Dynamic Response of AFM Cantilevers to Dissimilar Functionalized Silica Surfaces in Aqueous Electrolyte Solutions

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The dynamic response of an oscillating microcantilever with a gold-coated tip interacting with dissimilar functionalized silica surfaces was studied in electrolyte solutions with pH ranging from 4 to 9. Silica surfaces were chemically modified, yielding dissimilar surfaces with −Br, −NH₂, and −CH₃ functional group terminations. The relative hydrophobicity of the surfaces was characterized by contact angle measurements. The surface charge of the functionalized surfaces was first probed with commonly used static AFM measurements and serves as a reference to the dynamic response data. The amplitude and phase of the cantilever oscillation were monitored and used to calculate the effective interaction stiffness and damping coefficient, which relate to the electrical double layer interactions and also to distance-dependent hydrodynamic damping at the solid/water interface. The data for the dynamic response of the AFM over silica surfaces as a function of chemical functionalization and electrolyte pH show that the effective stiffness has a distinctive dependence on the surface charge of functionalized silica surfaces. The hydrodynamic damping also correlates strongly with the relative hydrophobicity of the surface. The data reported here indicate that interfacial properties can be strongly affected by changing the chemical composition of surfaces.

Introduction

Quantitative measurements of solid/water interfacial forces with atomic force microscopy (AFM) have been previously demonstrated in many studies using static force curves.1 In such studies, the deflection of a quasi-static microcantilever is measured as a function of the tip-sample distance. The electrical double layer interactions measured with static force curves have frequently been used to study surfaces that have been chemically functionalized,1−5 providing a quantitative description of the charging behavior of surfaces modified with specific chemical moieties. In contrast to the static measurements, dynamic AFM measurements are characterized by an oscillating microcantilever that is used to probe a sample surface while the phase and amplitude of the cantilever oscillation are monitored. It has been demonstrated that the dynamic response of the fundamental mode of cantilever oscillation is sensitive to solid/water interfacial forces, including solvation forces, van der Waals forces, and electrical double layer forces.6,7 In a previous study,8 Wu et al. demonstrated that the Debye length, which characterizes the interaction range of the electrical double layer forces, has a strong effect on the dynamic response of a microcantilever near a charged surface in water. Recently, other dynamic AFM measurements have provided correlations between surface interactions and the consequences of these interactions such as boundary slip and hydrodynamic damping,9−11 which are of central interest in engineered surfaces and nanoscale systems.10,12−17 In this study, small-amplitude dynamic responses of a microcantilever to silica surfaces with dissimilar functional moieties in aqueous electrolyte solutions were investigated to quantify the influence of surface charge on the aforementioned interaction forces.

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The oscillation amplitude of the cantilever in these experiments is kept small (less than 2 nm) compared to the Debye length (9.6 nm for 1 mM NaCl) to obtain force–distance data with spatial resolution better than 2 nm. The choice of small-oscillation amplitude is similar to that in other published studies\textsuperscript{6,7,9,11} to compare with established experimental methodologies.

Silica surfaces were chemically modified to yield surfaces with –Br, –NH\textsubscript{2}, and –CH\textsubscript{3} functional group terminations, respectively, according to a previously established methodology that relies on the use of well-established techniques of self-assembled monolayers and “click” chemistry.\textsuperscript{17} The well-studied native fused silica surfaces with silanol (–OH)-terminated groups were used as a reference surface for comparison to functionalized surfaces. The relative hydrophobicity of the surfaces was characterized by contact angle measurements before and after chemical modification. The charging states of the functional groups were first investigated with static force measurements with a silica colloidal probe interacting with the functionalized surfaces in 5 mM sodium chloride solutions. The charge polarity and effective charge density of the functionalized surfaces as a function of solution pH were extracted by the static force curves. The results of the static force measurements serve as a reference for the interpretation of the dynamic response to the charging behavior of the functional groups in aqueous electrolyte solutions. The purpose of this article is to report on the dependence of the dynamic response of a microcantilever to dissimilar functionalized silica surfaces in the presence of a pH-controlled aqueous environment.

The effect of distance-dependent damping and double-layer interactions on the cantilever oscillation is related to the phase $\phi_1$, and the hydrodynamic damping of the cantilever, $a_b$, are fundamental-mode amplitude and phase, respectively, when the AFM probe is far away from the solid/water interface. Both $k_c$ and $a_b$ can be determined by the thermal noise spectrum of the cantilever when the tip is far away from the surface.\textsuperscript{18,23} Because the amplitude of acoustic excitation, $a_b$, of the cantilever is not monitored by the laser in AFM, $a_b$ is approximated to be $A_{\phi}/Q_b$ where $Q_b$ is the quality factor of the cantilever resonance curve measured at a distance far away from the surface. After the contact point (zero tip sample distance point) was found in the mean deflection versus piezo displacement curves, the tip–sample distance was calculated using a previously established method.\textsuperscript{1} The amplitude versus tip–sample distance and the phase versus tip–sample distance were then replotted in terms of effective stiffness versus distance and damping versus distance using eqs \textsuperscript{1a} and \textsuperscript{1b}, respectively.

\textbf{Materials and Methods}

\textbf{Materials and Sample Preparation.} Round glass disks (Asylum Research) that match the fluid cell used in dynamic AFM measurements were degreased by rinsing with acetone, isopropanol (IPA), and deionized (DI) water, followed by drying under a constant stream of nitrogen. Then, the glass was cleaned via a standard piranha solution (4:1 H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O\textsubscript{2}) cleaning procedure for 30 min. (\textit{Caution!} Piranha solution is a strong oxidizing agent and must be used with proper safety procedures.) The samples were rinsed with copious amounts of DI water after the cleaning procedure and dried under a constant stream of nitrogen.

11-Bromoundecyltrichlorosilane (BUTS; Gelest, Inc., Morrisville, PA) was solution deposited in 1\% v/v anhydrous cyclohexane (Sigma-Aldrich, St. Louis, MO) by soaking the samples for 2 h. After the soak, the samples were rinsed with excess cyclohexane followed by methanol to remove physisorbed silane molecules. The samples were dried in a stream of nitrogen and stored in a drybox that was continuously purged with nitrogen until further use. The click functionalization was performed as described previously.\textsuperscript{17} Briefly, S\textsubscript{2} nucleophilic substitution replaces the surface bromo groups with azido groups after 48 h of soaking in a saturated solution of sodium azide (Acros Organics, Fair Lawn, NJ) in \textit{N,N}-dimethylformamide (DMF) (Sigma-Aldrich, Saint Louis, MO). The samples were rinsed with DMF and dried in a stream of nitrogen. Azide-terminated substrates were soaked in either propargyl amine (Sigma-Aldrich, Saint Louis, MO) or 1-ctoine (Sigma-Aldrich, Saint Louis, MO), each prepared as a 10 mM solution in ethanol to yield aminated or methylated surfaces after 2 h of soaking. The click solutions also contain equal volumes of CuSO\textsubscript{4}·5H\textsubscript{2}O (Sigma-Aldrich, Saint Louis, MO) and sodium l-ascorbate (Sigma-Aldrich, Saint Louis, MO).

Driving the oscillation frequency is less than the mean tip–sample distance $D$ and the contribution of the higher harmonics to cantilever oscillation is negligible, the effective stiffness, $k_s$, and the squeeze film damping between the tip and sample surface, $b_s$, can be expressed as

$$k_1 = \frac{(\cos \phi_1 - \cos \phi_2)}{A_1} A_a b_k$$

and

$$b_c = \left(\frac{b}{b_c} - 1\right) b_c = \left(\frac{A_{w_1} \sin \phi_1 - 1}{A_1} \sin \phi_1 - 1\right) b_c$$

where $k_c$ is the spring constant of the cantilever, $b_c$ is the hydrodynamic damping of the cantilever, and $A_w$ and $\phi_w$ are fundamental-mode amplitude and phase, respectively, when the AFM probe is far away from the solid/water interface. Both $k_c$ and $b_c$ can be determined by the thermal noise spectrum of the cantilever when the tip is far away from the surface.\textsuperscript{18,23} Because the amplitude of acoustic excitation, $a_b$, of the cantilever is not monitored by the laser in AFM, $a_b$ is approximated to be $A_{\phi}/Q_b$ where $Q_b$ is the quality factor of the cantilever resonance curve measured at a distance far away from the surface. After the contact point (zero tip sample distance point) was found in the mean deflection versus piezo displacement curves, the tip–sample distance was calculated using a previously established method.\textsuperscript{1} The amplitude versus tip–sample distance and the phase versus tip–sample distance were then replotted in terms of effective stiffness versus distance and damping versus distance using eqs \textsuperscript{1a} and \textsuperscript{1b}, respectively.


in DI water. Finally, the substrates were rinsed with a 1% v/v aqueous ammonia solution to remove any surface-trapped Cu catalyst and then further rinsed with DI water before being dried in a stream of nitrogen. Surface characterization was done by contact angle (CA) measurements (Rame-Hart model 250-00), measured as the advancing angle of a sessile drop of Millipore (18 MΩ) water, and X-ray photoelectron spectroscopy (XPS) (PHI model 5600) to determine the chemical composition of the adherent surface layers.

Native fused silica and DI water were used as the reference surfaces for comparison to functionalized surfaces. The native silica surfaces typically have a high density of silanol- or OH-terminated groups. A hydrophobic fused silica surface was prepared by dip cleaning in a mixture of sulfuric acid (98%) and nochromix reagent (GODAX Laboratories, Inc.), followed by extensive rinsing in deionized (DI) water (resistivity about 17.3 MΩ·cm) and drying with filtered nitrogen (N₂) gas.

Aqueous sodium chloride solutions (1 and 5 mM) were freshly prepared from reagent-grade chemicals (Sigma-Aldrich) and used without further purification. Electrolyte concentrations of 1 and 5 mM were chosen so that the characteristic length of the double-layer interaction (Debye length) is on the order of a few nanometers and will remain relatively the same when the electrolyte solution is titrated with NaOH and HCl from pH 3 to 9. The pH of the resulting NaCl solutions was confirmed via a digital pH meter (Accumet, Fisher Scientific). The solution pH levels were recorded before and after each measurement, and the mean values are reported in the results.

Static Force Measurements. The AFM force measurements were carried out on an Asylum Research (Santa Barbara, CA) MFP3 atomic force microscope. For the static force measurements, two kinds of colloidal probes (cantilevers with micrometer-sized spheres at the free end) were used. The first kind of colloidal probe uses silica spheres, and the second kind uses gold-coated silica spheres. Both have diameters of 5 μm and standard V-shaped silicon nitride cantilevers with a nominal spring constant of 0.06 N/m (Novascan Technologies Ames, IA). Static force measurements using the silica probes were carried out in 5 mM NaCl solutions. The purpose of this measurement was to provide data for surface charge analysis as detailed in the Results and Discussion section. We also measured the static force curves with gold-coated silica probes in 1 mM NaCl solutions so that we can make a direct comparison between static force and dynamic force measurements at the same solution concentration, pH level, and surface chemistry. Data are reported for two concentrations, 5 and 1 mM NaCl solutions. The silica spheres are nonporous and are similar to the flat substrates with surface-bound silanol groups. Before each measurement, the silica colloidal probe was treated with reactive oxygen in a molecular vapor deposition (MVD 100) tool (Applied MicroStructures, San Jose, CA) to eliminate organic contamination on the probes and to ensure that the silica probes have a high density of silanol groups. The spring constants of the cantilevers were calibrated for every experiment using the thermal noise method, where the power spectrum of the cantilever thermal fluctuation in air was fitted using a simple harmonic oscillator model. The force between the sample surface and the colloidal probe is sensed by the cantilever deflection as two surfaces are brought into contact at a constant velocity of 2 μm/s.

Dynamic Force Measurements. A gold-coated silicon nitride probe (Biolever, Olympus) with a rectangular cantilever (nominal spring constant of 0.03 N/m) was used. The probe has a pyramid-shaped tip with a typical tip height of 7 μm and a tip radius of 30 nm. The choice of cantilevers is critical to the experiments reported here. Low stiffness (0.03 N/m) was needed to satisfy the sensitivity requirements for double-layer interaction force measurements. With most compliant cantilevers, the resonance frequency is also low. However, the particular type of cantilever used here was very short (60 μm) and thus had a relatively high resonance frequency (around 11 kHz) compared to that of regular cantilevers with the same stiffness. Operating at a higher resonance frequency in liquid allowed an improved signal-to-noise ratio (SNR). To achieve this improved SNR, colloidal probes were not used in the dynamic measurements because the massive spherical probe renders a very low resonance frequency in liquid. When the cantilever is driven acoustically in liquids, there are usually multiple peaks in the resonance curve as a result of the convolution of the cantilever dynamics with the dynamics of the fluid cell hardware and the surrounding fluid. The thermal spectrum of the cantilever in liquids was measured as a guide to pick the drive frequency at the resonance frequency (around 11 kHz) of the cantilever for acoustic excitation. The amplitude of cantilever oscillation was tuned to be ~5 nm when the tip was about 6 μm away from the sample surface, and the Q factor of the resonance curve was recorded. Because the tip height is around 7 μm, measuring the Q factor of the resonance curve when the tip is 6 μm away from the surface would put the cantilever at around 13 μm away from the surface. This allowed an estimation of the acoustic excitation amplitude at the cantilever base in Eq 1 using the approximation . The thermal spectrum of the cantilever free from the impact of tip-sample interaction forces. The acoustic excitation amplitude was kept constant when the cantilever approached the sample surface. Thus, the estimation of far away from the surface still holds true when the dynamic response of the cantilever in the presence of the double-layer force was analyzed, including cases when the tip was within 15 nm of the surface. The cantilever oscillation amplitude was attenuated from ~5 to ~2.5 nm as the tip approached the sample surface from a distance of 6 μm to 15 nm as a result of increasing hydrodynamic damping that relates to fluid drainage between confined surfaces. Once the tip was within the 15 nm distance, in addition to the distance-dependent hydrodynamic damping, double-layer interaction forces further attenuated the cantilever oscillation amplitude to be less than 2 nm. The magnitude of the cantilever oscillation amplitude in the experiments fulfilled the small-amplitude assumption in our model. For each of the dynamic force curves, the mean cantilever deflection signal, the amplitude signal, and the phase signal were measured as a function of the piezo-actuator displacement. The contact point between the tip and the sample surface was calculated from the mean cantilever deflection versus the piezo displacement curve using the method described by Butt et al. As discussed by Butt et al., the error in the determination of the zero of separation is normally 1 to 2 nm with this method.

Results and Discussion

Contact Angle Measurements. The measured contact angles for each chemically modified surface are listed in Table 1. The relative hydrophobicity of the surfaces before and after the chemical modification provides a quick check of the surface chemistry by indicating changes in the surface energy. The measured contact angles for each of the surfaces are in agreement with previously reported values in the literature. Surface modification was also confirmed by XPS measurements (not shown), with XPS spectra similar to those that were previously reported.


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increasing negative charge density with increasing pH was also observed for the bromo (−Br)-terminated surfaces. The bromo group is a polar group and can easily acquire a partial negative charge.31−33 Furthermore, the hydroxyl radical and water molecules can also attach to the bromo-terminated surfaces with changes in the physical structure of the surface-attached water layer and possible changes in the surface charge density.31,32 The experimental results reported here show that the methyl (−CH3)-terminated surface (hydrophobic) in water is negatively charged over the pH range of 3 to 9, supporting the hypothesis that there is a preferential adsorption of hydroxyl ions at the hydrophobic surface and water interface. It is likely that with increasing pH a greater number of hydroxyl ions adsorb to the methyl surfaces, causing an increase in the negative charge. These results for the methylated surfaces are also in agreement with the sum frequency generation measurements that have recently been reported.34 The aminated (−NH2) surfaces are expected to undergo a change in surface charge polarity as a function of electrolyte pH. At low pH, the amine-terminated surfaces acquire positive charge through protonation. At high pH, the negative charge of the −NH2 surface probably has the same origin as that of the −CH3-terminated surface (i.e., adsorption of hydroxyl ions).35 Between pH 5 and 6, the aminated (−NH2) surface undergoes a surface charge polarity change. Note that in Figure 1 the effective surface charge density of the aminated surface at pH 3.5 is positive but...
with a very small calculated magnitude ($8.4 \times 10^{-6}$ C/m$^2$). The positive polarity of the surface charge can also be seen from the attractive force at pH 3.5 in Supporting Information 1. The smaller attractive force at pH 3.5 compared to that at pH 4.6 was most likely due to the decrease in the negative surface change of the silica surface from pH 4.6 to 3.5.

To maintain experimental uniformity between dynamic and static measurements, gold-coated tips in 1 mM NaCl solutions used for the dynamic measurements were complemented by static force measurements with the gold-coated colloidal probe interacting with the functionalized surfaces in 1 mM NaCl solutions, thereby facilitating a direct comparison. The results are shown in Figure 2. Chloride anions have a strong tendency to absorb onto gold surfaces$^{36}$ and render an overall negative surface charge density at the gold-coated colloidal probe in all tested pH ranges. The results in Figure 2 show that the interaction forces between the gold surface and the sample surfaces follow trends that are similar to those for the silica colloidal probe. The results from static force measurements demonstrated that the functionalized silica surfaces acquire distinct charge states in electrolyte solutions and the surface charge density can be changed by varying the solution pH.

**Dynamic Responses.** In previous work, the amplitude and the phase data of the cantilever dynamic response together were presented with a detailed discussion of the cantilever excitation spectrum. Because the cantilever dynamics is not the focus of this article, we include only the amplitude and phase data in Supporting Information 2. The focus of this article is the dynamic responses of the microcantilever to different functional groups of sample surfaces in terms of the effective interaction stiffness and hydrodynamic damping, along with reports of the drainage velocity that relate to the interfacial properties of the two surfaces confining the fluid. Figure 3 shows the effective interaction stiffness between a gold-coated vibrating probe and the chemically modified surfaces with $-\text{Br}$, $-\text{NH}_2$, and $-\text{CH}_3$ functional groups in 1 mM NaCl solutions at different pH values. Under the condition that the oscillation amplitude of the cantilever is much less than the characteristic length of the double-layer interaction, the effective interaction stiffness can be approximated to be the derivative of the interaction force over distance. With decreasing distance $D$, the magnitude of $k_i$ increases, indicating a stronger tip–surface interaction force. It can be seen from Figures 2 and 3 that this derivative correlation holds for all of the tested surfaces. It can also be noticed from Figure 3 that the effective stiffness

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Figure 3. Effective stiffness vs tip–sample distance for functionalized silica surfaces immersed in 1 mM NaCl solutions titrated at three different pH values.
Figure 4. Hydrodynamic damping vs tip–sample distance over functionalized silica surfaces immersed in 1 mM NaCl solutions titrated at three different pH values.
increases with increasing pH within the first 5 nm from the surface. It has previously been shown that to a first-order approximation the double-layer interaction force $F_{\text{dl}}$ is proportional to $k_c$. Therefore, a higher effective stiffness indicates a
stronger double-layer interaction force. The trends in $k_i$ and the implication for $F_d$ are also consistent with the surface charge dependence on pH that is shown in Figure 1.

The distance-dependent hydrodynamic damping at the dissimilar functionalized silica surfaces sensed by the microcantilever is shown in Figure 4. The data reported here in Figure 4 show that most of the changes in the damping curve for the chemically modified surfaces occur at a distance of greater than 3 nm. For comparison, we have listed the damping coefficients of the surfaces at 3 nm in Table 1. Figure 4 shows that there are distinct hydrodynamic damping responses among the silica surfaces with dissimilar functional groups. For example, there is a significant increase in the damping factor of the $\text{Br}$ surface as the distance between the probe and sample decreases, but by contrast, there is almost no change for the $\text{CH}_3$-terminated surface under similar test conditions. With each kind of surface, the solution pH value also has an impact on the damping curves, most likely because of the fact that pH acts as a control variable to modulate the effective surface charge density, thereby changing the interaction forces between the tip and the surface. Increasing pH leads to stronger damping responses for all of the surfaces, which relates to an increasing effective surface charge density as discussed above and shown in Figure 1. The discussion of hydrodynamic damping leads to two important implications of the trends observed for $b_d$. First, Table 1 shows that with increasing pH (and corresponding increases in surface charge density) the measured hydrodynamic damping increases. Second, it should also be noted from Table 1 that as the relative hydrophobicity of the surfaces increases, $b_d$ decreases.

Hydrodynamic damping coefficients are important because they can provide insights into the physical implications of surface—environment interactions. One particular surface—environment interaction of interest is the drainage velocity of the liquid thin film confined between two surfaces approaching one another. The drainage is related to the surface properties of the confining surfaces. For example, the drainage rate (or fluid drainage velocity) is often related to the equilibrium surface forces and can be used to determine the interfacial properties for both Newtonian and non-Newtonian fluids. Fluid drainage between surfaces with different combination of hydrophilicity and hydrophobicity has been used as an indirect way to characterize the boundary slip effect, with the underlying mechanisms being the subject of continued debate among the scientific community. Here with a first-order force balance, we derived the mean drainage velocity as a function of the dynamic response observables in AFM measurements as detailed in Supporting Information 3. Figure 5 shows the calculated mean drainage velocity for the different functionalized surfaces as a function of the tip—sample separation. Among the functionalized surfaces, the methyl ($\text{CH}_3$)-terminated surface has the highest contact angle and also has the highest drainage velocity. Followed by the methyl ($\text{CH}_3$)-terminated surface, the bromo ($\text{Br}$)-terminated surface has a higher contact angle and a mean drainage velocity for all pH values. One anomalous data point is noted at pH 4 for the positively charged aminated ($\text{NH}_2$) surface in Figure 5. The fact that the drainage velocity at pH 4 is much higher than for the bromo ($\text{Br}$)-terminated surface is not in agreement with the general trend that higher drainage occurs at a surface with a higher contact angle. Previously, molecular dynamics simulation results have suggested that water slips faster at positively charged surfaces than at negatively charged surfaces because of the moderate adsorption of mobile Cl$^-$ ions on such surfaces. Negatively charged surfaces may adsorb a significant number of immobilized Na$^+$ ions, leading to reduced slip at the solid/water interface. It should be noted here that the buffers used in the current work contain both Na$^+$ and Cl$^-$ ions. However, it must be pointed out once again that the results reported here are one of the first reports on the surface charge dependence on the drainage velocity, and the underlying mechanisms are the subject of continuing investigations.

Another observation from Figure 5 is that the drainage velocity also depends on the solution pH. Higher pH leads to a lower drainage velocity. The surface charge analysis in Figure 1 shows that the functionalized surfaces are charged more negatively at higher pH values. A hypothesis is presented next to enhance the scientific debate for the observed trends described above. It is hypothesized that the fluid drainage between the confining surfaces is strongly affected by the water structure at the solid/water interface. It has been well known for some time that because of the finite size of ions and solvent molecules electrolyte solutions demonstrate considerable structure at charged interfaces. As a consequence, it is not surprising that the structure of the solutions will have some dependence on the surface charge in confined systems or will be on the order of a few nanometers as in the dynamic measurements reported here. Furthermore, recent results for SFG measurements have shown that a higher interfacial charge density leads to more spatially aligned water molecules at the interface. Results reported here suggest that at higher solution pH the surface charge density is higher and the interaction between the functionalized surfaces and interfacial water is also stronger, leading to a slower drainage velocity.

**Conclusions**

When the oscillation amplitude of a microcantilever is much less than the electrical double layer interaction range, there are distinctive dynamic responses to dissimilar functionalized silica surfaces in aqueous electrolyte solutions within a few Debye lengths from the surface. The effective interaction stiffness is very dependent on the surface charge and can be altered by changes in solution pH. The hydrodynamic damping also shows a strong dependence on the surface hydrophobicity. With increasing hydrophobicity, the increase in the damping coefficient is lower as the tip—sample distance decreases. The impact of the surface functional groups on surface—environment interactions is demonstrated by the mean drainage velocity dependence on the systematically modified surfaces. Higher hydrophobicity leads to higher drainage velocity. The surface charge density can be manipulated by pH, which also influences the drainage velocity for a surface. The surface charge dependence of fluid drainage is attributed to the structuring of water and ions at charged interfaces. However, open questions remain with regard to the underlying mechanisms by which chemically modified surfaces acquire charge, and it is hoped that this experimental study will help spur theoretical investigations toward identifying these fundamental underlying mechanisms.

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Supporting Information Available: Force as a function of the tip–sample distance between the silica colloidal probe and functionalized silica surfaces immersed in 5 mM NaCl solutions with pH ranging from 3 to 9. Amplitude and phase variations as a function of the tip–sample separation near a functionalized silica surface coated with a −Br-terminated monolayer in a 1 mM NaCl solution. Derivation of the mean drainage velocity as a function of the dynamic response observables in AFM measurements. This material is available free of charge via the Internet at http://pubs.acs.org.