

STRUCTURED FLUID RHEOLOGY

Researchers are unraveling complex flow behavior of ordered polymeric and self-assembled fluids using custom-built X-ray shear cells.

Principal Investigator: Wesley Burghardt

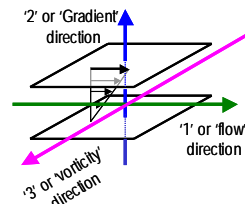
Collaborators: J. Kornfield, Caltech; J.-F. Berret, CNRS, France; T. Lodge & F. Bates, Minnesota; R. Krishnamoorti, U. Houston; J. Torkelson, Northwestern

Objective: Flow-induced molecular orientation underlies the complex flow behavior (rheology) of conventional polymers, which are usually processed in the liquid state, as well as has a profound impact on their microscopic morphologies and determines their technological utility. These phenomena are even more pronounced for polymers or other soft materials, in which self-assembly leads to higher levels of structure even in the equilibrium state. The Burghardt group is developing *in situ* x-ray scattering methods that provide detailed insights into the structural responses to flow, which in turn offer fundamental information about the microscopic molecular and supra-molecular scale dynamics of complex fluids.

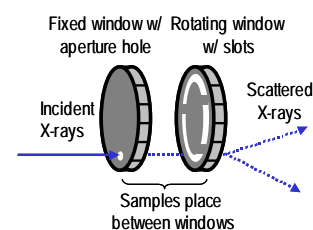
Approach: Complex fluid structures are typically studied using shear flow cells, in which the probing beams (x-rays, neutrons, light) measure structure factors in just one plane ('1-3'). The Burghardt group has constructed novel x-ray capable shear flow cells, in which structural factors can be measured in two perpendicular planes ('1-3' and '1-2' plane). The opportunity to interrogate multiple 'views' of fluid structure under shear greatly enhances the researchers' ability to study complex phenomena. In addition to idealized shear flow, capabilities have been developed to study polymer structure in complex flows within an extrusion die. These studies take advantage of Northwestern's synchrotron research center at the Advanced Photon Source, DND-CAT, which is a unique collaborative venture with DuPont and Dow located at nearby Argonne National Laboratory.

Results: The Burghardt group has investigated the complex flow behavior of a wide variety of ordered polymeric and self-assembled fluids, including lyotropic liquid crystalline polymer solutions (LCP), main-chain and side-chain thermotropic LCP melts, ordered block copolymers, nematic solutions of worm-like surfactants, bicontinuous polymer microemulsions, and polymer-clay nanocomposites. The researchers have demonstrated the power of *in situ* synchrotron x-ray scattering to provide detailed information on the non-equilibrium structure factor under flow. In a recent study, interrogation of structure in the '1-2' plane provided particularly direct and useful information about the shear-induced deformation and rotation of the bicontinuous microemulsion phase in a compatibilized polyethylene/polydimethylsiloxane (PEE/PDMS) blend. The high time resolution facilitated by brilliant synchrotron x-rays provided the ability to study structure development in a variety of transient flows, and facilitated deep tests of the connection between microscopic structural changes and bulk rheology. In this microemulsion sample, the effects of shear on the steady state structure differ from the predictions of a Landau-Ginzburg model, primarily in the strong enhancement in scattered intensity that is observed in experiment and not predicted by the theory. It is anticipated that shear measurements in '1-2' plane in other types of materials will also lead to new insights into the structural origins of complicated rheology in structured fluids.

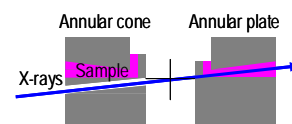
Selected Publications: Caputo FE, Burghardt WR, Krishnan K, Bates FS, Lodge TP *Phys. Rev. E* **2002**, 041401; Caputo FE, Burghardt WR *Macromolecules* **2001**, 34:6684.



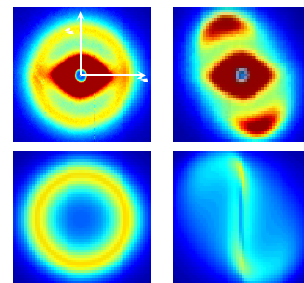
Structure can be measured in different planes.



Steady or oscillatory shear flows in '1-3' plane at temperatures up to 300°C are measured in a modified Linkam CSS-45 cell.



Unidirectional or oscillatory shear flows in '1-2' plane ($t = 20-250^\circ\text{C}$) are measured using a custom cone-and-plate cell.



Steady state SAXS images for PEE-PDMS microemulsion under shear (top) and their theoretical predictions (bottom).