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Probing oscillatory hydration potentials using thermal-mechanical noise in an atomic-force microscope

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Intermolecular forces between surfaces and molecules in aqueous solutions at distances below a few nanometers are critically important to the functioning of many systems, from colloidal to tribological and from geological to biological. These forces are not, however, well understood at present. We have made measurements of multiple, metastable states near the hydrophilic cleavage planes of the ionic crystals calcite ($CaCO_3$) and barite ($BaSO_4$) using a low-noise atomic-force microscope. The interaction potential of the cantilever tip is determined using the Boltzmann relation on histograms of the tip position as it hops between the metastable states, and is found to be oscillatory, indicating layering of the solvent at the tip or sample. These oscillations are spaced from 0.15 to 0.30 nm apart and are of order 5×10^{-21} J in amplitude, which is comparable to the thermal energy $k_BT=4\times10^{-21}$ J at room temperature.

The length scales over which intermolecular forces are most interesting are of the order of a few nanometers, since it is on this scale that properties like adhesion and specific molecular recognition are determined. In a vacuum, the forces between atoms and molecules on these length scales are fairly well understood; however, in liquids the presence of solvent and solute molecules in the gap between molecules can drastically alter the forces they experience. In fact, nature often exploits these alterations; for example, the presence or absence of ions plays an important role in many biological systems. At separations greater than a few nanometers, there are many molecules in the gap and continuum models have allowed a good theoretical understanding of the acting forces. Yet the same experiments that have verified these theories at larger separations have also shown them to break down at separations below a few nanometers, where the molecular size of the solvent becomes important.[1,2]

In the past ten to fifteen years computer simulation and direct measurement of these forces have contributed much to our still inadequate understanding of these forces. The surface-forces apparatus (SFA), developed by Israelachvili, Tabor, and Winterton, has been the source of much of the direct experimental data,[3–5] although a few other techniques can measure forces at such small separations.[6] A relative newcomer is the atomic-force microscope (AFM).[7–9] In many ways the AFM and the SFA are similar, but operate on different length and time scales. The SFA directly measures forces between two crossed cylinders of radius typically 1 cm, while AFM tips can range from 10-μm colloidal spheres to chemically sharpened tips a few nanometers in radius. When sharper tips are used, most intermolecular forces are too small to measure except at separations less than several nanometers with the AFM. Fortunately, the range where AFM has much to contribute is that where intermolecular forces are least understood. A recent example of a measurement on this scale is the observation of oscillatory solvation forces at graphite and mica surfaces in *n*-dodecanol and octamethylcyclotetrasiloxane by O'Shea and co-workers.[10,11] These oscillatory forces, first observed by Horn and Israelachvili with the SFA,[12] are due to layering of the solvent molecules at a hard wall and are a dramatic demonstration of how the molecular size of the solvent becomes very important at small separations. The interpretation of these forces is easier when the liquid is squeezed between two macroscopic, smooth plates, but is not as obvious when one of the surfaces has a radius of curvature of the order of a few nanometers. Luedtke and Landman have performed molecular-dynamics simulations of the forces between a realistic nickel AFM tip and a gold surface in hexadecane that show oscillatory force behavior.[13,14] Simulations of a spherical AFM tip at a hard wall in a Lennard-Jones fluid also show oscillatory solvation forces are expected.[15,16]

Water is a particularly important solvent since most natural chemistry (including biochemistry) occurs in aqueous solutions, yet modeling and understanding solvation forces in water (hydration forces) is extremely difficult. This is due to the unique properties of water including its small size, large dipole moment, and especially its hydrogen bonding abilities.[17] Here we present measurements of oscillatory hydration forces in aqueous solution at hydrophilic crystalline surfaces using a new, low-noise AFM. In previous work we had observed quantized values of adhesion on a glass surface using an AFM, but could not distinguish if the quantization was due to individual hydrogen bonds or thermal activation among hydration layers.[18] Here, we use a stiffer, sharper cantilever and observe the thermal fluctuations of the cantilever tip between metastable states due to layering of the water and/or hydrated ions at an ionic crystal surface (Fig. 1).

An important key to obtaining the data was reducing the noise present in the optical lever detection of the AFM cantilever. Although subangstrom sensitivities are achievable over short time scales (100 ms and less) for optical lever detection of an AFM cantilever,[19,20] we found spurious low-frequency fluctuations in the deflection signal corresponding to a few angstroms even when the cantilever was replaced by a fixed mirror. We traced these fluctuations back to angular instability in the output of the laser diode, and then minimized these low-frequency angular fluctuations by replacing the laser diode of a commercial AFM (Ref. 21) with the collimated output of a single mode fiber coupled to a laser

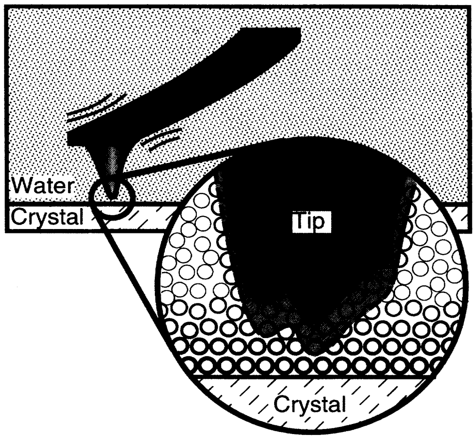

FIG. 1. A cantilever tip, held within a nanometer of a crystal surface in water, experiences an oscillatory potential near the surface due to layering of the water molecules and/or hydrated ions. If the amplitude of these oscillations is comparable to k_BT the tip hops between several metastable states. The potential the tip is moving in can be determined by examining the relative occupancy of these states.

diode.[22] Angular fluctuations in the laser-diode output only change the coupling to the fiber, so the output end of the fiber acts as a light source that is fixed in direction and shape and can only vary in intensity. These intensity fluctuations were eliminated in the bandwidth of interest by the standard practice of measuring the beam position with a split photodiode (which eliminates most of the intensity noise) and then dividing the photodiode difference signal by the total intensity of the light falling on the photodiode. We had used a single-mode optical fiber in a prototype AFM in our laboratory that was used for fibrinogen polymerization studies.[23] Many "improvements" were made at once in going to later prototypes, which eliminated the fiber and were much more convenient to use. Now it is clear that one of the "improvements," namely, eliminating the fiber, compromised the ultimate performance. Others have also noted the benefits of using a single-mode fiber.[24]

Another significant source of noise at low frequencies (<10 Hz) was air currents moving the laser beam (probably due to the changing index of refraction of air with temperature). This noise could be minimized simply by enclosing the small volume through which the laser beam travels. This improvement, coupled with the single-mode-fiber light source, improved the low-frequency signal-to-noise ratio by an order of magnitude. Since the thermal fluctuations of the cantilever were the signal being measured, we estimated other noise sources in the microscope by reflecting the light off a fixed mirror under the same experimental conditions. Our final noise figure was 0.036 nm rms in a bandwidth from 0.1 Hz to 50 kHz.

We used single-crystal silicon cantilevers,[25] not so much for their sharp tips, but for their low thermal drift compared to more commonly used silicon nitride cantilevers. The most significant drift affecting the tip-sample separation is usually the bending of the cantilever due to small temperature variations,[26] but with short silicon cantilevers this drift can be decreased to the point where other drifts in the microscope become dominant. The small thermal drifts (0.01–0.02 nm/s) achieved allowed us to hold the tip-sample separation nearly constant for longer times, allowing more data to be acquired.

Tip shape and chemistry obviously play very important roles in determining the forces acting between the tip and sample. One of the difficulties of using a sharp tip is the sharp tip itself; characterization at relevant length scales can be very difficult. Scanning electron microscopy (SEM) of the ends of several tips revealed that the shapes are variable on the 10–100-nm-length scale. The tip used in the measurements presented had a total opening angle of about 10° and terminated in a fairly flat surface about 60 nm across. It is not clear for this measurement that the sharpest tip is the best tip; the disadvantage of a sharper tip is a more localized interaction area and therefore smaller forces. Tip chemistry is also difficult to determine. It is known that these cantilevers have a native oxide layer about 2 nm thick.[25] Silicon oxide can be either hydrophobic or hydrophilic depending on the surface groups present. Cantilevers were irradiated with UV light before use; this caused them to become hydrophilic, so the predominant surface groups were probably silanol (Si-OH) and silicic acid (Si-O^-).[27]

All measurements were made in milli-*Q* (*p*H 6) water on the cleavage planes of a single crystal of calcite ($CaCO_3$) or barite ($BaSO_4$), both slightly soluble, divalent, ionic crystals. Freshly cleaved crystals were hydrophilic and grew hydrophobic after several hours in laboratory air, so crystals were immersed in water immediately (<5 min) after cleaving. The data shown were taken after the microscope had been operating for about 5 h. At this point the vertical drift in the microscope had stabilized to less than 0.02 nm/s and the water in the fluid cell was well equilibrated with the slightly soluble crystal. (Final concentration of Ca^{2+} and $CO_3{}^{2-}$ ions $\approx 100\ \mu M$; Ba^{2+} and $SO_4{}^{2-}$ ions $\approx 10\ \mu M$.)[28]

The photodiode signal measuring cantilever deflection was digitized at 100 kHz as the sample was moved towards or away from the cantilever. In some cases the sample was moved under piezo control at speeds of about 0.4–1 nm/s and in other cases the thermal drift of the microscope was used to control the cantilever-sample spacing at much slower speeds so that more data could be collected.

Figure 2 shows an oscilloscope trace of the cantilever deflection signal showing the thermal noise of the cantilever while the tip was positioned near a calcite surface. Four discrete levels with an average spacing of 0.20 nm can clearly be seen. Because the measurement shown is fast (20 ms) compared to the drift, the average tip-sample spacing only changed by 0.2 pm during the measurement, so the movement of the tip is entirely due to the cantilever thermally sampling different energy minima.

If we increase the observation time so that it is long enough compared to the vibrational period of the cantilever at the surface (≈ 0.01 ms) so that each state is visited many times, we can consider the cantilever to be in thermal equilibrium. If we ignore the small change in the potential in time due to drift then the distances should be distributed according to a Boltzmann distribution. That is $p(s)=C\exp[-V(s)/k_BT]$, where $p(s)$ is the probability of observing the tip at a deflection s, C is a normalization con-

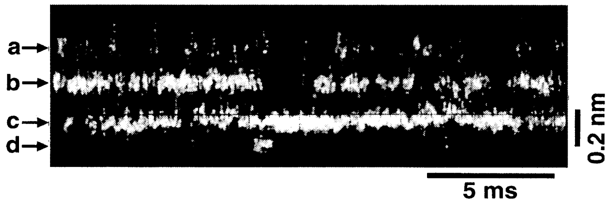

FIG. 2. A photograph of an oscilloscope trace showing the raw signal of cantilever deflection as a function of time. Position *a* is farthest from the surface while *d* is closest. In this case, the tip hopped between four distinct states, visiting *a*, *b*, and *c* several times in the course of the measurement (20 ms). The magnitude of the noise in each state contains information about the local curvature of the potential well. For instance, the tip is most tightly bound in *d* and least tightly bound in *a*. The occupancy of the four states is determined by their relative potential energies. Here *c* is the most energetically favorable and *d* the least. Since *d* was only occupied once, a longer observation would be necessary to consider the cantilever in thermal equilibrium amongst the four states.

stant, $V(s)$ is the potential the cantilever tip experiences as a function of deflection, k_B is the Boltzmann constant, and T is the absolute temperature.

We can invert this to give $V(s)$ in terms of the observed fluctuations of s:

$$V(s) = -k_B T \ln[p(s)] + \text{const.} \tag{1}$$

Since the potential is arbitrary to within an additive constant, (1) tells us that if we observe the cantilever for a long time then the potential at a particular deflection is simply proportional to the natural logarithm of the number of counts observed at that deflection. Figure 3 shows four such graphs generated from data taken as the sample drifted toward the surface of a cleaved calcite crystal. Nearly identical results were obtained on barite. It is important to note that $V(s)$ is not the pure interaction potential between the tip and sample since the harmonic potential of the cantilever is included in $V(s)$. This method of reconstructing the potential is similar to that used in another technique for measuring repulsive forces between a colloidal particle and a surface at larger separations.[29]

The harmonic potential due to the cantilever adds a controllable term to the tip-sample potential that can offset the long-range force gradients due to van der Waals attraction between a large portion of the tip and sample without greatly affecting the higher force gradients due to short-range interactions such as hydration layers. This prevents the cantilever tip from irreversibly snapping to the surface[30] as would occur for a weaker cantilever or a free particle. For instance, in the measurements presented in Fig. 3, the total depth of the attractive well between the tip and sample was about 4×10^{-19} J ($\approx 100 k_B T$). It is only because the cantilever potential has offset the longer-range attraction that the much smaller oscillations are visible; if the cantilever tip were a free particle these oscillations would not cause stable minima in the energy but would instead be imposed on a larger attractive well. By using a much stiffer spring, a single-welled equilibrium measurement could be made all the way to contact and no reconstruction of the potential would be necessary, but the distances the cantilever would deflect would become extremely small (subangstrom) and difficult to detect. The advantages of the method presented here are that the deflections involved remain measurable, and also that thermodynamics can be applied to measure the potential directly.

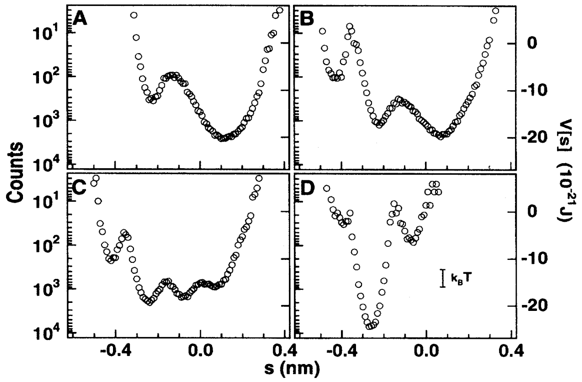

FIG. 3. Inverted histograms of the same type of data as shown in Fig. 2 taken at different average tip-sample spacing. The sample drifted about 10 pm closer to the cantilever during each histogram. The graphs are displayed on a log-linear scale with s corresponding to cantilever deflection. Negative values of s indicate deflections closer to the sample surface. There is 0.5 s of data in each histogram (50 000 points taken at 100 kHz). The cantilever is considered to be in thermal equilibrium among the potential wells observed and we interpret these graphs as the potential energy $V(s)$ experienced by the tip as a function of s. The right-hand axes are labeled in joules based on this relationship. Note that each graph is arbitrary to within an additive constant. *A* is taken when the sample is farthest from the cantilever and consists of the harmonic potential due to the cantilever with a small well due to the tip beginning to interact with the sample appearing on the left-hand side. In *B* the sample has drifted closer to the cantilever and the shallower well observed in *A* is now comparable to the central well and another minimum has appeared on the left-hand side. *C* shows four distinct minima with relative depths and widths comparable to the data observed in Fig. 2. Finally, *D* shows one central minimum approximately $6 k_B T$ deep, which is much steeper than the nearly free cantilever potential in *A*. The small minimum on the left-hand side indicates that the central minimum is still not the closest possible with the surface. The spacing between the minima vary between about 0.15 and 0.3 nm. This is similar to the size of a water molecule (about 0.3 nm); however, it is difficult to interpret the exact meaning of these lengths since they depend on the packing structure of the liquid at the surface, the path the tip follows as it moves through this structure, and also on the potential the oscillations are superimposed on.

The simulations of an AFM tip at a hard wall in liquid[13–15] indicate that, even with a tip of near-molecular dimension, these forces can still be interpreted as arising from the layering of solvent molecules at the surface of the tip and sample. Our system is more complicated in that there were also divalent ions present due to the crystals dissolving. From the data obtained so far, it is difficult to determine how hydrated ions from the bulk solution are involved in the layering at the crystal surface. Calcite has proven to be an excellent sample for the study of crystal growth,[31] and determining how hydrated ions from solution are incorporated into the growing crystal is important for understanding crystal growth from solution. Doing so will involve learning how the tip and its hydration layers affect the hydration measurements presented here. Calcite and other ionic crystals have also proven to be excellent samples for atomic resolution both in humid air[32] and in aqueous solution, where different forces have been measured when the tip is over different atoms in the crystal.[33,34] One tantalizing future direction is understanding the role hydration of the surface plays in atomic resolution imaging. On a broader scale, the measurements presented are extremely local measurements of hydration forces. If the technique can be extended to softer samples, it could greatly increase our understanding of the important role these forces play in biological systems.

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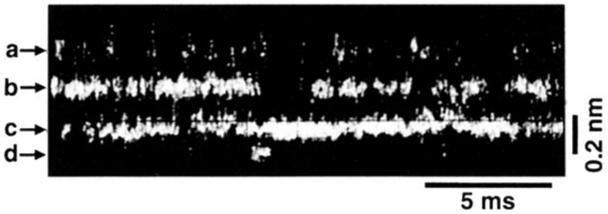

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