

How Confined Lubricants Diffuse During Shear

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The translational diffusion of a fluorescent dye embedded at a dilute concentration in a confined fluid was compared at rest and during shear. The fluid, octamethylcyclotetrasiloxane (OMCTS), was confined between step-free muscovite mica to thickness 3–4 layers. Fluorescence correlation spectroscopy showed that the time scales of intensity-intensity autocorrelation functions were essentially the same during shear and at rest, except they were faster during shear by a factor of 2 to 5. This dynamical probe of how liquids order in molecularly thin films fails to support the hypothesis that shear produced a melting transition.

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A curious fact about liquids is that they wrap themselves around solid surfaces to form layers; the simple reason is that space must be filled. Those molecules closest to the surface form the best-defined layer but the number of layers is believed to extend several molecular dimensions, to a distance normal to the surface approximately the correlation length of the bulk fluid. The layered structures on opposed surfaces interfere with one another when the spacing between two solids is less than twice this length [1]. Questions about confined fluid structure involve deep scientific puzzles. On the applied side, they also pertain directly to understanding the physics of porous media, of dense suspensions of colloidal particles in fluids, and of friction and lubrication.

Here we employ a fluorescence-based method to contrast the rate of Brownian diffusion during shear and at rest. Previously we introduced a method of few-molecule fluorescence to study confined fluids [2,3] but that study was restricted to fluids at rest. Here we describe what happens while sliding one surface past the other. The premise was that if the hypothesis of shear melting held, shear should induce speed up of the translational diffusion of a nonadsorbing fluorescent dye.

The fluid, containing dilute dye, was confined to a thickness of 3–4 molecular dimensions between parallel single crystals of muscovite mica. A large amount of prior study probed the *friction* of such systems. The hypothesis of a shear-induced phase transition, from solid to fluid, has been advanced based on the observation that, in most such experiments, static friction gives way to kinetic friction in molecularly thin liquid films [4]. The generality of this interpretation has been cast into doubt by the observation that fluids confined between rough metal surfaces behave similarly [5] and especially by recent experiments showing that the solidity of molecularly thin films in mica-based experiments depends on a particular method of surface preparation [6,7]. As arguments about experimental protocols are surely of no interest outside a specialized community, it is opportune to address the important question of order in confined fluids by an independent technique.

Fluorescence correlation spectroscopy (FCS) is usually used to study molecules dissolved in bulk solution [8,9]. As implemented here, the main idea is that as a small number of fluorescent molecules diffuse in and out of the focal point of a laser beam that causes two-photon excitation of fluorophores, the intensity rises and falls. The rate of change reflects the dye's local environment, on which translational mobility depends. The mean diameter of the liquid that we used, octamethylcyclotetrasiloxane (OMCTS), is ≈ 0.9 nm. The dimension of the dye, coumarin 153, is $\approx 1.2 \times 0.9 \times 0.37$ nm. This dye was selected after screening many alternatives because it has a high two-photon cross section at 800 nm and does not adsorb to mica from OMCTS. When in these experiments the OMCTS was confined, the nonadsorbing dye is believed to have resided in the middle fluid layers. However, whether the dye resided distinctly within given fluid layers, or also between them, is not known at this time. To anticipate results to be presented below, the data imply heterogeneous diffusion processes and suggest the existence of a distribution of subpopulations, possibly of dye orientation as well as of position normal to the surfaces.

Control experiments confirmed the picture of no dye adsorption. First, when the focus of the laser beam was scanned through the surface, into the bulk fluid, there was no jump in fluorescence intensity as the surface was crossed. Second, when the focus of the laser beam was scanned laterally across molecularly thin films within a flattened contact, large differences in the time scales of response were observed according to the mechanical pressure at that local spot [2], although the film thickness was measured to be the same everywhere. The dye concentration was 100 nM.

We begin with some technical comments about the enabling ideas that render the experiment possible. Briefly, a small homebuilt surface forces apparatus was placed on the sample stage of a Zeiss microscope. Near-infrared light from a Ti:Sapphire laser was focused through a long working distance objective between opposed mica sheets. Fluorescence was collected through the same objective and detected. Step-free single crystals

of mica were cleaved to thickness 2–4 μm using known methods, were draped over crossed cylinders placed at right angles to one another and glued in place, and finally were pressed together under a large load with liquid in between. The mica sheets deformed under load at the apex, producing a circular region of $\approx 50 \mu\text{m}$ diameter where the mica plates were parallel with fluid confined in between. Piezoelectric bimorphs were employed to apply oscillatory shear forces with frequency 1 to 250 Hz [2]. These forces were usually sinusoidal but sometimes they comprised a triangular ramp of constant slope, for better comparison with computer simulations that consider constant sliding velocity. The results presented below were unaffected by whether the shear was sinusoidal or a triangular ramp. Figure 1 illustrates the concept of this experiment.

To further enable these experiments, the silver sheets normally used for interferometric measurement of surface spacing [4,10] were replaced by multilayer dielectric coatings. Electron-beam deposition was used to coat 13 alternating layers of TiO_x and Al_2O_3 with high reflectivity in the region 600–700 nm (to determine surface-surface separation by multiple-beam interferometry) and translucent “windows” in the region ~ 800 nm (to allow fluorescence excitation) and 400–550 nm (to detect fluorescence). The combined effect of this complex optics and of relatively large background fluorescence, from mica and glue underneath the mica, rendered the FCS data noisier than is typical in bulk solution. This is why

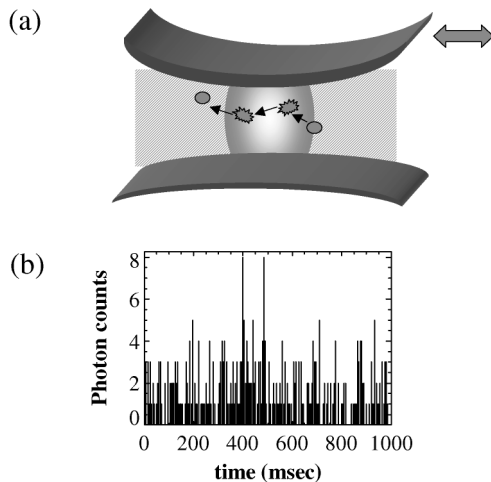


FIG. 1. Main idea of this experiment. A drop of fluid (OMCTS) containing nonadsorbing fluorescent dye (coumarin 153) was placed between crossed cylinders of mica, and load was applied causing formation of a flattened contact ($\approx 50 \mu\text{m}$ diameter) larger than the laser spot ($\approx 0.5 \mu\text{m}$ diameter). The load was 2–3 MPa; this is the force, squeezing the solid surfaces together, divided by contact area. A focused femtosecond laser caused two-photon excitation. The laser power was ≈ 1 mW at the sample and data were collected at 5–50 kHz sampling frequency. Fluorescence intensity fluctuations resulted as dye molecules diffused into and out of the focus spot. At an average instant, the signal resulted from one dye molecule.

the autocorrelation functions are noisier than is typical in bulk solution [8,9] although they were averaged for the unusually long time of 45 min.

The OMCTS molecule is ring shaped; it is the cyclic tetramer of dimethylsiloxane. There is a long tradition, reviewed elsewhere [6], of considering it to constitute a model system when studying friction and surface-induced structure of nonpolar confined fluids. OMCTS has a viscosity much like water (~ 0.002 Pa sec) and possesses the intriguing feature that it crystallizes near room temperature ($T_m = 17^\circ\text{C}$ at 1 atm), thus enhancing the possibility that a confinement-induced elevation of the melting temperature might be detected. The sample of OMCTS (Fluka, purum grade 99.8%) was used as received after drying over molecular sieves and filtering. Experiments were performed with P_2O_5 , a hygroscopic chemical, inside the sealed sample chamber. The experiments below refer to films of thickness 3.0 ± 0.4 nm relative to contact in air, corresponding to 3 or 4 dimensions of the fluid molecule. Only those experiments have been analyzed here for which photobleaching was minimal, $< 2 - 3\%$ during the duration of the experiments. In all of these experiments, various controls were performed. The film thickness was measured before and after sliding and found to be unchanged. The data acquisition times were kept the same to ensure similar signal averaging. The effect of shear on the autocorrelation curves was reversible.

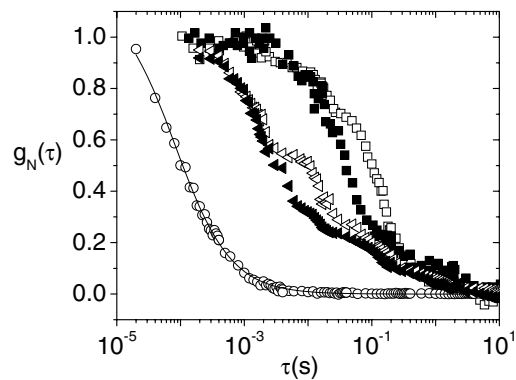


FIG. 2. Illustrative fluorescence intensity-intensity autocorrelation functions, $g_N(\tau)$, normalized to unity at short time and plotted against logarithmic time lag, τ . To cleave mica sheets, the conventional method was employed (see text). The thickness of the liquid film was 3.0 ± 0.4 nm relative to air, corresponding to $\approx 3-4$ molecular layers. The curves compare diffusion at rest in the unconfined bulk (circles; $D = 180 \mu\text{m}^2/\text{s}$) and at two radial positions (“ a ”) within the contact zone of radius $r \approx 25 \mu\text{m}$; $a/r = 0.7$ (triangles) and $a/r = 0.5$ (squares). The center is at $a = 0$. These data are taken at rest (open symbols) and while sliding (filled symbols) at shear rates 10^4 and 10^2 sec^{-1} , respectively. Sliding was performed at 1–256 Hz such that it was unidirectional for half the period then reversed direction, and so on repetitively; for the data shown here, it was 256 and 32 Hz, respectively. Lines through the data for the bulk are fits to a single diffusion process. As discussed in the text, diffusion during sliding was 2–5 times faster than at rest.

Figure 2 shows representative autocorrelation curves of the fluorescence intensity. Their time scale is governed by the diffusion time of the dye through the spot of calibrated diameter, $\approx 0.5 \mu\text{m}$, at which the interrogatory laser beam was focused. It is true that dye emission can also be intermittent owing to faster processes, such as the triplet lifetime, which do not reflect translational diffusion. But triplet-state dynamics occur on the microsecond time scale, faster than the autocorrelation functions shown in the Fig. 2. To begin, we verified what was already known from previous work, which is that *at rest*, the characteristic time scale of the autocorrelation curves decreased exponentially from the edges towards the center of the Hertzian contact [2]. The same was observed under shear. This is significant because if shear had caused the fluorescent dye to enter and leave the laser focus at a rate faster than the diffusion time [11], then autocorrelation curves everywhere in the confined spot should have been the same because velocity was the same. As this was not so, it shows that the time scales of autocorrelation functions analyzed in this study did indeed reflect Brownian diffusion. The reason that the autocorrelation functions were unaffected by motion is believed to be that the fluid undergoes partial “slip” when the moving surface is smooth. Friction measured in similar systems implies the same [6,7]. For two distinct posi-

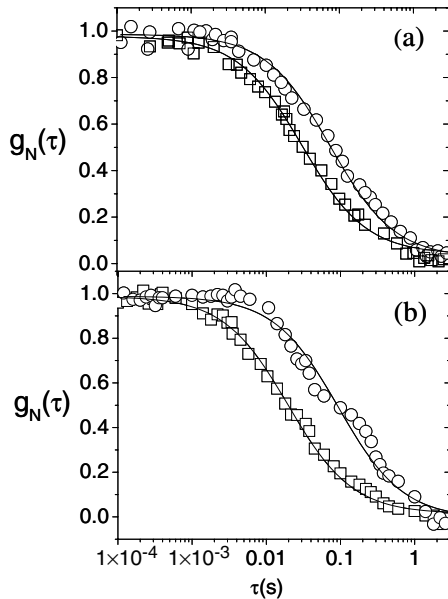


FIG. 3. Similar to Fig. 2 except using a different protocol to cleave mica sheets, the method of Frantz and Salmeron [16]. As in Fig. 2, the thickness of the liquid film was $3.0 \pm 0.4 \text{ nm}$ relative to air. The radial position within the contact spot was $a/r = 0.6$ (see legend of Fig. 2 to identify a/r). The data were acquired without sliding (circles) and during sliding at 256 Hz at peak shear rate $2 \times 10^4 \text{ s}^{-1}$ (squares). Panels (a) and (b) show results from independent experiments. As discussed in the text, these data are consistent with the conclusions from Fig. 2. Lines through the data show fits to the model of a single effective diffusion coefficient.

tions within the contact spot, autocorrelation functions at rest and under shear are compared in Fig. 2.

Next we varied the method by which the mica was cleaved. Data in Fig. 2 concern mica cleaved using the conventional protocol [12–15]. Data in Fig. 3 are based on experiments using the method of Frantz and Salmeron [16], which is reported to give very different friction and force-distance profiles [6,7,14]. In this method, first the mica sheets are cleaved and mounted using the customary protocol in this field of study, then recleaved immediately before an experiment, and finally a drop of fluid is added rapidly. Comparison to Fig. 2 shows no difference. One sees by eye in the raw data that the intensity-intensity fluorescence autocorrelation functions followed the same trend at rest and during shear, except that the time scale was moderately faster during shear. This suggests that explanation of marked differences in friction response [6,7] should not be sought in different local molecular mobility.

To quantify this data, the least model-dependent method is to compare times τ at which the autocorrelation functions $g(\tau)$ decayed by a given fraction. The difference in time, at rest and during sliding, was a factor of $\approx 2\text{--}5$ depending on the magnitude of $g(\tau)$ at which the comparison is made. It is true that spatially resolved measurements show that the time scale of autocorrelation functions slows with increasing proximity to the point of maximum load [2]. But concerning shear, there was no spatial dependence.

We now quantify the autocorrelation curves $g(\tau)$ in the language of an effective translational diffusion coefficient D . The idea is that as the diameter of the laser spot was known from calibration and the diffusion time was known from the autocorrelation decay time τ , it is reasonable to suppose that D equals distance squared divided by time. Quantitative elaboration of this idea, standard in fluorescence correlation spectroscopy, also takes into account the Gaussian shape of the spot illuminated by the laser beam [8,9]. The assumption of a single process is a simplification because of the fine structure in $g(\tau)$, suggesting the presence of several distinct processes. We emphasize that whatever the source of this heterogeneity, it was reproducible in independent experiments [2]. In preliminary experiments we find that it averaged out in time series that lasted 3–4 hr, but this is tentative because experiments that lasted so long also suffered from photobleaching. The main point to note at present is that the implied heterogeneity persisted so long—at least 45 min—without averaging out.

But to model $g(\tau)$ in terms of several distinct processes would require too many fitting parameters. The data do not admit a robust fit with more than two parameters. Therefore these curves were fit to the simplified model of a single Fickian diffusion process, an effective diffusion coefficient (D_{eff}). More than 30 experiments were analyzed in this way, results of those experiments conducted at the same shear rate being averaged. In Fig. 4, the ratio

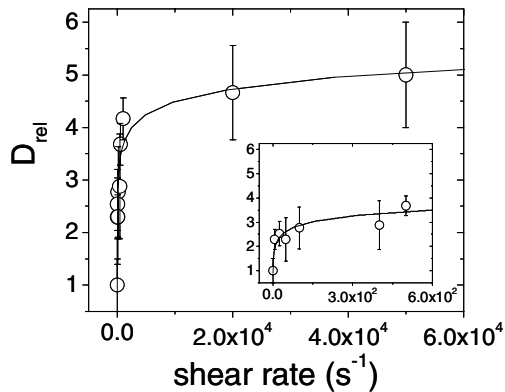


FIG. 4. Ratio (D_{rel}) of the effective diffusion coefficient during sliding (defined in text) to that at rest, plotted against peak shear rate. The data represent the average of more than 30 experiments, with error bars indicated. The inset shows the low shear part of this data.

of D_{eff} during sliding, to D_{eff} at rest, is plotted against the shear rate; the main figure shows the entire range of shear rate and the inset magnifies the regime of small shear rate. One sees that shear speeded up this measure of the time scale of the autocorrelation function by less than a factor of 5 in every case.

The significance is that this affords a direct (negative) test of the common hypothesis that the transition from rest to sliding reflected shear melting. An alternative picture might be that the fluorescent dye that we studied segregated into some kind of grain boundaries in the confined fluid, but this scenario relates only to the problem of why we observed fluidity in the rest state; it would not explain the minimal sliding dependence that we observed. It is true that this conclusion may seem inconsistent with friction experiments showing that the effective shear viscosity diverges when fluids become molecularly thin [4,17,18]. But remarkably, during the course of this study it emerged that this is not necessarily so; the observation of mechanical solidity depends on the method by which the confining surfaces are prepared [6,7,19]. Indeed, evidence of fluidity at the molecular level is mounting. A divergence of molecular relaxation times was not observed in dielectric measurements, neither in pores [20] nor in a sandwich geometry [21,22]. Loss of translational fluidity was not observed in molecular dynamics computer simulations (translational diffusion parallel to confining boundaries slowed by only 1-2 orders of magnitude) [23,24], nor in tracer diffusion experiments (translational diffusion slowed by only 2-4 orders of magnitude) [2].

Taken together, these considerations and the new data presented here show that these complex molecularly thin systems retain a high degree of fluidity at the molecular level. It is true that some kind of enhanced lateral ordering is indicated; computer predictions show that the structure factor of in-plane correlation is enhanced relative to the bulk [23,24] and experiments show that the

activation volume for diffusion exceeds that in the bulk liquid by ≈ 3 orders of magnitude [2]. However, shear did not modify substantially the Brownian diffusion reported in this study. An agenda for future investigation will be to understand better the relationship between mechanical friction response, which is an ensemble average, and measurements such as those presented here, which refer to the mobility of individual molecules.

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