

Critique of the Friction Coefficient Concept for Wet (Lubricated) Sliding†

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Complications in the traditional definitions of static and kinetic friction are discussed as they pertain to lubricated sliding. First, we discuss rate criteria to observe stick–slip motion and show that stick–slip occurs only when thin liquid films are deformed faster than their intrinsic relaxation time. This conclusion comes from experiments with confined aqueous films in a surface forces apparatus modified to measure interfacial rheology. The observation offers a new strategy to look for methods to avoid stick–slip motion by engineering the relaxation time of a confined fluid. Second, we consider the issue of transients and show, for the case of a polymer melt of PDMS (polydimethylsiloxane), that equilibration of the viscous forces was spectacularly slow to be achieved when the sliding velocity was changed. Overshoots of force were observed when the velocity was raised; undershoots of force were observed when the velocity was lowered. Third, we consider the question of how forces in the shear and normal directions are coupled. In systems comprised of polymer brushes in solution at near Θ solvent quality, we contrast the shear response for brush–brush sliding (both surfaces coated with end-attached polymer chains) and brush–mica sliding (one sole surface coated with end-attached polymer chains). Both systems gave nearly the same resistance to compression in the normal direction, but the latter system offered less shear resistance. The polymer brush experiments invite further theoretical interpretation.

Introduction—Classical Views of Friction

Much of the vocabulary to describe friction comes from years long gone. Leonardo da Vinci, Coulomb, and other intellectual giants defined the notions of static and kinetic friction in the midst of the explosive technological advances of those ages. The intellectual history of this is beautifully described by Dowson.¹ The fundamental distinction between static and kinetic friction^{2,3} is now taught even in secondary schools. The view holds that solid surfaces, when impelled to slide over one another, remain stuck until a critical force is overcome (the “static friction”) and thereafter slide with a friction force (the “kinetic friction”) that is independent of velocity. This classical view of friction is summarized schematically in Figure 1. The term, “friction coefficient,” derives from this point of view and refers to the experimental observation that, in dry sliding, the slope of force with normal load is often constant or nearly so.

It is fascinating to see that, largely independently of this, we know from everyday experience that friction can be regulated by oils. Sophisticated solutions of the Reynolds lubrication equation have evolved to explain friction on the basis of the continuum flow of liquids.³ The fundamental view here is that liquids resist deformation with force that *increases* with velocity. The dependence of force on velocity is linear for the simplest case (said to be “Newtonian” because the idea goes back to Isaac Newton). Even modern treatments consider that when velocity is increased, the force required to accomplish this increases with positive slope. When the slope is positive but less than unity, the liquid is said to “shear thin”.⁴

Recent experiments and simulations show that even the simplest Newtonian fluids (as concerns their bulk

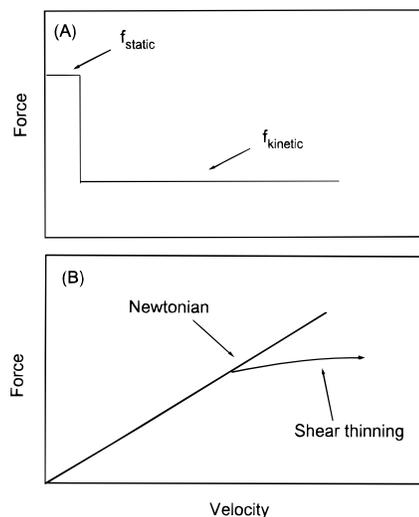


Figure 1. Schematic diagram in which the classical notions of friction (A) and fluid flow (B) are contrasted. As velocity approaches zero, the force required to slide approaches either a yield force, f_{static} (A) or zero (B). At finite velocity the viscous force required to slide either is velocity independent, with level f_{kinetic} (A), or increases with increasing velocity (B). If viscous force increases but less strongly than proportional to increases in velocity (B), the fluid is said to “shear thin”.

properties) are not totally expelled from between two solid surfaces when they are pressed together.⁵ In fact even the original experiments of centuries gone by, upon which the distinction between static and kinetic friction was based, involved solid surfaces in the presence of adventitious condensation from the ambient atmosphere and even solid surfaces with lubricants added deliberately.¹ This paradoxical consideration raises interesting questions of how to reconcile the two viewpoints: those based on solid friction and those based on fluid flow.

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Our motivation to pose these questions arises from recent experiments on idealized molecularly-smooth surfaces whose real contact area and separation could be directly measured *during* sliding. Most of this type of research has been done using the surface forces apparatus technique (SFA) involving independent researchers in different laboratories. In the SFA, the interaction forces between two curved, molecularly smooth surfaces are directly measured. The crossed cylinder geometry is equivalent to two spheres or to a sphere on a flat surface and thus mimics a single asperity contact. Typical surface radii are $R = 0.12$ cm, and typical contact diameters are 10–100 μm (depending on the applied load). An optical interference technique is used in which white light is passed normally through the interacting surfaces. The emerging beam is focused onto the slit of a grating spectrometer which splits up the beam into different wavelengths. This produces a series of colored fringes ("FECO fringes"—fringes of equal chromatic order) that provide a means for directly visualizing the surfaces, giving their shape and surface separation (to within ± 1 –2 \AA) and, for surfaces in contact, their exact area of contact (to $\pm 5\%$). The SFA can be used to measure both normal and lateral (shear) forces and normal pressures, under both static and dynamic conditions, and it is particularly well-suited for studying the structure of and interactions generated by thin liquid films between surfaces.

Modification of a surface force apparatus to measure dynamic oscillatory shear forces by use of piezoelectric elements was described previously.^{6,7} Briefly, to apply controlled shear motion in a surface forces apparatus, one surface was suspended as a boat from two piezoelectric bimorphs. Sinusoidal shear forces were applied to one piezoelectric bimorph, and the resulting displacement was monitored by a second piezoelectric bimorph by use of a sensitive lock-in amplifier. The method to separate apparatus compliance from true friction response, essentially by separate calibration of the apparatus response, was described in detail previously.⁷

The aims of this essay are, on the basis of this recent experimental data, to discuss (1) how far the classical views of friction apply to fluids under conditions of extreme confinement, as occurs during tribological processes, (2) to discuss how to link up, if possible, the classical views of dry friction with recent observations for wet friction in an atomically smooth sliding surface, and (3) to suggest improved approaches for interpreting these observations.

Relevance of Relaxation Time to Friction Experiments

Experiments show that, when the thickness of a liquid is reduced toward molecular dimensions, the times for the relaxation of shear stress are prolonged and nonlinear effects are set in at progressively lower shear rates for thinner and thinner films.⁸ It is even common to observe that the relaxation time slows to the point that the liquid seems to be solid over the accessible time scales.^{9,10} Various conflicting views have been advanced to explain this, but without resolution regarding the thermodynamic state of the observed solidity.¹ Recent experiments go a long way toward explaining the origin of the transition from the static to the kinetic state, however.

The key point is whether the fluid's relaxation time falls within the window of experimental deformation rates.

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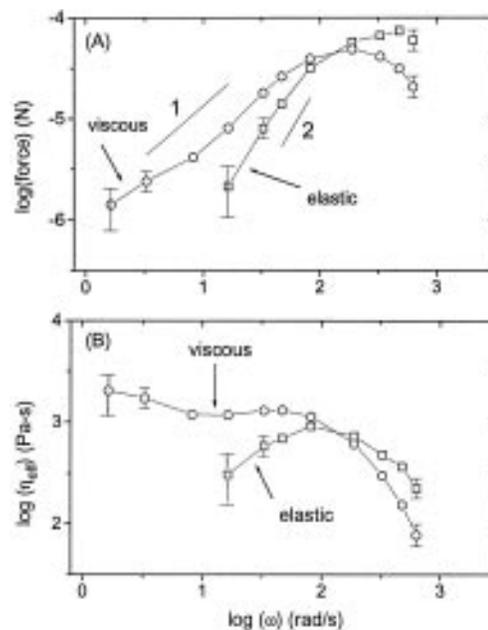


Figure 2. Two alternative representations of the frequency spectrum of linear viscoelastic response for aqueous MgCl_2 (100 mM concentration) confined between mica surfaces at thickness 0.6 ± 0.2 nm and contact area 2.6×10^{-9} m². (A) Raw force data for the constant deflection of 1 \AA . The viscous force (circles) and elastic force (squares) are plotted against radian frequency (ω) on log–log scales. The logarithmic slopes of +1 and +2 are the classical response of a fluid of constant viscosity. (B) Effective viscosity calculated from the raw data in part A. At frequencies below 100 rad/s the viscous component of viscosity (which measures the component of force that is in phase with the rate of deformation) is independent of frequency within the experimental uncertainty, indicating Newtonian behavior. But at higher frequencies the elastic component (which measures the component of force that is in phase with the absolute deformation) dominates.

An example follows. Figure 2A shows force (of small-amplitude linear response shear vibrations) plotted against drive frequency for aqueous films of MgCl_2 (concentration of 0.1 M) confined between mica surfaces to a thickness of 6 \AA . The scales are logarithmic. One observes that these forces are partially in phase with the shear deformations and partially in phase with the rate of deformation (i.e. 90° out of phase with the absolute shear deformation). Stated in another way, the forces are elastic and viscous, respectively, as indicated in Figure 2A. The frequency (ω) at which the elastic and viscous forces take the same magnitude defines the system's inverse longest relaxation time, $\omega = 1/\tau_1$.

These raw data were normalized to define an effective viscosity:

$$\eta_{\text{eff}} = FD/AV \quad (1)$$

Here, just as for the deformation of viscoelastic liquids in the bulk,⁴ F is force, D is film thickness, A is the true contact area (measured by multiple beam interferometry), and V is the peak deformation velocity, equal to the deformation frequency times the deformation amplitude.⁸ In Figure 2B, one sees that the viscous component of viscosity (in phase with the rate of deformation) dominated at the lower frequencies but that the elastic component dominated when the frequency was high. Stated in another way, the predominant force was proportional to the rate of deformation at low frequency but proportional to the absolute deformation when the frequency was high. Similar observations are familiar in many other well-known situations for other viscoelastic liquids.⁴ Other

experiments in this laboratory show that observation to be general: the relaxation times of even liquids that obey Newtonian behavior in the bulk are enormously prolonged when these liquids form thin films between solid surfaces. When they form thin films, they continue to deform as liquids, provided that the rate of deformation is sufficiently low. But above a critical frequency they deform as elastic solids instead.

Rate Criterion for the Stick–Slip Transition

When the distance slid greatly exceeds the thickness of an interfacial liquid film, the structure of this film cannot support static friction and must rearrange to allow a kinetic state. This may happen either by monotonic gradual rearrangement, as in shear thinning,^{4,8} or by intervention of the discontinuity of the shear response.^{11,12}

Well-known as a phenomenon in the engineering literature,³ the origin of the discontinuous start up of motion has been revisited in the modern literature. To explain stick–slip, the hypothesis has been advanced that sliding involves a dynamic phase transition in some kind of thermodynamic sense, some kind of shear-induced melting from a crystalline or glassy phase.^{13–16}

A contrary interpretation is suggested by the experiments shown in Figure 3 (they concern the same system whose small-deformation response is shown in Figure 2). In these experiments, it emerged that flow was fluid-like only when the frequency was less than the inverse natural relaxation time. To make these measurements, the force amplitude was increased past the point of linear response with the forcing frequency held constant. For low frequencies ($\omega < 1/\tau_1$) only dissipation resulted, as expected since the linear response was that of a liquid at this frequency. Figure 3A shows that the viscous force, proportional to shear rate (small deformations), subsequently increased more slowly, in the classical “shear thinning” manner of a viscous liquid.

In contrast to this, when the drive frequency was high relative to the natural relaxation time ($\omega > 1/\tau_1$), Figure 3B shows that the system switched from a predominantly elastic response (small deformations) to a predominantly viscous response (large deformations). This switch was accompanied by an abrupt jump in the distance slid in response to a given force, and in this sense the liquid displayed “stick–slip”.

The physical interpretation is that when the liquid was deformed faster than it could keep up, elastic forces built up to the point that catastrophic rupture intervened. The observed connection between stick–slip and forced motion at a rate that exceeded the inverse natural relaxation time has implications for predicting the onset of stick–slip behavior.

It is interesting to assess proposed theories of stick–slip in light of these observations. Stick–slip motion has been interpreted to signify that friction decreases with increasing distance traversed or velocity;³ however, this assertion does not include a mechanistic interpretation and provides no guide to predict the frequency or shear rate at which the effect will be observed. Another traditional explanation, in terms of the mechanical interlocking of rough surfaces, can be discounted since

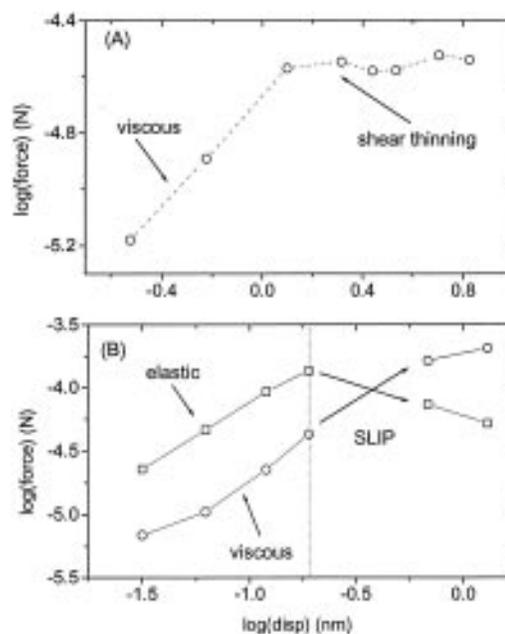


Figure 3. Contrast of sliding behavior at large deformation when the frequency is low relative to the inverse relaxation time of the confined fluid (A) and when the frequency is large relative to this (B). The system is the same as for Figure 2, aqueous MgCl_2 (100 mM) confined between mica surfaces at thickness 0.6 ± 0.2 nm and contact area 2.6×10^{-9} m². (A) At shear frequency 1 Hz, raw shear force data are plotted against sinusoidal displacement amplitude on log–log scales. Only the viscous component of force is measurable (any in-phase elastic component is less than the experimental uncertainty), indicating that the viscous force changes in response to shear rate (product of the sinusoidal displacement and the frequency).⁸ The viscous force grew in proportion to the shear rate when this was low but displayed shear thinning when the shear rate was large, as indicated in the figure. (B) At shear frequency 100 Hz, raw shear force data are plotted against sinusoidal displacement amplitude on log–log scales. The elastic component of force (in phase with the displacement) exceeded the viscous component (in phase with the rate of displacement) by nearly an order of magnitude when the displacement was small and increased in proportion to the displacement amplitude. Beyond a displacement amplitude of 4 Å there ensued a stick–slip transition, as described in the text. At larger shear amplitudes the viscous forces dominated.

these atomically-smooth surfaces were separated by water molecules. The more recent theory has been that confinement induces crystallization or some other phase change^{13–16} at rest; discontinuities when motion is forced are attributed to shear melting or some other shear-induced phase transition. However, these confined aqueous films were demonstrably in a fluid state to start with. Only when sheared faster than the natural relaxation time did they display discontinuous motion.

In fact, analogous phenomena are familiar in common experience when a fluid's natural relaxation time falls within the experimental window. Consider, for example, silly putty, honey, or tar. It is common experience that these fluids flow as liquids if a piece is pulled in opposite directions slowly but break into two if pulled in opposite directions rapidly. Of course this rate dependence could be described by some postulated relation between force and velocity that would imply instability when the velocity was high; but the description would risk being circular, being based on the postulated assumption. The new point is that the point of unstable motion was predictable on the basis of knowing the natural relaxation time of the confined fluid film.

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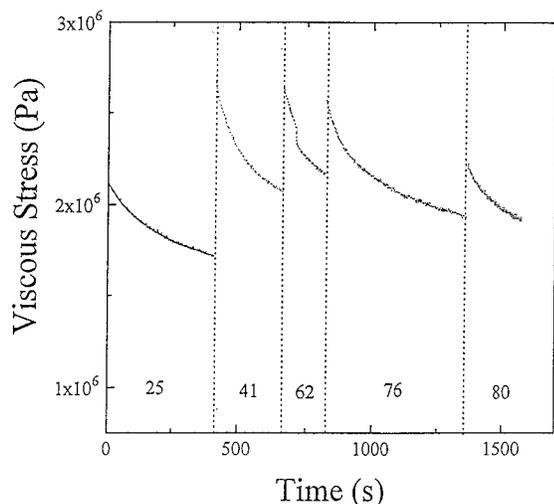


Figure 4. Viscous stress (stress is defined as force normalized by the area of contact) plotted against elapsed time after a sudden increase of oscillatory strain amplitude at 250 Hz. The system is polydimethylsiloxane (PDMS) confined between mica surfaces to a thickness of 30 Å. The number-average molecular weight is $M_n = 14\,760$. The ratio of number-average to weight-average molecular weight is $M_w/M_n = 1.11$. Measurements were taken with increasing strain amplitude (where strain is defined as the amplitude of oscillation divided by the film thickness of 30 Å). The dotted lines indicate a sudden increase of strain to the value (from 25 to 80) specified near the bottom of the figure.

Dependence of the Kinetic Friction on Velocity History

Long-lived transient behavior is often observed when the sliding velocity (or driving force) is switched from one level to another. This is another consequence of the fact that the transition to kinetic sliding involves modification of the interfacial fluid structure. In other words, shear-induced rearrangements of confined fluids can take spectacularly long times to be accomplished. In these cases, friction force is not sufficiently well-defined by specifying the velocity alone.

To illustrate the point, we consider a polymer melt of methyl-terminated PDMS (polydimethylsiloxane) of roughly 400 monomeric repeat units (a detailed specification of the sample is given in the figure caption). The unperturbed radius of gyration of PDMS of this molecular weight is 37 Å.¹⁷ On the basis of the known viscosity of the bulk fluid, the longest relaxation time of the bulk fluid is estimated to be 6×10^{-7} s.¹⁷

This polymer was first compressed to a film thickness of 30 Å; then sinusoidal shear of progressively increasing amplitude was applied at 250 Hz, with an amplitude from 25 to 80 times the film thickness. When sinusoidal shear amplitude so far exceeds the film thickness, the oscillatory experiment resembles an experiment at constant velocity, as discussed elsewhere.⁸ In Figure 4 the measured viscous stress (force 90° out of phase with the drive at 250 Hz and normalized by the contact area) is plotted against elapsed time. One observes that, even after equilibration of hundreds of seconds, the stress continued to change, indicating that steady state was not yet reached. The nature of the time dependence was an *overshoot* of the measured stresses as the distance of sliding (proportional to the velocity) was increased.

The converse situation, in which the effects of progressively lessening the shear amplitude were explored, is shown in Figure 5. In this case the nature of the

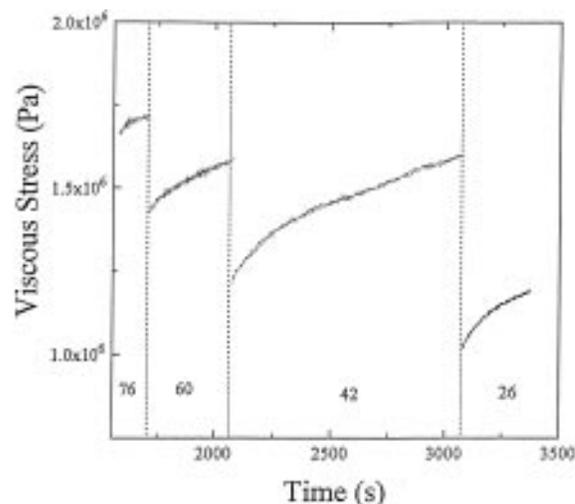


Figure 5. Viscous stress (stress is defined as force normalized by the area of contact) plotted against elapsed time after a sudden decrease of oscillatory strain amplitude. The system is the same as in Figure 4. Measurements were taken with decreasing strain amplitude (where strain is defined as the amplitude of oscillation divided by the film thickness of 30 Å). The dotted lines indicate a sudden decrease of strain to the value (from 76 to 26) specified near the bottom of the figure.

equilibration was an *undershoot* of the measured stresses as the distance of sliding (proportional to the velocity) was decreased. The measured viscous stress slowly *increased* with equilibration time at a specified new state.

The likely mechanism involves changes in the degree to which the polymer chains became aligned in the direction of flow and bridged the two solid surfaces.¹⁸ Analogous long transient effects, but over somewhat shorter time scales, are also observed even for small alkane chains when sliding velocity (or amplitude) is suddenly changed.

Coupling between Shear and Normal Forces

Statement of the Problem. This problem is exemplified by the interesting history of molecular dynamics (MD) simulations of Lennard-Jones particles confined to a molecular thickness between two parallel solid surfaces.^{5,13-16,19} It is now well understood that a liquid film supports a state of normal stress when the thickness is comparable to molecular dimensions; the film thickness adjusts to externally applied normal pressure because the liquid organizes into strata parallel to the surface. This is analogous to the radial distribution function of bulk liquids.^{5,13-16,19} But the initial simulations to explore consequences for diffusion and shear viscosity, employing solid surfaces that were modeled without structure in the plane, found minimal perturbations from bulk values.¹⁹ Only by allowing for atomic structure in the plane of the surfaces and incorporating this into the simulation model did these studies predict confinement-induced crystallization or vitrification.¹³⁻¹⁶ The moral of the story is that the normal forces were essentially the same for the two computer models, but the implied shear forces (and ensuing "friction") were qualitatively different.

A second thought experiment also illustrates this puzzle. Imagine that two solid surfaces, each with the same large electrical charge, are impelled to slide past one another while separated by a simple Newtonian fluid. Obviously

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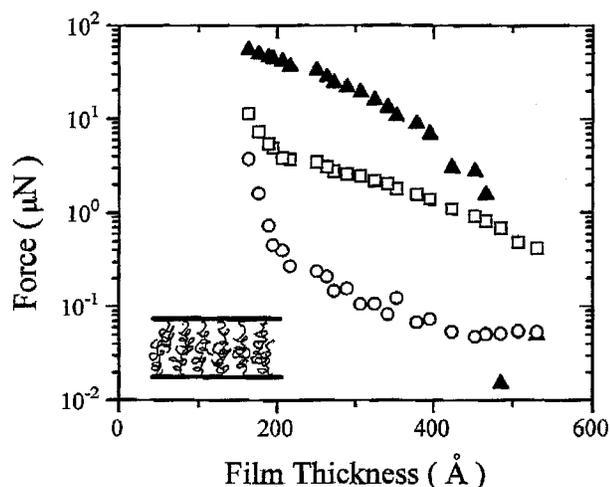


Figure 6. Dynamic forces in the shear direction (1 Hz, 5 Å displacement) and normal directions (static forces) contrasted for opposed PS–PVP (polystyrene–polyvinylpyridine) polymer brushes in *trans*-decalin at 24 °C. Forces are plotted against film thickness on semilogarithmic scales. The molecular weights of the diblock copolymer were 55 400 g mol⁻¹ (PS block) and 9200 g mol⁻¹ (PVP block). The ratio of weight-average to number-average molecular weight was $M_w/M_n = 1.05$. On the basis of the measured thickness of the polymer layers after drying the solvent, the average density between grafting sites was measured to be 54 Å, a number much less than the unperturbed brush thickness: (black triangles) static repulsive forces; (circles) shear viscous forces; (squares) shear viscous forces. Inset: schematic diagram of overlapping polymer brushes when compressed together.

the friction forces depend on the fluid viscosity and the shear rate, but the normal forces depend on electrostatic repulsion. Clearly, in this example also, the origins of the shear and normal forces are unrelated.

Contrast of Brush–Brush and Brush–Mica Systems. Analogous problems can arise in the case of sheared polymer brushes in solution. The configurational properties of polymer brushes are so well understood²⁰ that they present an attractive system in which to seek to relate structure and friction.²¹

A polymer system of near Θ solvent quality was selected. Details of the samples are given in the caption of Figure 6. In a manipulation performed outside the surface forces apparatus, the PS–PVP (polystyrene–polyvinylpyridine) samples of diblock copolymer were allowed to adsorb onto mica from dilute solution in toluene below the critical micelle concentration. The PVP adsorbs strongly while the PS block extends into solution. The coated surfaces were then placed within the surface forces apparatus, and a droplet of *trans*-decalin was placed between them. Experiments were conducted at 24 °C, which is ≈ 4 °C above the Θ temperature of a bulk PS solution in *trans*-decalin.

In Figure 6, the normal forces and shear forces (at fixed frequency, 1 Hz) are plotted against film thickness. The measurements correspond to shear displacements of only 5 Å, small enough to obtain a linear response, in which the force is strictly proportional to the displacement and the act of measurement does not perturb the film structure. The repulsive force–distance profiles showed that the polymer brushes began to overlap at the film thickness of 560 Å, as also shown in Figure 6. The force–distance profile fit quantitatively the well-known theoretical expressions.²⁰

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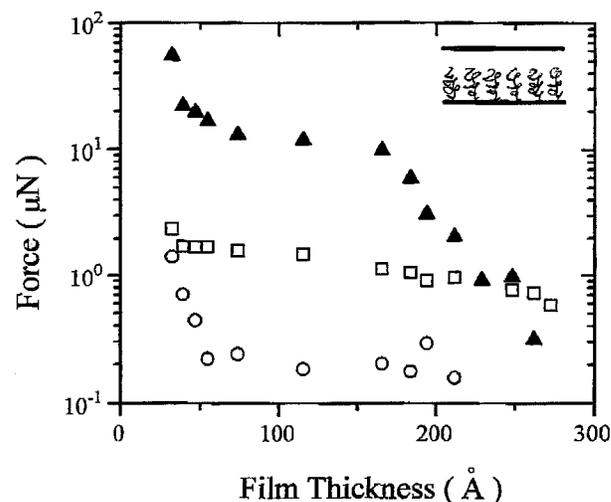


Figure 7. Dynamic forces in the shear direction (1 Hz, 5 Å displacement) and normal directions (static forces) contrasted for PS–PVP (polystyrene–polyvinylpyridine) polymer brushes opposed to a bare mica surface in *trans*-decalin at 24 °C. Forces are plotted against film thickness on semilogarithmic scales. Except for this asymmetry, all conditions and symbols are the same as for the brush–brush case shown in Figure 5. Inset: schematic diagram of polymer brush opposed to bare mica.

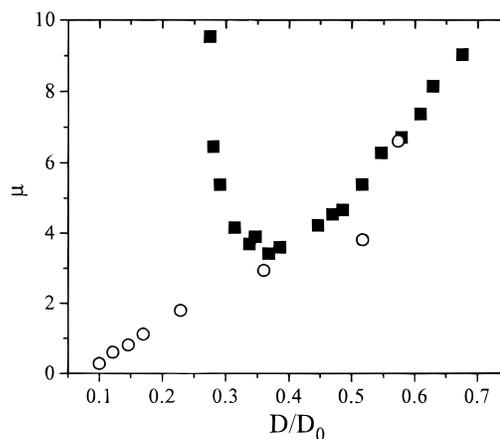


Figure 8. Thickness dependence of the small-amplitude friction coefficient, μ , defined as the shear elastic modulus at 1 Hz divided by the normal pressure. In the thickness scale, the actual thickness, D , is normalized by the film thickness at the onset of repulsive static forces, D_0 . The symbols refer to brush–brush contact (squares) and brush–mica contact (circles). Note that in brush–brush experiments D_0 was twice that for brush–mica experiments.

Analogous experiments were then performed in which the PS–PVP brush coated only one of the opposed surfaces. In this case the static force–distance profiles were again in reasonable agreement with the classical theory,²⁰ as expected since these theories for the origins of static forces do not distinguish the cases of brush–brush and brush–mica contact.

In Figure 7, the normal and shear forces (at fixed frequency, 1 Hz) are plotted against film thickness for brush–mica experiments. Again the data refer to a shear displacement of 5 Å. While the forces in Figures 6 and 7 may appear similar on logarithmic scales, Figure 8 (see discussion below) reveals qualitative differences.

Inspection of Figures 6 and 7 suggests limitations of the notion of friction coefficient in such systems:

(1) First, the normal and shear forces increased by orders of magnitude as the films were compressed, but these changes did not proceed in step with one another.

(2) Second, in comparing these two systems at the same level of normal force, the shear forces differed.

(3) Third, the ratio of viscous to elastic forces changed as the films were compressed. This indicates that the longest relaxation time (indeed, the entire spectrum of viscoelastic relaxation) shifted with increasing compression. Just as for the system discussed in connection with Figure 3, this carries implications for predicting the onset of stick–slip behavior.

Small-Strain Friction Coefficient. In order to compare shear and normal forces more quantitatively under conditions of linear response, the elastic and viscous shear forces were normalized, by the displacement amplitude and the effective area of contact, to give the effective shear moduli.⁷ The static repulsive forces were normalized by the effective area of contact to give normal pressure.⁷ The methods to do this are described in detail elsewhere.⁷ Having performed the normalization, it was meaningful to compare the dimensionless ratio of elastic shear modulus to normal pressure for the data in Figures 6 and 7.

The resulting small-strain friction coefficient, μ , is plotted against film thickness in Figure 8. The key points are two. First, the friction coefficient was decidedly not constant with normal load (i.e. film thickness). It decreased with increasing normal load when the compression was weak, indicating that normal forces increased more rapidly than shear forces. But at higher compression this pattern switched: the changes with normal load, for the brush–brush and the brush–mica systems, were in opposite directions.

The experiment also shows that both films presented greater elastic resistance to shear than to compression; the small-strain friction coefficient exceeded unity. The exception was the brush–mica case at high compression, presumably indicating that the polymer chains could slide more readily across the atomically-smooth, nonadsorbing mica surface than against an opposing brush layer.

These phenomenon can probably be understood as a consequence of interpenetration and entanglement of the polymer chains.¹⁸ Quantitative understanding of this linear-response dynamics, based on the known configurations of compressed polymer brushes and the well-developed statistical thermodynamics of long-chain polymers,²⁰ should be possible.

Conclusions

This essay has discussed complications encountered in applying traditional definitions of static and kinetic friction

to lubricated sliding. First, we discussed rate criteria to observe stick–slip motion. On the basis of experiments with confined aqueous films in a surface forces apparatus modified to measure interfacial rheology, stick–slip was shown to occur only when the films were deformed faster than the natural relaxation time. The proposal was advanced that this offers a direction to look, by tailoring the relaxation time of a confined fluid, for methods to avoid stick–slip motion.

Second, the issue of friction transients was discussed. In the case of an oligomeric polymer melt, equilibration of the viscous forces was shown to be spectacularly slow to be achieved when the sliding velocity was changed. Overshoots of force were observed when the velocity was raised; undershoots of force were observed when the velocity was lowered.

Third, we discussed the issue of coupling of forces in the shear and normal directions. In a system of polymer brushes, the shear responses for brush–brush sliding (both surfaces coated with end-attached polymer chains) and for brush–mica sliding (one sole surface coated with end-attached polymer chains) were contrasted. Both systems showed nearly the same resistance to compression in the normal direction, but the latter system offered much less shear resistance. The ratio of elastic shear modulus to normal pressure, defined as the small-strain friction coefficient, changed strongly with the normal load.

These three examples help to clarify the conditions when lubricated sliding will resemble dry sliding (Figure 1A) and when it will resemble fluid flow (Figure 1B). “Dry” sliding is observed if the velocity is infinitely rapid compared to the rate at which the interface reorganizes in response; this trade-off can be quantified by comparing the sliding rate to the system’s Brownian relaxation time. The work with polymer brushes shows further that the relaxation time for equilibration of the forces that resist compression is typically much more rapid than the relaxation time that governs shear displacement, but interpretation of the work with polymer brushes invites theoretical modeling.

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