

# Electrostatic interaction in atomic force microscopy

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**ABSTRACT** In atomic force microscopy, the stylus experiences an electrostatic force when imaging in aqueous medium above a charged surface. This force has been calculated numerically with continuum theory for a silicon nitride or silicon oxide stylus. For comparison, the Van der Waals force was also calculated. In contrast to the Van der Waals attraction, the electrostatic force is repulsive. At a distance of 0.5 nm the electrostatic force is typically  $10^{-12}$ – $10^{-10}$  N and thus comparable in strength to the Van der Waals force. The electrostatic force increases with increasing surface charge density and decreases roughly exponentially with distance. It can be reduced by imaging in high salt concentrations. Below surface potentials of  $\approx 50$  mV, a simple analytical approximation of the electrostatic force is described.

## INTRODUCTION

The atomic force microscope (AFM), invented by Binnig, Quate and Gerber (Binnig et al., 1986), has become an important tool for imaging surfaces (Wickramasinghe, 1989). In the AFM, a sharp stylus at the end of a cantilever is scanned over a surface. Surface features cause the stylus and thus the cantilever to deflect. By measuring the deflection of the cantilever, a topographic image of the surface can be obtained. In biology the AFM has been applied to proteins, lipid layers, DNA, and whole cells (Drake et al., 1989; Butt et al., 1990a; Edstrom et al., 1990; Egger et al., 1990; Weisenhorn et al., 1990; Meyer et al., 1991; Zasadzinski et al., 1991).

Many AFM studies were done in an aqueous medium. This is for two reasons. The force applied by the stylus to the surface can be reduced by a factor of 10–100 compared to the force in air as the meniscus force is absent (Weisenhorn et al., 1989). Second, for many applications water is the natural environment. Biological materials often denature if not kept in a buffer. Electrochemical processes, for instance, can only be observed in water.

To interpret AFM images correctly it is important to know which forces are acting between stylus and surface. In addition, knowledge about the different components of the force is important to minimize the total force and thus prevent possible deformation or destruction of the sample. When imaging in water, different forces act between stylus and sample (Burnham and Colton, 1991). The AFM is based on the repulsive force coming from overlapping electron orbitals between stylus and sample atoms. Another interaction is the Van der Waals attraction. The Van der Waals (VdW) force has been calculated for different stylus-medium-sample combinations

and for different geometries (Albrecht, 1989; Girard et al., 1989; Goodman and Garcia, 1991; Hartmann, 1991).

Burnham and Colton, 1991, already pointed out that in an aqueous medium the electrostatic force should be considered. In water, many surfaces are charged. The charging of surfaces can come about in two ways: by the dissociation of surface groups (e.g., the dissociation of protons from carboxylic groups), or by the adsorption of ions onto the surface. These surface charges cause an electric field which decreases roughly exponentially with increasing distance from the surface (McLaughlin, 1977). Even if the stylus surface does not bear free electric charges, polarization charges at the stylus/electrolyte interface caused by the electric field give rise to an electrostatic interaction. An additional effect is the osmotic pressure acting on the stylus. Surface charges attract counterions and the overall ion concentration increases near the sample. These ions cause an osmotic pressure which repels the stylus. In first experiments, the force versus distance above a mica surface, which is negatively charged, was measured. In addition to the VdW attraction, a repulsive force was observed which depended on the salt concentration (Weisenhorn et al., 1991, submitted for publication).

In this paper I calculated the electrostatic force with continuum theory for a conical stylus with a spherical end made of silicon nitride or silicon oxide. These calculations were done numerically, assuming that the surface charge density is fixed. The influence of the surface charge density and the salt concentration was studied. In addition, a simple analytical expression was derived which approximates the electrostatic force for low surface potentials. For comparison, the VdW force

was calculated for the same stylus-medium-sample configuration.

## THEORY

### Electrostatic force

The electrostatic interaction was evaluated in two steps. First, an expression of the force acting on the stylus was derived. This force depends on the electric field, which was calculated in a second step. For all calculations, the stylus was modeled by a cone with half angle  $\alpha = 45^\circ$  (Fig. 1). The cone was supposed to have a spherical end with a radius of curvature  $R$ . As the stylus geometry had a rotational symmetry, I used cylinder coordinates.

The electrostatic force acting on the stylus  $F_c$  was obtained by integrating the Maxwell electric field stress tensor and the osmotic pressure  $p$  over the whole stylus/electrolyte interface. As only the cross-sectional part of the interfacial area contributes to the force, the integral is

$$F_c = 2\pi \cdot \int_0^\infty (T_z + p) \cdot r \cdot \frac{dr}{dz} \cdot dz. \quad (1)$$

$r$  denotes the horizontal radius of the stylus at a certain height  $z$ . With  $D$  being the distance between stylus and surface,  $r$  is given by

$$r = \sqrt{R^2 - (D + R - z)^2}$$

in the spherical region and

$$r = tg\alpha \cdot (z - D - R + R/\sin\alpha)$$

in the conical region of the stylus.  $T_z$  is the  $z$  component of the Maxwell stress tensor which is given by (Becker

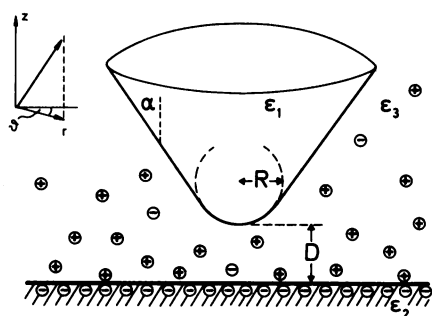


FIGURE 1 Conical stylus with half angle  $\alpha$  and a radius of curvature  $R$  at a distance  $D$  above a charged surface in electrolyte. The concentrations of counterions is increased near the surface.

and Sauter, 1973)

$$T_z = \epsilon_0 \epsilon_{30} \left( E_z^2 - \frac{\vec{E}^2}{2} + E_r E_z \right). \quad (2)$$

$\epsilon_0$  is the vacuum dielectric permittivity,  $\epsilon_{30}$  is the static permittivity of the electrolyte.  $\vec{E}$  is the electric field with  $E_z$  and  $E_r$  as  $z$ - and  $r$ -components.  $\vec{E}$  is related to the electric potential  $\Phi$  by  $\vec{E} = -\nabla\Phi$ .

The second term in Eq. 1 accounts for the force caused by the osmotic pressure. The osmotic pressure at any given point in the electrolyte is

$$p = kT \sum_i (n_i - n_i^\infty), \quad (3)$$

where  $n_i$  is the ion density related by  $n_i = n_i^\infty \cdot e^{-z_i e \Phi / kT}$  to the electric potential.  $n_i$  is the number of one sort of ions per unit vol,  $n_i^\infty$  is the bulk concentration,  $z_i$  represents the valency,  $e$  is the electronic unit charge,  $k$  is the Boltzmann constant,  $T$  the temperature. The sum runs over all sorts of ions present.

To solve Eq. 1, the electric potential needed to be evaluated. Therefore, two regions were considered. In the electrolyte, with ions present, the electric potential was calculated from the Poisson-Boltzmann equation:

$$\Delta\Phi_e = -\frac{\rho}{\epsilon_0 \epsilon_{30}} = -\frac{1}{\epsilon_0 \epsilon_{30}} \cdot \sum_i z_i e n_i^\infty e^{-z_i e \Phi / kT}. \quad (4)$$

$\rho$  is the charge density caused by the ions,  $\Delta$  is the Laplace operator. The sum runs over all sorts of ions present. In the stylus region only the Laplace equation,

$$\Delta\Phi_s = 0, \quad (5)$$

had to be solved as no free charges are present.

Rotational symmetry of the stylus implied that the potential must not depend on the angle around the axes of the cone. Then the Laplace operator could be simplified:

$$\Delta\Phi = \frac{d^2\Phi}{dr^2} + \frac{1}{r} \frac{d\Phi}{dr} + \frac{d^2\Phi}{dz^2}.$$

In addition to Eqs. 4 and 5, boundary conditions were necessary to determine  $\Phi$ . All calculations were done with a fixed surface charge  $\sigma$ . At the interface between electrolyte and stylus the equations

$$\Phi_s = \Phi_e, \quad \epsilon_{10} \frac{d\Phi_s}{dn} = \epsilon_{30} \frac{d\Phi_e}{dn}, \quad (6)$$

are valid (Landau and Lifschitz, 1967).  $d\Phi_s/dn$  and  $d\Phi_e/dn$  are the changes of the electric potentials perpendicular to the stylus/electrolyte interface.  $\epsilon_{10}$  is the static dielectric permittivity of the stylus material.

To solve the partial differential Eqs. 4 and 5, a

network of regularly spaced straight lines, each parallel to one of the coordinate axes, was superimposed over the  $r, z$ -region (Fig. 2). Instead of seeking the value of the solution of the differential equation at every point in the continuous region, I calculated approximate values of the solution at the mesh points. Mesh points are the intersections of the network lines with each other and with the boundary. The partial differential equation was replaced by a partial difference equation (Young, 1961).

The  $r, z$ -plain was subdivided into 118 (in  $r$ ) times 90 (in  $z$  direction) mesh points. At a certain mesh point  $(r_j, z_i)$ ,  $\Delta\Phi_{j,i}$  was approximated by (Kuipers and Timman, 1968):

$$\begin{aligned} \Delta\Phi_{j,i} &= \frac{1}{h_0} \left( \frac{\Phi_{j+1,i} - \Phi_{j,i}}{h_0} - \frac{\Phi_{j,i} - \Phi_{j-1,i}}{h_0} \right) \\ &+ \frac{1}{h_0} \left( \frac{\Phi_{j,i+1} - \Phi_{j,i}}{h_0} - \frac{\Phi_{j,i} - \Phi_{j,i-1}}{h_0} \right) \\ &+ \frac{1}{r_j 2h_0} (\Phi_{j+1,i} - \Phi_{j-1,i}) \\ &= \frac{1}{h_0^2} (\Phi_{j+1,i} + \Phi_{j-1,i} + \Phi_{j,i+1} + \Phi_{j,i-1} - 4\Phi_{j,i}) \\ &+ \frac{1}{(j-1)2h_0^2} (\Phi_{j+1,i} - \Phi_{j-1,i}) \end{aligned} \quad (7)$$

$h_0$  is the distance between two neighboring mesh points. Inserting this expression in Eq. 4 gives in the electrolyte region,

$$\begin{aligned} \Phi_{j,i} &= \frac{1}{4} (\Phi_{j+1,i} + \Phi_{j-1,i} + \Phi_{j,i+1} + \Phi_{j,i-1}) \\ &+ \frac{1}{8(j-1)} (\Phi_{j+1,i} - \Phi_{j-1,i}) + \frac{h_0^2}{4\epsilon_0\epsilon_{30}} \sum n_i e z_i. \end{aligned} \quad (8)$$

In the stylus region the last term could be omitted.

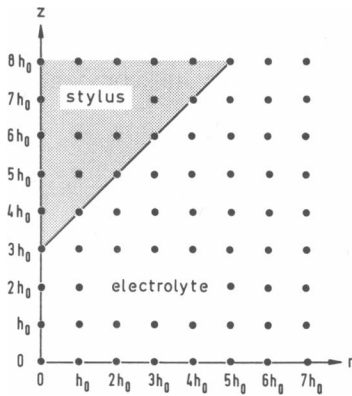


FIGURE 2 Distribution of mesh points in the  $r, z$ -region as it was used for the numerical calculations.

With the above equations, the electric potential could be evaluated iteratively. First,  $\Phi$  was set to an initial value. To avoid a long iteration process the potential was initially set to the Gouy-Chapman potential (Israelachvili, 1985). Then,  $\Phi$  was calculated for all mesh points. This calculation was repeated until the difference of subsequently calculated values  $\Phi_{j,i}$  became negligible. It can be shown that under normal circumstances  $\Phi$  converges (Kuipers and Timman, 1968) against a certain value. This value is identical with the true potential for an infinite number of mesh points. By varying the number of mesh points, it was checked that  $118 \times 90$  was a sufficient number of mesh points.  $h_0$  was set to 0.1 nm or 0.2 nm and it was 800 times iterated.

After solving Eqs. 4 and 5 numerically, the electrostatic force acting on the stylus was calculated with Eq. 1. If not otherwise mentioned, all calculations were done at  $T = 22^\circ\text{C}$ , with a static permittivity of 79 for the electrolyte (Pottel, 1973) and 6.0 for silicon nitride (Sze, 1988).

### Simple approximation of the electrostatic force

The exact, numerical calculation described above is a long, complicated procedure and inconvenient to use. To overcome this disadvantage, a simple analytical expression for the electrostatic force was derived.

Parsegian and Gingell, 1972, calculated the force per unit area between two planar, semiinfinite surfaces separated by a distance  $z$ . They assumed (a) that the surface potential  $\Phi_0$ , related by the Grahame equation

$$\sigma^2 - 2\epsilon_{30}\epsilon_0 kT \cdot \sum_i n_i^\infty (e^{-ze\Phi_0/kT} - 1) = 0,$$

to the surface charge density  $\sigma$  (McLaughlin, 1977) is low ( $e\Phi_0 \ll kT$ ); (b) that the distance  $z$  is larger than the Debye length  $\kappa^{-1}$  given by

$$\kappa = \sqrt{\frac{e^2}{\epsilon_0\epsilon_{30}kT} \sum_i n_i^\infty z_i^2}. \quad (9)$$

If the two surfaces bear surface charge densities  $\sigma_1$  and  $\sigma_2$  Parsegian and Gingell (1972) obtained a force per unit area of

$$f_e = \frac{2}{\epsilon_0\epsilon_{30}} \cdot [(\sigma_1^2 + \sigma_2^2) \cdot e^{-2\kappa z} + \sigma_1\sigma_2 \cdot e^{-\kappa z}]. \quad (10)$$

Eq. 10 includes components coming from the Maxwell electric field stress tensor and from the osmotic pressure. To estimate the force on the stylus, I integrated the

force on small circular cross-sections of  $2\pi r dr$ :

$$F_e = 2\pi \cdot \int_D f_e \cdot r \cdot \frac{dr}{dz} \cdot dz.$$

For a sharp, conical stylus, this integration yielded

$$F_e = \frac{\pi}{\epsilon_0 \epsilon_{30} \kappa^2} \cdot t g^2 \alpha \cdot [(\sigma_1^2 + \sigma_2^2) \cdot e^{-2\kappa D} + 4\sigma_1 \sigma_2 \cdot e^{-\kappa D}].$$

An analogous expression can be derived for a half sphere with radius  $R$ :

$$F_e = \frac{\pi}{\epsilon_0 \epsilon_{30} \kappa^2} \cdot [(\sigma_1^2 + \sigma_2^2) \cdot (2\kappa R + e^{-2\kappa R} - 1) \cdot e^{-2\kappa D} + 4\sigma_1 \sigma_2 \cdot (\kappa R + e^{-\kappa R} - 1) \cdot e^{-\kappa D}].$$

If  $\sigma_1 \ll \sigma_2$ , the electrostatic force on a cone with a spherical end becomes

$$F_e = \frac{\pi \sigma_2^2}{\epsilon_0 \epsilon_{30} \kappa^2} \cdot e^{-2\kappa D} \cdot g, \quad (11)$$

where the geometry factor  $g$  is

$$g = 2\kappa R - 1 + e^{-2\kappa R} \cdot e^{2\kappa R \sin \alpha} \cdot (1 + t g^2 \alpha).$$

This can be further simplified. For a sharp cone ( $R = 0$ )  $g$  becomes  $g = t g^2 \alpha$ . If on the other hand  $R$  is much larger than the Debye length  $\kappa^{-1}$ , the last two terms can be neglected and  $g$  becomes  $g = 2\kappa R$ .

With the integration leading to the last three equations, it was further assumed that the electric field between cross-sectional areas  $2\pi r dr$  equals the field of an infinite plane at the same distance and that the stylus shape does not influence this field (Ring, 1985). All assumptions could be tested with the numerical calculations described above.

## Van der Waals force

The VdW force between a conical stylus and sample was evaluated from:

$$F_{\text{vdw}}(D) = 2\pi \cdot \int_D f_{\text{vdw}}(z) \cdot r \cdot \frac{dr}{dz} \cdot dz, \quad (12)$$

where  $f_{\text{vdw}}$  is the force per unit area between two planar semiinfinite media separated by a distance  $z$ .  $f_{\text{vdw}}$  is given by (Dzyaloshinskii et al., 1961),

$$f_{\text{vdw}}(z) = \frac{kT}{\pi c^3} \sum_{n=0}^{\infty} \epsilon_3^{3/2} \xi_n^3 \int_1^{\infty} p^2 \left[ \frac{1}{\alpha e^x - 1} + \frac{1}{\beta e^x - 1} \right] dp, \quad (13)$$

with

$$\alpha = \frac{(s_1 + p)(s_2 + p)}{(s_1 - p)(s_2 - p)},$$

$$\beta = \frac{(s_1 + p\epsilon_1/\epsilon_3)(s_2 + p\epsilon_2/\epsilon_3)}{(s_1 - p\epsilon_1/\epsilon_3)(s_2 - p\epsilon_2/\epsilon_3)}$$

$$x = \frac{2p\xi_n}{c} z \sqrt{\epsilon_3},$$

$$s_1 = \sqrt{\frac{\epsilon_1}{\epsilon_3} - 1 + p^2},$$

$$s_2 = \sqrt{\frac{\epsilon_2}{\epsilon_3} - 1 + p^2}.$$

$c$  is the velocity of light in vacuum,  $p$  is an integration variable and  $\epsilon_1, \epsilon_2, \epsilon_3$  are the dielectric permittivities of stylus, sample and electrolyte depending on the imaginary frequency  $\omega = i\xi$ . The prime on the summation symbol indicates that the term in  $n = 0$  is to be taken with a factor  $1/2$ . The sum is to be taken over frequencies  $\xi_n = 2\pi n kT/\hbar$ .  $\hbar$  is Planck's constant. Eq. 13 contains the nonretarded as well as the retarded interaction.

The term in  $n = 0$  in the sum poses a problem: it is undetermined because the factor  $\xi_n^3$  vanishes while the integral over  $p$  diverges. This indeterminacy can be removed by replacing  $p$  by the variable of integration  $x$ . If then  $\xi_n$  is put to zero, the  $n = 0$  term in the sum can be approximated by (Dzyaloshinskii et al., 1961; Mahanty and Ninham, 1976)

$$f_{\text{vdw}}^0 \approx \frac{kT}{8\pi z^3} \cdot \frac{(\epsilon_{10} - \epsilon_{30})(\epsilon_{20} - \epsilon_{30})}{(\epsilon_{10} + \epsilon_{30})(\epsilon_{20} + \epsilon_{30})}.$$

The VdW force can be straightforward evaluated from Eqs. 12 and 13 if the dielectric permittivities are known. Convenient representations of the dielectric permittivities which incorporate experimental data as well as general constraints were obtained by Ninham and Parsegian, 1970. For water several components have to be considered:

$$\epsilon_3(i\xi) = 1 + \frac{C_{\text{MW}}}{1 + \xi/\omega_{\text{MW}}} + \frac{C_{\text{IR}}}{1 + (\xi/\omega_{\text{IR}})^2} + \frac{n^2 - 1}{1 + (\xi/\omega_{\text{UV}})^2}. \quad (14)$$

The term containing  $C_{\text{MW}}$  and  $\omega_{\text{MW}}$  accounts for the relaxation of the static dipol moments of water molecules; they were set to 73.8 and  $1.06 \cdot 10^{11} \text{ s}^{-1}$ , respectively. The next two terms are caused by vibration and electronic transition processes. According to Ninham and Parsegian, 1970, the values  $C_{\text{IR}} = 3.42$ ,  $\omega_{\text{IR}} = 5.66 \cdot 10^{14} \text{ s}^{-1}$ ,  $\omega_{\text{UV}} = 1.91 \cdot 10^{16} \text{ s}^{-1}$  were used. The refractive index  $n$  was set to 1.33.

For silicon nitride  $\epsilon(i\xi)$  was described by

$$\epsilon(i\xi) = 1 + \frac{C_{\text{IR}}}{1 - (\xi/\omega_{\text{IR}})^2} + \frac{n^2 - 1}{1 - (\xi/\omega_{\text{UV}})^2}, \quad (15)$$

$\omega_{\text{UV}}$  is the ionization potential value. For  $\omega_{\text{IR}}$ , an average infrared relaxation frequency of  $0.6 \cdot 10^{14} \text{ s}^{-1}$  and a value of 2 for  $C_{\text{IR}}$  was chosen (Mahanty and Ninham, 1976).  $n$  was set to 2.01,  $\omega_{\text{UV}}$  was taken to be  $7.6 \cdot 10^{15} \text{ s}^{-1}$  (Sze, 1988). For biological material the values  $C_{\text{IR}} = 1.5$ ,  $\omega_{\text{IR}} = 0.6 \cdot 10^{14} \text{ s}^{-1}$ ,  $n = 1.55$ , and  $\omega_{\text{UV}} = 3 \cdot 10^{16} \text{ s}^{-1}$  were chosen (Tredgold and Hole, 1976; Pethig, 1979; Persson, 1987; Warshel, 1989).

## RESULTS

Fig. 3 shows lines of equal potential within and around the stylus. The sharp ( $R = 0$ ), conical stylus is 1.1 nm above a surface which bears a charge density of  $\sigma = 0.4 \text{ e/nm}^2$ . Near and in, the stylus lines of equal potential are not parallel to the surface anymore. In the stylus region, the surface charges are screened less effectively than in the electrolyte. Consequently, lines of equal potential are shifted away from the surface.

The electrostatic force versus distance is shown in Fig. 4 for a sharp ( $R = 0$ ), conical stylus. The upper line was calculated for a surface charge density of  $0.4 \text{ e/nm}^2$  and a salt concentration of 0.03 M. The electrostatic force is repulsive. It decays roughly exponentially with increasing distance between stylus and surface. The line in the middle was calculated with the same salt concentration but a lower surface charge density ( $\sigma = 0.1 \text{ e/nm}^2$ ). The force on the stylus was lower but the slope of the curve, and hence the distance dependency, remained the same.

When the salt concentration was increased, the dis-

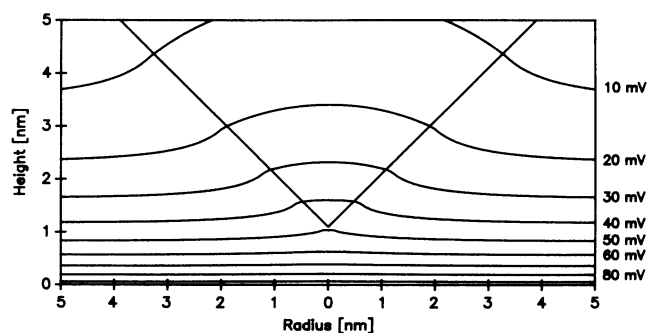


FIGURE 3 Lines of equal potential within and around the stylus calculated numerically. The sharp ( $R = 0$ ), conical silicon nitride stylus is 1.1 nm above a surface, which bears a surface charge of  $\sigma = 0.4 \text{ e/nm}^2$ . The concentration of a monovalent salt was 0.03 M.

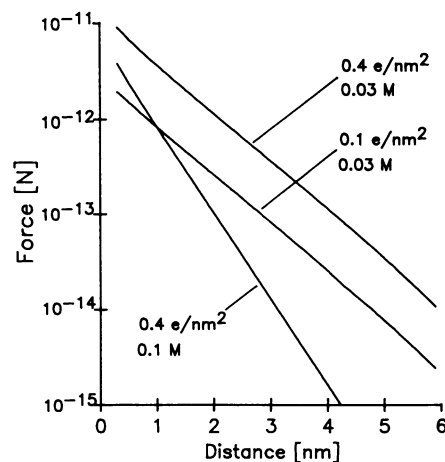


FIGURE 4 Repulsive electrostatic force versus distance of a sharp ( $R = 0$ ), conical silicon nitride stylus. The electrostatic repulsion was calculated numerically for  $\sigma = 0.4 \text{ e/nm}^2$  and  $C = 0.03 \text{ M}$ ,  $\sigma = 0.1 \text{ e/nm}^2$  and  $C = 0.03 \text{ M}$ , and  $\sigma = 0.4 \text{ e/nm}^2$  and  $C = 0.1 \text{ M}$ , where  $C$  is the concentration of a monovalent salt.

tance dependency of the electrostatic force changed. The lower curve was computed at a salt concentration of 0.1 M and a surface charge density of  $0.4 \text{ e/nm}^2$ . The decrease of the force with distance is steeper than in the curves obtained with a salt concentration of 0.03 M. In addition, the force is lowered due to a more efficient screening of the surface charges at high salt concentrations.

The dependence of the electrostatic force on the salt concentration is shown more accurately in Fig. 5 (*continuous lines*) at a surface charge density of  $0.2 \text{ e/nm}^2$ . The force at 0.5 nm distance and the decay length, defined as the distance where the force at 0.5 nm is diminished by a factor  $1/e$ , decreased with increasing concentration of a monovalent salt. Both effects are caused by the more efficient screening of surface charges at high salt concentrations. Hence, high salt concentrations can be used to reduce the electrostatic force.

The force at 0.5 nm obtained with approximation 11 (*dashed line*) for a sharp conical stylus approached the results obtained with the numerical procedure (*continuous line*) at high salt concentrations. High salt concentrations decrease the surface potential. Eq. 10, on which approximation 11 is based, was derived under the assumption that the surface potential is low (Parsegian and Gingell, 1972). At a concentration  $C$  of 0.01 M for instance, the surface potential  $\Phi_0$  is 88.0 mV and the force calculated with approximation 11 and the exact, numerical procedure differed by a factor of 4.5. At  $C = 0.1 \text{ M}$  and  $\Phi_0 = 39.8 \text{ mV}$  this difference is a factor of 1.9,

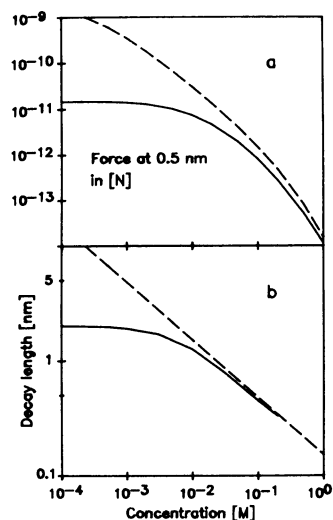


FIGURE 5 Dependence of the electrostatic repulsion on the concentration of a monovalent salt for a sharp, conical silicon nitrite stylus. The continuous lines were calculated numerically, the dashed lines were approximated with equation 11. (a) Force between stylus and surface at a distance of 0.5 nm. (b) Decay length (distance where the force at 0.5 nm decayed by a factor  $e$ , minus 0.5 nm). The surface charge density was  $\sigma = 0.2 e/\text{nm}^2$ .

at  $C = 1.0 \text{ M}$  and  $\Phi_0 = 13.7 \text{ mV}$  it is only a factor of 1.4. The same behavior was observed when the surface charge was varied and the salt concentration was kept constant (data not shown). At low surface charge densities and consequently low surface potentials the difference between approximation 11 and numerical results became small. At surface potentials below 50 mV approximation 11 differed less than a factor two from the exact, numerical results.

In Fig. 6, the electrostatic force is compared to the VdW force. This was done at a surface charge density of  $0.1 e/\text{nm}^2$  and a salt concentration of 0.02 M. The lower continuous line is the electrostatic repulsion for a sharp ( $R = 0$ ), conical stylus calculated numerically. With approximation 11 applied to the same stylus geometry, I obtained the lower dashed line. At a surface potential of  $\Phi_0 = 43.6 \text{ mV}$ , both curves differed by a factor of two. The lower dotted curve represents the VdW force. In contrast to the repulsive electrostatic force, the VdW force is attractive. The strength of both forces is in the same order of magnitude.

Also in Fig. 6 the force versus distance for a conical stylus with a spherical end is shown. The radius of curvature was set to 10 nm. The upper continuous line resulted from the numerical calculation, the upper dashed line was obtained with approximation 11. In this case, the numerical results differed only by about a factor of 1.7 from results obtained with the approxima-

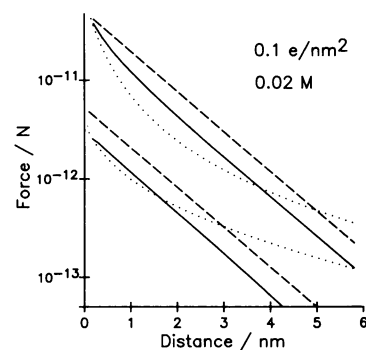


FIGURE 6 Electrostatic and VdW force versus distance at a surface charge density of  $0.1 e/\text{nm}^2$  and a salt concentration of 0.02 M. The lower three lines show results for a sharp ( $R = 0$ ), conical stylus, the upper three lines were calculated for a conical stylus with a spherical end ( $R = 10 \text{ nm}$ ). The electrostatic repulsion calculated numerically is shown in continuous lines, the approximation with Eq. 11 in dashed lines. The dotted lines show the attractive VdW force.

tion. Electrostatic repulsion and VdW attraction (*upper dotted curve*) were both stronger than forces acting on the sharp, conical stylus. The VdW force is proportional to  $1/D^n$ , with  $n$  being one for a conical stylus and two for a sphere (Hartmann, 1991). This agrees with my results. For the conical stylus,  $n = 1.0$  was obtained whereas for the conical stylus with a spherical end,  $n$  was 1.4.

In a series of calculations, the influence of a change in the dielectric permittivity was checked. Silicon oxide has a static dielectric permittivity of 4.1 (Sze, 1988). The electrostatic force calculated with this dielectric permittivity differed only negligibly from the force on a stylus with a permittivity of 6.0. Hence, forces given for silicon nitrite can also be used for silicon oxide. It is known that the dielectric permittivity of water decreases with increasing salt concentration. Ions bind water molecules in their hydration shell and these water molecules are not free anymore to rotate according to an external field. When describing the dielectric permittivity by the empirical expression (Conway et al., 1951; Pottel, 1973)  $\epsilon_{30} = 22 + 57 \cdot e^{-0.192C}$  with  $C$  as the local concentration of monovalent ions in  $M$ , the electrostatic force did not change significantly. Even at high salt concentrations and high surface charge densities, the difference of the dielectric permittivities of stylus and electrolyte is large and the electric field was not much different from the field calculated with  $\epsilon_{30} = 79$ .

## DISCUSSION

A repulsive force between a charged surface and the stylus agrees with results given in the literature for the

force between two spheres with fixed surface charge densities. Hogg, Healy, Fuerstenau and Wiese (Hogg et al., 1966; Wiese and Healy, 1970), and Bell and Peterson, 1972, always found repulsive forces when the two spheres had surface charges of the same sign. Even when the surface charges were of opposite sign, at small distances the force was always repulsive. Only in the case of  $\sigma_1 = -\sigma_2$  the spheres attract each other at all distances (Bell and Peterson, 1972).

Two complementary explanations can be given for the fact that the electrostatic force is repulsive rather than attractive. For a surface charge it is energetically favorable to be surrounded by a medium with a high dielectric permittivity like water (Born, 1920). If the stylus approaches the surface charge it replaces the water. Stylus material has a lower dielectric permittivity than water and the situation becomes energetically less favorable. Consequently, the stylus is repelled by the surface charge.

Another explanation of the repulsive character of the electrostatic force is based on the higher polarizability of water than that of the stylus material. If the surface of the sample is, for instance, positively charged, water molecules tend to orient with the positive side pointing away from the sample. This leads to a net positive charge at the stylus/electrolyte interface. The stylus is also polarized, resulting in a negative surface charge of the stylus. As the polarizability of water is higher than that of the stylus material, the positive poles of the water molecules more than compensate the negative charge of the stylus. This results in a net positive charge at the stylus/electrolyte interface, which is repelled by the positively charged surface of the sample.

Some work in atomic force microscopy was done with conducting stylus materials. One might speculate about the electrostatic force acting on a conducting stylus. Conductors have an infinite static permittivity and polarizability. Hence, based on the arguments given in the two paragraphs above, conducting styli should be attracted by a charged surface.

### Assumptions and limitations of the calculation

I used continuum theory for all calculations, where the discrete molecular nature of all materials was ignored. This excludes to consider hydration forces which are caused by the discrete nature of water. It is known that at distances below few molecular diameters repulsive hydration forces become important or even dominant (Israelachvili and Pashley, 1983; Rau and Parsegian, 1990; references therein). Another consequence of the discrete nature of water is that close to ions, the dielectric permittivity of water is changed. At a micro-

scopic level the averaged screening function corresponds to the dielectric permittivity in continuum theory. By molecular dynamics calculations, it could be shown that the averaged screening function around an ion in water deviates from the dielectric permittivity below a radius of 0.5 nm (Warshel and Russel, 1984).

The electric charge on the surface is not uniformly smeared out, as has been implicit in all the equations. Fortunately it can be shown that the electric field of discrete charges approaches the smeared-out field rather rapidly (McLaughlin, 1977). If the distance between the discrete charges is  $d$ , at a height  $z = d/2$  the actual field is at most 17% different from that of the smeared-out field (Israelachvili, 1985).

All calculations were based on the Poisson-Boltzmann equation. For very high surface potentials this leads to unrealistic results. If, for example, the surface potential is 250 mV and the bulk ion concentration is 0.01 M the local concentration of negative ions at the surface would be  $0.01\text{M} \cdot e^{250\text{meV}/kT} = 220\text{M}$ ! The problem is the assumption of point charges. Neglecting the ionic radius leads to wrong results at high surface potentials (Israelachvili, 1985).

The electrostatic force was calculated assuming that the ion concentration around the stylus is an equilibrium. To verify this assumption, the scan speed of the stylus has to be compared with the ionic mobility and diffusion coefficient of ions in water. Typical scan speeds range from 10 nm/ms to 0.1 nm/ms. Ionic mobilities are around  $6 \cdot 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  (Barrow, 1979). This means that it takes only 1  $\mu\text{s}$  for an ion to move 10 nm even if the potential difference is only 1 mV. In addition, diffusion coefficients for ions in water are  $\sim 2 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$  (Adam et al., 1977) so that diffusion in the 10 nm region takes about 0.1  $\mu\text{s}$  (Carslaw and Jaeger, 1959). As the distribution of ions in water reaches its equilibrium much faster than the stylus scans the sample, the above assumption is justified.

### Total force between stylus and sample

At distances  $> 2$  nm, the total force acting on the stylus is determined by the VdW attraction and the electrostatic repulsion. The electrostatic force depends on the surface charge density and the salt concentration, the VdW force is not directly affected by these two parameters. Hence, depending on the surface charge density  $\sigma$  and the salt concentration  $C$ , either the electrostatic force dominates and the total force is repulsive (high  $\sigma$ , low  $C$ ), or the VdW force dominates resulting in a net attractive force (low  $\sigma$ , high  $C$ ).

At small distances the total force should be attractive as the VdW force is proportional to  $1/D^{1\cdots 2}$ , whereas the

electrostatic force decays roughly exponentially. This agrees with the result of other researchers. When measuring the force between two cylinders of mica or mica covered with lipid layers they found long-range electrostatic interaction and a short-range VdW attraction (Israelachvili and Adams, 1978; Marra and Israelachvili, 1985; Marra, 1986; Ducker and Pashley, 1989). At small distances, the VdW attraction often became stronger than the electrostatic force. However, at distances below 2 nm the repulsive hydration force has to be considered (Israelachvili and Pashley, 1983; Rau and Parsegian, 1990). As a result, the total force might be repulsive at all distances.

### Practical consequences

Usually AFMs are operated in the contact mode, where the stylus is supposed to be in contact with the surface. Therefore, the externally applied force has to overcome the electrostatic repulsion. Otherwise, the charge distribution, and not solely the topography of the sample, is imaged. Hence, the electrostatic repulsion determines the minimal force which has to be applied.

It was shown that the electrostatic repulsion can be reduced by imaging in high salt concentrations. Thus, if the sample is soft or fragile and might be deformed or damaged, the electrolyte solution should contain a salt concentration higher than 50–100 mM.

As one example to estimate the possible influence of electrostatic repulsion, AFM experiments done with purple membranes (Butt et al., 1990b) shall be discussed. Purple membranes consist mainly of the membrane protein bacteriorhodopsin (Stoeckenius and Bogomolni, 1982). Bacteriorhodopsin forms trimers which are arranged in a hexagonal pattern with a unit cell size of 6.2 nm. The area between the proteins is filled with lipids, which are negatively charged. They give rise to a high average surface charge density of  $\sim -1 e/\text{nm}^2$  (Renthal, 1989; Szundi and Stoeckenius, 1989). The AFM measurements were done in electrolyte at a salt concentration of 0.06 M (Butt et al., 1990b). With a surface charge density of  $1 e/\text{nm}^2$ , the force on a conical stylus with a spherical end ( $R = 5 \text{ nm}$ ) at a distance of 0.5 nm would be  $0.6 \cdot 10^{-10} \text{ N}$ . The experiments were done with an external force of  $\sim 3 \cdot 10^{-10} \text{ N}$ . Hence, the force was high enough to overcome the electrostatic repulsion. If the measurements were done with a salt concentration of 0.001 M, the force on the stylus ( $R = 5 \text{ nm}$ ) would have been  $1.1 \cdot 10^{-10} \text{ N}$ . This might have been high enough to influence the AFM image.

I would like to thank E. Bamberg and K. Fendler for their help, many discussions and critically reading the manuscript; R. Petzoldt and H. Volk for excellent drawings and photographs.

This work was supported by a Max Planck Institute postdoctoral fellowship and the Deutsche Forschungsgemeinschaft Sonderforschungsbereich 169.

Received for publication 26 February 1991 and in final form 3 June 1991.

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