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Jacob Israelachvili†, Patty McGuiggan†, Michelle Gee†,
Andy Homola‡, Mark Robbins§ and Peter Thompson§

† Department of Chemical Engineering, and Materials Department, University of
California, Santa Barbara, CA 93106, USA
‡ IBM, Almaden Research Center, 650 Harry Road, San Jose, CA 95120, USA
§ Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD
21218, USA

Abstract. Using the surface forces apparatus technique we have measured the dynamic properties of ultrathin liquid films between two molecularly smooth solid surfaces sliding past each other. The results on several different liquids are reviewed; these reveal film properties that are profoundly different from those of the bulk liquids once the film thickness falls below five molecular diameters. For example, the liquids can now support a normal (hydrostatic) pressure as well as shear stresses, exhibiting upper and lower yield points (stick–slip friction). Certain molecular rearrangements can take 10^{10} times longer in a 10 Å film than in the bulk liquid. The experimental results are reproduced by computer simulations which indicate that liquid molecules in ultrathin films become ordered and solid-like, 'freezing' into discrete layers which also have lateral order. On applying a shear force, the film undergoes a melting transition from 'solid' to 'liquid' at the yield point. But even during slip some order remains within the film which therefore becomes more like a liquid crystal than a simple liquid. These phenomena and thin film properties do not appear to be readily describable in terms of mechanisms or concepts applicable to bulk liquids or solids.

1. Introduction

The last few years have witnessed renewed interest in the properties of liquids confined within very narrow spaces, e.g., in fine pores or capillaries, or in molecularly thin films between two surfaces. This interest has extended to both the static and dynamic properties of the confined liquids. The area itself is an old one, and has traditionally been part of colloid science, adhesion science, and tribology (the science of friction and lubrication). However, it is only recently that experimental techniques have developed to the stage where one can directly measure the physical properties of liquids in ultrathin films at the molecular level. This is due to the development of various Force balance techniques such as the surfaces forces apparatus (SFA), the scanning tunnelling microscope (STM), and the atomic force microscope (AFM). The SFA technique allows for measurements of the thickness of a liquid film between two molecularly smooth surfaces (to within 1 Å), the true area of molecular contact, the static adhesion force between the surfaces, the dynamic (frictional or shear) forces, the elastic or plastic deformations of the surfaces, and many other properties at the molecular level [1]. Only the molecular conformations of liquids in such thin films cannot yet be easily accessed experimentally.

On the theoretical side, advances in computer technology now enable molecular dynamics and other computer simulation techniques to study complex molecular systems with a detail that could not have been conceived of only a few years ago. These studies are providing quantitative data that link up nicely with the experimental findings, and further provide detailed insights into molecular events that cannot be accessed experimentally.

When a liquid is confined within a space whose dimensions are less than five to ten molecular diameters it ceases to behave as a structureless continuum, i.e., its properties can no longer be described in terms of its bulk properties or in terms of continuum or mean-field theories. Much work has been done on the static or equilibrium force laws between two surfaces across such thin films. These exhibit oscillations, varying between stable attractive wells and unstable repulsive peaks, with a periodicity equal to some molecular dimension. Such films can therefore sustain a finite normal stress, and the adhesion between two surfaces across such films may be thought of as being 'quantized' with the number of layers between the surfaces [2]. These forces are now well understood theoretically, at least for simple liquids [3].

Less work has been done on the dynamic, e.g., viscous or shear, forces across such films, though recent experiments and theory both indicate that even when two surfaces are in relative shear motion they still prefer to remain in one of their stable potential energy minima, i.e., the film remains structured (layered) normal to the surfaces [4]. Further, if the surfaces are themselves structured there can also be long-range lateral order within each layer. When this happens, the film becomes essentially solid-like and can sustain a finite shear stress (in addition to a normal stress) [5]. Simple spherical molecules such as cyclohexane between two mica surfaces show this type of behaviour [6]. These small quasi-symmetrical molecules readily pack in an ordered structure between the two crystalline surfaces of mica when these are brought close together. Such solid-like films exhibit yield-points or yield stresses, where the film 'melts' (shear-melting) [10] and begins to flow [7. 8]. The value of the yield stress depends on the number of layers comprising the film and represents another 'quantized' quantity associated with such films.

On the other hand, molecules with a more complex or asymmetric shape cannot conform as easily to the two surface lattices. Since they cannot adopt an ordered or layered structure, they remain more liquid-like even in very thin films. This occurs, for example, with 2-methyloctadecane (a branched paraffin) between mica surfaces [8]. However, as we shall see, the properties of such films may still be significantly different from those of the bulk liquid. For example, they may still exhibit a yield point even though this is no longer quantized.

The dynamic properties of a liquid film undergoing shear are very complex. During sliding, transitions can occur between n layers and $n - 1$ or $n + 1$ layers; the friction may be smooth (if the film is liquid-like) or of the 'stick–slip' type (if it is solid-like), and the details of the motion can depend critically on the area of contact, the externally applied load, the stiffness of the system, the sliding velocity, the angle between the two surface lattices and the angle of the sliding direction relative to either of these lattices.

In this brief review of the current state of understanding of these systems we shall concentrate on the simplest systems possible (which nevertheless are already quite complicated). The geometries of real systems can vary greatly and it is unlikely that one simple picture can represent them all. Such 'real' systems include flow in confined spaces, boundary or interfacial friction, the 'serrations' produced during the plastic deformations of metals, alloys and polycrystalline solids, and even squeaking doors and
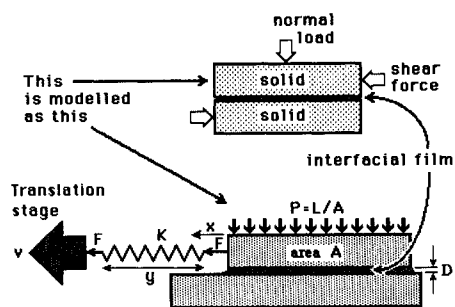
v   Velocity of translation stage
x   Total displacement of upper surface
v_x Velocity of upper surface ($v_x = dx/dt$)
K   Spring stiffness
y   Spring length
F   Frictional force (spring tension = K Δy)
A   Contact area
L   Externally applied load
P   Externally applied pressure (P = L/A)
D   Thickness of film

Figure 1. Schematic representation of experimental set-up used to measure shear forces and other dynamic properties of liquids in ultrathin liquid films between two molecularly smooth mica surfaces. The experimental details are given in [9].

earthquakes. In a first approximation all these may be modelled as shown in figure 1, where a rigid surface is pulled horizontally by a spring attached to a moving translation stage. This is essentially the experimental set-up of the friction device attachment for the surfaces forces apparatus [6, 9] that has been used for making these measurements.

2. Results and discussion

We first proceed with a qualitative description of what happens to a thin liquid film between two molecularly smooth surfaces, initially at rest, after we start moving the translation stage at some constant velocity, v. The changing pattern of events with time is shown in figures 2 and 3.

2.1. (T = 0) surfaces at rest (equilibrium)

The two surfaces are at rest. Even with no externally applied force, liquid–liquid and liquid–surface interactions forces the liquid molecules in the film to adopt a solid-like ordering (high order parameter, S, as shown in figure 3). Thus at rest the surfaces are pinned to each other through the film. The molecular ordering in the film extends both normally (forming quasi-discrete layers) and laterally (within each layer). This ordering depends not only on the types of intermolecular forces involved but more critically on the geometry of the liquid and surface molecules, and the relative orientation of the two surfaces. For simplicity, figure 2 (top left) shows the surface and liquid molecules as having the same spherical shape, and with the two surface lattices aligned (zero 'twist angle'). A more realistic situation could be much more complicated, as shown in the
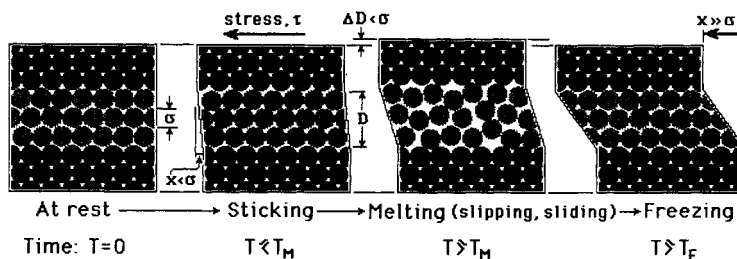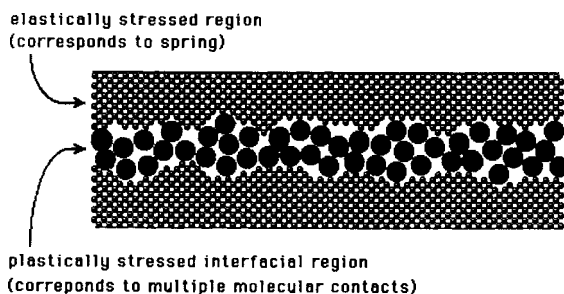
Figure 2. Upper part: idealized contact between two molecularly smooth surfaces separated by a thin liquid film comprised of three layers of solvent molecules. Initially, the film is solid-like (frozen) and the two surfaces remain pinned (stuck) to each other under an increasing shear stress. At the yield-point the film melts (shear–melting transition) and the two surfaces slip. The motion either continues (sliding) or comes to an abrupt stop if the film freezes again. Note that when the stress is increased during the sticking regime, the entire solid material on both sides of the film also deforms elastically and acts like a spring. Lower part: the geometry of a real friction boundary is generally much more complex, and cannot be represented in terms of one picture, however schematic. Real surfaces are usually rough on the molecular scale and the contact area and film thickness may be difficult to define (as illustrated here). For even rougher surfaces, contact may be occurring only at isolated points between the most protruding asperities.

lower part of figure 2. With rough surfaces and/or highly asymmetrically shaped molecules the molecular ordering is reduced or totally destroyed (see later).

2.2. $(T \to T_M)$ sticking regime

From time $T = 0$ onwards the stage is moved laterally at constant velocity v. A progressively increasing shearing force (shear stress) is therefore experienced by the interfacial film as well as by the material on either side of it. From $T = 0$ to $T = T_M$ this force is too weak to produce any irreversible deformations (e.g. plastic strains), and all the strains are elastic. Thus both the lateral displacement, x, and the film thickness, D, increase linearly with time, but only by a small fraction of a lattice or molecular dimension, σ (figure 2). During this time period the film retains its solid-like properties and one may consider the two surfaces as remaining 'pinned' or 'stuck' to each other across the film. As shown in figure 3 the shear stress, τ, displacement, x, and film thickness, D, increase roughly linearly with time up to $T = T_M$, whereas the order parameter of the
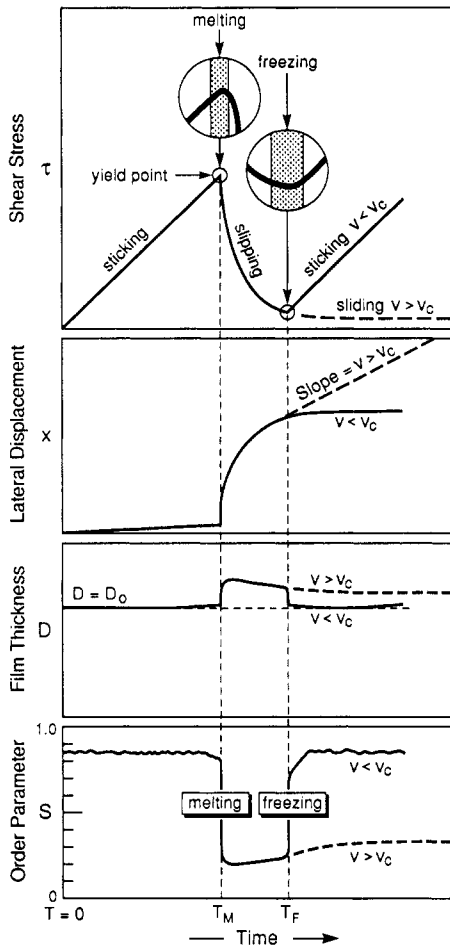
Figure 3. Changes of various film properties with time corresponding to the different stages shown in figure 2. The order parameter, S, measures the degree of crystalline order in the film (the Debye–Waller factor); definitions of other symbols are given in figure 1. (Adapted from [7].)
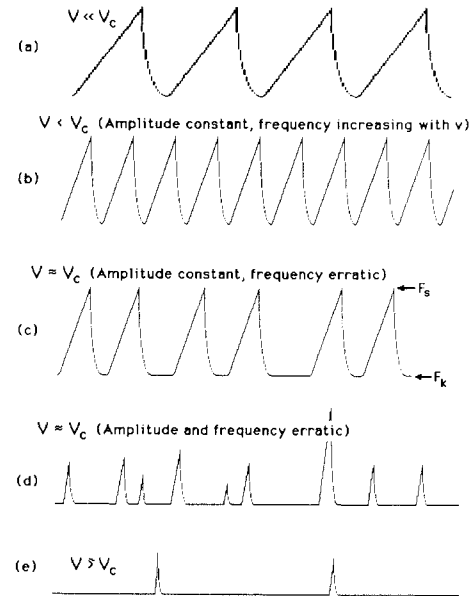
Figure 4. Changing shear stress versus time profiles associated with the transition from stick–slip to smooth sliding with increasing driving velocity, v. By convention, F_s and F_k define the 'static' and 'kinetic' friction (the latter may be finite or even zero). Details of each regime are discussed in the main text.

film remains high, though it too is changing slightly. Note that the bulk material on either side of the film also becomes elastically strained, with corresponding changes in its lateral and normal dimensions. Here, x and D refer to the film dimensions only, and it is implicitly assumed that the film constitutes the weakest part of the whole system (i.e., the region where non-elastic shear will eventually occur).

2.3. $(T = T_M)$ melting transition (yield point)

Over a very short time interval the film shear melts, which in a first approximation may be considered as a normal first-order solid-to-liquid phase transition [10] (though it is

worth bearing in mind that phase transitions in two dimensions can be continuous and have other unusual properties). In the language of tribology the 'static friction', F_s, has been reached; in the language of materials science the 'yield point' has been reached. At this point the shear stress, τ, suddenly drops as the two surfaces begin to slip past each other and the lateral displacement, x, now increases rapidly and with increasing speed. As shown in figure 3, during melting the film thickness, D increases, i.e., the film density falls, and the order parameter, S, drops. Much of this has been inferred from computer simulations. The melting period is extremely short, and cannot normally be seen during experiments which instead show an abrupt and discontinuous change in all the measured properties at the yield point (shown by the small circled region in figure 3). Computer simulations allow us to probe this short-time regime, and these show that the melting occurs over a finite time period of the order of a molecular relaxation time, as shown in the larger circled region in figure 3. However, this time scale may be much longer than normal molecular relaxation times, of order 10^{-9}–10^{-12} s, in bulk liquids because of the high compressive loads and small confined space. These factors will act to reduce both the local melting rate and the speed at which the liquid region grows. The good agreement between the experiments and simulations whenever these can be compared provides confidence that other computed values, such as the order parameter, are likewise reliable. However, one cannot be sure of this. It is entirely possible that molecular motions in thin films may also occur via the movement of dislocations or disclinations, or that different layers within the film move in very different ways. Future experiments and simulations should be able to further probe this interesting regime.

2.4. $(T_M \rightarrow T_F)$ slipping regime

The slip regime can be as short as one lattice spacing or it can continue over macroscopic distances. This depends on the material and spring stiffness, K, on the driving velocity, v, and on the 'dissipation mechanism' by which heat is dissipated away from the surfaces into the bulk material each time the liquid molecules bump into them. In the slip regime, the two surfaces start by slipping past each other at a velocity $v_x = \mathrm{d}x/\mathrm{d}t$ that is much higher than the stage velocity, i.e. $v_x \gg v$. Thus, as the slip proceeds the tension in the spring relaxes so that the shearing force, F, falls. This, and the energy dissipation, causes v_x to steadily fall and for τ to decrease less rapidly (roughly exponentially). In the slip regime v_x approaches v as the top surface races to catch up with the stage. Meanwhile, the film remains in a liquid-like or liquid-crystal-like state with low order parameter and $D > D_0$.

2.5. $(T = T_F)$

The slipping regime ends either by (i) the abrupt freezing of the film at T_F (freezing transition), when the surfaces once again become stuck and the whole process thereafter repeats itself in a periodic fashion (stick–slip friction), or (ii) the slip velocity v_x reaches the stage velocity v, and thereafter the surfaces continue to slide at a steady velocity v (smooth sliding regime). Whether we get stick–slip sliding or smooth sliding depends on whether the driving velocity is less than or greater than some critical velocity v_c, characteristic for the film (discussed later). We consider each of these in turn.

2.6. $(T > T_F$ and $v \ll v_c)$ freezing transition (to stick–slip friction)

During the slipping regime the slip velocity v_x approaches the stage velocity v. If v is less than the critical velocity v_c, then even though the surfaces are still moving relative to

each other, the film will suddenly refreeze at time $T = T_F$ (figures 2 and 3). Freezing is accompanied by an abrupt decrease in D, an increase in S, and the repinning of the two surfaces to each other. The surfaces once again find themselves in the 'sticking regime'. However, the initial 'refrozen' configuration generally retains some disorder, and slower molecular relaxations and rearrangements towards true equilibrium continue to occur in the film even as the surfaces have become pinned to each other (see the D and S curves in figure 3 just after T_F). Apart from that the sticking regime is much the same as before, except that now different regions of the two surfaces are facing each other. Note that during a slip two surfaces are more likely to move by many microns or even large macroscopic distances relative to each other rather than by one lattice spacing. The latter situation arises only when K is very high so that F relaxes immediately after slip occurs.

2.7. ($T > T_F$ and $v \gg v_c$) sliding regime

The stage velocity v is too high for the slip velocity to fall to the critical value v_c needed for a freezing transition to occur. There is no freezing at $T = T_F$ and all the properties continue to vary smoothly towards their steady state values (see dashed lines in figure 3). The stress settles down to some constant value, the sliding velocity v_x (previously the decaying slip velocity) is now constant and equal to v (given by the slope of the x-curve in figure 3), and both D and S settle at some constant values different from those at rest.

2.8. ($T > T_F$ and v near v_c) erratic friction

If the stage velocity v is not constant but is gradually increased from below v_c to above v_c, the transition from stick–slip to smooth sliding can occur in a number of ways, depending on the system and the type of liquid in the film. These are shown in figure 4. In general, as v increases the stick–slip frequency first increases (figure 4(b)) and then becomes erratic but the amplitude of the spikes does not change. Thus the 'static friction' (F_s) and the 'kinetic friction' (F_k) remain largely unchanged, as shown in figure 4(c). In the case of mica across simple spherical liquids the stick–slip then vanishes abruptly above the critical velocity v_c, and the friction becomes smooth and equal to the kinetic value, F_k. With more complex liquids, e.g., short chain molecules, the transition is less abrupt. In such cases both the amplitude and frequency of the spikes becomes progressively more erratic (figure 4(d)): the mean amplitude falls and the mean time between spikes increases, until at $v \geqslant v_c$ the sliding is essentially smooth but still punctuated by isolated stochastic spikes (figure 4(e)). With even more asymmetric molecules, such as branched isoparaffins and polymer melts, no regular spikes or stick–slip behaviour occurs at any speed since these molecules can never order themselves sufficiently to 'solidify'. Examples of such liquids are perfluoropolyethers and polydimethylsiloxanes (PDMS).

A novel interpretation of the well known phenomenon of decreasing coefficient of friction with increasing sliding velocity has been proposed by Thompson and Robbins [7] based on their computer simulation which essentially reproduced the above scenario. This postulates that it is not the friction that changes with v, but rather the time various parts of the system spend in the sticking and sliding modes. In other words, at any instant during sliding the friction at any local region is always F_s or F_k, corresponding to the 'static' or 'kinetic' values of figure 4(c). The measured frictional force, however, is the

Table 1. Tribological characteristics of some liquids and polymer melts in molecularly thin films between two shearing mica surfaces. Note that a low friction coefficient is generally associated with a high bulk viscosity.

Liquid (dry)	Type of sliding	Friction coefficient	Bulk viscosity (cP)
Spherical molecules			
Cyclohexane ($\sigma = 5$ Å)	stick–slip	$\geqslant 1$ (quantized)	0.6
OMCTS ($\sigma = 9$ Å)	stick–slip	$\geqslant 1$ (quantized)	2.35
Chain molecules			
Octane	stick–slip	1.5	0.5
Tetradecane	stick–slip	1.0	2.3
Octadecane (branched)	(stick–slip)	0.35	5.5
PDMS ($M = 3700$)	smooth	0.42	50
PBD ($M = 3500$, branched)	smooth	0.03	800
Water/mixtures			
Water, KCl solution	smooth	0.01–0.03	1
Hydrocarbon liquids (wet)	smooth	0.03	~ 1

sum of all these discrete values averaged over the whole contact area. Since as v increases each local region spends more time in the sliding regime (F_k) and less in the sticking regime (F_s) the overall friction coefficient falls.

The above scenario is already quite complicated, and yet this is the situation for the simplest type of experimental system. The factors that determine the critical velocity v_c depend on the type of liquids between the surfaces. Small spherical molecules such as cyclohexane and OMCTS have been found to have very high v_c, which indicates that these molecules can rearrange relatively quickly in thin films. Chain molecules and especially branched chain molecules have been found to have much lower v_c, which is to be expected, and such liquids tend to slide smoothly rather than in a stick–slip fashion (see table 1). However, the values of v_c also depend on number of liquid layers comprising the film, the structure and relative orientation of the two surface lattices, the externally applied load, and of course on the stiffness of the spring (and in practice of the material of the surfaces).

Seven organic and polymeric liquids have been studied so far [6, 8, 9]. These are listed in table 1, together with the type of sliding observed, the friction coefficient, and the bulk viscosity of the liquids (given for reference purposes).

From the data of table 1 (top part) it appears that there is a direct correlation between the shapes of molecules and their coefficient of friction. Small spherical or chain molecules have high friction with stick–slip because they can pack into ordered solid-like layers, whereas longer chained and branched molecules give low friction and smoother sliding. It is interesting to note that the friction coefficient generally decreases as the bulk viscosity of the liquids increases. This is because the factors that are conducive to low friction are generally conducive to high viscosity. Thus, molecules with side groups such as branched alkanes and polymer melts usually have higher bulk viscosities than their linear homologues for obvious reasons. However, in thin films the linear molecules have higher shear stresses. It is probably for this reason that branched liquid molecules are better lubricants—being more disordered in thin films because of this branching. In this respect it is important to note that if an 'effective' viscosity were to be

calculated for the liquids of table 1, the values would be 10^6 to 100 times the bulk viscosities (10^6 for cyclohexane, 100 for PBD). This indicates that the bulk viscosity plays no direct role in determining the frictional forces in such ultrathin films. However, the bulk viscosity should give an indication of the lowest possible viscosity that might be attained in such films. Based on this hypothesis we may surmise that friction coefficients as low as 10^{-4}–10^{-3} might be attainable with the right system.

The only exception to the above correlations is water, which has been found to exhibit both low viscosity and low friction, yet water is essentially a small spherical molecule. In addition, the presence of water can drastically lower the friction and eliminate the stick–slip of hydrocarbon liquids when the sliding surfaces are hydrophilic. On the other hand, we have noted that with certain (hydrophobic) surfactant-coated monolayer surfaces and polymer melts the presence of water can act very differently, e.g. enhancing stick–slip. However, our results with monolayers and other surfaces are too few and too preliminary to allow us to draw any general conclusions at this stage.

3. Summary and conclusions

The properties of molecularly thin liquid films between two surfaces depend not only on the types of forces between the liquids and surfaces, but also on the atomic structure of the confining surfaces and how easily the liquid molecules can order relative to the surfaces. Both the static and dynamic properties can be quantized with the number of molecular layers comprising the film, and these properties as well as the number of layers can depend not only on the structure of the liquid and surfaces but also on the externally applied load, the sliding velocity, the direction of sliding, the elastic properties of the material confining the films, etc. Many of these properties cannot be described, even qualitatively, by conventional parameters, such as viscosity or elasticity modulus, normally applied to bulk liquids or solids.

The results show that liquid molecules in thin films can freeze into solid-like structures or adopt properties more like thermotropic liquid crystals. The results also show that during normal sliding the films may undergo many freezing–melting cycles per second (solid–liquid–solid transitions). From our studies it appears that for such stick–slip behaviour to occur there must be good geometric compatibility between the shapes of the liquid molecules and the structure of the confining surfaces, and also that the forces between the two surfaces across the liquid be attractive (i.e., adhesive).

Our findings pose some interesting fundamental and potentially important questions such as: during boundary friction or during the shearing of two metallic junctions do the molecules within the sheared interfacial layers behave as a liquid (moving via Brownian diffusion), as a plastically deforming solid (moving via dislocations, disclinations or galling), or is the motion accomplished by completely different mechanisms? Clearly, there are many interesting new phenomena still to be discovered concerning the properties of liquids in ultrathin films.

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