Stick-slip motion in boundary lubrication

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Abstract

With the development of the surface force apparatus (SFA) and molecular dynamics (MD) simulations, boundary lubrication has been extensively studied over the last decades. Due to confinement, liquids in boundary lubrication regime become solid-like and behave remarkably different from their bulk properties. For simple fluids, a first order liquid-to-solid phase transition is observed. Due to the solid-like behavior in the boundary lubrication regime, the solid-like phase is able to sustain a finite stress and stick-slip motion is often observed at low shear velocity. MD simulations show that this solid-like phase may transit into liquid-like phase in the slip state and the fluid may recrystallize in the next stick state. Another possibility is that the order of the solid-like phase can be maintained but layer-over-layer slips occur in the slip state.

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1 Introduction

When two macroscopic solids slide relative to each other, instead of smooth sliding with constant kinetic friction force, stick-slip motion can sometimes be observed during which the friction force oscillates between a maximum and a minimum. As its name suggests, stick-slip occurs when the two solids stick together for some time then slip for some distance, and the cycle repeats. Figure1 is a schematic diagram of stick-slip motion without lubrication. One solid with mass M is driven by a spring which moves at constant velocity v.
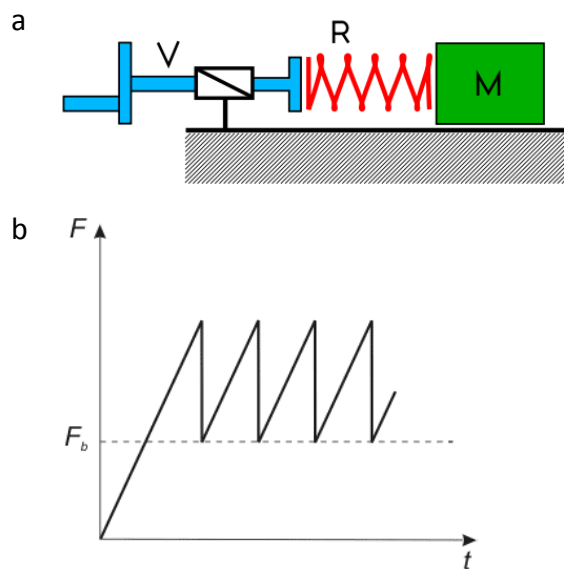

Figure1. (a)Schematic diagram of stick-slip motion without lubrication. (b)Typical friction profile as a function of time

The engineering explanation for the stick-slip motion is that the static friction force Fs is higher than the kinetic friction force F_k. As the spring stretches, shear force is applied to the solid, and finally exceeds the static friction force, then, the solid begins to slide. In the mean time, due to the sudden decrease in friction force caused by the smaller kinetic friction coefficient, the solid accelerates and makes a jump which is referred to as the slip state.

To diminish the friction between two solid surfaces, the usual way is to add liquid lubricants between them. An example is a Newtonian fluid whose viscosity η is independent of shear rate, in the space with dimension D between two parallel plates with area A and one plate shearing with velocity v. the friction force can be expressed as:

$$F = \frac{A\eta v}{D}$$

The bulk lubricant exhibits continuum properties which have no long-range order, cannot sustain shear strength, and constant viscosity. This regime may be referred as to hydrodynamic lubrication. To reach this regime, thick lubricant and high shear rate are needed and the load should be low or close to zero.

However, with the decreasing thickness of the lubricant down to the nanoscale, that is, a few layers of lubricant molecules, the properties of the lubricant layers change sharply. The viscosity of the lubricant increases dramatically and the thin film shows some solid-like behavior which is manifested by a finite yield strength. For simple molecules and linear alkanes, with progressive reduction of the confinement thickness, a sudden liquid-to-solid phase transition, which occurs at about 6-7 molecular layers, is observed in many experiments [1-3]. When the thin film is confined to about a few molecular layers, this kind of

lubrication is known as boundary lubrication.

Figure 2 is the Stribek curve [4], which empirically shows the three lubrication regimes: boundary lubrication, intermediate and hydrodynamic. The intermediate regime, between boundary lubrication and the hydrodynamic regime, shows intermediate properties but the film is still liquid.
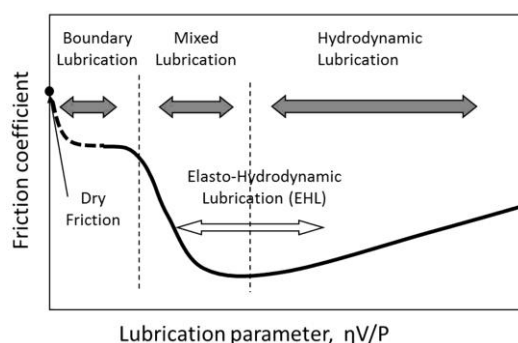

Figure 2. Stribek curve, friction force profile as a function of velocity, viscosity and load [4].

Interestingly, due to the solid-like behavior during boundary lubrication, when the molecular thin film is sheared under low shear rate, in most cases, stick-slip motion is observed. When the shear rate exceeds a critical velocity, the stick-slip motion disappears and the friction fluctuates gently around a smaller value. Experiments have shown that, for different molecules, the stick-slip motion behavior is also different. For branched alkanes, which are harder to pack in good order than simple molecules and linear alkanes, the transition from stick to slip is continuous and the relaxation time is longer [5-6], while the transition is abrupt for simple molecules and a critical velocity can be well-defined [7].

It is believed that a negative slope, dF/dv<0, where F is the friction force and v is the shear velocity, is necessary for the occurrence of the stick-slip motion [8]. If a friction force decreases with increasing shear velocity, the force (F_s) need to start the motion is higher than the force (F_k) to keep the motion going on. So long as the thin film is shearing at a constant velocity, the F(v) will lead to periodic motions of long stops, followed by fast acceleration and deceleration. However, experimental results [6] have shown that friction force is a multivalued funtion of velocity, with different behaviors in acceleration and deceleration during the slip state. This suggests a friction force profile, which is purely dependent on velocity, is not sufficient to explain the stick-slip motion and the states, or phases, of the thin film during the motion must be taken into account.
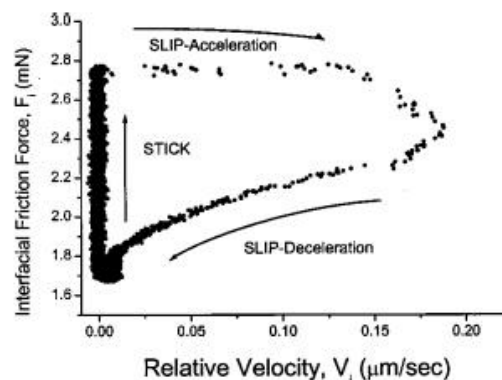

Figure 3. Intrinsic friction force as a function of relative velocity in a single stick-slip motion for thin lubricant confined by mica surfaces [6].

One of the first phase transition models, e.g. the shear-melting model, was proposed by Robbins and Thompson [9]. When the thin film is confined statically, the molecules arrange in order like in a solid state and

this order disappears in the following slip state. The order-disorder transition is not limited to solid-liquid transition. For example, the reform and breaking of domains, capillary bridges, chemical bonds, etc. are all possible.

This review is arranged as follows: first, the investigation methods, i.e. experimental and numerical methods, are introduced. The second part explains the confinement-induced solidification for boundary lubrication. After that, the dynamics of the confined thin film under shear, i.e., the stick-slip motion are present. Different models for the explanation of the stick-slip motion are described in section 5. The review ends with the conclusion.

2 Methods

2.1 Study materials

The most extensively studied lubricants are: nonpolar cyclic molecules usually referred as simple molecules, including Octamethyl-cyclotetrasiloxane (OMCTS) and cyclohexane; linear saturated alkanes such as dodecane, tetradecane, hexadecane, etc.; saturated branch alkanes such as squanlane; and polar aqueous liquids such as water [1-7]. The molecular structures of OMCTS and cyclohexane are shown in figure 4. Due to their cyclic structure, these nonpolar molecules are treated as simple quasispherical molecules.
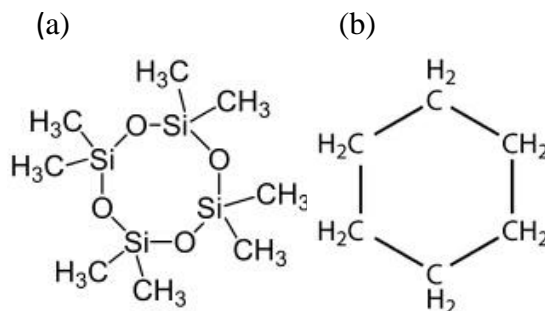

Figure 4. (a) Molecular structure of OMCTS (b) molecular structure of cyclohexane [1].

Atomically flat mica is widely used as a substrate in surface force measurements and its structure is shown in figure 5.
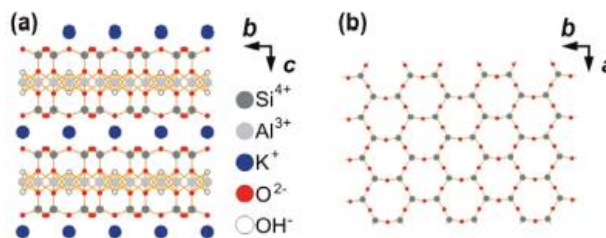

Figure 5. Crystal structure of mica. (a) viewed from [100] direction. (b) viewed from [001] direction [11].

A mica crystal consists of negatively charged aluminosilicate layers which are kept together by layers of positive potassium ions. The relatively weak electrostatic interaction between aluminosilicate and potassium layers results in easy cleavage along the {001} planes, which leading to an atomiclly flat surface. After cleavage, potassium ions assumed to be distributed randomly on each surface [11].

2.2 surface force apparatus (SFA)

With the development of atomic force microscope (AFM) [10] and

surface force apparatus (SFA), friction experimentS can be conducted at the microscale and nanoscale. Figure 6 is a typical SFA configuration for boundary lubrication measurements.
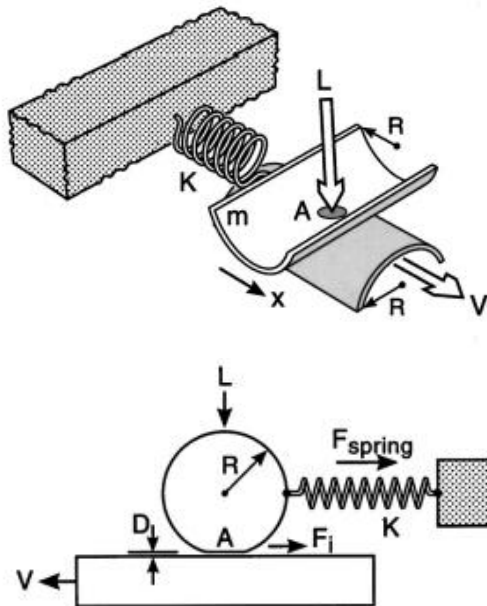

Figure 6. (a) Top view of a typical SFA. (b)Laterall view of (a) [6].

Two silica surfaces with radius R are coated by atomiclly flat mica. A load L is applied to the silica surface to make an elastic contact. The liquid thin film with thickness D is confined within the area A. The bottom surface is driven laterally at constant velocity V and a spring with spring constant K is attached to the upper surface to measure the friction force.

2.3 molecular dynamics (MD) simulations

Molecular dynamics is the computer simulation of movements of molecules by numerically solving Newton's equation of motions. Currently, molecular dynamics simulations are used extensively to study the mechanism of stick-slip, because it allows researchers to directly observe the configuration of molecules. For boundary lubrication, two solid walls are usually simulated with crystalline order containing hundreds of atoms. Several layers of lubricant atoms are confined by the walls and interact with each other with a potential U_{ij}, such as Lennard-Jones potential:

$$U_{ij} = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right],$$

where ε is the depth of the potential well, σ is the finite distance where the potential is zero, and r_{ij} is the distance between the molecules i and j. As shown in figure 7, a load L is applied to the wall to keep the lubricant atoms under confinement and the upper wall is fixed to a spring with spring constant k which drives at constant velocity. Compared to experiment, one of the biggest advantages of MD simulations is that the kinematics of the atoms are known, thus, the evolution of atomic dynamics can be directly observed.
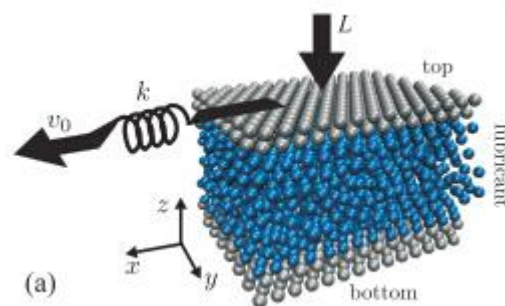

Figure 7. A typical model for MD simulations of boundary lubrication, grey atoms are wall and blue atoms are lubricant molecules [12].

On the other hand, MD simulations are limited by their time and length

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scales. Because the integration step is of the orders of about picoseconds, a long-duration MD simulation at the order of microseconds is computationally expensive. Moreover, MD simulations can only applied to small systems, i.e. of the order of tens of nanometers. Limited by scale, one solution, for example, coarse-graining model, is to define and work with pseudo atoms. This means that, by choosing appropriate parameters, the simple molecules mentioned earlier, e.g. OMCTS and cyclohexane, which are composed of many atoms, can be treated as one single atom in MD simulations.

The differences in time and length scales between experiments and MD simulations result in large discrepancies; for example, the critical velocity predicted in MD simulations is of the order of several meters per seconds while in experiments, it is of the order of micrometers per seconds. However, MD simulations are still quite accurate in predicting the physical behaviors.

3   Confinement of thin film down to molecular layers scale

With the development of the SFA, the properties of fluids under confinement of the order of nanometers have been extensively studied in the past two decades. For nonpolar simple molecules and linear alkanes, many SFA measurements and MD simulations [1-3,13-14] have revealed that progressively decreasing the thickness of the confined thin film, when exceeding a critical layer, usually about 6-7 layers thick, and depending on the type of molecules, an abrupt liquid-solid transition occurs, and the viscosity increases by several orders of magnitude.

Figure 8 shows the characteristic oscillatory normal force profile as a function of thin film thickness for OMCTS [1]. It is well known that nonpolar molecules without valence electrons interact with each other by van der Waals forces [15], as demonstrated by the attractive tail in the figure 8. For the OMCTS, with further confinement of the thin film whose thickness is corresponding to seven molecular layers, the separation of the walls decreases discontinuously to six molecular layers thick, and the liquid phase transits into the solid-like phase, in the sense that it is able to support a finite shear stress. After the liquid-solid transition, the normal force oscillates between a repulsive and an attractive value with periodicity about the mean diameter of the molecules.
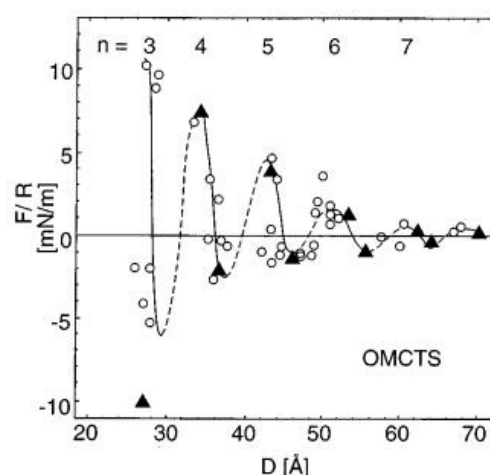

Figure 8. Oscillatory force as a function of distance of the confined walls for OMCTS.[1]

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It should be noted that this phase transition can be induced by geometric confinement alone, and high pressure is not necessary. Experiment [1] and MD simulations [13-14] have shown that the pressure on the surfaces is about atmospheric pressure.

It is surprising that MD simulations agree very well with the experimental results with regard to the number of molecular layers where the transition occurs. Also, MD simulations have revealed some possible explanations for the liquid-to-solid transition.

For example, Lei and Leng [11] performed liquid-vapor molecular dynamics (LVMD) simulations of simple spherical molecules under the confinement of face-centered cubic (fcc) crystal walls with the close-packed (111) plane. The confined liquid thin film is in equilibrium with surrounding vapor molecules, and the liquid molecules can be squeeze-out under compression. The transition occurs at seven molecular layers. Their work also demonstrates that the nucleation starts from the center of the thin film, and propagates to the edges, as shown in figure 9.
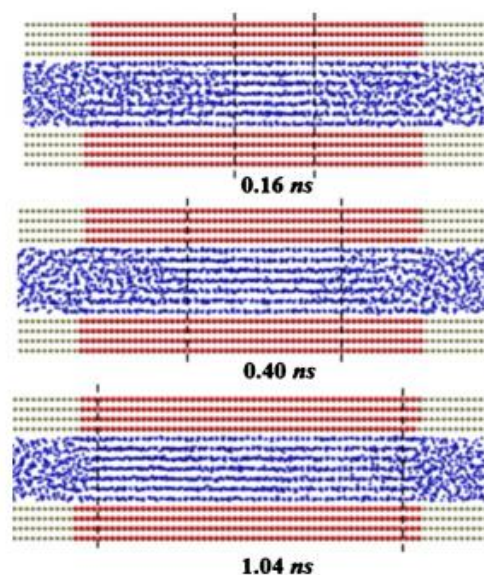

Figure9. Nucleation process of liquid-to-solid phase transition [13].

Cui et al. [14] simulated a thin film of dodecane, a linear alkane, under confinement, which displays similar abrupt liquid-to-solid phase transition when the film is reduced from seven to six molecular layers. Moreover, the simulation results directly reveal the in and out-of-plane order after the transition. Figure 10(a) shows the configuration of molecules in the disordered state, when the thickness of the thin film corresponds to eight molecular layers. When the thickness is reduced to seven layers, as shown in figure 10(b), the molecules exhibit partial order which can be seen at the edges. The liquid-solid transition occurs at seven to six layers. Figure 10(c) shows the configuration for film thickness corresponding to six molecular layers and the molecules lay orderly in six layers. Figure 10(d) is the perspective view of Figure 10(c) which shows the in-plane order of the thin film, i.e., the molecules tend to align
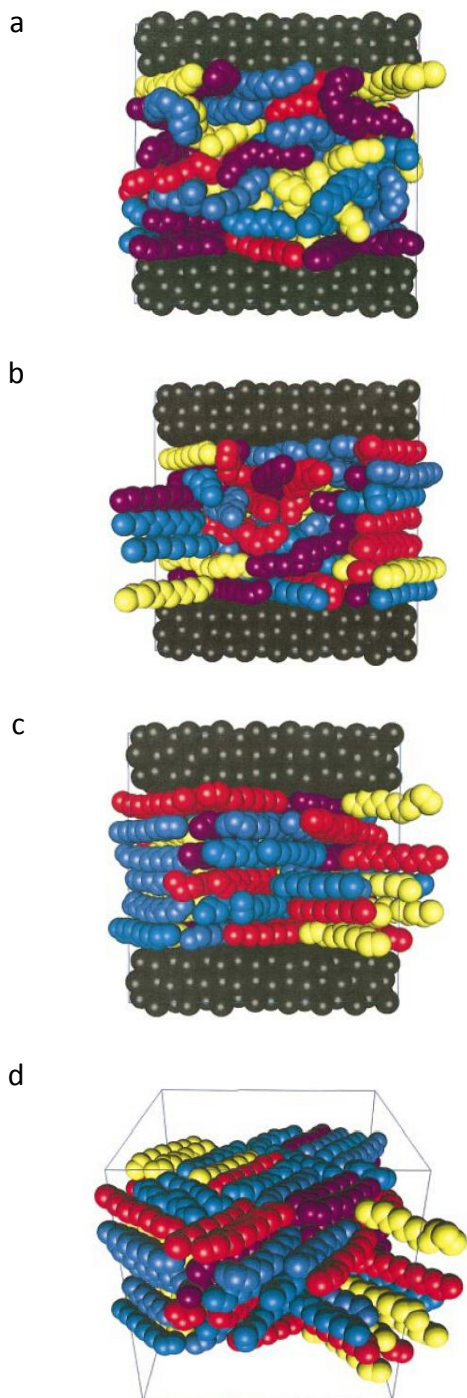
parallel or perpendicular with each other.

a

b

c

d

Figure 10. (a) Equilibrium configuration of dodecane thin film with thickness corresponding to eight layers. (b) Equilibrium configuration of dodecane thin film with thickness corresponding to seven layers (c) Equilibrium configuration of dodecane thin film with thickness corresponding to six layers (d) Perspective view of (c) [14].

Although MD simulations demonstrate elegant possible molecule rearrangement of the liquid-to-solid transition, the actual structure may not be as simple as MD simulations suggest. Mukhopadhyay et al [3] used fluorescence correlation spectroscopy, in which fluorescence dye are used to keep track of molecule movements, to study OMTS. The experiments confirmed the existence of the phase transition, but massively heterogeneous diffusion was observed suggesting that the confinement-induced solid-like state may not have a definite structure as in the case of bulk solids where molecules have fixed positions.

On the contrary, for branched alkanes [4], which are harder to crowd and pack in well order compared to simple molecules, decreasing film thickness only results in continuous monotonic increasing repulsion and liquid-to-solid transition does not occur.

There is also no liquid-to-solid transition for water confined by mica to a subnanometer film [16]. The viscosity of water remains within a factor of three of its bulk value even when it is confined to thin films whose thickness range from 3.5±1nm to 0.0±0.4nm.

4   Stick-slip dynamics

4.1   Transition of stick-slip to smooth sliding

Due to the solid-like properties of confined thin films in boundary lubrication, thin films can sustain a finite shear stress and, in most cases,

show stick-slip motion at low shear velocity. The static friction force F_s is the maximum force the thin film can support before slip and F_k is the kinetic friction force during the slip motion.

Figure 11(a) shows a discontinuous transition from stick to slip state in the sense that the friction spikes ($\Delta F=F_s-F_k$) remain roughly the same with different shear velocity and suddenly disappear a when the shear velocity, reaches a critical value. With the increase of velocity, the period of each stick-slip cycle decreases and the time intervals between each spike grow irregularly. For confined simple spherical or linear molecules [2], their transition between stick-slip and smooth sliding is discontinuous.

It should be pointed out that, although the height of spikes remains Bb roughly the same, the magnitudes of both the static friction F_s and the kinetic friction F_k decrease with increasing shear velocity, this negative slope, dF/dV<0 is thought to be necessary for stick-slip motion to occur [4].

On the contrary, for saturated branch alkanes, whether the transition is continuous or not is determined by the experimental conditions. For example, Gourdon and Israelachvili [5,6] studied the shear properties of confined thin films of squanlane. When the normal load applied to the film is high, the transition from stick-slip to smooth sliding is discontinuous as shown in figure 11(a). Under low load, however, a continuous transition is observed as depicted in figure 11(b). With the increase of driving velocity, the average height of the spike, $\Delta F=F_s-F_k$, decreases continuously. The inset shows that the friction pattern becomes irregular as

spikes with different heights appear. The critical velocity is defined at the point where no more stick is observed.

For both cases, i.e., continuous or discontinuous transition, when the system reaches at smooth sliding region, the friction force continuously decreases with the increasing driving velocity.
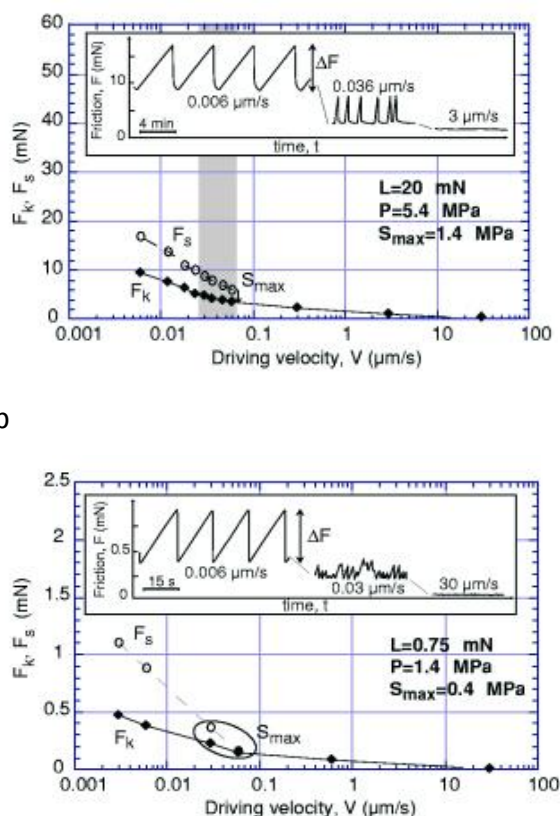

Figure11. Average static friction F_s and kinetic friction F_k as a function of driving velocity for (a) discontinuous transition, (b) continuous transition. The inset shows the friction spikes as a function of time for three different shear velocities [5].

4.2 Stop-start experiment

When the sliding is ceased, the lubricant molecules still undergo relaxation. Usually, a stop-start experiment is used to study the

transient evolution of force when the experimental conditions are suddenly changed [5,6]. The system is sheared above the critical velocity, followed by a sudden stop for some time t_s, and then the shearing is resumed. If the stop time t_s is longer than the latency time t_l, a stiction spike, corresponding to $F_{stiction}$ $-F_k$, as shown in the inset of figure 12, is observed when shearing resumes.
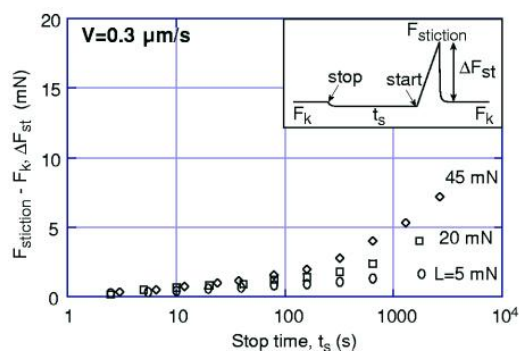

Figure 12. The increase of stiction spike height, $F_{stiction}$ $-F_k$ with longer stop time under three different loads for branches alkanes. The inset shows the transient profile of stiction [5].

For simple liquids, the height of the stiction spike remains roughly the same for varying stop times longer than the latency time, suggesting a fast relaxation of these molecules. On the contrary, for complex alkanes, the stiction spike height grows with the stop time even to four orders of magnitude, as shown in figure 11, and no trend for this increase to stop is observed. This suggests a much longer and complex relaxation than simple for molecules.

5   Models

5.1   Phase transition model

5.1.1 Shear-melting model

One of the first MD simulations to study the mechanisms of stick-slip motion was performed by Thompson and Robbins [9]. They proposed the shear-melting model and stated that stick-slip motion is caused by thermodynamic rather than dynamic instability. In this model, simple spherical molecules are confined by fcc walls with the (111) surfaces and the interaction of lubricant molecules with each other and with the wall is approximated by the same Lennard-Jones potential. As stated before, due to the confinement, the molecules lay in well order at rest even for zero normal load. A two dimensional factor, the Debye-Waller factor, is used to describe the in-plane order of the molecules of the layers next to the walls. For a perfect crystal at zero temperature, the value of Debye-Waller factor is 1 and drops to 0.6 at the melting point. When the plates stick together, the Debye-Waller factor is around 1, indicating a solidlike state. In contrast, when the two plates slide, the factor drop to 0.2, which suggests a liquid structure. This process is illustrated in figure 13.
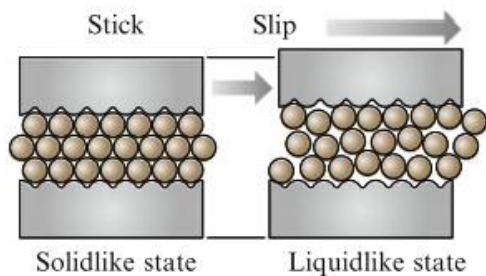
Figure 13. In the stick state, molecules are arrange in solid order and can support a finite shear force. In the slip state, this order disappears and a solidlike state transits to a more disordered liquidlike state [4].

When the shear velocity exceeds a critical value, the molecules do not have enough time to rearrange and the stick-slip motion disappears.

It should be noted that the recrystallization and melting transition within the layers, or at the boundary layer with the walls, may not be the same as the transition of bulk solid phase to liquid phase. If the molecules couple more strongly to the walls than within the thin film, the melting will start in the middle of the film. If the interaction of the lubricant molecules among themselves is stronger than that with the wall, the melting starts from the boundary layers [17].

Apparently, this order-disorder transition model is not limited to the solidlike state and liquidlike states. Other kinds of transitions between order and disorder state are also possible, as discussed in the next sections [18-19].

5.1.2 Domain reformation

The transition between domain reformation and domain breaking can also be regarded as a kind of order-disorder transition. Chen et al [18] studied a monolayer of simplified rigid bead-necklace liquid crystal confined by surfaces with different atomic arrangements as shown in figure 14. The monolayer of liquid crystals is sheared along the x aixs. The (111) plane of fcc crystal is close-packed, with six nearest neighbor atoms around a atom. The (110) plane only has two nearest neighbor atoms along the x axis, while the (100) plane has four nearest neighbor atoms along the diagonal of the xy plane. Due to the anisotropy of the liquid crystals, these tend to align with the surface mesh and form domains in the stick phase; these orders disappear or become less obvious in the subsequent slip state.
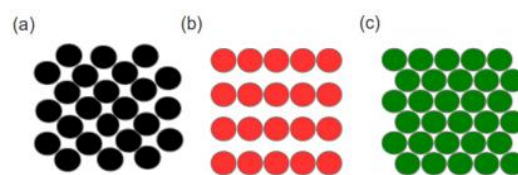

Figure 14. (a) (100), (b) (110),(c) (111) crystallography plane of face-centered crystals [15].

Figure 14 presents the snapshots of the arrangements of liquid crystals of planes (111), (100) and (110) in the stick-slip motions. For the (111) planes, it is clear from the snapshot that, in the stick state, the liquid crystals tend to organize in such a way so as to align their long axis parallel to the surface mesh, and a number of domains are formed. In the slip state, the domains decompose, and the orientations of liquid crystals, are distributed more randomly.
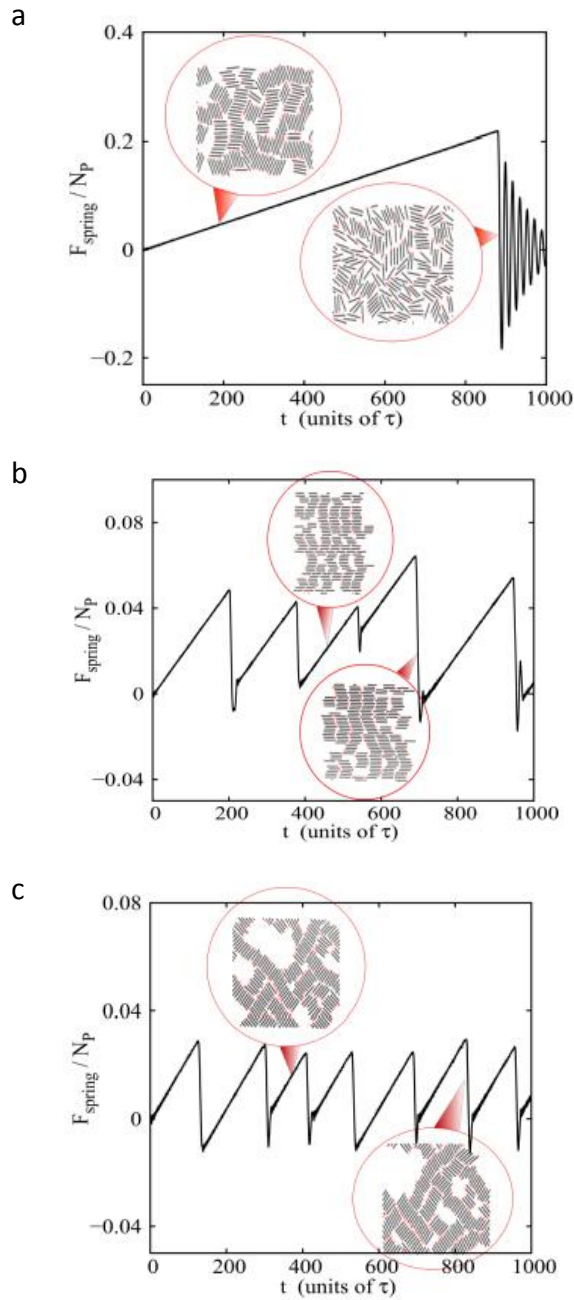
a

b

c

Figure 15. snapshots of liquid crystals arrangement in stick state and slip state for confined by (a) (100), (b) (110) and (111) planes of face-centered crystals, respectively[15].

The same mechanism also works for the (100) and (110) planes. For the (110) surfaces, as shown in figure 15(b), the atoms of the surface only have two nearest neighbors, which lie along the x axis so that the liquid crystals align themselves in this direction in the stick state. Because the shear direction is also along the x-axis, the preferential orientation does not change, and it is clearly shown in figure 15(b) that liquid crystals still orient their long axis in the x direction. In fact, it is hard to differentiate the stick and slip of the (110) planes from the snapshots. The authors used a global order parameter to study the difference between the slip and stick state, and, indeed, a small drop of the order parameter in the slip phase was observed.

For the (100) planes, liquid crystals align with the mesh, i.e. with the diagonals of the xy plane. Because there is no preferred orientation along the sliding direction, the molecules are aligned ±45° both in the stick and slip states as shown in figure 14(c).

Compared to (100) and (110) planes, molecules are more disordered in the slip state for the (111) plane. It is reasonable for these molecules to take more time to rearrange themselves back into the slip state, which is in agreement with the longer period shown in figure 15. When the shear rate exceeds the critical velocity, that is, in the smooth sliding state, the liquid crystals do not have enough time to rearrange, and finally align themselves with the shear direction.

5.1.3 Capillary bridge reformation

As mentioned previously, water confined by mica surfaces does not undergo liquid-solid transition even when the separation of mica surfaces at the range from 3.5±1nm to 0.0±0.4nm. [16]. In another study, Chen et al [19]

compared the difference of boundary lubrication of water confined by hydrophilic mica and hydrophobic graphene sheets. The result showed that the two mica plates lubricated by water show stick-slip dynamics, while there is only smooth sliding for graphene.

To mimic a real mica surface, half of the K^+ ions on the cleavage plane are placed randomly on the upper mica surface, and the rest half are placed at the corresponding position of bottom surface in the MD simulation. Because of the potassium ions, mica surfaces are hydrophilic in contrast with the hydrophobic graphene. In the stick state, the polar water molecules interact strongly with the K^+ by Coulomb interaction with the oxygen atoms. The density profile of water molecules shows that, in the stick state, as shown in figure 16(a), water molecules gather around the potassium ions, forming nanoscale capillary bridges which connect the upper and bottom mica surfaces and many empty areas without water molecules distributed in between the capillary bridges. These capillary bridges break in the following slip state and this cycle repeats, as illustrated in the figure 16.
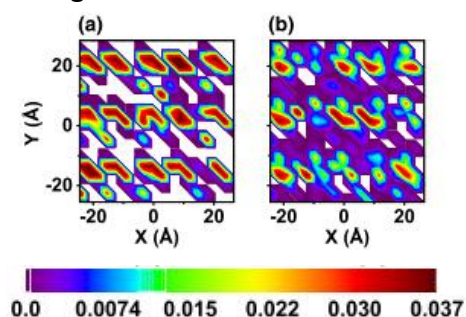

Figure 16. Contour graphs of density distribution of water molecules in (a) stick state and (b) slip state. White area means no water molecules [19].

The breaking and reforming process of nanoscale capillary bridges can also be regarded as an order-disorder transition. When the shear velocity exceeds the critical velocity, only smooth sliding is observed because there is not enough time to reform the capillary bridges. For thicker water films, the stick-slip motion also disappears because nanoscale capillary bridges cannot be formed. On the contrary, the carbon atoms in hydrophobic graphene interact weakly with water molecules and only show smooth sliding. The density profile of water confined by graphene only shows a single, large structure which looks more or less the same from the stick to the slip state[19].

5.2 Layer-over-layer sliding

In addition to the order-disorder transition, recent MD simulations [12,20] have shown that, in some cases, instead of shear-melting, slips of the layers within the thin film or with the walls may be the mechanism of stick-slip motion. Unlike the order-disorder phase transition, during each slip, the crystalline orders of the layers are well maintained in this case.

For example, Lei and Leng [20] performed liquid-vapor molecular dynamics (LVMD) simulations for nonpolar simple molecules under the confinement of (111) planes of face-centered crystals. Right after the liquid-to-solid phase transition, the upper plate is driven at a constant velocity far below the critical velocity. The bottom plate is fixed. The calculations demonstrate that

shear-melting is unfavorable in this case, because of the energy penalty of disorder during slips. Instead, slips between each interlayer or at the interface between an interlayer and the wall are observed, as shown in figure 17. For instance, at the first stick-slip cycle, layer 4 moves together with the upper wall and slips with layers below it. Then the layer 4 slip with the upper wall at the second stick-slip cycle, and so on. Moreover, Compared to the shear-melting model, the friction spikes are irregular with varying heights and periods.
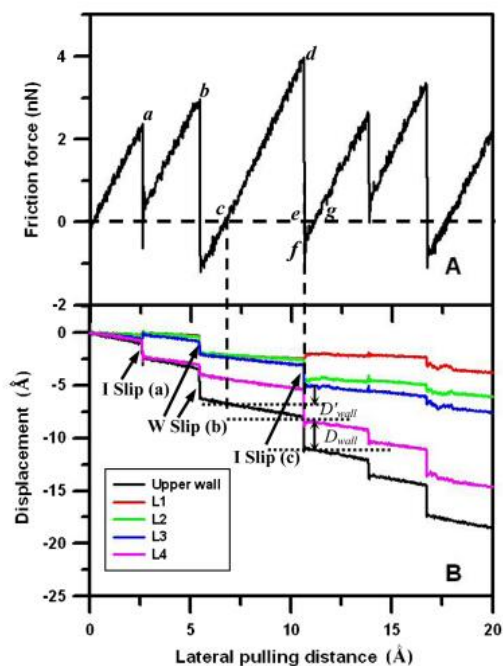

Figure 17. (a) Stick-slip friction force as a function of lateral pulling distance. (b) The displacement of each interlayer and upper wall for every slip state. Layer4 is right below the upper wall, followed by layer3, layer2 and layer1, respectively. [20].

A number of MD simulations [4,8,19] predict the increase, about 10%-15%, of the lubricant thin film thickness during the slip state; however, the resolution of the experiments performed thus far is not enough to validate these small change.

6 Conclusion

When a confined liquid thin film is reduced to nanoscale in thickness, its properties change remarkably in contrast to the bulk values. The fluid behaves more solidlike in terms of long-range order in the thin film, dramatically increasing its viscosity and the ability to sustain a finite stress. The properties of confined molecules, the atomic arrangement of the wall, shear velocity, temperature, load, etc., may all influence the behavior of the confined thin film.

For simple nonpolar molecules, systematic studies observed that abrupt confinement-induced liquid-to-solid phase transitions occur when the film is reduced to a critical number of molecular layers, usually 6-7. Note that the solid-like and liquid-like phases in confinement are not the same as these in the bulk solid and liquid phases. The solid-like phase in confinement may not have a definite crystalline structure as do bulk crystals. Due to the solid-like behavior, stick-slip motion occurs when the shear velocity is low. The stick-slip motion transits discontinuously to smooth sliding at a critical velocity. Shearing at the smooth sliding regime, if it is stopped for a time t_s which is longer than the latency time, a stiction spike is observed when the shearing resumes. Moreover, the height of the spike remains roughly constant for different stop time t_s as long as it is longer than the latency time.

In contrast, complex molecules, e.g. branched alkanes, do not undergo liquid-to-solid transition but only a monotoniclly increasing repulsive force is observed when reducing the scale of confinement. The transition from the stick-slip to the smooth sliding state is continuous, during which the heights of the friction spikes decrease continuously, and the transition is defined at the point where the friction spike disappears completely. There is also a latency time for complex molecules. However, the stiction spike grows with increasing stop time even when the stop time is longer by several orders of magnitude and no trend is observed towards a stop in growth, which suggest much longer relaxation time in contrast to simple molecules.

For nonpolar simple molecules and linear alkanes, the confinement induces solid-like order in thin films and the molecules arrange themselves in layers. Depending on the parameters of the simulation, this solidlike structure may be maintained but the molecular layers slip within the thin film or with the walls. Also this solidlike structure may melt in the slip state and recrystallize in following stick state. This order-disorder transition can have different forms, such as breaking and reforming domains, capillary bridges, and so on.

The number of published articles for boundary lubrication increases steadily over the last decades. For experiments, the type of sliding surface is limited because it is hard to get atomically flat surfaces from materials other than mica. To what extent the surface is clean should also be considered. The properties of the thin film should be decoupled from the whole system, and

so on. All these problems can be easily solved by MD simulations. Nowadays, researchers prefer MD simulations than experiments. With the development of computers, simulate complex molecules in detail may be possible in the future.

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8 Reference

1. Klein J, Kumacheva E. The Journal of chemical physics, 1998, 108(16): 6996-7009

2. Gee M L, McGuiggan P M, Israelachvili J N, Homola, A. M. The Journal of Chemical Physics, 1990, 93(3): 1895-1906.

3. Mukhopadhyay, A., Zhao, J., Bae, S. C., & Granick, S. (2002). Physical review letters,89(13), 136103.

4. Surface Forces and Nanorheology of Molecularly Thin Films. Marina Ruths and Jacob N. Israelachvili, in Handbook of Nanotechnology, 3rd edition, Chapter 29, B. Bhushan, Ed., Springer-Verlag. (2010) 857-922.

5. Gourdon D, Israelachvili J N. Physical Review E, 2003, 68(2): 021602.

6. Drummond C, Israelachvili J. Physical Review E, 2001, 63(4): 041506.

7. J. Israelachvili, P. McGuiggan, M. Gee, A. Homola, M. Robbins, and P. Thompson, J. Phys.: Condens. Matter 2, SA89 (1990).

8. Bowen, F.P., and Tabor D. Friction and Lubrication. Oxford Univ. Press, Oxford 1958

9. Thompson, Peter A., and Mark O. Robbins. Science 250.4982 (1990): 792-794.

10. Binnig, Gerd, Calvin F. Quate, and Ch Gerber. Physical review letters 56.9 (1986): 930.

11. Ostendorf, F., Schmitz, C., Hirth, S., Kühnle, A., Kolodziej, J. J., & Reichling, M. (2008). Nanotechnology, 19(30), 305705.

12. Vanossi, A., Benassi, A., Varini, N., & Tosatti, E. (2013). Physical Review B, 87(4), 045412.

13. Lei Y, Leng Y. Physical Review E, 2010, 82(4): 040501.

14. Cui S T, Cummings P T, Cochran H D. The Journal of Chemical Physics, 2001, 114(16): 7189-7195

15. Hamaker, H. C. physica 4.10 (1937): 1058-1072.

16. Raviv, U., Laurat, P., & Klein, J. (2001).. Nature, 413(6851), 51-54.

17. Braun O M, Peyrard M. Physical Review E, 2003, 68(1): 011506.

18. W. Chen, S. Kulju, A. S. Foster, M. J. Alava, and L. Laurson, Phys. Rev. E 90, 012404 (2014).

19. Chen W, Foster A S, Alava M J, Laurson L. Physical review letters, 2015, 114(9): 095502.

20. Y. Lei and Y. Leng, Phys. Rev. Lett. 107, 147801 (2011).