Formation, Manipulation, and Elasticity Measurement of a Nanometric Column of Water Molecules

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Nanometer-sized columns of condensed water molecules are created by an atomic-resolution force microscope operated in ambient conditions. Unusual stepwise decrease of the force gradient associated with the thin water bridge in the tip-substrate gap is observed during its stretch, exhibiting regularity in step heights (≈ 0.5 N/m) and plateau lengths (≈ 1 nm). Such “quantized” elasticity is indicative of the atomic-scale stick-slip at the tip-water interface. A thermodynamic-instability-induced rupture of the water meniscus (5-nm long and 2.6-nm wide) is also found. This work opens a high-resolution study of the structure and the interface dynamics of a nanometric aqueous column.

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Water is one of the most important substances of life and has been studied extensively for hundreds of years. Nonetheless, it is still quite a unique matter that keeps surprising us and exhibits peculiarities, in particular, when confined in a nanometric configuration. For example, water and simple organic liquids exhibit solid-like orderliness in molecularly thin films. Water molecules inside hydrophobic nanotubes manifest phases of ice that are not found under bulk conditions. However, since bulk water possesses only short-range order and water molecules move incessantly, it is usually difficult to experimentally investigate novel features of confined water structures other than thin films.

In this Letter, we have employed an atomic-resolution noncontact atomic force microscope (AFM) in air and achieved the spontaneous formation of a nanometric liquid column consisting of thousands of water molecules. We also have performed the sensitive measurement of the elastic property (or the force gradient) of the thin water column during its mechanical stretch. We have thereby demonstrated several novel phenomena: (i) the unusual stepwise decrease of the force gradient, associated with the atomic-scale stick-slip on the AFM-tip surface, (ii) the abrupt rupture of the thin water meniscus due to the thermodynamic instability of the liquid-vapor interface, and (iii) the manipulation of the thin aqueous column by repeated stretch-relaxation cycles, revealing the atomic-scale contact angle hysteresis.

Water molecules in ambient conditions produce a nanoscale water meniscus between a hydrophilic Si tip and a hydrophilic mica substrate, when capillary condensation occurs as the stiff AFM tip approaches the substrate within a nanometric distance (Fig. 1). Once the thin aqueous column is formed, it is stretched vertically upward by subsequent retraction of the tip. As the molecular water bridge of sub-zeptoliter (zepto = 10−21) volume is elongated thereby, the force gradient associated with the elasticity of the system is measured by an extremely small amplitude-modulation operation of AFM.

Figure 1 presents the schematics of a home-built AFM setup used for formation of a nanometric water column by capillary condensation as well as for simultaneous measurement of the force gradient of the elongated water meniscus, obtained at a given relative humidity (RH) and at room temperature (21 °C). A small-radius (≈ 10 nm) Si tip, having a nanometric discrete structure of atomic layers, is attached to a high-frequency \( f_0 = 1,002,198 \) Hz quartz crystal oscillator that has a very high stiffness \( k_0 \approx 5.4 \times 10^9 \) N/m and quality factor \( Q \approx 10^4 \). These parameters, under ambient conditions, allow the tip to be operated in extremely small amplitude-modulation (≈ 0.01 nm), noncontact, tapping mode suitable for high-resolution force-gradient measurement.

In contrast to a conventional micro-fabricated cantilever-based AFM used either in contact or noncontact operation mode, our AFM tip is stiff enough to pull the condensed water molecules without colliding with the substrate, as well as sensitive enough to measure the small changes of the force gradient (≈ 0.1 N/m). The minimum detectable force gradient using our detection scheme is estimated to be about 0.05 N/m. The RH was slowly decreased down to a desired value during several hours by using desiccant material placed inside a metallic enclosure box containing the AFM. The RH was also accurately monitored within 2% error by a digital hygrometer. Note that since our AFM did not employ a laser for the force-gradient measurements, there was very low electric power dissipation (< 1 nW) so that the local temperature variations near the tip were almost negligible. The inset of Fig. 1 shows an atomic-resolution AFM image of the mica substrate obtained at the RH of less than 5% (scan area of 1 nm × 1.5 nm).

In dynamic force microscopy, an oscillating probe detects the force gradient between the tip and sample along its oscillation direction. Such force gradient, \( k_{ts} = -\partial F_{ts}/\partial z \), detected by the probe is related to the reso-
The force gradient of mica substrate obtained in such a dry condition (inset of Fig. 1), indicated that there was neither capillary condensation of water nor any binding materials in between the tip-substrate gap. This was expected because the mica sample was placed, after in situ cleavage and subsequent chemical cleansing with dilute acid [10], inside an air-tight enclosure [11].

At 15% RH, on the other hand, similar measurements showed quite different results (Fig. 2b). As the tip approached the substrate, the force gradient increased abruptly as a result of the strongly attractive capillary forces arising from the Laplace pressure as well as the surface tension of condensed water [12]. Such capillary condensation occurred at less than ≈ 1-nm tip-substrate distance [2, 13], at which there was negligible tip-surface interaction in dry conditions (refer to Fig. 2a). Once the nanometric condensed water meniscus was formed and the tip modulation-amplitude is decreased by about 1%, the tip was computer-controlled to immediately retract in order to keep the meniscus as thin as possible.

As can be observed in Fig. 2b, the elastic force gradient decreased stepwise as the tip retracted in the nanometric range. There appeared three distinct steps (although the initial retraction region of 1.2 nm may as well be regarded as two additional steps) until the force gradient vanished (i.e. the water column was ruptured) at the distance of 4.2 nm from the retraction position. In particular, there was obvious regularity in the step heights (0.45 ± 0.03 N/m) as well as in then n step-plateau lengths (0.6 or 1.2 nm). It was also found that the rupture occurred abruptly within a distance of 0.1 nm, as manifested by the steep step edge.

Figure 2 presents experimental results of the force-gradient measurement: the magnitude of the force gradient versus the elongation of the water column, obtained at a given RH of (a) 2%, (b) 15%, (c) 31%, and (d) 45%. Each set of data represents one single approach (blue dots) and retraction (red dots) process obtained when the desired value of RH is established. The black solid line in (b) and (c) is a guide to the eye. The origin in (a) represents the tip-substrate contact point, whereas it denotes the position of tip retraction in (b) to (d). The approaching tip is computer controlled to retract immediately after its modulation amplitude is decreased by ≈ 1% due to the effects of capillary-induced damping.

In a very dry condition of the relative humidity (RH) of 2%, the measured elastic force gradient versus the tip-substrate separation showed no noticeable hysteresis behaviors during the tip approach and retraction (Fig. 2a). The force gradient of ≈ 1 N/m near the tip-substrate contact was originated from the typical short-range (< 1 nm) adhesive forces and the van der Waals forces between the tip and the substrate. Therefore, the absence of hysteresis in the approach-retraction curves, as well as the atomic-resolution noncontact AFM image of the mica substrate obtained in such a dry condition (inset of Fig. 1), indicated that there was neither capillary condensation of water nor any binding materials in between the tip-substrate gap. This was expected because the mica sample was placed, after in situ cleavage and subsequent chemical cleansing with dilute acid [10], inside an air-tight enclosure [11].

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pinned at the atomic step position of the discretely layered structures of the curved Si tip surface (Fig. 1), because Si atoms at the step edge with low bond-coordinate number exert extra attractive pinning forces on the water molecules. Once such a pinning process occurs, the magnitude of the force gradient in the vertical direction remains constant during subsequent stretch of the water column, like an elastic linear spring, as manifested by the plateaus in Fig. 2a.

While the surface area of the constant-volume water column increases as the tip retracts, the contact angle with respect to the tip surface as well as the Laplace pressure are decreased steadily. Then a slip of the contact line occurs when the water column is stretched enough so that the contact angle becomes equal to a critical angle, beyond which the pinning energy can no longer compensate for the extra surface energy needed in maintaining the same contact position. The force gradient decreases rather abruptly during the slip process and the slip stops when the contact angle restores its equilibrium value at the next atomic step position of the tip where the free energy is minimized. It is interesting that step-wise decrease with respect to elongation was observed in the measurement of the quantized conductance of a nanometric gold junction formed between two gold surfaces, which was shown to be highly correlated with the stiffness change of the metallic nanocontact.

The area under the last plateau before the rupture (≈ 600 pN) represents the capillary force at the last stick position of ≈ 3.1 nm. The corresponding work done until the rupture occurs (≈ 2.3 eV) is approximately equivalent to the overall loss of tens of hydrogen bonds during the last 1-nm elongation. A simple estimate of the meniscus-neck diameter, given the vertical force of 600 pN, presents a value of ≈ 2.6 nm, assuming the bulk value for the surface tension of the water-air interface (72.8 mN/m at 20 °C). [Note that simulation predicts this bulk value might be reduced by ≈ 20% in the nanometer dimensions.] Such a thin water meniscus with ≈ 5 nm in length (Fig. 2b) corresponds to a cylindrical liquid volume of ≈ 10^{-20} cm^3 (or 10 yoctoliter), consisting of only ≈ 10^3 water molecules. As the meniscus thins even more, the relative fluctuation of the liquid-vapor interface increases so that the meniscus becomes thermodynamically unstable. The observed rupture of the meniscus occurs when the neck has a width of ≲ 2.6 nm and this critical value is in agreement with the simulation results. Such interfacial instability also manifests itself as an increased level of fluctuations of the force gradient in the last plateau before the rupture (Fig. 2b).

The results at 31% RH (Fig. 2c), which were independently obtained with the same tip on a different day, showed overall step-like discrete characteristics similar to those in Fig. 2b, except that the step edges following the plateaus were broader (0.9 ± 0.1 nm). At a higher RH of 45% (Fig. 2d), the elasticity-distance curves exhibited smooth variations except for the final rupture process, as similarly observed in Ref. [22]. The continuous and monotonic decrease of the elastic-force gradient as well as the much larger initial values of the force gradient indicated that the water meniscus was already of bulk-like nature before retraction, smearing out the stepwise discrete changes.

In other words, as the initial amount of capillary-condensed water increased due to a uniform water layer formed on the mica substrate at an RH higher than 40%, the contact circle became larger in diameter and the effective pinning strength was diminished, resulting in the usual steady sliding of bulk water. The broadened step edges shown in Fig. 2c may be caused by mixed effects of the stick-slip and the steady sliding behaviors. Note that the elasticity measurements in Fig. 2 were performed during a single approach-retraction process, after waiting for many hours until the RH reached a given value, in order to avoid any unwanted ‘memory’ effects of the water meniscus as well as to form the thinnest possible meniscus width at a given RH.

To confirm that the measured force gradient during approach and retraction of the tip truly represented the elasticity of the system, and to explore the potential of the present technique for manipulation of the nanometric aqueous column, we repeatedly stretched and relaxed the water column by a slow (0.15 nm/s speed) cyclic motion of the tip. Figure 3a shows an approach-retraction curve, which was obtained when the approaching tip retracts as soon as its initial modulation amplitude is decreased by ≈ 10%, resulting in a ‘closer’ approach with respect to that in Fig. 2b obtained at a similar RH (note that the tip approached only until its initial modulation amplitude is decreased by ≈ 1% in Fig. 2b). The repeated cycles then start when the tip retracts from the origin up to ≈ 5-nm distance just before the rupture, and continue within the subsequent 2-nm range.

Figure 3b presents a close-up plot of the repeated cy-
cles in Fig. 3a, with an arbitrary vertical offset given between each cycle just for a clear eye guide. The vertical scale bar represents the force gradient of 1 N/m. The tip movement is in the order of the increasing arrow number. The retraction curve of the last cycle (arrow #6) is followed by an intentional rupture of the thin water column. The evident reproducibility of the repeated cycles in Fig. 3b represents that the force-gradient measurements indeed reveal the discrete elastic properties of the thin water column confined in between the tip-substrate gap. In particular, the repeated hysteresis behaviors within each cycle are indicative of the atomic-scale contact angle hysteresis of the nanometric liquid water on the tip surface [14], which is closely related to the atomic-scale friction.

The present work may provide a novel experimental tool for studying the kinematics of the condensed or adsorbed liquids on surfaces, which is of fundamental and technological interest in surface science and engineering. One can also study water molecules in nanoconfinement [26] that may behave unexpectedly by forming nanoclusters or by rearranging themselves to seek the energetically most favorable configurations by bending, but not breaking, the finite hydrogen-bonded network [27]. Furthermore, the current technique to form and manipulate a nanometric water column between two surfaces may provide a means to extend our understanding of the transport processes of ions through a nanometric water channel in biological cells.

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