

# Microscopic study of thin film lubrication and its contributions to macroscopic tribology

Yuan-Zhong Hu<sup>a,\*</sup> and Steve Granick<sup>b</sup>

<sup>a</sup> National Tribology Laboratory, Tsinghua University, Beijing 100084, PR China

<sup>b</sup> Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801, USA

This review article summarizes recent progress in investigation of nano-rheology and thin film lubrication, as well as their contributions to conventional tribology. As the thickness of a lubricating film becomes comparable to molecular dimensions, a lubricant confined between solid walls undergoes a dramatic transition in its rheological properties and physical state, including the formation of ordered structure, enhanced viscosity and slow relaxation, glass transition or solidification, and consequent stick-slip motion. As a result, it is recognized that there is special regime between EHL and boundary lubrication, identified as thin film lubrication, where lubricant flow and hydrodynamics are still in action but behave differently from expectations of the classical theory. Generalized theories of thin film lubrication are under development. Microscopic studies of thin film lubrication provide a solid theoretical basis to the development of high-tech and micro devices, the understanding of lubrication failure, the generalization of classical lubrication theory, and friction control and interface design.

**Keywords:** thin film lubrication, nano-rheology, molecular tribology

## 1. Introduction

As manufacturing technology progresses, there is a remarkable tendency in tribological design that the designed thickness of hydrodynamic or elasto-hydrodynamic films decreases continuously to meet the requirement for high performance [1–6]. Precision components with ultra-smooth surfaces are now used frequently in many high-tech and micro devices, where the distance between the sliding surfaces may reach nanometer scales, or become comparable to the dimension of the lubricant molecules. The consequent questions are: is the classical Reynold's equation still valid in such a thin film? where is the limitation of the continuum theory? and how to predict lubrication behavior of these nanometer thick films? In searching for the answer to these questions, it has been realized that there may be a new lubrication regime bridging between EHL (elasto-hydrodynamic) and boundary lubrication, where lubricant flow and hydrodynamics are still in action, but behave quite differently from the prediction of classical theory [7–10]. This new lubrication regime and related phenomena, generally known as “thin film lubrication”, have attracted recent attention of researchers who used to work on the more conventional problems of tribology.

It is well known that asperity contact and interference occur in mixed lubrication, where the lubricating films between the interacting asperities could become molecularly thin. Therefore, thin film lubrication is a phenomenon which exists universally in conventional tribology systems. A better understanding of thin film lubrication, including the rheological transitions referred to above confined lubri-

cants, as well as asperity deformation and adhesion, will improve our prediction of tribological failures.

It is technical advances of instrumentation and rapid development of computer power that provide the real opportunity for the first time to investigate these tribological processes on atomic and molecular scales. For example, the surface force apparatus (SFA), which can measure film thickness and friction force between two curved mica surfaces, has been widely used to study the rheological properties of confined liquids [11–23]. The high thickness resolution, up to 0.1 nm for the film thickness measurement, and the ability to detect the extremely small surface forces, make it a major instrument which promotes the experimental studies of nano-rheology. The atomic force microscope (AFM) is another powerful equipment for microscopic researches of tribological processes [1]. Its tiny cantilever deflects flexibly with fluctuating normal and lateral atomic forces when scanning across a surface. The friction force and its correlation with the microstructure of the interface can be traced precisely.

As film thickness comes to the nanometer scale, the validity of continuum theory becomes questionable, and there are no accepted existing theories available to predict the lubricant behavior and response in ultra-thin films. Molecular dynamics (MD) simulation has turned up recently as an alternative approach to study interfacial phenomena and thin film rheology. In these simulations, solid surfaces and the confined lubricant are considered as a particle system, in which the time evolution of every particle can be traced by solving Newton's equations of motion. The thermodynamic parameters and transport properties of the system are obtained through statistical averages of the molecular motion. The MD simulation approach has proved to be effective in theoretical studies of thin film lubrication [7,8,24–38].

\* Current address: Eaton Corp., 26201 Northwestern Highway, Southfield, MI 48037, USA.

In this review article, we summarize recent progress in studies of nanorheology and thin film lubrication, with emphasis on the connections with important prior contributions in conventional macroscopic tribology.

This review focuses on knowledge obtained from MD (molecular dynamics) simulations and from experiments that probe interfacial rheology. The important related areas of tribochemistry, chemical reactions at surfaces, and dry lubrication would require separate reviews of their own.

## 2. Nanorheology of confined lubricant

Lubricant materials properties, such as the density, viscosity and thermal conductivity, are considered to be independent of film thickness in the classical theory of lubrication. As the film thickness approaches molecular scales, however, the lubricant confined in such a narrow gap will undergo a dramatic change in the static and dynamic properties. This confinement-induced change is the central phenomenon we are going to discuss in this section.

For a bulk fluid at sufficient low shear rate, shear response obeys Newton's law

$$\tau = \eta \dot{\gamma},$$

where  $\tau$  is the shear stress,  $\dot{\gamma}$  is the shear rate and  $\eta$  is the viscosity.

The concept of viscosity may no longer be a proper description of fluid property at the atomic or molecular scale, but an effective shear viscosity, defined as  $\eta_{\text{eff}} = \tau / \dot{\gamma}_{\text{eff}}$ , may help us to understand what goes on in ultrathin films. We distinguish nominal shear rate  $\dot{\gamma}$  from  $\dot{\gamma}_{\text{eff}}$ , the effective shear rate defined as  $\dot{\gamma}_{\text{eff}} = U_f / h$ , where  $h$  is film thickness or distance between solid walls,  $U_f$  refers to the fluid velocity in neighboring region closest to the walls. Apparently, the  $\dot{\gamma}_{\text{eff}}$  will deviate from  $\dot{\gamma}$  if slip is a significant part of the rheological response.

The experiments with the surface force apparatus have shown that when the film thickness becomes comparable to the molecular dimension, the effective viscosity at low shear rate is much greater than in the bulk, and grows with decreasing thickness [11–13,15–18]. The enhancement in effective viscosity by many orders of magnitude implies a transition of the confined fluid to a solid state.

Computer simulations performed by many researchers, including one of the authors, have revealed the molecular ordering imposed by the confining surface: layering normal to the surface [24,26,30,34,35,38] and epitaxial order in the plane of the surface when the surface is crystalline [7,27–29]. The layered structure can be observed clearly in the segment density profile shown in figure 1, based on our recent MD study of confined decane films. The density oscillates with a period of approximately the width of a methylene segment, with sharp density increase in the fluid layers nearest the surfaces. When two surfaces separated by lubricant are pushed together, the oscillation in normal

force is believed to be a manifestation of this inhomogeneous density profile [17]. Figure 2 illustrates the in-plane order in a liquid argon film [7]. The amplitude of distribution functions in figure 2 reflects the probability of a particle to appear at a certain location in the  $x$ - $y$  plane. The first fluid layer adjacent to the solid wall shows a distinct in-plane structure while the structure gradually disappears for fluid molecules that are farther removed from the wall. Similar results can be found in many earlier studies [28–32]. For  $n$ -hexadecane films, certain sorts of in-plane structures were also reported by Landman and co-workers in their simulations [34,35].

As the film thickness decreases, the ordered structures induced by the two opposite walls begin to overlap or interfere. When the structure grows over the entire film, the confined fluid may undergo a phase transition to a crystalline or glass state. It has been long recognized that bulk lubricants experience a glass transition at high pressure [39]. Simulation results (figure 3) have shown that the critical pressure, at which phase transition begins, declines with decreasing thickness, and the transition may take place under very low pressure when the film is sufficiently thin [7]. Therefore, similar processes of solidification can be observed for various systems, from ultrathin film to the bulk lubricant, but at different pressure scales.

Viscous dissipation and elasticity of confined liquids at rest have been studied experimentally by applying very small periodic deformations that did not perturb the film structure [19–22]. The findings display a progressive transition from viscous response to a predominately elastic state, as the shearing frequency increases. This proves that the solidification should not be viewed as a first-order phase transition, as had been suggested in the earlier work. Meanwhile, the elastic modulus of the solidified liquid is found to be at least three orders of magnitude less than that typical of glass or crystal in the bulk; i.e., the liquid behaves as a “soft”, highly deformable solid [19].

As the deformation increases to a yield point, the glassy film starts to flow. The shear force at this point is recognized as the origin of static friction in lubricated contacts [13,19].

After yield, the thin films tend to shear in an unstable way. This long-noticed phenomenon in macroscopic friction, known as “stick-slip” motion, has been studied recently at molecular scales [12–16,18,26,27,30]. Simulations of confined liquids comprised of spherical molecules reported that transitions between sticking and sliding were accompanied by periodic shear-melting and recrystallization of thin films [26,27,30]. Sticking occurs in the frozen state and slipping occurs in the shear-induced melted state. However, the presumption did not receive solid support from experiments up to now. The dissipative stress in thin films, measured after yield, was found nearly independent of sliding velocity in the range of 1–100 nm s<sup>-1</sup> [19]. This weak dependence, unlike any response of a bulk liquid, suggests that the mechanism of after-yield flow may not involve a solid-liquid transition

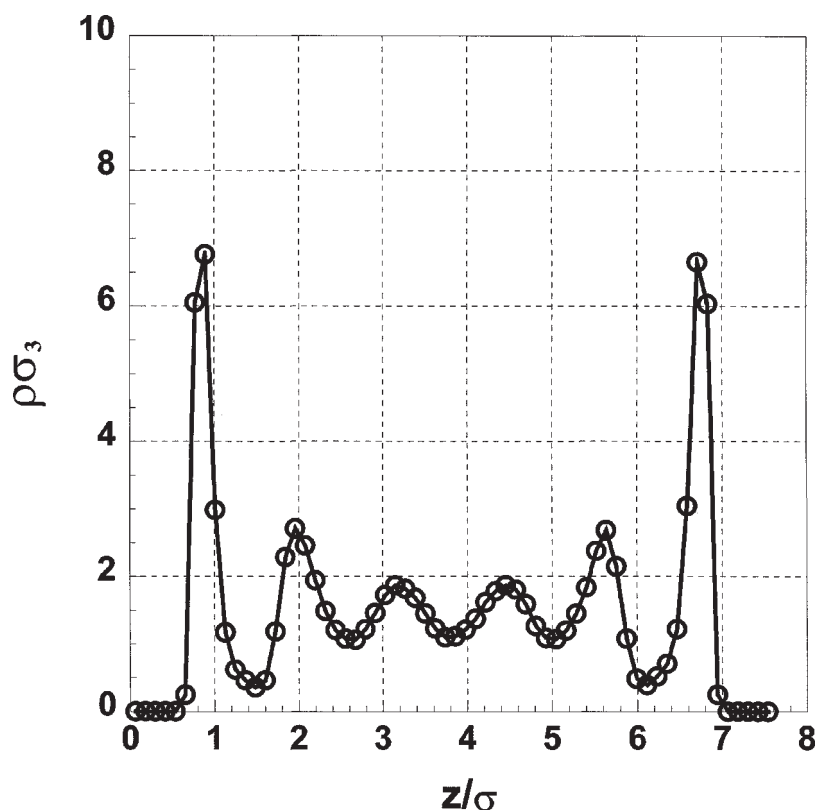


Figure 1. Layered structure in a confined decane film with system pressure  $P_z = 0.2 \epsilon/\sigma^3$  and temperature  $T = 360$  K.  $P_z$  is average normal stress applied by fluid molecules to solid walls,  $\epsilon$  and  $\sigma$  are the energy and length scale, respectively, of the inter-molecule Lennard-Jones potential. The segment density is observed to oscillate across the film and to increase sharply near the solid walls [63]. Similar figures can be found from many prior studies (see [33], as a recent example).

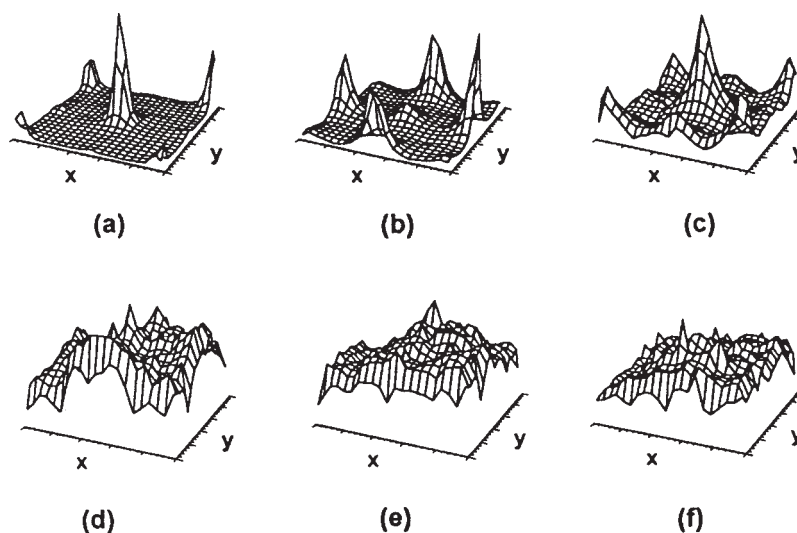


Figure 2. Spatial distribution in six layers nearest a solid wall, for an eleven layer argon film with  $P_z = 3.0 \epsilon/\sigma^3$ ,  $T = 144$  K and  $\epsilon_{wf}/\epsilon = 3.5$ . Epitaxial order can be seen in (a) and (b) while (d), (e) and (f) show relatively random structure [7], similar results can be found in earlier studies [27–32]).

(shear-melting). Figure 4 exhibits velocity profiles of a thin decane film in steady-sliding, obtained from our recent MD simulation [38]. The explicit slip observed at the solid walls and between two adsorbed layers of the decane molecules indicates that the film responds as a solid rather than a liquid, even during the kinetic sliding motion.

The controversy may open up an alternative interpretation for stick-slip motion – the periodic cracking transition [6]. When shear stress exceeds the yield point, cracking suddenly occurs along one of the walls or in the center of the film. Once enough stress is released, the crack re-heals and slip stops. The conventional tribological “expla-

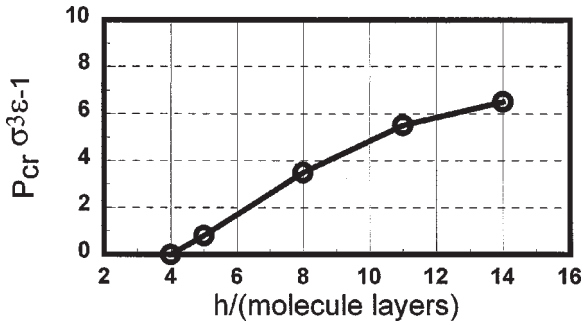
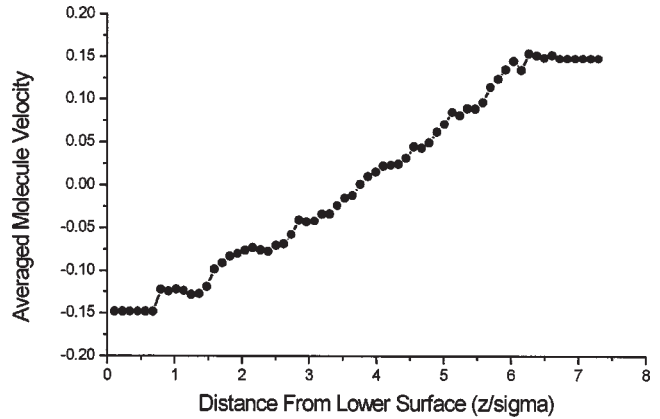


Figure 3. Critical transition pressure  $P_{cr}$  as a function of film thickness at a fixed temperature  $T = 144$  K for a liquid argon film with  $\epsilon_{wf}/\epsilon = 3.5$ .  $P_{cr}$  declines continuously as the film thickness decreases, which implies that in ultra-thin films solidification may occur under low pressure.  $P_{cr}$  is defined as the normal pressure in a liquid argon film, at which the effective viscosity and density of confined liquid jump suddenly [7].

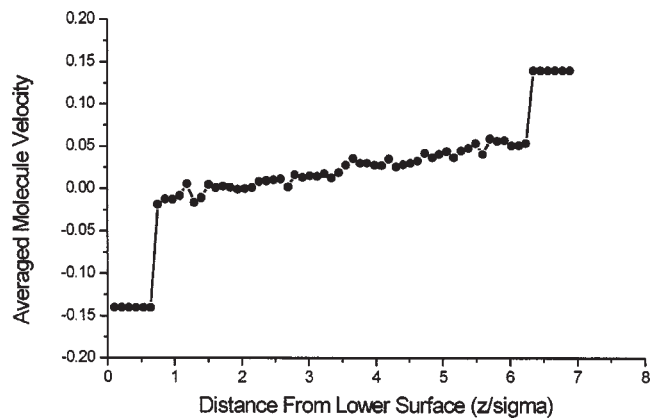
nation” for stick-slip, that friction decreased with velocity, thus finds molecular explanation.

Experiments by Dhinojwala, by shearing the film in periodic oscillation, reveal that stick-slip motion appears only if the shear rate exceeds the inverse natural relaxation time. Meanwhile, experiments with the surfaces sliding at a nominal constant speed show that stick-slip disappears when the sliding velocity goes beyond a critical value [12–14]. This indicates that the stick-slip phenomenon may be amenable to experimental control by strategies based on manipulating the lubricant’s natural relaxation time and the velocity of the tribological contact.

In the experiments where the films are sheared steadily, the confined lubricant exhibits a linear response if the shear rate is low, i.e., the effective viscosity,  $\eta_{eff}$ , remains unchanged, though its magnitude is much higher than that of bulk lubricant. As the shear rate exceeds a critical point,  $\eta_{eff}$  starts to drop extensively. The inverse of the critical shear rate is identified as an estimate of relaxation time for the confined system. The central theme is that relaxation in ultrathin films is much slower than for bulk films. For example, the longest relaxation time for dodecane films of thickness 2.7 nm is nearby 0.05 s – more than  $10^8$  times slower than in the bulk [17]. In the non-linear response region, the rate of decrease in viscosity follows an universal power law,  $\eta_{eff} \sim \dot{\gamma}^{-\alpha}$ . In the experiments at constant normal load, the power  $\alpha$  is found to be slightly more than 2/3, and to grow modestly as the load increases [15–18], reaching the limiting value  $\alpha \approx 1$  in the most confined state and the highest shear rates. Computer simulations at constant load show a similar power law for the shear thinning:  $\eta_{eff} \sim \dot{\gamma}^{-2/3}$  [32]. Simulations performed at constant film thickness, however, produce a different exponent  $\alpha \approx 1/2$  [31,33]. Therefore, the exponent may vary in the range 1/2–1, according to the specific system and condition. It is worthwhile to emphasize that both experiments and simulations display a similar power law behavior, but at different time scales: the relaxation times estimated by the MD simulations are several orders of magnitude more rapid than those observed in experiments. It is possible that



(a)



(b)

Figure 4. Velocity profiles in a confined film containing five layers of decane molecules. The film was sheared at  $\dot{\gamma} = 0.05\tau_0^{-1}$ ,  $T = 360$  K, and  $P_z = 2.0 \epsilon/\sigma^3$  (a) or  $P_z = 30.0 \epsilon/\sigma^3$  (b), where  $\dot{\gamma}$ ,  $T$  and  $P_z$  represent shear rate, temperature and normal system pressure (see the definition in figure 1);  $\tau_0$ ,  $\epsilon$  and  $\sigma$  are time, energy and length scales of the fluid molecule. A basically linear velocity profile with slight interlayer slips is shown for the lower pressure case but wall slip dominates at high pressure. The data at the two ends of the profiles are identical to the wall velocity [63].

the shear thinning predicted by simulations may correspond to a second region of non-linear response which occurs at high shear rate.

The mechanism of shear thinning has not been fully understood, but we would like to emphasize that wall slip may be an important origin leading to the decrease in effective viscosity. Figure 4 gives the velocity profiles obtained from simulation of decane films sheared at a relatively low shear rate ( $\dot{\gamma} = 0.05$ ). The velocity discontinuity between wall and adjacent fluid molecules indicates that slip occurs at the wall-fluid interface. The wall slip reduces the shear rate within the film and hence the shear stress. When this reduced shear stress is divided by the nominal shear rate, which is much higher than the actual shear rate within the lubricant, it gives an artificially small effective viscosity. The situation is analogous to “plug flow” of polymers and colloids. As the slip ratio grows with the increasing wall velocity [7,29], the shear stress, reduced by the slip, in-

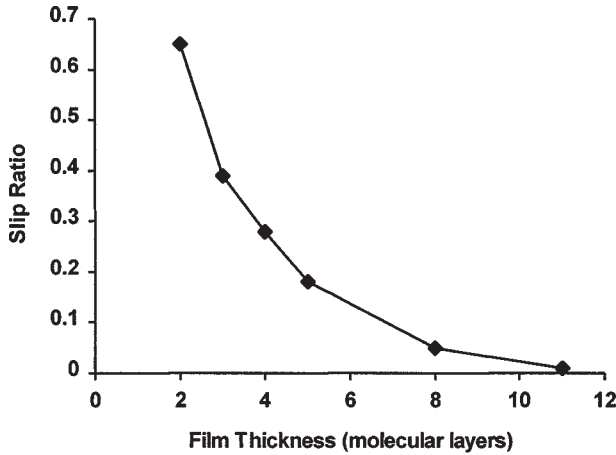


Figure 5. Slip ratio simulated under NVT conditions for confined decane of several film thicknesses, sheared at  $\dot{\gamma} = 0.02$ , with temperature  $T = 144$  K and segment density  $\rho = 1.50/\sigma^3$ . An NVT assembly means that the total number of fluid molecules, volume and temperature of the system are constant for each case of the simulation. The slip rate is defined as  $S = \Delta v_{wf}/v_w$ , where  $v_w$  is wall velocity and  $\Delta v_{wf}$  is the velocity difference between wall and adjacent fluid molecules. The increasing slip indicates that solidification progresses as the film thickness decreases [63].

creases slower than the nominal shear rate  $\dot{\gamma}$ , leading to a decreasing effective viscosity.

One reason for us to emphasize the contribution from wall slip to the phenomenon of shear thinning is that slip will become more significant in thin films. Figure 5 shows how slip ratio changes with film thickness. The slip ratio in the figure is defined as  $S = \Delta v_{wf}/v_w$ , where  $v_w$  is wall velocity and  $\Delta v_{wf}$  is the velocity discontinuity between wall and adjacent fluid molecules. The rapid growth of slip with the decreasing film thickness show in figure 5 indicates that slip may take place even at low shear rate when the film becomes molecularly thin. It has been widely recognized that lubricants confined in thin films exhibit solid-like behavior [6,7,17,21,26–38]. When the solidified film is sheared by the sliding walls, it could be transitioned back to a liquid state, or it could be split along a plane at wall/fluid interface or somewhere within the film, but still remains solid state. We believe that the rapid increase in slip rate provides some evidence for the second possibility, or in another word, the significant slip at low shear rate indicates solidification process with in the film.

As shear rate increases continuously, it was observed in recent experiments that the effective viscosity fell to a second Newtonian plateau with the bulk value of viscosity [41]. If the shear rate keeps growing, it was expected that the viscosity would again deviate from the bulk value and drop again, corresponding to the shear thinning expected even in a bulk system when the shear rate is high. Based on these experiments with a polymer sample, a generalized friction map was suggested by Luengo and coworkers [41] as shown in figure 6. The proposed map reveals that the first shear thinning process, at low shear rate, corresponds to a shear-induced transition from confined solidity to the bulk liquid state. We doubt the generality of this fig-

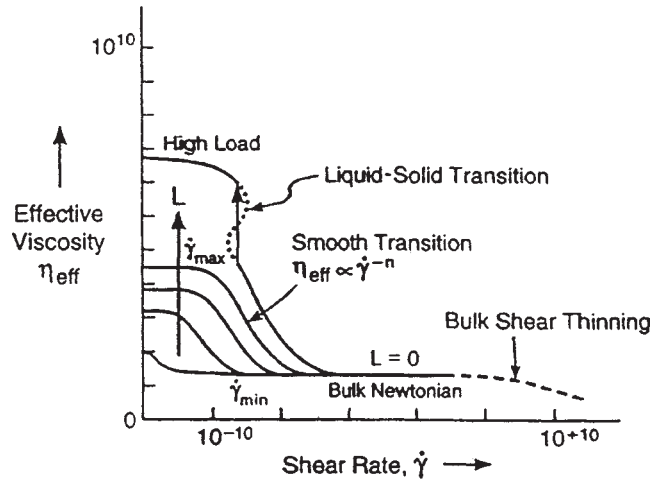


Figure 6. Proposed generalized friction map of effective viscosity plotted against effective shear rate. For ultrathin films at very low shear rate, the effective viscosity is independent of shear rate; this is known as a Newtonian regime. As  $\dot{\gamma}$  increases beyond  $\dot{\gamma}_{min}$ ,  $\eta_{eff}$  starts to decrease with a power law, which is followed by a second Newtonian plateau when the shear rate reaches and exceeds  $\dot{\gamma}_{max}$ . If the  $\dot{\gamma}$  is sufficiently large, bulk shear-thinning is expected [41].

ure however: the mechanisms of molecular motion that are responsible for viscosity are so completely different in bulk fluid and in confined films that we expect the coincidence of effective viscosity with the bulk viscosity to have been fortuitous.

### 3. Thin film lubrication

Lubrication with molecularly-thin films is a common practice in many modern technical devices. A key issue is whether the classical theory of lubrication (the Reynolds equation) is still applicable to the thin films; if not, where is the limit of application, and how alternatively can a tribologist model the thin film lubrication?

In experiments involving elasto-hydrodynamic lubrication, classical theory was found valid even for films of 10–15 nm [42,43]. For spacings less than 10 nm, however, ultrathin films behaved differently from the prediction of classical EHL theory. This is not surprising if we recall the rheological properties of confined lubricants discussed in the previous section. Recently, experimental studies on performances of thin EHL films have been reported by Luo and coworkers [9,10]. The film thickness  $h$  was measured as a function of rolling speed  $v$  with results plotted on logarithmic coordinates in figure 7. For films thicker than 25 nm, the variation of film thickness followed Dowson's classical prediction very well:  $h \sim v^\beta$ , where  $\beta$  is a constant. When the film thickness decreased to a certain limit, depending on the specific lubricant studied and on operation conditions, the  $h-v$  curves took a smaller slope and leveled off gradually. The author suggested that the changes in slope of  $h-v$  curves imply a transition from EHL to a new lubrication regime in which lubricant flow and hydrodynamic effects still exist but behave differently from the

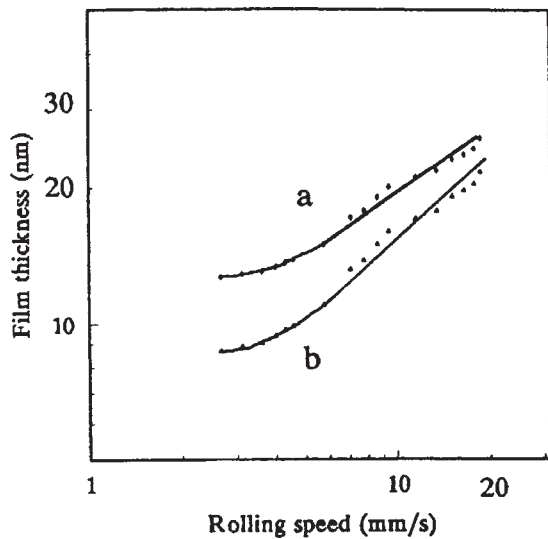


Figure 7. Film thickness measured in a EHL contact as a function of rolling speed. Lubricant: standard viscous liquid 13604, with viscosity of 17.4 mPa s (20 °C), environment temperature: 25 °C, load: 4 N, and ball diameter: 23.5 mm. In the high speed region (above 5 mm s<sup>-1</sup>), the film thickness  $h$  varies in a classical power law:  $h \sim v^\beta$ , where  $v$  is the rolling speed and the index  $\beta \approx 0.70$  for the present case. As the film thickness decreases to a certain limit, the  $h$ - $v$  curves take a smaller slope and level off gradually (see [9] for details).

expectations of classical theory. This new regime is identified as “thin film lubrication”; it bridges hydrodynamic and boundary lubrication [10]. However, since lack of roughness parameters in their report, there is another possibility that roughness may play a significant role in the transition of lubrication behavior.

Theoretical models have been developed to predict viscous flows in conditions of thin film lubrication [2,44–50]. Based on notions of ensemble average, Tichy [44] introduced a dimensionless vector – the director  $\vec{n}$  to describe the mean microstructural alignment of confined lubricants. Meanwhile, the viscous resistance resulting from the molecular orientation was considered to be proportional to a director viscosity  $\mu_1$ . In this approach, a generalized lubrication equation was obtained, in which the structure-oriented effects were described by the parameters  $\theta$  and  $\mu_1$ . In another model suggested also by Tichy [45], the lubricant layers near the solid walls were viewed as a porous medium, which leads to a modified Reynolds equation.

In gas-film lubrication with film thickness  $h$  comparable to the molecular mean free path  $\lambda$ , but still in a small Knudsen number regime ( $K_n \sim 1$ , where  $K_n$  is defined as  $K_n = \lambda/h$ ), modified Reynolds equations based on velocity boundary conditions of first or second order slip flow have been widely used to predict the performance of thin gas films [46,47]. When the film thickness decreases to the nanometer scale and the Knudsen number becomes high ( $K_n > 1.6$ ), molecular behavior has to be taken into account. A generalized lubrication equation was derived by introducing the kinetic theory of gases or molecular gas dynamics [48–50]. The validity of this approach was confirmed by experiments and simulations [2].

For rough engineering surfaces in mixed lubrication, asperities on the opposite surfaces begin to interfere. Numerical analyses, known as micro-EHL, have been performed to study tribological processes involving individual surface asperities [51]. However, the continuum assumptions used in these analyses, such as the rheological properties of lubricant and interfacial boundary conditions, become questionable as two asperities approach each other. Landman and coworkers [36,37] have used MD simulation to investigate asperity interactions in an ultrathin alkane film, providing new information from nanoscale regime to micro-EHL studies. The simulation results show that layered fluid structure is developed in the interasperity region, and that the number of fluid layers diminishes in a quantized manner as successive layers are squeezed out by the colliding asperities. These structural variations are accompanied by oscillation of the fluid-induced forces in the shear and normal direction; this is considered as a possible source of stick-slip motion observed in experiments. For the cases of asperity overlap or near overlap, high pressures are built up in the interasperity region, resulting in severe deformations of the asperities. In the asperity-overlapping case, drainage of lubricant molecules is completed when the asperities pass over each other, leading to formation of an intermetallic junction. Continued sliding shears and eventually breaks the connective junction, resulting in transfer of some metal atoms from one asperity to another [37]. To be a real micro-EHL system, however, the simulation has to consider the elastic deformation of bounding walls, which is difficult to deal with.

Lubrication with monolayers of ordered organic films is a new and rapidly developing topic in thin film lubrication [54–56]. The ordered films can be deposited on the surfaces (substrates) by several approaches such as Langmuir–Blodgett (LB) methods, self-assembly, adsorption, evaporation, etc. [54–56]. The purpose of using ordered films is to achieve low friction coefficients by manipulating molecular arrangement at the interfaces, or by grafting certain surfactant molecules to surfaces. Another advantage of this lubrication strategy is that the lubricant layers are prepared right from the start to provide the surfaces with self-lubricating films. Meanwhile, very small quantities of material are needed so that material cost should not be a major consideration even for fairly expensive lubricants [6].

#### 4. Connection to the macroscopic tribology

Nanorheology, thin film lubrication, or in a broader sense, nanotribology grow up from technical needs. Knowledge gained in these microscopic investigations can contribute to technical progress and better understanding of tribological processes in several aspects:

- (1) Understanding material behavior and lubrication performance on atomic and molecular levels provides a solid theoretical basis for the development of several kinds of high-tech micro devices. In computer hard

disk systems, for example, the disk surface is protected by a thin carbon film, covered with a layer of polymer lubricant several nanometers thick; the spacing between the magnetic recording head and disk surface has been reduced to the nanometer scale to achieve high density storage [3]. The design and smooth operation of such a tribology system depends, to a large extent, on the accumulation of knowledge about interfacial rheology of the lubricant and lubrication behavior of molecularly thin gas films. These issues are particularly critical at start-up of the hard drive – the phenomenon known as “stiction”. The theory of ultra-thin gas film lubrication and results of study on surface mobility have been applied successfully in the design of such a system. Other examples could be cited from the growing field of MEMS (micro-electromechanical system) devices.

- (2) Microscopic study of thin lubricating films may also provide direct contributions to the tribology design of traditional machine components, such as bearings, gears and piston/cylinders, since most of them operate in a mixed lubrication regime where surface asperities interfere with each other; lubricants are highly confined in the inter-asperity regions. Numerical analysis of component performance in mixed lubrication and micro-EHL simulation have become a routine procedure of design in automobile and other industries [57,58]. One growing difficulty in these analyses is the uncertainty of lubricant rheology in inter-asperity region where film thickness can be as low as several nanometers. Application of a traditional rheology model in such a thin film not only leads to unrealistic predictions of pressure distribution, but also brings about numerical instability. It is now possible for engineers to introduce the achievements of nanorheology study into their numerical analysis of mixed lubrication. In addition, the study of rheology in thin films may also play an important role in developing a continuum model of mixed lubrication which includes the effects of asperity interaction and transition of lubricant rheology. One strategy, for example, is to combine microscopic descriptions of interfacial chemical reactions, molecular orientation, and rheological transition with continuum lubrication theory. An alternative strategy for coupling atomic and molecular investigations with continuum-based theories is to establish a constitutive relationship, which would include the contributions from the confining walls and molecule architecture of the lubricant.
- (3) In spite of great progresses made through the past half century, yet many basic issues in fundamental researches of tribology, such as origin of friction, failure of lubrication, even those friction phenomena observed in daily life, remain unsolved mysteries. By revealing the mechanism of friction, lubrication and other interfacial phenomena at atomic and molecular scale, the study of nanorheology may carry new inspiration to the unsolved issues, and push forward the fundamental

study. For example, it is significant and inspiring for a traditional tribologist to know that the static friction in lubricated contact may originate from shearing of solidified lubricant, the stick-slip phenomenon may pertain to the periodic transition of rheological state, and wall slip may take place at very low shear rate if the lubricating film is sufficiently thin. In addition, the mixed lubrication model containing the knowledge of thin film rheology, as mentioned in the previous paragraph, and the friction mapping over a wide range of lubrication regimes, such as suggested in [41], may help engineers to gain a better understanding of the mechanism of lubrication failure and transition between different lubrication regimes.

- (4) Friction control and interface design have long been the desire of generations of tribologists. Studies on nanorheology and thin film lubrication now create new opportunities of interface manipulation and molecular surface engineering. For example, research using organized monolayers as lubricant, such as LB films or self-assembled films, are in progress [59,60]. The friction force may be significantly reduced by manipulating the molecular organization on sliding surfaces to produce a brush-like polymer structure [61], by embedding certain self-lubricating particles [62], or by grafting specific functional groups into the ordered molecule system [52]. Furthermore, based on the understanding that static friction is closely related to the commensurability of solid surfaces in contact, it is possible to limit the static friction by a single layer of lubricant since it does not have enough degree of freedom to lock into a state that is commensurate simultaneously with two walls [6]. Finally, from studies of confined lubricants, we know that the dramatic increase in viscosity due to confinement leads to a transition to the glassy state. This may provide a possibility to form a robust wear-protective layer at molecular scales.

Surfaces in relative motion, if tribologists are successful in tribological design, should be something like human bodies which have their own self-protection mechanisms and immunities. Studies of confined lubricant and thin film lubrication may help to determine how a protective layer is formed at atomic and molecular scales. The long-term purpose of microscopic studies is to understand how to arrange lubricant molecules at the interfaces to achieve low friction and zero wear, and to develop corresponding techniques, on the basis of this understanding, which are believed the most efficient, reliable and economic.

#### Acknowledgement

This research was supported by Chinese National Science Foundation through grant no. 59475035 and by the Pre-researching Foundation of Science Committee of Chinese Defense department. SG acknowledges support from the US National Science Foundation (Tribology Program).

## References

- [1] B. Bhushan, J.N. Israelachvilli and U. Landman, *Nature* 374 (1995) 607.
- [2] R. Kaneko, S. Umemura and M. Hirano et al., *Wear* 200 (1996) 296.
- [3] R. Kaneko, *Wear* 168 (1993) 1.
- [4] S. Granick, *MRS Bulletin* 17 (October 1991) 34.
- [5] J.N. Israelachvilli, in: *Handbook of Micro/Nanotribology*, ed. B. Bhushan (CRC Press, 1995) p. 267.
- [6] M.O. Robbins and E.D. Smith, *Langmuir* 12 (1996) 4543.
- [7] Y.Z. Hu, H. Wang, Y. Guo and L.Q. Zheng, *Wear* 196 (1996) 243.
- [8] Y.Z. Hu, H. Wang, Y. Guo and L.Q. Zheng, *Wear* 196 (1996) 249.
- [9] J.B. Luo, S.Z. Wen and P. Huang, *Wear* 194 (1996) 107.
- [10] J.B. Luo and S.Z. Wen, *Science in China A* 39 (1996) 1312.
- [11] D.Y.C. Chan and R.G. Horn, *J. Chem. Phys.* 83 (1985) 5311.
- [12] A.M. Homola, J.N. Israelachvilli, M.L. Gee and P.M. McGuiggan, *J. Tribol.* 111 (1989) 675.
- [13] M.L. Gee, P.M. McGuiggan, J.N. Israelachvilli and A.M. Homola, *J. Chem. Phys.* 93 (1990) 1895.
- [14] A.M. Homola, J.N. Israelachvilli, M.L. Gee and P.M. McGuiggan, *Wear* 136 (1990) 65.
- [15] J. Van Alsten and S. Granick, *Phys. Rev. Lett.* 61 (1988) 2570.
- [16] H.W. Hu, G.A. Carson and S. Granick, *Phys. Rev. Lett.* 66 (1991) 2758.
- [17] S. Granick, *Science* 253 (1991) 1374.
- [18] G.A. Carson, H.W. Hu and S. Granick, *Tribology Transaction* 35 (1992) 405.
- [19] G. Reiter, A.L. Demirel and S. Granick, *Science* 263 (1994) 1741.
- [20] G. Reiter, A.L. Demirel, J. Peanasky, L. Cai and S. Granick, *J. Chem. Phys.* 191 (1994) 2606.
- [21] S. Granick, A.L. Demirel, L. Cai and J. Peanasky, *Isrl. J. Chem.* 35 (1995) 75.
- [22] A.L. Demirel and S. Granick, *Phys. Rev. Lett.* 77 (1996) 2261.
- [23] A. Dhinowala, L. Cai and S. Granick, *Langmuir* 12 (1996) 4537.
- [24] S. Toxvaerd, *J. Chem. Phys.* 74 (1981) 1998.
- [25] J. Koplik, J.R. Banavar and J.F. Willemsen, *Phys. Rev. Lett.* 60 (1988) 1282.
- [26] M. Schoen, J. Cushman, D. Diestler and C. Rhykerd, *J. Chem. Phys.* 88 (1988) 1394.
- [27] M. Schoen, C.L. Rhykerd, D. Diestler and J.H. Cushman, *Science* 245 (1989) 1223.
- [28] U. Heinbuch and J. Fischer, *Phys. Rev. A* 40 (1989) 1144.
- [29] P.A. Thompson and M.O. Robbins, *Phys. Rev. A* 41 (1990) 6830.
- [30] P.A. Thompson and M.O. Robbins, *Science* 250 (1990) 792.
- [31] P.A. Thompson, P.A. Greast and M.O. Robbins, *Phys. Rev. Lett.* 68 (1992) 3448.
- [32] P.A. Thompson, M.O. Robbins and P.A. Greast, *Isr. J. Chem.* 35 (1995) 93.
- [33] E. Manias, G. Hadziioannou and G. Brinke, *Langmuir* 12 (1996) 4587.
- [34] T.K. Xia, J. Ouyang, M.W. Ribarsky and U. Landman, *Phys. Rev. Lett.* 69 (1992) 1967.
- [35] U. Landman, W.D. Luedtke, J. Ouyang and T.K. Xia, *Jpn. J. Appl. Phys.* 32 (1993) 1444.
- [36] J. Gao, W. Luedtke and U. Landman, *Science* 270 (1995) 605.
- [37] U. Landman, W. Luedtke and J. Gao, *Langmuir* 12 (1996) 4514.
- [38] Y.Z. Hu et al., STLE meeting, Detroit, MI (May 1998), to be presented.
- [39] M. Alsaad, S. Bair, D.M. Sanborn and W.O. Winer, *J. Lub. Tech.* 100 (1978) 404.
- [40] B.N. Persson, *J. Phys. Rev. B* 50 (1994) 4771.
- [41] G. Luengo, J.N. Israelachvilli and S. Granick, *Wear* 200 (1996) 328.
- [42] G.J. Johnston, R. Wayte and H.A. Spikes, *STLE Tribol. Trans.* 34 (1991) 187.
- [43] D. Cooper and A.J. Moor, *Wear* 175 (1994) 93.
- [44] J.A. Tichy, *STLE Tribol. Trans.* 38 (1995) 108.
- [45] J.A. Tichy, *J. Tribol.* 117 (1995) 16.
- [46] A.J. Burgdorfer, *Basic Engn.* 81 (1959) 94.
- [47] Y. Hsia and G.A. Domoto, *J. Lub. Tech.* 105 (1983) 120.
- [48] R.F. Gans, *J. Tribol.* 107 (1985) 431.
- [49] S. Fukui and R. Kaneko, *J. Tribol.* 112 (1990) 78.
- [50] S. Fukui and R. Kaneko, in: *Handbook of Micro/Nanotribology*, ed. B. Bhushan (CRC Press, Boca Raton, FL, 1995) ch. 13.
- [51] X.L. Ai, H.S. Cheng and L.Q. Zheng, *J. Tribol.* 115 (1993) 102.
- [52] H. Yoshizawa, P. McGuiggan and J.N. Israelachvilli, *Science* 259 (1993) 1305.
- [53] J. Klein, E. Kumacheva, D. Mahalu, D. Perahia and L.J. Fetters, *Nature* 370 (1994) 634.
- [54] I. Langmuir, *Trans. Far. Soc.* 15 (1920) 62.
- [55] K.B. Blodgett, *J. Am. Chem. Soc.* 57 (1935) 1007.
- [56] A. Ulman, *MRS Bulletin*, 21 (6) (1995) 46.
- [57] P.K. Goenka and P.R. Meernik, *SAE Technical Paper*, Ser. 920490 (1992).
- [58] D. Zhu, H.S. Cheng, T. Arai and K. Hamai., *ASME Paper*, 91-Trib-66.
- [59] E. Meyer, R. Overney and D. Brodbeck et al., *Phys. Rev. Lett.* 69 (1992) 1777.
- [60] A.O. David and H.G. Jcha, *Langmuir* 9 (1993) 3015.
- [61] J. Klein et al., *Nature* (11) July (1991) 352.
- [62] J. Zhang, Q.J. Xue and Z. Du, *Science Bulletin of China* 33 (1993) 1671.
- [63] Y.-Z. Hu et al., to be published.