

# Probing molecular ordering at a liquid-solid interface with a magnetically oscillated atomic force microscope

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We have demonstrated the ability of an atomic force microscope operated in the magnetic a/c mode to determine the layered structure of liquids at interfaces with high accuracy and reproducibility. Oscillations in surface stiffness were found for octamethylcyclotetrasiloxane (OMCTS) and mesitylene close to a graphite surface and the period of oscillation allowed us to determine the molecular packing to sub-Angstrom precision. The Young's modulus, measured at the peak stiffness of each layer, decreased exponentially with distance from the interface with a decay length of 8.8 Å for OMCTS and 6.5 Å for mesitylene. © 1998 American Institute of Physics. [S0003-6951(98)04013-3]

Ordering of the liquid at the interface with a solid is a phenomenon of fundamental importance in fields such as tribology and electrochemistry<sup>1</sup> and it has been studied extensively with the surface force apparatus.<sup>2,3</sup> This liquid structuring may also have a profound affect upon the operation of an atomic force microscope (AFM), causing the tip to hop between different stable configurations in the ordered region of the fluid.<sup>4</sup> The AFM has been used to study structure in interfacial water<sup>5</sup> and organic liquids.<sup>6,7</sup> In contrast to the surface force apparatus, 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 may be obtained despite variability in AFM tips.

If the microscope is operated with a probe that is oscillated at an amplitude  $x_0$  far from the surface, then, provided the oscillation frequency  $f$  is far below mechanical resonances, the surface stiffness at some distance  $z$  from the surface,  $S(z)$ , is given by<sup>7</sup>

$$S(z) = k \left( \frac{x_0}{x(z)} - 1 \right), \quad (1)$$

where  $k$  is the spring constant of the cantilever and  $x(z)$  is the amplitude of the tip oscillation. A number of simple models permit extraction of quantities such as Young's modulus from the surface stiffness.<sup>8,9</sup>

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<sup>7,10-12</sup> as opposed to indirect mechanical excitation with an acoustic transducer.<sup>13,14</sup> O'Shea *et al.*<sup>7</sup> 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, octamethyl-

cyclotetrasiloxane (OMCTS), was substantially smaller (5 Å) than the known smallest dimension of the molecule (8 Å) so that 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 [ $((\text{CH}_3)_2\text{SiO})_4$ ] and mesitylene [ $(\text{CH}_3)_3\text{C}_6\text{H}_3$ ] because they are relatively rigid and their dimensions are reasonably 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.<sup>15</sup> Ordered layers have been detected on mica with a period of 0.8 to 1.0 nm using the surface force apparatus.<sup>3</sup> Mesitylene or 1,3,5-trimethylbenzene molecule has a benzene ring with each  $-\text{H}$  at the first, third, and fifth carbon locations replaced by a  $-\text{CH}_3$  group. Crystal structure data<sup>16</sup> 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) and mesitylene was obtained from Alfa Aesar (Ward Hill, Massachusetts). Graphite obtained as highly-oriented pyrolytic graphite (HOPG) was from Advanced Ceramics (Cleveland, Ohio).

We used a PicoSPM from Molecular Imaging (Phoenix, Arizona) operated in the magnetic a/c mode (MAC Mode)<sup>12</sup> with a Molecular Imaging MAC Mode interface driving a Nanoscope E controller (Digital Instruments, Santa Barbara, CA). The spring constant of the magnetic cantilevers (Molecular Imaging) used was typically 0.5 nN/nm. Atomic force spectra (AFS) were obtained by driving the force input of the nanoscope controller with the demodulated amplitude signal from the MAC Mode controller and setting the nanoscope to record force curves. The tip oscillation frequency was between 200 and 500 Hz, far below the mechanical resonance of the cantilever in fluid (about 28 kHz).

The fluid cell and cantilever holder were thoroughly cleaned before each experiment. OMCTS was stored in a desiccator filled with  $\text{N}_2$  at 4 °C. It was warmed to ambient

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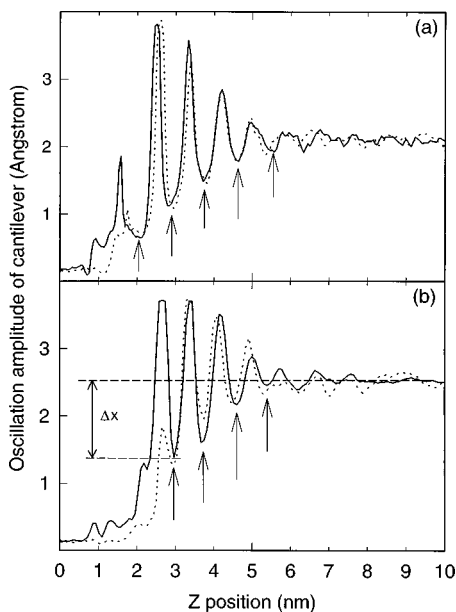


FIG. 1. Two independent measurements of force spectra of the MAC Mode AFM at OMCTS-graphite interface. The amplitude of oscillation of the magnetic cantilever driven by an external magnetic field oscillates in both approaching (solid line) and retracting (dotted line) curves in the region of a few nanometers away from the surface due to ordered layers of OMCTS molecules at the interface. The period of the oscillation,  $8.2 \text{ \AA}$ , precisely reflected the dimension of OMCTS molecules along the direction perpendicular to the layers. (a) Driving frequency  $500 \text{ Hz}$ , scan rate  $2.8 \text{ nm/s}$ . (b) Driving frequency  $200 \text{ Hz}$ , scan rate  $1.6 \text{ nm/s}$ . The arrows on this and subsequent plots correspond to repulsive-force maxima.

temperature before removal. 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 1(a) and 1(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 the approaching and the retracting curves were recorded. In Fig. 1(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  $8.7 \text{ \AA}$  for approaching, and  $7.9 \text{ \AA}$  for retracting. The difference was due to thermal drift. Seven molecular layers are also detected in the data shown in Fig. 1(b). Thermal drift was less in this case. The average spacing between two adjacent layers was  $8.2 \text{ \AA}$  for approaching and  $8.0 \text{ \AA}$  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  $8.2 \pm 0.3 \text{ \AA}$ , consistent with the minor axis of the molecule according to the oblate spherical model of OMCTS<sup>15</sup> and considerably smaller than the major axis. These results show that the layers stack along the minor axis of the molecules.

Figures 2(a) and 2(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 2(a) shows eight molecular layers on approach and six on retraction, presumably because of dis-

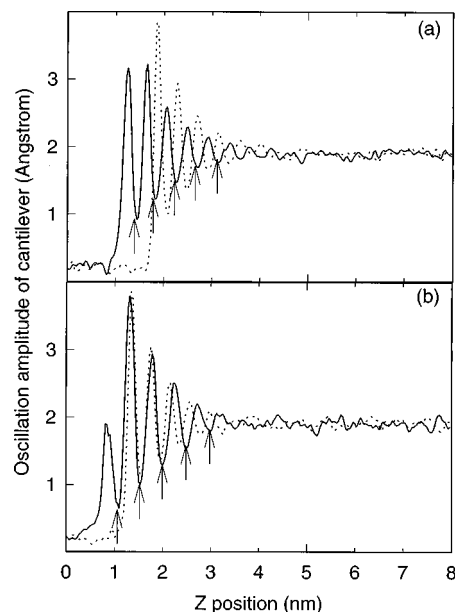


FIG. 2. Two typical force spectra at mesitylene-graphite interface in both approaching (solid line) and retracting (dotted line) processes. Up to eight layers of mesitylene were observed. The oscillatory period,  $4.4 \text{ \AA}$ , indicated that the ordered mesitylene rings arranged parallel to the graphite surface. Both (a) and (b) driving frequency  $500 \text{ Hz}$ , scan rate  $2.4 \text{ nm/s}$ .

ruption of the fluid structure by the tip. The average period of the layers was measured to be  $4.2 \text{ \AA}$  for approaching and  $4.3 \text{ \AA}$  for retracting. Figure 2(b) shows fewer layers (six approaching and five retracting) and slightly higher thermal drift. The average periods for approaching and retracting were  $4.7$  and  $4.1 \text{ \AA}$ , 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  $4.5 \pm 0.2 \text{ \AA}$ . Given the crystal structure data,<sup>16</sup> these results suggest that the mesitylene rings lie flat with respect to the graphite surface.

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<sup>17</sup> and this results in a corresponding oscillation in the surface stiffness.<sup>7</sup> The amplitude of oscillation of the tip was set at about  $2 \text{ \AA}$  far from the surface, and it can be seen that the layering introduces regions of both positive stiffness (decreased amplitude) and negative stiffness (increased amplitude).

The layer spacings varied from the average by an amount that was considerably in excess of the noise. For example, seven consecutive periods in the approaching curve of Fig. 2(a) are  $4.0$ ,  $4.1$ ,  $4.4$ ,  $4.2$ ,  $4.5$ ,  $4.0$ , and  $4.5 \text{ \AA}$  as measured outward from the graphite surface. These fluctuations changed from scan to scan, and probably arise from fluctuations in the interfacial structure, reflecting the fluid nature of these layers.

We looked for evidence of a systematic variation in layer separation with increasing distance from the interface. For OMCTS, the first pair of peaks were separated by  $8.05 \pm 0.14 \text{ \AA}$ , whereas peaks 6 and 7 were separated by  $8.31 \pm 0.12 \text{ \AA}$  where the uncertainty is plus or minus one standard error. Therefore any effect is barely significant. No effect was observed for mesitylene.

For discrete molecular layers, it is inappropriate to map

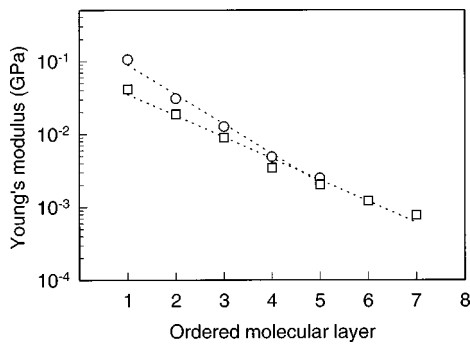


FIG. 3. The Young's modulus of OMCTS (circles) and mesitylene (squares) at centers of ordered layers. The lines are best-fit lines, indicating exponential decay of the Young's modulus with the number of molecular layers. Data from Fig. 1(a) and Fig. 2(a).

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 senses a local maximum repulsive force. These points are marked with arrows on both Figs. 1 and 2. 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 a simple model based Hertzian elasticity.<sup>9</sup> An effective Young's modulus for the  $n$ th layer,  $E_n^*$ ,<sup>8</sup> can be obtained from the surface stiffness for the  $n$ th layer,  $S_n$ , according to<sup>9</sup>

$$E_n^* = \sqrt{S_n^3/6RL_n}, \quad (2)$$

where  $R$  is the radius of the tip and  $L_n$  is the load on the  $n$ th layer.  $L_n$  is calculated from  $L_n = \Delta x_n k$ , where  $\Delta x_n$  is the amplitude decrease for the  $n$ th layer [see Fig. 1(b)]. Assuming that the radius of curvature of the tip is 30 nm and its spring constant is 0.5 nN/nm (specifications from Park Scientific Instruments, Sunnyvale, CA), the Young's modulus at the centers of each ordered molecular layer was calculated from Eqs. (1) and (2). The results are shown in Fig. 3 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.

In our analysis we have assumed a purely elastic interaction between the tip and the fluid. We expect viscosity to increase dramatically as the liquid takes on solid-like properties.<sup>18</sup> Assuming a harmonic process, we may write the time-dependent amplitude of oscillation as

$$x_0(t) = x'_0 e^{i\omega t}, \quad x(z, t) = x'(z) e^{i[\omega t + \phi(z)]}, \quad (3)$$

where  $\phi(z)$  is the phase shift due to the viscosity, and  $x'_0$  and  $x'(z)$  are time-independent parts of the amplitudes. The corresponding surface stiffness  $S(z)$  is complex and can be separated into real  $S_R(z)$  and imaginary  $S_I(z)$  parts,

$$S(z) = S_R(z) + iS_I(z). \quad (4)$$

Equation (1) can then be written as

$$kx'_0 e^{i\omega t} = [S_R(z) + iS_I(z) + k]x'(z) e^{i[\omega t + \phi(z)]}. \quad (5)$$

From which the real parts of the stiffness signal is

$$S_R(z) = k \left( \frac{x'_0}{x'(z)[1 + \sin \phi(z) \tan \phi(z)]} - 1 \right). \quad (6)$$

So the effect of a viscously-induced phase shift is a reduction in the apparent Young's modulus. A large effect might be manifest as a nonexponential decay in modulus, but we see no evidence for this, implying that the viscous contribution does not change by a large amount over the distance that our measurements are made. This may well be a geometrical effect since the contribution to damping provided by the tip is infinitesimal compared with that from the remainder of the cantilever structure.

In conclusion, we have used the AFS mode 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. Combining with the high lateral resolution feature of the MAC Mode AFM,<sup>19</sup> 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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