

## Glasslike Transition of a Confined Simple Fluid

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A simple globular-shaped liquid (octamethylcyclotetrasiloxane, OMCTS) was placed between two solid plates at variable spacings comparable to the size of this molecule and the linear shear viscoelasticity of the confined interfacial film was measured. Strong monotonic increase of the shear relaxation time, elastic modulus, and effective viscosity were observed at spacings less than about 10 molecular dimensions. Frequency dependence showed good superposition at different film thickness. The observed smooth transition to solidity is inconsistent with a first-order transition from bulk fluid to solidity. [S0031-9007(96)01142-8]

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The literature is conflicting on the question whether the observed reduction of molecular mobility, as a fluid is confined in one or more directions between solid surfaces to be molecularly thin, stems from a phase transition [1–16]. For fluid particles of regular shape, some interpretations show the possibility of surface-induced crystallization [3–7], others of a glass transition [9–11], both at temperatures well above the respective bulk transition temperature. This problem, with ramifications in tribology [14], geology [17], and biology [18], is important to decide in order to resolve the senses in which confinement-induced solidity has a thermodynamic or kinetic origin. It is unsatisfactory that the same basic experiment [1,13–16] has been interpreted in both terms.

The ambiguity stems from the problem that previous measurements and simulations have both been made at fairly high rates or frequencies—leaving unclear the response at sufficiently long times (or low frequencies) to actually measure the relaxation time, the characteristic time of Brownian motion. Such a measurement should involve linear response in order to rule out the possibility of shear-induced changes.

Here we provide the needed data by considering the linear-response shear viscoelastic spectrum of the liquid that has been considered to be the prototypical small-molecule fluid for experimental studies. This is octamethylcyclotetrasiloxane (OMCTS), considered to be a model liquid for comparison with “Lennard-Jones” liquids because of the globular shape of this ring-shaped nonpolar molecule [19,20]. The data presented below definitively rule out the possibility of the abrupt first-order transition whose possibility has been much discussed. Instead, the solidification is continuous with diminishing film thickness and the viscoelastic spectra at different film thickness appear to scale with reduced variables.

The frequency dependence of the shear modulus was measured using a modified surface force apparatus described in detail previously [21–23]. Briefly, a droplet of sample fluid was confined between two atomically smooth crystals of muscovite mica, glued onto crossed cylindrical lenses whose separation was controlled using a surface

forces apparatus. The surface separation was measured by interferometry. The radius of curvature of the mica sheets was large,  $\approx 2$  cm, giving a slitlike geometry when the surface separation was molecularly thin. To apply shear, sinusoidal shear forces were applied to one piezoelectric bimorph and the resulting sinusoidal displacement was monitored by a second piezoelectric bimorph; details of the piezoelectric circuitry are described elsewhere [21]. A lock-in amplifier (Stanford Research Instruments 850) was used to decompose the output into one component in phase with the drive and a second component out of phase with it, giving the elastic and dissipative shear forces as a function of the excitation frequency. The apparatus compliance was calibrated separately and taken into account in analyzing the data [22,23]. However, films thicker than three molecular dimensions were unaffected by this correction because the apparatus was then so much stiffer than the sample. Linear response, obtained for shear displacements less than  $\approx 20\%$  of the sample thickness, was verified. It is well known that a linear viscoelastic response characterizes the Brownian relaxation rate of a sample at rest [24].

Experiments were performed at 27 °C with  $P_2O_5$  (a highly hygroscopic chemical) inside the sealed sample chamber. The sample of OMCTS (Fluka, purim grade) was used as received after control experiments showed similar behavior following further purification [25].

As smooth solid surfaces separated by OMCTS were pushed together, fluid drained smoothly until oscillatory forces of alternative attraction and repulsion were first detected at thickness  $\approx 7$  molecular dimensions. As shown by others in earlier reports [19,20], the period of oscillatory forces was an integral multiple of the molecular dimension,  $\approx 9$  Å. These oscillatory forces extended to larger thickness than in our earlier preliminary study [15]; the present measurements agree with literature values [19,20], as shown in the inset of Fig. 2. These oscillatory forces arise from the tendency of fluid to form layers parallel to the surface. Application of pressure caused the fluid to drain in discrete steps corresponding to squeezing out of successive molecular layers.

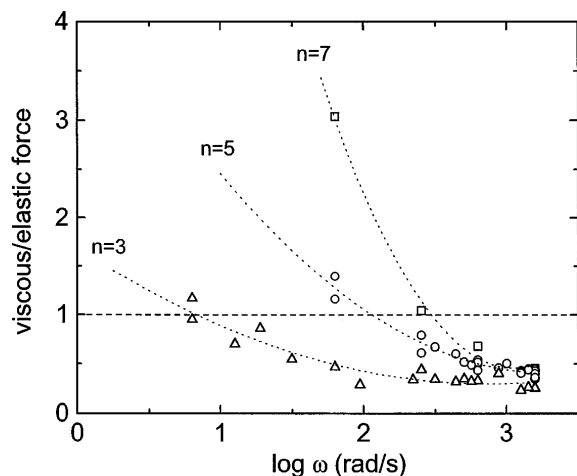


FIG. 1. Ratio of dissipative to elastic shear force plotted against logarithmic frequency for OMCTS confined between mica sheets at film thickness  $n = D/\sigma = 3, 5,$  and  $7$  molecular dimensions of the OMCTS molecule (indicated by numerals next to lines in the figure). Temperature was  $27^\circ\text{C}$ . The relaxation time was quantified as  $\tau_1 = 1/\omega_c$ , with  $\omega_c$  the frequency at which the ratio of dissipative and elastic force was unity. The associated rigidity ( $1, 3,$  and  $60 \mu\text{N}$ , respectively, for  $2 \text{ \AA}$  deflection) is analyzed in Fig. 3.

Figure 1 shows shear measurements at three illustrative levels of film thickness:  $3, 5,$  and  $7$  molecular dimensions. In order to avoid the need for normalization (problematical aspects of normalizing shear forces between curved surfaces were discussed previously [22]), the dimensionless ratio of dissipative to elastic force is plotted against logarithmic frequency.

The viscoelastic frequency spectra in Fig. 1 are typical of liquids in a frequency range near  $1/\tau_1$ , where  $\tau_1$  is the inverse longest relaxation time. The films relaxed shear stress predominantly in the manner of viscous liquids when the frequency was less than  $1/\tau_1$ , but predominantly in the manner of solids when the frequency was higher; at high frequencies the perturbation was not relaxed during the period of oscillation and energy was stored. From common experience, the analogous viscoelastic phenomenon is known for silly putty: It bounces when dropped on a floor (high-frequency response) but flows when it sits on a table.

These raw data show definitively that the change of viscoelastic response was continuous rather than abrupt with decreasing film thickness. To quantify  $\tau_1$ , a useful measure was the inverse frequency at which the ratio of dissipative and elastic force was unity. In Fig. 2,  $\tau_1$  is plotted semilogarithmically against film thickness expressed as multiples of the molecular diameter of OMCTS. The inset of Fig. 2 shows the normal forces required to produce this change of thickness. The sudden slowing down of  $\tau_1$  by 3 orders of magnitude, as the film was squeezed from a thickness of  $7$  to  $2$  molecular dimensions, is striking. Though the limited range of thickness admits various functional fits, the increase of  $\tau_1$  appears to be more rapid than expo-

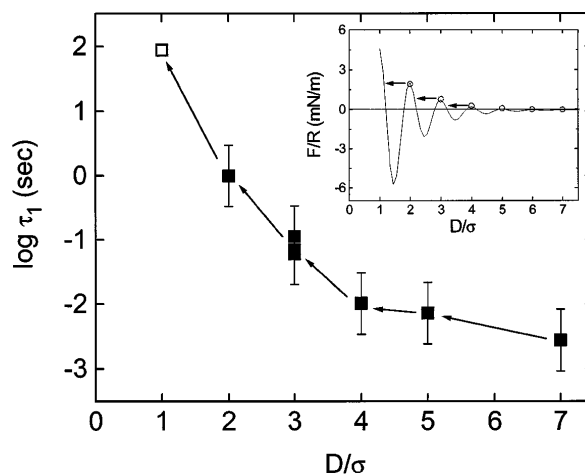


FIG. 2. Longest relaxation time  $\tau_1$  plotted logarithmically against film thickness expressed in multiples of the molecular dimension of OMCTS. Data at different thickness were acquired by squeezing the surfaces together progressively as shown in the inset (data for  $D/\sigma = 6$  are missing owing to thermal drifts). Inset shows the force  $F$  (normalized by the radius of curvature of the mica sheets,  $R$ ) required to squeeze the films to the given thickness. As the normal force was increased beyond the values indicated by circles, film thickness decreased abruptly by the thickness of a single molecule, as indicated schematically by the arrows. Control experiments show that for a given  $D/\sigma$  but  $F/R < 0$ ,  $\tau_1$  was slightly less than plotted in the figure, but still within the indicated error bars. Open square: extrapolated  $\tau_1$  used for frequency-thickness superposition shown in Fig. 4. Filled squares: measured values.

ponential. Well-known viscoelastic relations show that the effective viscosity of a viscoelastic body is proportional to  $\tau_1$  [24], indicating a similarly sudden increase of the viscosity. Control experiments confirmed this result also for noncrystalline surfaces [26].

Why are the error bars so large? The large error bars in Fig. 2 were intrinsic to these experiments: In repeated experiments, variations of the compression rate resulted in somewhat different  $\tau_1$  at a given film thickness. Others also have noticed dependence on the compression rate for experiments involving chain molecules [27]. This dependence on sample history is consistent with the hypothesis of a glassy state. If liquid exchange between the confined volume and the reservoir outside were suppressed by the sluggish mobility upon confinement, molecules might become trapped within the gap when the solid surfaces were squeezed together rapidly.

We now discuss elastic rigidity of these confined films: the in-phase component of the viscoelastic response. The elastic shear forces were normalized by the displacement amplitude ( $0.1$ – $0.5 \text{ nm}$ ) to give the elastic shear constant  $g'(\omega)$ , which is roughly proportional to the shear storage modulus [24]. The dissipative shear forces were normalized in the same fashion to give the viscous shear constant  $g''(\omega)$ , which is roughly proportional to the shear loss modulus [24]. Figure 3 shows that the longer the relaxation time, the stiffer the confined fluid at  $\omega = 1/\tau_1$ .

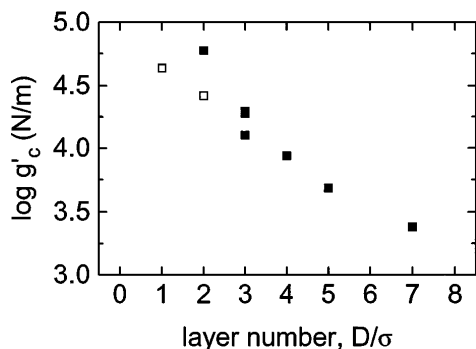


FIG. 3. Elastic spring constant of confined OMCTS at the frequency ( $1/\tau_1$ ) where elastic and dissipative shear forces are equal, plotted logarithmically against film thickness expressed in multiples of the molecular dimension  $n = D/\sigma$ . The elastic spring constant is the measured elastic shear force normalized by shear displacement (0.1–0.5 Å). Open squares: extrapolated values used for frequency-thickness superposition shown in Fig. 4. Filled squares: measured values.

This elastic rigidity  $g'_c$  was rather soft. It can be normalized roughly as follows. The effective contact area between curved surfaces in this experiment is on the order of  $10 \mu\text{m}$  on a side; this gives an estimate of the frequency-dependent elastic shear modulus, with units of energy per unit volume. From this reasoning, it follows that the volume attributable to a  $k_B T$  of elastic energy ranged from  $\approx 300$  molecules (thickness of 7 molecules) to  $\approx 60$  molecules (thickness of 2 molecules). Clearly, an explanation should not be sought in single molecule-molecule interactions, but rather in collective interactions at larger length scales than molecular—again consistent with the hypothesis of glassy response.

To describe the viscoelastic spectrum at *all*  $\omega$  (not just at the crossover frequency  $1/\tau_1$ ), it was tempting to search for a method of reduced variables. To describe bulk liquids in the vicinity of a glass transition, reduced variables that relate time, temperature, and pressure are fundamental [24,28]. Though initial attempts to superpose the data solely by shifts along the frequency axis were not successful, superposition was possible with an additional vertical shift, as we now discuss.

Figure 4 shows a master curve consisting of data taken at six different film thicknesses but shifted on both the horizontal and vertical scales to coincide at  $\omega = \omega_c$ . The elastic and viscous spring constants are plotted against frequency on log-log scales. The reference state is the film of thickness  $n \equiv D/\sigma = 7$  molecular dimensions. For films of lesser  $n$ , the data are shifted on the frequency scale by  $a_n \equiv \tau_1(n)/\tau_1(7)$ . On the vertical scale, they are shifted by  $b_n \equiv g'(1/\tau_1(n))/g'(1/\tau_1(7))$ . A viscoelastic property measured at frequency  $\omega$  and a given thickness was equivalent to the same viscoelastic property measured at a different frequency  $\omega a_n$  and different thickness  $n$ .

This superposition was self-consistent as shown by the following test. The raw data [Fig. 4(a)] were consistent with the classical slopes of +1 (viscous component  $g''$ )

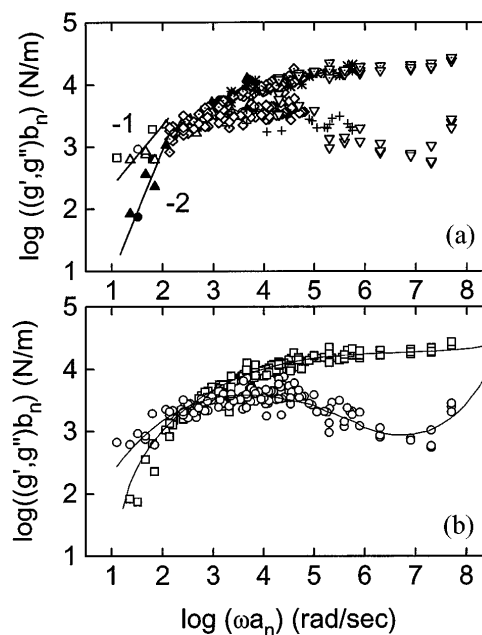


FIG. 4. Master curve describing frequency-thickness superposition of the viscoelastic response. The  $g'$  and  $g''$  are the elastic and viscous shear forces, respectively, normalized by shear displacement (approximately 2 Å). The reference state is  $n \equiv D/\sigma = 7$  molecular layers. Data at other film thickness were shifted vertically (shifts denoted  $b_n$ ) and horizontally (shifts denoted  $a_n$ ) as described in text, to make the elastic and dissipative spring constants coincide at  $\omega_c$ . (a) The following symbols indicate real and imaginary components, respectively. Filled and open squares ( $D/\sigma = 7$ ). Filled and open circles ( $D/\sigma = 5$ ). Filled and open triangles to right ( $D/\sigma = 4$ ). Diamonds with and without center dot ( $D/\sigma = 3$ ). Stars and plus sign ( $D/\sigma = 2$ ). Triangles with and without center dot ( $D/\sigma = 1$ ). The logarithmic slopes of +1 and +2 are the classical response of a fluid dictated by the Kramers-Kronig relations. (b) Imaginary component (dotted curve) calculated from the real component (solid curve) using the Kramers-Kronig relation. Data taken at different  $D/\sigma$  are identified in (a).

and +2 (elastic component  $g'$ ) required for a fluid by the Kramers-Kronig relation (the necessary relation between the real and imaginary parts of the response to a sinusoidal excitation) [24]. Furthermore, from the Kramers-Kronig relation, one spring constant could be calculated from the other; Fig. 4(b) shows  $g''$  calculated from  $g'$ . The quantitative overlap of measured and calculated quantities shows consistency of the frequency-thickness superposition over the reduced frequency scale of 7 logarithmic decades. The shifts were not arbitrary; the measured viscoelastic response at  $1/\tau_1$  determined the shift for superposition at every other  $\omega$ .

We now discuss the main features of the phenomenological master curve and ignore aspects of fundamental interpretation. The key point is wide separation between two families of viscoelastic relaxation. Figure 4 shows a broad maximum in  $g''(\omega a_n)$  at low reduced frequency, indicating one cluster of relaxation times. At much higher reduced frequency the  $g''(\omega a_n)$  rises sharply, indicating

the onset of additional relaxation processes. It is curious that these two clusters of relaxation times seem to be separated by a constant distance on the reduced frequency scale. This constitutes an important difference from the well-known  $\alpha$  and  $\beta$  relaxations of bulk glasses, whose separations certainly increase with increasing pressure or diminishing temperature [24,28]. A point for future work will be to expand the experimental frequency window to better probe the relaxation processes at high  $\omega a_n$ , to test more strictly whether the observed frequency-thickness superposition will hold as well at high frequency as at low. This, however, is not yet feasible with our present experimental setup.

In summary, the linear viscoelastic responses described here, for a confined molecule selected because of its ideally simple globular shape, are inconsistent with a first-order freezing transition from bulk fluidity to crystallinity. The nature of solidification is instead a smooth transition towards slower relaxation and increasing rigidity with decreasing film thickness. There is obvious phenomenological similarity to a bulk glass transition [24,28]; the usual roles of temperature or pressure are played by the film thickness, which in turn depends on the pressure that squeezes the films together. The frequency spectra of viscoelastic relaxation, measured at different confined film thickness, appear to scale with reduced variables.

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