

X-RAY SCATTERING STUDY OF SHEAR EFFECTS ON INTERFACIAL STRUCTURE IN LIQUIDS

The effect of shear flow on interfacial structures is a relatively unexplored phenomenon, particularly at nanoscale dimensions. While x-ray scattering is a useful technique in the study of liquid structure near interfaces, it is difficult to study shear effects with this means because of the necessity of enclosing the liquid under study within solid surfaces and the resultant attenuation and scattering of the x-ray beam caused by the surfaces. Under such limitations, only strong signals from bulk liquid structure are normally detectable, rather than weaker signals from interfacial boundaries. A team from Northwestern University managed to overcome these difficulties in order to study shear flow effects on the interfacial structures of two nonpolar liquids, tetrakis (2-ethylhexoxy)silane (TEHOS) and poly(dimethylsiloxane) (PDMS), using the MR-CAT 10-ID beamline at the APS and the MATRIX beamline X18-A at the National Synchrotron Light Source.

The Northwestern team created a sample chamber consisting of a stainless steel liquid sample holder encased in a circular housing with a Kapton window allowing access by the x-ray beam. A silicon substrate protruded slightly above the top of the sample holder, permitting x-rays to encounter the sample at small incidence angles. To apply shear, the outer housing of the sample chamber was rotated, with the sample liquid confined between the Kapton window and a magnetic seal.

X-ray scattering data from unsheared TEHOS shows a scattering maximum at 0.63 \AA^{-1} , which indicates layering of the interfacial TEHOS with an approximately 10 angstrom spacing between individual layers. After shear stress is applied at a rate of 0.17 turns per second for 1 minute, and reflectivity is measured at various distances from the center in regions with different shear rates, the diffraction peak diminishes, while maintaining the same shape and position as observed without shear. This suggests that the number of ordered layers is not reduced but an increasing part of the substrate surface is covered by disordered rather than layered TEHOS. The peak takes several hours to recover following the removal of shear stress.

These effects are quite distinct from those observed by the Northwestern researches in PDMS, a polymeric liquid of long and flexible molecules. Without the application of shear stress, PDMS displays no diffraction peak attributable to layering. Only at very high shear rates, approximately 104 s^{-1} , does a change occur, demonstrating molecular layering at a thickness of approximately 30 angstroms in the ordered region of the interface. Because the layered PDMS region returned to a disordered state in approximately 3 hours, the experimenters suggest that the layering observed under shear stress is due to the disentanglement of the polymeric chains.

The team discounts the possibility that other factors such as contaminant adsorption or chemical molecular damage are responsible for their experimental results. The reproducibility of the observed effects rules out contamination, and the brief duration of the shear application and consequent minimal interfacial heating make molecular damage unlikely.

The Northwestern/MR-CAT sector 10 results provide a clear demonstration of the usefulness of shear effects in the observation and study of interfacial molecular structure. Shear effects can be applied in order to manipulate molecules at interfacial regions to provide direct evidence of microscopic structure under x-ray reflectivity observation. ^m

See: C. Yu, G. Evmenenko, J. Kmetko, and P. Dutta, "Effects of Shear Flow on Interfacial Ordering in Liquids: X-ray Scattering Studies," *Langmuir* **19**, 9558-9561 (2003).

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