Molecular Scale Liquid Lubricating Films

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A number of recently-developed experimental techniques, such as force balance, atomic force microscopy and ultrathin film interferometry have enabled the direct study of the properties of very thin liquid lubricating films between solid surfaces. These have been used to demonstrate the structure and rheology, and thus the lubricating ability, of monolayer additive films in rolling and sliding contacts. They have also been used to investigate the thin film properties of simple, additive-free fluids such as hydrocarbon base stocks.

This paper reviews previous work on the thin film-forming properties of simple lubricant base fluids. New work is carried out using ultrathin film interferometry and a rolling-sliding friction test apparatus. It is found that the quasi-spherical molecules, cyclohexane and OMCTS form enhanced film thicknesses in high pressure, slow speed, rolling contacts. There is also an indication of a step-wise dependence of film thickness on rolling speed, in accord with finding using atomic force microscopy and surface forces apparatus. Friction measurements in mixed rolling-sliding show that these fluids also reduce friction in the boundary film regime.

1. INTRODUCTION

Over the last twenty years, a number of techniques have been developed which are able to study the properties of very thin liquid films confined between a pair of solid surfaces. These techniques range from general-purpose tools devised by surface physicists to investigate the behaviour of interfaces, such as the surface force apparatus and atomic and friction force microscopy, to tools developed specifically for studying lubricated contacts, such as ultrathin film interferometry.

One obvious use for such techniques has been to probe the origins of boundary lubrication, both in terms of the nature of films formed by lubricant additives in solution and also the behaviour and properties of very thin, molecular-scale, layers of base fluid. For the former, the various methods employed have shown quite good agreement; for example in indicating that close-packed, monolayer-thick, adsorbed surfactant films on polar solid surfaces are able to survive in very high

pressure, rubbing contacts and to reduce friction (1)-(3).

In the study of simple non-polar base fluid behaviour however, results have been more disparate. Some studies have indicated that liquids form an organised, layered structure, several molecules thick, between solid surfaces. Others have shown no evidence of any anomalous boundary film properties down to the thickness of a single molecule.

The aim of this paper is to discuss existing work in the area of boundary film formation by simple liquids and combine this with some new work using ultrathin film interferometry and rolling-sliding contact friction measurement, in order to assess the presence and practical significance of molecular-scale films formed by lubricant base fluids.

The paper first reviews the main findings made by each of the main techniques in turn. It then brings all of these together to discuss the practical role, if any, of molecular-scale base fluid films in lubrication.

2. SURFACE FORCES APPARATUS

One of the most extensively-used techniques for investigating the properties of thin liquid films between solid surfaces has been the surface forces apparatus (SFA), otherwise called the force balance method. In this, the surfaces of two, very smooth, non-conforming bodies are brought into very close proximity using piezo-electric positioning techniques, to produce a known and controllable gap between them, down to fractions of a nanometer in thickness. One of the surfaces is then moved normally or laterally against the other while monitoring the consequent normal or shear force. Surface separation is either measured optically or from capacitance, or simply inferred from normal force measurements. A typical test apparatus is shown in figure 1 (4).

Figure 1. Typical surface forces set-up (from ref. 4)

This technique was first developed in the late 1960s to investigate the van der Waal force between dry, solid surfaces (5). In the late 1970s it was extended to examine liquid-filled gaps, looking first at normal, steady-state forces and later, damping forces due to sinusoidal approach, and shear forces due to sliding. In order to ensure atomically-smooth surfaces, most work has employed thin sheets of mica, glued onto crossed-cylinders of glass.

Using this apparatus, Israelachvili showed in the early 1980s that the presence of some simple liquids within a mica-mica contact modified the monotonic force-distance relationship characteristic of van der Waal's attraction, to produce a normal force whose magnitude varied periodically with separation out to several molecular dimensions (6). This is shown in figure 2 and results from an

ordering in the packing of the molecules within the gap, imposed by the confining solid walls (6). Low normal force occurs when a stable configuration having an integer number of molecular layers is present, while a high normal force results from a non-integer number of monolayers.

Figure 2. Schematic of periodicity of normal forces for alkane in very thin gap (from ref. 7)

This type of force, resulting from near-surface ordering is termed a "structural" or "solvation" force. The main features of this type of solvation have been summarised by Israelachvili (7). The effect is particularly strong and can extend over up to 10 monolayers for rigid, near-spherical molecules such as cyclohexane and octamethylcyclotetrasiloxane (OCMTS), where the layer spacing correspond to the molecular diameters of approximately 0.5 nm and 0.8 nm respectively. It is also found for linear alkanes, with a layer spacing matching the width of the carbon chain, i.e. 0.4 nm. However branched or small, flexible molecules show much smaller, if any, periodicity, presumably because molecular packing to form a regular structure cannot take place. It has also been suggested that the periodicity in normal force is lost if the solid surfaces have any significant roughness, even at the sub-nanometer level (8), and that the presence of adsorbed water can also disrupt the ordering. It should, however be noted that the

purported effect of roughness did not arise from real solid surface roughness but from the uneven deposition of an adsorbed surfactant film on the mica surfaces.

In the late 1980s, both Israelachvili, and Granick superimposed lateral motion on one of the two mica surfaces and measured the consequent shear forces present in very thin liquid films. Granick applied a low amplitude sinusoidal lateral motion and measured effective shear viscosity as a function of separation for dodecane and OCMTS (9). He found that this rose rapidly as the film thinned from five down to two monolayers, as shown in figure 3). However, as the shear rate was increased, this viscosity enhancement was progressively lost. Granick also noted that this thin film viscosity enhancement was time-dependent, taking several minutes to develop to its full value.

Figure 3. Influence of film gap on effective viscosity for dodecane (from ref. 9)

Israelachvili and co-workers noted that, for quasi-spherical molecules such as OMCTS and cyclohexane, the film gap during sliding was effectively quantised, with a sudden transition from three to two and then two to one molecular layer as the applied load was increased (10)(11). These transitions also corresponded to sudden increases in effective viscosity or shear stress, with, for cyclohexane, an increase in shear stress from 0.1 MPa for three molecular layers to 10 MPa for one layer.

Both researchers suggest that very thin, confined films of regularly-shaped liquids form an ordered, essentially crystalline structure in a

stationary or very low shear rate contact. As shear rate increases this structure breaks down, with consequent shear thinning. For very thin films, where structure is lost at relatively high shear rates but reforms rapidly upon halting, this can even result in stick-slip action since the dynamic friction is less than the static value (12).

Matsuoka and Kato have also used the force balance method with crossed cylinders of mica to study very thin, liquid film behaviour (4). Their approach was more strongly focussed towards lubrication than Israelachvili's and Granick's, the main difference being that they imposed a much higher sliding velocity of one surface against the other, up to 0.2 mm/s in magnitude, to generate a film pressure due to fluid entrainment. For thick films, Matusoka measured an hydrodynamic fluid force which varied with film thickness in accord with hydrodynamic lubrication theory. However, for very thin fluid films of some fluids, the film thickness could only adopt values corresponding to an integral number of molecular layers, as indicated in figure 4. At these thicknesses, there was a solvation force superimposed upon the hydrodynamic force, which was independent of sliding speed and had a value ranging from 10 μ N for six molecular layers, up to 500 μ N for one monolayer. Such layering was found for cyclohexane and for OMCTS, but not for hexadecane.

Figure 4. Variation of fluid force with film thickness for OMCTS at 0.2 mm/s (from ref. 4)

All of the above work employed a mica-mica, crossed cylinder contact. One limitation of this is that, largely because of the low modulus of the adhesive used to fasten the mica to the cylindrical substrate, the contact pressures possible are quite low, typically 1 to 10 MPa. In the early 1990s, Georges and co-workers developed a new force balance system, comprising a ball against a flat (13)(14). Both ball and flat could be steel or metal-coated glass, which enabled considerably higher pressures to be obtained than using mica (typically 20 to 100 MPa) and also allowed the influence of a metallic surface and of surface roughness to be studied.

Georges investigated the thin film rheological properties of simple fluids, including alkanes and OCMTS, by monitoring the damping that resulted when the ball approached the flat with a very slow velocity overlaid with a small, sinusoidal acceleration. Georges found that, as the film gap was progressively reduced, the fluid viscosity retained its bulk value until the gap thickness was typically four to six times the liquid's molecular size (the molecular diameter for OCMTS but the chain thickness for linear alkanes). The effective viscosity then rose with further film thickness reduction until the gap corresponded to twice the molecular dimension, at which point the remaining film was essentially solid-like. There was thus an immobile layer of molecules, one molecular dimension thick, present on each solid surface. From the damping-separation curve it was apparent that these two layers were present even when the separation was much thicker; i.e. they were not produced by the fluid confinement but simply associated with each independent surface. They were also present regardless of the roughness of the solid surfaces.

From all of the above it can be seen that a very thin fluid film confined between two solid surfaces can possess three separate features of interest. One is a periodicity in structure and density up to ten molecular layers thick. However this only occurs with regularly-shaped molecules and may be absent for non-atomically smooth surfaces. A second is a progressive increase in effective viscosity for films less than about six molecular dimensions thick. This effect can produce very high shear stresses and is effective even for irregular molecules, but much of it appears to be lost at high shear rates. Finally

there is the presence of immobile monolayers of base fluid on each surface. These appear to be very persistent, and, indeed, irremovable in most surface forces work.

3. ATOMIC FORCE MICROSCOPY

In atomic force microscopy (AFM), a tiny, very sharp tip, with a radius of a few nanometers, is pressed against a solid surface and dragged across it at constant normal force. The tip is mounted on a cantilever whose deflection is used to measure the normal force, which is then maintained at a constant value by moving the tip up and down using a piezo-electric system. This produces a map of constant attractive-repulsive force, which is effectively one of surface topography. The cantilever can also bend in the sliding direction, parallel to the surface, and this can be used in friction force microscopy (FFM) to determine how friction between surface and tip varies at the nanometer scale (15). The overall set-up is shown schematically in figure 5 (16).

Figure 5. Schematic diagram of atomic force and friction force microscopy (from ref. 16)

In its conventional form as outlined above, AFM/FFM has been used to study the topography, friction and endurance of additive films, such as Langmuir Blodgett films and antiwear coatings (2)(16)(17). However, because it traces the friction and topography of just one, constant force surface, it cannot be used to study how film properties vary with thickness, or depth. To address this limitation, in the last few years, AFM has been modified to permit new types of tip motion, including rapid oscillation or tapping, so as to generate information

about the viscous and viscoelastic properties of the fluid in the tip/substrate gap. By backing the tip off different distances from the substrate, it is then possible to probe thin film properties as a function of thickness, in a fashion not dissimilar to that used in SFA, although with a very different contact geometry.

This technique has been used by Welland and co-workers to investigate the viscous and elastic properties of very thin liquid films between a Si_3N_4 tip and a freshly-cleaved graphite or a mica surface (18)(19). Figure 6 shows how both measured interaction stiffness and effective viscosity vary with tip-substrate separation for OMCTS. The stiffness clearly varies periodically with a spacing of 0.8 nm, characteristic of the diameter of the OMCTS molecule. The variation of viscosity with film gap is less regular, but does show a marked increase when the gap corresponds to two molecular diameters of fluid or less.

Figure 6. Variation of stiffness (dashed line) and effective viscosity (solid line) with tip-sample separation for OMCTS on HOPG in AFM apparatus (from ref. 19)

One severe practical problem with AFM used in this configuration is to compensate for the viscous damping of the cantilever in the fluid. A second is that because there is no independent measure of film gap, it is not possible to categorically establish zero separation. This has to be inferred from the force/distance plot. A third complication is that it is very difficult to estimate the contact pressure, since the area of contact is problematic, and pressures are usually very high, of the order of GPa. However even with these provisos, the work has served to demonstrate that simple liquids can form ordered

layers, with a shear strength which varies with distance from the surface, in the very localised contact of a 14 nm radius tip on a flat. The implication of this is that fluid ordering, with possible consequent rheological effects, may occur at an asperity-contact scale. It also supports the SFA finding of a very highly viscous, or immobile monolayer on each of the solid surfaces.

4. ULTRATHIN FILM INTERFEROMETRY

Unlike SFA and AFM, ultrathin film interferometry was developed specifically to study very thin lubricating films. It measures lubricant film thickness in the contact formed by a steel ball rolling against the flat surface of a transparent glass or sapphire disc, using an extended form of optical interferometry (20). The principle is shown in figure 7.

Figure 7. Schematic diagram of ultrathin film interferometry

The disc surface is coated with a very thin film of semi-reflective chromium on top of which is a 400 nm thick layer of transparent silica. White light is shone through the glass surface into the contact region. Some is immediately reflected from the chromium layer, whilst the rest passes through any oil film present and also a silica spacer layer before being reflected back from the steel ball surface. Because the two beams of light thus travel different distances they interfere constructively at wavelengths, λ which obey the relationship;

$$(N - \phi)\lambda = 2n_{oil}h_{oil} + 2n_{spacer}h_{spacer}$$

$$N = 1, 2, 3, \dots \quad (1)$$

where N is the fringe order, h_{oil} and h_{spacer} are the thickness of oil and spacer layer films, n_{oil} and n_{spacer} the refractive index of these films and ϕ is a phase change that is characteristic of the surfaces and takes place upon reflection. Clearly, if the wavelength of maximum constructive interference, λ can be measured and h_{spacer} is known, h_{oil} can be determined. To determine this wavelength, interfered light from the central region of the contact is dispersed in a spectrometer and the resulting spectrum is frame-grabbed and image-analysed. Over the last ten years the precision of the technique has been gradually extended and it can now measure film thickness to less than ± 1 nm for films below 20 nm and $\pm 5\%$ above this.

This technique is not able to measure such thin films as SFA or AFM, nor can the normal or shear force be accurately measured. However, the contact conditions present are far more realistic of most lubricated contact than these methods, with pressures of 0.2 to 1 GPa, rolling speeds up to greater than 1 m/s, and a conventional ball bearing surface.

Figure 8 shows how film thickness depends upon mean rolling speed for three fluids, purified hexadecane (21), a mineral oil (22) and a polyalphaolefin-based, synthetic hydrocarbon. The first two of these were measured in pure rolling and the last in pure sliding with the ball stationary, using a synthetic hydrocarbon of viscosity 1.03 Pas at 40°C.

Figure 8. Film thickness/speed plots for three hydrocarbon-based fluids using ultrathin film interferometry

According to elastohydrodynamic (EHD) lubrication theory, film thickness, h , depends upon mean rolling or entrainment speed U and lubricant viscosity, η according to (23);

$$h \propto (U\eta)^{0.7} \quad (1)$$

This means that, for constant η , a plot of $\log(h)$ versus $\log(U)$ should be linear. This is seen to be the case down to about 1 nm for all three fluids in figure 8. (The differing gradients in figure 8 result from slight differences in the index in equation 1, which can range from 0.6 to 0.75 for different fluids.) In EHD, the critical viscosity for determining film thickness is that of the fluid in the immediate contact inlet, since this determines how much fluid is dragged into the contact (24). Because the plots in figure 8 remain linear down to 1 nm, this indicates that the effective fluid viscosity remains constant at its bulk value down to about this thickness.

Some ester base fluids show a deviation from linearity in film thickness/speed plots, to form thicker than expected films in the very thin film regime (21). This is indicative of a local increase in effective viscosity close to the solid surfaces. However it has not been demonstrated whether this results from the adsorption of viscous, polar impurities in the ester or from a true viscosity enhancement of the base fluid in the confining inlet. It has also been shown that cyclohexane forms a boundary film of about 2 nm thickness, but no purification of the fluid was carried out, so it is not clear if this is intrinsic or results from impurities (25).

In order to compare very thin film EHD measurements made using ultrathin film interferometry with SFA and AFM work, tests have been carried out on cyclohexane and OMCTS. Both fluids were purified by passage through an alumina column and tested immediately to prevent water contamination. Film thickness measurements were made in pure rolling, using a 19 mm steel ball, root mean square roughness (rms) 8 to 10 nm, at a load of 20 N corresponding to a maximum Hertz pressure of 0.52 GPa and at a controlled temperature of 25°C. Ball, disc and test chamber were scrupulously cleaned in Analar toluene followed by isopropylalcohol prior to use.

Figure 9 shows a plot of film thickness versus speed for OMCTS. There is marked deviation from linearity in the thin film region, with a thicker film than predicted from EHD theory.

Figure 9. Film thickness/speed plot for OMCTS

Above 6 nm thickness, corresponding to 0.1 m/s entrainment speed, a fully linear plot is seen. Below this, the film thickness appears to fall in a series of steps, at 6 nm, 4 nm and, less clearly, just below 2 nm. Between these steps, the $\log(\text{film thickness})/\log(\text{speed})$ plot is linear. This behaviour that would be expected if the viscosity of the fluid in the immediate, converging, inlet varied in a layered fashion, approximately doubling from 6 to 4 and then again from 4 to 2 nm. At the end of a test, the film thickness was measured in the static contact. No residual film greater than 0.3 nm was detected.

Figure 10 shows a similar plot for cyclohexane at 25°C.

Figure 9. Film thickness/speed plot for cyclohexane

Again, there is a considerable enhancement in film thickness at slow speeds. This begins at 5 nm and, as for OMCTS, increases progressively as the film thickness is reduced. Because of the scatter in measurements of approximately ± 0.25 nm, it is not possible, to identify layering behaviour categorically from the results. However there does appear to be a levelling-out at 1, 1.5, 2, 2.5 and 5 nm. In the static contact at the end of the test, a residual 1 nm film remained separating the surfaces for at least 30 minutes.

These results suggest that in a rolling, high pressure contact, the quasi-spherically shaped OMCTS and cyclohexane both show anomalous viscosity below about 5 to 6 nm film thickness, corresponding to up to 10 molecular layers. However hexadecane, which has a linear structure shows no such effect. There is also some evidence of layering, in that the film thickness/speed curve shows steps at specific film thickness values. For cyclohexane, this appears to correspond to the molecular size of 0.5 nm. For OMCTS, the layering is more obvious but appears to occur in steps of approximately two molecular layers. This may conceivably correspond to layering on the two surfaces as the approach in the converging inlet.

Cyclohexane appears to form a strong, bilayer film, which can withstand Hertzian pressures for long periods. OMCTS does not show this behaviour, in that any film present is very rapidly squeezed out of the static contact. This may be because solvation pressure of one molecular layer of OMCTS is only ≈ 174 MPa, which may not be large enough to prevent its displacement under high static pressure (26).

5. FRICTION-SPEED MAPPING

All of the above methods involve idealised contact systems, with either very low contact pressure, very small amounts of sliding or non-engineering surfaces. It is of interest to determine whether a simple, non-polar liquid can provide any significant degree of surface protection and thus friction reduction in rubbing, metallic contact. To do this, a sliding-rolling ball on disc test apparatus, the mini-traction machine or MTM test rig has been used. This is shown schematically in figure 11. A steel ball is rotated against the flat surface of

a smooth steel disc, with both surfaces driven independently. The ball shaft is angled to minimise spin, and a transducer on this shaft monitors the lateral force and thus the friction at the ball/disc contact.

Figure 11. Schematic diagram of MTM rig

The test rig is fully computer-controlled so that a test sequence can be carried out over any desired rolling/sliding speed combination. In the current study, the friction properties of purified base fluids were measured at a series of entrainment speeds, while maintaining a constant slide-roll ratio. The advantage of this type of test is that, friction/speed results can be correlated with film thickness/speed ones obtained using ultrathin film interferometry, so as to derive the friction properties of films of known thickness.

Tests were carried out using a 19 mm diameter steel ball, rms = 8 to 10 nm, against a steel disc, rms = 8 nm. The applied load was 5 N to give the same maximum Hertz pressure of 0.52 Pa as that present in the film thickness measurements described in the previous section. All tests were conducted over a range of rolling speeds and a fixed slide-roll ratio (ratio of sliding speed to entrainment speed) of 50%. The temperature was controlled to $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$. The cleaning procedure used was the same as for ultrathin film interferometry, as described above.

For each fluid, the apparatus was assembled with a fresh ball and disc and the test liquid added. A series of successive friction scans were then conducted, following one after the other without disassembling the rig or changing specimens or fluid. In each scan, load was applied and the entrainment speed gradually raised in steps from

0.005 to 1 m/s while monitoring friction. Load was then removed.

Figure 12 shows the friction behaviour of purified hexadecane.

Figure 12. Series of friction/entrainment speed scans for hexadecane at 50% slide-roll ratio

It can be seen that the first scan gives relatively low friction coefficient, of around 0.2. In this scan, as the entrainment speed and thus the sliding speed is increased, friction rises, before falling, probably due to the onset of mixed boundary/EHD lubrication. In subsequent scans, the behaviour is quite different, in that the friction coefficient remaining at a very high value between 0.4 and 0.7 for most of the scan, before falling slightly above about 0.4 m/s.

These results suggest that hexadecane is a very poor boundary lubricant, being unable to protect surface and protect adhesive junction growth in rolling-sliding contact. Initially some degree of protection is afforded, possibly due to the presence of an oxide film, but this does not survive the first encounter of the surfaces to high levels of sliding.

Figure 13 shows the friction behaviour for OMCTS. For this fluid, after the first scan, the system settles into a very repeatable response. (For clarity only the first four scans are shown but scans 2 to 6 were almost identical.) At very slow entrainment speed there is very high friction, comparable to that of hexadecane. However, as the speed increases above 0.01 m/s, the friction coefficient falls sharply to 0.2. It then remains at this value, before starting to fall once more at a speed of above 0.1 m/s. Thereafter it shows a fall in

friction and levelling-out characteristic of the transition from mixed to full EHD behaviour. The final friction coefficient level of 0.04 reached at high speed is a typical EHD value.

Figure 12. Series of friction/entrainment speed scans for OMCTS at 50% slide-roll ratio

The behaviour between 0.01 and 0.1 m/s is unusual and revealing. It clearly represents the presence of some form of entrained or speed-dependent film, since below 0.01 m/s very high friction ensues. From the film thickness/speed behaviour in figure 9, it can be seen that the entrainment speed range 0.01 to 0.1 m/s corresponds to film thicknesses between 2.5 nm to 6 nm, where layering behaviour is in evidence. The plateau region at friction coefficient 0.2 thus results from the enhanced film formation of OMCTS.

Figure 14 shows the behaviour of cyclohexane.

Figure 14. Series of friction/entrainment speed scans for cyclohexane at 50% slide-roll ratio

Again, in the very first scan, a relatively low friction is observed at slow speeds, but the pattern then stabilises in subsequent scans of which only the first two are shown. Unlike OMCTS, cyclohexane shows relatively low friction even at the lowest speed tested. At higher speeds, it behaves similarly to OMCTS, with friction starting to drop due to EHD film formation when the entrainment speed reaches 0.1 m/s (film thickness 5 nm). EHD friction is higher than for OMCTS, as might be expected for a less flexible molecule (28).

6. MOLECULAR MODELLING

As well as the above experimental techniques, molecular modelling methods have also been extensively applied to study the properties of very thin, confined, liquid films. Using molecular dynamics simulation, it has been shown that simple liquids form ordered layers within thin gaps, in confirmation of SFA work (29)-(31). The AFM tip/substrate geometry has also been modelled and it has been shown that local layering should occur in this system (32).

Molecular dynamics simulation can also be used to model the molecular behaviour of a liquid close to a single solid surface. This shows that some layering can occur even in such unconfined systems. Figure 15 shows a typical molecular arrangement calculated from a molecular dynamics simulation of hexadecane against a gold surface at 350K (33). It can be seen that a layer of molecules is preferentially aligned parallel to the surface, of thickness 0.4 nm. Beyond this, a second, less regular layer is present at 0.8 nm.

Using molecular dynamics simulation, it is also possible to impose shear on a thin film of fluid confined between two solid surfaces and determine the resultant molecular motion. So far it has proved very difficult to obtain reliable rheological data from such systems, mainly because of the problem of accounting for the large amounts of thermal energy dissipated. However a simulation of the shear of hexadecane indicates that the first, ordered, molecular layer on each solid surface is effectively immobile under such shear, so that the Couette velocity profile shifts outward from the solid surface by 0.4 nm, to beyond this first hexadecane layer (33)

Figure 15. Molecular dynamics simulation of arrangement of hexadecane near a gold surface (from ref. 33)

7. GENERAL DISCUSSION

From all of the above, an overall pattern can be seen to emerge. Very thin liquid films can show two effects. One is a strongly bound monolayer on each solid surface, the so-called “immobile layer”. This appears to be present on polar surfaces regardless of the proximity of any counterface. It has a dimension characteristic of the molecule concerned; a chain width of 0.4 nm for alkanes and the molecular diameter for quasi-spherical molecules such as OMCTS and cyclohexane. With SFA, these layers are almost impossible to displace. However in the static condition of ultrathin film interferometry, only the cyclohexane layers are able to withstand the pressure applied: hexadecane and OMCTS monolayers are squeezed out. In practical terms, this means that, in rolling-sliding metal-metal contact, cyclohexane continues to provide a modicum of boundary lubrication even at very slow entrainment speeds, while the other two fluids do not.

The second thin film effect is a layering that occurs next to solid surfaces for fluids with regularly-shaped molecular structure, at least when

confined between a pair of solid surfaces. This effect is demonstrated very clearly using SFA and from molecular modelling, and results in an oscillation in film density and normal force that can extend across a film of up to 10 monolayers (5 to 7 nm). It is also associated with an increase in shear strength or viscosity of the fluid in very thin fluid films. Some of the literature suggests that this ordering effect may be absent or ineffective for rough surfaces (8). However a similar layering has been seen using both AFM and in modelling with rough surfaces, which suggests that significant surface ordering may occur even when roughness is present (19)(29). One practical question concerns the rate at which surface ordering takes place, since Granick’s work indicates that the recovery of enhanced viscosity of disturbed thin films may be quite slow (9). In this context, the studies of Matsuoka are important in that they show a significant layering effect even at quite high sliding speeds, when fresh surface and fluid is entering the contact at 0.2 mm/s (4). This suggests that, if layering takes place only due to confinement, it is very rapid.

For quasi-spherical molecules, this ordering and its associated viscosity increase has been shown, in this paper, to make a significant contribution to film formation and thus to friction in high pressure, lubricated contacts. Ultrathin film interferometry indicates that both OMCTS and cyclohexane form thicker films in the thin film regime than expected from their bulk viscosity. There is also some indication of a step-wise film thickness/speed variation, indicative of layering, although this phenomenon occurs at the threshold of the sensitivity of the current experimental method. Interestingly, liquids based primarily on linear or branched alkanes show no such surface effects, even for very high viscosity fluids.

At a more practical level, this enhancement in film thickness produced by OMCTS and cyclohexane has also been shown to be associated with a friction reduction in rolling-sliding contact. For hexadecane and for OMCTS at very slow speeds, very high friction coefficient is seen, of around 0.6. However, for cyclohexane and for OMCTS in the intermediate speed range, friction is stabilised at a value of 0.2. This is not a very low friction in view of the fact that surfactant additives often give values of around 0.1. But it is evidence

of a true contribution to boundary lubrication by simple base fluids.

The precise mechanism by which cyclohexane and OMCTS provide such boundary lubrication is not yet clear. For rough surfaces, the classical asperity contact model of friction predicts friction coefficients of around 0.2 for solids. Higher values of 0.5 to 0.7 as found with hexadecane are considered to result only from adhesive junction growth (27). Thus, one possibility is that cyclohexane and OMCTS are inhibiting such junction growth. Alternatively, the deformed surfaces, even in the MTM, may be so conforming that smooth-surface adhesion may be occurring. In this case, the role of the boundary fluid films may simply be to reduce such adhesion.

There are clearly many unanswered questions. These include whether simple fluids can influence film thickness at asperity contact between real rough surfaces. Can multilayer ordering can take place in the contact inlet where the fluid is not fully confined and thus influence liquid entrainment? How do we disentangle physical responses of the fluid at surfaces from possible chemical changes induced by rubbing? These questions can only be addressed by further research. However this study has shown quite clearly that simple base fluids may make a significant contribution, in some circumstances, to boundary friction reduction.

8. CONCLUSIONS

Ultrathin film interferometry has been used to compare the film-forming properties of the simple fluids, hexadecane, cyclohexane and octamethylcyclotetrasiloxane (OMCTS). Hexadecane shows no anomalous film-forming behaviour down to a film thickness of one nanometer. However the more rigid, quasi-spherical molecular structures, cyclohexane and OMCTS, form thicker than expected films, based on their bulk viscosities, at below 6 nm. There was also an indication of a step-wise dependence of film thickness on rolling speed, in accord with finding using atomic force microscopy and surface forces apparatus.

Friction measurements in mixed rolling-sliding indicate that both cyclohexane and OMCTS limit the value of friction coefficient at very slow entrainment speeds, probably by virtue of forming a

molecularly-layered structure, as found using AFM and SFA.

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