Effects of Shear Flow on Interfacial Ordering in Liquids: X-ray Studies

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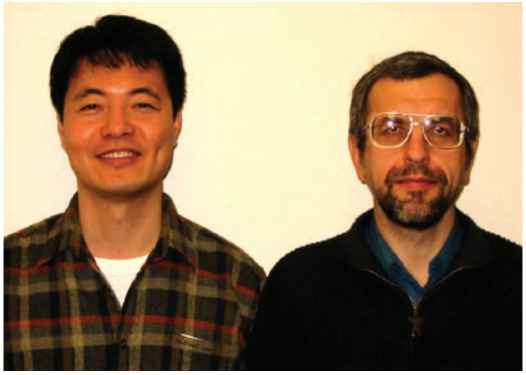
We have directly observed shear-induced structural changes in two interfacial liquids using x-ray reflectivity. The liquids are tetrakis (2-ethylhexoxy) silane (TEHOS) and polydimethylsiloxane (PDMS). Both are insulating, nonpolar liquids, but TEHOS molecules are spherical (non-entangling), while PDMS molecules are linear (entangling). The static interfacial structure of TEHOS, approximately three layers at the interface, was gradually destroyed as the shear rate increased. PDMS, which has no observable interfacial layers when unsheared, developed approximately four layers at the interface at the shear rate of about 10^4 units/second (s^{-1}), applied for 1.5 minutes. We suggest possible correlations between our observations and unusual shear responses reported by other researchers.

Classical hydrodynamics assumes isotropic, continuous media, but this assumption is likely to fail near interfaces, and there is considerable evidence that it does fail. Many experiments have showed a non-classical shear response in interfacial liquids, but the relation between this response and structural changes in the interfacial liquid is not clear. We have directly observed structural changes in interfacial liquids under shear. We used the liquids tetrakis(2-ethylhexoxy)silane (TEHOS) and polydimehylsiloxane (PDMS) in this study. These materials are chemically similar (both are insulating, nonpolar, nonreactive van der Waals liquids), but the molecules are geometrically very different (TEHOS is spherical and PDMS is spaghetti-like).

Surface Force Apparatus (SFA) experiments on nanoscopic round-molecule liquids confined between two smooth solid surfaces have showed shear thinning (reduction of shear viscosity) above a threshold shear rate about 10^8 times smaller than that for bulk liquids. The reduction follows a power law. Computer simulations indicate that shear thinning occurs only in the interfacial region. While our experiments used much thicker liquid films than the SFA experiments, we applied the same shear rates and looked at the structure in the interfacial region. For this purpose we fabricated a shearing apparatus that maintains micrometer-thick liquid films while rotational shear is applied (**Figure 1**).

When no shear is applied, TEHOS is known to develop layers (density oscillations) near hard surfaces. Our shear-dependent x-ray reflectivity data show that these density oscillations are gradually lost above a threshold shear rate, as indicated by the loss of scattering peak height. The relaxation time of the interfacial TEHOS, 0.01 s, can be estimated from the inverse of the threshold shear rate. However, we observed that the disrupted diffraction peak did not significantly redevelop for at least a few hours. We attribute this discrepancy to



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the fact that the shear rate we quote is based on the bulk viscosity of TEHOS, while near the interface a far higher viscosity is likely to exist. The anomalous increase of viscosity at the solid-liquid interfaces has been observed experimentally and is supported by computer simulations.

A very different behavior was observed for PDMS. Unsheared PDMS has a featureless reflectivity pattern (no layering). After shear of $10^4\ s^{-1}$ was applied for 1.5 minutes, a peak developed corresponding to a spacing equal to the backbone diameter of PDMS. This ordering persisted after the shear was no longer being applied, returning to the unsheared state in approximately three hours. The peak is probably a consequence of the disentanglement of PDMS molecules (**Figure 2**).

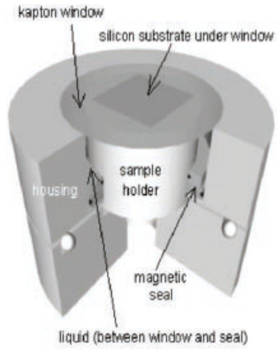
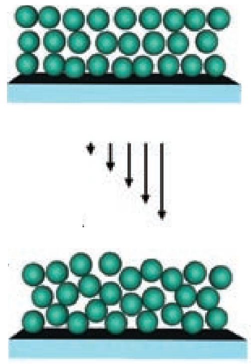


Figure 1. Schematic diagram of the experimental setup. The outer housing and attached kapton window are rotated to apply shear.

(a)



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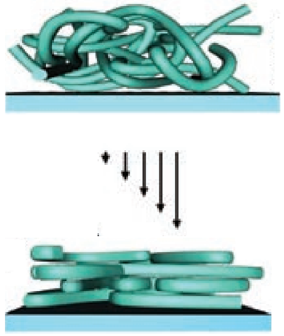

Figure 2. Schematic representation of the effect of shear stress near an interface on (a) TEHOS and (b) PDMS