Structure of an Interfacial Liquid under Shear

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Introduction

The study of liquids under shear is essential for understanding rheology (i.e., chemical and mechanical processes). Complex fluids under shear show phase transformations, change of phase boundaries, etc. The corresponding microscopic structures have been extensively studied by neutron scattering and x-ray scattering [1-4]. In contrast, Newtonian fluids under shear, under normal conditions, do not behave like complex fluids. However, it has been reported, mostly from using surface force apparatus (SFA), that interfacial Newtonian liquid films show complex shear responses that may originate from the ordered molecular structures as a result of confinement [5-7].

X-ray reflectivity is a popular technique to probe the structures of soft matter with less-than-angstrom resolutions along the normal direction to the solid substrate. However, the experimental setup to combine the x-ray reflectivity and the apparatus controlling the shear rate of very thin film confined between two solid substrates is difficult to achieve. The difficulty is mainly due to the attenuation of x-ray intensity passing through the solid substrate and the strong background scattering. Thus, probing molecular structures of confined fluids at embedded interfaces is a challenging task.

Methods and Materials

We designed a sample chamber (Fig. 1). The surface of the silicon substrate slightly protrudes above the top surface of the stainless steel sample holder and housing. This chamber allows the reflectivity signal to hit at angles as low as possible and helps the estimation of the liquid film thickness (see below). The shear was applied by rotating the housing part while the liquid was kept in the sample cell by a Kapton film on the silicon surface side and a magnetic seal on the other side. The silicon substrate was cleaned in strong oxidizer and kept in water before use [8]. The x-ray beam size was 0.2 to 0.3 mm vertically and 1 mm horizontally.

A slightly negative pressure in the chamber reduced the liquid thickness and decreased the bulk tetrakis(2-ethyl-hexoxy)silane (TEHOS) scattering at high angles. The resulting thickness was found to be ~13 μm after fitting data (see text below). Although much thinner films (less than 10 molecule sizes using SFA) than ours are required to show non-Newtonian behavior for Newtonian liquids,

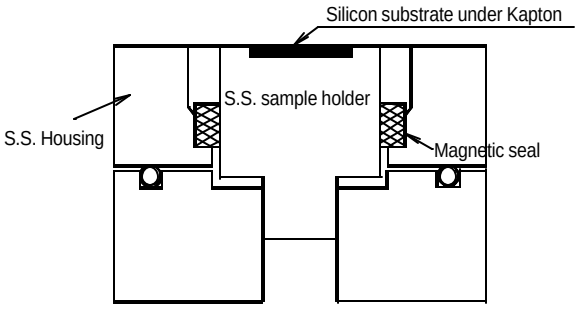

FIG. 1. Schematic diagram of the sample setup. (S.S. = stainless steel).

we think that the interpretation of our experiment with ~13 μm could be extended to SFA experiments as long as the electron density profile of the liquid near the solid-liquid interface is not affected by the film thickness.

The film thickness could actually disrupt or enhance the electron density profile if it is within the range of 1 to 3 molecular sizes, which is manifested as a structural force [9]. In this structural force regime, stick-slip motion is the typical dynamical response to shear stress, However, in the thickness regime of 3 to 10 molecular sizes, confined Newtonian fluids show shear thinning, which is a typical behavior of complex fluids. A computer simulation study shows that shear thinning occurs only at solid-liquid interfaces and that the liquid molecules in the middle of confined liquids act as a bulk liquid [10]. This is consistent with our previous experimental results showing that the significant structural changes exist only within a distance of less than 3 to 6 molecular sizes from the isolated solid interface [8, 11, 12].

Results

In our previous work [12], we showed that liquid layering is at the solid-liquid interface but not in any other region of ~5000-Å-thick TEHOS film bounded by air-liquid and solid-liquid interfaces. Although the air-liquid interface is replaced with a Kapton-TEHOS interface in this case, the relatively rough surface of Kapton polymer film should not induce the liquid layering at the interface. Therefore, the diffraction peak in Fig. 2(a) is from layered TEHOS molecules at the solid-liquid interface.

We obtained the TEHOS film thickness (d_T) and roughness of the silicon (σ) to be 13 μm and 4.3 Å by fitting it with:

$$\frac{R}{R_F}(q) = N \exp\left(-2\left(\frac{d_k}{\delta_k} + \frac{d_T}{\delta_T}\right)\Big/ \sin\theta\right) \exp\left(-\sigma^2 q^2\right),$$

where R = reflectivity, R_F = Fresenel reflectivity, $q = 4\pi/\lambda \sin\theta$, λ = wavelength of the x-ray, θ = incident angle, N = normalization constant, d_k = thickness of 25.4 μm, and $\delta_k(\delta_T)$ = attenuation length of Kapton (TEHOS). The diffraction peak around 0.63 $Å^{-1}$, which shows the layering of the TEHOS at the solid-liquid interface, was expected to be similar to previously reported data, but the peak intensity and full-width, half-maximum (FWHM) of the peak was different from the data [12]. We attribute this effect to the roughness of the silicon substrates: 3 Å for Ref. 12 and 4.3 Å here.

To apply shear stress, we rotated the stainless steel housing in Fig. 1, while the Kapton film was held down on top of it, at a rate of 0.17 turn/s for 1 min, stopped the rotation, and measured the reflectivity from every 0.33-cm interval away from the center to 1 cm. In Fig. 2(b), the x-ray reflectivity was measured at the center part of the sample of the approximately zero shear region, and the data were not distinguishable from Fig. 2(a), as expected. Figures 2(c)-2(e) show the data for distances of 0.33, 0.67, and 1 cm from the center, respectively; each scan took about 45 min. The shear rates ranged from 0 to ~800 ± 40 s^{-1} where the error of 40 was calculated from the horizontal size (1 mm) of the x-ray footprint at the sample.

We found structural changes in TEHOS liquid at the solid-liquid interface as a result of shear. We could clearly see the diffraction peak was disrupted as the x-ray footprint point got away from the center or as the applied shear rate got higher. Another interesting observation was that the position of the dip (~0.55 $Å^{-1}$) before the diffraction peak and the center of the diffraction peak did not distinguishably change during the disruption of the diffraction peak. This means that the spacing and the number of liquid layers were almost the same and that only the domains of the layered region were reduced as a result of shear.

Discussion

Figures 2(a) and 2(c)-2(e) were fitted with an exponentially decaying curve and a Gaussian diffraction peak from 0.6 to 0.9 $Å^{-1}$. Figure 2(a) was fitted first to obtain the FWHM of the Gaussian curve and the peak position, and these were fixed in other fits for Figs. 2(c)-2(e). The inset of Fig. 3 shows a representative fit from the data in Fig. 2(a). In Fig. 3, we plotted the amplitude with respect to the shear rate in log-log plot. The shear rate for the data point at the lowest shear rate was arbitrarily selected to represent a very small shear rate, and the amplitude value was from the fit for Fig. 2(a). This plot is very similar to the shear thinning plot for 3- to 10-molecular-size-thick Newtonian fluids studied by surface force measurement where the y-axis value was the shear viscosity [7]. The slope in the log-log plot from that work was about –2/3, and it was about –1 in ours. That research also stated that –1 was observed for the thinnest films [13].

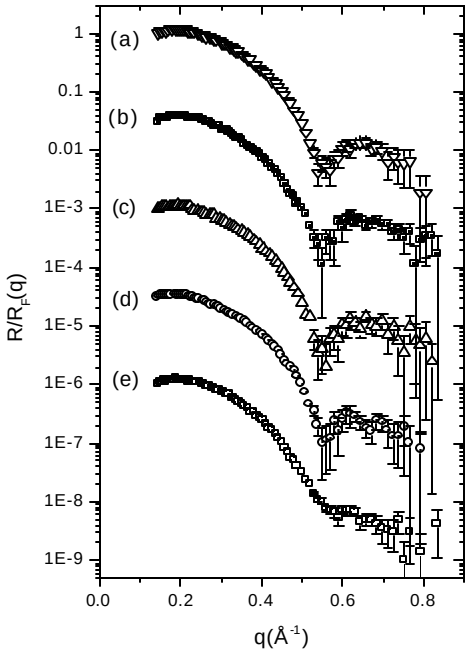

FIG. 2. Normalized x-ray reflectivity data for ~13-mm-thick TEHOS film. (a) Unsheared. (b-e) After rotational shear for 1 min at a shear rate of (b) 0 s^{-1}, (c) 270 ± 40 s^{-1}, (d) 540 ± 40 s^{-1}, and (e) 800 ± 40 s^{-1}.

In summary, we observed that shear flow affects the structure of TEHOS adjacent to the solid substrate. The relation between the amplitude and shear rate behaves in a manner similar to the relation between the shear viscosity and shear rate reported by other researchers. This suggests, for the first time, that the anomalous dynamic properties of normal fluids confined between two surfaces could be linked to the their structures by using x-ray probes.

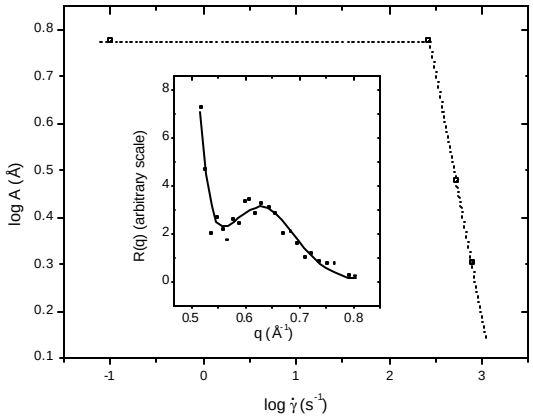

FIG. 3. The amplitude (A) of the diffraction peak is plotted with respect to the shear rate applied for 1 min. After a threshold shear rate, the amplitude drops rapidly. The dotted line through the data point is a guide to the eye. The inset shows the fit to the data in Fig. 2(a), as an example, with an exponentially decaying function and a Gaussian curve. The values of FWHM and peak position obtained from the Gaussian fit are fixed for the fits [Figs. 2(c)-2(e)].

Acknowledgments

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