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Advancements in superlubricity

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Superlubricity is a new area in tribology, in which the slide friction coefficient is about 1/1000 to 1/100 of the general ones. Since the concept of superlubricity was proposed, it has attracted more and more attentions from researchers in fields of tribology, physics, chemistry, materials, etc. Many significant progresses have been made during the last two decades in experimental studies on superlubricity. In the present work, the recent advancements in solid superlubricity and liquid superlubricity are reviewed and the lubricating mechanisms of different superlubricity systems are discussed. Finally, the problems on the superlubricity mechanism and the development of superlubricity in the future are addressed.

friction, superlubricity, solid superlubricating lubricants, liquid superlubricating lubricants

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1 Introduction

The concept of superlubricity was proposed by Hirano and Shinjo [1, 2] at the beginning of 1900s to describe a theoretical sliding regime in which the friction between two contact surfaces completely vanishes. Theoretically, the superlubricity is the realization of zero friction force. But in practice, due to the limited precision of measurement and other influencing factors, it is considered that when the friction coefficient (the ratio of friction force to load) is less than 0.01, the lubrication condition is called as superlubricity [3]. Due to the ultra-low friction force in superlubricity, the energy dissipation and the wear on the surfaces in the sliding process would become very small. Therefore, the investigations on superlubricity will help human get free from the yoke of friction and wear in the future, which will be extremely beneficial to industrial technology and energy conservation.

During the last two decades, superlubricity has attracted more and more attentions from researchers in many fields, including tribology, machinery, physics, material and chemistry. Their works on superlubricity can be divided into two areas. One is in theory, where most works were focused on investigating the condition of superlubricity and the mechanism of superlubricity. Another one is in experiment, where great efforts have been made for finding out more kinds of superlubricity materials. As a result, a significant progress has been made in experimental studies on superlubricity in recent years. The development of atomic force microscope (AFM) and surface force apparatus (SFA) give an enormous impetus to the investigation of superlubricity mechanism at nano-scale [4–11]. In addition, the molecular dynamics simulation (MDS) also provides an effective tool for studying the mechanism of energy dissipation in superlubricity [12–14].

Superlubricity materials can also be divided into two kinds. One is solid lubricant, such as diamond like carbon (DLC), molybdenum disulfide (MoS_2), graphite, and CN_x films [15–19]. These solid lubricants are found to own superlubricity phenomena under certain conditions when the two friction surfaces are contacting with each other directly. The other is liquid lubricant, such as polymer brushes with water [20], ceramic materials with water [21, 22], glycerol

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solution with acid or polyhydric alcohol [23, 24], and some kinds of polysaccharide mucilage from plants [25, 26]. In these cases, the two friction surfaces are separated by liquid molecules. Due to the difference in contact model, the mechanism of superlubricity for solid lubricants is very different from that for liquid lubricants. Therefore, the solid superlubricating lubricants, the liquid superlubricating lubricants, and their mechanisms are reviewed and discussed here, respectively.

2 Solid superlubricating lubricants

At the beginning of 1900s, Hirano and Shinjo [2] proposed that the friction force would disappear when the two contact crystal planes slid with each other in a certain direction. This is the earliest work on the solid superlubricity. After that, how to find a solid lubricant with superlubricity property was a big problem in the tribology world or physics world. There were some people working on such area found some materials having superlubricity under certain conditions, including DLC, MoS_2, graphite and CN_x [15–19]. Particularly, the finding of superlubricity of DLC film brought the superlubricity from theory into practice [27]. The superlubricity mechanism for these materials was mainly attributed to the incommensurate contact, coulomb repulsion or weak interfacial interaction in the condition of high vacuum or nitrogen protection [28–30]. More detail analyses and discussions on the four typical kinds of solid super-lubricants (DLC, MoS_2, graphite and CN_x) are introduced as follows.

2.1 Diamond like carbon (DLC)

The research on DLC film can be traced back to 1970s. Because the DLC film has good wear characteristics, chemical inertness, and optical properties, the early studies were mainly focused on how to use the DLC film to protect the tribo-surfaces of hard disk drivers [31–34]. In the past two decades, Erdemir and his coworkers have done many good works on the superlubricity of DLC film with the rapid development of chemical deposition techniques and they have made a great progress of superlubricity [16, 27, 35–38].

As shown in Figure 1, it was found that the friction coefficient would become lower with the increase of hydrogen density on the DLC film [37]. When the concentration of hydrogen gas reached 75% during deposition, the lowest friction coefficient could reduce to 0.001. However, if the DLC film was hydrogen-free, the friction coefficient would become quite high (more than 0.2) even if it was tested in the high vacuum or in the dry nitrogen environment [16]. In recent years, some researchers supplied the hydrogen gas into the test chamber, where the hydrogen-poor or -free DLC films were subjected to sliding tests. It was found that the superlubricity could also be achieved as long as the sliding contact interfaces of sliding DLC films were supplied with sufficient amount of hydrogen gas [39, 40]. Based on these friction results, it can be concluded that the hydrogen plays a very critical role on the superlubricity. The superlubricity mechanism is attributed to the positively charged plane formed by the hydrogen terminated carbon atoms, which can produce the weak van der Waals forces and provide the strong repulsive electrostatic forces to reduce friction, as shown in Figure 2 [38].

At present, it is possible to synthesize all kinds of DLC films, ranging from hydrogen-free to hydrogen-rich that can meet the increasingly multi-functional needs of industrial applications. A large number of experiments have shown that the superlubricity of DLC is not only dependent on the hydrogen density on its surface, but also closely linked to the test conditions and environments. Erdemir et al. [41] found that an ultra-low friction coefficient of 0.004 could be achieved in a nitrogen atmosphere between two DLC films

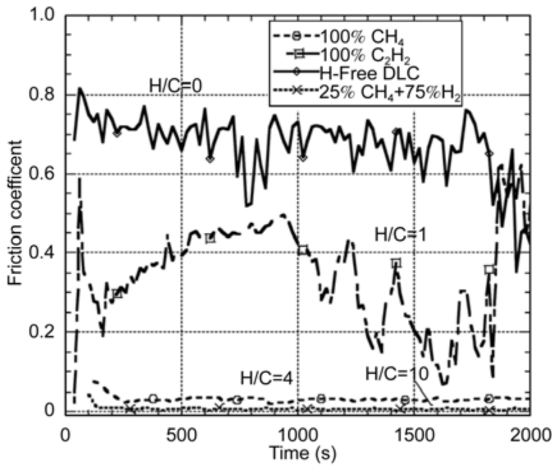

Figure 1 Friction coefficients of DLC films derived from various source gases in a plasma enhanced CVD system [37]. Copyright 2000, Elsevier.

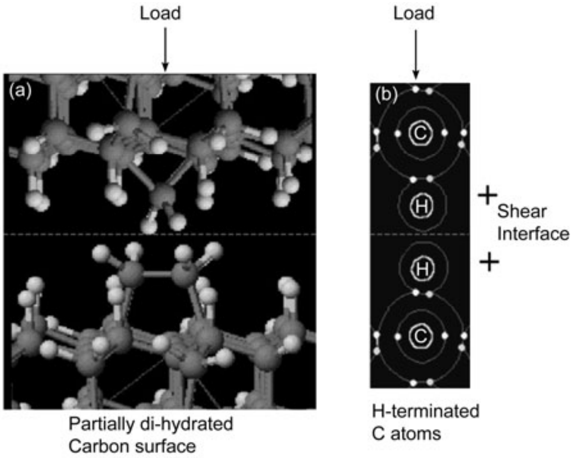

Figure 2 Schematic illustration of (a) partially di-hydrated carbon surfaces sliding against one another and (b) surface carbon atoms terminated by hydrogen whose positively charged core is exposed to surface [38]. Copyright 2001, Elsevier.

with high hydrogen content. But the friction coefficient in the air was higher than 0.01 with the same DLC films. Their studies showed that the interaction between air and DLC films played the key role in preventing the superlubricity. Other related literatures have reported that the friction coefficients of different kinds of DLC films in different test environments can reduce to as low as 0.001, but can also increase to as high as 0.7 [27, 42–45]. In order to improve the properties of DLC film in the high humidity condition, Freyman et al. [46] added sulfur into hydrogenized DLC film so as to get a friction coefficient of about 0.004 for 40 min with a humidity of 50%, as shown in Figure 3.

Ma et al. [47, 48] used DMS to investigate the variation of DLC layers during sliding of H-free DLC films. They found the atomic orientation towards the sliding direction, the alignment of atoms within the horizontal planes, and the formation of grapheme-like layers. In particular, by controlling the surface and the structural chemistry of DLC film, it is easy to achieve friction coefficient as low as 0.001 on highly hydrogenated DLC films and they do not require a special sliding orientation or incommensurability to achieve superlubricity due to their amorphous structure.

2.2 Molybdenum disulfide (MoS_2)

MoS_2 is a well-known lamellar solid lubricant with a hexagonal structure [49]. Martin et al. [15] found that the MoS_2 film could obtain a low friction coefficient of 0.002 under the high vacuum, as shown in Figure 4(a). It can be seen that the friction coefficient would become negative sometimes, which is due to the measuring errors of the system [50]. They found that with the induction of friction, the orientation of basal planes of MoS_2 grains in the interface was parallel to the sliding direction. In addition, the high resolution TEM image showed that the wear fragments of MoS_2 presented moire patterns as shown in Figure 4(b), which indicated that there existed superimposed MoS_2 crystals with a rotation angle between themselves [15]. Therefore, the superlubricity mechanism of MoS_2 is attributed to the frictional anisotropy of sulphur-rich basal planes during intercrystallite slip.

However, if there are any impurity oxygen atoms in the crystal of MoS_2 to replace the sulfur atom, the friction coefficient will be higher than 0.01. This result explains that the superlubricity of MoS_2 can be achieved only in a vacuum or in an inert gas (such as pure nitrogen and argon) [51]. In other words, the oxygen atoms from the air and the presence of water vapor can prevent the superlubricity of MoS_2 in natural conditions. This is because the water molecules or oxygen atoms can be chemically adsorbed on the crystal surface of MoS_2, thereby preventing the formation of orientation and the easy shear plane.

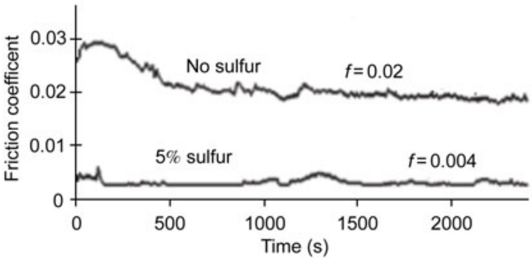

Figure 3 Friction coefficient of hydrogenated carbon films doped with 5 at.% sulfur with the 50% relative humidity [46]. Copyright 2006, Elsevier.

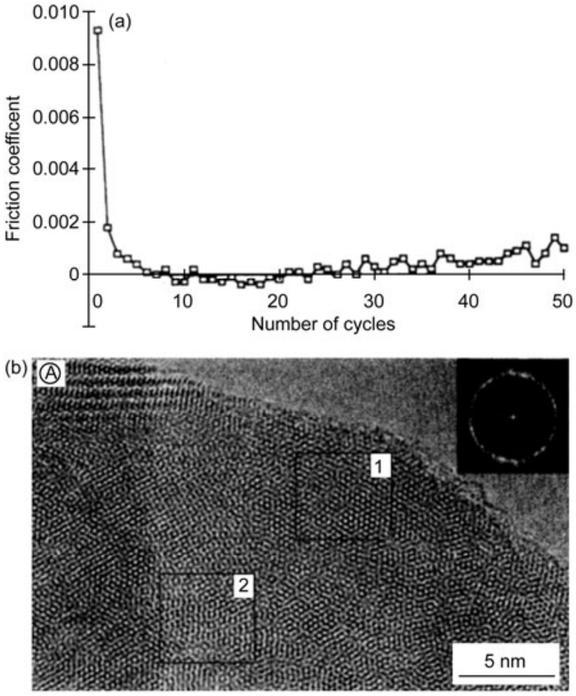

Figure 4 (a) Friction coefficient of MoS_2 as a function of number of cycles in the high vacuum (b) TEM image of MoS_2 wear particles [15]. Copyright 1993, American Physical Society.

To improve the friction properties of MoS_2 in natural conditions, Grossiord et al. [52] added some additives into the MoS_2 film, such as molybdenum dithiocarbamate (Modtc), molybdenum dithiophosphate (Modtp). However, the effect of these additives was not very good, and the lowest friction coefficient was only 0.04 [53]. After that, Chhowalla et al. [54] successfully manufactured the MoS_2 film composed by the hollow fullerene-like nanoparticle of MoS_2. It was found that the lowest friction coefficient could reduce to 0.003 even in the humidity of 45%. They attributed the excellent friction properties to the bending of S-Mo-S that prevents the oxidation of surface as well as protects the lamellar structure from being destroyed by water vapor.

2.3 Graphite

Graphite is one of the most familiar solid lubricants and the research works on the graphite have a very long history. It was found many years ago that the graphite had lamellar structure similar to that of MoS_2, and the interaction force between layers was also very weak. Large amounts of data show that the friction coefficient between graphite and other materials is between 0.08 and 0.18 in natural condition. In 1987, Mate et al. [55] found that the superlubricity could be achieved between graphite and graphite under some certain conditions. They obtained an ultra-low friction coefficient of 0.005 between a tungsten tip and a graphite substrate by using the frictional force microscope. At the beginning of the test, the flake of graphite was transferred onto the tungsten tip, and then the tip presented the "stick-slip" movement, which would lead to the friction force changing periodically with crystal lattice of graphite.

After that, many studies on superlubricity of graphite were taken experimentally and theoretically. Dienwiebel et al. [18] found that the friction coefficient changed with the rotation angle between two sheets of graphite, as shown in Figure 5. It was found that there were two narrow peaks of high friction when the rotation angle was 0° and 61°. If the angle was in the other region, the friction force was too low to measure by their measuring system, which indicated that the graphite was in the regime of superlubricity. It is obvious that the distance between the two peaks of high friction is about 60°, which is in accordance with the 60° symmetry of individual atomic layers in the graphite lattice. Therefore, it can be concluded that the superlubricity mechanism of graphite is attributed to the incommensurate contact between the two rotated graphite layers [56].

Recently, Zhen et al. [57] found that the self-retraction could occur between two graphite surfaces over a contact area of up to 10 μm×10 μm under ambient conditions, which indicated that the superlubricity occurred between the two incommensurate graphite surfaces. They found that the self-retraction was dependent on the rotation angle between the two graphite surfaces, which was also in accordance with the lattice of graphite as shown in Figure 6.

In addition, Miura et al. [58] found that the friction properties of graphite that was embedded with C_{60} was more excellent than the common graphite. An ultra-low friction coefficient of less than 0.001 could be obtained on the frictional force microscope in all sliding directions. The same friction in all directions indicates that the incommensurate contact is not the superlubricity mechanism. They found that the very weak interaction between C_{60} and graphite was the key reason for superlubricity. Moreover, they thought that the molecules of C_{60} could act as rolling bearing sliding on the graphite smoothly, which also played an important role in the ultra-low friction [59, 60].

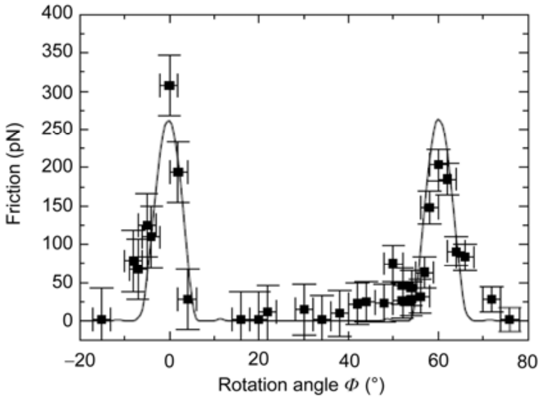

Figure 5 Average friction force versus rotation angle of the graphite sample around an axis normal to the sample surface [18]. Copyright 2004, American Physical Society.

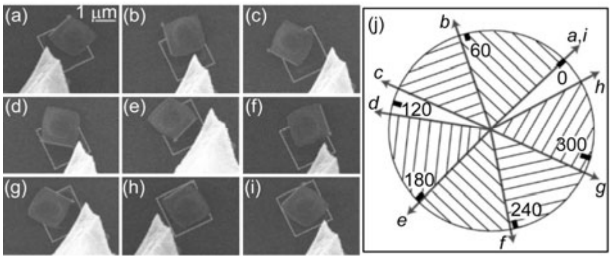

Figure 6 Self-retraction between two graphite with different rotation angles [57]. Copyright 2012, American Physical Society.

2.4 CN_x

The carbon nitride is supposed to have the hardness higher than that of diamond if it has the ideal atomic structure of β-C_3N_4 [61]. However, such ideal structure can hardly be formed by the deposition of carbon in the presence of nitrogen. Therefore, the actual carbon nitride contains 12%–13% nitrogen in an amorphous structure of carbon giving hardness value of about 30 GPa, which is referred to as CN_x coating. Kato's group found that the CN_x coating exhibited a friction coefficient less than 0.01 when tested in a nitrogen gas atmosphere during sliding against itself, Si_3N_4, or steel. However, these material combinations gave friction coefficient higher than 0.1 in air [62, 63]. If the running-in process was taken place in oxygen gas during the initial sliding cycles, the following sliding in nitrogen gas would give a friction coefficient less than 0.005 and a wear rate less than 10^{-7} mm^3/Nm. Sanchez et al. [64] studied the friction properties of CN_x under different surrounding atmospheres, as shown in Figure 7. They found that the superlubricity could be achieved under dry nitrogen gas. Moreover, the superlubricity was independent of the mating materials (steel or sapphire). They found that the CN_x film could translate onto the mating materials, leading to a very low shearing strength between the two sliding surfaces.

At present, the superlubricity mechanism of CN_x is not very clear, but is closely linked to the tribolayer formed during the running-in process. The Raman spectrum shows that there exists a graphite-like structure in the tribolayer. Therefore, the mechanism of low friction is attributed to the weak interaction between the graphite-like structure of tribolayer and the surrounding nitrogen.

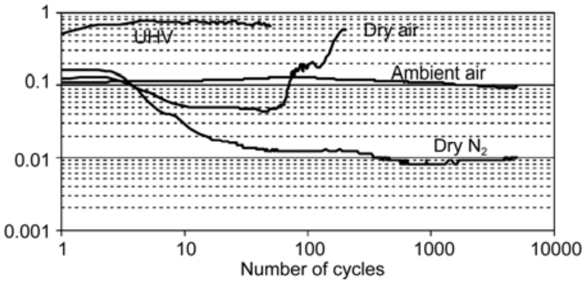

Figure 7 Changes in the friction coefficient of the carbon nitride film under different environments [64]. Copyright 2002, Elsevier.

3 Liquid superlubricating lubricants

For liquid lubricant, how to reduce friction coefficient to save energy, how to become green for environmental protection and how to be beneficial to the nature will be very important in the near future [65–67]. It can be divided into two kinds, i.e., water-based lubricants and oil-based lubricants. Because the oil-based lubricants have a higher viscosity-pressure coefficient and a higher viscosity than those of water-based lubricants in general, the sliding friction coefficient is usually above 0.04. Due to its high viscosity in the contact region, it can lubricate well under heavy load, low speed and high temperature. However, the big problem for oil lubricants is how to reduce friction coefficient to save energy and how to keep its properties without petroleum in the future. For water-based lubricants, their viscosity hardly increases with the increasing pressure [68]. Moreover, the water has excellent fluidity even under a high pressure [69]. Both of them provide the favorable conditions to achieve superlubricity. However, how to form a lubricant film in the contact region is a key problem. Generally, the hydrodynamic effect is very important to form a thick lubricant film in the contact region to prevent the solid contact. Therefore, how to form a lubricant film with very low friction coefficient at very low speed or under heavy load is a barrier to overcome. So both of them are required for achieving superlubricity.

The first liquid with superlubricity in the world is Helium II that was found by Tisza et al. [70] in 1938, which is called as superfluidity. It can move with very little viscosity ($<10^{-11}$ mPa s) at a temperature lower than 2.172 K. The current research works for liquid superlubricity are mainly focused on water-based lubricants. At present, there are several kinds of liquids found having superlubricity properties, such as ceramic materials with water, polymer brushes, phosphoric acid solution, glycerol solution with acid or polyhydric alcohol, and some kinds of polysaccharide mucilage from plants. More detail analyses and discussions on these liquid superlubricants will be taken as follows.

3.1 Ceramic materials with water

In 1987, Tomizawa and Fisher [71] found that the friction coefficient between Si_3N_4 ceramics with the lubrication of water became less than 0.002 after a running-in process, which was the first time to see that water used as lubricant can achieve superlubricity. After that, other ceramics, such as SiC and CN_x were also found having an ultra-low friction coefficient less than 0.01 with the lubrication of water [72, 73]. These works showed that the tribochemical reaction on the surface of ceramics in the running-in process and the electric double layer of the water film played the important role in superlubricity [74, 75]. Kato's and Adachi's group [76–79] have studied the friction properties of ceramics with the lubrication of water systematically.

As shown in Figure 8, they used Si_3N_4/Si_3N_4 as friction pairs, and found that the friction coefficient after a running-in period dropped to about 0.007. It was found that the tribochemical reaction of the ceramic surfaces occurred in the running-in process as follows:

$$Si_3N_4+6H_2O=3SiO_2+4NH_3 \quad (1)$$

$$SiO_2+H_2O=Si(OH)_4 \quad (2)$$

Thus, a silica layer would be formed on the two ceramic surfaces in the running-in process. The silica layer can produce the electrical double layer, which would lead to a very low friction in the boundary lubrication, but cannot sustain a pressure larger than tens of megapascals. Moreover, the surface becomes very smooth and the contact pressure becomes much lower due to the wear in the running-in process. In this case, the hydrodynamic lubrication can be obtained and the friction coefficient is very low because of the low viscosity of water. Thus, a very low friction coefficient can be gotten in the mix lubrication (boundary lubrication and hydrodynamic lubrication) under low pressure [74]. They also tested other ceramics, such as SiC/Si_3N_4, SiC/SiC, and CN_x/Si_3N_4 [21, 22, 72]. It was found that the friction coefficient between them with the lubrication of water could reduce to 0.01 or less, but the running-in period was much longer than that of Si_3N_4/Si_3N_4 [80]. In order to improve the lubricating properties of ceramic with the lubrication of water, they also produced the surface texture by laser (such

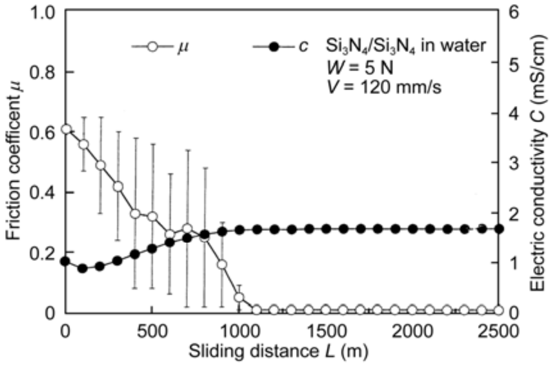

Figure 8 Friction coefficient and electrical conductivity as a function of sliding distance at 20°C [74]. Copyright 2000, Elsevier.

as micro-pores), which could increase the load carrying capacity greatly [81, 82].

3.2 Polymer brushes

Since 1990s, Klein et al. [83–85] have done a lot of works on the lubrication of polymer brushes by using SFA. At the beginning, they grafted the polymer film (polystyrene with polar end) on the mica surfaces firmly. The long chain molecules of the polymer were immersed in the toluene solution to form a layer of "molecular brush", and it was found that the chain extended in the solvent without departing from the surface of mica. Thus, it would produce a strong osmotic pressure between brushes. In addition, with the effect of electrical double layer repulsion and the dispersion force, the force between polymer brushes was in the range of repulsion. The repulsive force increased rapidly as the gap between the mica decreased. Due to the large repulsive force, the two mica surfaces were separated by the brushes, which could lead to an ultra-low friction coefficient of 0.001 [83].

Because the water molecules have a stronger polarity than that of organic solvents, and they have more excellent fluidity, the water used as solvent can make the polymer brushes spread in it very well, and thereby producing a repulsive force to achieve superlubricity. Klein et al. [20] found that the charged polymer (such as polyelectrolytes) had better lubricating properties compared with other polymers when water was used as solvent, as shown in Figure 9. As for these charged polymers, an ultra-low friction coefficient less than 0.0006 could be obtained at a pressure of 0.3 MPa. It is because the potential opposing interpenetration for the charged brushes is augmented relative to that of neutral brushes by the presence of mobile counterions within the brush layers, which can suppress the mutual interpenetration further [86]. In this case, the weak interpenetration would result in a sheared zone that is rather narrow and within which the polymer segments are short and unlikely to be entangled with each other, which would reduce the dissipation of energy and hence the frictional force [87]. A second and important effect is due to the hydration layers surrounding each of the charged segments on the ionized polymers, which can forms many hydration sheaths [68, 69]. Because these hydration sheaths still have good mobility even under pressure, which can play the role of molecular ball bearings, thereby effectively reducing the friction coefficient.

Spencer' group grafted the polyethylene glycol (PEG) onto the poly-lysine (PLL), and made them be adsorbed on the charged surfaces by electrostatic adsorption [88–92]. Thus, the PEG chains could extend to the aqueous solution to form the molecular brushes, therefore greatly reducing the friction coefficient. They obtained an ultra-low friction coefficient of 0.0001 on the rolling friction testing machine, where the hydrodynamic effect was quite strong. In summary, polymer brush used as lubricant has to dissolve in a good solvent. Only by this, the presence of solvent molecules can make polymer brushes have a good stretch so as to produce an osmotic pressure to bear the load. Otherwise, the ultra-low friction coefficient cannot be achieved.

3.3 Phosphoric acid solution

The phosphoric acid solution has never been used as lubricants before. However, it was found having superlubricity properties by Li et al. [93] in our group in 2011. As shown in Figure 10, a friction coefficient about 0.004 has been gotten between glass plate and Si_3N_4 ball with the lubrication of phosphoric acid solution (pH=1.5) after a short running-in period. According to the evolution of friction coefficient with time, the friction process was divided into three stages. The first stage within the first 120 s was the friction reducing rapidly process. In this stage, the wear occurred on the friction surfaces, which would increase the contact area and reduce the contact pressure. In addition, the tribochemical reaction between hydrogen ions and friction surfaces occurred in the contact region as follows [94, 95]:

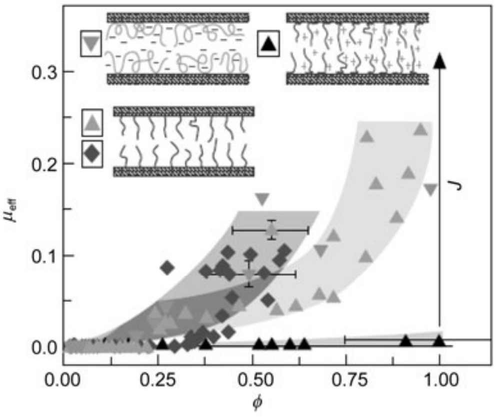

Figure 9 Variation of the effective friction coefficient between mica surfaces bearing different types of polymeric surfactants [86].

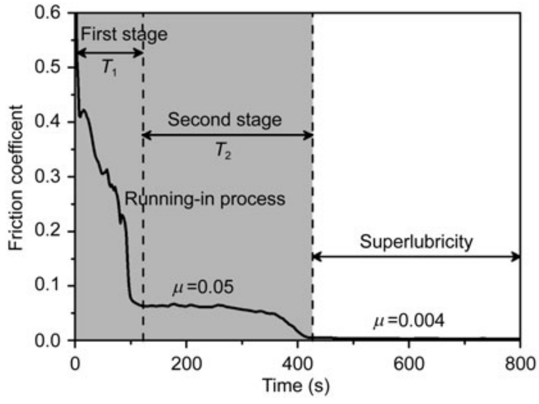

Figure 10 The friction coefficient with time under the lubrication of H_3PO_4 solution (pH 1.5, Volume=20 μL).

$$\mathrm{SiOH+H^{+}\rightarrow SiOH^{2+}} \tag{3}$$

Thus, the friction surfaces would become positively charged, which could form the electrical double layer and the stern layer to reduce friction force [96]. In addition, the period of this stage was dependent on the concentration of hydrogen ions. The second stage from 120 s to 430 s was the low friction reducing slowly process. During this stage, the free water in the solution was evaporating out gradually, which would lead to a reduction of proportion of water molecules. When the proportion of water molecules reduced to a constant (the water molecules and the phosphoric acid molecules were in an equilibrium state), the lowest friction coefficient appeared. At this moment, Raman spectrum showed that there was a stable hydrogen bond network between phosphoric acid molecules and water molecules formed on the two friction surfaces. The third stage from 430 s to the end of the test was the superlubricity process. In this stage, the superlubricity would keep constant as long as the equilibrium state between water molecules and phosphoric acid molecules was not broken. Therefore, the superlubricity mechanism of phosphoric acid is attributed to the hydrogen bond network between phosphoric acid and water molecules formed on the stern layer that is induced by the attached hydrogen ions [93, 96, 97].

3.4 Glycerol solution with acids or polyhydric alcohol

Glycerol molecules have three hydroxyl groups, which can form strong hydrogen bond network among themselves. In 2008, the superlubricity of pure glycerol was observed at 80°C by Matta et al. [23]. They deposited the hydrogen-free tetrahedral coordinated carbon (ta-C) on the steel surfaces by physical vapor deposition. In the presence of glycerol, the friction coefficient was below 0.01 at the steady state. They attributed the superlubricity to the easy sliding on triboformed OH-terminated surfaces. In addition, at a lower temperature (20°C), by adding the polyhydric alcohols in the glycerol, the superlubricity of steel surfaces could also be achieved. It is due to the triboinduced degradation of glycerol that produces a nanometer-thick film containing organic acids and water. The film can form a hydrogen bond network consisting of glycerol molecules adsorbed on the OH-terminated surface by hydrogen bond.

At the same time, Ma et al. [24] in our group found that the superlubricity could be obtained between glass plate and Si_3N_4 ball with the lubrication of mixture of glycerol and boric acid after a running-in process of few minutes. The lowest friction coefficient was about 0.0028. The superlubricity mechanism is attributed to the strongly adsorbed diglycerin borate layer on the sliding surface and the hydration effect that makes water molecules act as a lubricant in the contact region. After that, Li et al. [98] promoted the superlubricity phenomenon of glycerol. They found that all the acid solution mixed with glycerol solution could realize superlubricity, which indicated that the superlubricity was independent of the kinds of acid. They also found that the ultra-low friction was also closely related to the pH value of acid and the concentration of glycerol. The superlubricity mechanism is attributed to a fluid hydrated water layer between the hydrogen bond networks of glycerol and water molecules on the positively charged surfaces, as shown in Figure 11. Because the glycerol belongs to polyhydroxy alcohol, they used other polyhydroxy alcohols (such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, and 1,5-pentanediol) to replace glycerol and then mixed them with acid solution. It was found that the superlubricity could also be achieved once these polyhydroxy alcohols were mixed with acid solutions, as shown in Table 1 [99]. It was also found that the superlubricity was closely dependent on the concentration of polyhydroxy alcohol and the number of hydroxyl groups in the molecular structure of polyhydroxy alcohol. However, the number of carbon atoms and the arrangement of hydroxyl groups in the molecular structure almost had no effect on superlubricity.

3.5 Polysaccharide mucilage from plants

Some natural lubricants that are water-based also have

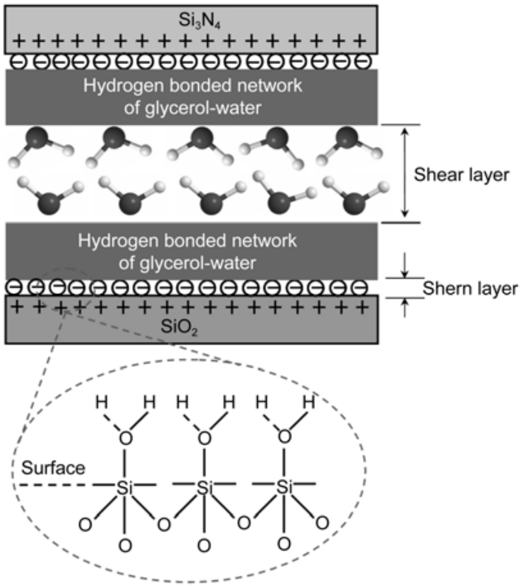

Figure 11 Schematic illustration of possible structure between two friction surfaces [98]. Copyright 2013, American Chemical Society.

Table 1 Final friction coefficient with the lubrication of mixtures of four kinds of polyhydroxy alcohols and three kinds of acid solutions ((HCl, $H_2C_2O_4$ and H_3NO_3S, pH 1) with the volume ratio of 10:1 [99]. Copyright 2012, American Chemical Society

	HCl	$H_2C_2O_4$	H_3NO_3S
1,2-ethanediol	0.004	0.004	0.003
1,3-propanediol	0.003	0.003	0.003
1,4-butanediol	0.005	0.005	0.004
1,5-pentanediol	0.006	0.004	0.003

excellent lubricating properties [100]. For example, the hyaluronic acid in the joint of animal can protect the organs from abrasion, which induces a friction coefficient lower than 0.003 [101]. In addition to the superlubricity of internal organs of human and animals, some mucilage from plants can also realize superlubricity. In 2006, Arad et al. [25] obtained an ultra-low friction coefficient (less than 0.003) by the use of polysaccharides extracted from the red algae. They attributed the superlubricity to the spiral chain structure, which can preserve a thin layer of water at the interface under low loads. Recently, Li et al. [26] found that an aquatic plant named Brasenia schreberi (B.S) can realize superlubricity. They designed a novel measuring system to investigate the lubrication characteristics of the B.S mucilage, and an ultra-low friction coefficient of 0.005 between the mucilage and glass surface was obtained. The microstructure analysis indicated that the mucilage surrounding B.S formed a kind of polysaccharide gel with many nano-sheets. A lubrication mechanism was proposed that the formation of hydration layers among these polymer nano-sheets with plenty of bonded water molecules caused the ultra-low friction, as shown in Figure 12.

4 Discussions

As shown above, the superlubricity is another hot topic in the field of tribology after nanotribology [102, 103] and biotribology [104–107]. The solid superlubricity lubricants are mainly based on the incommensurate contact and the weak interfacial interaction between layers. Most solid lubricants that have superlubricity properties have laminate structure. Because the laminate structure can provide weak interaction between layers and it can also realize incommensurate contact, it would provide a favorable condition for superlubricity. However, the superlubricity is closely dependent on the test condition and environment. So far, not one single solid lubricant has been found to realize superlubricity in all environments. Some kinds of solid lubricants, such as graphite, require humid environments or other gases with high concentration to achieve superlubricity. Some kinds of other solid lubricants, such as MoS_2 and DLC, require high vacuum or protection of inert gas or doped with sulfur to achieve superlubricity, as shown in Table 2. It poses many restrictions for the application of solid lubricant in actual condition. Therefore, how to reduce the effect of environment on superlubricity by adding some elements or change the microstructure is the focus of study for solid lubricants.

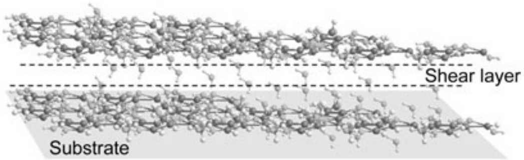

Figure 12 The molecular schematic representation of mucilage surrounding the B.S sample during lubrication. The nano-sheet structure is formed by polysaccharide which comprises eight kinds of monosaccharide. Between the nano-sheets, it is filled with water molecules to form hydration layer [26]. Copyright 2012, American Chemical Society.

Table 2 Relationship between solid superlubricity and the test load, enviroment and friction coefficient

Solid Superlubricity	Load	Environment	Friction coefficient
DLC	10 N	nitrogen	0.001
MoS_2	1.2 N	vacuum	0.002
Graphite	100 nN	humidity	0.005
CN_x	100 mN	vacuum	0.005

Compared to the solid lubricant, the environment has much less limitations to the liquid lubricant. It is easy to found that all of the present superlubricity liquids are water-based due to the very low coefficient of viscous pressure of water. However, not all the liquid superlubricity has engineering application due to its low contact pressure. For example, the polymer brush can only achieve superlubricity on SFA with a pressure less than 7.5 MPa. The other liquid superlubricity such as ceramic materials with water, phosphoric acid solution, and glycerol solution with acid or polyhydric alcohol has potential application, because all of them can achieve superlubricity on traditional tribometer (load is greater than 1 N, and velocity is greater than 1 mm/s). In addition, it is found that the liquid superlubricity is dependent on the characteristic of solid surfaces [93, 99]. For example, the hydration model requires the surface charged, the tribochemical model requires the surface reacting with water, and the hydrogen bond network requires the surface OH-terminated. It is totally different from traditional hydrodynamic lubrication that is mainly dependent on the hydrodynamic effect which is related to the lubricant viscosity, speed, etc. As for solid tribo-surfaces, there are several methods to meet the requirement of liquid superlubricity. The first method is to choose the surface on which the tribochemical reaction can occur, such as ceramic. The second one is to treat the surface by grafting molecular brushes, self-assembled monolayers, or changing the hydrophobicity. The third method is to choose the soft surface with high content of water, such as hydrogel.

5 Conclusion

In the present paper, the recent progresses mainly in solid superlubricity and liquid superlubricity have been reviewed. Then, some superlubricity phenomena and their mechanisms have been discussed. Although many progresses have been achieved on superlubricity for the last two decades, there are still many problems to be solved as follows.

(1) Is there a uniformed mechanism of the superlubricity?

(2) What kind of molecular structure can realize superlubricity?

(3) Is there a relationship between nano-scale superlubricity and macro-scale superlubricity?

(4) Can the superlubricity be obtained from the oil-based liquids?

In summary, with the rapid development of computer technology and measuring technique, the research on superlubricity develops very fast. We believe that in the near future, the superlubricity can be applied to the practical engineering so that it not only saves energy during the friction process but also reduces the environmental pollution.

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