.\(^{56}\)

In 1983 Gruen and Marčelj published a model to explain the presence of hydration forces between lipid bilayers.\(^{57,58}\) Since they implicitly assumed the same hypothesis than the nonlocal electrostatic theory, their model is target of the same criticisms exposed by Attard et al.\(^{56}\)

The idea of a variable dielectric constant is also used by Basu and Sharma to explain the existence of a short-range repulsion between mica surfaces and the dependence of this repulsion on pH and salt concentration.\(^{59}\) The same behavior as for mica is predicted by this model for silica surfaces. However, it is known from experimental works that hydration forces between silica and mica surfaces are different and do not follow similar trends as a function of pH and salt concentration.\(^{1,2,60–62}\)

A different approach was proposed by Spitzer, who stated that hydration forces could be explained by including a modification in the structure of the electrical double layer.\(^{63–65}\) The adsorbed counterions, which constitutes the Stern layer, are at a distance \( a \) from the surface; the region comprised within the plane \( a \) and an outer plane \( b \) only contains counterions; the diffuse layer extends from the plane \( b \). The counterions adsorb on or desorb from the Stern layer depending on the number of counterions in the region between the planes \( a \) and \( b \). Spitzer assigned an equilibrium constant \( K_d \) to this process. With this model, Spitzer found that the interaction between two surfaces separated by a distance \( x > 2h \) is given by similar equations to those of the DLVO theory. However, a new repulsion appears at separation distances \( 2a < x < 2b \) due to the electrostatic interaction between the counterions, repulsion whose mathematical expression (between a plane and a sphere of radius \( R \)) is
\[
F(x) = \frac{2\pi \sigma_0^2 kT}{
\varepsilon^2 \varepsilon_0 \varepsilon_{r0}(a) \left( K_d \right)^2 \left( \frac{1}{(x/2) - a} - \frac{1}{b - a} \right)
+ 2\pi \varepsilon_0 \varepsilon_r \varepsilon_{r0} \left( \frac{K_d \varepsilon_{r0}}{\varepsilon_{r0} \varepsilon_r} \right)^2
\]
(17)
where \( \sigma_0 \) is the surface charge density, \( n_{i0} \) is the counterion concentration in the bulk (number of counterions per unit volume), and \( z_+ \) and \( z_- \) are the valences of counterions and ions, respectively. Taking \( a \) as the hydrated radius of the counterions and \( \sigma_0, K_d, 1/b \) and \( b \) as the fitting parameters, we have tried to fit our experimental results using Spitzer’s model. In spite of Spitzer successfully applied his model to the interaction between montmorillonite surfaces, we have not observed the same success with silica surfaces; the theoretical curves do not fit the experimental data suitably and, in many cases, the van der Waals attraction is stronger than the short-range repulsion predicted by this model (results not shown).

The theories arisen in the literature about hydration forces usually consider the interaction between homogeneous surfaces. Leikin and co-worker—taking as starting points the Marčelj andRadić model, the continuum electrostatic theory or the nonlocal electrostatic theory—analyzed the effect of the inhomogeneity of the surfaces on the hydration forces between lipid bilayers.\(^{60–68}\) That inhomogeneity was characterized by surface structure factors. The limitations of the mathematical treatment of Leikin and co-worker are the same as those of the theoretical model used as starting points.

It is also possible to find in the literature different simulation studies (by Monte Carlo methods or molecular dynamics) which try to gain an insight into the origin of the hydration forces. But the conclusions are not always coincidental; Kjellander and Marčelj related the hydration forces to the breakage of hydrogen bonds.\(^{52}\) Forsman et al. concluded that the range of the hydration forces mainly depends on the intensity of the interaction between the surfaces and the water molecules.\(^{69,70}\) Marčelj found that the interaction between hydrated ions increases the intensity of the electrical double-layer repulsion at short distances.\(^{71}\)

We can finish this section by mentioning the molecular theory developed by Trokhymchuk et al.\(^{12,2}\) These authors used a model in which the solvent molecules are treated as dipolar hard spheres and the ions are considered as point ions. By means of complex integral equations, Trokhymchuk et al. found two contributions to the hydration forces: one of them related to the volume exclusion of the solvent spheres and the other to the orientation of the dipoles. These two contributions give rise to an oscillatory interaction with an exponential repulsion decay superimposed on the oscillations. These results are qualitatively in agreement with the experimental data about interaction between mica surfaces obtained by Israelachvili and Pashley.\(^{72}\) However, oscillatory forces have not been found between silica surfaces so far. Among the main limitations of this model we underline that, on one hand, it is valid only at dilute concentrations of electrolyte and, on the other hand, it does not take into account the contribution due to the formation and breakage of hydrogen bonds between the water molecules themselves and between the water molecules and certain surface groups (which seems of great importance in the case of silica).

**IV. CONCLUSIONS**

In this paper we have presented a review of the different theoretical models arisen in the literature—from the phenomenological model proposed by Marčelj and Radić until nowadays—to explain the microscopic nature of the, in principle, surprising hydration forces. Each model associates the appearance of hydration forces to different mechanisms: polarization of water molecules by surface dipoles, changes in the dielectric constant of the medium, adsorption of counterions, breakage of hydrogen bonds, etc. It is important to em-
phazise that the origin of the short-range repulsive hydration forces may be different in different systems (mica, lipid bilayers, silica, proteins,...).

An original contribution of the work presented in this paper has been to directly test the validity of these theories for the case of silica. With this purpose, the theoretical curves given by each theory have been compared with the experimental data of interaction between silica surfaces obtained by means of an AFM. Although it is possible that several mechanisms proposed by different authors come into play jointly to give rise to a net short-range repulsion, it seems clear, however, that in the case of silica the main contribution comes from the formation and rupture of hydrogen bonds. This is specially important in the case of silica due to the formation of hydrogen bonds between the surface silanol (Si–OH) groups and the neighboring water molecules.

ACKNOWLEDGMENTS

This work was supported by the Spanish “Technology and Science Ministry” (Project Nos. MAT 2001-1743 and AGL 2001-3843-C02-02) and by a grant of the same Ministry to one of the authors (J.J.V.D).

APPENDIX: REPULSIVE CONTRIBUTION TO THE INTERACTION ENERGY IN THE RUCKENSTEIN AND MANCIU MODEL

The repulsive contribution to the interaction potential energy per surface unit between two infinite planes in the Ruckenstein and Manciu model can be expressed as

\[ V_R(x) = G(x) - G(x \to \infty), \]

where the free energy of the system \( G(x) \) is given by (at boundary conditions of constant surface charge)

\[ G(x) = \frac{\varepsilon_0 e_0 \kappa^2}{2} a_1^2(x) \sinh \left( \frac{x}{\lambda_1} \right) - \frac{C_1 \Delta^2}{2} a_1^2(x) \sinh \left( \frac{x}{\lambda_1} \right) + \frac{\varepsilon_0 e_0 \kappa^2}{2} a_2^2(x) \sinh \left( \frac{x}{\lambda_2} \right) - \frac{C_1 \Delta^2}{2} a_2^2(x) \sinh \left( \frac{x}{\lambda_2} \right) - \frac{\varepsilon_0 e_0 \kappa^2}{2} a_1(x) a_2(x) - \frac{C_1 \Delta^2}{2} a_1(x) a_2(x) \sinh \left( \frac{x}{2 \lambda_1 \lambda_2} \right), \]

(A2)

where

\[ a_1' = a_1 e_0 \varepsilon_0 \lambda_1 \left( \frac{1}{\lambda_1^2} - \varepsilon_0 \kappa^2 \right), \quad a_2' = a_2 e_0 \varepsilon_0 \lambda_2 \left( \frac{1}{\lambda_2^2} - \varepsilon_0 \kappa^2 \right), \]

(A3)

\[ \lambda_{1,2} = \sqrt{\left( 1 + \frac{\lambda_m^2}{2} \pm \sqrt{1 - \frac{\lambda_m^2}{2}} \right) + \frac{1}{4} + \left( \frac{\lambda_m^2}{2 \lambda_m^2} \right)(1 - (2/\varepsilon_0))}, \]

(A4)

\[ \lambda_m^2 = e_0 \varepsilon_0 (\varepsilon_r - 1) C_1 \Delta^2, \]

\[ a_1(x) = \frac{(\sigma_0 / e_0 \varepsilon_0 \kappa^2) h(x) - \lambda_2 K \sinh(x/2 \lambda_2)}{\lambda_1 h(x) \sinh(x/2 \lambda_1) - \lambda_2 g(x) \sinh(x/2 \lambda_2)}, \]

(A5)

\[ a_2(x) = \frac{K}{h(x)} \left[ \frac{g(x)}{h(x)} \right] \frac{(\sigma_0 / e_0 \varepsilon_0 \kappa^2) h(x) - \lambda_2 K \sinh(x/2 \lambda_2)}{\lambda_1 h(x) \sinh(x/2 \lambda_1) - \lambda_2 g(x) \sinh(x/2 \lambda_2)}, \]

(A6)

\[ g(x) = \left[ e_0 \varepsilon_0 \lambda_1 \left( \frac{1}{\lambda_1^2} - \varepsilon_0 \kappa^2 \right) \left( 1 - e_0 \varepsilon_0 \kappa^2 \right) (1 - e_0 \varepsilon_0 \kappa^2) \right] \sinh \left( \frac{2 \Delta' - x}{2 \lambda_1} \right) - e_0 \varepsilon_0 \kappa^2 (e_r - 1) C_0 \]

\[ X \left( \frac{1}{\lambda_1^2} - \varepsilon_0 \kappa^2 \right) \sinh \left( \frac{2 \Delta' - x}{2 \lambda_1} \right), \]

(A7)

\[ h(x) = \left[ e_0 \varepsilon_0 \lambda_2 \left( \frac{1}{\lambda_2^2} - \varepsilon_0 \kappa^2 \right) \left( 1 - e_0 \varepsilon_0 \kappa^2 \right) (1 - e_0 \varepsilon_0 \kappa^2) \right] \sinh \left( \frac{2 \Delta' - x}{2 \lambda_2} \right) - e_0 \varepsilon_0 \kappa^2 (e_r - 1) C_0 \]

\[ X \left( \frac{1}{\lambda_2^2} - \varepsilon_0 \kappa^2 \right) \sinh \left( \frac{2 \Delta' - x}{2 \lambda_2} \right), \]

(A8)

\[ K = \left( \frac{\rho}{e_0} \right) \frac{\varepsilon_0 (e_r - 1)}{2 \pi (A/\pi) + \Delta^2}, \]

(A9)

\[ C_0 = - \frac{3.766}{4 \pi e_0 \varepsilon_0 \lambda_1^2}, \quad C_1 = - \frac{1.828}{4 \pi e_0 \varepsilon_0 \lambda_2^2}, \]

(A10)

where \( \sigma_0 \) is the surface charge density, \( \Delta' \) is the distance between the surface and the first water layer, \( p \) is the perpendicular (to the surface) component of the dipolar moment of
the surface dipoles, $A'$ is the area per surface dipole, $\epsilon_r'$ is the effective relative dielectric constant for the interaction between a surface dipole and a neighboring water molecule, and $\epsilon_r''$ is the effective relative dielectric constant for the interaction between two neighboring water molecules in the bulk. The meaning of the rest of the parameters has been already explained in the text. The parameters $K$—related through Eq. (A9) to the intensity $p/e_r'$ and the density $(A')^{-1}$ of the surface dipoles—and $\sigma_0$ have been used as the fitting parameters. According to Ruckenstein and Manciu, the values assigned to the rest of variables were $\epsilon_0 = 8.85 \times 10^{-12} \text{C}^2/\text{N m}^2$, $\epsilon_r' = 78.5$, $\epsilon_r'' = 1$, $\Delta' = 0.1 \text{nm}$, $l = 0.276 \text{nm}$, $\Delta = 0.368 \text{nm}$, $v_0 = 0.0324 \text{nm}^3$, and $T = 295 \text{K}$.

27 In the Ref. 25 there is a mistake in the calculus; thus, the final expression for $V_d$ is different from Eq. (4).