

# Combined Atomic Force Microscopy and Fluorescence Correlation Spectroscopy Measurements to Study the Dynamical Structure of Interfacial Fluids

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We have studied the dynamic structure of thin (approximately a few nanometers) liquid films of a nearly spherical, nonpolar molecule tetrakis(2-ethylhexoxy)silane (TEHOS) by using a combination of atomic force microscopy (AFM) and fluorescence correlation spectroscopy (FCS). Ultra-sensitive interferometer-based AFM was used to determine the stiffness (force gradient) and the damping coefficient of the liquid film. The experiments show oscillations in the damping coefficient with a period of  $\sim 1$  nm, which is consistent with the molecular dimension of TEHOS as well as previous X-ray reflectivity measurements. Additionally, we performed FCS experiments for direct determination of the molecular dynamics within the liquid film. From the fluctuation autocorrelation curve, we measured the translational diffusion of the probe molecule embedded within the fluid film formed on a solid substrate. The autocorrelation function was best fitted with two components, which indicate that the dynamics are heterogeneous in nature. However, the heterogeneity is not as pronounced as had been previously observed for molecularly thin liquid films sandwiched between two solid substrates.

## Introduction

The properties of molecularly thin fluid films are important in numerous areas of nature and technology, among them lubrication, adhesion, lithography, and colloidal particles suspended in liquids.<sup>1–5</sup> It is also relevant to the understanding of the structure and transport properties of complex fluids localized in self-assembled fluid structures such as polymers, vesicles, and biomembranes. During the last two decades, significant experimental and theoretical studies have been carried out to understand the interfacial behavior of liquids.<sup>6–15</sup> The structure of liquids near a solid surface has been analyzed by different techniques. Experimental methods such as using a surface forces apparatus (SFA)<sup>16</sup> and atomic force microscopy (AFM)<sup>17–20</sup>

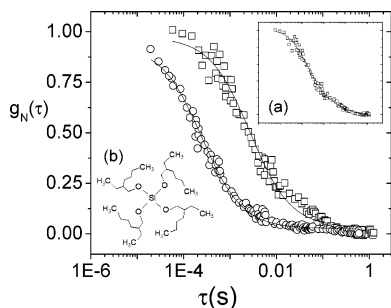
measure the force required to bring two solid surfaces from a large distance into close proximity.<sup>7,21,22</sup> These experiments have revealed that when two surfaces approach closer than a few molecular diameters, continuum theories often break down, and an oscillatory solvation force, which arises from the discrete molecular nature of the liquids, comes into play.<sup>17,23</sup> Theoretical work and computer simulations of fluids at solid surfaces have shown that the origin of this oscillatory solvation force is the ordering of molecules in layers parallel to the surface.<sup>24</sup> More recently, it has become possible by using advanced synchrotron X-ray reflectivity to directly observe such molecular layering in thin liquid films.<sup>25</sup>

The mechanical properties of the first few molecular layers of a liquid close to a solid surface have also been found to be significantly different as compared to the bulk.<sup>26–28</sup> When a liquid is confined to a thickness comparable to the size of the molecules, the viscosity and the effective shear modulus can increase by several orders of magnitude, and the terminal relaxation times are enormously prolonged.<sup>29–33</sup> The majority of the experimental results came from using modified SFA and AFM, both of which can measure the rheological or tribological properties of molecularly thin films of precisely controllable thickness. It is unclear at present how the mechanical properties measured in these experiments relate to individual molecular

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- (1) Bhusan, B.; Israelachvili, J. N.; Landman, U. *Nature* **1995**, *374*, 607.
- (2) Cohen, I.; Mason, T. G.; Weitz, D. A. *Phys. Rev. Lett.* **2004**, *93*, 46001.
- (3) He, M.; Szuchmacher, A.; Overney, G.; Overney, R. M. *Phys. Rev. Lett.* **2002**, *88*, 154302.
- (4) Maeda, N.; Chen, N. H.; Tirrell, M.; Israelachvili, J. N. *Science* **2002**, *297*, 379.
- (5) Urbakh, M.; Klafeter, J.; Gourdon, D.; Israelachvili, J. *Nature* **2004**, *430*, 525.
- (6) Becker, T.; Mugele, F. *Phys. Rev. Lett.* **2003**, *91*, 166104.
- (7) Heuberger, M.; Zach, M.; Spencer, N. D. *Science* **2001**, *292*, 905.
- (8) Mugele, F.; Balselli, S.; Somarjai, G. A.; Salmeron, M. *J. Chem. Phys.* **2001**, *114*, 1831.
- (9) Mugele, F.; Salmeron, M. *Phys. Rev. Lett.* **2000**, *84*, 5796.
- (10) Mukhopadhyay, A.; Bae, S. C.; Zhao, J.; Granick, S. *Phys. Rev. Lett.* **2004**, *93*, 236105.
- (11) Raviv, U.; Laurat, P.; Klein, J. *Nature* **2001**, *413*, 51.
- (12) Schuster, J.; Cichos, F.; Wrachtrup, J.; von Borczyskowski, C. *Single Mol.* **2000**, *1*, 299.
- (13) Yu, C. J.; Richter, A. G.; Datta, A.; Durbin, M. K.; Dutta, P. *Phys. Rev. Lett.* **1999**, *82*, 2326.
- (14) Zhu, Y.; Granick, S. *Phys. Rev. Lett.* **2004**, *93*, 96101.
- (15) Zilberman, S. B. T.; Mugele, F.; Persson, B. N. J.; Nitzam, A. *J. Chem. Phys.* **2003**, *118*, 11160.
- (16) Israelachvili, J. N.; Pashley, R. M. *Nature* **1983**, *306*, 249.
- (17) Antognozzi, M.; Humphris, A. D. L.; Miles, M. J. *Appl. Phys. Lett.* **2001**, *78*, 300.
- (18) Jarvis, S. P.; Uchihashi, T.; Ishida, T.; Tokumoto, H.; Nakayama, Y. *J. Phys. Chem. B* **2000**, *104*, 6091.
- (19) Jeffery, S.; Hoffmann, P. M.; Pethica, J. B.; Ramanujan, C.; Özer, H. Ö.; Oral, A. *Phys. Rev. B* **2004**, *70*, 54114.
- (20) O'Shea, S. J.; Welland, M. E. *Langmuir* **1998**, *14*, 4186.

- (21) Cappella, B.; Dietler, G. *Surf. Sci. Rep.* **1999**, *34*, 1.
- (22) O'Shea, S. J.; Welland, M. E.; Pethica, J. B. *Chem. Phys. Lett.* **1994**, *75*, 336.
- (23) Lim, R.; O'Shea, S. J. *Phys. Rev. Lett.* **2002**, *88*, 246101.
- (24) Gao, J.; Luedtke, W. D.; Landman, U. *J. Chem. Phys.* **1997**, *106*, 4309.
- (25) Seeck, O. H.; Kim, H.; Lee, D. R.; Shu, D.; Kaendler, I. D.; Basu, J. K.; Sinha, S. K. *Europhys. Lett.* **2002**, *60*, 376.
- (26) Burns, A. R.; Houston, J. E.; Carpick, R. W.; Michalske, T. A. *Langmuir* **1999**, *15*, 2922.
- (27) Drummond, C.; Israelachvili, J. *Phys. Rev. E* **2001**, *63*, 41506.
- (28) Thompson, P. A.; Grest, G. S.; Robbins, M. O. *Phys. Rev. Lett.* **1992**, *68*, 3448.
- (29) Cui, S. T.; Cummings, P. T.; Cochran, H. T. *J. Chem. Phys.* **2001**, *114*, 7189.
- (30) Demirel, A. L.; Granick, S. *J. Chem. Phys.* **2001**, *115*, 1498.
- (31) Filipov, E.; Klafeter, J.; Urbakh, M. *Phys. Rev. Lett.* **2001**, *87*, 275506.
- (32) Khare, R.; de Pablo, J. J.; Yethiraj, A. *J. Chem. Phys.* **2001**, *114*, 7593.
- (33) Klein, J.; Kumacheva, E. *J. Chem. Phys.* **1998**, *108*, 6996.



**Figure 1.** Normalized autocorrelation function of coumarin diffusing through TEHOS in bulk (circles) and within a thin film,  $L \approx 14$  nm (squares). The graph has been fitted with a single diffusion coefficient ( $D$ );  $D_{\text{bulk}} = 70 \mu\text{m}^2/\text{s}$  and  $D_{\text{film}} = 6 \mu\text{m}^2/\text{s}$ . Inset a shows the fitting of the thin film autocorrelation function data assuming two diffusing species, having a fast ( $D_{\text{fast}} = 10 \mu\text{m}^2/\text{s}$ ) and a slow component ( $D_{\text{slow}} = 0.2 \mu\text{m}^2/\text{s}$ ). Inset b provides the molecular structure for TEHOS.

dynamics because although the thickness of the studied liquid films is molecular in the force-based experiments, the area dimension is not. The measurements in such experiments typically represent an average over ensembles of many molecules.<sup>34</sup>

In the past few years, optical spectroscopy at the level of a single or a few molecule has grown into a powerful technique for exploring the nanoscale behavior in complex condensed matter environments.<sup>35,36</sup> The direct measurement of the dynamics of individual molecules within an SFA has been achieved recently.<sup>37</sup> The experiments revealed a massively heterogeneous molecular mobility within fluid films. It has been speculated that the origin of the heterogeneous dynamics is the layering of the molecules parallel to the confining surfaces, in which both the local density and the diffusion rate can differ. Because of several technical challenges to perform single molecule spectroscopy within SFA, it is difficult to definitively correlate the heterogeneous dynamics with the layering. It is also relevant to point out here that the computer simulations of confined fluids of a few nanometers in thickness have also indicated that the dynamics of molecules at individual layers could be different.<sup>38</sup>

Thin (approximately a few nanometers) films of tetrakis (2-ethylhexoxy)silane (TEHOS), a nearly spherical and nonpolar molecule, have been model systems to investigate the interfacial organization of liquids near a solid surface.<sup>39</sup> The molecule is comprised of a silicon atom bound to four oxygen atoms, which are surrounded by branched alkanes (see Figure 1).<sup>40</sup> The freezing point and critical point for TEHOS have yet to be precisely determined, although X-ray scattering in transmission and differential scanning calorimetry has found no evidence of a bulk phase transition down to 190 K.<sup>41</sup> We have chosen this system because evidence of molecular layering of TEHOS near a solid substrate has previously been demonstrated by X-ray reflectivity experiments.<sup>13,42,43</sup> One of our goals is to investigate

how this layering affects the lateral translational diffusion of fluorescent dye molecules embedded within the film. This will be accomplished by utilizing the single molecule sensitive technique of fluorescence correlation spectroscopy (FCS). A second objective of this paper is to investigate the mechanical responses of the film, which are expressed in terms of stiffness and damping coefficients. A novel liquid-based AFM,<sup>44</sup> which can measure forces associated with molecular ordering, will be used for this purpose. Both FCS and AFM results will be compared with previous experiments, which used another model liquid, OMCTS (octamethylcyclotetrasiloxane).

## Experimental Procedures

**FCS.** FCS is an experimental method that extracts information on dynamical processes from the tiny fluctuations that can be observed in the emission of a small ensemble of fluorescent molecules. The fluctuation of fluorescence is due to dynamic processes such as diffusion, aggregation, and chemical reactions, which occur in very small volumes ( $\sim 10^{-15}$  L) in very dilute systems (from picomolar to nanomolar concentrations). By calculating the autocorrelation function ( $G(\tau)$ ) of this fluctuation ( $F$ ),  $G(\tau) = \langle \delta F(t)\delta F(t + \tau) \rangle / \langle F(t) \rangle^2$  and by choosing a suitable model to analyze the autocorrelation function, the rate of the dynamic process can be obtained.<sup>45</sup> If the primary reason for fluctuation is two-dimensional translational diffusion, one can calculate the translational diffusion coefficient ( $D$ ) from the autocorrelation function by using the relation  $G(\tau) = G(0)/(1 + 8D\tau/\omega_0^2)$ , where  $\omega_0$  ( $\sim 0.35 \mu\text{m}$ ) is the width of the laser focus. As the thickness of the film ( $L \approx 10$  nm) is much smaller as compared to the size of the laser focus in the axial direction ( $z_0 = \sim 2 \mu\text{m}$ ), the analysis of the autocorrelation function using two-dimensional diffusion is justified. The magnitude of the autocorrelation function at time zero,  $G(0)$ , is related to the average number of fluorophores ( $N$ ) in the observation volume by  $G(0) = 1/(2N)$ . The concentration of dye molecules in these experiments has been selected such that  $N < 10$ . As compared to other methods such as scattering, fluorescence recovery after photobleaching (FRAP), and laser induced transient grating spectroscopy, FCS is capable of measuring extremely dilute systems with high spatial resolution down to the optical diffraction limit.

FCS experiments have been performed by two-photon excitation of fluorescence. A femtosecond titanium-sapphire laser (Mai Tai, Spectra-Physics) generates laser pulses with a fwhm (full width at half-maximum) of 100 fs at a repetition rate of 80 MHz. A Zeiss inverted microscope (Axiovert S200TV, Carl Zeiss) serves as the operational platform for the experiment. By introducing the laser beam through the objective lens ( $63\times$ , NA = 0.75), a very small excitation volume is generated within the sample solution. Fluorescence is collected through the same objective and detected by a single photon counting module (Hamamatsu). The sensitivity of this technique to the diffusion of a single molecule both in bulk and within thin films has been demonstrated previously.<sup>46</sup>

**AFM.** AFM was used to sample the stiffness, mechanical damping, and mechanical relaxation time of a TEHOS layer confined between the tip and the substrate. In general, when a liquid is confined, mechanical measurements often exhibit an oscillatory profile as the separation of the two confining surfaces is changed. Broadly speaking, we expect a high stiffness when the separation allows the molecules to neatly fit between the two surfaces and form an integer number of layers. If the tip is at a separation that is not an integer multiple of the molecule size, the layering is disturbed, and we would expect to measure a low stiffness of the confined liquid film. So, as we approach the two surfaces (the tip and substrate in our case), we would expect the stiffness to go through several local maxima, as molecular layer after layer is squeezed out.<sup>19,47</sup>

(34) Mukhopadhyay, A.; Granick, S. *Curr. Opin. Colloid Interface Sci.* **2001**, *6*, 423.

(35) Moerner, W. E.; Orritt, M. *Science* **1999**, *283*, 1670.

(36) Xie, X. S.; Trautman, J. K. *Annu. Rev. Phys. Chem.* **1998**, *49*, 441.

(37) Mukhopadhyay, A.; Zhao, J.; Bae, S. C.; Granick, S. *Phys. Rev. Lett.* **2002**, *89*, 136103.

(38) Gao, J. P.; Luedtke, W. P.; Landman, U. *Phys. Rev. Lett.* **1997**, *79*, 705.

(39) Forcada, M. L.; Mate, M. C. *Nature* **1993**, *363*, 527.

(40) Yu, C. J.; Richter, A. G.; Kmetko, J.; Datta, A.; Dutta, P. *Europhys. Lett.* **2000**, *50*, 487.

(41) Mo, H.; Evmenenko, G.; Kewalramani, S.; Kim, K.; Ehrlich, S. N.; Dutta, P. *Phys. Rev. Lett.* **2006**, *96*, 96107.

(42) Yu, C. J.; Evmenenko, G.; Kmetko, J.; Dutta, P. *Langmuir* **2003**, *19*, 9558.

(43) Yu, C. J.; Evmenenko, G.; Richter, A. G.; Dutta, A.; Kmetko, J.; Dutta, P. *Appl. Surf. Sci.* **2001**, *182*, 231.

(44) Patil, S.; Matei, G.; Dong, H.; Hoffmann, P. M.; Karakose, M.; Oral, A. *Rev. Sci. Instrum.* **2005**, *76*, 103705.

(45) Berland, K. M.; So, P. T. C.; Gratton, E. *Biophys. J.* **1995**, *68*, 694.

(46) Mukhopadhyay, A.; Granick, S. *Rev. Sci. Instrum.* **2003**, *74*, 3067.

(47) Patil, S.; Matei, G.; Oral, A.; Hoffmann, P. M. *Langmuir* **2006**, *22*, 6485.

For our measurements, we used a home-built AFM,<sup>44</sup> which uses a fiber-interferometric deflection sensor to boost sensitivity. With this, we were able to perform measurements in the small amplitude, linear regime.<sup>48</sup> In this regime, the stiffness and damping coefficient can be calculated from

$$k = k_L \left( \frac{A_0}{A} \cos \varphi - 1 \right) \quad (1)$$

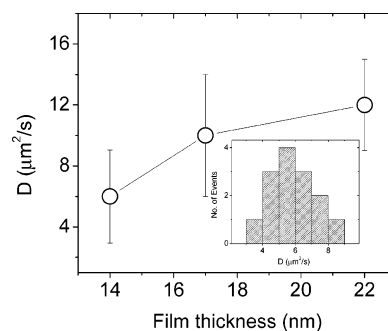
$$\gamma = \frac{k_L A_0}{A \omega} \sin \varphi \quad (2)$$

where  $k_L$  is the stiffness of the cantilever,  $A_0$  is the amplitude far from the surface,  $A$  is the measured amplitude as the surface is approached with the tip,  $\omega$  is the angular frequency of the tip oscillation, and  $\varphi$  is the phase angle between the piezo drive and the tip end. Our measurements were performed far below the resonance frequency of the lever, and in the absence of a tip-sample interaction, the phase angle  $\varphi$  would be zero and  $A = A_0$ . A change in the phase angle indicates a dissipative interaction with the substrate and intervening medium.<sup>49</sup>

**Sample Preparation.** The sample of TEHOS (Gelest) was used as received. The substrates used were quartz cover slips (Esco Products) for FCS experiments and silicon wafers for ellipsometry and AFM experiments. Prior to use, the cover slips were kept in an acid bath overnight, rinsed with deionized water, ultrasonicated in acetone, and finally rinsed with distilled ethanol. Si wafers were cleaned with a piranha solution, rinsed in deionized water several times, and kept in oven at 110 °C overnight to remove water. This cleaning procedure left the Si wafer surface hydrophilic with a thin passive oxide layer. For AFM experiments, a small amount of liquid was injected into a liquid cell containing the clean Si wafer substrate.<sup>44</sup> The cantilever and tip were immersed in the liquid to avoid snap-to-contact due to capillary forces. For FCS and ellipsometry experiments, the deposition of the thin film was carried out as described in ref 13. The substrate was immersed in a dilute solution of TEHOS in hexane and then withdrawn at a constant speed ( $\sim 1$  mm/s). The thickness of the film was varied by changing the concentration of TEHOS in the hexane solution. The film thickness was measured by using a commercial phase-modulated ellipsometer (Beaglehole Instruments). For FCS experiments, the solution also contained  $\sim 50$  nM fluorescent dye coumarin 153 (Exciton). The dye was selected because it has a high two-photon cross-section at an excitation wavelength of 800 nm and does not adsorb to the substrate as verified by control experiments. The mean diameter of the liquid TEHOS is  $\approx 0.9$  nm, and the dimensions of the dye, coumarin 153, are  $\approx 1.2$  nm  $\times$  0.9 nm  $\times$  0.37 nm.<sup>37</sup>

## Results and Discussion

**Diffusion Dynamics.** Figure 1 shows the illustrative autocorrelation function obtained from FCS experiments. From the time series of fluctuations of the fluorescence intensity, the intensity-intensity autocorrelation function was calculated and plotted against the logarithmic time lag. The time scale of diffusion, which can be estimated as the time at which the autocorrelation function decays to one-half its initial value, is larger within the fluid film as compared to the bulk. The autocorrelation function in the bulk can be fitted very well with a single diffusion coefficient  $D \approx 70 \mu\text{m}^2/\text{s}$ . For thin films ( $L \approx 14$  nm), fitting the data with a single diffusion coefficient yields  $D \approx 6 \mu\text{m}^2/\text{s}$ , indicating that dye molecules within the fluid films have slowed down by a factor of  $\sim 10$ . This result is consistent with previous experiments, which have also found a slowing down of the molecules near a solid surface.<sup>12,37</sup> In the present experiments, however, we found a weak dependence of



**Figure 2.** Diffusion coefficient ( $D$ ) as a function of film thickness.  $D$  has been obtained by fitting the autocorrelation functions with a single diffusion coefficient. The inset shows the histogram of measured  $D$  at  $L = 14$  nm.

the measured diffusion coefficients on the thickness of the films, which was varied between 14 and 22 nm (Figure 2). Surprisingly, even for the thickest films, which correspond to  $\sim 25$  or more molecules thick, the diffusion dynamics are at least 5 times slower as compared to the bulk value. A histogram of the diffusion coefficients measured at a fixed film thickness has been shown in the inset of Figure 2. To obtain this histogram, curves were fitted with a single diffusion coefficient.

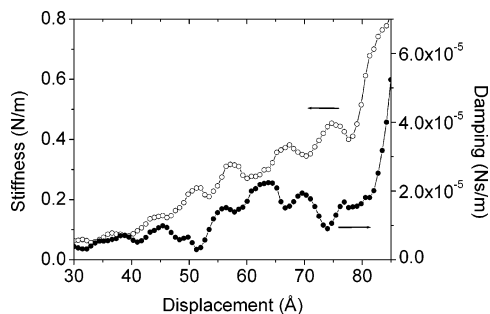
A closer look at the autocorrelation function for thin films, however, showed that comparably good fitting results were obtained (Figure 1 inset) if the curves were evaluated under the assumption of two diffusing species having a faster and a slower component. To obtain these components, the autocorrelation function in Figure 1 was fitted using the functional form  $G(\tau) = G_1/(1 + 8D_{\text{fast}}\tau/\omega_0^2) + G_2/(1 + 8D_{\text{slow}}\tau/\omega_0^2)$ , giving  $D_{\text{fast}} = 10 \mu\text{m}^2/\text{s}$  and  $D_{\text{slow}} = 0.2 \mu\text{m}^2/\text{s}$ . These results can be compared to single molecule microscopy experiments performed by Cichos et al. for the same system.<sup>12,50,51</sup> In their experiments, the mean diffusion coefficient of the dyes and its distribution were obtained by averaging over hundreds of individual single molecule trajectories. A broad distribution of diffusion coefficients was found, which was attributed to diffusion within distinct layers of the liquid. They have interpreted the results in terms of dynamics that depend strongly on the distance of the molecules from the solid surface. In contrast to single molecule tracking experiments, FCS is an intrinsically statistical method, and a typical FCS measurement averages many individual molecules diffusing in and out of the focal volume during data recording. This causes some loss of information on dynamic properties. Nevertheless, previous FCS experiments in thin films ( $\sim 4$ – $5$  nm) of OMCTS confined between two solid substrates within an SFA have observed massively heterogeneous molecular dynamics.<sup>37</sup> This heterogeneity did not disappear, even when it was averaged over an extended period of time ( $\sim 45$  min). It has been speculated that the heterogeneity arises because of different translation diffusion rates in different layers. For the system studied in the present experiments, X-ray reflectivity experiments have shown density oscillations, although the amplitude is less than 10% of the average liquid density.<sup>13</sup> AFM experiments have also indicated layering of the confined TEHOS (see Mechanical Measurements). Taken together, our data are consistent with the interpretation that the layering of molecules in thin films is responsible for the heterogeneous dynamics. It is important to note that the film could also be laterally heterogeneous, especially for thinner films. But, the effect of those is likely to be weak,

(48) Hoffmann, P. M. *Appl. Surf. Sci.* **2003**, *210*, 140.

(49) Hoffmann, P. M.; Jeffery, S.; Pethica, J. B.; Özgür, Ö. H.; Oral, A. *Phys. Rev. Lett.* **2001**, *87*, 265502.

(50) Schuster, J.; Cichos, F.; von Borczyskowski, C. *Eur. Phys. J. E* **2003**, *12*, 75.

(51) Schuster, J.; Cichos, F.; von Borczyskowski, C. *Eur. Polym. J.* **2004**, *40*, 993.

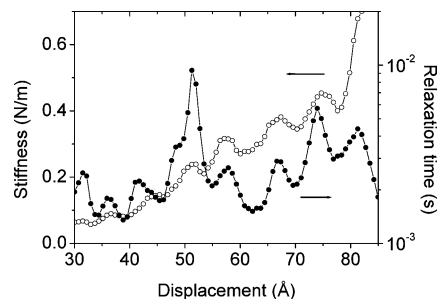


**Figure 3.** Simultaneously measured stiffness (open circles) and damping (filled circles) of a confined TEHOS film. The measuring tip was approached at a rate of 12 Å/s. The surface is located to the right.

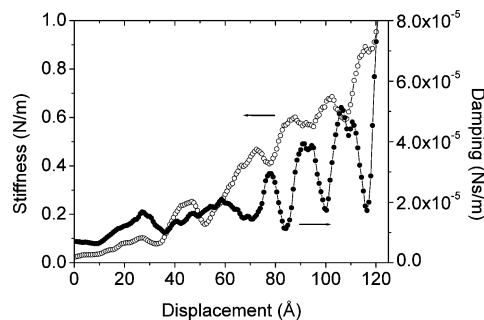
based on our FCS measurements of different film thicknesses (Figure 2). However, we note that the heterogeneity in the diffusion dynamics is not as pronounced in these films as compared to when the liquid is confined between two solid substrates. The thicknesses of the films in these experiments are also much larger as compared to SFA experiments. We found thickness variations across the film when we tried to prepare thinner films (by using more dilute TEHOS in a hexane solution). This made it difficult to measure the diffusion dynamics as a function of film thickness in a more systematic way. In all these experiments, it was also difficult to determine whether the dye resided distinctly within given fluid layers or also between them. The axial length of the laser focus, which is  $\sim 2 \mu\text{m}$ , is orders of magnitude larger than the thickness of the film. So, the question of how the diffusion dynamics depends upon the distance from a solid surface still remains open to debate. Experiments are currently under progress in our laboratory to answer this question.

**Mechanical Measurements.** Figure 3 shows the stiffness,  $k$ , and damping coefficient,  $\gamma$ , measured with our AFM at an amplitude of 3.4 Å and a frequency of 465 Hz. The approach speed of the two surfaces (tip and substrate) during the measurement was 12 Å/s. Stiffness and damping maxima can be clearly discerned over a monotonically increasing background as the tip approaches the surface. It is also apparent that the stiffness and damping are out of phase for the last few layers (i.e., at displacements where the stiffness is at a local maximum and the damping is in a local minimum (or vice versa)). The average spacing of the stiffness peaks in this measurement was  $7.6 \pm 1.1 \text{ Å}$ , while the spacing averaged over all measurements obtained at an approach speed of 12 Å/s was  $9.9 \pm 2.7 \text{ Å}$ , consistent with the size of the molecules. Differences in spacing between measurements are most likely due to thermal drift.

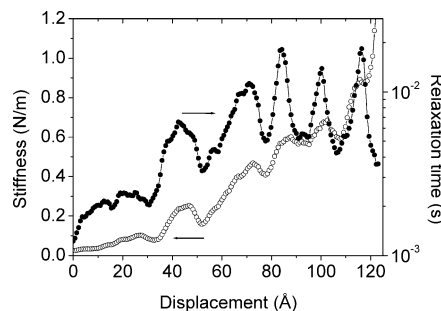
From the stiffness and damping data, we can also calculate a characteristic mechanical relaxation time  $t_R = k/(\gamma\omega^2)$ , which corresponds to the time it takes for any stress to dissipate in a system when an external strain is imposed.<sup>19</sup> This time would be expected to be short in a liquid and large in a solid. Figure 4 shows the mechanical relaxation time versus displacement. It can be seen that the relaxation time has prominent peaks associated with the stiffness maxima, indicating a solid-like, elastic behavior when the molecular layers are allowed to order between the tip and the substrate. From previous experiments on OMCTS,<sup>47</sup> we found that this elastic solid-like behavior is not necessarily associated with the solidification of the confined film at thermal equilibrium but rather is induced kinetically. In OMCTS, we found that the peaks in the relaxation time disappear when the tip is approached at a rate slower than about 5 Å/s toward the substrate.



**Figure 4.** Simultaneously measured stiffness (open circles) and relaxation time (filled circles) of a confined TEHOS film. The measuring tip was approached at a rate of 12 Å/s. The surface is located to the right.



**Figure 5.** Simultaneously measured stiffness (open circles) and damping (filled circles) of a confined TEHOS film. The measuring tip was approached at a rate of 3 Å/s. The surface is located to the right.



**Figure 6.** Simultaneously measured stiffness (open circles) and relaxation time (filled circles) of a confined TEHOS film. The measuring tip was approached at a rate of 3 Å/s. The surface is located to the right.

Figure 5 shows a measurement of the stiffness and damping of TEHOS at a free amplitude of 5.6 Å, a frequency of 265 Hz, and an approach rate of 3 Å/s. Again, we see periodic maxima in the stiffness and damping, with an average spacing of the stiffness peaks in this measurement of  $13.8 \pm 2.1 \text{ Å}$ . Averaged over all measurements at an approach speed of 3 Å/s we found a spacing of  $10.3 \pm 2.7 \text{ Å}$ , consistent with the molecular size and the spacing measured at a higher approach rate. As in the case of the previously published OMCTS measurements, we found that the amplitude (as long as we stay in the linear regime) and the frequency (as long as we stay far below the cantilever resonance) have no systematic influence on the results. As can be seen in this figure, the stiffness and damping are again out-of-phase close to the surface, similar to Figure 3.

Figure 6 shows the corresponding relaxation time, which also shows peaks, indicating solid-like, elastic behavior. This is in contrast to the OMCTS data,<sup>47</sup> where the peaks in the relaxation time disappeared when lowering the approach rate to 3 Å/s. Unfortunately, we cannot go any slower in our measurement due to software and thermal drift limitations and thus at the moment

cannot determine if a solid-like mechanical response in TEHOS is induced kinetically at a very low speed or exists at thermal equilibrium.

We also note that at both approach speeds, the stiffness and damping are in-phase far from the surface and only become out-of-phase in the last few layers. This suggests that the induced solid-like behavior only happens in the last few molecular layers. This correlates well with our FCS results stated previously, where we obtained two distinct diffusion coefficients even for a free, unconfined liquid. This would suggest that solid-like mechanical behavior may occur in TEHOS even at thermal equilibrium, in contrast to our previous results on OMCTS.

### Conclusion

The objective of the experiments described in this paper was to understand the dynamical structure of interfacial fluids by performing both mechanical and spectroscopy measurements. We have chosen the model liquid TEHOS, which has been used before to study molecular ordering near a solid surface. Spectroscopy experiments showed a slowing down of the diffusion of embedded dye molecules due to the confinement and signature

of heterogeneous dynamics. This can be interpreted in terms of a different diffusion coefficient in different layers. Our AFM results suggest that kinetic solid-like behavior in nanoconfined liquid films depends strongly on the nature of the molecules involved. Even though OMCTS and TEHOS are chemically similar and of comparable size, their kinetic mechanical behavior appears to be different. While confined OMCTS remains as a liquid up to a speed of about 5 Å/s, TEHOS already behaves as a solid when squeezed at a rate of only 3 Å/s. We also note that TEHOS has a higher viscosity than OMCTS and that this fact may have a bearing on the observed differences in kinetic mechanical behavior. These observations would have to have a firmer basis by further experiments and appropriate theory.

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