Modification of boundary lubrication by oil-soluble friction modifier additives

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The molecular-level function of model and commercial friction modifier additives in lubricants of the type used at the wet clutch interface in automatic transmissions has been studied using a surface forces apparatus (SFA) modified for oscillatory shear. The nanorheological properties of tetradecane with and without a model friction modifier additive (1-hexadecylamine) were examined in the boundary lubrication regime and compared to a fully-formulated automatic transmission fluid (ATF). 1-Hexadecylamine adsorbed as a single layer on the sliding surfaces, reduced the static frictional force and the limiting shear stress, and eliminated the stick–slip transition that exists in pure tetradecane. The ATF, which contains commercial-grade friction modifiers, showed nanorheological properties similar to those observed for tetradecane containing 0.1–0.2 wt% 1-hexadecylamine.

KEY WORDS: friction modifiers, automatic transmission fluids, thin-film lubricating, nanorheology, molecular tribology, surface forces apparatus

1. Introduction

In the automotive industry, a better understanding of lubrication phenomena is an ongoing challenge. The automatic transmission fluids (ATFs) are among the most sophisticated types of lubricants known to the industry. Their functions include lubricating wet clutch interfaces, transmitting energy/torque (via wet clutches), fluid coupling in a torque converter, and moderating temperature [1]. Fully-formulated ATFs contain a small amount of *friction modifier* (FM) additives, which provide smooth and efficient operation of transmission wet clutches [2–5]. The aim of our work is to study the boundary and near-boundary lubrication mechanism of ATFs, and especially the function of the FM additives at the molecular level. The operating conditions of model wet clutch systems should be similar to the bench test conditions proposed by automotive manufacturers [6–9]. The average pressures used in these bench tests range from 0.7 to 2 MPa, but the local pressure can be up to 4 MPa due to non-uniform contact [4]. The sliding speed can change from 0 to 2 m/s in slipping clutch interfaces, and from 0 to ~ 20 m/s for shifting clutches.

A wide variety of FMs have been reported in the literature [2,10–12]. Typical FMs used in ATFs are oil-soluble molecules that consist of alkane chains with 10 or more carbon atoms and a complex surface-active group at one end. For this study, we have designed model lubricant systems that consist of tetradecane, a model of a non surface-active solvent, and 1-hexadecylamine, a model of an oil-soluble FM additive.

The experimental technique used was a surface forces apparatus (SFA) modified for dynamic (oscillatory) shear. Our setup was developed by Granick and coworkers and is capable of probing the nanorheological properties of films confined between well-defined surfaces down to nanometer (10^{-9} m) length scales [13–15]. This method has provided the means to investigate how lubricant molecules react at a single asperity contact in relative motion, and it has provided new insights into molecular-level tribology [16–22].

In this paper, we present work on model lubricants at various concentrations in tetradecane as well as on a fully-formulated ATF.

2. Materials

1-Hexadecylamine ($CH_3(CH_2)_{15}NH_2$, Aldrich 99%), a model compound for a friction modifier additive, was used as received. A mineral-oil based ATF containing a complete performance additive package was provided by Lubrizol Corporation. The tetradecane ($CH_3(CH_2)_{12}$-CH_3, Aldrich 99%) and the fully-formulated ATF were dried over molecular sieves (Aldrich, pore size 5 Å) before use. Dilute solutions of 1-hexadecylamine (0.05–0.2 wt%) in tetradecane were prepared by agitation in a hot water bath and then in an ultrasonic bath.

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3. Experimental

3.1. Surface forces apparatus

Modification of a surface forces apparatus (SFA) for oscillatory shear experiments was described previously [13,15]. The surfaces were thin sheets of muscovite mica, silvered on one side and glued with their silvered side down onto fused silica discs with 1,5-diphenylcarbazide. The discs were mounted in the instrument with the mica surfaces facing each other in a crossed-cylinder geometry that can be thought of as a single asperity contact. When the two surfaces were pressed together, a region of contact was produced in which the surfaces are locally planar and parallel due to the compliance of the underlying glue. This flattening happened at very small separation, when the confined fluid can support the normal load. The changes of the surface separation were measured with a sensitivity of 2–3 Å by multiple beam interferometry of white light reflected between the silvered backsides of the mica sheets. The contact area was calculated from the shape of the interference fringes. A droplet of the sample solution was injected slowly between the surfaces through a flush-cleaned Millex-SR syringe filter (Millipore, pore size $0.5\,\mu$m). The measurements were started 30 minutes to 1 hour after injecting the solution. The atmosphere in the instrument chamber was kept dry with P_2O_5. All experiments were conducted using droplets inserted between the mica sheets, at $25 \pm 0.2\,^{\circ}$C.

3.2. Static force–distance measurement

The interaction force between the two mica surfaces was measured as a function of surface separation (film thickness) as the two surfaces were brought toward each other, brought into contact, and separated. The zero distance between the surfaces was defined as mica–mica contact in dry air. The force in the direction normal to the surfaces, F, was calculated from the deflection of the leaf-spring (of known stiffness, $k = 927\,$N/m) that supported the lower surface. The force F was normalized by the geometric-mean radius of curvature of the crossed cylinders R (typically 1.6–2 cm), since the value F/R is proportional to the interaction energy per unit area between two parallel plates (the Derjaguin approximation) for undeformed surfaces [23]. The interaction force measured as a function of distance gives information about the adhesion and repulsion between the two surfaces during loading/unloading cycles, as well as a means to infer the structure, orientation, and rearrangement of confined liquid molecules.

3.3. Oscillatory shear experiments

The rheological properties of a confined liquid film can be studied by measuring its response to oscillatory shear with a modified SFA. The shear device has two piezoelectric bimorphs attached to the holder for the top mica surface. Shear was induced by the input of a sinusoidal signal from a function generator (at the radial frequency ω) to the 1st (sender) bimorph. The resulting motion of the surface induced an electrical signal in the 2nd (receiver) bimorph.

The applied shear force, $f(t) = f_0 \sin \omega t$, causes a displacement of the top mica surface with respect to the bottom surface, $x(t) = x_0 \sin(\omega t + \delta)$, where δ is the phase shift. The value x_0 was deduced from the output signal measured with a lock-in amplifier. The velocity of the top surface with respect to the bottom one was $v(t) = \partial x(t)/\partial t = v_0 \cos(\omega t + \delta)$, where the velocity amplitude was $v_0 = x_0 \omega$. Similarly, the shear rate amplitude $\dot{\gamma}_0$ was defined as the ratio of the velocity amplitude v_0 to the film thickness h. In contrast to our previous publication [24], the film thickness h was defined here as the distance between the mica plates, which includes the thickness of adsorbed molecular layers on surfaces. The shear rate cycles from zero to $\dot{\gamma}_0$ during each oscillation.

The responding stresses generated within the confined liquid film were measured by a lock-in amplifier, decomposed into their in-phase and out-of-phase components, and compared to the signal when the two surfaces were separated [13,17,19,25]. The in-phase component, i.e. the component that followed Hooke's law of elastic deformation, gave the storage (or elastic) modulus (G') after normalizing by measured strain amplitude ($\gamma_0 \equiv x_0/h$). The out-of-phase component of the imposed shear stress, i.e. the component that followed Newton's law of viscous flow, gave the loss (or viscous) modulus (G'') after normalizing by strain amplitude. The storage modulus represents the energy stored during each oscillation, while the loss modulus represents the energy dissipated. The effect of the device and glue impedance was eliminated through a calibration procedure by comparing the signal in mica–mica contact, i.e., without the liquid film, with the out-of-contact signal [17,19,25]. With this instrumentation, the rheological properties of confined fluids in the linear response region as well as in the non-linear response regions can be deduced [17,25,26].

The average contact pressure during shear was maintained at $1 \sim 4\,$MPa in accordance with actual operating conditions of wet clutch interfaces [4,6–9]. In SFA experiments, average pressures were calculated using Hertz theory for contact between non-adhering surfaces [27]. The sliding speeds attained in SFA experiments were quite small ($\sim 10\,\mu$m/s) but allowed us nevertheless to observe the molecular-level mechanism of lubricants in the boundary lubrication regime, which was the primary purpose of this work.

4. Results

4.1. Model lubricants tetradecane with and without 0.1 wt% 1-hexadecylamine

The static interaction forces as a function of separation D are shown in figure 1. The separation D
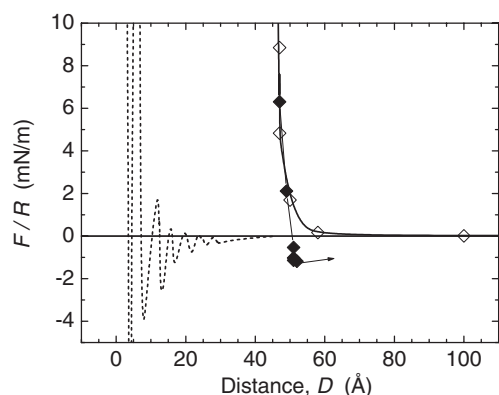
Figure 1. The normalized static force F/R versus the film thickness D (distance between the upper and lower mica surfaces) for pure tetradecane (shown as a dashed line) [28] and 0.1 wt% 1-hexadecyla-mine in tetradecane (open diamonds indicate compression and filled diamonds separation) [24]. R is the geometric-mean radius of curvature of the crossed cylinders (typically 1.6–2 cm). The curves through the 1-hexadecylamine data are meant as guides to the eye. The arrow indicates a jump out of contact.

was defined to be zero at mica–mica contact in dry air. The data for 0.1 wt% 1-hexadecylamine in tetradecane are shown as diamonds [24]. Open symbols denote the forces measured upon bringing the surfaces closer together, and filled symbols denote the forces measured upon separation. As the two surfaces were brought together from a large separation, a repulsive force was detected at a separation of about 60 Å. The repulsion then monotonically increased as the two surfaces were brought closer. The "hard-wall film thickness" was determined to be 47 Å. For comparison, the data for pure tetradecane found in the literature [28] are plotted as a dashed curve. Pure tetradecane showed an oscillatory force as a function of separation, with the period of the oscillations equal to the alkane chain cross-sectional diameter of 4 Å. In tetradecane, the two surfaces were able to approach to within 10 Å when compressed with moderate forces. Shown in figure 2 is the proposed model of the tetradecane with 0.1 wt% 1-hexadecylamine between the sliding surfaces based on
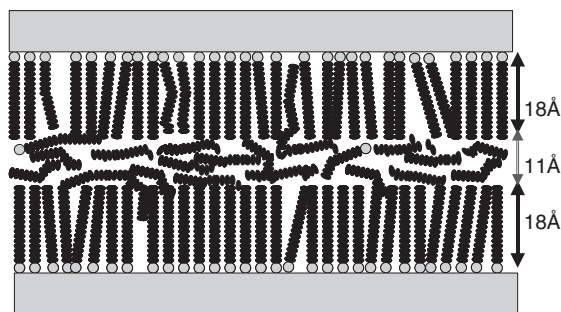

Figure 2. Schematic diagram of the proposed "hard-wall" structure of the FM solution (0.1 wt% 1-hexadecylamine in tetradecane) confined between two atomically flat mica surfaces. The FM molecules are adsorbed to each mica surface through the headgroup, forming a disordered, single layer. Two to three layers of the randomly oriented solution molecules reside between the adsorbed FM layers.

the experimental data, as discussed in detail in the discussion section.

Next we measured the shear forces by imposing sinusoidal shear stresses parallel to the surfaces. Figure 3(a) shows the amplitudes of elastic (in-phase) and viscous (out-of-phase) forces as a function of deformation amplitude. Figure 3(b) shows the normalized forces (the moduli, G' and G'') as a function of deformation amplitude. The data were obtained at a fixed oscillation frequency, 13 Hz for tetradecane and 2.6 Hz for 0.1 wt% 1-hexadecylamine in tetradecane, and at a fixed normal pressure, 3.2 MPa for tetradecane and 3.3 MPa for 0.1 wt% 1-hexadecylamine in tetradecane. Below we discuss the distinctly different responses that tetradecane with and without 0.1 wt% 1-hexadecylamine shows to oscillatory shear, including the presence of stick–slip behavior for pure tetradecane (indicated by arrows).

In order to quantify the resistance observed during sliding at large deformation, we have plotted the viscous shear stress (σ_{vis}) as a function of shear-rate amplitude (figure 4). The data for pure tetradecane were taken at 3.2 MPa (shown as open circles). The data for 0.1 wt% 1-hexadecylamine were taken at a pressure of 1.1 MPa (shaded circles) and 3.3 MPa (filled circles). The viscous stress stayed essentially the same at higher shear rates as the load was increased from 1.1 to 3.3 MPa for 0.1 wt% 1-hexadecylamine.

4.2. Fully-formulated automatic transmission fluid

We have conducted similar experiments for a mineral-oil-based commercial ATF currently used in the auto industry. The static interaction force versus film thickness is shown in figure 5. The open diamonds denote the forces measured upon bringing the surfaces closer together, and filled diamonds denote the forces measured upon separation. Upon approaching, a repulsive force started to appear at very large distance (~ 700 Å). The steepest slope (hard wall) in the force versus distance curve was observed at a surface separation of approximately 47 Å.

The responses to oscillatory shear are shown in figures 6 and 7. Figure 6(a) shows the elastic (in-phase) and viscous (out-of-phase) forces as a function of deformation amplitude. Figure 6(b) shows the normalized forces (the moduli, G' and G'') as a function of deformation amplitude. The data were obtained at fixed oscillation frequency (2.6 Hz) and at fixed normal pressure (4.2 MPa). The forces observed were an order of magnitude smaller than the forces for pure tetradecane, and no stick-to-slip transition was observed. The viscous forces at low deformations and elastic forces at high deformations were comparable to those of the 0.1 wt% 1-hexadecylamine in tetradecane. While the crossover point from predominantly elastic to viscous response occurred at smaller deformations in the ATF,
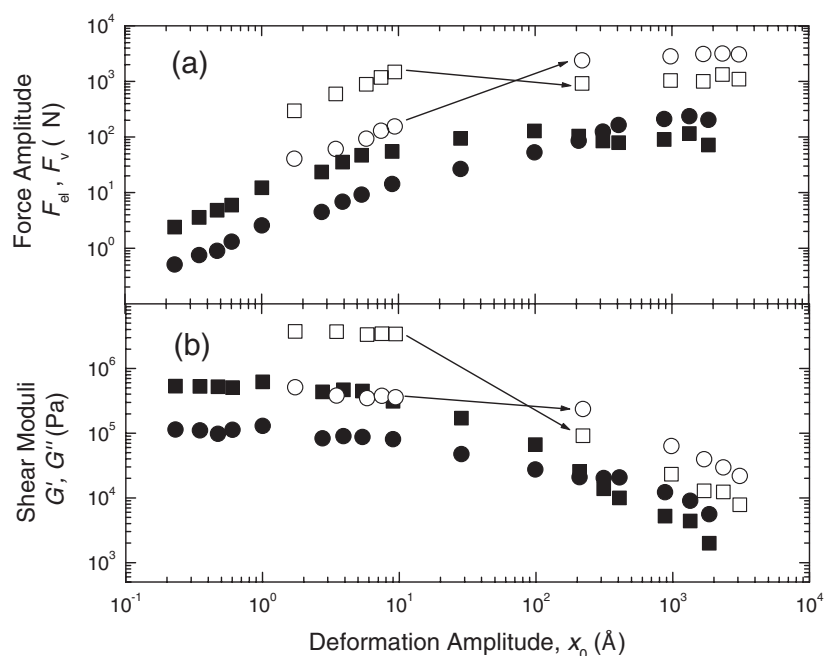
Figure 3. (a) The amplitude of elastic force (shown as squares) and viscous force (circles) plotted against deformation amplitude x_0. Results are shown for pure tetradecane at film thickness 20 Å (open symbols) and for the model FM 0.1 wt% 1-hexadecylamine in tetradecane at film thickness 47 Å (filled symbols). The measurements were made at a fixed oscillation frequency and normal pressure ($f = 13$ Hz and $P_{ave} = 3.2$ MPa for pure tetradecane, and 2.6 Hz and $P_{ave} = 3.3$ MPa for 0.1 wt% 1-hexadecylamine in tetradecane). The discontinuous transition in the data for pure tetradecane indicates that the onset of sliding occurs as slip, whereas the transition is continuous in the FM system. (b) The amplitude of elastic and viscous forces in panel (a) normalized by strain and area of contact to give the storage and loss shear moduli, G' (squares) and G'' (circles), as a function of the deformation amplitude.

the stress was similar to that in the 0.1 wt% 1-hexadecylamine solution. This is related to the faster increase in viscous forces with deformation amplitude in the ATF, which is accompanied by an increase in G'' at intermediate shear amplitude. Figure 7 is a plot of viscous shear stress (σ_{vis}) versus effective shear rate for the ATF at a pressure of 1.6 MPa (shaded circles) and

4.2 MPa (filled circles). The viscous shear stresses were significantly lower than the values observed for pure tetradecane. It appears that the shear stress did not quite approach a constant value as the shear rate increased. Therefore we can only make a rough estimate of the limiting shear stress for this ATF (table 1).
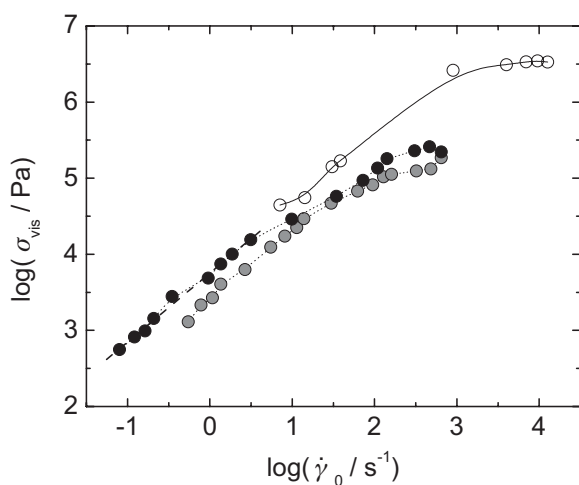

Figure 4. Log–log plot of the amplitude of viscous shear stress as a function of shear-rate amplitude for pure tetradecane at 3.2 MPa (open circles), and 0.1 wt% 1-hexadecylamine at 3.3 MPa (filled circles) and 1.1 MPa (shaded circles). The film thickness for the latter case was 48 Å.
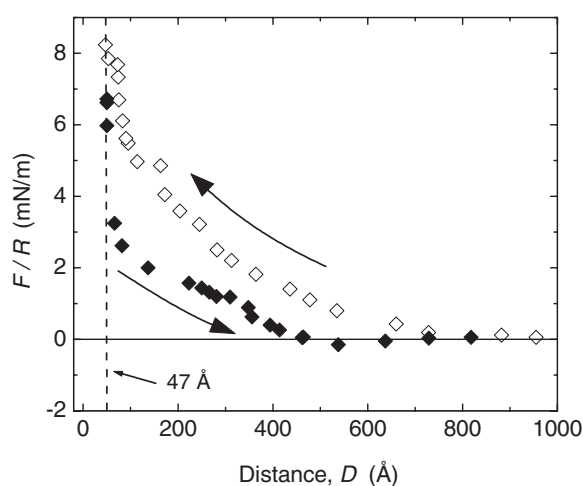

Figure 5. The normalized static force F/R versus the separation D between the mica plates for a fully-formulated ATF confined between two mica surfaces (open diamonds indicate compression and filled diamonds separation). The same hard-wall film thickness was found in this commercial sample and in the model system (47 Å, cf. figure 1).
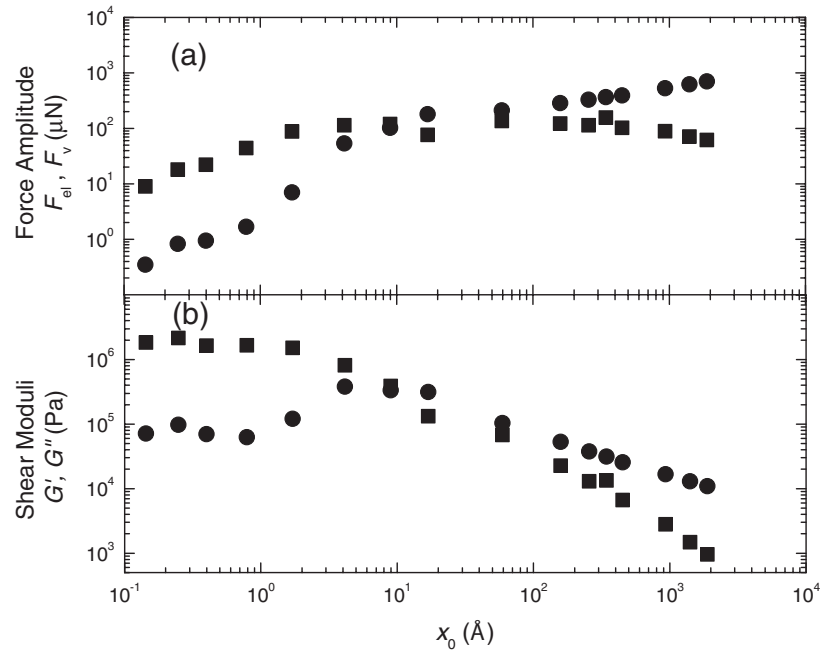
Figure 6. (a) The amplitude of elastic force (shown as filled squares) and viscous force (filled circles) for a fully-formulated ATF at film thickness 48 Å, plotted against deformation amplitude. The measurements were made at a fixed oscillation frequency ($f = 2.6$ Hz) and normal pressure of 4.2 MPa. No discontinuous transition was observed. (b) The amplitude of elastic and viscous forces in panel (a) normalized by strain and area of contact to give the storage and loss shear moduli, G' (squares) and G'' (circles), as a function of the deformation amplitude.

4.3. Model lubricants with FM at different concentrations

We then conducted SFA experiments for the 1-hexadecylamine solutions in tetradecane at different concentrations. 1-Hexadecylamine did not completely dissolve in tetradecane to more than 0.4 wt% at room temperature. Measurements were thus not possible at higher concentrations, because solid particles of 1-hexadecylamine disturbed the experiments. The results

are summarized in table 1. Already 0.05 wt% 1-hexadecylamine provided a hard-wall distance comparable to that found for the 0.1 wt% solution and caused a decrease of the limiting shear stress. However, this amount was not sufficient to eliminate the stick–slip (the stick persisted up to the deformation amplitude of ~ 6 Å), which was removed only at an increased concentration of 0.1 wt%.

5. Discussion

Discerning molecular-level contributions to boundary lubrication is difficult due to the complicated mixtures involved. Fully-formulated ATFs contain many performance additives besides friction modifiers, such as viscosity-index improving agents, anti-oxidants, detergents, and dispersants [3,11,12]. The exact formulations are proprietary. The sliding components in a wet clutch are also a complex mixture. A resin-treated, paper-based friction material contains additional components, such as activated carbon, graphite, and diatomaceous earth (sedimentary rock composed of the silicate cell walls of diatoms), and it slides against a steel mating surface [29]. In addition, the sliding surface changes chemically during usage. In the past, macroscopic friction testers have been used to obtain friction performance data, but they afforded no understanding of surface and interfacial interactions.

We decided to start our research using a very simple system, a well-defined model lubricant confined between
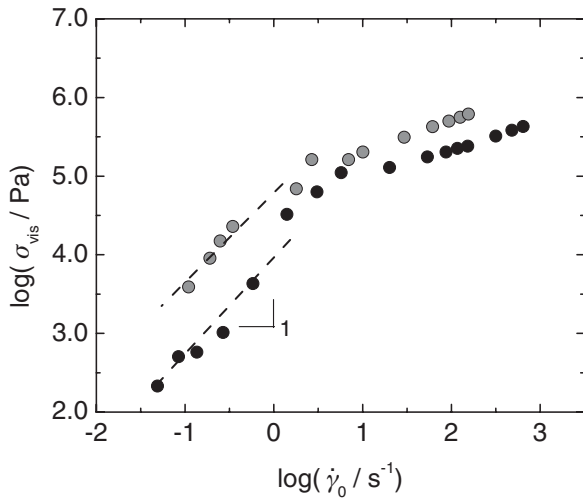

Figure 7. Log–log plot of the amplitude of viscous shear stress as a function of shear-rate amplitude for a fully-formulated ATF at 4.2 MPa (filled circles) and 1.6 MPa (shaded circles). The film thickness for the latter case was 49 Å.

Table 1
Comparison of model lubricants and fully-formulated automatic transmission fluid (ATF).

Lubricants	Pure tetradecane	Tetradecane + 1-hexadecylamine (0.05 wt%)	Tetradecane + 1-hexadecylamine (0.1 wt%)	Tetradecane + 1-hexadecylamine (0.2 wt%)	Fully-formulated ATF
Hard-wall film thickness	<10 Å	46 Å	47 Å	~42 Å[b]	47 Å
Abrupt stick–slip transition[a]	Observed	Observed	Not observed	Not observed	Not observed
Limiting shear stress[a] (log σ, Pa)	6.5	5.0	5.4	5.2	~5.6

[a]These shear response data were obtained with applied pressures ranging from 3.3 to 4.4 MPa.
[b]A very limited amount of data was taken for this fluid.

sliding, atomically flat mica surfaces. We then compared this system to a commercial ATF. Through their precise composition and positional control, SFA experiments have provided an ideal way to investigate the action of friction modifier additives between a single asperity contact *in situ*.

The use of a well-defined model friction modifier (1-hexadecylamine) made the interpretation of SFA data more straightforward. The structure model of FM layers (figure 2) was inferred from the force-distance profiles (figure 1) as follows: The hard-wall distance for the 0.1 wt% model FM solution was much larger than the value observed for pure tetradecane. This indicates that the model FM molecules adsorbed on each mica surface and stayed there as the two surfaces are pushed together. It has been reported that dry single layers of various surfactants with hydrocarbon chains containing 16 carbon atoms have thicknesses of 17–20 Å [30,31], values that closely match the length of an alkane chain with 16 C–C bonds in an all-trans configuration. For an all-trans chain, the average projection of each bond along the chain contour equals $L \sin(\theta/2)$, where θ is the C–C–C bond angle. Typical values ($L = 1.53$ Å, $\theta = 109.5°$) lead to an extended chain length of 1.25 Å per bond, or 20 Å for a linear molecule of 16 bonds (15 C–C and 1 C–N). Additional space would occur between the end group and the surface atoms. Since this length is less than half the hard-wall thickness measured in our system, the adsorbed layers are likely separated by an additional thin layer of solution that could not be squeezed out. Shown in figure 2 is the resulting model of the confined lubricant with a small amount of 1-hexadecylamine. Since the oscillatory force observed for neat tetradecane was removed by the addition of model FM molecules, the non-adsorbed layer consisting of both tetradecane and model FMs is probably highly disordered rather than layered. The molecular dynamics simulations of similar systems have shown results consistent with these data [32].

Figure 1 also clearly showed that the adhesion force was diminished by the addition of model FM molecules. The free energy minima have depths for pure tetradecane that are of order 1–3 mJ/m² more negative than those for 1-hexadecylamine/tetradecane.

The dynamical shear experiments showed two clear distinctions between the tetradecane without and with 1-hexadecylamine: the presence or absence of stick–slip motion and the magnitude of elastic and viscous forces.

As shown in figure 3, pure tetradecane (open symbols) showed stick–slip. Elastic forces dominated at small deformation amplitude, increasing in proportion to the amplitude of deformation. This is the linear-response region, where the surfaces are not yet sliding and where the force is proportional to the deformation amplitude. In this region, the deformation amplitude of the top mica surface stayed small (smaller than ≈ 10 Å) as the amplitude of the signal to the 1st bimorph was increased. At a deformation amplitude of about 10 Å, the imposed force overcame resistance to sliding, and deformation amplitude increased suddenly as the amplitude of the signal to the 1st bimorph was increased. This behavior indicates the end of the stick region, in which the confined fluid had behaved like an elastic solid. Figure 3(a) shows the abrupt start of sliding and the switch to a predominantly viscous response at large deformation amplitude (>200 Å). The "stick" region is characterized by the elastic modulus G' being much greater than the viscous modulus G'', and the "slip" region by the loss modulus G'' being much greater than the storage modulus G'. In this non-linear slip region, both elastic and viscous forces were nearly independent of deformation amplitude. This has been attributed to sliding along an interface [19,20].

For tetradecane with 0.1 wt% 1-hexadecylamine (filled symbols in figure 3), the elastic and viscous forces increased smoothly as a function of deformation amplitude. Linear response was again observed at deformation amplitudes up to ca. 10 Å. This was followed by a gradual transition from linear to non-linear response with increasing deformation amplitude, in contrast with the stick–slip response observed for pure tetradecane. In addition, the magnitude of the viscous and elastic forces observed for tetradecane with 0.1 wt% 1-hexadecylamine were an order of magnitude smaller than the forces for pure tetradecane.

In the viscous shear stress plot of the model lubricants (figure 4), we observed a transition from Newtonian response at low shear rate to strongly non-

Newtonian response at higher shear rate. Also observed was that the shear stress appeared to approach a constant value as the shear rate increased. This constant value of the shear stress is called the "limiting shear stress", where the system undergoes pure sliding. The magnitudes of the limiting shear stress (cf. table 1) for the model FM solutions ($\log \sigma \cong 5.0$–5.4) were significantly lower than the value observed for pure tetradecane ($\log \sigma \cong 6.5$). This is clear evidence that adsorbed FM layers are responsible for reducing the sliding resistance of confined liquids.

The commercial ATF had very similar properties as tetradecane containing a small amount of 1-hexadecylamine. It was striking that the hard wall distance observed for the ATF was the same as the one observed for tetradecane containing 0.1 wt% model FM (47 Å), and that the hard wall was reached at a similar magnitude of the compressive force. It is possible [11,12] that the commercial ATF contained an FM molecule with chain length similar to the one for 1-hexadecylamine and formed a structure similar to the one shown in figure 2, although further work would be needed to prove this. The commercial ATF differs from the 0.1 wt% hexadecylamine in tetradecane by exhibiting long-range repulsion upon approach and separation, rather than adhesion upon separation with a jump out of contact. The cause of this long-range repulsion has not been investigated. It likely arises from adsorption of the ester-type viscosity-index improving agent (VI improver) that has a large molecular weight (number average molecular weight $M_n \approx 150,000$ g/mol). Since the size of the VI improver changes significantly with temperature, SFA measurements at different temperatures would provide insight into this phenomenon.

The dynamical shear responses of the fully formulated ATF were distinctly different from the properties observed for pure tetradecane; instead they were similar to the properties observed for tetradecane containing 0.1–0.2 wt% of 1-hexadecylamine. The deformation amplitude increased gradually with applied shear force, rather than showing the stick–slip behavior observed for tetradecane. The viscous forces were Newtonian at lower shear rates, as in the tetradecane containing 0.1 wt% of 1-hexadecylamine, and were similar in magnitude. This also indicates that commercial FMs, which typically occur in ATFs in amounts comparable to those in our model systems, work in a way similar to the 1-hexadecylamine in tetradecane.

6. Conclusion

We have used a surface forces apparatus (SFA), modified for oscillatory shear experiments, to study the action of friction modifier additives in lubricants. We have examined simple model systems as well as a commercial automatic transmission fluid (ATF). It was found that a small amount of 1-hexadecylamine (a model friction modifier) caused a large change in the nanorheological properties in a favorable way. Specifically, we found that the model FM molecules increased the hard-wall distance, removed the oscillatory force observed for pure tetradecane, reduced the adhesion force, eliminated the stick–slip, and lowered the magnitude of the limiting shear stress. A fully-formulated ATF containing a complete additive package showed interfacial properties similar to those of tetradecane containing small concentrations (0.1 to 0.2 wt%) of model FMs.

The experimental approach described here provide a means to measure important tribological quantities such as viscous and elastic forces, and the limiting shear stress of lubricants. The nanorheological data obtained with model lubricant systems were useful references in interpreting the data obtained for commercial lubricants of which the exact formulation was unknown and proprietary.

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