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# Non-linear rheology of a nanoconfined simple fluid

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We probe the rheology of the model liquid octamethylcyclotetrasiloxane (OMCTS) confined into molecularly thin films, using a unique Surface Forces Apparatus allowing to explore a large range of shear rates and confinement. We thus show that OMCTS under increasing confinement exhibits the viscosity enhancement and the non-linear flow properties characteristic of a sheared supercooled liquid approaching its glass transition. Besides, we study the drainage of confined OMCTS via the propagation of “squeeze-out” fronts. The hydrodynamic model proposed by Becker and Mugele [Phys. Rev. Lett. **91**, 166104 (2003)] to describe such front dynamics leads to a conclusion in apparent contradiction with the dynamical slowdown evidenced by rheology measurements, which suggests that front propagation is not controlled by large scale flow in the confined films.

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Supercooled liquids share qualitative rheological features upon approaching the glass transition: (i) their viscosity increases dramatically, and (ii) as shown by experiments on metallic glass formers [1] or silica melts [2], they exhibit non-newtonian properties (shear thinning) when the time scale of mechanical forcing is comparable or shorter than that of structural relaxation. The precise origin of such a behavior is the subject of active theoretical and numerical investigations [3]. Fuchs and Cates have recently proposed an extension of mode-coupling theory (MCT) to flow situations, in order to describe this non-linear rheology [4]. Now, a stringent test of theoretical predictions against experimental results requires measurements, over a large range of shear rate ( $\dot{\gamma}$ ), of the non-linear properties as jamming is gradually approached. These are extremely challenging to perform on atomic glass formers, because of their elevated glass transition temperature and flow stress. The most comprehensive studies to date have focused on colloidal suspensions of thermosensitive particles, in which the particle volume fraction, hence the distance to jamming, can be finely tuned [5]. It has thus been shown that, in very good agreement with MCT, the flow stress of such colloidal suspensions, measured over eight decades of  $\dot{\gamma}$ , exhibits a rate dependence all the weaker that the distance to glass transition is small, until a yield stress develops when the suspension gets jammed [5]. Such a behavior can be considered as the rheological hallmark of the approach to glass transition.

Here, we show that increasing confinement may represent an alternative pathway to bring a system close to its jammed state under well-controlled conditions. Surface Forces Apparatus (SFA) experiments have shown that simple newtonian liquids confined between solid walls below thicknesses of a few molecular diameters exhibit enhanced flow resistance. From SFA experiments probing the linear shear response of molecularly thin films, Demirel and Granick concluded to a confinement-induced dynamical slowdown, akin to what occurs in supercooled

liquids [7]. However, this conclusion has been challenged by other groups probing the large strain shear response of confined fluids [8, 9]. Moreover, recent experiments by Becker and Mugele (BM) have shown that under increasing pressure, a confined simple liquid drains stepwise by expelling monomolecular layers via the propagation of “squeeze-out fronts” [10]. A 2D hydrodynamic model of the front dynamics, proposed by BM as an extension of the work by Persson and Tosatti [11], led them to the conclusion that the confined fluid retained its bulk viscosity, dissipation enhancement arising from high friction on the confining walls. The nature of the mechanism by which the properties of simple liquids are affected by confinement therefore remains an open question.

In this Letter, we report on the first SFA study in which *both* large strain shear rheology and squeeze-out fronts measurements are performed, in the same experimental run, on the nonpolar liquid octamethylcyclotetrasiloxane (OMCTS), which has been used as a model system in the aforementioned works.

(i) We thus show unambiguously, from flow curves measured over six decades of shear rates, that the behavior of increasingly confined OMCTS exhibits the viscosity enhancement and non-newtonian features of a supercooled liquid approaching the glass transition. We therefore reach a conclusion which is fully consistent with that of Demirel and Granick [7].

(ii) We observe squeeze-out front dynamics in quantitative agreement with that previously reported [10]. When analyzed within the framework of the BM model, it results in an effective viscosity two orders of magnitude lower than that directly measured in shear. We conclude that such an apparent contradiction arises from an improper assumption by BM about the nature of the mass transport mechanism at play during front propagation.

Experiments were performed on a home-built SFA [12] (inset of Fig. 1). The liquid under study is confined between two atomically smooth backsilvered mica sheets glued onto crossed cylindrical lenses (radius of curvature

$\sim 1$  cm). The normal force  $F_n$  applied to the confined liquid is measured by means of a load cell of stiffness  $9500 \text{ N.m}^{-1}$ . The “contact” area  $A$ , over which the mica sheets elastically flatten to form a circular parallel gap in which the liquid is confined, is monitored by videomicroscopy. The thickness of the film,  $d$ , is determined by white light multiple beam interferometry [13] and fast spectral correlation, as described in [12, 14]. Once confined under a given load, over an area  $A$ , the liquid is sheared, in a parallel Couette geometry, by moving laterally one surface at a velocity  $V$  in the range  $10^{-4} - 10^2 \mu\text{m.s}^{-1}$ , while measuring the resulting tangential force  $F_t$  with a load cell of stiffness  $5200 \text{ N.m}^{-1}$ . The shear stress sensitivity of the instrument is  $F_t/A \sim 200 \text{ Pa}$ . Our SFA has the unique feature of using the normal force signal as the input of a feedback loop, which allows to perform steady-state experiments over large shear amplitudes (up to hundreds of microns) under constant normal load conditions, whatever the level of confinement of the liquid. The mica sheets were prepared as described in [15], glued onto the cylindrical lenses using a UV curing glue (NOA 81, Norland), and cleaved with adhesive tape immediately before being installed in the SFA, so as to obtain contaminant-free surfaces [16]. OMCTS from Fluka (purum grade  $\geq 99\%$ ) was vacuum distilled before use. A drop ( $\sim 150 \mu\text{L}$ ) of the liquid, filtered through a  $0.2 \mu\text{m}$  membrane, was injected between the surfaces. It was then left for equilibration at  $T = 20 \pm 0.01^\circ\text{C}$  for 12h in the sealed SFA, containing  $\text{P}_2\text{O}_5$  to scavenge residual moisture, before beginning experiments.

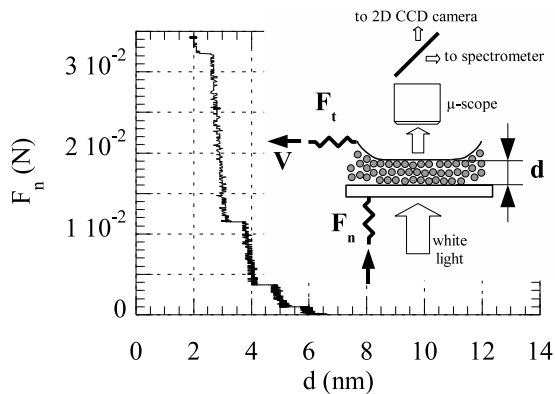


FIG. 1: Force *vs* distance curve measured during quasi-static approach of the surfaces immersed in OMCTS. Inset: scheme of the experimental setup. The fluid is confined and sheared between mica sheets which form a Fabry-Perot cavity. White light is shone on this cavity, and the transmitted intensity is sent (i) to an imaging spectrometer for spectral analysis of the Fringes of Equal Chromatic Order [13], from which  $d$  is deduced, and (ii) to a 2D CCD camera acquiring images of the contact area  $A$  at a frame rate of  $55 \text{ s}^{-1}$ .

Fig. 1 shows a force-distance profile measured upon

quasi-static approach of the surfaces: it is clearly seen that below  $6 \text{ nm}$ [17], the thickness of the confined liquid decreases by steps of approximately  $8 \text{ \AA}$ , which corresponds to the minor diameter of the slightly oblate OMCTS molecule. Such a stepwise drainage under increasing normal load reflects the well-documented wall-induced layered structure of the fluid, which gives rise to the so-called solvation forces [18].

We first focus on shear experiments performed on layered OMCTS films with thicknesses ranging from 6 down to 2 monolayers. Over the whole range of confinement and velocity explored, we have observed: (i) a smooth stable shear response (see time trace in the inset of Fig. 2b), and (ii) a steady-state value of the tangential force  $F_t$  which increases with the driving velocity. On Fig. 2a, we plot the steady-state flow stress  $\sigma = F_t/A$  as a function of the shear rate  $\dot{\gamma} = V/d$  for the different film thicknesses. The same data are plotted on Fig. 2b as the effective viscosity  $\eta_{\text{eff}} = \sigma/\dot{\gamma}$  versus  $\dot{\gamma}$ .

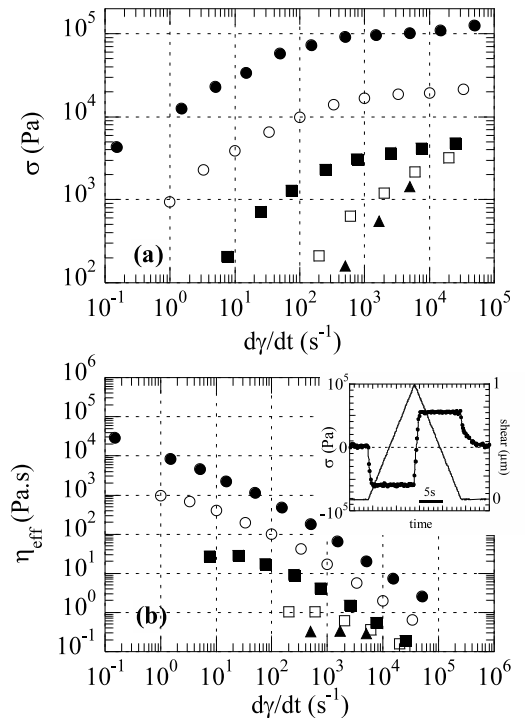


FIG. 2: (a) Flow stress versus shear rate for OMCTS films of ( $\blacktriangle$ ) 6, ( $\square$ ) 5, ( $\blacksquare$ ) 4, ( $\circ$ ) 3, and ( $\bullet$ ) 2 monolayers. (b) Effective viscosity versus shear rate, symbols as in (a). Inset: time trace of ( $\bullet$ , left scale) the shear stress measured at  $V = 0.1 \mu\text{m.s}^{-1}$  on a 2nm-thick film, (line, right scale) the forth and back shear motion applied.

It can be seen that, as the OMCTS thickness is reduced from  $n = 6$  to 2 monolayers:

(i) The flow stress, and hence the viscosity, steadily increases [19].

(ii) The dependence of  $\sigma$  on  $\dot{\gamma}$  shifts from linear (newtonian) to sublinear (shear-thinning).

(iii) The crossover from linear to non-linear shifts to smaller  $\dot{\gamma}$ , until shear-thinning spans the entire range of shear rate.

(iv) Shear thinning at low  $\dot{\gamma}$  becomes more pronounced.

(v) For  $n \leq 4$  monolayers, power-law shear thinning ( $\sigma \sim \dot{\gamma}^\alpha$ ,  $\alpha < 1$ ) at low  $\dot{\gamma}$  crosses over to a quasi-plateau regime.

This set of features is characteristic of the approach to jamming, as reported for colloidal suspensions [5] and predicted by MCT and numerical simulations [3, 4]. It shows that the flow behavior of OMCTS under increasing confinement is akin to that of a supercooled liquid approaching its glass transition. Furthermore, the observation of a plateau regime which does not extend down to the lowest shear rates, even under the highest confinement, indicates that, in the present experiments, confined OMCTS approaches but does not reach jamming. This is consistent with the fact that, as seen on the inset of Fig. 2b, upon cessation of shear, the stress relaxes (i) very slowly, over  $\sim 5$  s, and (ii) down to a non-measurable level.

These observations lead us to conclude, in good agreement with Demirel and Granick [7], that OMCTS undergoes dynamical slowdown upon increasing confinement, similarly to a glassy system close above jamming. Such a conclusion contrasts with that of Kumacheva and Klein [8] or Yoshizawa and Israelachvili [9], who observe shear responses exhibiting a stick-slip dynamics which they interpret in terms of shear-melting of a confinement-induced ordered solid-like structure. We discuss later a possible explanation for such differences.

We now present the results from squeeze-out experiments. While the surfaces are approached, we record the light intensity transmitted through the contact area, along with the normal force and the film thickness. We observe, as previously reported [10, 15], that a film of thickness  $n$  monolayers thins down via nucleation/growth of a circular region of thickness  $(n - 1)$  layers (see Fig. 3a-d). Nucleation is accompanied by elastic relaxation of the confining mica sheets, which are locally bent in the boundary zone connecting the regions of thickness  $n - 1$  and  $n$  (Fig. 3d). This creates a 2D pressure gradient which then drives the expulsion of one monolayer [10]. Our imaging technique allows us to follow with time the position of the “squeeze-out” front, where the local curvature of the mica sheets induces a contrast in the transmitted intensity (Fig. 3a-c). We have thus measured, for successive  $n \rightarrow n - 1$  transitions, the squeeze-out time  $\tau$  needed to fully expel one monolayer from the contact area  $A$ . We have done so before and after rheology experiments, and did not observe any influence of shear history on front dynamics.

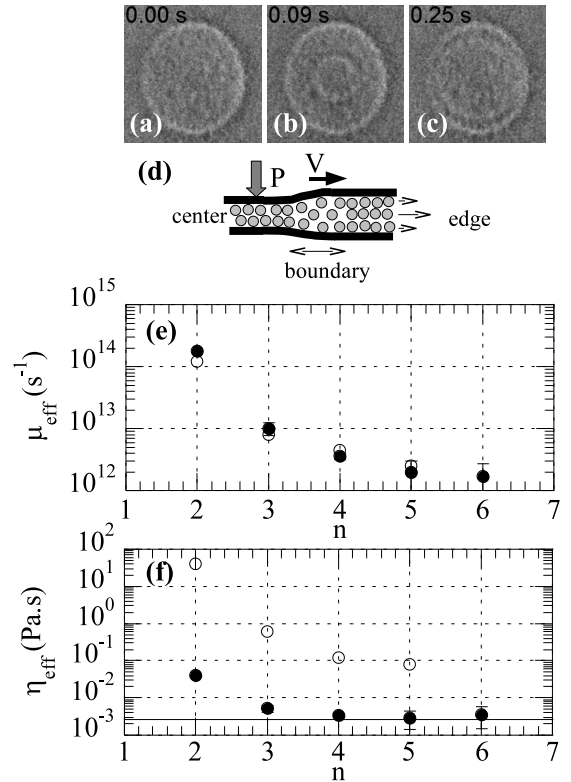


FIG. 3: (a-c): Sequence of images ( $96 \times 96 \mu\text{m}^2$ ) showing the front propagation during a transition from 3 to 2 monolayers. (d): schematic cross-section of the film during squeeze-out. Within the BM picture, front propagation at velocity  $V$  is controlled by the flow between the boundary and the contact edge. (e):  $\mu_{\text{eff}}$  vs film thickness (in number of monolayers) for squeeze-out experiments. ( $\bullet$ ) our results, ( $\circ$ ) BM results, adapted from [10]. (f): viscosity vs film thickness. ( $\circ$ ) measured in shear experiments, and ( $\bullet$ ) deduced from squeeze-out experiments. The horizontal line indicates the bulk viscosity of OMCTS.

In the Persson and Tosatti (PT) model [11], the front velocity is related to the 2D pressure gradient by:  $\nabla p_{2D} = -\rho_{2D}\mu_{\text{eff}}V$ , where  $p_{2D} \sim Pa$  and  $\rho_{2D} = \rho a$  [10, 11] ( $P = F_n/A$  is the applied pressure,  $\rho$  the fluid density and  $a$  the molecular size),  $V$  is the front velocity and  $\mu_{\text{eff}}$  a viscous drag coefficient. The latter is deduced from the squeeze-out time as [11]:  $\mu_{\text{eff}} = 4\pi\tau P/(\rho A)$ . On Fig. 3e we have plotted  $\mu_{\text{eff}}$  as a function of film thickness for the present experiments, along with the values obtained by Becker and Mugele (BM) [10]. There is quantitative agreement between both data sets. BM have extended the PT model by assuming that front propagation is controlled by a “layered” Poiseuille flow between the front and the edge of the confinement area (Fig. 3d), and thus proposed that  $\mu_{\text{eff}}$  should identify with the drag coefficient of a Hele-Shaw flow, *i.e.*  $\mu_{\text{eff}} = 12\tilde{\eta}_{\text{eff}}/(\rho d^2)$ , with  $\tilde{\eta}_{\text{eff}}$  a shear viscosity and  $d$  the film thickness [10].

We use this expression to infer  $\tilde{\eta}_{\text{eff}}(d)$  from the front dynamics. On Fig. 3f, we compare it to the characteristic [20]  $\eta_{\text{eff}}(d)$  obtained from our shear data. It thus appears that  $\tilde{\eta}_{\text{eff}}$ , which stays close to the bulk value down to 3-layer-thick films, is about two orders of magnitude lower than  $\eta_{\text{eff}}$ .

We propose the following explanation to this apparent paradox. Simple shear experiments are a straightforward way to measure  $\eta_{\text{eff}}$ , in contrast to squeeze-out experiments, which require modelling of the front dynamics to infer a viscosity. Therefore, we consider that the reliable results regarding  $\eta_{\text{eff}}(d)$  are those from shear rheology. We are then left with the observation of squeeze-out fronts which, given the  $\eta_{\text{eff}}(d)$  obtained in shear, travel much faster than expected from the drag mechanism assumed in the BM picture. This suggests that the front dynamics is not controlled by the coherent sliding of adjacent incompressible molecular layers ahead of the front. Indeed, another piece of information emerges from the force-distance profile of Fig. 1: between two steps, the film thickness is observed to decrease by about 3 Å as the force is increased. We have checked that such a thickness variation is reversible upon load reduction. This shows that layered OMCTS films are substantially compressible, hence contain a non-negligible amount of free volume, which is consistent with the fact that confined films do not reach jamming. This certainly facilitates local rearrangements, and it is therefore likely that during propagation of a squeeze-out front, molecules in the layered region ahead of it permeate between layers in order to accommodate for density variations in the vicinity of the front. The apparent low resistance to front propagation suggests that permeation, rather than large scale coherent sliding of layers, controls mass transport ahead of propagating fronts. This implies that, pending further modelling, front dynamics cannot be used to infer a shear viscosity.

In summary, we have probed the non-linear rheology of a simple fluid under molecular confinement, and conclude that its behavior is akin to that of a sheared supercooled liquid close above the glass transition. This shows, as suggested by recent experiments on colloidal suspensions [21], that confinement can be used as an alternative route to finely control the approach to jamming. Our results, which show a liquidlike behavior down to the thinnest film investigated, raise the issue of how to cross the jamming transition under confinement. Two routes can be envisaged in order to achieve this. It can be done by varying the chemical corrugation of the walls, as it has already been shown in friction experiments [22] or in numerical simulations [23]. This can also be done, in the SFA, by changing the relative orientation between the crystalline lattices of the confining surfaces. Indeed, the lattice mismatch is expected to strongly affect the structure and the shear response of the intercalated molecular film [24], and this might be the origin of the differences

between the results of Klein [8] and Israelachvili [9] and those reported in the present study.

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