Relaxation Time of Confined Liquids under Shear

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Ultrathin films of simple nonpolar molecular fluids (3–8 segmental dimensions thick) show a strikingly long relaxation time in response to oscillatory shear when confined between mica plates at 27 °C. When the shear rate exceeds this inverse time, the effective viscosity decays as an apparent power law in the shear rate, implying considerable distortion of the dynamic structure. The relaxation time is orders of magnitude longer than the Brownian relaxation time in the bulk state and may reflect collective motions induced by confinement.

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A system of finite size in one or more directions can have properties strikingly different from the bulk. We are concerned here with the solid-liquid interface, where the disordered liquid state contends with the ordering potential of the surface; other examples are monolayers and multilayers,[1] molecular clusters,[2] and nanosized powders.[3] Recently methods were devised to measure the shear response of liquid films so thin that their thickness approaches molecular dimensions.[4-6] In this rapidly developing area, most studies have concerned the loss of fluidity and subsequent dynamic friction when the film thickness is in the range of 1–3 molecular dimensions. The origin of solidification—epitaxial crystallization or trapped vitrified states—has excited much discussion.[5-9] An important open question is: What happens at slightly larger thickness, on the order of 3–10 molecular dimensions, where the response to shear remains liquidlike but different from that in the bulk? Earlier we showed that at this thickness the effective shear viscosity is orders of magnitude larger than the bulk viscosity.[5] However, those measurements employed a single frequency and a narrow range of amplitude, too narrow to draw definite conclusions about relaxation times.

In this Letter, we describe the first experiments to identify a Brownian relaxation time. Using simple nonpolar liquids whose longest relaxation time in the bulk is $< 10^{-10}$ sec, we infer a viscous relaxation time under confinement that is tens to hundreds of milliseconds, i.e., $> 10^8$ times longer than in the bulk. When the inverse shear rate is less than this time, the nonlinear effective viscosity suggests considerable shear-induced distortion of dynamic structure. These observations are tentatively interpreted to imply that the relaxation time reflects collective motions rather than motions of single molecules.

The principle of the measurement, described in detail elsewhere,[4] was to apply a sinusoidal time-varying shear force and measure the viscous dissipation. Ultrathin liquid films (dodecane and the silicone oil, octamethylcyclotetrasiloxane, "OMCTS," purchased from Fluka and dried over molecular sieves), surrounded by a drop of the liquid, were confined between circular parallel plates of single crystals of muscovite mica whose diameter was vast (on the order of 100 μm) compared to the thickness between them. At molecular thicknesses a liquid film supports a state of normal stress;[9-12] the film thickness adjusts to externally applied normal pressure. The thickness at a given net normal pressure, < 10 nm, was measured to ±0.1 nm by optical interferometry between the back sides of the mica sheets. The temperature was 27±1 °C. The amplitude of sinusoidal oscillation was 0.4 nm to 6 μm. The frequency was 0.02 to 52 Hz. Under dry conditions, the static force-distance profiles used to thin these liquids are known[11,12] and were verified by control experiments. As in previous work,[11,12] sensitivity to trace moisture and other polar impurities was noted.

First we discuss the simple flexible chain molecule, dodecane. The bulk shear viscosity is 0.01 P, independent of shear rate up to $> 10^{10}$ sec^{-1}. The bulk freez-

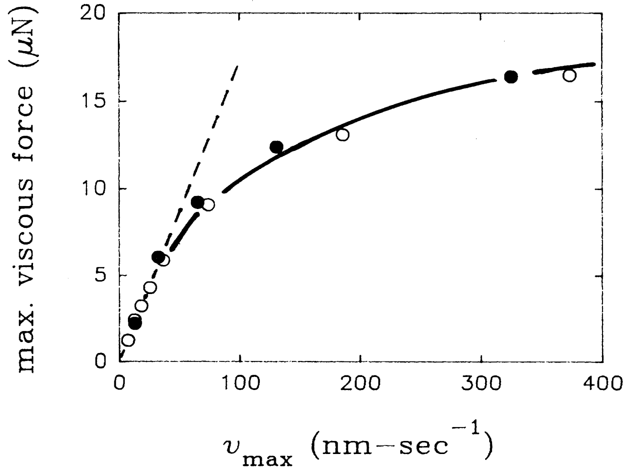

FIG. 1. Maximum viscous force plotted vs maximum velocity during a cycle of oscillation, for dodecane film of thickness 2.7 nm and net normal pressure 0.12 MPa. Open circles: amplitude varied from 0.9 to 180 nm at 1.3 Hz. Solid circles: frequency varied from 0.02 to 52 Hz at amplitude 40 nm. Dotted line extrapolates the zone of linear response.

ing temperature is −9.6 °C. The chain length is approximately 1.8 nm and the width of each methylene segment is approximately 0.4 nm. The essentially nonlinear shear response is illustrated in Fig. 1 for a film confined at thickness 2.7 nm and small net normal pressure 0.12 MPa (approximately 1.2 atm). The maximum viscous force during a cycle of oscillation ($f_{\max}$) is plotted against the maximum velocity ($v_{\max}$). The data demonstrate two immediate conclusions. First, $f_{\max}$ was linear in $v_{\max}$ when the latter was sufficiently low, but became nonlinear at a modest velocity ($v_{\max} > 40$ nm sec^{-1}). Second, the data show that the reducing variable by which to analyze the viscous force was indeed velocity, not frequency, over the range of frequency overlap studied (0.05–5 Hz). This follows because when amplitude and frequency were varied separately, the viscous force depended only on their product.

We assume that the length scale of this problem is the thickness of the fluid film (the assumption is not restrictive because other conceivable length scales have similar magnitude; see discussion below.) Figure 2 shows the effective viscosity ($\eta_{\rm eff}$) deduced from such data, plotted against effective strain rate ($\dot{\gamma}_{\rm eff}$) on log-log scales in view of the large changes in magnitude. The effective viscosity is the viscous stress [(maximum force) $\times$(area)$^{-1}$] divided by the effective strain rate [(maximum velocity)(film thickness)$^{-1}$]. At low strain rate, $\eta_{\rm eff}$ was constant. This was followed by extensive shear thinning. The rate of shear thinning followed an empirical power law, $\eta_{\rm eff}\dot{\gamma}_{\rm eff}^{-a}$. The power, slightly less than $-\frac{2}{3}$, increased modestly in absolute value with increasing net normal pressure (as may be inferred from data in Fig. 4). At every shear rate, $\eta_{\rm eff}$ exceeded the viscosity of bulk dodecane, but decayed by more than 2 orders of magnitude as the shear rate was raised. Measurements of film thickness failed to detect any changes with shear (<0.1 nm); this puts the upper limit of 4% on possible shear-induced changes in the mean liquid density. Other control experiments showed reversibility when the velocity was raised and lowered.

What of the generality of this behavior? Figure 2 shows that this was confirmed in experiments using OMCTS, a silicone oil of different chemical composition than dodecane. For some years, OMCTS, a compact-shaped (but flexible) ring molecule with diameter approximately 0.9 nm, has been a reference liquid in studies of liquid microstructure.[5,6,12] The different quantitative response from that for dodecane probably reflects differences in intensity of wall-liquid interactions as well as in molecular packing; a detailed comparison is not offered at this time. For the present we emphasize the qualitative agreement: The effective viscosity was controlled by the velocity or normalized velocity of the experiment and showed extensive shear thinning. Thus this pattern of behavior held even for a molecule that is not a linear chain. In what follows, we return to dodecane.

In the relaxation of liquids, a nonlinear viscous response sets in when the experimental time scale is less than a characteristic time scale of Brownian motion. We estimated the onset of nonlinear response by extrapolating the linear and power-law zones until they crossed. The conclusion that the nonlinear response set in at $\dot{\gamma}_{\rm eff} > 20$ sec^{-1} implies that the longest system relaxation time was approximately 5×10^{-2} sec. This is the central result: the experimental determination of a relaxation time consistently so much longer than in the bulk.

This pattern of behavior—linear response followed by extensive shear thinning—was also observed at other

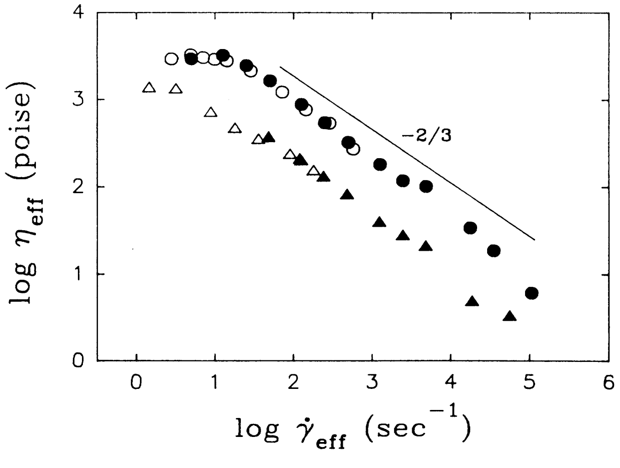

FIG. 2. Log-log representation of changes in the effective viscosity as a function of strain rate. Circles: dodecane film specified in Fig. 1. Triangles: OMCTS film of thickness 2.7 nm and net normal pressure 0.14 MPa. Open symbols: amplitude varied at constant frequency. Solid symbols: frequency varied at constant amplitude.

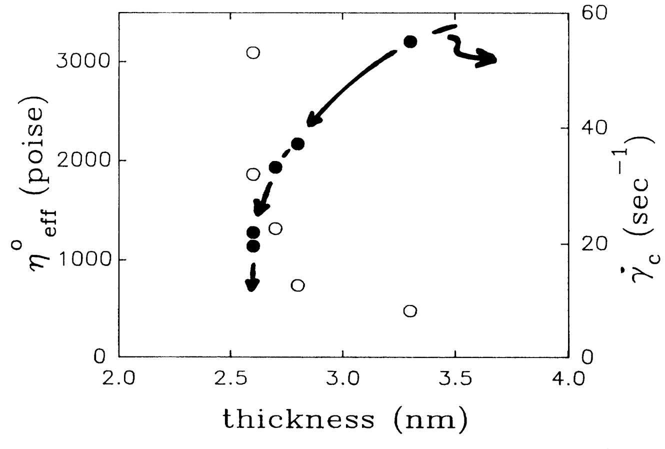

FIG. 3. Effective limiting viscosity at low shear rate (open circles), and critical effective strain rate at onset of nonlinear behavior (solid circles), plotted against film thickness for confined dodecane films. Arrows indicate direction of increasing net normal pressure.

film thicknesses and net normal pressures. Figure 3 shows changes, with film thickness, of both the effective viscosity in the zone of linear response ($\eta^0_{\rm eff}$) and the critical strain rate at onset of nonlinear response ($\dot{\gamma}_c$). The four data pairs at 2.6 ± 0.1 nm all refer to a layer of approximately 6 segmental widths. The adjustments of thickness by 0.1–0.2 nm, less than the segmental width, reflect compressibility of the liquid film. The associated increase of $\eta^0_{\rm eff}$ with increasing net normal pressure is in general agreement with what we found previously for hexadecane.[5]

The new observation is the strain rate at onset of nonlinear response. The large increases of $\eta^0_{\rm eff}$ were accompanied by decreases in $\dot{\gamma}_c$, i.e., apparent divergence of a relaxation time. In fact, these changes largely offset one another, so that the shear stress at onset of nonlinear response (product of $\eta^0_{\rm eff}$ and $\dot{\gamma}_c$) rose by only a factor of 2 as the film of 6 segmental widths was compressed. At still higher compressions than indicated in Fig. 3, there ensued solidlike behavior.[5,6] We remark that because the film thickness was practically constant, the calculated increases of $\eta^0_{\rm eff}$ and decreases of $\dot{\gamma}_c$ are robust to any other sensible choice of length by which to normalize the velocity.

Further experimental insight comes from an activation energy analysis. If one postulates that $\Delta\eta^0_{\rm eff}$ was proportional to a Boltzmann factor in energy ($e^{\Delta E/kT}$, where E is the energy, k the Boltzmann constant, and T the absolute temperature which is constant), then ΔE can be regarded as the net differential normal pressure $\Delta P_\perp$ times an activation volume $\Delta V_{\rm act}$. When $\log(\eta^0_{\rm eff})$ is plotted against $P_\perp$, the data are indeed consistent with exponential growth of $\eta^0_{\rm eff}$ with $P_\perp$, in spite of the fact that $P_\perp$ is not the usual isotropic pressure. From the slopes in Fig. 4, one deduces that $\Delta V_{\rm act} \approx 80$ nm^3 (linear response), 40 nm^3 ($\dot{\gamma}_{\rm eff} = 10^3$ sec^{-1}), and 20 nm^3 ($\dot{\gamma}_{\rm eff} = 10^5$ sec^{-1}). In the bulk, by contrast, the activation volume for diffusion is[13] < 0.03 nm^3 (approximately 1 segment of the molecule).

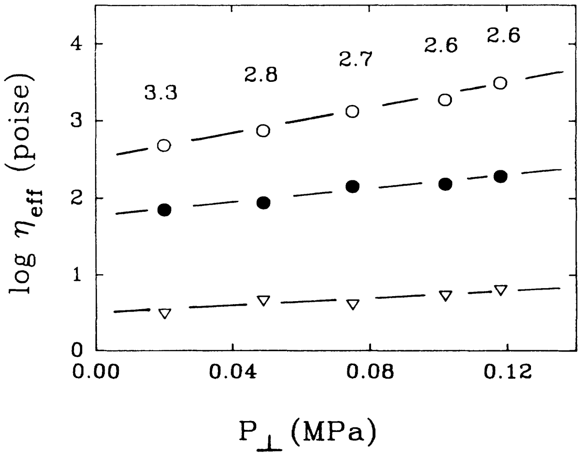

FIG. 4. Effective viscosity of dodecane plotted logarithmically against net normal pressure. Open circles: limiting linear response at low strain rate. Solid circles: 10^3 sec^{-1}. Triangles: 10^5 sec^{-1}. Numerals show the associated film thickness in nm.

The activation volumes for flow under confinement correspond to approximately 200, 100, and 50 molecules, respectively, implying that the unit event in shear flow was collective and that shear thinning involved breaking up some structure. This is the second hint (the first was the ultraslow viscous relaxation time) that this viscosity stems from intermolecular ordering, not single-chain motion.[14] If so, the activation volume in the zone of linear response is an estimate of the size of correlations in the quiescent state.

What of possible artifacts? Shear-induced chemical degradation is ruled out by the observation of reversibility. Reflection of shear waves in the apparatus is ruled out by the velocity (rather than frequency) dependence illustrated in Figs. 1 and 2. As for heat generated by viscous dissipation, straightforward calculation[15] shows that this was efficiently dissipated because the area of the films was also large relative to their thickness. One might question analysis of the data in terms of an effective viscosity; but even cursory inspection of raw data such as in Fig. 1 shows these effects. While it is true that the length scale by which to normalize the velocity might be somewhat less than the total film thickness (one or two layers of fluid might be pinned to each surface over the time scale of the experiment), such fine tuning of the analysis would not change the relative numbers analyzed above, nor their orders of magnitude. The consistent measurements obtained in repeated experiments using different liquids persuades us that the results are generic and must be examined at face value.

Let us now restate the problem to be explained. Density oscillation of fluid segments in the direction normal to a solid boundary is well understood in principle from arguments of geometric packing,[10-12] but the question of a liquid's positional order parallel to a solid boundary has surfaced only recently.

Clearly under some circumstances (spherical particles) the problem is one of wall-induced crystallization.[8,9] Our problem here is different: to understand the ordering of molecules of complex shape and many internal degrees of freedom, when the film is still fluid. It is conceivable that the crystalline clusters might form, analogous to incommensurate phases in adsorbed monolayers,[1] but a mechanism to form such clusters is not evident. Long-time tails of velocity correlations resulting from hydrodynamics[16] could in principle come into play, but are not expected to be prominent at high density[17] as in the present systems. The scenarios remain that the preferred direction introduced by the shear motion, and possibly also long-range (algebraically decaying) interactions as a state of two dimensions is approached,[18] could cause long-range orientational correlations.

Confinement might also induce a glass in the sense that molecules become logjammed, as has been argued elsewhere.[5,7]

In summary, these are the first experiments to show the limits of linear and nonlinear viscous shear response of confined fluids. It emerges that a boundary can profoundly slow down the dynamics of the liquid state. There are a variety of physical situations, especially lubrication, fluids in porous media,[19] and the wall-stick condition of fluid flow,[20] to which this new physics may apply by rational extension.

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