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Minitips in Frequency-Modulation Atomic Force Microscopy at Liquid–Solid Interfaces

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A frequency-modulation atomic force microscope was operated in liquid using sharpened and cone-shaped tips. The topography of mica and alkanethiol monolayers was obtained with subnanometer resolution, regardless of nominal tip radius, which was either 10 or 250 nm. Force–distance curves determined over a hexadecane–thiol interface showed force modulations caused by liquid layers structured at the interface. The amplitude of force modulation and the layer-to-layer distance were completely insensitive to the nominal tip radius. These results are evidence that minitips smaller than the nominal radius are present on the tip body and function as a force probe. © 2012 The Japan Society of Applied Physics

1. Introduction

Atomic force microscopy (AFM) has been a powerful tool for the investigation of liquid–solid interfaces. It is now possible to observe the structure of interfacial liquid in addition to the topography of a solid. When a liquid is structured over a solid to form liquid layers on the surface, modulations appear in the tip–surface force as a function of tip–surface distance. Liquid layers have been found by AFM on a number of interfaces, as summarized in recent reviews.[1–4]

The latest technical development by Fukuma *et al.*[5] reduced the noise of frequency-modulation AFM (FM-AFM) to less than $20 \, \mathrm{fm \, Hz^{-1/2}}$. Using improved microscopes, layered liquids have been identified over polydiacetylene,[6] mica,[7–9] TiO_2,[10] Al_2O_3,[11] graphite,[12] thiol monolayers,[13,14] and a lipid bilayer.[15] The improved force sensitivity allows weak-force detection. With such weak forces, a small tip apex functions as the force probe without collapse. A small tip apex is desirable to improve spatial resolution. The tip apex was shown to play an important role in simulations of AFM at liquid–solid interfaces.[16,17] Experimental knowledge of the tip apex is quite limited, especially for tips scanned in liquids. In the present study, we compared two commercially available silicon cantilevers with sharpened or cone-shaped tips over water–mica and alkane–thiol interfaces. Topography and force–distance curves obtained in water or hexadecane were totally insensitive to the nominal radius of the tips, suggesting the presence and critical role of atomistic minitips on the tip bodies.

2. Experimental Methods

2.1 Microscope and cantilevers

Topography and force–distance curves were determined in an aqueous KCl solution or neat *n*-hexadecane at room temperature, using a modified Shimadzu SPM 9600 microscope. The deflection noise of the microscope had been reduced to less than $20 \, \mathrm{fm \, Hz^{-1/2}}$. The low deflection noise is critical for the observation of weak tip–surface forces in liquids. The absolute deflection of cantilevers was estimated by comparing the theoretical amplitude of the cantilever Brownian motion to the deflection sensor output recorded with a spectrum analyzer.

Two commercial silicon cantilevers with different tip radii, 10 nm (Nanosensors NCH) and 250 nm (Team Nanotech

LHCR250), were used. The shape of the tips was checked after imaging scans using a scanning electron microscope (JEOL JSM-5610). The nominal spring constants provided by the suppliers, $40 \, \mathrm{N \, m^{-1}}$ for each cantilever, were used for calibrating the deflection sensor sensitivity. NCH cantilevers were coated with aluminum on the back surface (NCH-R) when used in hexadecane and with gold in the aqueous solution. LHCR cantilevers were coated with aluminum on the back surface. The quality factor (Q) of resonance was 5–10. To remove spurious oscillation in low Q environments, a bandpass filter of $Q = 20$ was inserted in the feedback loop to regulate the oscillation amplitude constant. The resonance oscillation frequency was in the range of 140–190 kHz measured in liquids.

2.2 Substrates and solutions

Muscovite mica (Furu-uchi Chemical) was cleaved with scotch tape. The KCl solution was prepared at a concentration of $1 \, \mathrm{mol \, L^{-1}}$ with KCl (Nakarai, >99.5%) and Millipore water. The dodecanethiol self-assembled monolayer (SAM) was prepared on Au(111) films of 150 nm thickness. Cleaved mica wafers were annealed at $450 \, °C$ in a vacuum of $10^{-5} \, \mathrm{Pa}$ and exposed to a gold vapor source. The gold-deposited wafers were soaked in a 1 mM ethanol solution of 1-dodecanethiol (Wako, >98%) for 24 h. The soaked wafers were rinsed several times with pure ethanol and immersed in hexadecane (Wako, >97%).

3. Results and Discussion

3.1 Tip body shape

Figure 1 presents the SEM images of the tips after scans. There was no sign of tip–surface collisions during the scans. The tip of the NCH-R cantilever remained sharp, as expected from the nominal radius of 10 nm. The tip of the LHCR cantilever retained its cone shape with a 250 nm radius.

### 3.2 Topography obtained with sharpened and cone-shaped tips

Figure 2 shows the topography of mica measured in the KCl solution with the two cantilevers. The vertical tip position was regulated to keep the frequency shift (Δf) constant. The repulsive tip–surface force was estimated to be on the order of 0.1 nN using the quantitative relationship developed by Sader and Jarvis.[18] The topography observed with the two tips shows equivalent honeycomb structures with hexagons of 0.5 nm. The honeycomb structure observed agreed with an earlier report.[6] Note that subnanometer resolution was achieved with the cone-shaped LHCR tip. The topographic
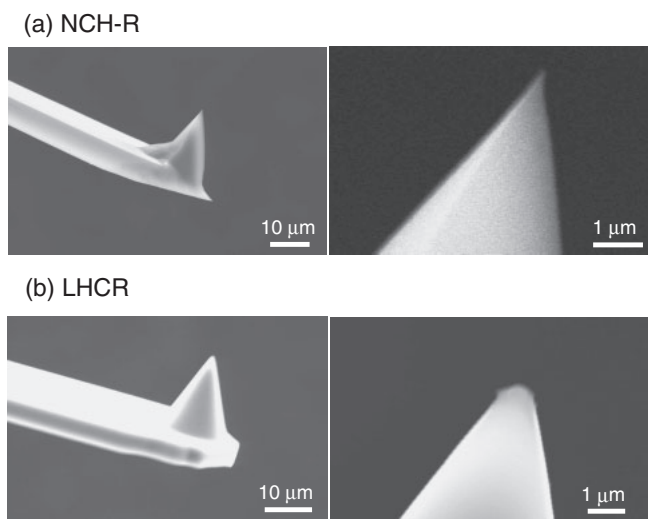
(a) NCH-R

(b) LHCR

Fig. 1. SEM images of the (a) NCH-R and (b) LHCR cantilevers after use in AFM measurements of the interface of hexadecane and dodecanethiol SAM. The right-hand-side images are close-ups of the tip apex.

(a)

(b)
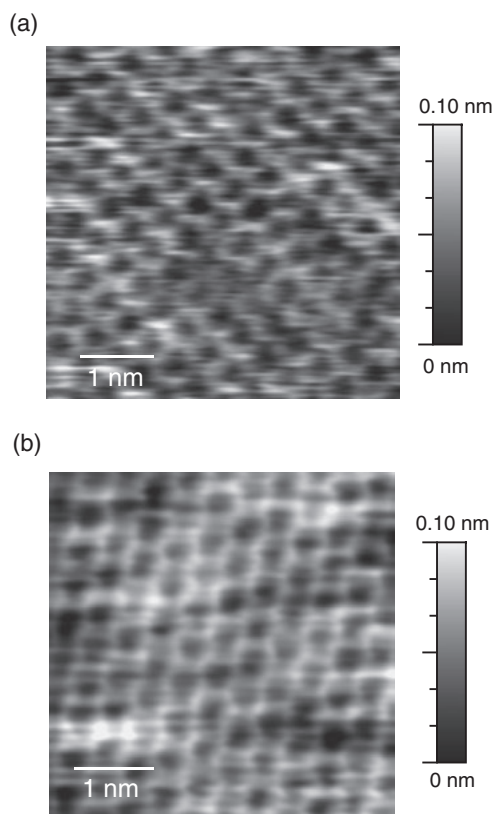
Fig. 2. Topography of mica in the 1 M KCl aqueous solution using (a) the sharpened and (b) the cone-shaped tip. Oscillation amplitude: 0.2 nm. Frequency shift: (a) +350 Hz and (b) +300 Hz.

resolution and contrast of mica was insensitive to the shape of the two tips. It was difficult to deduce a possible contribution of long-range force to the topography observed with the cone-shaped tip.

Subnanometer resolution was also achieved on a soft, organic surface using the two tips. Figure 3 shows the topography of the dodecanethiol SAM in hexadecane. Protrusions appeared with a hexagonal arrangement of 0.5 nm spacing and are assigned to the methyl head groups of

(a)

(b)
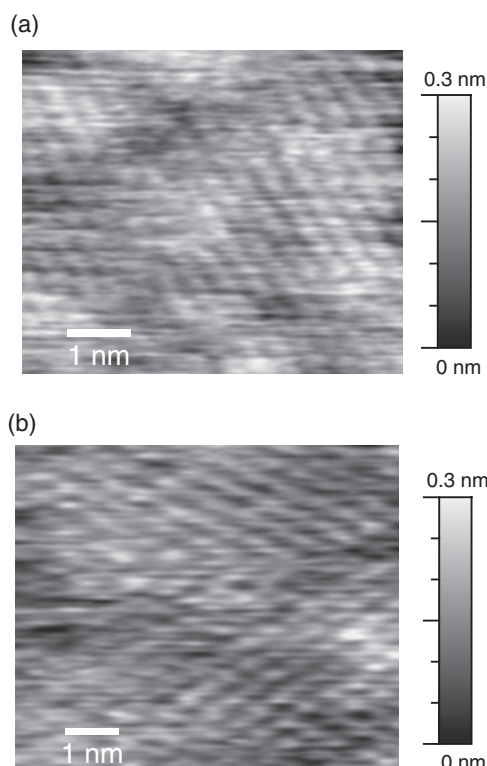
Fig. 3. Topography of the dodecanethiol SAM in hexadecane using (a) the sharpened and (b) the cone-shaped tip. Oscillation amplitude: 0.2 nm. Frequency shift: (a) +1300 Hz and (b) +800 Hz.

the ($\sqrt{3} \times \sqrt{3}$)-ordered thiol monolayer. It was difficult to resolve the $\sqrt{3}$ structure at the thiol monolayer facing water. The hydrophobic property of the thiol monolayer may be the reason for the insufficient resolution.

These results show that subnanometer resolution was achieved with the sharpened NCH tip and the cone-shaped LHCR tip. The topography obtained with AFM is generally a convolution of the surface corrugation and tip. The subnanometer resolution thus suggests a subnanometer-sized apex present on both the sharpened and cone-shaped tips. This suggestion is in line with the minitip assumption frequently assumed in scanning probe microscopy. Protrusions may be naturally present on a tip body. One such protrusion, which is closest to the surface, exclusively receives the short-ranged repulsive force response from the surface in atomic force microscopy.[19–22]

3.3 Force curves obtained with sharpened and cone-shaped tips

Force–distance curves were measured at the hexadecane–thiol SAM interface using the two cantilevers. The oscillating cantilever was scanned vertically from the liquid to the surface until Δf exceeded a threshold, +1000 Hz. The vertical scan was limited to the height of the threshold to avoid the tip tapping the surface. Δf was monitored as a function of the vertical coordinate to produce a Δf-distance curve at one lateral coordinate. The tip was then shifted laterally by a fixed amount and another vertical scan was conducted. By repeating the vertical scan-lateral shift cycle, a two-dimensional Δf distribution was constructed. Liquid hexadecane structured on the thiol monolayer presented an
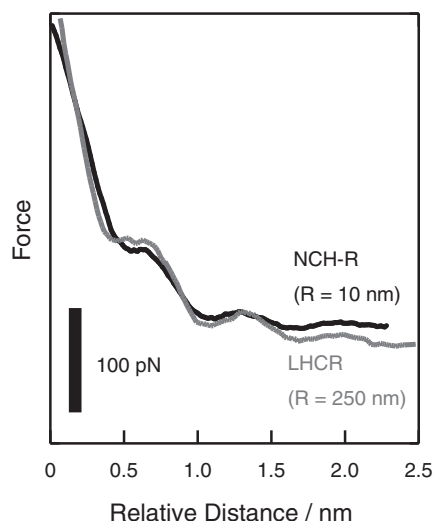
Fig. 4. Averaged force–distance curves at the hexadecane–dodecanethiol SAM interface. The dark and gray curves were determined with the sharpened and cone-shaped tips, respectively. The curves are vertically shifted to overlap, to aid comparison. The origin of the relative distance is set to the distance at which Δf of the NCH-R cantilever exceeded the threshold of $+1000$ Hz.

Fig. 5. (Color online) Minitip penetrating the structured hexadecane.

uneven Δf distribution as a function of the vertical distance from the surface. We found, in a recent study,[13] that the Δf distribution was, on the other hand, homogenous along lateral coordinates. Fifty Δf-distance curves were observed in scan-shift cycles in the present study and summed to obtain an averaged curve. The water–mica interface was not favorable for averaging, since the interfacial water was laterally structured to give heterogeneous Δf curves along lateral coordinates.[8,9] The Δf curves in hexadecane were converted to force–distance curves and then averaged. The nominal spring constants provided by the suppliers were used in the conversion. Detailed insight on applied force was gained by quantitatively comparing the averaged curves.

Figure 4 shows force–distance curves obtained with the sharpened and cone-shaped tips. The horizontal axis of the figure represents relative tip–surface distance, as the two curves were adjusted at the second local maximum. Three local maxima were identified on each of the two curves, with the same peak-to-peak distances and modulation amplitude. The modulation amplitude was insensitive to the tip body radius, which deviates from the Derjaguin approximation.[23] This approximation relates the radius of a spherical tip (R_{tip}) to the tip–surface force strength (F), and predicts a constant ratio, F/R_{tip}, in a continuum liquid. The approximation works well with micrometer-sized colloidal tips. Lim *et al.*[24] pointed out that the modulation amplitude deviated from the prediction of the Derjaguin approximation when they used tips of 15–100 nm radius in organic solvents over graphite. If we applied the approximation to the two tips, the modulation amplitude would be larger by 25 times with the cone-shaped tip than with the sharpened tip. This was clearly not the case, as the results show in Fig. 4.

The measured force modulation amplitude was totally insensitive to the tip body radius. This suggests that the effective area loading the force to hexadecane is smaller than the nominal radius, which was 10 nm in the present study.
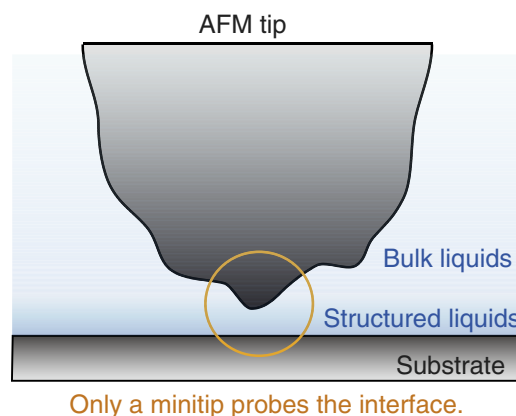
Here, we return to the minitip assumption mentioned in §3.2. The thickness of the region occupied by layered hexadecane was 2 nm, as seen in Fig. 4. When the minitip closest to the surface penetrates that region, it receives force modulated by the structured hexadecane, and the resonance oscillation of the cantilever is accordingly affected. Hexadecane density should be uniform outside of the 2-nm-thick layer. The rest of the tip body and entire cantilever are surrounded by hexadecane liquid of uniform density, as illustrated in Fig. 5. Hence the tip body cannot contribute to the amplitude of force modulations caused by the structured hexadecane.

3.4 Fluctuating minitip

The amplitude of force modulations fluctuated in scan-shift cycles to a limited extent. Figure 6(a) shows a cross-sectional presentation of Δf distributions over the hexadecane–thiol interface obtained with the cone-shaped tip. Positive (negative) Δf is shown to be bright (dark). The brightest region at the bottom represents the contour on which Δf exceeded the threshold. Three pairs of dark and bright layers appeared from the surface to the liquid, showing the uneven density distribution of structured hexadecane. This layered feature was disturbed occasionally. One of disturbances appeared in the region marked by a broken line. The shape of force curves discontinuously fluctuated to a limited extent at the disturbance.

Force curves before and after the disturbance are compared in Fig. 6(b). Fifty curves in each of boxes (1) and (2) were averaged to produce curves (1) and (2). The two averaged curves presented the same peak-to-peak distances with different modulation amplitudes. The amplitude from the second minimum to second maximum was 18 pN in curve (1) and 13 pN in curve (2). The different amplitude should reflect the different effective area of the minitip. By accumulating similar events observed in repeated scans, the amplitude of the second minimum and second maximum was seen to fluctuate in the range of 10–30 pN. This range of force fluctuation is consistent with the minitip assumption, in which only a few atoms are exposed to the liquid. In an earlier study of water on $CaCO_3$,[25] attractive forces on the order of 10 pN acting between single atomic sites on the sample and the front atoms of the tip were measured.

Consider here the extent of confinement caused by our minitip. When solid walls pinch a liquid, diffusion of liquid
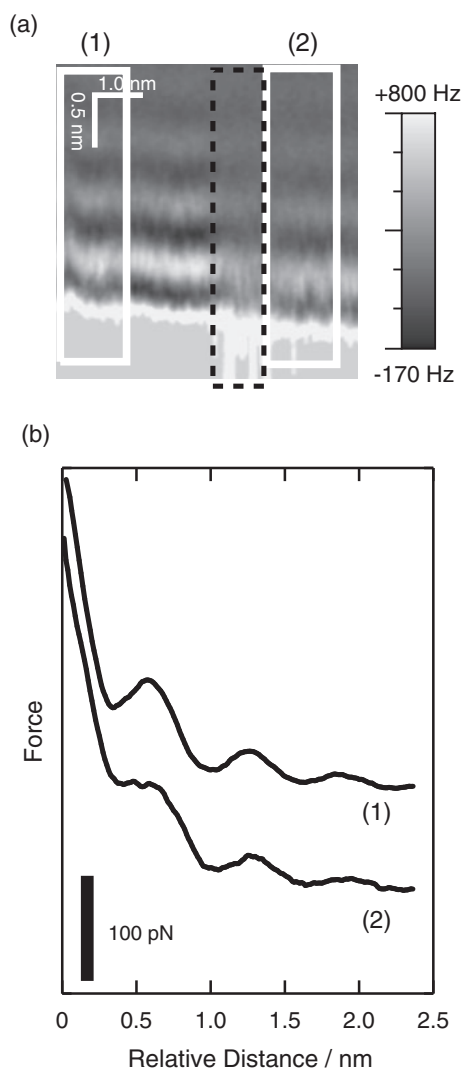
Fig. 6. Force distribution on the hexadecane–thiol SAM interface observed with the cone-shaped tip. A cross-sectional Δf distribution is shown in (a). The disturbed region is marked with a broken line. Fifty force–distance curves accumulated in regions (1) and (2) were averaged and presented in (b). Each curve is laterally adjusted to each force maxima and staggered vertically for viewing ease. The origin of the relative distance is set to the distance at which Δf of curve (2) exceeded the threshold of +1000 Hz.

molecules is limited. The number density of the molecules consequently increases. The pressure applied by the walls also enhances the dense packing of the liquid molecules. These effects of confinement distinctly appear in surface force apparatus (SFA) studies.[26] *n*-undecane presented layer-to-layer distances of 0.3–0.4 nm when confined by octade-cyltriethoxysilane-covered mica wafers.[27] On the other hand, the force curves shown in Figs. 4 and 6 presented longer peak-to-peak distances of 0.6 nm. The longer distance is a sign of less confinement. The two force curves in Fig. 6(b) exhibit the same peak-to-peak distances accompanied by different force amplitudes. The different force amplitudes indicate differently sized minitips. The peak-to-peak distance insensitivity to the minitip size may suggest that our minitip was not large enough to cause the confinement of hexadecane. We thus infer that the intrinsic structure of an open liquid–solid interface is observable by atomic force microscopy with a 10-pN-order force sensitivity.

4. Conclusions

Using sharpened and cone-shaped tips, constant frequency-shift topography and force–distance curves were obtained on hexadecane–thiol SAM and water–mica interfaces. The topography of SAM and mica was obtained with atomistic resolution regardless of the nominal radius of the tips. The amplitude of force modulation and layer-to-layer distances of the interfacial hexadecane were totally insensitive to the nominal tip radius. These results revealed that minitips smaller than the nominal radius, 10 nm in the current study, are present on the tip body and function as a force probe.

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