

Relaxations in molecularly thin liquid films

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 9537

(<http://iopscience.iop.org/0953-8984/8/47/058>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 04:34

Please note that [terms and conditions apply](#).

Relaxations in molecularly thin liquid films

A Levent Demirel[†] and Steve Granick

Materials Research Laboratory, University of Illinois, Urbana–Champaign, Urbana, IL 61801, USA

Received 15 July 1996, in final form 25 August 1996

Abstract. The linear viscoelastic behaviour of molecularly thin OMCTS (octamethylcyclotetrasiloxane) films has been studied as a function of film thickness using a modified surface forces apparatus. The frequency spectra of viscoelastic relaxation measured at different film thicknesses superposed onto a master curve when each spectrum was shifted horizontally and vertically with respect to the frequency spectrum at a reference film thickness. The master curve indicates a wide separation between two sets of viscoelastic relaxations and suggests a gradual glass-like transition to solidity.

The viscoelastic properties of liquids confined between solid surfaces down to thicknesses comparable to the molecular dimensions are significantly different from the bulk properties. It has been previously observed that the viscosity of the liquids increases by orders of magnitude with increasing confinement (decreasing separation of the solid surfaces confining the film) [1, 2], and that a confinement-induced elastic state is reached when the surface separation is less than 2–3 molecular diameters [3–5]. However, there is disagreement as to the nature of the transition from bulk viscous behaviour to the confinement-induced elastic state. While computer simulations found that spherical molecules show a phase transition and chain molecules undergo a glass transition [6], the experimental results have been interpreted in both terms [7, 8].

Here we present the results of small-amplitude oscillatory shear experiments as a function of the film thickness and oscillation frequency, and show that the frequency spectra of viscoelastic relaxation measured at different film thicknesses superpose onto a master curve when shifted both along the frequency and the viscoelasticity axis, supporting a gradual glass-like transition and ruling out the possibility of an abrupt transition to solidity. The experiments were done using a surface forces apparatus modified for oscillatory shear [9]. Globular OMCTS molecules, mean molecular diameter $\sigma \approx 9 \text{ \AA}$, were confined between two atomically smooth mica surfaces at surface separations close to integer numbers of molecular diameters. For a given number of molecular layers between the surfaces, the surface separation can be changed within $\approx \sigma/2$ by changing the normal pressure on the surfaces. The superposition also holds for the viscoelastic responses measured in such cases [9]. The confined film was subjected to sinusoidal shear forces. The amplitude of deformation was 2–4 \AA . The resulting stress was normalized by strain and decomposed into two components, in phase and out of phase with the drive, giving the storage modulus G' and the loss modulus G'' , respectively.

[†] Present address: FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands.

At a constant oscillation frequency, the linear response of the OMCTS film changed from a predominantly viscous response ($G'' > G'$) to a predominantly elastic response ($G' > G''$) with decreasing film thickness. For larger oscillation frequencies, the crossover from viscous to elastic response happened at larger film thicknesses. At 250 Hz, the largest frequency used, the crossover happened at a surface separation of 9 molecular diameters ($\approx 81 \text{ \AA}$).

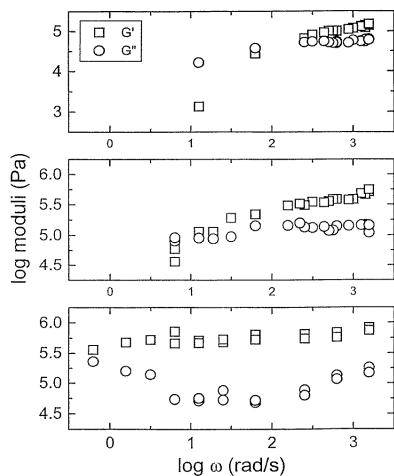


Figure 1. The storage modulus, G' , and loss modulus, G'' , plotted against logarithmic frequency for OMCTS confined between mica surfaces at film thicknesses of 5, 3 and 1 molecular layer, from top to bottom.

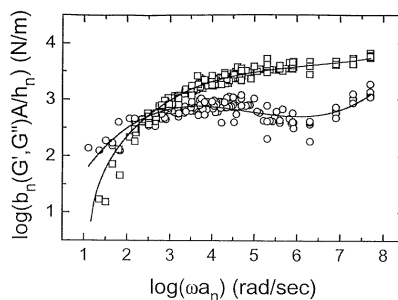


Figure 2. The master curve describing the time–thickness superposition of the viscoelastic response at a reference film thickness of $n_0 = 7$ molecular layers. The solid line for G' (squares) was calculated from the polynomial fit to G'' (circles) using the approximate Kramers–Kronig relation.

The frequency spectra were measured at different film thicknesses. Figure 1 shows three illustrative frequency spectra of the linear viscoelastic response corresponding to film thicknesses of 5, 3 and 1 molecular layers (≈ 45 , 27 and 9 \AA , respectively) from top to bottom. For 3 and 5 molecular layers, the moduli increased with frequency. One observes a crossover frequency ω_c within the experimental frequency window below which the response was predominantly viscous. When $\omega > \omega_c$, G' exceeded G'' . The crossover frequency for the bottom panel, corresponding to film 1 molecular layer thick, was to the left of the experimental frequency window. The response was predominantly elastic with G' being nearly independent of frequency and G'' showed a minimum. With decreasing film thickness, the magnitude of the moduli increased while the crossover frequency progressively moved to lower frequencies. A relaxation time τ can be defined as the reciprocal of the crossover frequency, $\tau = 1/\omega_c$. The relaxation time increased gradually by more than two orders of magnitude from 7 to 2 molecular layers, while the moduli increased by approximately an order of magnitude.

The frequency spectra of viscoelastic response measured at different film thicknesses, normalized by h/A where h is the film thickness and A is the contact area, superposed onto a master curve when shifted horizontally and vertically with respect to the frequency spectrum at a reference film thickness. The shift factors for each spectrum were determined from the experimental data such that the crossover points of each normalized spectrum coincided on the master curve. The horizontal shift factor a_n is then the ratio of the relaxation time at

a film thickness n to that at the reference film thickness, n_0 , and the vertical shift factor b_n is the ratio of the magnitude of the moduli, normalized by h/A , at the crossover point of the reference spectrum to that at a film thickness n . Figure 2 shows the master curve consisting of data taken at six different film thicknesses, including the data of figure 1, and spanning a frequency range of more than six orders of magnitude. The reference film thickness corresponded to 7 molecular layers. The solid line for G' was calculated from the polynomial fit to G'' using the approximate Kramers–Kronig relation. The quantitative overlap of measured and calculated quantities shows consistency of the time–thickness superposition over the frequency scale of more than six decades. The master curve of figure 2 indicates a wide separation between two families of viscoelastic relaxation. The broad maximum in G'' at low frequencies, indicating one set of relaxation times, is clearly seen. At higher frequencies G'' rises sharply, indicating the onset of additional relaxation processes.

Superposition of the frequency spectra of viscoelastic response taken at different film thicknesses separates the effects of the frequency and the film thickness. The master curve gives the frequency dependence at a constant film thickness and shows that a viscoelastic property measured at frequency ω and a given film thickness n_0 is equivalent to the same viscoelastic property measured at a different frequency ωa_n and different thickness n . This suggests that the elastic state will also be observed for thicker films, if the oscillation frequency can be taken to high enough values. Because the oscillation amplitude is small, the equilibrium structure of the film at each thickness is weakly perturbed. The observed solidity is then the result of shearing the system at a rate faster than it can relax at, which rules out the possibility of a phase transition from a viscous liquid to an elastic solid. The thickness dependence of shift factors represents the basic effect of the thickness on the viscoelastic properties. a_n , and thus the relaxation time, increases exponentially with $1/n$. b_n , and thus the elasticity, decreases exponentially with n . The significant increase in the relaxation time with decreasing film thickness and the superposition of the data suggest a gradual glass-like transition of OMCTS under confinement.

Acknowledgments

This work was supported by grants from the Exxon Research & Engineering Corporation, the US National Science Foundation (Tribology Program) and the US Air Force (AFOSR-URI-F49620-93-1-02-41).

References

- [1] van Alsten J and Granick S 1988 *Phys. Rev. Lett.* **61** 2570
- [2] Hu H W, Carson G A and Granick S 1991 *Phys. Rev. Lett.* **66** 2758
- [3] Gee M L, McGuiggan P M and Israelachvili J N 1990 *J. Chem. Phys.* **93** 1895
- [4] Israelachvili J, McGuiggan P, Gee M, Homola A, Robbins M and Thompson P 1990 *J. Phys.: Condens. Matter* **2** SA89
- [5] Reiter G, Demirel A L and Granick S 1994 *Science* **263** 1741
- [6] Thompson P A, Grest G S and Robbins M O 1992 *Phys. Rev. Lett.* **68** 3448
- [7] Granick S, Demirel A L, Cai L L and Peanasky J 1995 *Israel J. Chem.* **35** 75
- [8] Klein J and Kumacheva E 1995 *Science* **269** 816
- [9] Demirel A L 1996 *PhD Thesis* University of Illinois