Probing the Double Layer: Effect of Image Forces on AFM

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ABSTRACT Force probes such as AFM tips or laser trap latex beads have a dielectric constant much less than that of the water that they displace. Thus when a probe approaches a charged surface under water it will be repelled simply based upon the image forces, and these can be of nN magnitude.

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The AFM has exquisite sensitivity for displacements normal to the tip, and that sensitivity has been used to probe the properties of the electrical double layer (1–4). These measurements typically examine forces as they vary with charge on the substrate or the tip, and the variation with ionic strength. However, the dielectric constant of the probe tip is much smaller than the water it displaces, and in the presence of an electric field, this discontinuity produces image forces (5). Thus, even neutral probes are repelled from a charged surface. In the case of deformable objects like membranes, these forces will push the membrane away from the tip, flattening the force-distance relationship and complicating interpretation of the data.

The effect of image forces applies to other force probes such as latex beads in a laser trap (6). The effect on beads is larger than that on the AFM tip because the dielectric constant of the bead (~2) is lower than that of an AFM tip (4–7) and the radius of curvature is larger. This article is a numerical analysis of the image force effects in the context of an AFM tip approaching an immobilized membrane.

The Poisson-Boltzmann equation was integrated using finite elements (FlexPDE, v5.0.9, www.pdesolutions.com) over an axially symmetric model centered about the middle of the tip (Fig. 1). The program scripts, including graphics, were less than one page and are available from the author. The AFM tip was approximated as a spherical cap with a radius of curvature of 10–50 nm mounted on a cone with a half-angle of 57°, emulating the pyramidal structure of AFM tips. The tip was Si_3N_4 with a dielectric constant of 7.4 (SiO_2 has a dielectric constant of ~4.5 and would increase the effects), and the surface was neutral unless noted otherwise. The membrane was electrically unsupported, 3-nm thick, and with a dielectric constant of 2. The lower surface was neutral and the upper surface was charged as noted. The lipid charge density was parameterized assuming an area of 7 nm^2 per lipid. The system was embedded in salt water with a dielectric constant of 80 and monovalent salt concentrations from 1 mM to 1 M. Unless otherwise stated the default values were a tip radius of 50 nm and a salt concentration of 150 mM. The effects are larger at lower ionic strength.

The force distance curve between the tip and the membrane is shown in Fig. 2. The AFM feels nN forces arising from the electrical double layer despite the fact that the tip is uncharged. For comparison to an ideal probe, Fig. 3 shows the force-distance curve for an imaginary 0.2-nm diameter sphere of dielectric constant 80 charged with +1e. The image force on a neutral AFM tip is that of an ideal probe of ~200e.

If the tip has the opposite charge from the surface being probed, the tip can overcome the repulsive force. At a distance of 1 nm, this balance of forces occurs with a tip surface charge 0.8% that of the membrane.

The image forces will lead to errors in the measured force and thus the estimated strength of the double layer, and the forces will also bend the membrane.

The radius of curvature of the tip has little effect on the force because the fields are broadly distributed and averaged over the tip. At a tip spacing of 1 nm, the force decreased by only 20% when the tip radius decreased from 50 to 10 nm.

The image forces increase with a decrease in ionic strength because the electric field increases (Fig. 4). Since the Poisson-Boltzmann distribution relates the ion concentration to the potential, the divergent field produced by the presence of the tip will also lead to changes of ionic composition and osmotic pressure that may affect the sample properties near the tip.

This study utilizes an equilibrium model. In tapping mode (7), there will be additional electroosmotic effects as the intervening fluid is sheared parallel to the bilayer. This will modify the electric field and require corrections to the resulting forces, although the magnitude of these forces relative to the fluid dynamic contributions is not known.

In summary, image forces resulting from insertion of low dielectric probes into the electrical double layer can produce significant perturbation of the AFM and other probes.

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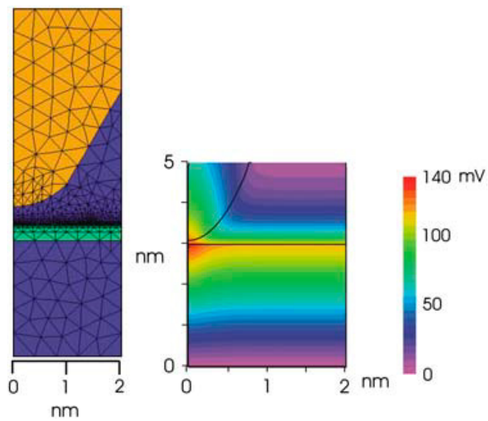

FIGURE 1 Left panel shows the basic geometry of the simulation with the automated grid set by the program. The right panel is a potential map with the tip 0.1 nm from the membrane, illustrating the gradient of the electric field produced by the low dielectric tip. The upper surface of the membrane is located at 3 nm.

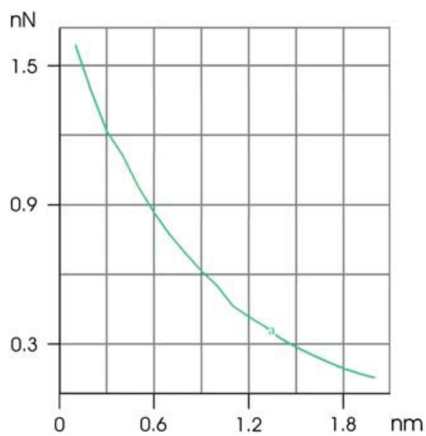

FIGURE 2 The repulsive force for an uncharged Si_3N_4 tip as a function of distance from the surface of a membrane containing 100% positively charged lipids.

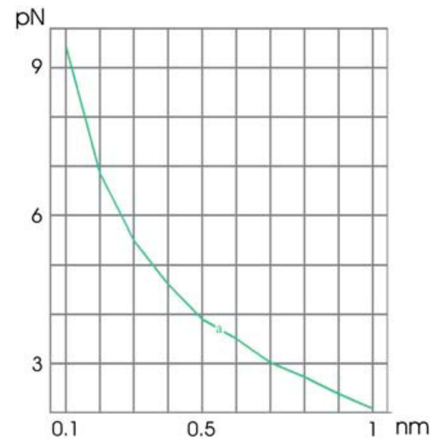

FIGURE 3 The force-distance relationship for a 0.2-nm diameter sphere charged with 1e approaching a uniformly charged lipid membrane (1e/lipid). The image force on this neutral AFM cantilever at the same distance is equivalent to ∼200e.

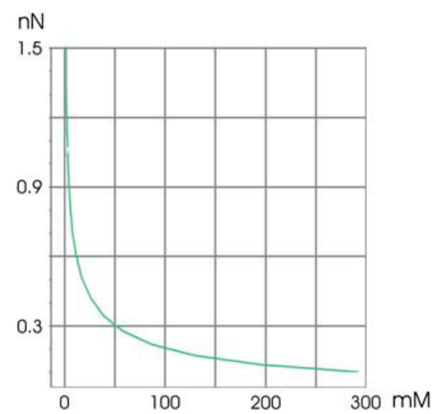

FIGURE 4 Variation of repulsive image force with salt concentration at a tip spacing of 1 nm over a charged lipid membrane.

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