Surface force apparatus for nanorheology under large shear strain

Lionel Bureau
Institut des Nanosciences de Paris, UMR 7588 CNRS-Université Paris 6, 140 Rue de Lourmel, 75015 Paris, France

(Received 24 April 2007; accepted 20 May 2007; published online 27 June 2007)

We describe a surface force apparatus designed to probe the rheology of a nanoconfined medium under large shear amplitudes (up to 500 μm). The instrument can be operated in closed loop, controlling either the applied normal load or the thickness of the medium during shear experiments. Feedback control allows us to greatly extend the range of confinement/shear strain attainable with the surface force apparatus. The performances of the instrument are illustrated using hexadecane as the confined medium. © 2007 American Institute of Physics. [DOI: 10.1063/1.2748362]

I. INTRODUCTION

The surface force apparatus (SFA) has been developed more than 30 years ago to probe surface interactions through a direct determination of force versus separation between two atomically smooth surfaces. This technique, originally designed to measure forces between surfaces separated by an air gap, has then been extended to force measurements across liquids of various natures. It appears from the large body of work done in the field that many liquids, when confined down to molecular thickness, tend to order into layers parallel to the confining walls.

The existence of such a molecular layering of simple liquids is at the origin of a number of studies which addressed the question of the lubricating properties of nanoconfined fluids subjected to shear. To do so, different versions of the SFA have been designed, which allow for tangential displacement of one of the confining surfaces and for shear force measurement. The studies performed with these friction devices focus either on the viscoelastic behavior of the confined fluid (i.e., on the response to small amplitude oscillatory shear) or on its frictional response when one of the surfaces is driven at constant speed in one direction. The following central result emerges: when confined to thicknesses on the order of five molecular diameters, many liquids exhibit a finite yield stress and strongly non-Newtonian flow properties. Moreover, such a solidlike behavior is most sensitive to the number of molecular layers between the walls. Maintaining a constant thickness, to within a few angstroms, of the medium during shear is thus of primary importance in these experiments.

Now, unavoidable mechanical imperfections of the instruments usually cause a slight nonparallel motion of the surfaces, which typically results in thickness variations of 10–30 Å for a shear amplitude of 1 μm. For a weakly confined medium of thickness h ~ 100 Å, the useful range of shear amplitude is thus limited to about 500 nm if one prescribes relative variations of h of less than a few percent. For a medium confined under a finite normal force applied through a spring of typical stiffness of 300 N m−1, if one wants the above-mentioned nonparallelism to cause an “acceptable” load variation of, say, 5%, over a shear amplitude of 100 μm, the applied load must therefore be of at least 1 mN. Such a load level corresponds to strongly confined regimes where the thickness is typically one to two molecular layers.

Such conditions are not limiting as long as molecules of simple structure are confined, for which a shear amplitude of about 1 μm is enough to establish a steady-state regime. However, they may become more of a concern when investigating the rheological properties of more complex molecules like branched hydrocarbons or polymers, which exhibit transients corresponding to sliding distances of more than 100 μm.

To our knowledge, only two devices have been designed to allow for compensation of nonparallel motion and thus extend the range of shear amplitude and confinement to be investigated. In the present article, we describe a surface force apparatus with unique performances in terms of intersurface distance stability over large shear amplitudes. This apparatus relies on a well-established mechanical design, and uses multiple beam interferometry to determine the thickness of the confined medium. The particularity of the SFA presented here is to allow for time-resolved distance and normal force measurements that are used as input signals of a digital feedback loop. This enables us to operate the apparatus either at constant thickness or constant force during shear motion over up to 500 μm.

II. GENERAL DESCRIPTION

The general design of the surface force apparatus is given in Fig. 1. The medium of interest is confined between two molecularly smooth mica sheets glued on crossed cylindrical lenses, of radius of curvature 1 cm. The mechanical arrangement is very similar to that proposed by Parker et al.: the SFA is made of an aluminum alloy cylindrical cell closed by a horizontal circular flange on which all the mechanical parts are mounted.

The lower mica surface is held at one end of a vertical spring, the other end of which is attached to a shaft that can...
be moved vertically (z axis) and horizontally (x axis). A coarse vertical motion is produced by a miniature translation stage equipped with a stepper motor (Physik Instruments PI-M1111.12s, total travel of 15 mm, positioning accuracy of 100 nm, with controller PI-C630). A fine vertical approach of the surfaces is made by means of a hysteresis-free piezoactuator (PI-P753.11C and control electronics PI-E509.C3A) of 12 μm range, which includes a built-in capacitive sensor allowing for closed-loop operation with a positioning accuracy of 0.5 Å. The motion along the x axis is produced by a piezoactuator using the same technology, but with a total travel of 500 μm (PI-P625.1CD and controller PI-E509.C1A).

The upper mica surface is held by a horizontal spring which serves as a shear force sensor. The apparatus is placed on an active antivibration table (MOD-1M, Halcyonics GmbH, Germany), and the whole setup is housed in a home-made thermally regulated enclosure. Four low-noise ventilators are used to maintain forced convection inside the enclosure, where the temperature can be adjusted at ±0.02 °C in the range of 10–45 °C by means of a thermoelectric cooling/heating assembly controlled by a commercial regulation unit (SuperCool PR-59).

A. Force measurement

Both vertical and horizontal springs are deformable parallelograms with flexure hinges, each of them being preci-
Instruments, 1340 × 400 pixels) is placed at the exit port of the spectrometer. With the 1200 g/mm grating, the spectral resolution is of 30 pm/pixel over a wavelength range of 40.2 nm. Good quality images of the spectrograph exit field are obtained with exposure times $t_{\text{exp}} \geq 20$ ms. The readout time of the full charge-coupled device (CCD) array is of 280 ms, which yields a rate of about 3 frames/s for acquisition of the FECO along a spatial coordinate. If measurements of the FECO are made only at the point of closest distance, the readout time is that of a single row of pixels and drops to 17 ms, which, added to $t_{\text{exp}} = 20$ ms, yields a maximum rate of about 27 Hz for spectrum acquisition at a single location.

The distance between the mica surfaces is deduced from the FECO using a LABVIEW-based implementation of fast spectral correlation (FSC) and multilayer matrix method (MMM), as introduced recently by Heuberger. We briefly describe the protocol followed for distance measurements.

(i) The mica surfaces are brought into contact, a spectrum is acquired in the flattened contact zone, and the wavelengths $\lambda_i$ of the transmission maxima are determined.

(ii) For the set of $\lambda_i$ determined at the mica-mica contact, we calculate, using the MMM, the transmissivity of the silver/mica/mica/silver layered medium for a range of plausible mica thickness $d_{\text{mica}}$ (typically 10 000–100 000 Å, with 1 Å steps). We choose for $d_{\text{mica}}$ the value that maximizes the function $T = \sum T_i$, where $T_i$ is the transmissivity calculated at the wavelengths $\lambda_i$. We finally calculate for this value of $d_{\text{mica}}$ the transmissivity over the full experimental wavelength window in order to check if both the number and the position of the calculated transmission maxima are in agreement with the experimental spectrum. The time needed for the determination of $d_{\text{mica}}$ is of a few seconds and is limited by the time for transmissivity calculation over the chosen thickness range.

(iii) The surfaces are separated by ~1 mm, and the liquid is injected between them using a microsyringe.

FIG. 3. Normal load as a function of hexadecane thickness for two approach velocities: 0.2 nm s$^{-1}$ (solid line) and 5 nm s$^{-1}$ (dashed line with symbols).

FIG. 4. Friction experiment at controlled normal load over a sliding distance of 100 μm. (a) Shear displacement. (b) Normal load (the horizontal dashed line indicate the setpoint). (c) Distance (the apparent increase/decrease of distance on a 20 s time scale actually corresponds to the point of closest distance moving slightly off axis of the microscope objective during shear). (d) Friction force.
(iv) The mica sheets are approached down to a separation of a few microns.
(v) The initial thickness of the liquid, $d_0$, is determined as in step (ii) above: we acquire a spectrum at the point of closest distance between the curved surfaces, locate the position of the transmission maxima, and calculate for these positions the transmissivity of the silver/mica/liquid/mica/silver multilayer for a range of plausible thickness (typically 0–50 000 Å, with 10 Å steps), assuming that the refractive index of the liquid is the bulk one. Once again, the time needed to complete this step is limited by the transmissivity calculation over the range chosen for the trial values of $d_0$.
(vi) Once $d_0$ is known, at each time $t_i$ a new spectrum is acquired. The intersurface distance $d_i$ is calculated as in step (v), with a range of plausible distance $d_i-\Delta d$, where $d_i-\Delta d$ is the distance determined at time $t_{i-1}$. The time for transmissivity calculations using $\Delta d=100$ and 1 Å increments is on the order of 1 ms, and distance measurements can thus be performed at a rate limited only by spectra acquisition.

C. Data acquisition and feedback operation

Spectra are transferred to the host computer via its universal serial bus and treated immediately to deduce the intersurface distance as described above. The signals corresponding to the normal and tangential forces and to the positions of the normal and tangential piezoactuators are measured by four digital multimeters (DMM) (34401A, Agilent, 6½ digits). The synchronization output of the PIXIS camera is used to trigger the multimeters each time a spectrum has been acquired. Measurements from the DMMs are transferred to the host computer between each trigger event, via a GPIB-PCI card. Feedback operation can be performed using either the intersurface distance or the normal force signal as the input of a digital loop with proportional and integral control, which acts on the voltage of the normal piezoactuator. The gains of the loop were set as described in Ref. 22 we first lower it by a few percent from this value, then increase the integral gain in order to reduce the offset to setpoint.

III. PERFORMANCES

A. Sample preparation

Mica sheets are cleaved down to a thickness of 2–5 μm and cut into approximately 1 cm² squares by means of surgical scissors. These samples are put on a clean mica backing substrate with one angle lying on a thin Teflon ribbon in order to allow for subsequent easy deadhesion. The back side of the mica samples is evaporated with a 45-nm-thick silver layer. The results presented hereafter have been obtained using glucose to glue the samples on the cylindrical lenses.

We demonstrate the performances of the apparatus using a linear alkane as a confined medium. We use anhydrous grade n-hexadecane (99±%, Sigma-Aldrich) filtered through a 0.2 μm Teflon membrane. A droplet of the liquid (30–50 μl) is injected between the mica surfaces; a beaker containing phosphorus pentoxide is placed inside the vessel which is then sealed and left for thermal equilibration for 12 h before starting experiments.

B. Layering under confinement

We first report the force-distance curve obtained when the surfaces are approached by driving the free end of the normal spring at a constant speed of 2 Å s⁻¹. Figure 2 clearly shows that the alkane exhibits layering under confinement, as seen from the 0.4–0.5 nm jumps in the intersurface distance, in agreement with previous studies of the same liquid.6,15

The present experimental setup allows for straightforward studies of dynamical effects which manifest when the fluid is confined at high enough velocities, and this without the need for postanalysis of recorded FECO patterns. This is illustrated in Fig. 3, where we have plotted two approach curves obtained at 0.2 and 5 nm s⁻¹. It is seen in Fig. 3 that for thicknesses ranging from 1 to 4 nm, high velocity confinement leads to much less molecular layering and to an upward shift of the force-distance profile, characterizing the out-of-equilibrium response of the fluid.

C. Large strain shear experiments

We now illustrate the shear capabilities of the instrument.

In Fig. 4, we show an experiment where a confined film of hexadecane is sheared at a speed of 5 μm s⁻¹ over a total sliding distance of 100 μm. This experiment was performed with a normal load setpoint of 185 μN and an acquisition rate of 25 Hz. Under such conditions, the normal load is found to settle at 178 μN during forward shear and at 192 μN during backward motion [Fig. 4(b)]. Increasing further the integral gain of the feedback to reduce the offset to the setpoint was found to destabilize the control loop. The film thickness is measured to be 9 Å, and the noise amplitude of ±2 Å visible in Fig. 4(c) is not affected by shear motion and corresponds to the measurement sensitivity at the chosen acquisition rate. Steady sliding is observed under a shear force of 8 μN [Fig. 4(d)]. In open-loop conditions, i.e., without normal load feedback, the nonparallelism of the surfaces (5×10⁻⁵ rad for this experiment) would yield a load variation of about 15 μN/μm, resulting in a complete loss of confinement after 20 μm of forward shear.
Larger shear amplitudes and lower load levels can readily be achieved. This is illustrated in Fig. 5, where a load of 21±3 μN (setpoint of 24 μN) is maintained over 400 μm at a sliding speed of 2 μm s⁻¹.

Experiments can also be performed under low confinement by using the intersurface distance as the input signal of the feedback control. In Fig. 6, we show such an experiment where a film of hexadecane is sheared over 250 μm at a velocity of 0.5 μm s⁻¹, while maintaining its thickness at 60±1.5 Å (distance setpoint of 60 Å). Under these confinement conditions, normal and shear forces are below the instrument resolution.

The maximum acquisition rate of 27 Hz for a simultaneous measurement of forces and distance limits the overall performances of the digital feedback loop and the range of accessible sliding speed. Typically, fluctuations of 20–30 μN or 10–20 Å are observed on normal force or distance when using a sliding speed of 20 μm s⁻¹. No noticeable noise is induced by the feedback control when the sliding velocity stays below 2 μm s⁻¹.

IV. DISCUSSION

We have built a surface force apparatus specially designed for shear experiments over large sliding distances (>100 μm). Feedback control is used in order to keep the normal load or the thickness of the confined medium constant during motion. The instrument exhibits exceptional performances in terms of force or distance stability, even in situations of weak confinement under small or zero applied load. We now plan to use this apparatus to investigate the shear behavior of glassy polymer thin films under low pressure and, more generally, of media presenting a complex molecular architecture, where large shear strains are needed in order to establish a steady-state regime.

ACKNOWLEDGMENTS

The author wish to thank Eric Perez, Philippe Richetti, and Carlos Drummond for valuable discussions and for their advice during the development of the instrument.

17 C. Drummond and J. Israelachvili, Macromolecules 33, 4910 (2000), and references therein.