MAC Mode Atomic Force Microscope

for Precision Interfacial Force Measurements [†]

Application Note

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Since its introduction, it has been recognized that the atomic force microscope (AFM) offers a unique ability to probe surface forces with nanometer resolution and that these surface forces play a vital role in the operation of the AFM (1). We (2, 3) and others (4, 5) have introduced a new approach to AFM in which a force is applied directly to an AFM tip using a magnetic field (MAC Mode AFM), rather than by pressing the tip into the sample with the scanning transducer. This method eliminates the spurious resonances seen in fluid tapping mode (3), leading to substantial improvements in image quality (6). Here, we discuss the application of MAC Mode AFM to the measurement of surface forces.

Ordering of the liquid at the interface with a solid is a phenomenon of fundamental importance in fields such as tribology and electrochemistry and it has been studied extensively with the surface force apparatus (SFA) (7). This liquid structuring can also have a profound effect upon the operation of an AFM, causing the tip to hop between different stable configurations in the ordered region of the fluid (8). The AFM has been used to study structure in interfacial water (9) and organic liquids (5, 10). In contrast to the SFA, the AFM suffers from a lack of reproducibility of one surface (the tip) but it has a number of advantages, among them the ability to produce high-resolution images of the surface along with high vertical (z) sensitivity and low mechanical drift. We show here that highly reproducible

and accurate data can be obtained despite variability in AFM tips.

If the microscope is operated with a probe that is oscillated at an amplitude x far from the surface, then, provided the oscillation frequency is far below mechanical resonances, the surface stiffness at some distance z from the surface, $S(z)$, is given by $S(z) = k [x_0 / x(z) - 1]$ where k is the spring constant of the cantilever and $x(z)$ is the amplitude of the tip oscillation (5). A number of simple models permit extraction of quantities such as Young's modulus from the surface stiffness (1, 11).

A substantial signal-to-noise advantage is obtained for A/C mode AFM in fluids if the tip is oscillated by direct application of a magnetic force, as opposed to indirect mechanical excitation with an acoustic transducer. O'Shea *et al*. (5) used a magnetically-oscillated-tip microscope to show evidence of up to seven ordered layers of liquid at an interface with graphite. However, the spacing between layers of the quasi-spherical molecule studied, octamethylcyclotetrasiloxane (OMCTS), was substantially smaller (5 Å) than the known smallest dimension of the molecule (8 Å); thus, an orientation could not be determined. We have repeated these measurements with a microscope designed for stable operation in fluids and show that for both OMCTS and another small molecule (mesitylene) we obtain data in excellent agreement with known molecular dimensions.

We chose OMCTS $(((CH_3)_2SiO)_4)$ and mesitylene $((CH_3)_3C_6H_3)$ because they are relatively rigid and their dimensions are well characterized. The oblate spherical model of OMCTS has a major diameter of 1.0 – 1.1 nm and a minor diameter of 0.7 – 0.8 nm (12). Ordered layers have been detected on mica with a period of 0.8 – 1.0 nm using the SFA (13). Mesitylene or 1,3,5-trimethylbenzene molecule has a benzene ring with each –H at the 1st, 3rd, and 5th carbon locations replaced by a –CH_3 group. Crystal structure data show that the ring-to-ring spacing in stacked layers is 3.6 Å in the solid, and that the end-to-end length of the molecule along the major axis is a little over 6 Å. OMCTS was obtained from Sigma (St. Louis, Missouri); mesitylene was obtained from Alfa Aesar (Ward Hill, Massachusetts). Highly oriented pyrolytic graphite (HOPG) was obtained from Advanced Ceramics (Cleveland, Ohio).

We used an Agilent AFM operated in MAC Mode (see Figure 1). The spring constant of the MAClevers (magnetically coated cantilevers) used was typically 0.5 nN/nm. Atomic force spectra (AFS) were obtained by driving the force input of the controller with the demodulated amplitude signal from the MAC Mode and setting the controller to record force curves. The tip oscillation frequency was between 200 – 500 Hz, far below the 28 kHz resonance of the cantilever in fluid.
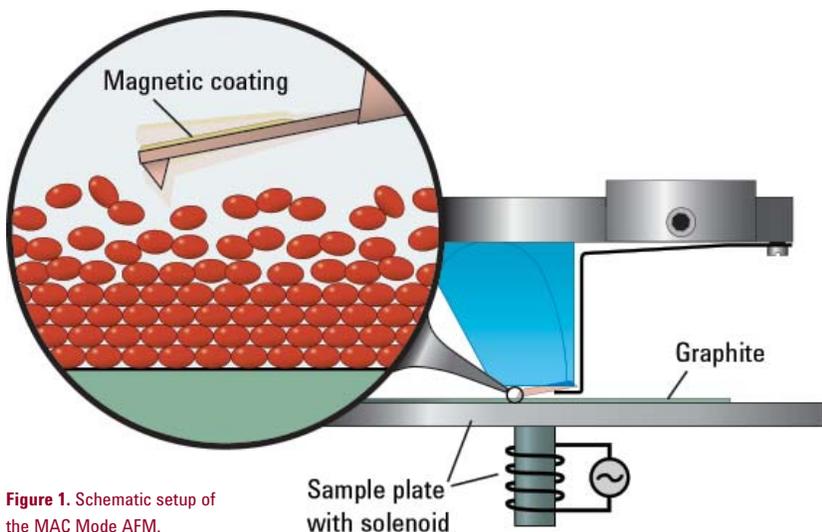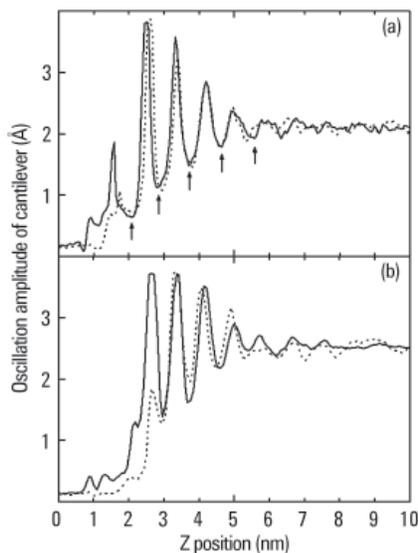
Figure 1. Schematic setup of the MAC Mode AFM.

The fluid cell and cantilever holder were thoroughly cleaned before each experiment. OMCTS was always stored in a desiccator filled with N_2 at 4 °C. It was warmed to ambient temperature before being taken out. In each experiment, graphite was cleaved immediately before being covered by fluid. All experiments were carried out at room temperature in air. The characteristics of AFS data presented here did not change over hours of measurements in our experiments.
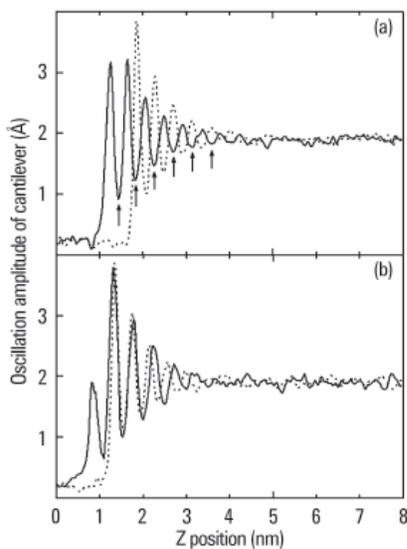
Figures 2(a) and (b) are typical force spectra from two independent experiments at OMCTS-graphite interfaces. They demonstrate the reproducibility of the spectra obtained with different tips. Both approaching and retracting curves were recorded. In Figure 2(a), seven layers of OMCTS molecules at the interface are clearly detected. The average spacing between two adjacent layers, which reflects the size of an OMCTS molecule along the direction perpendicular to the layers, was measured to be 8.7 Å for approaching and 7.9 Å for retracting. The difference was due to thermal drift along the approaching direction. In Figure 2(b), seven molecular layers are also detected. Thermal drift was less in this case. The average spacing between two adjacent layers was 8.2 Å for approaching and 8.0 Å for retracting. After analyzing 22 force spectra from three separate experiments, we found that the average size of OMCTS molecules along the direction of the ordered layers at the interface was 8.2 ± 0.3 Å, consistent with the minor axis of the molecule according to the oblate spherical model of OMCTS (12) and considerably smaller than the major axis. These results show that the layers stack along the minor axis of the molecules.

Figures 3(a) and (b) show two measurements of typical force spectra at mesitylene-graphite interface. Once again, the general features of the AFS are seen to be independent of the tip used. Figure 3(a) shows eight molecular layers on approach and six on retraction, presumably because of disruption of the fluid structure by the tip. The average period of the layers was measured to be 4.2 Å for approaching and 4.3 Å for retracting. Figure 3(b) shows less layers (six approaching and five retracting) and slightly higher thermal drift. The average periods for approaching and retracting were 4.7 and 4.1 Å, respectively. After averaging 22 force spectra in three separate experiments, we found the size of mesitylene molecules along the direction perpendicular to the ordered layers is 4.5 ± 0.2 Å. Given the crystal structure data (14), these results suggest that the mesitylene rings lie flat with respect to graphite surface.

Figure 2. Two independent measurements of force spectra of the MAC Mode AFM at OMCTS-graphite interface. The amplitude of oscillation of the cantilever oscillates in both approaching (solid line) and retracting (dotted line) curves in the region of a few nanometers away from the surface due to ordered layers of OMCTS molecules. The period, 8.2 Å, precisely reflects the layer thickness of OMCTS molecules. (a) Driving frequency = 500 Hz; scan rate = 2.8 nm/sec. (b) Driving frequency = 200 Hz; scan rate = 1.6 nm/sec. The arrows on this and subsequent plots correspond to the repulsive-force maxima.


Figure 3. Two typical force spectra at mesitylene-graphite interface in both approaching (solid line) and retracting (dotted line) processes. Up to eight layers of mesitylene were observed. The oscillatory period, 4.4 Å, indicated that the ordered mesitylene rings arranged parallel to the graphite surface. For both (a) and (b): driving frequency = 500 Hz; scan rate = 2.4 nm/sec.

The liquid density profile at liquid-solid interface oscillates due to the constraint of the solid surface and interactions between the surface and the liquid (15), thus resulting in a corresponding oscillation in the surface stiffness. The amplitude of oscillation of the tip was set at about 2 Å far from the surface. It can be seen that the layering introduces regions of both positive stiffness (decreased amplitude) and negative stiffness (increased amplitude).

For discrete molecular layers, it is inappropriate to map the liquid Young's modulus (compliance) continuously away from the surface because negative stiffness occurs around centers between two neighboring layers. However, it is possible to estimate the Young's modulus at centers of molecular layers where the tip sensed a local maximum repelling force. These points are marked with arrows on both Figures 2 and 3. Note that the amplitude of these minima changes in a consistent way from run to run, while the peak positions, corresponding to negative stiffness, do not.

The minima correspond to stable repulsive mechanical contacts and can be analyzed with simple model-based Hertz elasticity (11). An effective Young's modulus for the nth layer, E_n^*, can be obtained from the surface stiffness for the nth layer, Sn, according to $E_n^* = S_n [S_n / 6RL_n]^{1/2}$ where R is the radius of the tip and Ln is the load on the nth layer (11). Ln is calculated from $L_n = x_n k$ where x_n is the amplitude decrease for the nth layer. Assuming that the radius of the tip is 30 nm and its spring constant is 0.5 nN/nm, the Young's modulus at centers of each ordered molecular layer was plotted in Figure 4 for both OMCTS (circles) and mesitylene (squares). The best-fit lines yield decay lengths of 1.07 layers for OMCTS, corresponding to 8.8 Å, and 1.48 layers for mesitylene, corresponding to 6.5 Å.
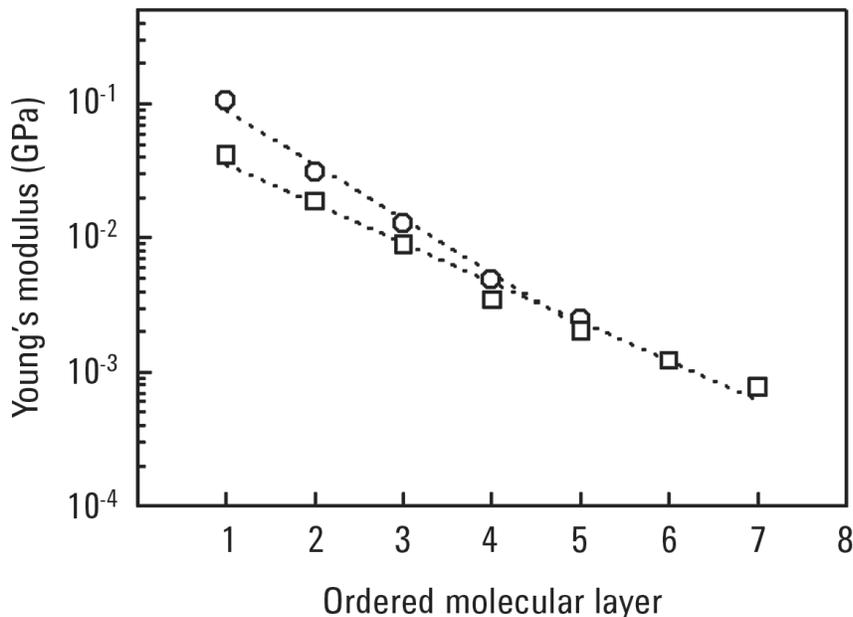
Figure 4. The Young's modulus of OMCTS (circles) and mesitylene (squares) at centers of ordered layers. The lines are best-fit lines, indicating exponential decay of the Young's modulus with the number of molecular layers. Data from Figure 2(a) and Figure 3(a).

In conclusion, we have used AFS of the MAC Mode AFM to probe ordered liquid molecules of OMCTS and mesitylene at the graphite surface with sub-angstrom vertical resolution. Elastic compliance at the center of each layer was found to exponentially decrease versus the number of layers. Combined with the high lateral resolution feature of the MAC Mode AFM (6), we believe this study will open a possible way of precisely identifying properties of molecules at surfaces and interfaces from solid to liquid.

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