# Shear-induced dilation of confined liquid films

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We demonstrate that sheared molecularly-thin fluid films dilate at the point of stick-to-slip (which is the transition from static to kinetic friction), indicating that density decreases when sliding occurs. This contrasts with incompressibility characteristic of bulk fluids when they are deformed. The magnitude of dilation was less than the size of the molecule and was larger in a polymer system (large molecules) than for small-molecule fluids. The experiments employed a surface forces apparatus modified to measure, using piezoelectric methods, sub-angstrom variations of film thickness during dynamic shear excitations that were performed at rates too rapid to allow fluid to enter and exit the zone of shear contact during the period of shear excitation. To demonstrate generality of the dilation effect, the specific systems studied included nonpolar fluids whose complexity was varied (a globular-shaped molecule, OMCTS; a branched alkane, squalane; a tethered diblock copolymer, polyvinylpyridine–polybutadiene) and also an aqueous electrolyte, $MgCl_2$ dissolved in water. Extensive analysis is also presented of the piezoelectric methods that were employed to detect volume changes too small to observe by the methods of multiple beam interferometry that are traditional for thickness measurement in a surface forces apparatus.

**Keywords:** shear-induced dilation, confined liquid films, surface forces apparatus, stick–slip

## 1. Introduction

The study of dilation began in 1885 when Osborne Reynolds noted "the existence of a singular fundamental property of granular media which is not possessed by known fluids or solids ... any disturbance whatever (of shape or distortional strain) causing a change of volume and generally dilation" [1]. This phenomenon can be observed on a beach when one walks on wet sand. The surface of the sand in a footprint appears dry. This is because interstitial water drains to fill the additional voids created, in the sand below the surface, by the pressure of walking.

Reynolds quantified these volume changes with the beautifully elegant approach of confining No. 6 rifle shot immersed in water inside a bag of India rubber connected to a graduated vessel of water [1]. He concluded this pioneering discussion by musing about implications for motion of the aether – it leads a reader to reflect, more than a century later, to wonder about the genesis of scientific creativity. Today the aether is discredited as a useful scientific concept but the concept of dilatancy is a firm and seminal bedrock of the phenomenology of granular material when it is distorted. Modern experiments in the topical physics literature continue to investigate the phenomenon of deformation-induced dilatancy, especially in wet granular media [2]. Here, when we employ the term "granular matter," we refer to sheared objects so large that their Brownian motion is negligible relative to mechanical deformations that are driven by external forces.

The past 10 years have seen remarkable progress towards the goal of understanding the mechanisms by which energy is dissipated when molecularly-thin films of liquids confined between opposed solid surfaces are slid, producing friction [3,4]. The demonstration that enhanced friction is observed even when asperity-free surfaces slide past one another was a new discovery, showing that the viscosity of fluids in the bulk cannot be used for correct prediction of energy dissipation in molecularly-thin films. It is now established that the effective shear viscosity of molecularly-thin liquid films is many orders of magnitude that of these same fluids if they were in the bulk state at the same temperature and pressure.

The schematic diagram in figure 1 illustrates a notional experiment to the effect that if solid bodies without thermal motion are at mutual equilibrium of mechanical force, changes of their mutual position must be accompanied by change of volume. We have recently developed methods that allow for quantitative measurements of displacements in the normal direction when confined fluids are sheared within a dynamic surface forces apparatus [5]. Since the methods developed appear to be applicable not only to the

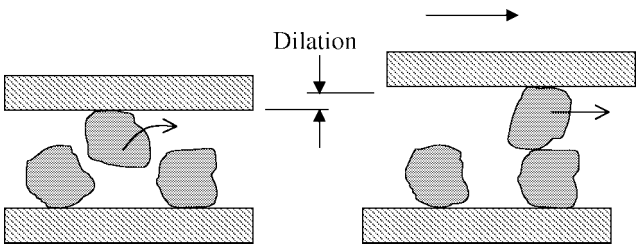


Figure 1. Hypothetical sketch illustrating the origin of dilation when two planes comprised of discrete objects slide over one another. The phenomenon is believed to be general for objects whose Brownian motion is negligible relative to external forces. It applies to objects of macroscopic size such as cobblestones and to granular materials such as sand. In this experimental paper devoted to observing the effect in a molecular system, we explore the usefulness of the concept when applied to molecules confined to molecularly-thin volumes. The horizontal arrows denote shear direction.

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relatively large surface separations to which they were applied to date [6,7], but also to films of lesser thickness, we adapt them here to this new problem.

In this work we present what we believe to be the first laboratory results to demonstrate the phenomenon of shear-induced dilation in confined liquid films. This conclusion, being based on analysis of sub-angstrom displacements of piezoelectric bimorphs, rests on the validity of the calibration of these piezoelectric materials in the case of ultra-small deflections. To confirm validity of the analysis, careful ancillary optical-based calibrations of the piezoelectric devices were also performed.

## 2. Experimental

The experimental setup was based on a surface forces apparatus, modified to measure time-dependent forces [3,4], in which fluids are confined between atomically smooth, step-free, single crystals of muscovite mica that are close to one another but not actually touching. The mica substrate can be modified by deposition of thin films of other materials. In such experiments, the area of contact between the solid surfaces is vast compared to the thickness between them; the extent of confinement differs in this respect fundamentally from the tip–surface interactions studied by atomic force microscopy and friction force microscopy.

Experiments were conducted by placing a droplet of liquid between two solid surfaces, one of which hangs as a boat from two piezoelectric bimorphs, which are placed symmetrically. In our experimental approach, the bottom surface was supported by a double-cantilever bimorph assembly similar to the one we use for shear, but rotated by 90° [5–7]. A shear excitation was applied to one of these bimorphs (the "sending" bimorph) and the responding motion of the other bimorph (the "receiver" bimorph) was detected. A schematic diagram is shown in figure 2. The general principle of using piezoelectric drives to both measure and detect the dynamic oscillatory shear responses of fluids confined between atomically smooth mica sheets was introduced some years ago [8]. Analysis of various experimental uncertainties has been presented [9,10]. Voltages induced in the piezoelectric bimorphs were detected using a digital lock-in amplifier (Stanford Research Instruments 850) whose resolution was 1 $\mu$V.

The strategy, by which we detected changes of film thickness too small to measure by the methods traditional for measurement of film thickness in a surface forces apparatus, consisted in orienting crossed mica cylinders such that shear displacements were not absolutely transverse to the normal direction. With the device sketched in figure 2, it was a simple matter to quantify the extent of this misalignment, as we have described in detail elsewhere [5]. Briefly, shear displacements caused accompanying vertical displacements. These displacements were quantified from calibration of the piezolectric bimorphs.

In figure 3, voltage induced in the piezoelectric bimorph that sensed vertical displacement is plotted against voltage

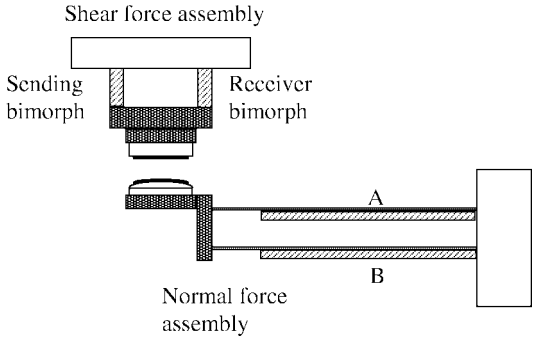


Figure 2. The experimental setup to measure shear-induced dilation in a modified surface forces apparatus. Two freshly-cleaved surfaces of atomically-smooth and step-free mica, glued onto cylindrically-shaped quartz supports, were oriented in a crossed cylinder geometry and placed within a surface forces apparatus. The top sheet of mica was hung as a boat from two piezoelectric bimorphs that are configured as a double cantilever spring. Application of voltage to the "sending" bimorph produced a shear force and the voltage induced in the "receiver" bimorph was used to sense the resulting shear deflection. Meanwhile, the bottom sheet of mica was placed on a double-cantilever spring that was oriented orthogonal to the shear direction and was therefore sensitive to displacements in the direction normal to the surfaces. The bimorphs labelled A and B, which were mounted symmetrically, refer to the forcing and sensing bimorphs; A and B were used interchangeably for forcing or sensing. In order to couple motion in the shear and normal directions, the mica cylinders were positioned so that shear was at an angle of approximately 2° off the parallel direction. The rectangle on the right-hand side of the figure indicates a positioning mechanism used to adjust the surface separation.

applied to impel forced shear excitation. The angle of shear motion, ∼2° to the parallel direction, caused these surfaces in adhesive contact at first to oscillate up and down in unison – as shown by the fact that these two voltages increased in strict proportion to one another. However, at the point where the "stick" characteristic of the rest state turned to kinetic sliding ("slip"), deviation from linearity was observed. Deviations at the stick–slip transition signify a change of the surface separation. The data in this figure are generic, as will be shown below. The particular system to which these data refer is specified in the figure caption.

### *2.1. Calibration of bimorph sensitivity (constant velocity changes of film thickness)*

The following procedure was used. First, the opposed surfaces were placed in an air environment at separations so large that surface forces between the mica cylinders were zero. Multiple beam interferometry was used to calibrate the bimorph displacement when we applied a drive voltage to the forcing arm of the normal translation stage. Stiff bimorphs were employed such that the shear displacement was approximately 2000 Å per forcing input volt. Their resonance frequency was 800 Hz. For the experiments presented here, the spring constant of the bimorphs used to sense normal displacements was $1 \times 10^4$ N/m (determined from the resonance frequency of the spring assembly and its known mass). Their resonance frequency was 235 Hz. Because the calibration was performed in air without added

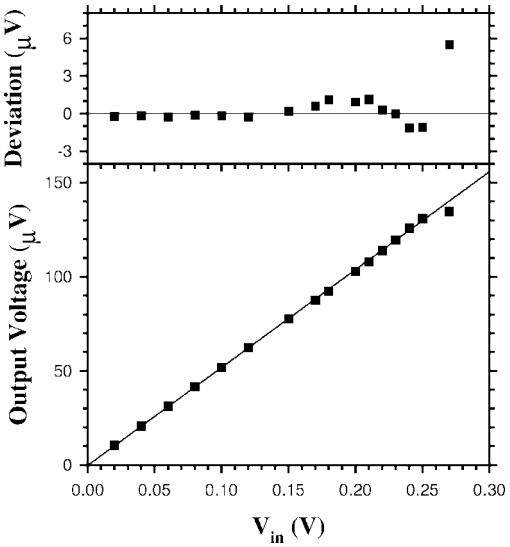


Figure 3. Coupling between motion in the shear and normal directions. When voltage was applied to the sender shear piezoelectric bimorph, shear at approximately 2° off the parallel direction caused deformation of the receiver piezoelectric bimorph that sensed displacements in the direction normal to the opposed mica surfaces. Bottom panel shows the relationship between induced voltage (normal sensing bimorph) versus shear deformation was linear at first but deviated when the shear input voltage ($V_{\text{in}}$) exceeded a critical level. The linear dependence means that the two opposed surfaces moved up and down in the lab frame of reference but without changing their separation. Deviations at the stick–slip transition signify that the surface separation changed. Top panel shows deviations from linearity concerning data in the bottom panel. Deviations from a linear fit are plotted against shear deformation. The data in this figure are generic but are taken from an experiment involving OMCTS (octamethylcyclotetrasiloxane) of thickness $20 \pm 2$ Å and sheared at 1 Hz. The data imply that the film thickness increased, at the point of stick–slip, by 0.05 nm.

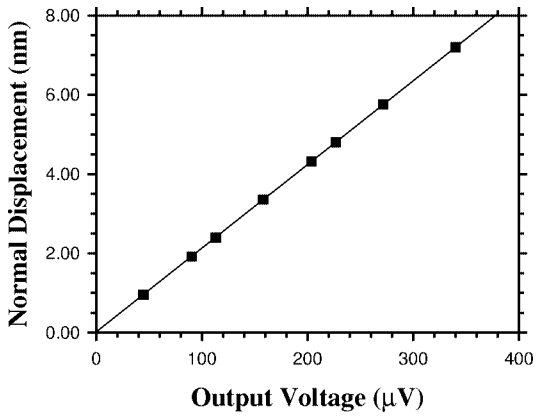


Figure 4. Calibration by multiple beam interferometry. A constant velocity displacement was produced by applying forcing voltage to the lower mica surface at 1 Hz in gas atmosphere at surface separations so large that surface forces were zero. The sensing voltage induced in the symmetrically-placed bimorph was detected. The graph showing *changes* of surface separation as a function of sensed voltage, was linear to excellent accuracy and showed a resolution of $\pm 0.02$ nm $\mu\text{V}^{-1}$.

liquid, the environment between the surfaces presented no complicating viscous drag.

As one observes in figure 4, the voltages induced by shear displacement were about three orders of magnitude less than those applied to force shear. The reasons for this difference were modeled quantitatively several years ago [9,10].

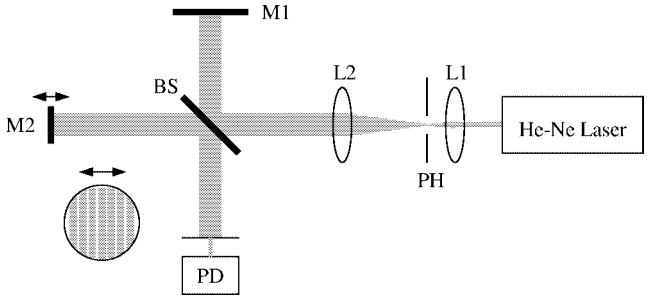


Figure 5. Schematic diagram of the interferometric setup for bimorph calibration. Laser light passed through an aspheric lens L1 (focal length 11 mm), a pinhole PH (diameter 25 $\mu$m), a collimating lens L2 (focal length 50 mm) and was separated by a beamsplitter BS. One portion passed to a fixed mirror M1, another portion to a moving mirror M2 rigidly attached to the moving bimorph, and the interference fringes produced by the reflected re-combined beams was imaged on a photodiode PD. The interference fringes oscillated with the bimorph motion as sketched in the bottom left of this figure.

To complete the calibration, one more number was needed, the output from the sensor bimorph in response to this deflection. The relation between output voltage and bimorph deflection (that is, changes of separation between the opposed mica cylinders), shown in figure 4, demonstrates the resolution of $\pm 0.02$ nm $\mu\text{V}^{-1}$. Discussion of possible nonlinearities and other complications in the interpretation of this number follows later in this paper.

### *2.2. Verification of bimorph sensitivity under sinusoidal displacement (optical interferometry)*

Applicability of the calibration just summarized was limited by the fact that surface separations changed slowly, slowly enough to be visible to the eye used to observe interference fringes. This left open the question whether bimorph responses would also be well-behaved at the higher frequencies at which measurements of shear-induced dilation are made typically. Therefore we set out to test, by direct measurement, the assumption that in response to a time-varying input voltage $V(t)$, the output deformation, $D(t)$, is $D(t) = \alpha V(t)$.

A schematic diagram of the optics used for interferometric calibration is shown in figure 5. This Twyman–Green interferometer is a variation of the traditional Michelson interferometer. A 2 mW He–Ne laser (Melles Griot 05LHP121) was used as the light source. It had a linear polarization and the beam size was 0.59 mm at $1/e^2$ intensity. A spatial filter (Thorlabs, KT300-B) was used to expand the beam size and produce a clean Gaussian beam. It was composed of an aspheric lens whose focal length was 11 mm, a 25 $\mu$m pinhole, and a collimating lens whose focal length was 50 mm. The beam size was expanded $\sim$4.5 times using these components. A beamsplitter (CVI, BS1-633-50-1037-45P) divided the incoming beam into two, one segment traveling to the fixed mirror M1 and one to the mirror M2 attached to

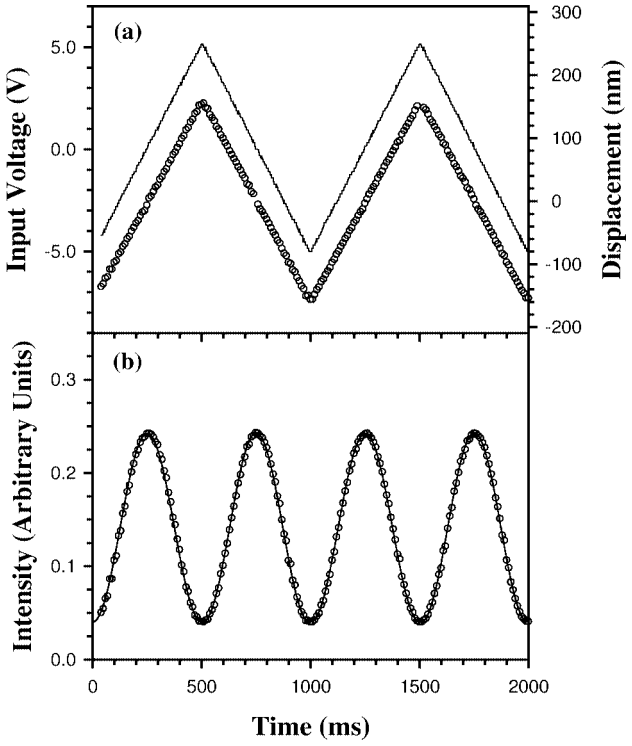


Figure 6. Examples of photodiode signal and bimorph motion at 1 Hz. A triangular-shaped input voltage was applied ((a), left ordinate axis), producing modulation of interference fringes that was sensed as a sinusoidally-varying intensity of signal at the photodiode. Using equation (3), the bimorph deflection was calculated ((a), right ordinate axis).

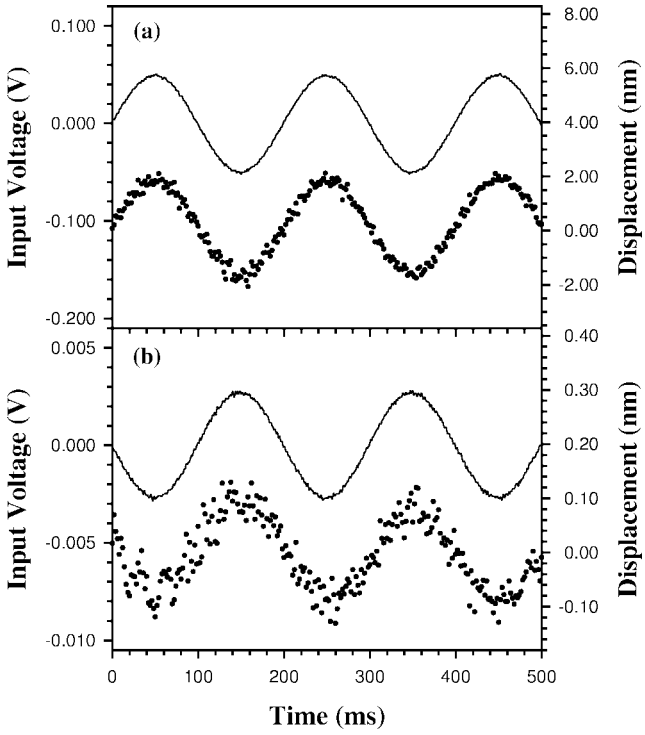


Figure 7. Bimorph response to 4 Hz sinusoidal input voltage of 50 mV (a) and 2.5 mV (b) after averaging for 20 and 300 cycles, respectively. The input waveform is plotted on the left ordinate and the resulting bimorph deflection, calculated from the photodiode signal (not shown) using equation (3), is plotted on the right ordinate. Displacements of 2.0 and 0.1 nm were easily resolved.

the bimorph whose calibration was intended. The bimorph assembly was the same as described above.

The two beams were reflected by mirrors and returned to the beamsplitter, the beam from M1 passing through the beamsplitter and the beam from M2 being deflected by the beamsplitter toward the detector. Here the two beams met and the resulting interference pattern was imaged, as shown schematically in figure 6.

A 200 $\mu$m slit was positioned at maximum interference irradiance and a Si photodiode detector (Thorlabs, PDA55) was used to monitor the irradiance changes caused by the displacement of mirror M2 attached to the moving bimorph. Provided that the two beams are coherent and have equal irradiances $I_0$, the interference irradiance $I$ at this position can be written as

$$I = 4I_0 \cos^2 \frac{2\pi(2D)}{2\lambda} = 2I_0\left\{1 + \cos\left(\frac{4\pi D}{\lambda}\right)\right\}, \quad (1)$$

where $D$ is the displacement of M2 from the position it takes in the absence of driving voltage, and $\lambda$ is the wavelength of the laser beam, 632.8 nm. Considering the offset and the gain of the photodiode detector, the photodiode signal intensity $S$ can be written as

$$S = S_0 + GI = S_0 + 2GI_0 + 2GI_0 \cos\left(\frac{4\pi D}{\lambda}\right)$$
$$= a + b\cos\left(\frac{4\pi D}{\lambda}\right), \quad (2)$$

where $S_0$ is the signal offset and $G$ is the gain of the photodiode. Then the temporal oscillation period of the signal corresponds to a displacement of amplitude $\lambda/2$.

Figure 6 shows an example of operation of this device. A triangular-shaped waveform was applied with amplitude 5 V and frequency 1 Hz. The photodiode signal showed the expected sinusoidal waveform and this was fitted to equation (2). The fit yielded a period of 0.488 s. During this period, the displacement of M2 should be $\lambda/2 = 316.4$ nm with corresponding voltage change 9.76 V, from which we deduce that the voltage constant for this bimorph assembly was $\alpha = 32.4$ nm/V.

One of the advantages of this interferometric method is that it shows directly the bimorph's motion. From equation (2), the bimorph displacement can be written as

$$D = \frac{\lambda}{4\pi} \arccos\left(\frac{S-a}{b}\right). \quad (3)$$

From the data in figure 6, the constants $a$ and $b$ were found to be 0.1417 and 0.1013, respectively. Using these constants, we calculated the displacement of the bimorph, with results included in figure 6(a). (Similar results were obtained using sinusoidal input voltages.) It is evident that the traditional assumption, $D(t) = \alpha V(t)$, was satisfied in this instance.

In order to check the sensitivity of this method, we applied progressively smaller sinusoidal input forcing volt-

ages, with amplitude as small as 2.5 mV. After averaging over 300 cycles, sinusoidal shear displacements as small as 1 Å could be resolved, as illustrated in figure 7. Direct optical detection of sub-angstrom displacements would have required prohibitive additional averaging of the output signals. From the data in figure 7, we conclude that the validity of calibration in response to dynamic oscillatory excitations was confirmed down to this level of sensitivity.

## 3. Results and conclusions

For several years it has been clear that much of the shear flow behavior of confined fluids strangely resembles that of granular materials such as sand, powder, and colloidal particles; an observer could not distinguish between the two if the experiment were performed in a black box [4]. Here, to further explore how far this analogy goes, we set the goal of measuring shear-induced changes of density when molecularly-thin films of simple liquids undergo shear. The problem is quite different from the known changes of film thickness that occur for well-understood hydrodynamic reasons. Regarding hydrodynamic-induced increases of film thickness during sliding, careful measurements of refractive index during shear confirm that enhanced film thickness is caused by entry of liquid into the confined gap such that the volume of confined liquid increases in proportion to the amount of dilation, but without change of density [11]. Here we enquired: what happens when hydrodynamic-based changes are avoided? What happens if the changes of shear direction are too fast to allow hydrodynamic entry of fluids into (and exit from) the confined gap? This was accomplished by reversing the direction of shear motion involving a large contact area at a rapid rate, multiple times per second.

Shear-induced changes of film thickness for non-hydrodynamic reasons have been predicted regarding molecularly-thin films but have not, so far as we are aware, been observed previously. In a pioneering investigation based on computer simulation, Grest and Robbins found by molecular dynamics (MD) simulation that film thickness increased when shear was induced relative to the rest state [12]. But relevance to laboratory experiments was unclear because the effective rates of shear exceeded, by several orders of magnitude, time scales of laboratory experiments. From another point of view entirely, Cushman, Fuchs and coworkers employed Monte Carlo simulations to predict quasistatic shear-induced deformations, and also predicted that shear would produce increased film thickness [13]. Shear dilatancy in simple fluids in the bulk state was also investigated by other molecular dynamics simulations [14]. When one endeavors to test these important physical issues in a laboratory experiment, it is obvious that the capacity is needed to monitor changes of film thickness that might, in magnitude, be less than the thickness of a single molecule.

Within the resolution of multiple beam interferometry in our (and most) laboratories, 1–2 Å, the film thickness was always the same for samples at rest and under shear. This is why piezoelectric responses were analyzed to seek a higher resolution than this. The piezoelectric setup, which is incapable of measuring *absolute* film thickness, proved to be sensitive to *variations* of film thickness during dynamic oscillatory measurements.

### *Shear-induced dilation*

Inspection of figure 3 shows a discontinuous 0.05 nm change of film thickness. From other experiments (cf. figure 8, for example), similar to those we have presented in detail elsewhere [15,16], it was clear that this occurred at the point of stick–slip: the passage from static to kinetic friction.

Given the novelty of these conclusions, it is appropriate to consider potential artifacts. An anonymous reviewer has asked about potential nonlinearity of the piezoelectric bimorphs employed to observe this effect. With the

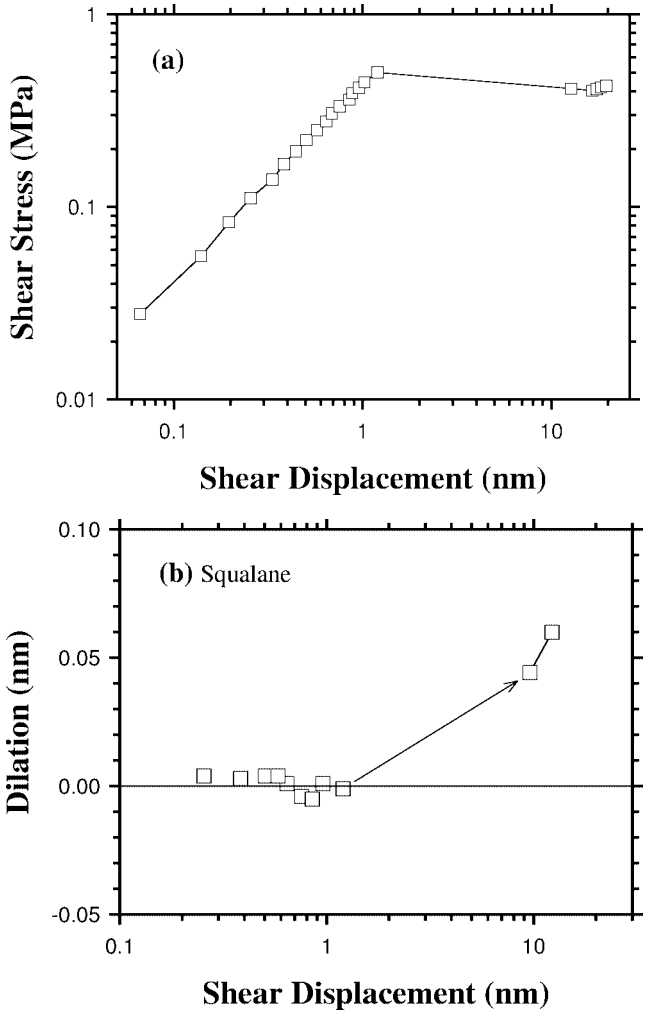


Figure 8. Correlation between shear response and dilation for a multiply-branched alkane, squalane. First (a), shear stress is plotted as a function of shear displacement at 1 Hz (the fluid was confined between mica surfaces at thickness $1.8 \pm 0.2$ nm). The resulting dilation at 1 Hz is plotted in (b). In other experiments, this result was confirmed for shear displacements at 256 Hz.

Table 1

| Confined liquid | Characteristic dimension of the liquid molecule (nm) | Total film thickness (nm) | Amount of dilation (nm) |
|---|---|---|---|
| OMCTS | 0.9[a] | 2.0 | $0.05 \pm 0.02$ |
| Aqueous $MgCl_2$ | 0.25[b] | 0.6 | $0.06 \pm 0.02$ |
| Squalane | 0.4[c] | 1.8 | $0.05 \pm 0.02$ |
| Diblock copolymer | 1.6[d] | 5.5 | $0.7 \pm 0.02$ |

[a] Period of oscillation in the force–distance profile between mica [16].
[b] Characteristic dimension of a water molecule [17].
[c] Period of oscillation in the force–distance profile of a confined linear alkane [15].
[d] Dry film thickness of an adsorbed layer of this polymer when coated onto a single mica surface [6].

current calibration instrumentation is difficult to calibrate the bimorph directly with a peak-to-peak displacement of 0.01 nm, although we have gone some distance in this direction with the data in figure 7(b). More essentially, we are looking at abrupt changes that take place at a stick–slip transition. Nonlinearities would be expected to manifest themselves in gradual deviations from linear dependence, and this we did not observe. We observed a strictly linear dependence until the system passed the stick–slip transition.

Alternative explanations suggested by the anonymous reviewer were also considered. First, one might suppose that the mica surfaces would be configured unevenly if the glue beneath them were spread unevenly. But unevenness would be expected to manifest itself in gradual deviations from linear dependence and this we did not observe. Secondly, one must consider the possibility of artifacts arising from parasitic deficiencies in the electric circuitry. However, measurements using an oscilloscope give the same conclusion as using a lock-in amplifier. In parallel work, to be reported elsewhere, we also find this effect when measurements are made at constant sliding velocity; in other words, the effect persisted even when the deflection of the bottom piezoelectric bimorphs was constant rather than changing with time. To be sure, confirmation by independent measurements will be desirable in future work, and we are working in this direction using both optical and capacitance-based detection methods.

Using the piezoelectric methods that form the detection scheme in this paper, several systems were studied, as summarized in table 1, at several shear frequencies between 1 and 256 Hz. The phenomenon of dilatancy based on the evidence presented was common to all of these systems:

- First, an alkane with extensive branching, squalane, was brought to film thickness $1.8 \pm 0.2$ nm. Shear experiments for this same system were presented previously [15,16]. Shear stress versus shear deformation is illustrated in figure 8(a). Measurements of shear-induced changes of film thickness, shown in figure 8(b), showed no detectable dilation in the rest state, but dilation by 0.05 nm at the point of stick–slip. The data concern shear displacements at 1 Hz; in other experiments, this result was confirmed for shear displacements at 256 Hz. Note that in figure 8, the "gap" of data on the displacement axis just reflects the fact that stick–slip motion is jerky; under a given sliding force, deflection increases so rapidly at a stick–slip transition that intermediate deflections are inaccessible when the spring constant of the device is exceeded.
- An aqueous system was also considered, in order to test generality of these effects in fluids comprised of nonpolar molecules. Distilled water containing 0.1 M $MgCl_2$ salt was confined between two mica sheets to a thickness of $0.6 \pm 0.02$ nm. Shear experiments for this same system were reported previously [17]. Results, shown in figure 9(a), showed no dilation in the rest state, but dilation by 0.05 nm at the point of stick–slip, similar to the behavior of nonpolar fluids, OMCTS (figure 3) and squalane (figure 8(b)).

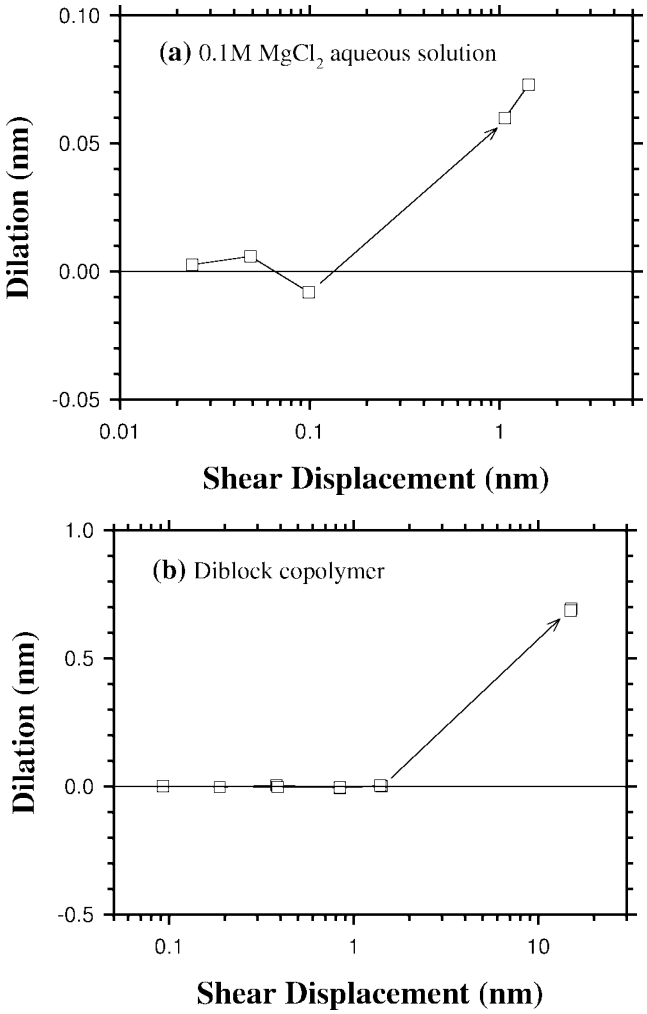


Figure 9. Correlation between shear response and dilation in two other systems. First (a), dilation is plotted as a function of shear deformation for an aqueous system, 0.1 M $MgCl_2$, confined between mica surfaces to a separation of $0.6 \pm 0.2$ nm and subjected to shear at 256 Hz. Next (b), dilation is plotted as a function of shear deformation for a polymer brush immersed in the good solvent, tetradecane, and subjected to shear at 1 Hz. Details of the molecular weight of the polymer brush and its grafting density are given in the text. Comparison of panels (a) and (b) shows that the magnitude of dilation increased with size of the confined molecule.

- Next a system comprised of larger molecules was investigated. A polymer was investigated, instead of a small molecule: diblock copolymers of polybutadiene and polyvinylpyridine (PB-PVP), immersed in the good solvent, tetradecane, at film thickness 5.5 nm. The molecular weights were 38 500 g mol$^{-1}$ (PB) and 23 700 g mol$^{-1}$ (PVP). The ratio weight-average to number-average molecular weight was $M_w/M_n < 1.05$. Since tetradecane is a nonsolvent for the PVP block but a good solvent for the PB block, the block polymers adsorbed onto the mica by selective adsorption of the PVP block. Extensive tapping force measurements on this same system were presented previously [6]. These larger molecules displayed dilation of $\sim$0.5 nm, as shown in figure 9(b) – larger by an order of magnitude than for the smaller molecules. Therefore, for films of confined fluid whose thickness was roughly the same, the magnitude of dilation appeared to correlate with the size of the molecule.

A confined molecular fluid displays stick–slip when it is deformed more rapidly than it can respond by Brownian motion; it yields to externally-applied shear forces discontinuously, like a solid, rather than continuously in the manner of a liquid's shear-thinning [18]. The intriguing analogy of sheared confined molecular fluids to mechanical deformations of granular systems comprised of macroscopic-sized objects was the subject of this paper.

A key point is that the periodic dilation that we infer was too rapid to allow equilibration of fluid within the confined space with the reservoir of fluid outside. For example, in the experiments performed during shear at 256 Hz, dilation was observed to occur twice during each cycle of rapid periodic shear, 512 times each second; for 1 Hz shear deformations, dilation occurred twice each second. Consider the fact that the linear dimension of the contact zone was $\sim$10 $\mu$m, about $10^4$ larger than the thickness. The viscous loss required to allow fluid to enter and exit the zone of contact is readily estimated from the Reynolds equation. Even if one takes the viscosity of the confined fluid to be the same as in the bulk (which is not realistic for confined fluids [3,4]), it follows for typical values of the experimental setup that 1–2 s is needed for fluid to enter or leave the gap in the case of fluids of low viscosity such as OMCTS and aqueous electrolyte [19] (the required time would obviously be far longer in the diblock copolymer system that we studied). In every case, the observed more rapid occurrence of dilation during periodic sliding signifies that the average density of fluid, within the gap must have been altered at the point of stick-to-slip.

The magnitude of dilation was in general sub-angstrom (except for the polymer system), but it constituted a substantial fraction of the total film thickness and also a substantial fraction of the size of the confined molecules. Characteristic dimensions of the molecules we have studied are summarized in table 1.

The known dilatancy of granular materials in bulk systems, although larger in magnitude, is smaller in a relative sense. For example, in a granular system of particles 100 $\mu$m in linear dimension and film thickness 3 mm, the amount of dilation was only 4–5 $\mu$m [2] – the amount of dilation, expressed as a fraction of either the particle dimension or the film thickness, was much larger for the present confined fluids.

Looking to the future, it will be important to learn whether the density of the confined fluid was lessened by the same amount everywhere, or inhomogeneously so. The possibility that density was low in some spots, higher in others, is an appealing hypothesis. If so, pockets of low density might serve as embryos for cavitation when lubricants are swept out of a contact zone. Shear-induced cavitation, a challenge for understanding as concerns even bulk fluids, is known as a source of damage to surfaces during sliding [20]. The results presented in this paper present the clear implication, which we hope to test in future experiments, that the abrupt change in average density demonstrated in this paper shows the occurrence of incipient cavitation within the confined liquid. Also important to test in future work will be dependence of the dilation magnitude on the normal load and on the spring constant of the device through which normal load is applied to the sample.

These constitute, to the best of our knowledge, the first experimental demonstration of shear-induced change of fluid density when molecularly-thin films of molecular fluids were sheared past the point of stick–slip at a rapid rate – many times per second. These findings are phenomenologically like the behavior of granular materials such as sand and seed grains. They reinforce the view that molecularly-thin fluid films of molecules display shear behavior similar to that of granular material [4].

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