Measurement of dynamic viscoelasticity of confined lubricant by using oscillating optical fiber probe

S Itoh 1, K Fukuzawa 1,2, Y Hamamoto 1 and H Zhang 1

1 Department of Micro-Nano Systems Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan.
2 JST, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan.

E-mail: s_itoh@nuem.nagoya-u.ac.jp

Abstract. When a liquid is confined in molecularly narrow gaps, it shows characteristic viscoelasticity such as enhanced viscosity or prolonged relaxation time. In order to investigate the dynamic viscoelasticity of the confined liquid, we developed a new shear force measuring method that uses a ball-ended optical fiber as a shearing probe. Our method can measure the shear force of 0.1 nN order with the oscillation frequency of up to 10 kHz. In addition, the gap that confines the liquid can be set at any constant value ranging from 10 μm to 0.1 nm. In this study, we measured the gap dependence of viscoelasticity of confined liquid lubricants. The gap ranged from 200 nm to a few nm. The tested lubricant was Fomblin Z03 and Zdol4000. A magnetic disk was used as the solid substrate. Oscillation frequency was set at 800 Hz. The experiment showed the viscosity of both Z03 and Zdol4000 gradually increased as the confining gap decreased. The gap width where the viscosity increase started was wider than 100 nm, which is dozens of times larger than the gyration diameter of lubricant molecules. Although Z03 and Zdol4000 have negligibly small elasticity in a bulk state, elasticity suddenly appeared at gaps less than about 8 nm with Zdol4000, and at gaps less than about 4 nm with Z03. Stronger affinity of Zdol4000 molecules to the solid substrate could cause the wider gap width of elasticity appearance.

1. Introduction

A liquid which is confined in a molecularly narrow gap has characteristic viscoelastic properties that are greatly different from those in a bulk state [1,2]. Characterization of the confined liquid is important not only for scientific investigations but also for industrial applications, such as lubrication for magnetic storage devices or a design for micro-fluidic devices. In measuring viscoelasticity of confined liquids, the surface force apparatus (SFA) is a well-established method. Previous researchers tested various kinds of confined liquids using the SFA and reported many important findings that include the molecular ordering of liquid molecules, the enhancement of viscosity, the prolonged relaxation time, and so on. However, the SFA has to use mica sheet as the solid substrates which confine the liquid. Therefore, the effect of physical and chemical properties of solid surface on the viscoelasticity of confined liquid has been unknown. Considering the industrial applications, it is especially important to clarify how the molecular interaction between the solid surface and the liquid molecules affects the lubricity or fluidity of the confined liquid in different kinds of mechanical devices. Consequently, to obtain an extensive understanding of the confined liquid, we require a new method that can utilize a variety of materials as confining solid surfaces. In our research, we have
developed a novel shear force measuring method that uses an optical fiber as a shearing probe [3]. One end of the optical fiber was shaped like a ball and sheared a liquid on a solid substrate. The liquid was confined in the gap between the ball-end and the substrate, and the shear force acting on the ball-end was measured by detecting the deflection of the probe. Any type of material can be used as a solid substrate. The material of the ball-end, which is the other side of the confining solid surface, is silicate glass. Silicate glass is widely used in the micro fluidic devices and its surface can be modified by coating it with other industrial materials, such as a diamond-like carbon overcoat. Therefore more varieties of solid surfaces can be used in our new method. We have named this the “fiber wobbling method” (FWM). In this study, we measured the gap dependence of viscoelasticity of confined liquid lubricants on a magnetic disk surface. The surface of magnetic disk is covered with a diamond-like carbon overcoat. As a liquid lubricant, we used two different types of perfluoropolyether lubricants, which are Z03 and Zdol4000. Difference between Z03 and Zdol4000 is the affinity to the magnetic disk surface. We revealed that the difference in affinity caused the different dependence of viscoelasticity on confining gaps.

2. Fiber wobbling method

2.1. Principle of the fiber wobbling method

The basic principle of the fiber wobbling method (FWM) is briefly outlined in this section. Figure 1 shows the schematic of the FWM. A ball-ended optical fiber is used as the shearing probe. The probe is positioned perpendicular to the sample surface and the liquid coated on the substrate is confined between the surfaces of the ball-end and the substrate. When the probe is moved horizontally, it deflects due to a shear force acting on the ball-end. The shear force can be measured by detecting this deflection. The probe is so small that it has high resonant frequency of more than 10 kHz. This means that the probe can be used for the shearing at a high oscillation frequency up to a few kHz. In addition, it is inherently much easier to deflect an optical fiber probe than to extend or contract it. Therefore, when it is positioned perpendicular to the sample surface, the weak shear force deflects the probe while the stiction or adhesion causes negligible change in the gap. This means that the shear force can be accurately measured and the gap can be precisely controlled with the FWM.

The accuracy of shear force measurement depends on how sensitive the deflection measurement is. The conventional method to obtain highly sensitive deflection measurement has involved the optical lever method. However, this is difficult to apply to the FWM because it uses the reflection of the laser beam from the plane surface of the probe tip. The end of the optical fiber probe has a round-shaped and transparent. Therefore, we have developed a novel method of measuring deflection that was

![Figure 1. Schematic of the fiber wobbling method. A ball-ended optical fiber is used as the shearing probe. Liquids are confined and sheared in the molecularly narrow gaps between the ball-end and a solid substrate. Shear force acting on the ball-end can be determined by measuring the fiber deflection using the optical technique which was originally developed by authors.](image-url)
extremely sensitive (Fig. 1) [4,5]. The fiber is used as a micro-cylindrical lens and the laser beam is focused onto the position sensitive detector (PSD). If the probe deflects, the laser spot on the PSD moves. The deflection of the probe is therefore measured by detecting the position of the laser spot on the PSD. The theoretical detection limit with this method was calculated as 4 pm. The experimental detection limit was around 10 pm. Compared with the theoretical detection limit, the experimental detection limit is about one order larger. The main reason for this discrepancy is the spherical aberration of the fiber used as the micro-cylindrical lens. In calculating the theoretical detection limit, the lens was considered to be ideal, which meant it had no spherical aberrations. However, the actual lens used in the experiment had spherical aberrations, weakening the intensity of the laser spot. This meant that the output signal from the PSD decreased. The spring constant of the optical fiber probe we used in this experiment was 66.1 N/m. Considering Hook’s law as a rough estimate, the detectable minimum shear force is about 0.7 nN. This indicates that the FWM can be used to measure shear forces below 1 nN.

2.2. Viscoelastic measurement
To measure the viscoelastic properties of liquid, the optical fiber probe is vibrated sinusoidally and both the amplitude and phase of vibration at the fiber end are measured. Viscosity $\eta'$ and elasticity $\eta''$ are calculated using amplitude ratio $\kappa$ and phase shift $\delta$, comparing when the ball-end is shearing the sample and when it is not making contact. Viscosity $\eta'$ and elasticity $\eta''$ are written as follows [3].

$$\eta' = \frac{(k - m\omega^2)\sin\delta}{\kappa \omega \Omega}$$  (1)

$$\eta'' = \frac{(k - m\omega^2)(\cos\delta - \kappa)}{\kappa \omega \Omega}$$  (2)

where $\omega$, $k$, $m$, and $\Omega$ are the driving frequency, spring constant of the optical fiber probe, effective mass of the ball-end, and geometric parameter calculated from the shape of the sliding surfaces, which are the sphere and the plane in the FWM. When a sphere with diameter $d$ moves parallel to the plane surface with a gap $h$, the geometric parameter $\Omega$ is obtained as follows,

$$\Omega = 3\pi l \left[ \log \left( \frac{d}{h} \right) + \cdots \right] \approx \frac{8}{5} \pi l \log \left( \frac{d}{h} \right)$$  (3)

The approximation for the right-hand side of equation (3) can be applied when $h << d$.

3. Experiments
3.1. Materials
Perfluoropolyether lubricants used in this experiment were Fomblin Z03 (Mw=4000) and Fomblin Zdol4000 (Mw=4000). The chemical formulas for these lubricants are shown in table 1. Both of them have the same flexible linear chain structures with the same molecular weight and size. The gyration diameters of Z03 and Zdol4000 are around 3 nm [6]. The only difference is that Zdol4000 has polar end groups, which are hydroxyl groups, on both sides of the chain. With the polar end groups, Zdol4000 molecules can adsorb onto the solid surface much stronger than Z03 molecules which has
Table 1. Lubricant used in this study.

| Lubricant | Chemical formula |
|-----------|------------------|
| Z03       | CF₃-CF₂(OCF₂CF₂)ₙ(OCF₂)mOCF₂-CF₃ |
| Zdol4000  | HO-CH₂-CF₂(OCF₂CF₂)ₙ(OCF₂)mOCF₂-CH₂-OH |

no polar end groups. We used a magnetic disk as the solid substrate. The surface of the magnetic disk was coated with a diamond-like carbon overcoat. We measured the surface roughness of the magnetic disk by atomic force microscopy (AFM). The root mean square roughness of the magnetic disk surface was 0.59 nm.

### 3.2. Experimental setup and measurement procedure

Figure 4 shows a schematic diagram of the experimental setup we developed. The piezo translator X (Piezo X) vibrated the optical fiber probe with the amplitude and the frequency we set. The gap between the ball-end of the probe and the sample surface was controlled with the piezo translator Z (Piezo Z) at a resolution of 0.1 nm. Output current from the PSD was converted to voltage at the pre-amplifier and measured with the lock-in amplifier using the driving signal for the Piezo X as a reference signal. The probe used in this experiment had a spring constant of 66.1 N/m. The ball-end diameter \( d \) was 0.204 mm, fiber diameter \( d_p \) was 0.114 mm, and fiber length \( l \) was 3.12 mm. Its resonant frequency was 10.186 kHz. Micrographs of the optical fiber probe are shown in figure 3. In addition, we evaluated the surface roughness of the ball-end by AFM. The surface of the ball-end was extremely smooth. At a scanning distance of 1 \( \mu \)m, root mean square roughness was 0.21 nm. Material of the optical fiber probe is silicate glass. Although in this study we used the probe as it is, the surface of the ball-end can be modified by coating it with other materials.

The measurement procedure for evaluating the gap dependence of viscoelasticity is described below. First, before shearing the sample, we measured initial amplitude \( a_0 \) and the phase shift from driving signal \( \delta_0 \). Next, we prepared a lubricant droplet on the substrate using a micro-syringe and immersed the ball-end completely into the droplet. Therefore the viscoelastic measurement in this study is the immersed system. Then probe amplitude \( a_1 \) and phase shift \( \delta_1 \) were measured with gap \( h \) gradually and continuously decreased from 200 nm to the solid contact at a constant rate of 10 nm/s. By substituting the amplitude ratio \( \kappa = a_1/a_0 \) and the phase shift \( \delta = \delta_1 - \delta_0 \) into equations (1) to (3), we obtained the viscosity \( \eta' \) and elasticity \( \eta^\ast \). In this experiment, the driving amplitude of the optical fiber probe was 30 nm and its frequency was 800 Hz. The conditions for driving vibration did not change throughout the experiment. The gap width was determined from the displacement of Piezo Z. The origin of the gap width was defined as the gap when the ball-end and the disk first made contact. The solid contact between the ball-end and the disk can be detected by the sudden decrease of the probe amplitude [3].

![Figure 2. Schematic of the experimental setup.](image-url) Amplitude and phase of the probe vibration were measured by using the lock-in amplifier and recorded in the personal computer.
Figure 3. Micrographs of the optical fiber probe. The end of the fiber was fabricated in a ball shape by annealing with CO2 laser.

Figure 4. Gap dependence of viscosity. Blank circles represent viscosity of Z03 and crosses represent that of Zdol4000. Inset shows the enlarged view at the gap width ranging from 100 nm to 200 nm.

Figure 5. Gap dependence of elasticity at the gap width less than 15 nm. Blank triangles represent elasticity of Z03 and filled triangles represent that of Zdol4000.

4. Results and discussion

Figure 4 shows the gap dependence of viscosity, and figure 5 shows that of elasticity measured with Z03 and Zdol4000. As shown in figure 4, viscosity of both Zdol4000 and Z03 increased with decreasing gaps up to dozens of times larger than those of bulk state. The inset of figure 4 shows an enlarged view of the measured viscosity in the gap range of 100 nm to 200 nm. The viscosity increase of both Zdol4000 and Z03 already started at gaps larger than 100 nm. Considering that the gyration diameters of Zdol4000 and Z03 are around 3 nm, the gap width where the viscosity started to increase was much larger than the molecular size. This means that the viscosity increase was not caused by the molecules that were directly adsorbed onto the solid surfaces. The confining surfaces might affect the mobility of molecules which were not proximate to the solid surface. The detailed mechanism of the viscosity increase is the subject for the future study. At a bulk state, both Z03 and Zdol4000 have negligibly small elastic properties. However, as shown in Fig. 5, when they were confined, elasticity appeared at gaps less than about 8 nm with Zdol4000, and at gaps less than about 4 nm with Z03. In both lubricants, the gap width where the elasticity appeared was equivalent to 1-3 molecular sizes. Therefore the appearance of elasticity could be caused by the lubricant molecules which were adsorbed onto the solid surfaces. Elasticity of Zdol4000 appeared at wider gap width than that of Z03. This could be caused by the stronger affinity of Zdol4000 molecules to the solid substrate.
5. Conclusions
We measured the gap dependence of viscoelasticity of confined lubricants by using the fiber wobbling method (FWM). The FWM is the highly sensitive shear force measurement method which we originally developed. We used two different types of lubricant that were the non-polar lubricant: Z03 and the polar lubricant: Zdol4000. Zdol4000 molecules have stronger affinity to the solid substrate than Z03 because of their polar end groups. Experimental results obtained in this study are summarized as follows.

- The viscosity of both Z03 and Zdol4000 increased as the gap decreased. At the narrowest gap of a few nanometers, their viscosity was dozens of times larger than that observed in a bulk state.
- The gap width where the viscosity increase started was wider than 100 nm.
- The elasticity of both Z03 and Zdol4000 is negligibly small in a bulk state. However, elasticity appeared at the gap of less than 4 nm with Z03, and at the gap of less than 8 nm with Zdol4000. Once the elasticity appeared, it increased as the gap decreased. The difference of the gap width where the elasticity appeared between Z03 and Zdol4000 is considered to be due to the difference in affinity of lubricant molecules to the solid surface. The stronger affinity of Zdol4000 might cause the appearance of elasticity at wider gaps.
- Considering that the gyration diameter of the lubricant molecules is around 3 nm, the gap width where the elasticity appeared was equivalent to 1-3 molecules. Therefore, the appearance of elasticity could be caused by the molecules which were adsorbed onto the solid surfaces. On the other hand, the viscosity increase was started at gaps of wider than 100 nm. This means that the viscosity increase was not caused by the molecules that were directly adsorbed onto the solid surfaces. The confining surfaces might affect the mobility of molecules which were not proximate to the solid surface.

References
[1] Luengo G, Schmitt F J, Hill R and Israelachvili J 1997 Macromolecules 30 2482-2494
[2] Granick S 1991 Science 253 1374-1379
[3] Fukuzawa K, Itoh S and Mitsuya Y 2003 IEEE Trans. Magn. 39-5 2453-2455
[4] Itoh S, Fukuzawa K, Takahashi K, Ando T, Zhang H and Mitsuya Y 2005 Microsystem Technologies 11 894-900
[5] Fukuzawa K, Itoh S, Ando T, Takahashi K, Zhang H and Mitsuya Y 2004 J. Appl. Phys. 95-9 5189-5191.
[6] Ma X 1998 Spreading of Perfluoropolyalkylether Films on Amorphous Carbon Surfaces (Pittsburgh: Carnegie Mellon University, Ph. D. Thesis)