

Contrasting Friction and Diffusion in Molecularly Thin Confined Films

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We study, using fluorescence correlation spectroscopy, translational diffusion in molecularly thin liquids confined within a surface forces apparatus. The diffusion coefficient decreases exponentially from the edges towards the center of the Hertzian contact and further suggests the presence of a small number of distinct diffusion processes. This holds alike a crystallizable fluid (OMCTS) and a glass-former (1,2-propane diol), both of which displayed static friction. We conclude that friction, the average of an ensemble of molecules, masked massively heterogeneous molecular mobility.

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What is the structure of confined fluids? The question of the order imposed on liquids by proximity to a surface is now of emerging interest in studies of lubrication, of force-distance profiles between surfaces in liquids, and of the physics of liquids in porous media [1–7]. The issues raised are also clearly relevant to many other diverse physical phenomena, among them the organization of complex fluids in vesicles and biomembranes. Here we describe what we believe to be the first experimental study of translational diffusion in molecularly thin liquid films. The results raise many questions concerning the packing and crowding of fluid molecules in constricted geometries. Mobility depends remarkably strongly on the local pressure squeezing on the film such that the large deduced activation volume indicates a collective process. Although the films appeared to be “solidified” (in the mechanical sense that static friction was observed), we conclude that friction, an average number, masked a rich pattern of heterogeneous molecular mobility. These experiments put to direct test, with a negative conclusion, the hypothesis that confinement-induced “solidification” consists of a definite crystallized structure in which molecules are fixed in space.

The principle of the measurement was fluorescence correlation spectroscopy (FCS) [8], performed here for the first time within a surface forces apparatus (SFA). Two-photon excitation at the diffraction-limited focus of a laser beam allowed us to measure diffusion within spots of submicron size, thus enabling spatially resolved measurements. The main idea of this technique as implemented here is that because the fluorescence intensity rises and falls as molecules diffuse into and out of the focus of the laser beam, the rate of diffusion can be inferred from the rate at which light intensity fluctuates. Briefly, a small homebuilt SFA was placed on the sample stage of a Zeiss microscopy (Axiovert 135). Near-infrared light from a femtosecond Ti:sapphire laser (800 nm, 80 MHz, pulse width ~ 100 fsec) was focused, through a long working distance objective ($63\times$, NA = 0.75), into the contact between opposed mica sheets. Fluorescence was excited only at the focus of the laser

spot, the laser power at the sample being ≈ 1 mW. It was collected through the same objective and detected by a single photon counting module (Hamamatsu). The silver sheets normally used for interferometric measurement of surface spacing [1,2] were replaced by multilayer dielectric coatings. Thirteen alternating layers of TiO_x and Al_2O_3 deposited on mica produced 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). Phosphorous pentoxide was kept inside the enclosed and sealed apparatus to scavenge rogue moisture during the experiment.

The usual force balance experiment measures an interaction between two smoothly curved crossed mica cylinders, as sketched in Fig. 1(a). However, as the cylinders separated by a liquid droplet are pressed together, fluid drains smoothly until oscillatory forces of alternate attraction and repulsion appear; these forces arise from the tendency of fluid to form layers parallel to the surface [2]. In these experiments, a soft glue (a UV-curing optical glue) underneath the mica sheets deformed instead. This resulted in a circular contact area of diameter ~ 20 μm [as sketched in Fig. 1(b)] of constant separation which made possible spatially resolved measurements as the diameter of the focused laser spot was 350 nm. Long averaging times (about 40 min) were needed to acquire good signal-to-noise ratio; this required the film thickness to be stable throughout. To achieve this, a large force was applied to the surfaces and the resulting thickness was selected by the mechanical pressure squeezing the surfaces together (for the experiments described here, mean normal pressure \equiv force divided by contact area = 2–3 MPa). When curved surfaces flatten as happened here at their apex in the absence of strongly attractive forces, the resulting pressure distribution is known to be “Hertzian”; zero at the edges of the contact zone and, at the center, $3/2$ the mean value [9]. This was important because it enabled us to infer the local, spatially resolved normal pressure.

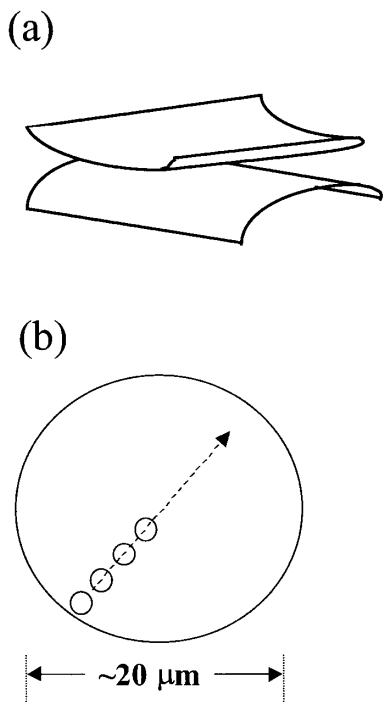


FIG. 1. Experimental scheme. (a) Crossed cylinder configuration. Droplets of fluid were placed between crossed cylinders of mica and force was applied in the normal direction, causing the formation of a circular area of flattened contact. (b) Fluorescence correlation spectroscopy (FCS) was performed after compressing the films with a mean normal pressure of 2–3 MPa to 2.5 nm (1,2-propane diol) and 3.0 nm (OMCTS). The sequence of smaller circles illustrates that the focus of the laser beam (diameter $\approx 0.35 \mu\text{m}$) was scanned across the contact (radius $\approx 10 \mu\text{m}$), enabling spatially resolved measurements.

First we discuss findings using a glass-former fluid, 1,2-propane diol, containing 50 nM of the fluorescent dye, rhodamine 123. This low-viscosity fluid (~ 0.4 poise) has glass transition temperature far below room temperature ($T_g = -105^\circ\text{C}$). Friction experiments in the SFA confirmed the same pattern of confinement-induced “solidification” that is observed systemically for other fluids when they are confined [1–7] and verified that friction was unaffected by the presence of fluorescent dye. Other control experiments were performed to test that the dye failed to adsorb, as it was critical for interpretation of the experiments that retarded diffusion should reflect confinement rather than trivial effects of adsorption. First, when the focus of the laser beam was scanned through the surface, into the bulk fluid, there was no jump in fluorescence as the surface was crossed, indicating no surface excess. Second, the density of fluorophores when the fluid was confined into thin films was only ~ 1 nM, 50 times less than in the bulk, showing that dye was depleted from the confined films as anticipated if there were no adsorption. There is admittedly uncertainty in these two statements because of the ambiguity of separating signal from

background. The third piece of evidence is independent of this. 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, although the film thickness was measured to be the same everywhere.

Figure 2(a) shows illustrative results. From the time series of fluctuations of the fluorescence intensity, the intensity-intensity autocorrelation function was calculated and plotted against logarithmic time lag. It is obvious that the time scale of diffusion, which can be estimated as the time at which the autocorrelation function decayed to one-half its initial value, increases with increasing proximity to the center of the contact area.

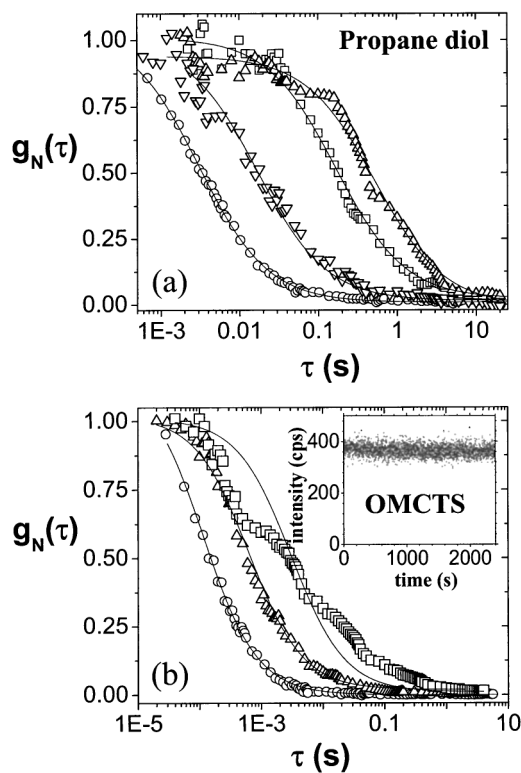


FIG. 2. Fluorescence autocorrelation functions, normalized to unity, are plotted against logarithmic time for rhodamine 123 in 1,2-propane diol (a) and coumarin 153 in OMCTS (b). The focus was at distances a from the center of the contact and the ratio $x \equiv a/r$ was considered, where r is the contact radius. In (a), $x \approx 0.95$ (circles), 0.82 (down triangles), 0.7 (squares), and 0.6 (up triangles). In (b), $x = 0.95$ (circles), 0.8 (up triangles), and 0.7 (squares). Lines through the autocorrelation curves are the least-squares fit to a single Fickian diffusion process. The magnitude of the fluorescence autocorrelation function at short times implies that, on average, one sole dye resided within the focus. The averaging time was 45 min. In the inset of (b), fluorescence counts (counts per second) are plotted against time for the same data that led to the slowest autocorrelation curve for the OMCTS system, demonstrating photostability (less than 3% decrease of counts in 2400 sec).

Assuming Fickian diffusion in a plane, the diffusion coefficient D scales as the square of the width of the focused laser beam divided by this time [8]. In addition to this qualitative observation, below we discuss the fact that, with increasing proximity to the center of the contact zone, the autocorrelation function showed fine structure. The slowing down that we observe cannot be dismissed as aggregation, as detailed inspection of the photon counting histogram showed no aggregates.

What happened when the confined fluid was crystallizable instead? The second system that we studied was octamethylcyclotetrasiloxane (OMCTS) containing ~ 50 nM coumarin 153. The same control experiments were performed to ensure that the dye did not adsorb. OMCTS is a low-viscosity fluid (~ 0.02 poise) that crystallizes near room temperature ($T_m = 17^\circ\text{C}$), so one may suppose the experimental conditions to be ideal to satisfy the hypothesis of confinement-induced crystallization [3,5]. Figure 2(b) shows spatially resolved measurements of the fluorescence autocorrelation function for this system, and we emphasize the qualitative agreement with findings obtained for the glass-forming fluid, Fig. 2(a). The fact that the same pattern was observed for both fluids, one a glass former and the other crystallizable, with different fluorescent dyes in the two instances, suggests that the conclusions of this study are generic. These measurements appear to be inconsistent with the common hypothesis that enhanced viscosity reflects confinement-induced crystallization [1–7]. According to that hypothesis in its simplest form, diffusion should have been quenched.

What of possible artifacts? The inset of Fig. 2(b) illustrates that photobleaching was minimal even for the set of data from which the slowest autocorrelation function for OMCTS was generated. However, it is true that photobleaching intervened when motion became even slower such that the same dye molecules resided even longer within the illuminated spot. This is why, in Fig. 2, we cannot present data for the points closest to the center of the contact.

Neglecting for the moment the fine structure in the autocorrelation curves, we begin by analyzing them in terms of a single Fickian diffusion process, as the model to do so [8] contains only one parameter, the effective diffusion coefficient, D_{eff} . The results are shown by the solid lines through the data in Figs. 2(a) and 2(b). Separately, we also used FCS to measure D_{bulk} in the bulk fluid. Figure 3(a) shows the logarithmic ratio, $D_{\text{eff}}/D_{\text{bulk}}$, plotted against position within the contact. Equivalently, knowing the expected [9] Hertzian pressure distribution, this same logarithmic ratio, $D_{\text{eff}}/D_{\text{bulk}}$, is plotted in Fig. 3(b) against relative pressure at the spot of spatially resolved measurement. It is worth emphasizing that the spatially resolved slowing down summarized here—3 orders of magnitude are visible over the dynamic range of the experiment—does not depend on the model

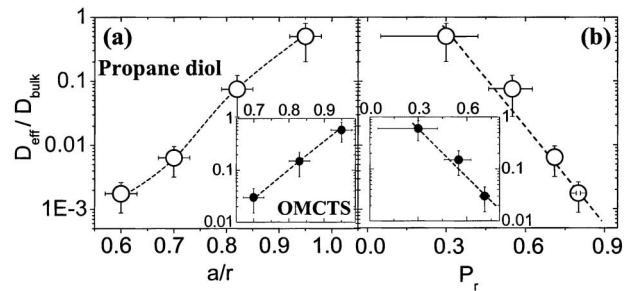


FIG. 3. Quantification of the effective diffusion coefficients (D_{eff}) inferred from the raw data in the previous figure. (a) The ratio, $D_{\text{eff}}/D_{\text{bulk}}$, is plotted against focus position, a/r . (b) The ratio, $D_{\text{eff}}/D_{\text{bulk}}$, is plotted against relative pressure squeezing the surfaces together, $P_r = P/P_{\text{max}}$ ($P_{\text{max}} \approx 4$ MPa), assuming Hertzian pressure distribution. Open circles (main figures) denote rhodamine 123 in 1,2-propane diol ($D_{\text{bulk}} \approx 8 \mu\text{m}^2 \text{sec}^{-1}$). Filled circles (insets) denote coumarin 153 in OMCTS ($D_{\text{bulk}} \approx 190 \mu\text{m}^2 \text{sec}^{-1}$). Because photobleaching was prohibitively large, it was not possible to make measurements closer to the center than shown. Because mechanical pressure is believed to be overestimated near the edge of the contact (see discussion in Ref. [10]), the apparent slowing down only above a critical pressure is not believed to be significant.

used here to interpret the data. It is already apparent in the raw data illustrated in Fig. 2 [10]. Furthermore, postulating that D_{eff} was proportional to a Boltzmann factor in energy ($\Delta E/kT$, where E is the energy, k the Boltzmann constant, and T the absolute temperature which was constant), ΔE can be regarded as the net differential normal pressure, ΔP , times an activation volume, ΔV_{act} . Figure 3(b) shows that the data are consistent with the implied exponential decrease of D_{eff} with P , in spite of the fact that P is mechanical pressure squeezing the confined fluid, not the usual isotropic pressure. From the slope in Fig. 3(b), one deduces that $\Delta V_{\text{act}} = 15\text{--}20 \text{ nm}^3$. It is intriguingly close to the activation volume obtained some years ago from independent friction measurements [4]. In the bulk, by contrast, the activation volume for diffusion is only $\approx 0.2 \text{ nm}^3$, the size of a fluid molecule (as also confirmed by our own experiments in which the bulk pressure was varied) [11]. This analysis highlights the key conclusion that diffusion appeared to involve cooperative rearrangements of many molecules. But as it assumes a single reaction coordinate and a fully equilibrated homogeneous system, it does not seem physically meaningful to identify the deduced activation volume with the lateral size of cooperatively rearranging regions within the confined films.

We now turn to the inflections in the intensity-intensity autocorrelation functions, shown in Figs. 2(a) and 2(b). They were quantitatively reproducible on different days with fresh samples, and cannot be easily dismissed as artifact when one considers that the signal-to-background fluorescence was the same at all points in the contact area. Physically, they signify some kind of long-lived but

quantitatively reproducible heterogeneity, which became increasingly intense moving from edges of the contact towards the center. To make this more precise, it is worth remembering that molecules in confined fluid films are known to organize into layers parallel to the confining surfaces, in which local density differs. In this scenario, we may conjecture that the multiple processes suggested in the autocorrelation curves signify that translational diffusion rates differed in these layers. For example, for OMCTS the slowest curve in Fig. 2(b) can be decomposed into subprocesses with $D_{\text{eff}} = 0.1, 0.7, 2.9,$ and $40 \mu\text{m}^2 \text{s}^{-1}$, the average being $5.5 \mu\text{m}^2 \text{s}^{-1}$ because the slowest two processes had the smallest amplitude and contributed least. This interpretation is consistent with the observation that the heterogeneity was more pronounced for OMCTS than for 1,2-propane diol, which is not expected to organize so definitively into distinct layers. From still another perspective, these data are qualitatively reminiscent of the “cage” slowing down observed in autocorrelation curves from dynamic light scattering studies of colloidal glasses [12]—some kind of incipient but incomplete solidification. From the available data we are unable to assess the relative importance of these two scenarios, but one conclusion is firm: the scale of heterogeneity must have been impressively large, when one considers that these heterogeneities did not average out in spite of the long averaging time and the fact that the laser beam spot (350 nm diameter) so much exceeded the size of the diffusing molecules [13].

In summary, we have introduced a new experimental method to study the dynamic structure of confined fluids. Using it, we have identified massively heterogeneous dynamics—more rich and complex than appears to be anticipated by the current notions of “confinement-induced solidification,” the term commonly used in this field of study. Looking to the future, the feasibility of time-correlated fluorescence measurements in a single confined contact, demonstrated here for the first time, will open up a class of experiments not previously possible regarding molecular understanding of lubrication, adhesion, transport in colloidal dispersions, and liquid interfaces in other confined environments.

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