Theory of Electrostatic Effects in Soft Biological Interfaces Using Atomic Force Microscopy

V. G. Levadny,*† M. L. Belaya,†§ D. A. Pink*, and M. H. Jericho‡

*Department of Physics, St.Francis Xavier University, Antigonish, Nova Scotia, Canada B2G 2W5, †Departamento de Ciencies Experimentals, Universidad Jaume 1, Ap.224, 12080 Castellon, Spain, ‡Department of Physics, Dalhousie University, Halifax, N.S., Canada B3H 3J5, and §Institute of Plant Physiology, Russian Academy of Sciences, Botanicheskaya 35, 127276 Moscow, Russia

ABSTRACT We calculated the electrostatic force between a planar interface, such as a planar-supported lipid bilayer membrane, and the tip of a stylus on which another lipid bilayer or some other biomacromolecular system might be deposited. We considered styli with rounded tips as well as conical tips. To take into account the effect of dynamical hydrogen-bonded structures in the aqueous phase, we used a theory of nonlocal electrostatics. We used the Derjaguin approximation and identified the systems for which its use is valid. We pointed out where our approach differs from previous calculations and to what extent the latter are inadequate. We found that 1) the nonlocal interactions have significant effects over distances of 10–15 Å from the polar zone and that, at the surface of this zone, the effect on the calculated force can be some orders of magnitude; 2) the lipid dipoles and charges are located a distance L from the hydrophobic layer in the aqueous medium and this can have consequences that may not be appreciated if it is ignored; 3) dipoles, located in the aqueous region, can give rise to forces even though the polar layer is uncharged, and if this is ignored the interpretation of force data can be erroneous if an attempt is made to rationalize an observed force with a knowledge of an uncharged surface; 4) the shape of the stylus tip can be very important, and a failure to take this into account can result in incorrect conclusions, a point made by other workers; and 5) when L is nonzero, the presence of charges and dipoles can yield a force that can be nonmonotonic as a function of ionic concentration.

INTRODUCTION

The measurement of intermolecular forces is a necessity if the interactions between biomacromolecules, such as proteins or polysaccharides, in aqueous media are to be understood. The Atomic Force Microscope (Binnig et al., 1986) images surfaces by exploiting the very short-range repulsive force between the surface and the tip of the stylus. It can, however, be used to measure the dependence of longer-range forces as a function of distance from the surface by recording the force needed to bring it to within a distance, H, of the surface. In this case one component can be deposited on the surface and the other deposited on the tip of the stylus (Rabinovich and Yoon, 1994). Recently, Butt (1991b) performed measurements on surfaces in aqueous solutions using silicon nitrite or silicon oxide tips. In addition, Butt (1991a) carried out calculations for various tip geometries relevant to his experiments by making use of the expressions of Parsegian and Gingell (1972) and the Derjaguin approximation (Derjaguin, 1934; Derjaguin, 1940; Derjaguin and Landau, 1945). He interpreted his experiments using the equations that he derived, and he found, among other results, that surfaces that were expected to be uncharged exhibited forces between them that appeared to suggest that they were indeed charged, a result that he was unable to account for. It is our intention to point out some unresolved questions raised by Butt's calculations and interpretation of experimental data, to present a model that takes into account physical phenomena not accounted for in his model, and to show that this accounts for observations in a reasonable way.

To interpret experimental data, it is necessary to develop a sufficiently accurate model of the system. This model must include a consideration of the geometry of the stylus tip. It must also take into account the positions and conformational arrangements of all charges in the system. In this regard it is important to note that in biological systems these charges generally are located in the aqueous medium, even though they may be physically attached to the interface or to a hydrophobic layer into which water does not penetrate. Further, a system might possess a net zero charge, while simultaneously possessing nonzero electric dipole moments located a distance L from the hydrophobic region in the aqueous medium (Belaya et al., 1994a). Such a case occurs, for example, with phosphatidylcholine and phosphatidylethanolamine lipids. L is, thus, the characteristic thickness of a polar zone. In general, these are dynamic systems, so that changes in L, due to conformational changes in the polar region, are brought about by external forces (such as thermal fluctuations). Here we were concerned only with electrostatic interactions and not with Van der Waals forces. We took account, however, of the fact that an aqueous medium has dynamic hydrogen-bonded clusters, each with a characteristic lifetime of picoseconds at ~300K, which is the temperature with which we are concerned. This lifetime is one or two orders of magnitude faster than times character-

istic of molecular conformational changes in the polar region at an interface at that temperature. Accordingly, because we attempted to take into account the effects of such dynamic hydrogen-bonded water clusters upon electrostatic interactions involving charges and dipoles, we could then use a model that treats those electrostatic interactions in an average way. One such model entails the use of a nonlocal permittivity function (Kornyshev, 1985; Cevc, 1985; Belaya et al., 1986a,b, 1987, 1994b). This approach describes electrostatic interactions by using a permittivity function that contains a characteristic length reflecting the correlations set up in the system by the existence of time-averaged hydrogen-bonded structures.

Our intention was to derive expressions for the electrostatic force between a planar surface on which an amphiphilic layer has been deposited, and for the tip of a stylus on which another amphiphilic layer has been deposited. The hydrophobic parts of the layers were in contact with the planar surface and the tip, with the hydrophilic regions extending into an aqueous solution that filled the remaining space. The hydrophilic layers were modelled to contain constant charge and dipole densities. These densities were assumed to reside on surfaces located fixed distances away from both the planar surface and the tip. That charge and dipole densities lie a characteristic distance, L, away from a hydrophobic layer in an aqueous solution leads to effects not manifested if L is taken to be zero. The distance L represents the "thickness of the polar region."

THEORY

General expression for the electrostatic force

We considered a tip of an arbitrary shape immersed in an aqueous solution above a planar surface, $z = 0$. The plane $z = 0$ represents the boundary between a hydrophobic medium ($z < 0$) and an aqueous medium ($z > 0$). The dielectric filling the space $z < 0$ represents the hydrophobic region of a supported lipid bilayer. It has been shown (Aytyan and Belaya, 1980) that such a region possessing a thickness of ≈ 50 Å can be replaced by one of infinite thickness if

$$\frac{\epsilon_m}{\epsilon_s ks} \ll 1 \qquad (1)$$

where $\epsilon_s \approx 81$ is the static permittivity of water, ϵ_m is the static permittivity of the hydrophobic region, k is the inverse Debye length, and s is the thickness of the lipid bilayer. The z axis is perpendicular to the plane, and the tip is assumed to exhibit cylindrical symmetry around the z axis. We refer to such a tip as a "symmetrical tip." The shape of the rotationally invariant surface of the tip is defined by the equation,

$$z = h(H) + S((x^2 + y^2)^{1/2}) \qquad (2)$$

where H is the minimum distance between the planar surface and the tip, $h(H)$ is some function of H, and $S(\rho)$ is a function that defines the shape of the tip surface and a function of a single variable representing radial distance from the z axis in an x-y plane. In general, both the tip and the planar surface possess surface electric charges and dipoles. The surfaces on which the charges and dipole densities are located represent, for example, the approximate time- and space-averaged positions of the charges and the dipoles associated with the polar groups of lipid bilayers. Although we could have represented these by discrete objects, each possessing independent z-coordinates, such a general model would have been unwieldy and was unnecessarily complex for our purposes.

To calculate the electrostatic force between tip and surface it is necessary to calculate the electric field distribution in this system and then to use it to calculate the free energy of interaction from which the force can be obtained (e.g., Landau and Lifshitz, 1960). However, the calculation of electric fields in nonplanar geometries usually involves complex mathematics. If the conditions required by the Derjaguin approximation are satisfied, however, then results for planar systems can be used in other geometries. The Derjaguin approximation has been discussed by Senden and Drummond (1995) and Drummond and Senden (1994). The Derjaguin approximation is valid if

$$kS(k^{-1}) \ll 1 \qquad (3)$$

For a hemispherical tip of radius R this condition reduces to

$$kR \gg 1 \qquad (4)$$

Butt (1991a) used this approximation when modelling a cone, which corresponds to $R \to 0$. In this limit, however, it is necessary to use a different approximation. For a conical tip with half-angle α, the requirement for the validity of the Derjaguin approximation is

$$\tan(\alpha) \gg 1 \qquad (5)$$

The total electrostatic free energy, $W(H)$, of the system is determined by the free energy density (per unit area of surface) of the electrostatic interaction between two charged surfaces, $w(z)$, at a position z along the z axis. The interaction between the planar interface at $z = L_2$ and the conical or spherical interfaces at the stylus tip will be approximated by interactions between the planar surface and a sequence of infinitesimal steps that approximate the curved surface of the tip. In the framework of the Derjaguin approximation (Derjaguin, 1979), this is

$$W(H) = 2\pi \int_H^\infty w(z) g(z) \, dz \qquad (6)$$

where $g(z) = rdr/dz$. Here, the smooth surface was approximated as a sequence of steps, with changes in the surface accounted for by the term $g(z)$. When we calculated this, we were concerned, therefore, with calculating the interactions between the planar surface at $z = L_2$ and a sequence of infinitesimal planes that approximate the curved stylus tip.

The force due to the electrostatic interaction between the tip and the planar surface was, therefore

$$F(H) = -\frac{\partial W}{\partial H} = 2\pi\left[w(H)g(H) - \int_H^\infty w(z)\frac{dg}{dH}\,dz\right] \quad (7)$$

This satisfied the boundary condition that $\lim_{H\to\infty} F(H) = 0$. Bearing in mind that the functions $g(z)$ for the hemisphere and the cone are

$$g(z) = R = \text{constant} \quad \text{(hemisphere)} \quad (8a)$$

$$g(z) = (z - H)\tan^2(\alpha) \quad \text{(cone)} \quad (8b)$$

then, using Eq. 7, we obtained the forces for these systems,

$$F(H) = 2\pi R w(H) \quad \text{(hemisphere)} \quad (9a)$$

$$F(H) = 2\pi\tan^2(\alpha)\int_H^\infty w(z)\,dz \quad \text{(cone)} \quad (9b)$$

The tip of the stylus can be described as a hemisphere attached to a truncated cone (Fig. 1). If $kR\cos(\alpha) \gg 1$, the interaction of the tip with the planar surface is completely determined by the interaction of the hemisphere with the planar surface, i.e., Eq. 9a. If, however, $kR\cos(\alpha) \sim 1$ and $\tan(\alpha) \gg 1$ then the interaction force is

$$F(H) = 2\pi R\left[w(H) - w(H_s) + \frac{\tan^2(\alpha)}{R}\int_{H_s}^\infty w(z)\,dz\right] \quad (10)$$

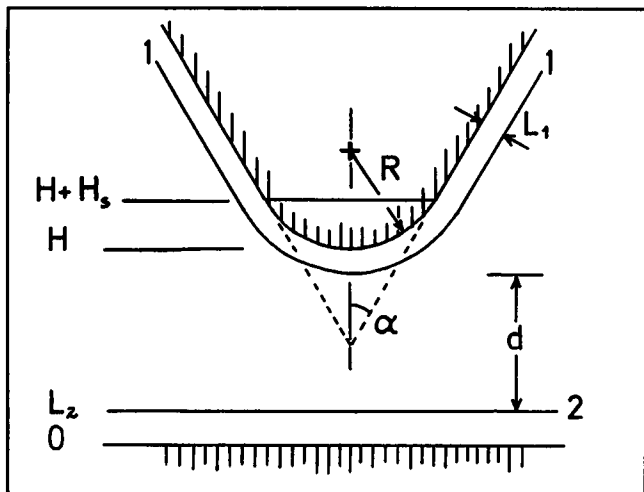FIGURE 1   Schematic diagram of the model planar surface-stylus tip system. The region $z < 0$ represents a dielectric (cross-hatched) layer such as the hydrophobic part of a lipid bilayer. Located on the plane $z = L_2$, referred to as layer 2, are surface charge and dipole densities, σ_2 and ν_2. The tip is described by a hemisphere of radius R attached to a cone with matching surfaces and slopes. The position of the join between the cone and the hemisphere is at $z = H + H_s$. The lowest point of the hemisphere is at $z = H$. A surface 1, $z = H + S((x^2 + y^2)^{1/2})$ is concentric with the dielectric surface of the hemisphere-cone combination. If $R \to 0$ then the tip is pointed with a half-angle α and the tip is at $z = H$.

where

$$H_s = H + R(1 - \sin(\alpha)) \quad (11)$$

Note that in this case if the cone is sufficiently sharp, i.e., $\tan(\alpha) \leq 1$, then the Derjaguin approximation is not valid.

The free energy density for a planar geometry

Fig. 1 shows a cross section through the system in which the z axis is perpendicular to the lower plane at $z = 0$. Uniform distributions of charge and point dipole densities are located on the plane at $z = L_2$. This plane is labeled 2, and the charge and dipole densities located on this plane have magnitudes σ_2 and ν_2, respectively. A portion of a spherical surface, of radius R with centre as shown representing the tip of the stylus, with rotation symmetry around the z axis exists for $H < z < H + H_s$. A cone with a half-angle (projected as shown) of α exists for $z > H + H_s$. The slopes of the cone and the sphere are equal on the plane $z = H + H_s$. We may wish to coat the tip of the stylus with a hydrophobic layer, which is attached to a surface on which charge and dipole densities are located. The shape of this polar surface, labeled 1, is defined by Eq. 2 with $h(H) = H$. The charge and dipole densities on the tip are denoted by σ_1 and ν_1. The perpendicular distance from the spherical and conical surfaces to the polar surface is equal to L_1, as shown. A significant result of this geometry is evident when the radius of the sphere, R, goes to zero. In this case, we considered a conical (pointed) stylus, making a half-angle of α at its tip that was located at $z = H$.

The free energy density must be calculated for the interactions between a planar surface at $z = L_2$ and a sequence of infinitesimal planar surfaces that represent the curved surface of the stylus tips. To obtain an expression for the free energy density, $w(z)$, of a system with the planar geometry appropriate to our model in terms of the charges and dipoles located at $z = z_i$ ($i = 1, 2$) on the planes labeled 1 and 2 respectively, we needed to obtain the electric potential, $\psi(z)$. In this geometry, the electric displacement vector, D, points along the z axis and depends functionally only on z, so that $D = D(z)z$ where z is a unit vector along the z axis. Then,

$$\nabla \cdot D = D' = 4\pi\rho_{\text{ion}} + \sum_{i=1}^2[\sigma_i\delta(z - z_i) - \nu_i\delta'(z - z_i)] \quad (12)$$

where the planes are $z_1 = H - L_1$ and $z_2 = L_2$, and the prime indicates the derivative with respect to z. Here ρ_{ion} is the average ion density, σ_i and ν_i are the magnitudes of the surface densities of charges, and point dipoles located on the planar surfaces z_i and $\delta(z)$ are Dirac delta functions. The boundary conditions are

$$\frac{\partial\Psi(z=0)}{\partial z} = 0; \quad \frac{\partial\Psi(z=H)}{\partial z} = 0 \quad (13)$$

The solution for the forces given in Eqs. 9a and b are outlined in the Appendix and are,

$$F(H) = \frac{4\pi^2 R}{\epsilon_s}\left\{\frac{1}{k}\frac{1}{sh(kH)}\left[(\sigma_{1k}^2 + \sigma_{2k}^2)e^{-kH} + 2\sigma_{1k}\sigma_{2k}\right]\right.$$

$$\left. + \frac{C_1}{n}\frac{1}{N(nH)}\left[(\sigma_{1n}^2 + \sigma_{2n}^2)\frac{1 + C_3}{2}e^{-nH} + \frac{2\sigma_{1n}\sigma_{2n}}{C_3}\right]\right\}$$

(hemisphere)   (14a)

$$F(H) = -\frac{4\pi^2}{\epsilon_s}\tan^2(\alpha)\left\{\frac{1}{k^2}\left[(\sigma_{1k}^2 + \sigma_{2k}^2)\ln(1 - e^{-2kH})\right.\right.$$

$$\left.+ 2\sigma_{1k}\sigma_{2k}\ln\left(\frac{1 - e^{-kH}}{1 + e^{-kH}}\right)\right]$$

$$+ \frac{C_1}{n^2 C_3^2}\left[(\sigma_{1n}^2 + \sigma_{2n}^2)\left(\frac{1 + C_3}{2}\right)\ln(1 - C_3^2 e^{-2nH})\right.$$

$$\left.\left.+ 2\sigma_{1n}\sigma_{2n}\ln\left(\frac{1 - C_3 e^{-nH}}{1 + C_3 e^{-nH}}\right)\right]\right\}$$ (cone)   (14b)

where the various quantities are defined in the Appendix.

If the stylus carries zero charge and dipole densities, i.e., $\sigma_{1k} = \sigma_{1n} = 0$, then these simplify to

$$F(H) = \frac{4\pi^2}{\epsilon_s}R\left[\frac{\sigma_{2k}^2 e^{-kH}}{k\,sh(kH)} + C_1\frac{(1 + C_3)\sigma_{2n}^2 e^{-nH}}{2n\,N(nH)}\right]$$

(15a)

(hemisphere)

$$F(H) = -\frac{4\pi^2}{\epsilon_s}\tan^2(\alpha)\left[\frac{\sigma_{2k}^2}{k^2}\ln(1 - e^{-2kH})\right.$$

(15b)

$$\left.+ C_1\frac{(1 + C_3)}{2C_3^2}\frac{\sigma_{2n}^2}{n^2}\ln(1 - C_3^2 e^{-2nH})\right]$$ (cone)

The first terms in each of these equations are the (classical) Debye terms, whereas the second terms arise because of the nonlocal interactions. Note that the first term of Eq. 15b differs from that of Butt (1991a, Eq. 11) for the same system. It does, however, reduce to his expression when $kH \gg 1$, i.e., when the separation between the tip of the stylus and the planar surface is much greater than the Debye length. In the next section we applied our results to the two cases, conical and hemispherical tips. In all calculations, wherever necessary, we assumed that the temperature is 300K. Elsewhere, we used the expressions obtained here to make comparisons with experimental results.

RESULTS

Results are presented for the force, F, as a function of the distance, d, between the planar surface and the tip. We were concerned almost exclusively with uncharged tips ($\sigma_1 = 0$) that possess zero dipole density ($\nu_1 = 0$). We chose the half-angle, α, to be $\pi/4$ and considered cases for which L_2

= 5 Å or L_2 = 0. On the planar surface we chose $\sigma_2 = 0.1$ e/nm² and ν_2 = 5.0, 3.3 and 1.7 in units of 10^{-3} e/nm, where e is the unit of electronic charge. We concerned ourselves, predominantly, with two values of ionic concentration, 0.1 M and 0.03 M, except when we considered the dependence of the force upon this quantity. In the latter case we considered d = 5 Å and 10 Å. Recalling that ν is the component of the dipole perpendicular to the surface, we chose a small value, because experiments (e.g., Brumm et al., 1994) suggest that the P-N dipole makes a very small angle with the bilayer plane in a fluid phase.

Conical tip and planar surface

Fig. 2 shows the dependence of the forces on the distance, d ($d = H - L_1 - L_2$), between a conical tip of half angle 45°, and a planar surface for L_2 = 5 Å (Fig. 2 A) and for L_2 = 0 (Fig. 2 B), when the ionic concentration is 0.1 M. This gives k = 0.1 Å⁻¹ at ~300K. At this temperature the relationship between c (in M) and k (in Å⁻¹) is $c = 9k^2$. We chose some of our parameters to make a comparison with the results of Butt. The intention here was to illustrate the effect of the presence of charges or dipoles bound at an interface located a distance L in the aqueous region, and the effect of including hydrogen-bonded water clusters via the nonlocal theory. The tip possessed zero charge and dipole density on layer 1, whereas the charge density on the planar surface, layer 2, was chosen to be σ_2 = 0.1 e/nm². We chose three dipole densities, ν_2 = 5.0, 3.3, and 1.7, in units of 10^{-3} e/nm. In Fig. 2 A the effect of the dipoles, when L is nonzero, is to decrease the force as the magnitudes of the dipoles decrease. The pronounced effect of the nonlocal interactions that come into play when $d < 20$ Å can be seen. Also shown is the calculation of Butt (1991a) for the same ionic concentration and charge density, which yields a linear dependence of $\log(F)$ upon d. Butt, of course, had no dipoles present. When $L = 0$, all forces became equal for $d > 17$ Å, but the nonlocal effect can still be seen for values of d smaller than this. Again the calculation of Butt yields a linear dependence.

Conical tip and planar surface

Fig. 3 again shows the dependence of the forces on the distance, d, between a conical tip of half-angle 45° and a flat surface, but now with a lower ionic concentration, 0.03 M. This gives k = 0.057 Å⁻¹. Again, we chose various dipole densities, with L_2 = 5 Å (Fig. 3 A) and L_2 = 0 (Fig. 3 B), with both the charge and dipole densities on the tip being zero and σ_2 = 0.1 e/nm². A comparison of Figs. 2 B and 3 B, for L_2 = 0, shows that the nonlocal effect had the same range and yielded the same value of the force as $d \to 0$. The difference between them lies in the distance-dependence of the force determined by the different values of k. It is again evident that the difference in the force at the surface is two orders of magnitude larger because of the nonlocal effects.
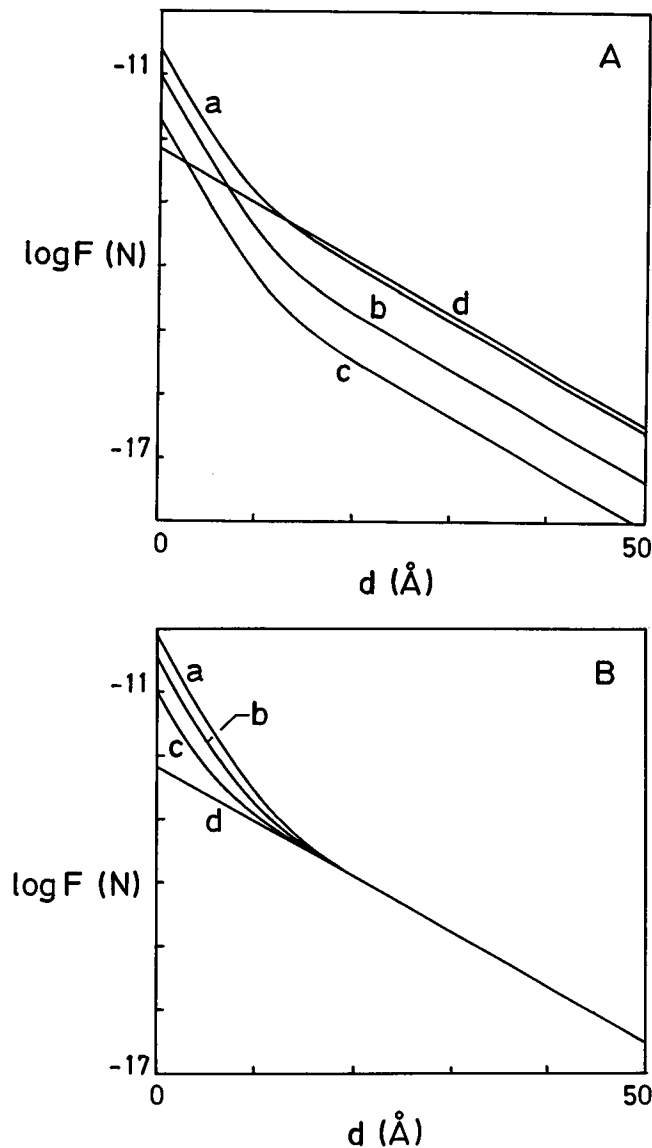
FIGURE 2 Conical stylus tip. Dependence of force upon distance. A: k = 0.1 Å^{-1} (0.1 M) and L_2 = 5 Å. Force (in Newtons) as a function of separation, d, with α = 45°, σ_1 = ν_1 = 0, with σ_2 = 0.1e/nm². a) ν_2 = 5.0 × 10^{-3} e/nm; b) ν_2 = 3.3 × 10^{-3} e/nm; c) ν_2 = 1.7 × 10^{-3} e/nm. d) Calculation of Butt (1991a) for α = 45°, concentration 0.1 M and charge density = 0.1 e/nm². B: All parameters are the same as in A, except that L_2 = 0. a) ν_2 = 5.0 × 10^{-3} e/nm; b) ν_2 = 3.3 × 10^{-3} e/nm; c) ν_2 = 1.7 × 10^{-3} e/nm. d) Calculation of Butt (1991a) for α = 45°, concentration 0.1 M and charge density = 0.1 e/nm².

FIGURE 3 Conical stylus tip. Dependence of force upon distance. A: k = 0.057 Å^{-1} (0.03 M) and L_2 = 5 Å. Force (in Newtons) as a function of separation, d, with α = 45°, σ_1 = ν_1 = 0, with σ_2 = 0.1e/nm². a) ν_2 = 5.0 × 10^{-3} e/nm; b) ν_2 = 3.3 × 10^{-3} e/nm; c) ν_2 = 1.7 × 10^{-3} e/nm; d) σ_2 = 0 and ν_2 = 1.7 × 10^{-3} e/nm. e) Calculation of Butt (1991a) for α = 45°, concentration 0.03 M and charge density = 0.1 e/nm². B: All parameters are the same as in A, except that L_2 = 0. a) ν_2 = 5.0 × 10^{-3} e/nm; b) ν_2 = 3.3 × 10^{-3} e/nm; c) ν_2 = 1.7 × 10^{-3} e/nm. d) Calculation of Butt (1991a) for α = 45°, concentration 0.03 M and charge density = 0.1 e/nm².

Fig. 3 A illustrates, as in Fig. 2 A, the effect of dipoles located on a plane in the aqueous medium. Here we show an additional result in the case that layer 2 is uncharged (σ_2 = 0) but possesses an nonzero dipole density, ν_2 = 1.7 × 10^{-3} e/nm. A consequence of L_2 > 0 is to cause a force to appear even though the surface is uncharged. If L_2 = 0, no force will be observed. This has relevance for the measurements reported by Butt (1991b) where a force was experimentally observed, and unaccounted for, in the case of an uncharged surface.
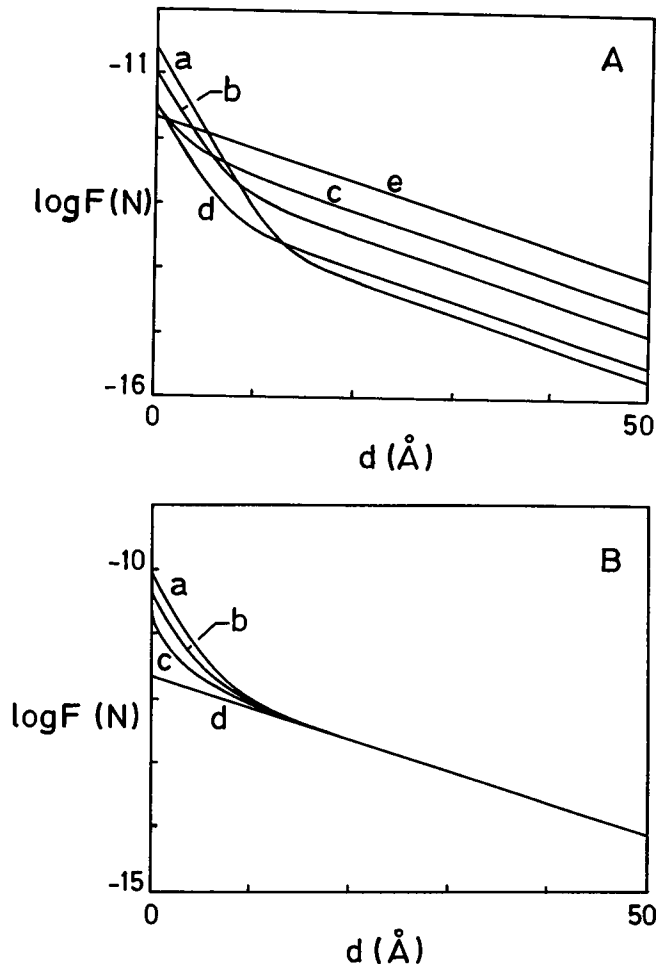
Spherical or conical tips and planar surface

Fig. 4 shows a comparison between spherical (*solid lines*) and conical tips (*dashed lines*) and a flat surface, with an ionic concentration of 0.03 M, giving k = 0.057 Å^{-1}. The intent here was to show that the force observed can be very sensitive to the shape of the tip. The half-angle of the cone is α = 45°, and the radius of the spherical tip is R = ~8.8A. Again, we chose the charge and dipole densities on the stylus to be zero, with the charge density on the planar surface being σ_2 = 0.1 e/nm². We compared the cases of L_2 = 5 Å (Fig. 4 A) and L_2 = 0 (Fig. 4 B) and again used the three values of dipole density, ν_2, of 5.0, 3.3, and 1.7 × 10^{-3} e/nm. Fig. 4 B shows that near the surface, the effect of hydrogen bonding in the aqueous solution gives rise to a difference in the forces due to the different tips. For the
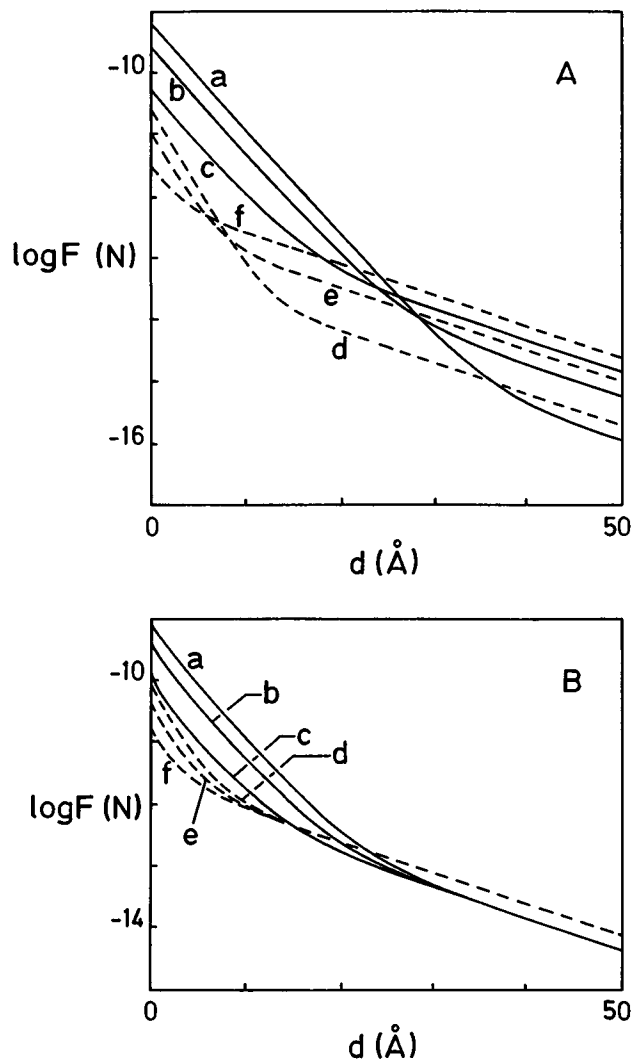
FIGURE 4   Comparison of spherical (*solid lines*) and conical (*dashed lines*) tips. Dependence of force upon distance. A: $k = 0.057$ Å^{-1} (0.03 M), $R = \sim 8.8$ Å, cone angle $\alpha = 45°$ and $L_2 = 5$ Å. Force (in Newtons) as a function of separation, d, with $\sigma_1 = \nu_1 = 0$ and with $\sigma_2 = 0.1e/nm^2$. *a, d)* $\nu_2 = 5.0 \times 10^{-3}$ e/nm; *b, e)* $\nu_2 = 3.3 \times 10^{-3}$ e/nm; *c, f)* $\nu_2 = 1.7 \times 10^{-3}$ e/nm. B: All parameters are the same as in A except that $L_2 = 0$. *a, d)* $\nu_2 = 5.0 \times 10^{-3}$ e/nm; *b, e)* $\nu_2 = 3.3 \times 10^{-3}$ e/nm; *c, f)* $\nu_2 = 1.7 \times 10^{-3}$ e/nm.

parameters chosen here, this difference manifests itself for $d < \sim 15$–20 Å. Because $L_2 = 0$, however, there are no other consequences; and for d greater than these values, both tips appear equivalent. Fig. 4 *A*, however, for which $L_2 = 5$ Å shows the effect of dipoles and charges located some distance from the hydrophobic layer in the aqueous solution: comparing curves a and d, b and e, c and f, we see that the forces are not identical and that the effect extends out to at least between ~ 20–35 Å. Even beyond this distance there could be observable differences between the two kinds of tip. Our results confirmed the claim of Rabinovich and Yoon (1994) that the shape of a tip is very important, especially at short distances.

Ionic concentration

Fig. 5 shows the effects upon the force of changing the ionic concentration for selected values of L_2 and d for a conical tip for which the half-angle is $\alpha = 45°$ and on which the charge and dipole densities are zero. The charge density on the planar surface is $\sigma_2 = 0.1$ e/nm^2. The dipole densities on the planar surface are $\nu_2 = 5.0$, 3.3, and 1.7×10^{-3} e/nm as used before and labeled a, b and c. Curve d (*dashed*) shows the results of Butt (1991a) for the same charge density on the planar surface and the same values of d. Figs. 5 *A* and *B* show the nonmonotonic behavior of the force as a function of ionic concentration for $L_2 = 5$ Å and $d = 5$ Å and 10 Å, respectively. The approximate value of k at which the minimum occurs is

$$k^* \approx \frac{1}{H}[1 + \zeta + \zeta^2] \qquad \zeta = \frac{\sigma_2 H^2}{\nu_2 L_2} \qquad (16)$$

CONCLUSIONS

We have derived expressions for the electrostatic force between a planar surface on which an amphiphilic layer has been deposited and the tip of a stylus on which another amphiphilic layer can be deposited. The hydrophobic parts of the layers were assumed to be in contact with the planar surface and the tip, with the hydrophilic regions extending into an aqueous solution that was assumed to fill the remaining space. The hydrophilic layers could contain both electric charges and dipoles, described by constant charge and dipole densities. It was assumed that charge and dipole densities associated with the planar surface or the stylus tip were located on surfaces that were fixed distances away from both the planar surface and the tip, respectively. We used a nonlocal electrostatics theory of hydrogen-bonded liquids to take into account the effect of space- and time-averaged dynamic hydrogen-bonded water clusters on the electrostatic interactions among charges and dipoles. The fact that these charges and dipoles lie a characteristic distance, L, away from the hydrophobic layer and in the aqueous solution leads to effects not manifested if L is taken to be zero. We have studied this so-called "L-effect" in calculating forces as functions of distance between the planar surface and the stylus tip and as a functions of the ionic concentration. We considered two kinds of stylus tips: a conical tip characterized by a half-angle of α that, for the purposes of illustrating our results, we took to be 45° to compare our results with other calculations, and a truncated cone surmounted by a spherical tip, the whole structure being identified by the conical half-angle α and the radius, R, of the sphere. We obtained inequalities describing conditions under which the Derjaguin approximation, which we used here, is valid and pointed out that this approximation has not always been applied consistently. In illustrating the results of our approach, we have made comparisons with those of Butt (1991a,b). We intend to apply the expressions derived and presented here to analyze the results of experimental studies that we are now carrying out.
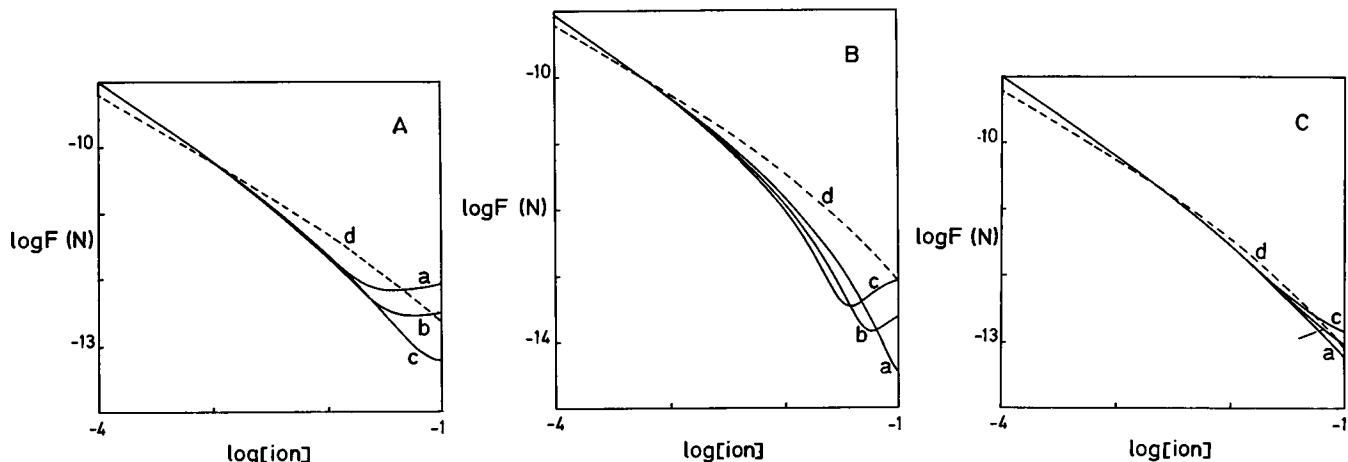
FIGURE 5   Conical stylus tip. Dependence of force (in Newtons) upon ion concentration for various distances with $\alpha = 45°$, $\sigma_1 = \nu_1 = 0$ and $\sigma_2 = 0.1$ e/nm². a) $\nu_2 = 5.0 \times 10^{-3}$ e/nm; b) $\nu_2 = 3.3 \times 10^{-3}$ e/nm; c) $\nu_2 = 1.7 \times 10^{-3}$ e/nm. d) Calculation of Butt (1991a) for $\alpha = 45°$ and charge density $= 0.1$ e/nm². Butt's distances are the same as d. A: $L_2 = 5$ Å and $d = 5$ Å. B: $L_2 = 5$ Å and $d = 10$ Å. C: $L_2 = 0$ and $d = 10$ Å.

APPENDIX

Outline of derivation of Eq. 14a and b

In what follows we take into account the possible change in the permittivity of the aqueous solution near the planar surface by making use of nonlocal electrostatics (Belaya et al., 1994b). We also define, for use below, the distance, d, between the planes $z = z_1$ and $z = z_2$: $d = H - L_1 - L_2$. In all of this we have indicated only the functional dependence upon H, the smallest distance between the polar layers on the stylus and the planar surface. The quantities L_1, L_2, H_s, and α are treated as parameters. Making use of the results of Belaya et al. (1994b) we obtain the electrostatic free energy density,

$$w(H) = \frac{2\pi}{\epsilon_s} \left\{ \frac{1}{k} \frac{1}{sh(kH)} \left[(\sigma_{1k}^2 + \sigma_{2k}^2) e^{-kH} + 2\sigma_{1k}\sigma_{2k} \right] \right.$$

$$\left. + \frac{C_1}{n} \frac{1}{N(nH)} \left[(\sigma_{1n}^2 + \sigma_{2n}^2) \frac{1 + C_3}{2} e^{-nH} + \frac{2\sigma_{1n}\sigma_{2n}}{C_3} \right] \right\} \quad (A1)$$

where

$$C_1 = \frac{\epsilon_s}{\epsilon_\infty} - 1 \qquad C_3 = \frac{\epsilon_\infty^{1/2} - \epsilon_s^{1/2}}{\epsilon_\infty^{1/2} + \epsilon_s^{1/2}}$$

$$N(x) = \frac{e^x - C_3^2 e^{-x}}{2} \quad (A2)$$

$$\sigma_{ik} = \sigma_i ch(kL_i) + \nu_i k sh(kL_i)$$

$$\sigma_{in} = \sigma_i cn(nL_i) + \nu_i n sn(nL_i) \quad i = 1, 2$$

with

$$ch(x) = (e^x + e^{-x})/2 \quad h(x) = (e^x - e^{-x})/2$$

$$cn(x) = (e^x + C_3 e^{-x})/2 \quad sn(x) = (e^x - C_3 e^{-x})/2 \quad (A3)$$

Substituting (A1) into (9a) and (9b), we obtain Eq. 14a and b for the force for the general cases in which both surfaces possess electric charges and dipoles.

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