Shear thinning behavior of monolayer liquid lubricant films measured by fiber wobbling method

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Abstract. It is essential to clarify mechanical properties of monolayer lubricant films coated on magnetic disks under shearing motion for designing future hard disk drives with ultra-low flying height. Many of previous researchers reported that strong shear rate dependence of viscoelasticity was one of the typical phenomena observed with molecularly thin liquid films. However, it has not been clarified whether or not perfluoropolyether (PFPE) lubricant films, which are used for the head-disk interface (HDI) lubrication, show shear thinning behavior under actual HDI conditions. In this study, we used the fiber wobbling method that can achieve both highly-sensitive shear force measurement and precise gap control and measured shear rate dependence of viscoelastic properties of monolayer PFPE films coated on the magnetic disk. Our experimental results showed that shear thinning does occur at high shear rate ranged from $10^2$ to $10^6$ s$^{-1}$.

1. Introduction

To achieve further increase in recording density of hard disk drives (HDDs), the gap between the magnetic head and the disk must be reduced to less than 5 nm [1]. Taking into account this reduced gap, lubricant films used to lubricate head-disk interface (HDI) of HDDs must be a monolayer, with a thickness of around 1-2 nm. In addition, HDI must be designed to allow continuous or frequent contact between the head and the disk. In order to ensure durability and reliability of future HDDs, it is essential to characterize mechanical properties of monolayer lubricant films under shearing motion.

A surface force apparatus (SFA) is widely used to measure the viscoelasticity of molecularly thin liquid films. Ruths and Granick reported that the perfluoropolyether (PFPE) lubricants, which are used for HDI lubrication, showed shear thinning behavior under confined and sheared conditions [2]. On the other hand, no shear thinning behavior was observed with PFPE films by Bhushan’s experiments using their original viscometer [3]. This discrepancy can be attributed to the differences in experimental conditions between the SFA method and Bhushan’s method. Major differences are shear rate and materials of the substrate. In Bhushan’s method, higher shear rate ($10^4 – 10^7$ s$^{-1}$) was achieved and the substrate was comparable to actual magnetic disks. However, the shearing gap was not well determined. In the SFA measurements, although the shearing gap was precisely determined, the shear rate was much lower (around 1 – 10 s$^{-1}$) and the mica was essential for the substrate. Since the
shearing speeds dynamically change in the actual HDDs’ operation, it is important for the lubrication
design to clarify whether or not shear thinning occurs in HDI.

In our previous study, we originally developed a highly-sensitive shear force measurement method
that utilized a ball-ended optical fiber as a shearing probe. We called this method the “fiber wobbling
method (FWM)” [4, 5]. In FWM, the shearing probe was oscillated sinusoidally and the probe’s tip
sheared the sample to detect its dynamic viscoelasticity. We succeeded in measuring the viscoelastic
properties of monolayer lubricant films coated on the magnetic disks [6]. There are many other
methods using cantilevers placed orthogonal to the sample to achieve the sensitive detection of shear
force [7-9]. One of the typical differences with our method was they used resonant oscillation of the
probe to attain high sensitivity. In FWM, we can achieve high sensitivity without resonant oscillation.
This means that we can choose any oscillation frequency to evaluated viscoelastic properties of
samples. FWM also achieves a shear rate comparable to Bhushan’s method. In this study, we used
FWM to measure shear rate dependence of viscoelastic properties of monolayer lubricant films coated
on the magnetic disk. Non-polar PFPE: Fomblin Z03 was used as the sample lubricant.

2. Measurement of viscoelastic properties of monolayer lubricant film by FWM

2.1. Principle of the fiber wobbling method (FWM)
The experimental setup for FWM is outlined in figure 1(a). The optical fiber probe positioned
perpendicular to the sample was oscillated sinusoidally using a piezo actuator, and the lubricant-film
sample on the substrate was sheared with the probe end. To measure the oscillation of the probe, the
optical fiber probe was used as a cylindrical lens and the deflection of the probe was measured by
detecting the displacement of the laser spot formed onto the position sensitive detector (PSD). The
displacement signal from the PSD was synchronously detected with a lock-in amplifier referring to the
forced oscillation signal for the piezo actuator. A laser Doppler velocimeter with detection limit of 1
nm (LV-1500, Ono Sokki) was used to calibrate the displacement signal. Our previous study showed
that the detection limit of the displacement by using our technique was around 1-10 pm [10]. This
detection limit corresponds to the shear-force detection limit of 1-100 pN considering that spring
constant of the probe was usually around 1-10 N/m. The viscoelastic properties of the lubricant
confined and sheared in the gap between the probe end and the substrate surface were obtained by
measuring the change in probe amplitude and the phase shift.

In FWM, however, it is difficult to measure the shearing gap directly. Therefore, the gap width is
determined by the displacement of the piezo stage from the point where solid contact occurred, which
is a gap width of 0 nm. The accuracy with which the gap is controlled depends both on the resolution
of the piezo stage and the sensitivity with which solid contact is detected. The resolution of the piezo
stage is on the order of 0.1 nm. The point of solid contact is determined by using the following
procedure. Both of the two shearing surfaces - the surface of the probe end and that of the substrate -
have surface roughness. Therefore, at the beginning of solid contact, asperity collisions occur and impulsive forces are applied to the probe. The impulsive forces can excite resonant oscillation on the probe. Thus, solid contact is detected by monitoring the excitation of the resonant-frequency component that is included in probe oscillation. The experimental setup that we used to detect solid contact is indicated in the dotted box in figure 1(a). To detect the resonant-frequency component in probe oscillation, we prepared another lock-in amplifier. A sinusoidal wave synchronized with the resonant frequency of the probe was used as the reference signal and it was input into the lock-in amplifier from the function generator. In our previous study, an accuracy of 0.2 nm was achieved in determining the solid-contact point [6].

There is a micrograph of the optical-fiber probe we used in this study in figure 1(b). The fiber diameter was about 100 µm, and the probe’s end had a curvature radius of about 8 µm. The probe was 4.2 mm long. The probe’s resonant frequency was 4945 Hz and its spring constant was 20 N/m. The surface roughness of the probe’s end was measured by atomic force microscopy. The average roughness, root-mean-square roughness, and peak-to-valley roughness were 0.20 nm, 0.27 nm and 1.27 nm, respectively.

2.2. Calculation of viscoelastic properties
In viscoelastic measurement using FWM, the damping coefficient \( c_f \) and elastic coefficient \( k_f \) of the sheared samples are obtained as follows [4]:

\[
\begin{align*}
    c_f &= \frac{a_0(k - m\omega^2)\sin\delta}{a_0} \\
    k_f &= \frac{(a_0\cos\delta - a)(k - m\omega^2)}{a_0}
\end{align*}
\]

where \( a \) and \( \delta \) are the probe amplitude and phase shift measured at the shearing of samples, and \( a_0, \omega, k, m \) correspond to the forced oscillation amplitude, the forced oscillation frequency, the spring constant of the probe, and the effective mass of the probe end, respectively. Dynamic viscoelasticity is often evaluated by the complex viscosity coefficients expressed as \( \eta = \eta' - i\eta'' \). Here, \( \eta' \) is the dynamic viscosity and \( \eta'' \) is the dynamic elasticity. We can relate \( \eta' \) and \( \eta'' \) to \( c_f \) and \( k_f \) as follows:

\[
\begin{align*}
    c_f &= \eta\Omega \\
    k_f &= \eta^*\Omega
\end{align*}
\]

Here, \( \Omega \) is the geometric parameter calculated from the shape of the sliding surface. If the sliding surfaces are flat plates and they move parallel to each other with the gap width of \( h \), \( \Omega \) is expressed as follows [11]:

\[
\Omega = \frac{S}{h}
\]

where \( S \) represents the contact area. Since the range of gap widths we focused on was sufficiently smaller than the curvature radius of the probe end, the geometric configuration of the sliding surfaces in our setup can be assumed to be two flat plates. However, it is difficult to determine an accurate value for \( S \) experimentally, because of the small curvature radius of the probe end, which was around 8 µm. Additionally, the dynamic deformation of the lubricant film expected during shearing motion makes it difficult to determine an accurate value. Therefore, we evaluated the viscoelasticity of the lubricant films with \( c_f \) and \( k_f \) and discussed their shear rate dependence.

3. Method and materials

3.1. Experimental procedure
We started to oscillate the optical-fiber probe sinusoidally using a piezo actuator. The gap width between the probe tip and the sample was decreased at a constant rate of 2 nm/s using the piezo stage. At an initial state, the probe tip did not make contact with the sample. As the gap was gradually decreased, the probe started to shear the lubricant film on the disk and finally made contact with the substrate. We defined this process as the “approaching process”. Subsequently, measurement was conducted in the “separating process”, which is a process whereby the gap width was increased at a constant rate of 2 nm/s. In the separating process, the probe first sheared the substrate and then only sheared the lubricant film. Finally, the probe and sample lubricant came off completely. Both in the approaching and separating processes, we measured change in probe amplitude and phase shift, and evaluated \( c_f \) and \( k_f \). The oscillation frequency was fixed at 1000 Hz in all of the experiments. The frequency of 1000 Hz was smaller than the resonant frequency of the probe, which was 4945Hz. To discuss shear rate dependence, we conducted each measurement at different oscillating amplitude: 50 nm, 25 nm, 17.5 nm, 10 nm and 5 nm. Corresponding shear rate ranged from \( 10^2 \) to \( 10^6 \) s\(^{-1}\).

Both in the approaching and the separating processes, gap range whereas the probe tip is shearing lubricant film must be determined. In the approaching process, we defined the gap width at which the probe tip began to contact the lubricant film as the “touch-down gap”. Touch-down gap was defined as the point where decrease in the probe amplitude or increase in the phase shift first exceeded noise levels. The noise levels of the measured probe amplitude and phase shift were determined by calculating the threefold variance in the measured data at a time when the probe did not contact the lubricant film. Similarly, we defined the gap width where the probe and the lubricant film completely came off in the separating process as the “take-off gap”. Take-off gap was defined as the point where both the increasing probe amplitude and the decreasing phase shift first agreed in the range of noise levels with their average values measured when the probe and the sample were completely apart. These touch-down and take-off gaps represent the gap range whereby the probe end shears the lubricant film and they are not necessarily equal to the film thickness since the lubricant film can be deformed.

3.2. Materials
We used a magnetic disk with a carbon overcoat as a substrate. The surface roughness of the disk was measured by atomic force microscopy. The root-mean-square roughness was 0.45 nm and the peak-to-valley roughness was 1.96 nm. For the sample lubricant we used the non-polar perfluoropolyether lubricant, Fomblin Z03 (Solvey Solexis Inc.). Its chemical formula is,

\[
\text{CF}_3 - \text{CF}_2 (\text{OCF}_2 \text{CF}_2)_n (\text{OCF}_2)_m \text{OCF}_2 - \text{CF}_3.
\]

The molecular weight was 4000 amu and the length of the main chain was around 14 nm. Since the main-chain structure is quite flexible, the Z03 molecule has random coil structures in the bulk state. Dip coating was used to form the molecularly thin lubricant films on the magnetic disk. In dip coating, we prepared the lubricant solution and dipped the disk at a constant speed. When the disk was fully immersed, the disk was pulled out at the same speed as when dipping. Thickness of the film was controlled precisely by the concentration of the solution and the speed of dipping and pulling out. All samples we prepared in this study had a thickness of 2.0 nm, which was verified by an ellipsometer.

4. Experimental result and discussion
Figure 2 shows the experimental results measured with the oscillation amplitude of 25 nm. The longitudinal axes plot the probe amplitude \( a \), phase shift \( \delta \) and resonant-frequency component \( a_r \). The plotted values of \( a_r \) are normalized using their average value measured while the probe and sample did not make contact. The transverse axes plot the gap width between the probe end and the disk. Origins of the gap width were defined as the solid-contact point determined by the increase in the measured resonant-frequency component. The touch-down gap was 4.5 nm and the take-off gap was 150 nm. For the other oscillation amplitudes, quantitatively identical results were obtained (data not shown).

Since the thickness of the lubricant film was 2.0 nm, the touch-down gap of 4.5 nm indicates that the contact between the probe tip and lubricant film started at a gap width larger than the thickness of the
lubricant film. We considered that the attractive intermolecular force from the approaching probe surface caused the formation of a liquid bridge between the probe tip and the disk. This was not the case with different type of lubricant that strongly adsorbed on to the disk surface [6]. Due to the strong adsorption to the disk surface, the lubricant film cannot be deformed by the attractive force from the probe tip. Therefore, the touch-down gap is equivalent to the film thickness. The take-off gap of 150 nm was much larger than the film thickness. This can be due to the elongation of lubricant gathered near the probe tip during the contact. The formation of liquid bridge in approaching process and its elongation during the separating process are schematically summarized in figure 3. We calculated damping coefficient $c_f$ and elastic coefficient $k_f$ from the measured probe amplitude and phase shift by using equation (1) and (2). Results for different oscillation amplitudes are plotted in figure 4 to 8. The longitudinal axes plot $c_f$ and $k_f$ and the transverse axes plot the gap width. The horizontal dotted lines show the magnitude of noise levels in the determination of $c_f$ and $k_f$. They were obtained by substituting the threefold variance of the measured probe amplitude and phase shift into equations (1) and (2). The variance was evaluated from the data obtained when the probe did not make contact with the sample. As shown in figure 4 to 8, the elasticity $k_f$ was quite small and comparable to the noise level in most cases. Therefore, we cannot discuss the shear rate dependence of $k_f$ in this study. In contrast, the damping coefficient $c_f$ were sufficiently larger than the noise level at the smaller gap widths. We discuss the shear rate dependence of $c_f$ at the gap range where measured values of $c_f$ sufficiently exceeded the noise level, which were the gap widths less than 3 nm in approaching process and the gap widths less than 40 nm in separating process.

The relationships between $c_f$ and shear rates at representative gap width, which are 0.2, 1.0, 2.0, 3.0 nm in the approaching process and 2, 10, 20, 40 nm in separating gap process, (shown as vertical dotted lines in figure 4 to 8) were shown in the figure 9 with double logarithmic plot. Transverse axes show shear rates calculated from the gap widths and the maximum shearing speed, which were...
**Figure 3.** Schematic of configuration of lubricant molecules between the probe tip and the substrate in approaching and separating processes.

**Figure 4.** The relationship between gap width and damping coefficient, $c_f$ and elastic coefficient $k_f$ with oscillation amplitude of 50 nm in (a) approaching and (b) separating processes.
Figure 5. The relationship between gap width and damping coefficient, $c_f$ and elastic coefficient $k_f$ with oscillation amplitude of 25 nm in (a) approaching and (b) separating processes.

Figure 6. The relationship between gap width and damping coefficient, $c_f$ and elastic coefficient $k_f$ with oscillation amplitude of 17.5 nm in (a) approaching and (b) separating processes.
Figure 7. The relationship between gap width and damping coefficient, $c_f$, and elastic coefficient $k_f$ with oscillation amplitude of 10 nm in (a) approaching and (b) separating processes.

Figure 8. The relationship between gap width and damping coefficient, $c_f$, and elastic coefficient $k_f$ with oscillation amplitude of 5 nm in (a) approaching and (b) separating processes.
Figure 9. The relationship between shear rate and damping coefficient, $c_f$, in (a) approaching and (b) separating processes. Both in (a) and (b), damping coefficient decreased exponentially at every gap width. These results indicate the shear thinning behavior of Z03 films on the magnetic disk surface.

Figure 10. The relationship between shear rate dependence, $\alpha$, and the gap width, $h$, in (a) approaching and (b) separating processes.

determined by oscillation frequency and amplitude. Shear thinning behavior is often well expressed by the empirical power law:

$$\log c_f = -\alpha \log \gamma + \beta,$$

where $\alpha$ and $\beta$ are fitting parameters and $\gamma$ represents shear rate. The broken lines in figure 9 are the calculation results obtained by fitting the equation (6) to the experimental data. As shown in figure 9, shear rate dependence of $c_f$ was well represented by the empirical power law. These results indicate that shear thinning does occur with molecularly thin Z03 lubricant films coated on the magnetic disk surface. At the other gap width, which should be less than 3 nm in approaching and less than 40 nm in separating, similar shear thinning was observed. We plotted the $\alpha$ against the gap widths as shown in figure 10. The values of $\alpha$ were obtained by the results of a fitting calculation, and they represent the inclination of the fitted line of equation (6). A larger value of $\alpha$ represents a more prominent decrease in viscosity along with increasing shear rate caused by shear-thinning. As shown in figure 10, shear dependence, $\alpha$ ranged from 0.4 to 0.8 in approaching process. On the other hand, it remained constant at around 0.4 in separating process. Although this difference might have some kind of physical origins, future investigations must be performed to explain the details.
5. Summary
To clarify whether or not shear thinning occurs with lubricant films coated on the magnetic disk, we measured the shear rate dependence of the viscoelastic properties of 2 nm-thick lubricant films, using the fiber wobbling method (FWM). In the viscoelastic measurements, oscillation frequency was fixed at 1000 Hz and the oscillation amplitude was varied from 5 nm to 50 nm to change the shear rate. Corresponding shear rates examined in this study ranged from $10^2$ to $10^6$ s$^{-1}$. Our experimental results revealed that shear thinning does occur both in the approaching and separating processes at nanometer-sized gap widths. We consider this result is important in the design of head disk interface lubricating systems since the shearing speed dynamically changes during an HDDs’ operation.

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