

# Molecular tribology of lubricants and additives

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Knowledge of the bulk viscosity provides little guidance to predict accurately the interfacial shear strength and effective viscosity of a fluid in a lubricated contact. To quantify these differences between bulk and thin-film viscosity, an instrument was developed to measure the shear of parallel single crystal solids separated by molecularly-thin lubricant films. The effective shear viscosity is enhanced compared to the bulk, relaxation times are prolonged, and nonlinear responses set in at lower shear rates. These effects are more prominent, the thinner the liquid film. Studies with lubricant additives cast doubt on the usefulness of the concept of a friction coefficient for lubricated sliding. © 1998 Elsevier Science Ltd. All rights reserved.

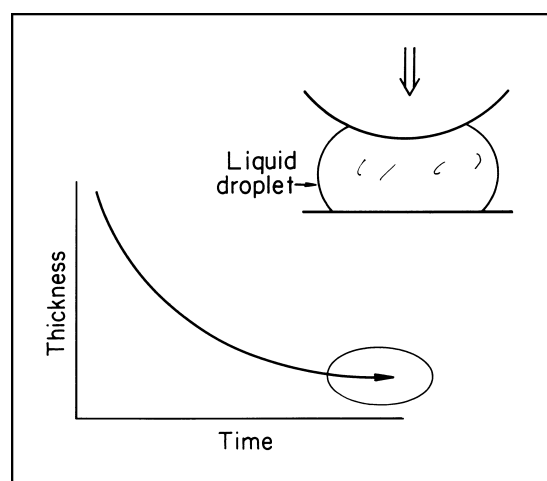
**Keywords:** *nanotribology, friction, SFa, lubricants, nanorheology*

## Introduction

In surveying the present situation, one notices that one of the major difficulties in explaining tribology is the paucity of direct, experimental information concerning dynamic events on a microscopic scale. With macroscopic approaches one can measure, for example, the friction between surfaces (and other global properties) while the surface are actually in contact. Such macroscopic measurements are often difficult to interpret from a molecular point of view. Most of the questions regarding mechanisms are molecular in nature. With microscopic analytical methods, one generally examines surfaces before and after sliding has occurred. As such, these approaches yield incomplete information concerning the many interfacial situations where the presence of a lubricant is an essential part of the physical situation.

A further major problem is to characterize the true contact area and thickness of fluid films during flow. They can be gauged by resistance, capacitance, and other measurements, but of course many distributions of surface roughness are compatible with a given measurement. Furthermore, to the degree that a surface is rough, the surface separation and the thickness of the intervening film must be described by a distribution rather than any single number.

Consider now the canonical experiment depicted in Fig 1. Imagine that one takes a droplet of liquid, puts it between a ball and a table, and lets the ball fall. Of course the liquid squirts out, initially rapidly, then slower and slower as the liquid thickness becomes less than the radius of the ball. This problem was solved



*Fig. 1 Hypothetical experiment showing that a liquid can support a normal force. A liquid droplet is placed between a ball and a flat surface. The graph, in which liquid thickness is plotted schematically against time after the ball has begun to fall, shows that the film thickness remains finite (a few molecular dimensions) even at equilibrium.*

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*Received 12 December 1996; accepted 6 November 1997*

over 100 years ago in the classic analysis of Reynolds.<sup>1</sup> Experiment shows that the film eventually stabilizes at a *finite* thickness of a few molecular diameters.<sup>2</sup> The liquid film supports the weight of the ball! Of course the heavier the ball, the less the ultimate thickness of the liquid film, but this is a general result: an extraordinarily large pressure is needed to squeeze out the final few layers of liquid between two solid surfaces. This experiment shows that when the thickness of a liquid film becomes comparable to molecular dimensions, classical intuition based on continuum properties no longer applies.

In this rapidly developing area, the experimental picture that has emerged to date is summarized in Fig 2. Energy dissipation of a fluid film is sketched schematically against thickness of the lubricant film. When the film is sufficiently thick ( $\mu\text{m}$  or more), it obeys well-known continuum relations. At smaller film thickness (in the order of nm) the effective viscosity rises, and the characteristic relaxation times are prolonged. At still smaller film thickness (in the order of  $\text{\AA}$  to nm), the films become solid-like in the sense that sliding does not occur unless a certain shear stress (or "yield stress") is attained.

### Experimental approach

The frequency-dependence of the shear viscosity was measured using an interfacial rheometer described in detail previously.<sup>3</sup> Briefly, a droplet of sample fluid was confined between two anatomically smooth crystals of muscovite mica glued onto crossed cylindrical lenses whose separation was controlled using a surface forces apparatus. The radius of curvature of the mica sheets was  $\approx 2\text{ cm}$ , giving a slit-like geometry for molecularly-thin surface separations. To apply shear, sinusoidal shear forces were applied to one piezoelectric bimorph and the resulting sinusoidal displacement was

monitored by a second piezoelectric bimorph details of the piezoelectric circuitry were described previously.<sup>3</sup> A lock-in amplifier was used to decompose the resulting sinusoidal response into one component in phase with the drive and a second component out of phase with it, giving the elastic and dissipative shear forces as a function of the excitation frequency. Linear response for shear displacements less than 20% of the sample thickness was verified. All experiments were performed with  $\text{P}_2\text{O}_5$  (a highly hygroscopic chemical) inside the sealed sample chamber, so that measurements of thin films would not be complicated by the adsorption of ambient moisture to the hydrophilic solid surfaces. Other experiments with surfaces chemically modified to be hydrophobic have also been performed.<sup>4</sup>

### Interfacial viscosity contrasted with the viscosity of the thick-film viscosity

First we consider the interfacial viscosity of two fluids of nearly the same bulk viscosity. These are samples of perfluoropolyether fluids that are commonly used in the magnetic storage industry: Krytox-AZ (bulk viscosity 0.744 P at 20°C) and Demnum S-20 (bulk viscosity 0.781 P at 20°C).<sup>5</sup>

As smooth solid surfaces of mica separated by these two fluids were pushed together, fluid drained smoothly until repulsive forces appeared at a thickness of roughly five times the molecular size.<sup>5</sup> These forces arise from entropic elasticity as chain molecules, anchored to the solid surfaces by adsorption, are compressed. The fluid supported a normal load.<sup>5,6</sup>

To quantify the effective viscosity, a useful measure was the dynamic viscosity. The dynamic viscosity, measured when a surface is sheared in oscillatory displacement, is the peak shear stress during a cycle, divided by peak shear rate. The dynamic viscosity has two components: a dissipative component,  $\eta'$ , that is in-phase with the shear rate, and an elastic component,  $\eta''$ , that is in-phase with the displacement amplitude. The dynamic viscosity is commonly used to characterize polymers and other viscoelastic fluids.<sup>7</sup> For a Newtonian fluid (the fluid modelled by the Reynolds equation)  $\eta'$  is frequency-independent and  $\eta'' \approx 0$ .

In Fig 3(A), the effective viscosity of Krytox-AZ is plotted against shear frequency on log-log plots. Fig 3(B) contrasts the response of Demnum S-20. The normal load was small—4 MPa or less. The data show clearly that in both cases the response was decidedly non-Newtonian. The data also show spectacular differences between the two lubricants. The elastic component of effective viscosity dominated for Demnum S-20, but was less by orders of magnitude for Krytox-AZ. Detailed consideration shows that this is correlated with stiction behavior in the former case, but smooth start-up of sliding in the latter case.<sup>5</sup> Measuring the frequency dependence of the dynamic viscosity thus permits one to predict the occurrence (or not) of stiction behavior.

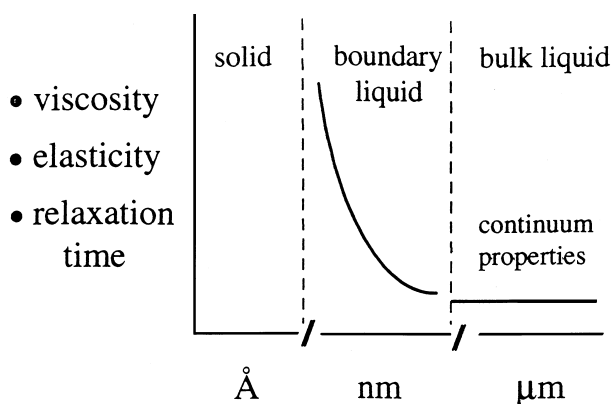


Fig. 2 Schematic diagram of how the effective viscosity depends on thickness of a lubricant film. When the thickness is comparable to the dimensions of the lubricant molecules themselves, the effective viscosity grows with diminishing thickness and diverges when the film thickness is sufficiently small. Classical continuum considerations do not apply. The shear elastic modulus and the longest relaxation time of the fluid structure also diverge with diminishing film thickness. This has consequences for predicting the onset of stiction.

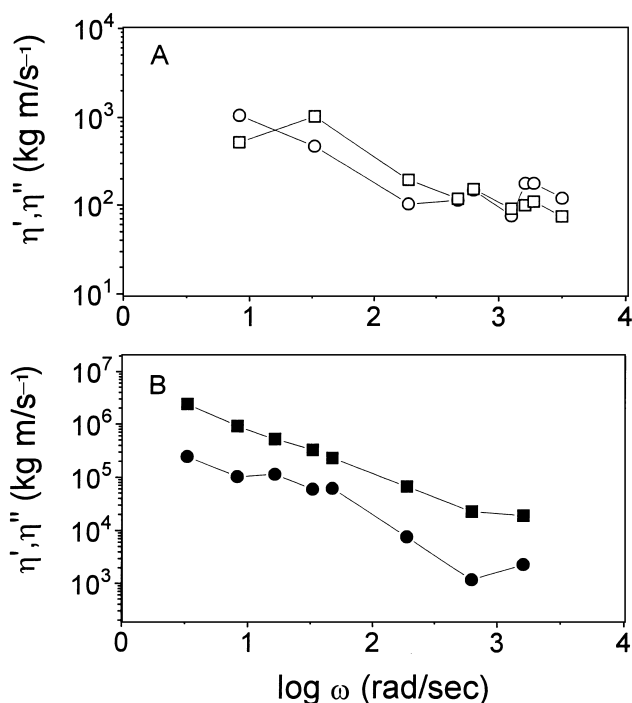


Fig. 3 Comparison of Krytox and Demnum at molecularly-thin spacings between solid surfaces. The viscosity of these fluids is dramatically different although nearly the same, 0.744 P (Krytox-AZ) or 0.781 P (Demnum S-20) in the bulk. Dynamic viscosity is plotted against frequency. Circles denote the dissipative response (in-phase with the shear rate). Squares denote the elastic response (in-phase with the shear amplitude). (A)  $\circ$ ,  $\square$ , Krytox-AZ; (B)  $\bullet$ ,  $\blacksquare$ , Demnum S-20.

#### Microviscosity-dependence on the shear rate

Shear rate can be approximated, for large amplitudes of sinusoidal displacement, to be the product of oscillation amplitude and oscillation frequency.<sup>6</sup> It is of particular interest to consider the dependence of effective viscosity on shear rate for perfluoropolyether fluids, of interest in the magnetic recording and in the aerospace industries. In Fig 4, effective viscosity plotted against effective shear rate on log-log scales. The data refer to the above-mentioned sample of Demnum S-20.<sup>5</sup> Data from two experiments are shown: one at 1.3 Hz, the other at 200 Hz. The closed symbols represent data taken with increasing strain and the open symbols data taken with decreasing strain. In the stick regime, the effective viscosity was constant. After the stick-slip transition from the elastic to the dissipative state, shear thinning was observed. The effective viscosity decreased as a power law in the shear rate, with slope increasing in magnitude (from  $-2/3$  to  $-1$ ) with increasing shear rate. Interestingly, the data of the two experiments at two different frequencies but sufficiently high shear rate extrapolated to fall on the same line.

Various theoretical models predict this result.<sup>8</sup> At higher shear rates, as the limiting shear stress of the lubricant is approached, the power-law of shear thinning approached the slope of  $-1$ , indicating that the dissipative shear stress reached a limiting plateau.<sup>9</sup>

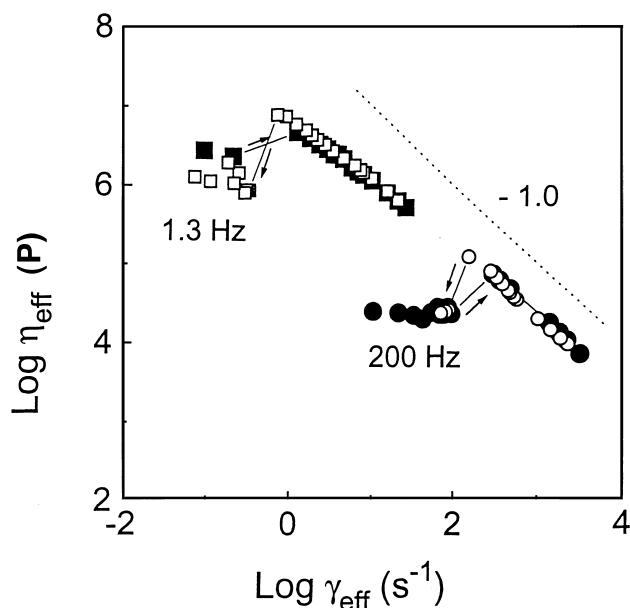


Fig. 4 Effective viscosity of Demnum S-20 plotted against the effective shear rate at two frequencies, 1.3 and 200 Hz.<sup>5</sup> In the stick regime, the effective viscosity was constant. After the stick-slip transition from the elastic to the dissipative state, shear thinning was observed. The effective viscosity decreased as a power law in the shear rate, with slope  $-2/3$  at moderate shear rate and  $-1.0$  at sufficiently large shear rate. Interestingly, the data of the two experiments at two different frequencies but high shear rate extrapolate to fall on the same line.

#### Coupling of forces in the shear and normal directions

This problem is exemplified by the interesting history of molecular dynamics (MD) simulations of Lennard-Jones particles confined to molecular thickness between two parallel solid surfaces. 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. But the initial simulations to explore consequences for diffusion and shear viscosity, employing solid surfaces that were modelled without structure in the plane, found minimal perturbations from bulk values.<sup>10</sup> 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.<sup>11</sup> 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 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 understood<sup>12</sup> that they present an attractive system in which to seek to relate structure and friction. Polymer brushes present a case study of polymer lubrication additives.<sup>13</sup>

A polymer system of near-theta solvent quality was selected. Details of the samples are given in the caption of Fig 5. 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  $\approx 4^\circ\text{C}$  above the theta temperature of a bulk P5 solution in trans-decalin.

In Fig 5, the normal forces and shear forces (at fixed frequency, 1 Hz) are plotted against film thickness. The

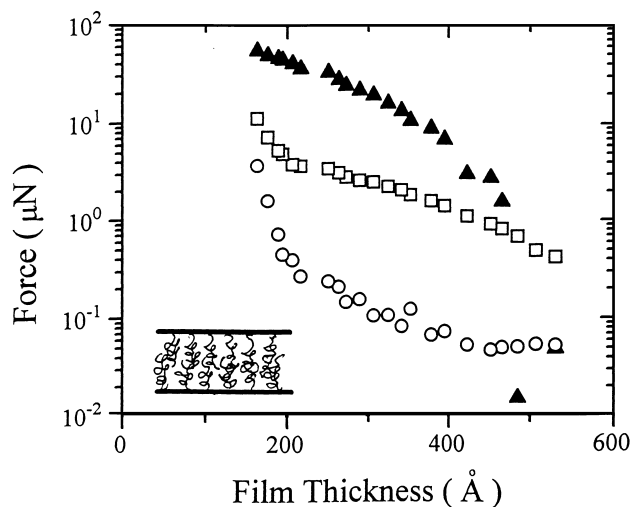


Fig. 5 Dynamic forces in the shear direction (1 Hz, 5 Å displacement) and normal directions (static forces) contrasted for opposed PS–PVP (polystyrene–polyvinylpyridine) polymer brushes in trans-decalin at 24°C. Forces are plotted against film thickness on semi-logarithmic scales.<sup>13</sup> The molecular weights of the diblock copolymer were 55,400 g mol<sup>-1</sup> (PS block) and 9200 g mol<sup>-1</sup> (PVP block). The ratio of weight-average to number-average molecular weight was  $M_w/M_n = 1.05$ . Based on 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. ▲, Static repulsive forces; ○, shear viscous forces; □, shear viscous forces. Inset shows a schematic diagram of overlapping polymer brushes when compressed together.

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 Fig 5. The thickness at a given normal load fit quantitatively the well-known theoretical expressions.<sup>12</sup>

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,<sup>12</sup> as expected since these theories for the origins of static forces do not distinguish the cases of brush–brush and brush–mica contact.

#### 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. The static repulsive forces were normalized by the effective area of contact to give normal pressure. The methods to do this are described in detail elsewhere.<sup>13</sup> Having performed the normalization, it was meaningful to compare the dimensionless ratio, elastic shear modulus to normal pressure.

The resulting small-strain friction coefficient,  $\mu$ , is plotted against film thickness in Fig 6. 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 comparison was weak, indicating that normal forces

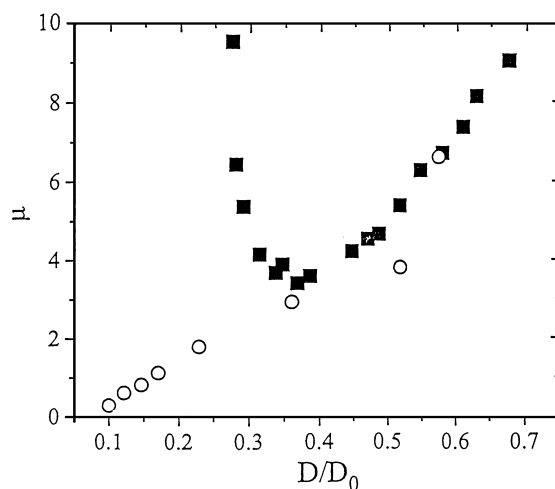


Fig. 6 Thickness dependence of the small-amplitude friction coefficient,  $\mu$ , defined as the shear elastic modulus at 1 Hz divided by the normal pressure. In thickness scale, the actual thickness,  $D$ , is normalized by the film thickness at onset of repulsive static forces,  $D_o$ .<sup>13</sup> ■, Brush–brush contact; and ○, brush–mica contact. Note that, in brush–brush experiments,  $D_o$  was twice that for brush–mica experiments.

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, non-adsorbing 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.<sup>14</sup> 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,<sup>12</sup> should be possible.

## Conclusions and engineering significance

In summary, these experiments show the limits of linear and nonlinear viscous shear response of confined lubricating fluids. It emerges that a boundary can profoundly slow down the dynamics of the liquid state and enhance the effective viscosity. Lubricants with the same bulk viscosity may have very different interfacial viscosity.

One tends to take friction, wear, and tear for granted. While tribology design and tribology-based applications are rooted in our economic life, too often the technologies and formulations are empirically-derived.

On the scientific side, appreciation is growing that scientific understanding is possible of these systems that are so complex and so far from equilibrium. Surfaces in sliding contact are more amenable to rational inquiry than might be feared. Tribology is becoming recognized as an area with many opportunities to do exciting and useful surface science.

The engineering significance is that the flow of these—the simplest fluid lubricants—under extreme confinement could not be understood simply by intuitive extrapolation of bulk properties. Features of specific engineering significance are:

1. *It is possible to predict the film thickness at which these boundary layer effects set in.* The film thickness grows with the strength of attraction between lubricant and solid and in proportion to the molecular size or radius of gyration, unless the surfaces is coated with bonded lubricants.<sup>4,15</sup>
2. *Stick versus slip boundary conditions of lubrication.* Traditionally one solves lubrication problems by assuming the "stick" boundary condition in the Reynolds equation. But this fails, unless the shear rate is exceptionally low when lubricant films are sufficiently thin. This explains why kinetic friction is essentially velocity-independent in boundary lubrication.<sup>16</sup>
3. *The magnitude of static friction force, determined by the yield point of the solidified lubricant, is*

*typical of a "soft" or "waxy" solid.* The significance is that a crystalline or glassy solid had been widely expected from molecular simulations. The engineering implication of this finding is to better understand what determines the magnitude of static friction as well as the magnitude of succeeding kinetic friction. Static friction can be larger than, equal to, or actually less than the kinetic friction.<sup>16</sup>

4. *Load-bearing capacity of lubricants.* Systematic work shows that adhesion during sliding is approximately one-half that in the static state. Certain additives present even larger load-carrying capacity.<sup>17</sup>
5. *Limiting shear stress behavior correlates with substantial fluctuation of the friction coefficient.* The limiting shear stress involves wall slip and in this circumstance the friction coefficient includes large variation around the mean. This fluctuation cannot be explained by traditional explanations of friction fluctuations.<sup>18</sup>
6. *The friction coefficient presents an imperfect description of friction forces.* Though the forces in the normal direction can be essentially the same, the forces that resist shear can be essentially different.<sup>13</sup>
7. *Prospects for design of lubricant formulations.* The patterns described in this article appear to be general, but their magnitudes depend on particular properties of the lubricant (the molecular size, shape, polarity, and chemical composition), as well as on the strength of surface-fluid attraction.

## Acknowledgements

Financial support was provided by the Exxon Research and Engineering Corporation, and by the taxpayers of the United States through the Air Force (AFOSR-URI-F49620-93-1-02-41) and the National Science Foundation (Tribology Program).

## References

1. Dowson, D., *History of Tribology*. Longman, London, 1979.
2. Israelachvili, J. N., *Intermolecular and Surface Forces*, 2nd edn. Academic Press, New York, 1991.
3. Peachey, J., Van Alsten, J. and Granick, S., Design of an apparatus to measure the shear response of ultrathin liquid films. *Reviews of the Science Institute*, 1991, **62**, 463–473.
4. Peanasky, J., Cai, L., Kessel, C. R. and Granick, S., Nanorheology of confined polymer melts. III. *Weakly adsorbing surfaces*. *Langmuir*, 1991, **10**, 3874–3879.
5. Cho, Y. -K. and Granick, S., Shear of confined perfluorinated polyethers: effect of side-branching. *Wear*, 1996, **200**, 346–352.
6. Granick, S., Motions and relaxations of confined liquids. *Science*, 1991, **253**, 1374–1379.
7. Ferry, J. D., *Viscoelastic Properties of Polymers*, 2nd edn. Wiley, New York, 1980.
8. Urbakh, M., Daikhin, L. and Klafter, J., Dynamics of confined liquids under shear and references therein. *Journal of Physics Review E*, 1995, **51**, 2137–2141.
9. Davis, H. T., Kinetic theory of strongly inhomogeneous fluids. In *Fundamentals of Inhomogeneous Fluids*, ed. Henderson, D., Marcel Dekker, New York, 1992, pp. 551–598.
10. Luengo, G., Israelachvili, J.N., Dhinojwala, A. and Granick, S., Generalized effects in confined fluids: new friction map for boundary lubrication. *Wear*, 1997, **205**, 246.

11. Thompson, P. A., Robbins, M. O. and Grest, G. S., Structure and shear response in nanometer-thick films. *Israel Journal of Chemistry*, 1995, **35**, 93–106.
12. Halperin, A., Tirrell, M. and Lodge, T. P., Tethered chains in polymer microstructures. *Advances in Polymer Science*, 1991, **100**, 31–86.
13. Dhinojwala, A., Cai, L. and Granick, S., Critique of the friction coefficient concept for wet (lubricated) sliding. *Langmuir*, 1996, **12**, 4537–4542.
14. Hirz, S., Subbotin, A., Frank, C. and Hadziioannou, G., Static and kinetic friction of strongly confined polymer films under shear. *Macromolecules*, 1996, **29**, 3970–3974.
15. Granick, S. and Hu, H.-W., Nanorheology of confined polymer melts. I. Linear shear at strongly adsorbing surfaces. *Langmuir*, 1994, **10**, 3857–3866.
16. Reiter, G., Demirel, A. L. and Granick, S., From static to kinetic friction in confined liquid films. *Science*, 1994, **163**, 1741–1744.
17. Reiter, G., Demirel, A. L., Peanasky, J., Cai, L. and Granick, S., Stick to slip transition and adhesion of lubrication surfaces in moving contact. *Journal of Chemistry and Physics*, 1994, **101**, 2606–2615.
18. Demirel, A. L. and Granick, S., What is fluctuating in a confined liquid in the stick-slip regime? In *Physics of Sliding Friction*, ed. B. Persson. Kluwer Academic Publishers, Boston, 1996, pp. 93–102.