

Experimental Study on Molecular Arrangement of Nanoscale Lubricant Films— A Review

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Received March 19, 2015; revised July 27, 2015; accepted July 30, 2015

Abstract: In order to understand lubrication mechanism at the nanoscale, researchers have used many physical experimental approaches, such as surface force apparatus, atomic force microscopy and ball-on-disk tribometer. The results show that the variation rules of the friction force, film thickness and viscosity of the lubricant at the nanoscale are different from elastohydrodynamic lubrication (EHL). It is speculated that these differences are attributed to the special arrangement of the molecules at the nanoscale. However, it is difficult to obtain the molecular orientation and distribution directly from the lubricant molecules in these experiments. In recent years, more and more attention has been paid to use new techniques to overcome the shortcomings of traditional experiments, including various spectral methods. The most representative achievements in the experimental research of molecular arrangement are reviewed in this paper: The change of film structure of a liquid crystal under confinement has been obtained using X-ray method. The molecular orientation change of lubricant films has been observed using absorption spectroscopy. Infrared spectroscopy has been used to measure the anisotropy of molecular orientation in the contact region when the lubricant film thickness is reduced to a few tens of nanometers. In situ Raman spectroscopy has been performed to measure the molecular orientation of the lubricant film semi-quantitatively. These results prove that confinement and shear in the contact region can change the arrangement of lubricant molecules. As a result, the lubrication characteristics are affected. The shortages of these works are also discussed based on practicable results. Further work is needed to separate the information of the solid-liquid interface from the bulk liquid film.

Keywords: nano-scale lubricating film, in situ measurement, molecular arrangement

1 Introduction

Lubrication originated from the attempts to reduce the friction force between sliding surfaces. Today, the most common lubricants are fluids, and the technique is closely related to hydromechanics^[1-2]. A lubricant film with a thickness of several microns or greater is generally treated as a continuous medium. Based on this idea, hydrodynamic lubrication and elastohydrodynamic lubrication have been produced^[3-5]. The characteristics of this lubrication regime have been investigated by various methods, including numerical methods^[6-9] and experimental methods^[10-11]. Under some special conditions, such as bearings working at low speed and heavy loads, the lubricant film is often produced at the nanoscale. For molecularly thin lubricant films, boundary lubrication^[12-14] and thin-film lubrication^[15-18] have been put forward. The former mainly describes the lubricant film formed by absorbed molecules. The latter describes the films in which molecular behavior can be affected by both surface absorption and flow. In these cases, the physicochemical properties of the liquid

film, solid surfaces, and liquid-solid interfaces surfaces exert obvious effects on the lubrication performance. However, most of the information on the molecular level is provided by computer simulation. For example, DAVIS, et al^[19], investigated several molecular layers between two solid surfaces under shearing and observed a layered film structure when the thickness was less than 6–10 times the molecular diameter. SCHOEN, et al^[20-21], proved that the molecular arrangement changed from a disordered fluidity structure to an ordered solid-like structure under similar conditions. HU, et al^[22-23], investigated the rheological behavior of a spherical molecule and observed that the ordered structure near solid surfaces extended to the middle of the lubricant film with increasing pressure.

On the experimental side, experiments focused on the physical properties of nano-thin lubricant films have revealed many new phenomena. Researchers have produced different models of molecular arrangement to explain the changing rules of friction force, viscosity, and film thickness (gap size). In addition, with the development of optical and spectroscopic measuring techniques, many new experimental methods have been used to detect the molecular arrangement of lubricant films in-situ. In this review, the experimental method and results from different experiment methods are summarized.

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Supported by National Natural Science Foundation of China(Grant Nos. 51335005, 51321092)

2 Analysis of Physical Parameters

2.1 Atomic force microscopy

The experimental study of lubricant molecules at the nanoscale is based on the measurements of physical parameters. Recently, much work has been performed using atomic force microscopy (AFM). AFM was designed for micro force and morphology measurements. The apparatus uses a nano-size tip fixed on a micro cantilever approaching the sample surface. When scanning a liquid sample on the substrate, the cantilever works in tapping mode. Molecules of the liquid film will affect the vibrating parameters of the tip, and the information is collected from the changing electric signal. As a result, the tribological properties such as the shear force, film thickness, and viscosity can be obtained. By correctly designing the test, these parameters can reflect the difference in the microstructure in different sample areas.

O'SHEA, et al^[24], investigated the tribological properties of octamethylcyclotetrasiloxane (OMCTS) molecules absorbed on a graphite substrate. As shown in Fig. 1(a), the tip surrounded by liquid molecules was approaching the solid surface. In Fig. 1(b), it is demonstrated that the effective viscosity increases significantly when the distance decreases less than 2 nm. The difference between the trends of effective viscosity and stiffness is possibly due to the ordered layer structure near the solid surface. The molecules are arranged against the shear; therefore, the viscosity measured near the surface is higher than in the bulk liquid. KARUPPIAH, et al^[25], investigated a self-assembled monolayer on a substrate using AFM. An external electric field was applied in this experiment. When a forward voltage was applied, the friction force was 3 times that observed under reverse voltage. These researchers attributed this phenomenon to the vertical molecular orientation of the monolayer caused by the electric field.

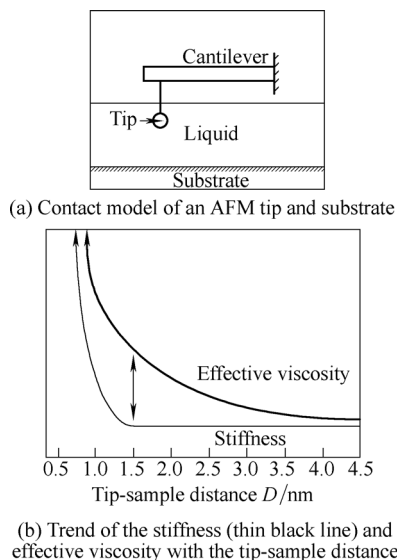


Fig. 1. Tribological property of liquid film on the substrate^[24]

2.2 Surface force apparatus

Surface force apparatus^[26] (SFA) is another important experimental method to investigate this problem. The sliding solid surfaces are two cross-placed pieces of mica. Using the fringes of equal chromatic order (FECO) method, the lubricant film thickness can be acquired. The friction force and effective viscosity can be obtained simultaneously.

ISRAELACHVILI, et al^[27], analyzed the mechanical properties of liquid films when the distance between the mica sheets was only several times the molecular dimension. It was observed that the force changed discretely with the molecular layers between the solid surfaces. This finding was attributed to the layered arrangement of molecules near the surface, as described in Fig. 2^[28]. From the shear force curves and interference patterns, it was inferred that the arrangement of liquid molecules changed from liquid to solid-like as the gap size decreased. GRANICK, et al^[29], observed an ordered molecular arrangement between the mica sheets of SFA when the film was molecularly thin. KLEIN, et al^[30], investigated the arrangement of a confined liquid film at the molecular scale.

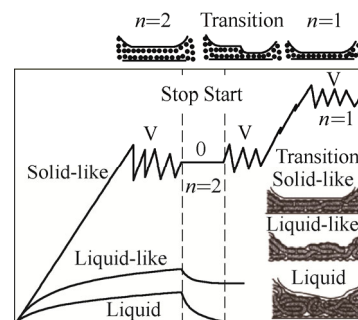


Fig. 2. Structure change of confined liquid molecules

All these results indicate that the physical properties of a lubricant film change when the thickness is reduced to the nanoscale. Researchers have attributed these phenomena to the ordered molecular arrangement near the surface, such as a layered structure or uniform orientation. However, the tip system in AFM and the mica sheets in SFA are all highly improved conditions compared with a real friction pair such as bearings or pistons.

2.3 Lubricant film-thickness-measuring apparatus

The experimental study of thin lubricant films has been greatly improved by the optical interference technique, which is usually used to measure the lubricant film thickness. The friction pair of these interfering film-thickness-measuring meters usually consists of a transparent disk and a reflective ball, which is very close to the practical working condition. Therefore, this technique has been applied to investigate the film forming property of oils and greases. In a traditional interferometer, the resolution is submicron-to-micron. To obtain sufficient measuring accuracy at the nanoscale, researchers have

made various improvements. For example, SPIKES, et al^[31–32], improved the measuring resolution of the film thickness using chromatic lights. HARLT, et al^[33], applied colorimetry interferometry to the interferometer. LUO, et al^[17, 34], used the relative intensity of optical interference rings to measure the oil film thickness, and the resolution was improved to 0.5 nm. These researchers investigated the film-forming property of various lubricants at the nanoscale. A special lubrication state called thin film lubrication (TFL) was observed between the boundary and elastohydrodynamic lubrication. This finding is based on the unique rheological behavior of the nanoscale lubricant film. For example, the film thickness measured in the experiment increases over working time, which is precisely the opposite of the shearing thinning phenomenon of EHL. It was believed that lubricant molecules out of the absorbed layer still exhibit an ordered arrangement within a certain range. In addition, these molecules remain considerably fluid-like in behavior. Thus, when the shearing stops, part of this ordered layer remains, and the static film thickness after the experiment is higher than the value before. XIE, et al^[35], observed that this ordered structure could be enhanced by an electric field. This conclusion is based on the finding that the tail area in Fig. 3(a) in the lubricating outlet region gradually decreases when an external voltage is applied, as shown in Fig. 3(b). These researchers believed that the applied electric field enhances the surface absorption and weakens the fluidity of the ordered fluid molecules. Thus, the tail area originating from the fluidity of the lubricant film shrinks. This phenomenon weakens when the film thickness increases with speed and disappears when the lubricating state enters elastohydrodynamic lubrication (EHL).

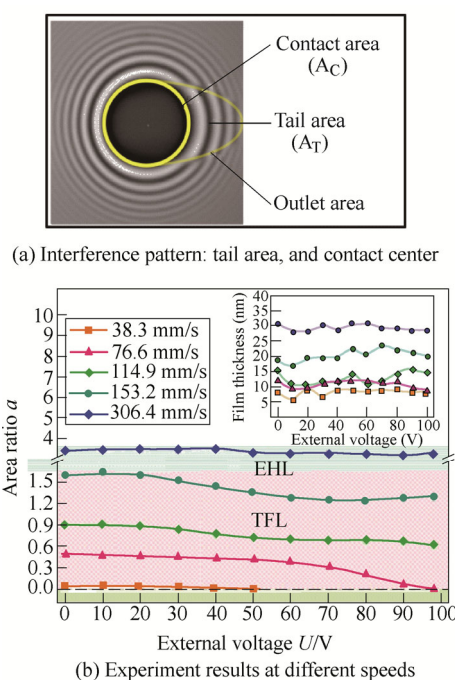


Fig. 3. Area ratio between tail area and contact area vs. external voltage^[35]

There are many other ways to investigate the special physical characteristics of nanoscale lubricant films, such as using ball-on-disk or cylinder-on-disc tribometers^[36–37]. The values or changing rules of physical parameters such as the friction coefficient, film thickness, and viscosity have been used to speculate the molecular arrangement of lubricant films. However, these results were not directly obtained from the layer structure at the nanoscale, and the conclusions are not entirely convincing.

3 In Situ Spectral Measurements

Spectral methods, such as X-ray diffraction, absorption spectroscopy, infrared spectroscopy and Raman spectroscopy, have been widely used to analyze material microstructures, including the chemical structure, crystal structure, molecular spatial distribution, and orientation. In previous tribological tests, spectral techniques have been mainly utilized to describe the chemical properties of solid surfaces or lubricants before and after rubbing.

Recently, in the fields of surface physics, chemistry, and tribology, researchers have applied spectral methods to traditional physical tests and attempted to find direct evidence of the molecular arrangement of nanoscale lubricant films under confinement and shear.

3.1 X-ray diffraction

X-ray diffraction (XRD) is generally used to analyze the structure of metals and crystals. The peak site, width, or intensity in an XRD spectrum can be used to characterize the microstructure of the material. GOLAN, et al^[38–39], investigated the arrangement of liquid crystal molecules with an XRD-combined SFA, as shown in Fig. 4(a). The new apparatus is called “XSFA” and can be used to measure the shear force, film thickness, and XRD spectrum simultaneously.

The result shows an orientation change induced by shear. Spectra in Fig. 4(b) were acquired over time. The diffraction peak “b” in the spectra represents the initial structure of the liquid crystal film. The new peak “a” in Fig. 4(b) represents the orientation change of some molecules. This orientation originates from the boundary layer near the solid surface. As the experiment proceeds, the peak intensity of peak “b” decreases and the peak intensity of peak “a” increases gradually, as observed in Fig. 4(b). This finding suggests that the range of this shear-induced orientation in the liquid film increases over time.

Note that the film thickness of the lubricant film in X-ray experiments is hundreds of microns. In general, to enhance the X-ray diffraction intensity, the thickness of the measured film must be greater than the wall of the container or at least on the same order. Currently, X-ray diffraction is not suitable at the nanoscale.

3.2 Absorption spectroscopy

The molecular alignment affects the light absorption

efficiency. The absorption intensity is the strongest when the light polarization is parallel to the long molecular axis and weakest when the light polarization is perpendicular to it^[40]. BAE, et al^[41], investigated the arrangement of a dye molecule dissolved in toluene. The experiment was performed on a modified SFA, which had the function of recording the absorption spectrum. Spectra in Fig. 5(a) demonstrates that the absorption peak intensities under orthogonal incident light polarizations are almost the same only in confinement and the difference finally appears after shear. This finding suggests that the molecular orientation has been changed by shear. The degree of this anisotropic absorption is defined by the relative difference between the peak intensities polarized parallel and perpendicular to the shear direction. Fig. 5(b) reveals that the magnitude and symbol of this value vary stochastically from one experiment to another. This finding indicates that the shear-induced orientation of the dye molecules is not constant during shearing. The reciprocating shearing direction of mica surfaces is a possible cause for the unstable molecular orientation.

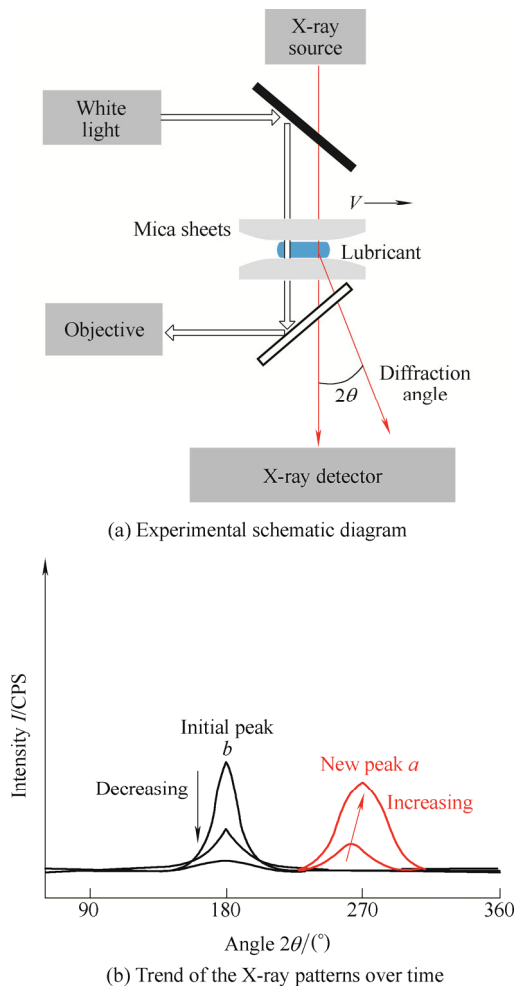


Fig. 4. In situ orientation change observed by X-ray diffraction during shearing^[38]

These researchers also performed photoluminescence (PL) measurements of dye molecules. The PL spectra were acquired at two orthogonal directions of the analyzer, one

parallel and one perpendicular to the laser polarization. The relative peak intensity of the dye molecule changes after shearing and evaporation. The result also demonstrates that the arrangement of the dye molecules is changed by rubbing.

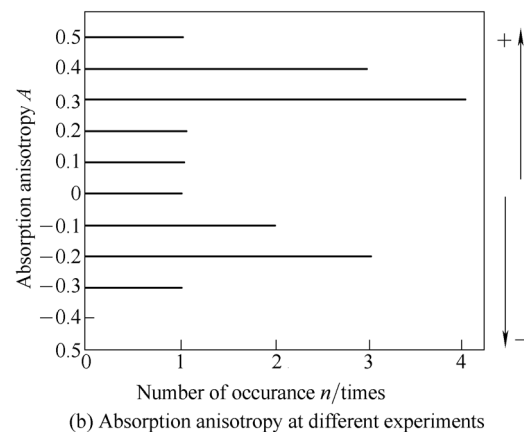
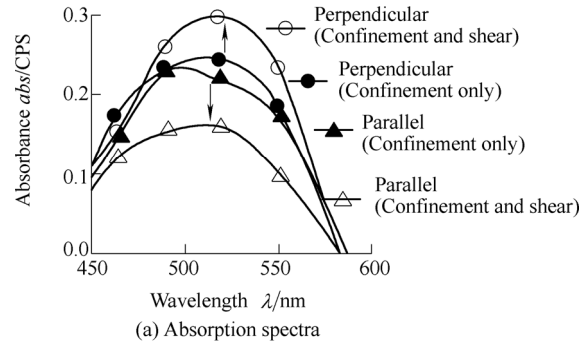


Fig. 5. Shear-induced anisotropy of absorption spectrum^[41]

This method has obvious shortcomings: it cannot be applied to molecules without chromophore. In practice, dye molecules and fluorescent nanoparticles have been added to lubricants to represent the characteristics of the lubricating film. However, this step could have a dramatic impact on the molecular arrangement. The results obtained using lubricants with dye molecules are not always the same as those obtained with pure lubricants.

3.3 Infrared spectrum

When a continuous infrared light illuminates sample molecules, some wavelengths are absorbed based on the molecular vibrational modes. As a result, the site of the absorption peak in the spectrum depends on the molecular structure. The peak intensity of some molecules with an asymmetric structure can be used to calculate the orientational information of molecular arrangement^[42].

CAN, et al^[43-44], invented an apparatus for in-situ IR spectral measurements, as shown in Fig. 6(a). Based on the FTIR and optical interference techniques, the lubricant film thickness and IR spectral information were effectively acquired. The minimum lubricant film thickness measured by the apparatus is dozens of nanometers. The infrared absorption characterization of a polyolefin lubricant was

analyzed during lubrication, as shown in Fig. 6(b). The intensity ratio of CH₂ asymmetric (ν_{asym} , 2924 cm⁻¹) and CH₂ symmetric (ν_{sym} , 2853 cm⁻¹) stretching vibration is closely related to the conformation of the alkyl chain. In their experiment, when the polyolefin film thickness was reduced below 200 nm, the intensity ratio of 2924 cm⁻¹/2853 cm⁻¹ began to decrease with decreasing film thickness. The result indicates that the molecular alkyl chain is orientated parallel to the solid surface when the film thickness is on the nanoscale. This finding also directly demonstrates that the molecular arrangement of the lubricant film becomes increasingly ordered when the film thickness becomes molecularly thin.

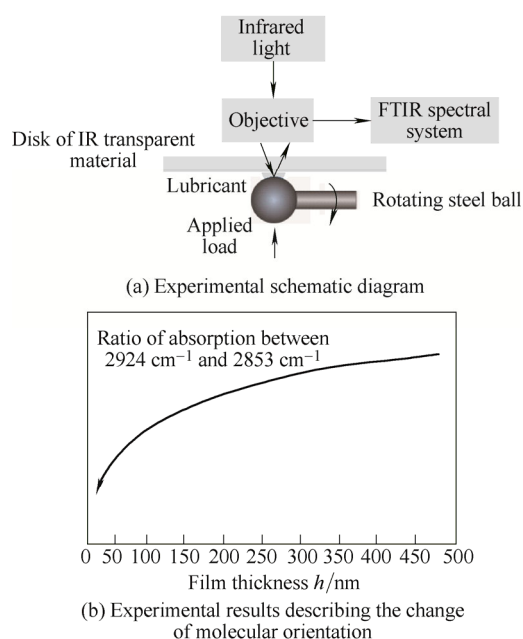


Fig. 6. Schematic and experiment results of in situ FTIR measurements^[43]

The disadvantage of in situ IR spectral measurements is the spatial resolution. The wavelength of the infrared light makes this technique poor for scanning the molecular arrangement in the contact region of hundreds of microns. When the film thickness is several nanometers thick, it is difficult to separate the information about the lubricant film from the background noise in the infrared absorption spectrum.

3.4 Raman spectroscopy

Raman scattering occurs when a polarized laser beam illuminates a sample liquid. The change in the photon energy shown in the wavenumber in the Raman spectrum is related to the vibrational energy of the liquid molecules, which depends on the molecular structure and environment.

In the field of hydrodynamic lubrication, BONGAERTS, et al^[45], analyzed the film thickness and chemical composition of micron-sized fluid films using Raman spectroscopy. The value of the film thickness was determined by the Raman peak intensity, which is proportional to the number of molecules in the measuring

range. Thus, the film forming and chemical information were measured simultaneously. JUBAULT, et al^[46-47], and YAGI, et al^[48], analyzed the composition and pressure profile in the lubricating point contact area. The theory of their experiments is that the Raman shift will change with the intermolecular force between liquid molecules. The pressure profile they measured was consistent with the theoretical prediction. In this state, no anisotropic arrangement was observed in their experiments. Most of the lubricant molecules were arranged in the state of fluid.

JIANG, et al^[49-50], improved SFA to investigate the spectral characteristics of molecularly thin films in situ. These researchers changed the silver coating on the bottom side of the lower mica sheet to a half transparent and half reflecting material, as illustrated in Fig. 7(a)^[50]. The Raman spectrum, film thickness, and friction force could be obtained in the same sliding process. The molecular orientation change of a polydimethylsiloxane (PDMS) melt under confinement was investigated. The experimental result is presented in Fig. 7(b). The peak intensities of the CH₃ symmetric stretching vibration in the Raman spectra were recorded at two orthogonal polarized incident lights, one parallel and one perpendicular to the optic axis of the mica sheet. The anisotropy is defined by the difference between the two values, which was measured and is shown in Fig. 7(b). When the film thickness gradually decreases from 20 nm to 2 nm, the average molecular anisotropy value increases. This finding suggests that the molecular chain has a lateral orientation and that the anisotropic degree increases near the mica surface.

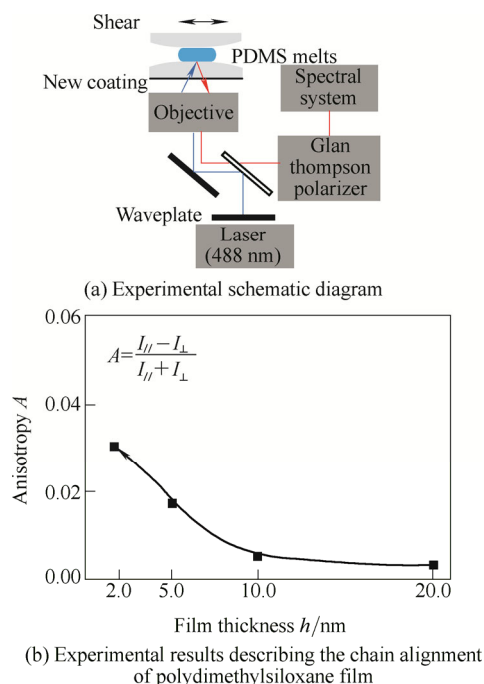


Fig. 7. Schematic and experiment results of in situ Raman measurement^[50]

ZHANG, et al^[51], investigated a nematic liquid crystal in a lubricating point contact area at the nanoscale. A shear-induced orientating process was observed. The

experimental system that they used was developed from an interference film thickness measuring apparatus^[17], as shown in Fig. 8(a). The Raman data at the center of the contact area was recorded during shearing, and the 1607 cm^{-1} peak intensities at different polarization angles are summarized in Fig. 8(b).

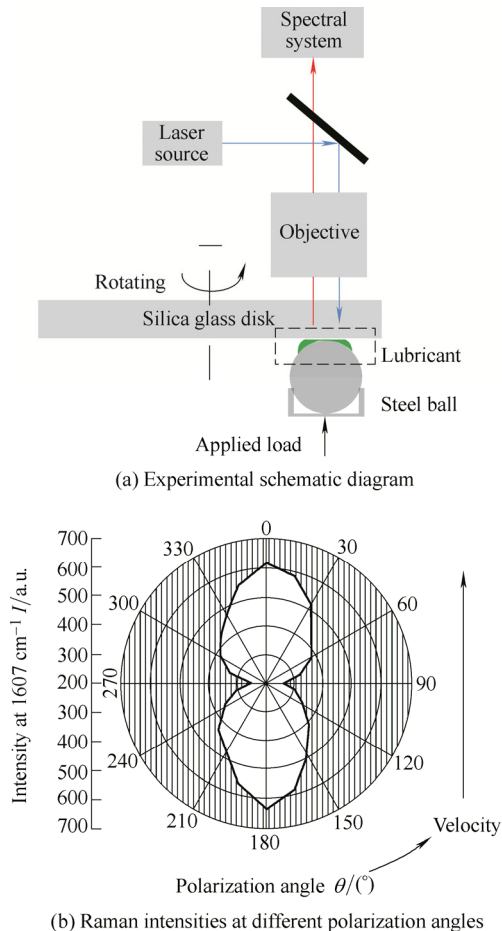


Fig. 8. Schematic of Raman measuring system and experimental results

The angular distribution of the polarized Raman peak intensity exhibits obvious anisotropy. The maximum peak intensity appears in the rolling direction, which indicates that the rod-like liquid crystal molecules are orientated in this direction. The anisotropy value of this orientated arrangement increases with rolling speed unlike the flow alignment of liquid crystal, which is independent of the velocity of flow. An isotropic arrangement of molecules is also observed in the tail area of the outlet region, which is attributed to the lack of confinement. It is believed that confinement and shear are the major factors affecting the orientation in the contact region when the film thickness is less than the transfer thickness of flow alignment.

In traditional spectral experiments, the signal is recorded from molecules throughout the entire film thickness. The problem is that the spectroscopic information is a statistical average. It is difficult to separate the signal of the molecules at the interface from the signal of the bulk liquid. In practice, some researchers have investigated the average

molecular arrangement under increasing distance between solid surfaces. The experimental results can partly illustrate the structure of the arranged lubricant molecules.

BEATTIE, et al^[52], used total internal reflection Raman spectroscopy to investigate the arrangement of molecules in and near an adsorbed layer. The spatial resolution can reach dozens of nanometers, which is more accurate than traditional Raman spectroscopy.

Another way to acquire information about molecules at an interface is to use the sum-frequency generation (SFG) technique and SFG spectroscopy. SFG can only occur when the following condition is satisfied: the matter that light is interacting with must be asymmetric. Surfaces and interfaces are the most common conditions. In other words, molecules in a bulk liquid exhibit no SFG effect, and the spectrum response curve originates only from the molecules at the interface. For example, NANJUNDIAH, et al^[53], investigated the structure of water molecules confined between PDMS and sapphire surfaces. The molecular orientation was measured using polarized SFG spectroscopy, which is similar to Raman spectroscopy but more refined. The result describes the detailed molecular arrangement of adsorbed water molecules. In reality, there are also problems with this measurement—the testing sensitivity is poor, and the horizontal resolution in the contact plan is low. It is difficult to focus the two incoming lights on the area of interest when the surfaces are moving. A combination of SFG and Raman spectroscopy may be a practical solution.

4 Conclusions

The study of the molecular arrangement of lubricating films originates from the experimental analysis of tribological behaviors. AFM, SFA, and film thickness measuring apparatus are common equipment. The change rules of friction force, film thickness, viscosity and other physical properties are sometimes different from the traditional theoretical prediction when the gap size is confined to tens of nanometers or several nanometers. Therefore, the possible structures arranged by lubricant molecules are demonstrated and compared with theoretical computation results.

Currently, direct and detailed information on molecular arrangement is obtained by spectral methods. The X-ray method has been employed for SFA experiments, and the shear-induced film structure of a liquid crystal has thus been obtained. However, it is difficult to apply this method when the film thickness is less than the X-ray penetrating depth. To investigate the molecular arrangement of nanoscale lubricant films, absorption spectroscopy has been used on SFA. The shear-induced orientation change of dye molecules in nanoscale lubricant films has been observed using the polarized dichroic absorption method. This method can only be applied to molecules with chromophores.

Infrared spectroscopy can be used in a tribological ball-on-disk testing system. The anisotropy of molecular orientation has been measured when the lubricant film thickness is reduced. Agreement is observed between theoretical predictions and experimental results. The disadvantages of this approach are the poor spatial resolution and accompanying background noise.

In situ Raman spectroscopy and film thickness measurements have been successfully implemented both on SFA and ball-on-disk testing systems. The results verify the feasibility that confinement and shear can change the arrangement of lubricant molecules. Further work is needed to separate the information concerning molecules at the interface from that concerning the bulk.

Benefiting from the development of nanometer testing technology, experimental studies of the molecular arrangement of lubricants have been growing rapidly. However, research in this field has just begun, and much more work must be performed. For example, what will happen to the molecular arrangement when the lubricating state changes? Are the molecular configuration, conformation, and orientation uniformly distributed in the lubricating contact region? Addressing these questions will contribute to the understanding of the relationship between the molecular-level characteristics and macroscopic properties of lubricants.

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