SOFT MATTER

Spatiotemporal stress and structure evolution in dynamically sheared polymer-like micellar solutions

Small-angle neutron-scattering diffractometer D22

One fundamental challenge in studying soft material under deformation is establishing a quantitative connection between the deformation field, local microstructure and macroscopic dynamic flow properties, i.e. the rheology. To address this, we present a new method coupling simultaneous small-angle neutron scattering (SANS) with nonlinear oscillatory shear deformation to study the dynamics of soft matter. This is demonstrated by investigating the structure-property relationship for a worm-like micellar solution (WLM) [1].

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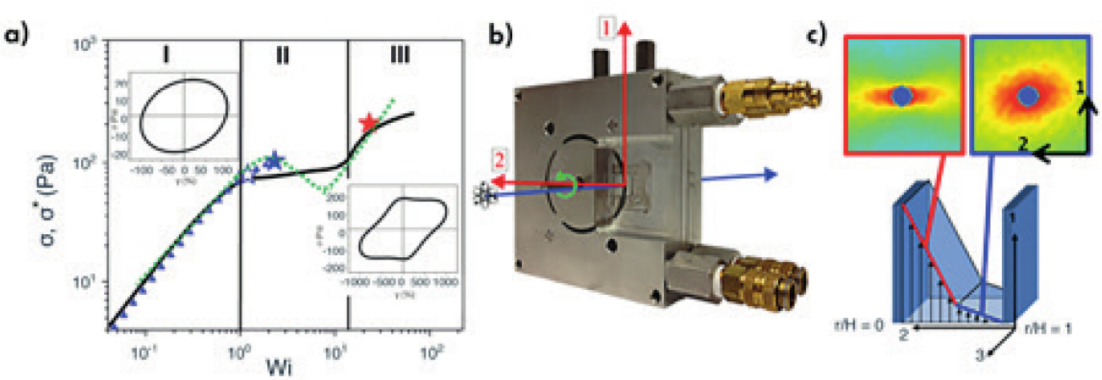
A new, state-of-the-art flow SANS sample environment **(figure 1b)** developed in the ILL Large-Scale Structures group in collaboration with the Center for Neutron Science (CNS) and NIST Center for Neutron Research (CNR) enables simultaneous, quantitative measurements of the spatially resolved composition and microstructure alignment and orientation in the most influential velocity-velocity gradient [1-2] plane of shear [2]. From these structural measurements it is then possible to predict, through molecular-based theory and constitutive equation, the resulting shear stress properties measured macroscopically [3].

So-called shear-banding instabilities are present in many industrial processes and are macroscopically characterised by a stress plateau over a significant range of shear rates, meaning that material flow rates can increase by orders of magnitude with additional small amounts of energy **(figure 1a)**. Microscopically, the solution presents inhomogeneous velocity fields: a distinct high shear band typically exhibits strong flow alignment while a low shear band has nearly isotropic microstructure **(figure 1c)**. While theoretical and experimental research efforts have been successful in defining and predicting

Figure 1

a) Shear stress as a function of dimensionless shear rate (Wi) for WLM solution (black line). The green line shows the underlying constitutive equation and the stars denote conditions studied under LAOS.
b) Flow-SANS 1-2 plane shear cell developed at the ILL in collaboration with NIST CNR and CNS University of Delaware.
c) Schematic of the 1-2 plane of shear with corresponding 2D SANS scattering patterns of oriented and isotropic structure in the high and low shear bands [1].



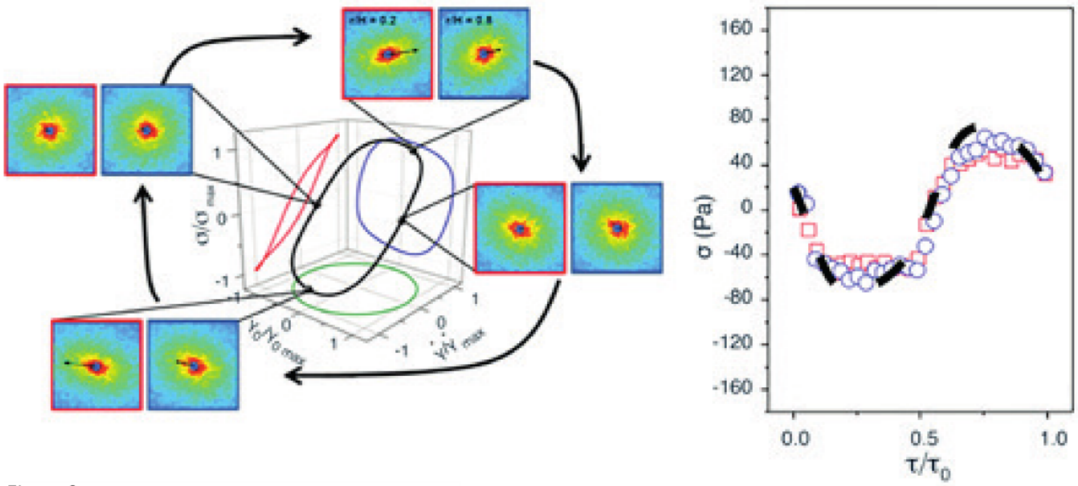


Figure 2

Left: Lissajous-Bowditch diagram for De = 0.23 and Wi = 1.2 where ω = 0.56 rad s-1 and γ_0 = 5. SANS scattering patterns inner (r/H = 0.2) and outer (r/H = 0.8) positions have red and blue borders, respectively. For the 2D SANS patterns the angle of the arrow reflects the average orientation angle ϕ_0 and the length of the arrow indicates the magnitude of alignment factor A_f.
Right: Rheometry experiment stress reported (dashed line). Symbols use the stress-SANS rule.

the onset and microstructure of steady shear banding, the challenge now is to understand the dynamics of shear banding at a more fundamental level, including the spatiotemporal microstructure evolution that lies at the foundation of the mechanism. Nonlinear oscillatory shear is thus applied because of the method's ability to create and probe experimentally inaccessible metastable states using traditional steady shear methods. By changing the frequency at which strain is applied, we can tune the time it takes to reach the maximum shear rate or deformation and then control the viscoelastic states of the WLM otherwise known to exhibit shear banding during steady shear.

The worm-like micellar solution investigated in this work comprises 5.1 % w/w cetylpyridinium chloride and 1.1 % w/w sodium salicylate (1:1 molar ratio) in a 0.5 M NaCl and D_2O brine. The large amplitude oscillatory shear (LAOS) applied to the solution is defined by a frequency f = 0.089Hz and a strain amplitude of deformation of 500 %. These conditions correspond to the metastable state of shear banding (blue star on **figure 1**).

Time-resolved, small-angle neutron-scattering (TR-SANS) methods are used to capture 30 different measured microstructures over the course of a single oscillatory cycle during LAOS experiments at two positions in the gap (inner and outer positions r/H = 0.2 and 0.8 where H is the gap size therefore r/H = 0 & 1 correspond to the inner rotating wall and the outer fixed wall respectively, see **figure 1c**). The data are collected over multiple oscillation cycles such that statistically sufficient scattering events are recorded in each bin. The range of scattering vectors probed by SANS is appropriate for defining the stress-SANS relationships between microstructure and shear and normal stresses under flow: $\sigma \sim \sqrt{A_f}\sin(2\phi_0)$.

The nonlinear stress response shown in **figure 2a** corresponds with microstructures measured at the inner and outer positions, with slightly more alignment (A_f) and flow orientation (ϕ_0), observed nearer to the inner wall as expected for a shear thinning fluid in Couette flow. The highest alignment indicating the greatest microstructural deformation corresponds to the largest stress response. We observe an isotropic scattering pattern that is indicative of an entangled PLM solution when the stress is at a minimum during the cycle.

Figure 2b shows quantitative agreement between shear stress measured by rheometry and the predicted shear stress at both positions in the gap, calculated using the ϕ_0 and A_f values gained from SANS measurements where the stress-SANS rule coefficient is independently defined from steady shear measurements. Thus, for this condition the validity of the stress-SANS rule relating segmental alignment to the polymeric stress tensor shows that the material behaviour is equivalent to that under steady shear conditions, as expected from theory. The three distinct material states (see **figure 1a**) have also been investigated and are reported in detail in [1]. We anticipate that this new combined method of LAOS rheometry and 1-2 flow-TR SANS will provide new opportunities to understand a broad range of nonlinear flow phenomena in shearing complex fluids. The authors encourage interested scientists to view reference [2] for further information.