

Dielectric constant measurements of interfacial aqueous solutions using atomic force microscopy

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Abstract

Dielectric constant variation at aqueous solution/mica interfaces is shown to be responsible for the force acting on tips immersed in the double layer. The exchange of the volume of a region of the electric double layer of a mica surface immersed in aqueous solutions, with a dielectric constant, by the silicon nitride tip, with a dielectric constant ϵ_{Tip} , is responsible for the repulsion at large distances from the surface (starting at ~ 100 nm, diffuse layer) and followed by an attraction when the tip is immersed in the inner layer (≤ 10 nm). The force versus separation measured curves were fitted to the expression of the dielectric exchange force derived by using a continuum theory for a sharpened conical tip immersed in a spatially variable dielectric constant double layer electric field. The dielectric exchange effect gives a consistent description of the force acting on the tip by assuming a double layer region of water with $\epsilon_{\text{DL}} \approx 80$ at distances far away from surface (~ 100 nm), followed by a region of lower dielectric constant at the inner layer. Support for the proposed model (dielectric exchange force) is given by the observation of an attractive force when metal (platinum) coated tips ($\epsilon_{\text{Tip}} \approx \infty$) are immersed in the mica double layer and the measurements of only repulsive force components when silicon nitride tips are immersed in solvent where there is no interaction between the mica surface and the solvent and consequently, no solvent structuring at the interface. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The vast majority of molecular interactions in living systems occur in an aqueous environment. Water is complex and has some unusual, if not unique, property [1]. The complexity of liquid water is due to a combination of the small size and distinct polar charge distribution of the water molecule [2]. The charge dis-

tribution can be modeled by four charges located along the four arms of a tetrahedron [2,3] which allows each water molecule to participate in strong polar (electrostatic charge-dipole or hydrogen-bonding) interactions [4] with a high degree of spatial directionality. The strong hydrogen-bonding water-water interaction results in a large cohesive energy or latent heat, a high boiling point, a high surface tension and a reluctance to dissolve inert (non-polar or hydrophobic) solutes with which it cannot interact through similarly strong polar forces [5].

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Water can strongly bind to and dissolve polar and hydrophilic compounds and it is an excellent solvent for a wide variety of solute molecules and ions and for suspending colloidal particles and biological structures such as proteins, DNA, viruses and cells. To explain the powerful solvent properties of water, scientists naturally turned to consider the intermolecular forces acting between the dissolved species in water and aqueous electrolyte (salt) solutions. The two major forces operating between two macromolecules in liquids are the attractive van der Waals (vdW) and repulsive electric double layer force [6]. The former is always present; the latter depends on the existence of charged surface groups. But even uncharged molecules and particles are often dispersed in water; an observation that led Langmuir [7] and Derjaguin [8] to postulate the existence of an additional force that turned out to be unique to water. This hydration or structural force is believed to arise from the strongly bound and oriented first layer of water molecules on surfaces. There was good experimental and theoretical evidence for the existence of such a primary hydration shell or layer. But to explain an attraction that exceeded the vdW attraction in both magnitude and range, this force had to propagate further than one or two molecular layers. It seemed natural that the first oriented layer could induce a second layer to orient, the second would likewise influence a third and so on.

An alternative possibility is that the origin of short-range forces do not arise from water structuring effects associated with some peculiar property of water-water interactions intrinsic to water, but has more to do with the chemical and physical nature of the surfaces. With this new interpretation of the origin of these forces, many colloidal and biological interactions in water are seen in a completely different light, with different mechanisms for controlling phenomena such as particle adhesion, membrane recognition and fusion, biochemical reactivity and the rates of complementary associations. Here we present experimental evidence that leads to this hypothesis. We will measure the force resulting from water molecule dipolar reorientation at solid/liquid interfaces.

Due to the large significance of electrostatic double layer interactions, numerous attempts to quantify them have been described in the literature, including the pio-

neering work of Derjaguin–Landau–Verwey–Overbeek [9,10] known as the DLVO theory. The force and energy of interactions between plates and spherical particles were determined in the DLVO theory using the simple Gouy–Chapman–Stern [11–14] double layer model based on the continuous Poisson–Boltzmann (PB) equation. Later, many attempts were made to derive more general equations formulated on the basis of statistical mechanics. This led to complicated non-linear integro-differential equations whose solutions became mathematically prohibitive. More successful were the phenomenological theories based on the local thermodynamic balance in which various corrections of the governing PB equation were considered. The simplicity, consistency and an understanding of the limitation of the original DLVO theory have recently being reported by Ninham [15]. The electrostatic force acting on a tip immersed in aqueous solution may be obtained by integrating the Maxwell electric field stress tensor and the osmotic pressure over the whole tip/electrolyte interface or by using the free energy method [6]. The exact numerical calculation of the field stress tensor and the osmotic pressure over the interface is a long, complicated procedure and inconvenient to use [16]. To overcome this disadvantage a simple analytical expression for the electrostatic force was derived [17]. The electrostatic interaction between the charge mica surfaces and charged tips was calculated and the derived electrostatic force on a cone was shown to be $\propto e^{-\kappa H}$, where H is the distance between the tip and mica surface and κ^{-1} is the Debye–Huckel's length.

In this paper we will calculate the force acting on an uncharged tip using the Maxwell stress tensor. The force calculated values for distances far away from the interface is identical to the ones previously derived expression using the DLVO theory. The difference between our treatment and the previous one is that we assume that the repulsion and attraction close to the surface (≤ 10 nm) is associated with the spatial variation of the water dielectric constant; while previous treatments assign this attraction to only vdW forces. A support for the proposed model is given by observation of force versus separation curves for platinum coated tip ($\epsilon_{\text{Tip}} \approx \infty$) immersed in the mica double layer and experiments performed in other solvents (DMSO and formamide) where vdW forces should be observed.

2. Experimental

In our experiments a commercial AFM instrument, Topometrix TMX2000, was used where the movement of the cantilever was detected by the conventional deflection sensor using a 4-quadrant detector enabling vertical as well as lateral force measurements. A special cell was built in order to perform observations in liquid media [18,19]. The cell was made of TeflonTM and the sample is fixed at its bottom. It is moved in the x , y and z directions with respect to a stationary tip. The laser beam enters and leaves the cell through a glass plate and thus, does not cross the air–liquid interface, which is usually curved. The top confining surface of the solution in the cell is far removed from the cantilever beam. In this geometry the displaced liquid follows a path that is perpendicular to the cantilever beam. We have obtained best results in these measurements with very soft cantilevers, typically ~ 0.03 N/m (MicroleverTM, type B, Park Scientific Instruments). Verifications of the spring constants of the cantilever by the method of Sader [20] gave values not statistically different from the manufacturer's values. Water (Milli-Q Plus quality, resistivity ~ 15 M Ω /cm), dimethylsulphoxide (DMSO), formamide, NaCl and KCl solutions were introduced into the cell after freshly cleaved mica was mounted on the xyz translator of the AFM. The experiments were performed at a temperature of 20°C. Each presented curve was registered using at least five different mica substrates and three different tips with various approach velocities averaged using measurements at different point of the sample. Airborne contamination is minimised by preparing samples in a compact laminar flow cabinet and scanning samples in a clean air hood. Forces were measured between a commercial silicon nitride ($\epsilon_{\text{Tip}} = 7.4$) and a flat mica surface ($\epsilon_{\text{mica}} = 5.4$) [21] after 1, 24 and 36 h of immersion in water. Identical force versus separation curves were registered, consequently we did not observe effects of tip aging.

Metal (platinum-iridium) coated tips were also used. These conical tips (Ultralevers, ThermoMicroscopes) are mounted in hard cantilevers with nominal spring constants of 3.3 N/m.

When the mica basal plane is placed within water, the mechanism for the formation of the double layer is assumed to be the dissolution of K^+ ions as well as ion exchanging of K^+ by H^+ or H_3O^+ ions. It

should be noted that the K^+ ions initially held on the mica surface in the high resistivity water (10 M Ω /cm, $\sim 5 \times 10^{-6}$ M 1:1 electrolyte at pH ~ 6) should be at least partially H_3O^+ ion-exchanged. Considering that the solvent volume of the cell was 300 μl and the mica exposed area was 1.13 cm^2 , if all K^+ ions on the mica surface were exchanged into solution, the K^+ concentration would be about 8.3×10^{-8} M, almost two orders smaller than the calculated concentration of the H_3O^+ present in the solution. The charge residing within the double layer has the same net magnitude but opposite sign as the charge present at the mica surface. The zeta potential at the macroscopic mica surface–water interface, was measured using the plane-interface technique in the presence of 10^{-3} M KCl, and was found to be ~ 125 mV within the pH range from 5 to 6 [6].

3. Results and discussion

A typical force versus sample displacement curve is shown in Fig. 1a, for pure water. The vertical axis represents the force acting between tip and sample surface. It is obtained by multiplying the deflection of the cantilever with its spring constant. The horizontal axis represents the distance the sample is moved up and down by the xyz translator. In this, curve repulsive and attractive forces act between tip and sample before contact. Hence, when the sample approaches the tip, the cantilever bends upwards. At a certain point **A** the tip is attracted to the surface. Finally, moving the sample still further causes a deflection of the cantilever by the same amount the sample is moved, because tip and sample are in contact (point **O**). The approaching force curve (Fig. 1a) collected on a mica surface in water is a plot of the change in cantilever deflection (ΔY) versus sample displacement (ΔX). On a hard non-deformable surface, ΔY is proportional to ΔX while the tip and the sample are in contact. Rather than using sample position (X), it is more useful to use an absolute distance (H) that is relative to the separation between the tip and the sample surface. The correction to produce a force versus absolute distance curve uses the relationship $H = \Delta X - \Delta Y$ [22,23]. Fig. 1b shows the force versus separation.

Fig. 2 shows the tip approach for DMSO and formamide. Observe that there is no jump onto the surface that is present in the water measured curve (point

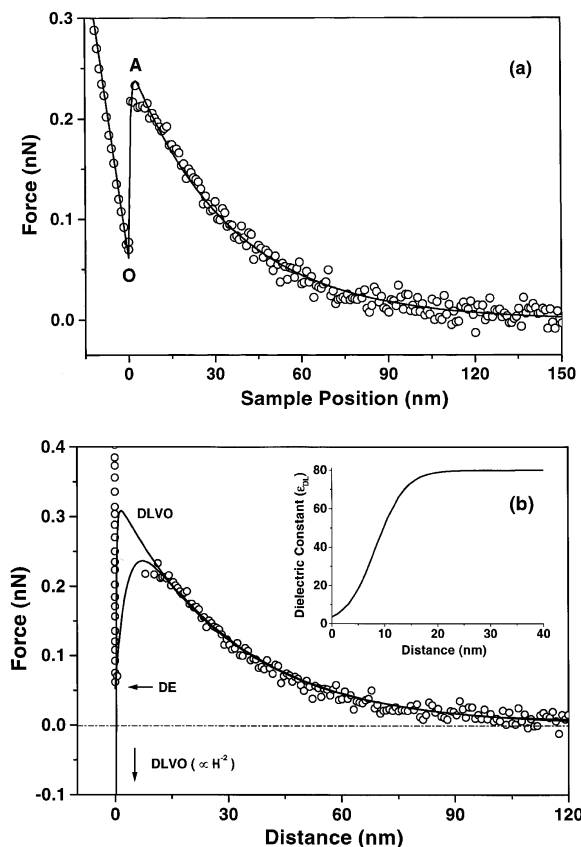


Fig. 1. Force vs. sample displacement measured curves (\circ) for a Si_3N_4 tip and a mica sample immersed in water: (a) measured curve (the line is drawn to guide the eye) (b) corrected curve (absolute tip/substrate distance). The full line indicated by DE (dielectric exchange force) corresponds to the fitting by Eq. (1) and the full line indicated by DLVO corresponds to fitting by the DLVO theory. Observe that DLVO theory fit well only the experimental points for distances from the interface >10 nm. Inset: calculated dielectric constant vs. separation curve that results in the best fitting of the experimental points.

A in Fig. 1a). Fig. 3 shows force versus separation curves measured with a silicon nitride tip on mica obtained at a 10^{-3} M NaCl concentration. The force versus separation curve was also measured for various salt concentrations. For 0.1 M NaCl solution forces act on the tip at smaller distances away from the mica surface than for 10^{-3} M NaCl, but larger than for 1.0 M solutions. These observations indicate that these forces are the result of the presence of a double layer. For 1.0 M NaCl solution, where the expected double

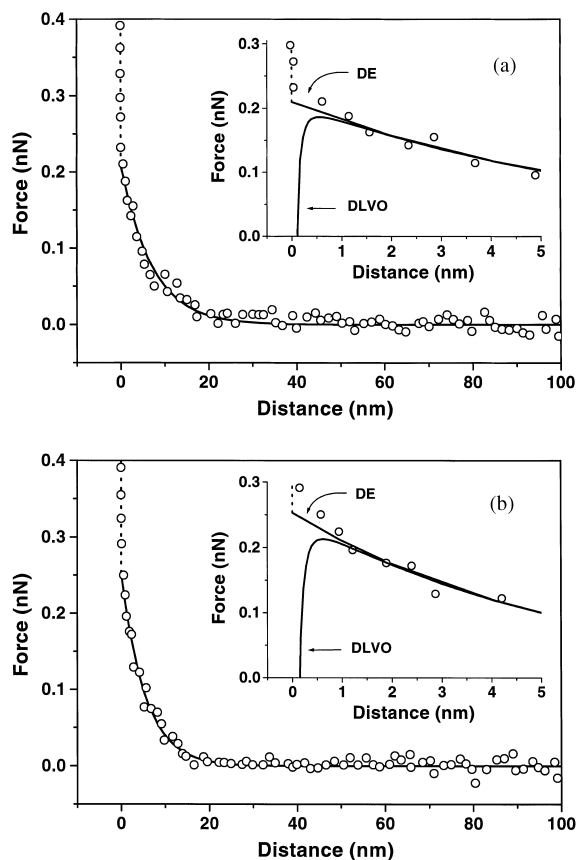


Fig. 2. Force vs. absolute tip/substrate distance curve for a Si_3N_4 tip and mica sample immersed in (a) dimethylsulphoxide (DMSO) and (b) formamide. The full line corresponds to the fitting by Eq. (1) using the parameters shown in Table 1. The dashed line indicates the region where tip and substrate are in contact. Inset: calculated force vs. separation curves by Eq. (1), indicated by DE (dielectric exchange force) and DLVO theory, indicated by DLVO.

layer thickness is <5 nm, the repulsive force described above when the tip was approaching the surface was not detected, indicating that this force is not derived from thin film viscosity nor compression effects.

Force versus separation curves were then measured for a tip with different dielectric constant. Platinum coated tips were then used and the force versus separation curve is shown in Fig. 4. Distinct force curves were measured when compared to the ones measured for silicon nitride tips. The difference observed is an attraction of the tip at distances far away from the interface when compared to the repulsion observed

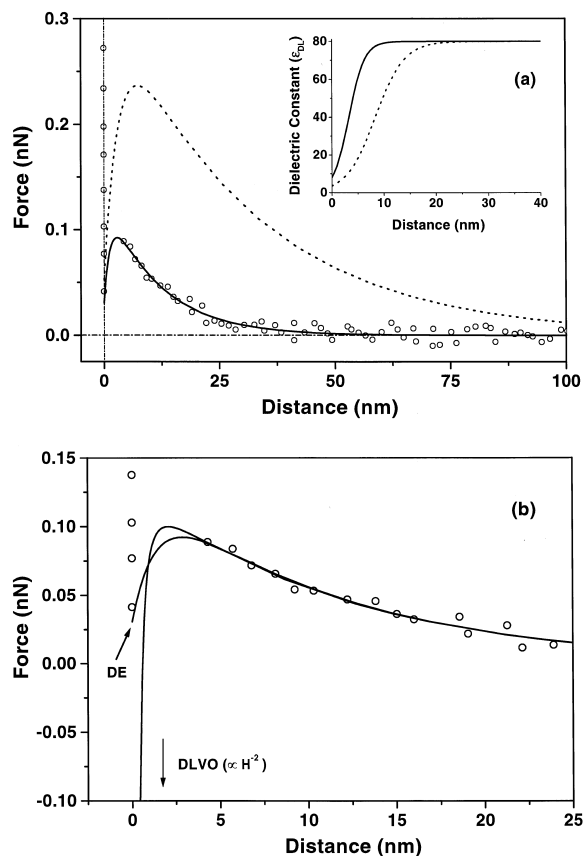


Fig. 3. Force vs. separation curve for a Si_3N_4 tip and a mica sample immersed in 10^{-3} M NaCl solutions (a) the full line corresponds to the fitting by Eq. (1) using the parameters shown in Table 1. The dashed line shows the force vs. separation fitted to the data measured in Milli-Q water. Inset: the full line corresponds to the dielectric constant spatial variation that results in the best fitting to the experimental points. For comparison the corresponding dielectric constant spatial variation for pure water is shown by the dashed line (b) plot of the dielectric exchange force (full line indicated by DE), given by Eq. (1), fitted to the force vs. separation measured points (\circ); and the calculated curve using DLVO theory (full line indicated by DLVO). Both fitted curves are coincident for distances far away from the interface up to 5 nm. For distances shorter to the interface than 5 nm only the dielectric exchange force shows a good fitted curve.

for silicon nitride tips. The repulsive and attractive forces observed at large distances from the interface for silicon nitride and platinum tips, respectively, clearly indicates that the dielectric constant of the tips plays a determinant role in the force acting on the tips. This is the result of the fact that metal coated

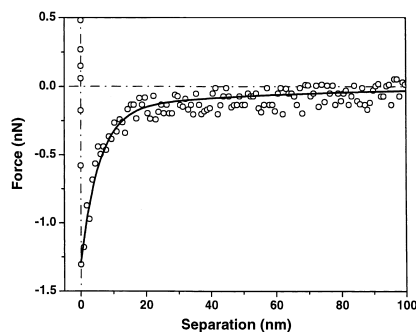


Fig. 4. Force vs. absolute distance measurements for a hard cantilever with a platinum coated tip using the same parameters to fit the experimental data as the ones used for the silicon nitride tips. The full line corresponds to the fitting by Eq. (1).

tips, have dielectric constant $\sim \infty$, which corresponds to a null electric field inside the tip and consequently, zero electric energy stored inside the tip volume. The corresponding force on the tip is attractive since the immersion of the tip in the double layer electric field minimises the total energy of the configuration. The energy variation obtained by the immersion of a metal coated tip is given by Eq. (1) were $1/\epsilon_{\text{Tip}} \approx 0$.

The DE fitting of the experimental points, shown in Figs. 1b and 4, were obtained using the same ϵ_{DL} and κ^{-1} parameters summarised in Table 1. Observe that, in Eq. (1), there is no attractive component acting on the metal tip when it is immersed in the regions near to the interface, since the calculated dielectric exchange force is proportional to $1/\epsilon_{\text{DL}}$ and is always positive for any value of ϵ_{DL} .

Attractive components shown near point A (Fig. 1a) for water are not present for solvents such as DMSO

Table 1
Measured and calculated parameters (in parenthesis) of the double layer (for silicon nitride tips)

Solvent	Dielectric constant spatial variation ($\epsilon_{\text{bulk}}/1+B[\phi(x)]^2$)		κ^{-1} (nm)	ϵ_{DL} (surface)
	ϵ_{bulk}	B		
H_2O	79	35	60	3.64
DMSO	46	0	14	–
Formamide	109	0	11	–
10^{-3} M KCl	80	20	9 (10)	3.81
10^{-3} M NaCl	80	15	11 (10)	8.00

and formamide, therefore, we assumed that the presence of the repulsive force followed by an attractive part close to the surface on the neutral tip in the double layer region is associated with its variable dielectric constant ϵ_{DL} . Several estimates have been given in the literature for the value of the dielectric constant as a function of the distance to the liquid/solid interface in the electric double layer. Bockris and Reddy [24] and Kaatz [25] suggest that for a fully oriented primary water layer, the dielectric constant is about 6, as compared to a bulk value of ~ 80 . James and Healy [26] provide an expression for the dielectric constant of water in the double layer. A similar expression for $\epsilon_{DL}(z)$ was used in this work, i.e. $\epsilon_{DL}(z) = [\epsilon_{bulk}/1 + B\phi^2(z)]$, where ϵ_{bulk} is the dielectric constant in the bulk medium, B is an adjustable parameter, $\phi = \exp(\kappa_{Stern}^{-1}z)$ is a function of the distance z to the surface and has an exponential variation inside the Stern layer characterised by Stern's length κ_{Stern}^{-1} . A plot of $\epsilon_{DL}(z)$ as a function of the distance to the surface is shown as an inset in Figs. 1b and 3a.

The surface of a silicon nitride tip in aqueous solution is composed of amphoteric silanol and basic silylamine (secondary (silazane, $-\text{Si}_2\text{NH}_2$) and possibly primary (silylamine, $-\text{SiNH}_3$) amines though the latter is rapidly hydrolysed) surface groups [27,28], at pH ~ 6 ; with no added electrolyte the silicon nitride surface is either zwitterionic (zero net charge) or slightly negatively charged [29], consequently, we assumed that the surface charge density in the tip $\sigma_{Tip} \ll \sigma_{Mica}$ in water (pH ~ 6.3). To verify the surface charging behaviour of the tips, force versus distance curves in solutions with pH between ~ 5.2 and 6.8 were measured, and the isocharging (icp) point for silicon nitride was determined to be $\text{pH}_{icp} \sim 6.3$.

The analysis of the force acting on the cantilever is as follows: one side of the cantilever is gold covered, therefore, there is a charge difference between the cantilever surfaces, which may cause cantilever deformation or deflection. However, this deflection is present throughout the duration of the approach and adds to the baseline force. The influence of the cantilever charge on the measured force variation during the tip approach to the surface is negligible since the Debye–Huckel's length of mica immersed in Milli-Q water is around one hundred nanometers and the tip height is $\sim 3 \mu\text{m}$. Therefore, only the tip is immersed in the mica double layer region. Supertips of soft can-

tilevers used in this experiments are sharpened conical tips with a $\sim 18^\circ$ angle apex and $\sim 100 \text{ nm}$ height etched at the end of $\sim 3 \mu\text{m}$ height tips. Consequently, the main interaction region of the tip/cantilever with the mica double layer is the sharpened region of the tip and the force variation measured by the AFM during the tip immersion in the mica surface double layer is the force experienced by the tip. Platinum coated tips have a $\sim 25 \text{ nm}$ tip radius of curvature and a 12° angle apex.

Since the charge distribution is assumed constant, the electrostatic energy density is written as a function of the electric displacement vector [30–32]. We also assume that the displacement vector is equal to the field of an infinite plane and that the tip shape does not influence this field. A simple analytical expression for the electrostatic force was derived based on the following principle: it is energetically favourable for a surface charge to be surrounded by a medium with large dielectric constant like water. If the tip approaches the double layer region it replaces the water and since the tip material has a lower dielectric constant than water [21], the configuration becomes energetically unfavourable. Consequently, the tip is repelled by the double layer charge. To estimate the size of this exchange repulsion force we assumed, for a measured double layer width, that the energy change involved in the immersion of the sharpened conical shaped tip inside the double layer, is given by the product of the immersed tip volume times the dielectric constant variation and times the square of the electric displacement vector. The tip was defined to have a sharpened conical shape with one flat end with an area of πR^2 (see Fig. 5), where R is the tip radius. The schematic diagram of a truncated cone compared to a cone with a spherical tip end is shown in the inset of Fig. 5. Since our model proposes that the force on the tip is associated with the tip immersion in the electric field generated at the mica interface and the double layer width is $\sim 100 \text{ nm}$, the effect of a 5 nm radius spherical end tip when compared to a truncated conical tip with a 5 nm flat end radius is negligible. The difference in cross-sections is indicated by the dashed area. Numerical calculations support our claims.

The double layer is characterised by the surface potential and its Debye–Huckel's length is given by $\kappa^{-1} = \sqrt{\epsilon_0 \epsilon_{bulk} kT / e^2 \sum n_i^\infty Z_i^2}$ where ϵ_0 is the vacu-

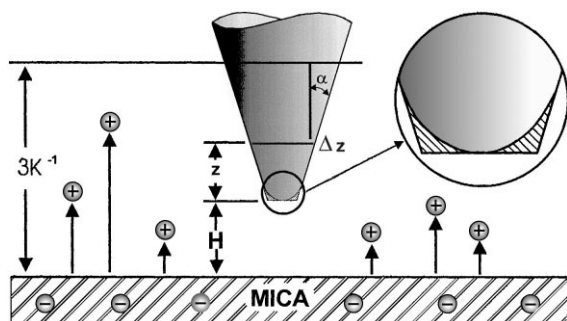


Fig. 5. Conical shaped tip with a cone angle α , a flat end with an area of πR^2 immersed in the double layer region, z is the integration variable of the elemental volume with a width Δz and H is the distance between the surface and the end of the tip. Inset: schematic diagram of a truncated cone with one flat end compared to a cone with a spherical tip end. The dashed region indicates the difference in cross-sections.

um permittivity, k is the Boltzmann constant, T is absolute temperature, e is the electronic unit charge, n_i^∞ is the ion density in the bulk solution and Z_i represents the valency. The sum is over all species of ions present. The electric displacement vector (D) is assumed to have an exponential spatial dependence $D(z) = D_0 e^{-\kappa z/2}$, where D_0 is determined by the ionic charge distribution at the mica surface by using Gauss' Law. A schematic diagram of the tip immersion in the double layer region is depicted in Fig. 5, where z is the integration variable of the trapezoidal volume and H is the distance between the surface and the end of the tip. The elemental volume (dv) of the trapezoidal tip immersed in the double layer region is given by $dv = \pi[R + (tg\alpha)z]^2 dz$ and the change in the electric energy involved in the exchange of the dielectric constant of the double layer by that of the tip is calculated by integrating the energy expression over the tip immersed volume in the double layer region. The force is obtained by the gradient of the energy expression, i.e. $F_z = -\text{grad } \Delta E$, where

$$\Delta E = \frac{1}{2} \int_0^{10\kappa^{-1}H} \left[\frac{1}{\varepsilon_{\text{DL}}(z)} - \frac{1}{\varepsilon_{\text{Tip}}} \right] \times \frac{D^2(z)}{\varepsilon_0} \pi [R + (tg\alpha)z]^2 dz \quad (1)$$

To quantify the characteristic range of the repulsive and attractive forces and to compare the experiments

with calculations, we tried to fit the repulsive part of the force versus separation curves with the gradient of Eq. (1), where the Debye–Huckel's decay and the displacement vector amplitude were the fitting parameters. By adjusting the parameters in the expression of ε_{DL} it possible to fit the attractive part of the curve. The best results of the fitting are shown in Figs. 1b, 2, 3 and 4 by the full lines and the corresponding values are plotted in Table 1. The measured thickness of the diffuse double layer (κ^{-1}) for aqueous solution ($\sim 10^{-6}$ M ion concentration) is ~ 60 nm, in agreement with the value (56 nm) measured by Kékicheff et al. [33]. The Debye–Huckel's lengths values published in the literature are determined by the slope in a logarithmic scale of the force versus separation curves, i.e. $\log(\text{force})$ versus separation. For 10^{-3} M NaCl solution the calculated value is 10 nm and the measured value is ~ 11 nm: for 10^{-3} M KCl the calculated value is 10 nm and the measured value is ~ 9 nm (see Table 1).

The inner layer calculated dielectric constant is ~ 4 for pure water, in agreement with the value of 4.66 given in [25]. This decrease of the double layer dielectric constant from its bulk value, is associated with the tip attraction near the surface. This attraction arises from a particular water dipolar reorientation that is generated by the interfacial electric field. The attribution of this short-range force in water to surface charge induced change in the water dielectric constant accounts for the experimental results shown in this work. The model formulated here, in terms of a water reoriented layer, predicts an attractive force (or less repulsive force when compared to the double layer repulsion) that is determined by the degree of polarisation of the layer of water molecules at the solid/liquid interface, which decreases the water dielectric constant from ~ 80 to a value ~ 6 . The difference between the tip dielectric constant immersed in the double layer and double layer dielectric constant determines the sign of the force (see Eq. (1)).

The measured water reoriented layer present at the mica/liquid interface is in agreement with the results of several studies that have been recently devoted to the layering and orientation of water molecules on surfaces [34–39].

The experimental curves measured for DMSO and formamide do not show an attractive force close to the interface as the one shown in water. Our model

then assumes that there is no variation of the dielectric constant close to the interface and consequently we assume that the dielectric constant $\varepsilon(z)$ is equal to the bulk dielectric constant.

Observe that our model fits well the data at distances shorter than 10 nm. The attractive behaviour of the tip when immersed in the inner layer is associated with the water dipoles partial reorientation at the interface and not the van der Waals attraction which has a much too short range (~ 1 nm) [40]. A possible influence of the vdW attractive force on the shape of the force curve was investigated. The vdW force between a conical tip with a spherical end is given by $-A(H)R/6H^2$ [41], where $A(H)$ is the Hamaker constant for a mica substrate and a silicon nitride tip. The calculated force versus separation curves are shown in Figs. 1b, 2a,b and 3b. The vdW attraction decays, $\propto 1/H^2$, are clearly shown to be inadequate to match the force at close distances (< 10 nm) to the interface for pure water, DMSO, formamide and 10^{-3} M NaCl solutions.

One point that deserves attention is the low calculated value of the dielectric constant of water close to the surface over ~ 10 nm distance. In the literature low values of ε are expected at distances on the order of few (~ 3) molecular diameters close to the surface. Few points have to be considered in order to explain the values measured in this work. The classical description [24] of the water inner double layer is based in inner Helmholtz layer capacitance measurements. The saturation layer (reoriented water molecules layer) is determined using capacitance measurements at interfaces in highly concentrated solutions with κ^{-1} small values. A $\sim 10 \mu\text{F}/\text{cm}^2$ capacitance is associated with a hydrated layer thickness of ~ 1 nm and $\varepsilon \approx 6$. In these measurements, only the ratio of the dielectric constant and the layer width is determined; in our work both the distance of the attraction region corresponding to layer width and the dielectric constant are determined simultaneously. If, arbitrarily, we assume the saturation layer width to be the one corresponding to the half maximum amplitude of the dielectric constant variation in Figs. 1b and 3a (inset), we obtain for Milli-Q water and for 10^{-3} M NaCl solutions ~ 8 and 3 nm, respectively, for the water dipole reoriented layer width. For highly concentrated solutions ($\sim 10^{-1}$ M), the value determined by capacitance measurements is ~ 1 nm [24].

We measured water dielectric constant variations in very diluted solutions thus, layer widths much larger than the ones in concentrated solutions are expected. Water dipoles may be partially oriented in a region close to the interface estimated as follows: for mica immersed in solutions with low ionic concentrations the electric field orients water molecules up to a distance L from the interface, given by the expression $kT \approx \vec{p} \cdot \vec{E}(L)$, where $kT \approx 4.11 \times 10^{-21}$ J is the energy responsible for the thermalisation of the molecular orientation distribution of water molecules (dipole moment $p \approx 6 \times 10^{-30}$ C m); the electric field generated by the mica for surface charges fully dissociated is D (electric displacement vector) ≈ 0.17 C/m². The water dipoles show an orientational effect generated by mica interfacial charges up to ~ 7 nm away from the interface which corresponds to $\varepsilon(L) \approx 27$, calculated using expression $kT \approx \vec{p} \cdot \vec{D}/\varepsilon_0\varepsilon(L)$, where L is determined using the dielectric constant versus separation curve shown in the inset of Fig. 1.

In conclusion both the repulsive and later attractive components of the force acting on the tip during its approach to the surface when immersed in the double layer were associated with the exchange of a double layer region with $\varepsilon_{\text{DL}}(z)$ by the tip with a ε_{Tip} . The dielectric exchange effect gives a consistent description of the force acting on the tip by assuming a double layer region with a variable polarisation profile as function of the distance to the surface. The polarisation variation is associated with the reorientation of the water molecular dipoles in the presence of the mica interfacial charges.

Support for the proposed model (dielectric exchange forces) is given by the observation of an attractive force when metal coated tips are immersed in the double layer. This corresponds to a decrease of the electric field and of the total energy of the field, since the electric field is null inside the metal coated tip and in solvents like DMSO and formamide, where there is no orientational and water effect, no attraction was detected giving further support to our model and weakening the previous argument that the attraction of the tip when it gets close to the interface is due to vdW attraction. A simple description of the water as a media with a variable dielectric constant explains attraction and repulsion components when the tips are immersed in the double layer region.

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