RheoSANS of Nanocrystalline Cellulose in a Wormlike Micelle Solution

Small-Angle Neutron Scattering (SANS)

Neutron scattering measures the change in momentum (mass and velocity) of neutrons as they pass through a material and interact with nuclei. This change in momentum can reveal information about the structure (usually in elastic scattering) and motions within the material (typically seen in inelastic scattering). In contrast to x-ray scattering or visible light scattering, neutrons interact with the nuclei and not the electron cloud. As a result, neutrons often have very different interactions with a given material than those seen with electromagnetic radiation.

All neutron techniques interact with nuclei, however different techniques measure different properties of the neutron as they pass through the material. Small Angle Neutron Scattering (SANS) measures the elastic scattering function of the neutrons, meaning there is an inherent assumption that the neutrons have not lost energy (or changed wavelength) as they passed through the material. In most cases, this is a reasonable assumption. As in other forms of neutron scattering, SANS measures the change in momentum of the neutrons, where the momentum is defined as ½ m * **v**, m is the neutron mass and **v** is a vector of the neutron velocity (vectors are denoted here as boldface letters). When the assumption of purely elastic collisions is valid, the magnitude of the m and **v** are constant. As a result, we measure the momentum change, **q**, by simply measuring the change in direction of the scattered neutrons:

$$|\mathbf{q}| = |\mathbf{k_o} - \mathbf{k_i}| = 4\pi/\lambda \sin(\theta) \qquad \text{(Eqn. 1)}$$

Here, the change in momentum is the difference in outgoing ($\mathbf{k_o}$) and incident ($\mathbf{k_i}$) momentums,and is expressed using simple vector mathematics as an inverse function of wavelength (λ) and a trigonometric function of the half angle of scatter between the outgoing and incoming neutrons (θ). At small angles, note that $\sin(\theta) \sim \theta$. This relationship is often useful for back of the envelope estimates, however we will be using the full expression for our measurements. If the wavelength is constant, the SANS experiment is simply the measurement of scattered neutron intensity as a function of scattering angle at fixed wavelength, providing us with I(**q**).

Scattering intensity as a function of **q** is determined by measuring the neutrons that hit a detector located at some distance from the sample. By adjusting the instrument optics and the sample to detector distance a relatively large **q**-range is measured. For instance, on the 10 m SANS we typically measure scattering over $0.003<q<0.6$ Å^{-1}. For most scattering experiments the samples will scatter isotropically – scattering with no preferred direction – and a circular average of the reduced 2D detector intensity as a function of **q** will result 1D plot of differential scattering cross-section versus **q**. However, when nanostructural orientation is expected, such as in the cases of flowSANS or polarized beam SANS, the resulting scattering can be anisotropic. An example of this would be in the scattering from wormlike micelles undergoing flow induced alignment. For anisotropic systems such as these, an alternate approach accounting for the scattering variation as a function of angle ϕ or direct analysis of the 2D data is required. In fact, one simple way to quantify alignment in these systems is to take an annular average about some limited q-range and plot the intensity as a function of ϕ. An even Legendre expansion can be used to fit this data and extract the Hermann orientation parameter. While there a number of methods by which we quantify

alignment, it is challenging to extract more information from partially aligned samples, though there are ongoing efforts to improve the information we can extract from these experiments.

Methods for Measurement Structure in Complex Fluids under Flow at the NCNR

Many complex fluids are known to exhibit either shear thinning or thickening under shear flow. This non-linear rheological behavior is typically tied to changes in the nanostructure of the material (Fig 1). Two examples of such complex fluids are dense colloidal suspensions (shear thickening) or wormlike micelle solutions (shear thinning). Complex flow behavior is one reason why complex fluids are frequently utilized in commercial formulations. In fact, in many cases a particular type of non-Newtonian fluid response may even be deliberately engineered for a specific application. Over the last few decades, small angle neutron scattering has been used to directly measure the scattering of complex fluids as they undergo flow induced structural transitions.

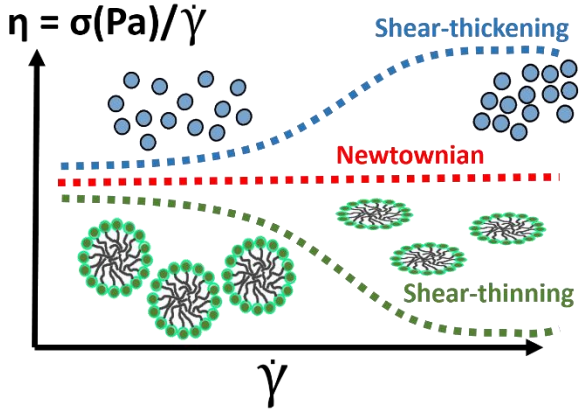

Figure 1:Many systems undergo structural changes under flow, which is strongly correlated to changes in their mechanical response.

One of the most frequently used and well established flowSANS techniques is rheoSANS. For these measurements, a rheometer is placed directly into the neutron beam, and scattering is collected simultaneously with the rheological data. Use of the rheometer rather than a flow cell ensures both high precision control of the shear field and simultaneous measurement of the sample rheology. The rheoSANS tool that is currently available in the user program is an Anton Paar rheometer with specially designed Couette geometries made from either quartz or titanium (owing to the relatively low interaction of neutrons with these materials) (See Figure 2). Furthermore, the temperature can be controlled between -40 and 300 °C. Shear rates as high as ~3,500 or ~10,000 s^{-1} can be achieved in low volume (~5-7 mL) and high volume (~9~15 mL) geometries respectively. With this instrument, measurements can be made to probe the flow-vorticity or shear gradient-vorticity planes (radial or tangential measurements respectively).

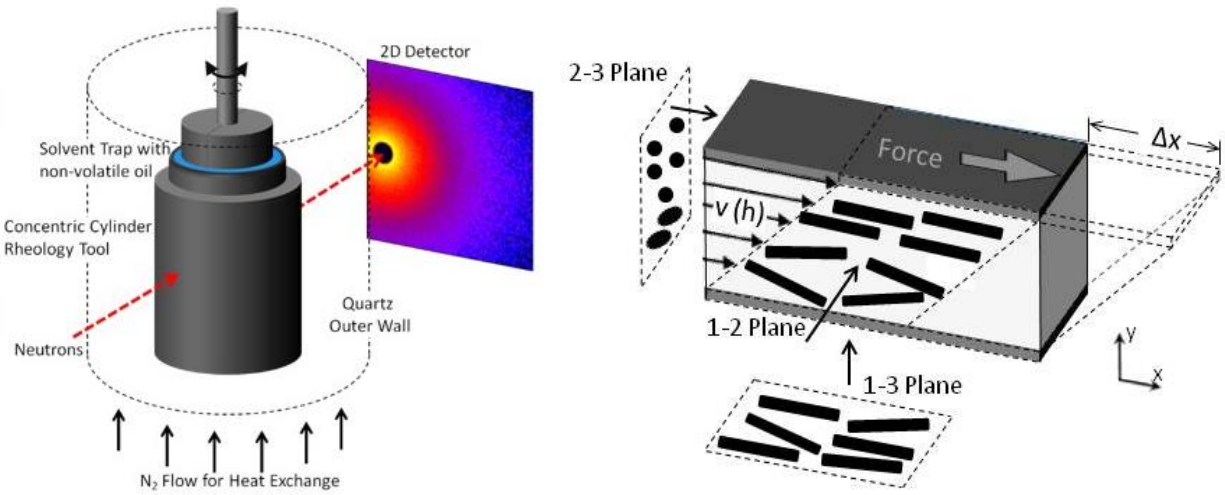

Figure 2: Left - Schematic of Couette rheoSANS instrument. Right – Diagram to define the various flow planes.

Due to the physical constraints, both in terms of space and construction, rheoSANS measurements cannot be made in the flow-shear gradient (1-2 plane, See Figure 2). However, purpose built devices, such as the 1-2 shear cell, can be used to measure in this orientation. [5] This device makes it possible to measure gap resolved structure, which is critical to understanding the structural origin of shear banding in some viscoelastic fluids. Furthermore, the alignment angle can be determined relative to the shear gradient only when measured in this orientation. It is important to note that the 1-2 shear cell is not a rheometer and no rheological data are collected during these experiments. [5]

Neither of these measurements can be made at very high shear rates (>10,000) that are frequently observed in industrial applications. An example of a high shear rate industrial application is the injection of pharmaceuticals through very small needles as shown in Figure 3. Achieving high shear rates approaching or exceeding 10^6 s^{-1}, however, will require a shift away from simple Couette flow. Capillary rheometers (diameters on the order of 10 – 100 μm) can be used to reach the desired shear rates, however such capillary devices are far too small to be effectively coupled to SANS measurements. Instead, we will use a microfluidic slit rheometer with very high aspect ratios (cross-sections on the order of 1 cm x 100 μm).

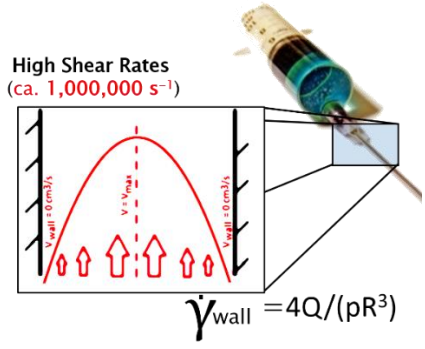

Figure 3: Industrial processing frequently requires pumping highly viscous fluids through narrow constrictions.

Experiment Introduction

Typically, non-Newtonian fluids are sufficiently concentrated that interparticle interactions are not only present, but are also responsible for the non-Newtonian properties of the fluid. For instance, in semi-dilute to concentrated wormlike micelles, a pseudo-network of entangled micelles exists when the solutions are rest. The entangled micelles give rise to a relatively high zero shear viscosity and an elastic response over some frequency range in oscillatory rheology measurements. At sufficiently high shear rates (this scales with the relaxation time and occurs at Weisenberg number ~1) the micelles will start to disentangle and align leading to lower resistance to flow, or lower viscosity (shear thinning). As we strain the sample, we expect that other structural changes may be occurring in additional to the observed alignment. Wormlike micelles are sometimes referred to as living polymers, because they are composed of individual surfactant molecules that have self-assembled into long flexible threadlike structures at thermodynamic equilibrium. As we increase the strain rate, some have predicted that the length distribution of the micelles should become shorter, but how might we be able to quantify such changes…???

Interpreting our scattering data when we have partially aligned objects is particularly challenging, even when there is no structure factor contribution. Furthermore, structure factors for anisotropic particles at rest is also nearly uncharted territory. For the most part, with a few exceptions, the analysis of partially aligned anisotropic scattering has been limited to simple methods for quantifying alignment and a variety of qualitative arguments. Recently the fitting software SASview has been updated to include the ability to fit a variety of 2D form factors for anisotropic particles, and this approach should work well for samples that are either dilute (such that there is no structure factor) or when fitting form factors over a q-range where the structure factor is expected to be negligible. For this module, we will explore various methods of fitting anisotropic data that results from rheoSANS experiments including quantification of anisotropy with an alignment factor and fitting partially aligned anisotropic particles with 2D fitting in SASView.

A series of complex fluids including SDS wormlike micelles and nanocrystalline cellulose will be prepared. Both single component solutions and multicomponent solutions are available. Using contrast variation (by adjusting the H to D ratio) of either the solvent ($Al(NO_3)_3$ brine or water) or the SDS molecules we can selectively highlight scattering of the surfactant or cellulose particles in a mixed complex fluid. By suspending a very small quantity of nanocrystalline cellulose (~0.1% mass/volume) into a contrast matched concentrated SDS wormlike micelle solution, we expect that we will be able to induce alignment of what appears to be a dilute solution of nanocrystalline cellulose particles at shear rates where the invisible wormlike micelles are aligning.

The primary goals of your experiment are:

1. Experimentally determine the scattering length densities of your samples and determine appropriate sample compositions for your experiment.
2. Characterize the static structure of the SDS wormlike micelles and the nanocrystalline cellulose solutions.
3. Measure the alignment of SDS wormlike micelles using rheoSANS and determine the alignment factor as a function of shear rate.

4. Use rheoSANS measurements to determine whether a dilute suspension of nanocrystalline cellulose in water will align at the shear rates where alignment was observed in the wormlike micelle solution.
5. Use rheoSANS measurements to determine whether a dilute suspension of nanocrystalline cellulose in SDS wormlike micelles will align at the shear rates where alignment was observed in the wormlike micelle solution.
6. Characterize the alignment of the nanocrystalline cellulose in the wormlike micelle solutions and compare with the pure SDS results… Discuss…
7. If time allows, use SASView to fit the 2D form factor for the dilute nanocrystalline cellulose. If you apply a fixed orientation distribution, do you think that the nanocrystalline form factor should change? If you assume that the form factor parameters won't change, can you accurately determine your alignment distribution?

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