RheoSAXS studies of anisotropic complex fluids under shear

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Abstract. We discuss the application of in-situ rheological small angle X-ray scattering experiments to the study of complex fluids under shear, implemented using custom Couette cylinder rheometers mounted on the SWING beamline of the SOLEIL Synchrotron. We discuss several applications of this technique to the study of phase transitions in nanoparticle doped liquid crystals and shear alignment of clay suspensions. The concurrent capture of rheological and scattering data provides vital information that relates macroscopic properties such as viscosity to the microstructure of the fluid.

1. Introduction

The study of complex fluids and of their rheological properties is an active area of research with a wide range of applications. The bulk macroscopic properties of complex fluids, such as rheological properties such as shear viscosity, for example, will often depend on the structure of the fluid on a microscopic level. Thus it is often convenient to combine various techniques in order to study macroscopic and microscopic properties at the same time. Investigations using small angle scattering techniques (SAS) (light, neutrons, X-rays) can be performed on such fluids directly under flow; this allows the simultaneous recording of rheological quantities (such as flow-curves and viscosity profiles) and structural information. In the case of strongly anisotropic fluids, small angle X-ray or neutron scattering (SAXS/SANS) experiments are particularly well suited to following orientation phenomena of structured fluids under flow. Using new rheological small-angle (Rheo-SAXS) instruments developed at the SWING SAXS beamline of the SOLEIL synchrotron, we present some examples of results demonstrating in detail the behaviour under shear of doped surfactant lamellar phases and colloidal clay suspensions.

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2. Rheo-SAXS setups

The first Rheo-SAXS instruments were developed in the 1990’s and today several such instruments are available around the world, both at neutron and synchrotron facilities. Following the design of these previous instruments, a concentric cylinder Couette shear cell geometry has been chosen for the new instruments installed on the SWING beamline. Two different instruments are available: a custom built Couette cell and a commercial Anton Paar MCR 501 rheometer, both of which are directly installed on the beamline as illustrated in figure 1 below. Between these two instruments a great amount of flexibility exists for the user in terms of the kind of experiments that can be performed.

![Custom Couette instrument (left) and the commercial MCR-501 rheometer (right) installed on the beamline.](image)

**Figure 1.** Custom Couette instrument (left) and the commercial MCR-501 rheometer (right) installed on the beamline. The nose of the detector is visible on the left in both images.

The mean stress $\langle \sigma \rangle$ and shear rate $\dot{\gamma}$ in Couette cylinder geometry for a Newtonian fluid, assuming no shear-banding or wall slippage and to a linear approximation, are given by

\[
\langle \sigma \rangle = \frac{(R_e^2 + R_i^2)}{4\pi HR_e^2 R_i^2} M, \\
\dot{\gamma} = \frac{(R_e^2 + R_i^2)}{(R_e^2 - R_i^2)} \Omega,
\]

where $R_i$ and $R_e$ are the interior and exterior Couette cylinder radii respectively, $H$ is the cylinder height, $M$ is the measured torque on the interior cylinder and $\Omega$ is the angular velocity. The shear viscosity $\eta$ can now be calculated through the relation $\langle \sigma \rangle = \eta \langle \dot{\gamma} \rangle$. This calculation is valid if the contribution of the fluid located in between the bases of the two Couette cylinders is negligible. We find that, for example, if the bases of the exterior cylinder ‘cup’ and the interior cylinder are both conical, which may be useful for reducing sample volume, then a correction is applied to the viscosity calculation form of the shear viscosity again for a Newtonian fluid and is now given by

\[
\eta = \frac{M}{4\pi\Omega} \left[ \frac{HR_e^2 R_i^2}{(R_e^2 - R_i^2)} + \frac{R_i^4}{4.232(18 - H)} \right]^{-1}
\]
where all parameters are as previously defined. The custom shear device is fully integrated into SWING’s control systems, while the Anton-Paar rheometer is controlled by the accompanying RheoPlus software.

Two types of measurements are made, in ‘tangential’ or ‘radial’ geometry. These positions correspond to the X-ray beam either parallel or perpendicular to the flow direction, as illustrated in figure 2. These two positions are realised by displacing the entire rheometer laterally with respect to the incoming X-ray beam. The combination of the scattering patterns of these two configurations make it possible to reconstruct in 3D the orientation distribution of anisotropic nanoparticles with respect to the shear flow directions (velocity direction and velocity gradient direction).

![Figure 2](image.png)

**Figure 2.** Schematic illustration of the concentric cylinder Couette cell in tangential and radial geometries.

### 2.1. Description of the instruments

In the case of both instruments (Table 1), identical concentric cylinder Couette cells are fabricated of polycarbonate because it is an inexpensive material and it is relatively easy to obtain small wall thicknesses (less than 0.3 mm in this case), its absorption coefficient for X-rays is small (the attenuation length at 12 keV is 3.8 cm$^{-1}$), and the scattering contribution in the small q-range is reasonably low. Measurements are then made at an energy value ranging from typically 10 to 12 keV.

The transmission $T_n(r)$ of the cell at some radial position $r$ for any particular medium $n$ is given by

$$T_n(r) = \exp\left(-\frac{2\left(\sqrt{R_e^2 - r^2} - \sqrt{R_i^2 - r^2}\right)}{\mu_n}\right),$$

for $r < R_i$, $\sqrt{R_e^2 - r^2} = 0$ for $R_e > r > R_i$, where $\mu_n$ is the absorption coefficient of the medium involved. When multiple media are involved, such as when the cell is filled, the compound transmission of all the included media can simply be taken. In order to account for the width of the X-ray beam in the horizontal plane (around 200 microns), the compound transmission function is convoluted with a Gaussian function where the FWHM is of 200 microns.
Figure 3. X-ray transmission data and model fits scanning the cell gap (0.5 mm) corresponding to the tangential position.

X-ray transmission data and model simulations are presented in figure 3, in this case scanning across the gap corresponding to the tangential geometry. Good agreement is found between the convoluted transmission model and the X-ray transmission data for the empty and water-filled polycarbonate cell. Absorption coefficients of polycarbonate and water at 12 keV are taken as 3.8 and 2.27 cm$^{-1}$ respectively.

2.1.1. Custom Couette apparatus. A complete Couette shear cell apparatus where the lower outer cylinder cup is rotated by a precision stepper motor has been constructed. The speed of rotation is controlled (thus we impose the shear rate). The main characteristics are the possibility to impose large shear rate values, a range from 1 s$^{-1}$ to 5000 s$^{-1}$ is accessible with this setup, without any Taylor-Couette instabilities that develop only when the inner cylinder is rotated. The standard polycarbonate cells have an average radius of 10 mm, a height of 17 mm and gap values ($R_o - R_i$) of 0.5, 0.2 or 0.1 mm with a sample volume of around 1 ml. Smaller cells of average radius 3 mm and height 10 mm permit one to work with very small sample volumes (about 0.2 ml), which is particularly suited to the case of biological samples for example. The measurement of the torque transferred by the sample to the inner cylinder is made using a force sensor at a distance of 20 mm from the rotation axis. The accessible torque range is from $10^{-5}$ to $2 \times 10^{-2}$ Nm corresponding to a stress range from 1 to 2000 Pa. If needed, the cell is thermostated by water circulating within the fixed inner cylinder. Constant shear rates and oscillating stresses can be applied to the sample using this apparatus.

|                      | Custom Couette | Commercial rheometer |
|----------------------|----------------|----------------------|
| Min torque (mN.m)    | 0.01           | $5 \times 10^{-5}$   |
| Max torque (mN.m)    | 20             | 200                  |
| Min speed (rpm)      | 0.6            | $10^6$               |
| Max speed (rpm)      | 960            | $3 \times 10^7$      |
| Average radius (mm)  | 3/10           | 10                   |
| Gap size (mm)        | 0.2/0.1, 0.2 or 0.5 | 0.2 or 0.5         |
| Sample volume (ml)   | 0.2/1          | 1                    |

Table 1. Technical data for both instruments equipped with similar polycarbonate SAXS cells.
2.1.2. *Commercial rheometer.* A commercial rheometer, the Anton Paar MCR 501, has also been directly installed and integrated into the beamline. Identical polycarbonate cells to those described for the previous apparatus have been fabricated by Anton Paar for this rheometer (Table 1). The two main advantages compared to the custom setup are, firstly, that very low stress values are accessible (minimum torque value of 5×10⁻⁸ Nm), which is particularly important for dilute colloidal suspensions, and secondly, that a wider range of rheological measurements are possible, including imposed shear rate or stress, oscillatory stress mode, creep-recovery, etc. Because the inner cylinder is rotating rather than the outer one, Taylor-Couette instabilities along the neutral axis at high shear rates may be observed, which is not the case with the previous setup. Temperature control is made via thermostated air circulation around the cell.

2.2. Calibration procedure
The calibration of the cells for each instrument has been performed using Newtonian standards of known viscosity such as PDMS oils and hexadecane. The results compare favourably with calculations based purely on the physical dimensions of the cell. X-ray data conversion to absolute intensity can be performed in the radial geometry by subtracting the scattering of the empty cell from that of the same cell filled with water, as the sample thickness is equal to twice the gap size in this geometry. In the tangential position, transmission scans across the gap allows one to accurately find the gap centre and the tangential sample thickness, taking into account the width of the X-ray beam in the horizontal plane and the absorption coefficients of polycarbonate and sample (see previous description and figure 3). Making the assumption that along the neutral Z-axis the scattered intensity is the same in the radial and tangential geometries, then the radial and tangential intensities can be both scaled to absolute units.

3. **Examples of anisotropic complex fluids**

We will now give two examples (doped lamellar phases and clay suspensions) of some of the first results obtained using these RheoSAXS instruments in order to illustrate the type of structural information that they provide. Both examples concern very anisotropic complex fluids, which undergo orientational changes and/or structural transitions under shear. Experiments were performed at 11 keV and the distance between the sample and the CCD detector was 1.4 m for the lamellar phases and 6 m for the clay suspensions.

3.1. Doped lamellar phases

Concerning the rheological properties of surfactant lamellar phases, a wide range of properties may be observed, including shear-alignment and thinning of the lamellar phases and shear-induced transitions from lamellae to multilamellar vesicles (MLVs) that have been already observed in a wide range of systems using a variety of optical and particle scattering techniques.¹ Our aim is to determine how the addition of inorganic nanoparticles to such a lamellar phase will influence and modify the rheological behaviour.

3.1.1. *Doping with spherical nanoparticles.* Small spherical polyoxometallate (POM) inorganic nanoparticles derived from phosphotungstic acid (diameter 1.1 nm) can be incorporated into the liquid crystalline lamellar phase of Brij30/water, where Brij30 is a non-ionic surfactant mainly composed of C₁₂EO₄.⁸ It is observed in this ternary system that the POMs are preferentially located close to the EO groups of the surfactant membrane rather than remaining dispersed within water between the bilayers, while the inter-lamellar spacing remains unmodified by the presence of the particles.⁸

In pure systems under shear, previous studies of C₁₂E₄/water⁹ and similar C₆₇E₂₅/water¹⁰ lamellar phases have characterised the shear viscosity and a structural transition from the lamellar state to a multi lamellar vesicle (MLV) or ‘onion’ phase. On increasing the POMs doping concentration, this
The shear-induced transition is offset to higher shear rates (for applied shear rates less than $50 \text{ s}^{-1}$). The SAXS signature of the MLV state can be seen in Figure 4.

For a shear rate of $5 \text{ s}^{-1}$, three resolution-limited Bragg peaks due to the lamellar stacking are recorded. The intensity modulations, with the second order peak weaker than the first one, are related to the spatial distribution of the POMs nanoparticles, that are preferentially located close to the EO groups of the surfactant membrane. In the tangential geometry, the intensity of the Bragg peaks is reinforced in the horizontal direction, indicating a preferred alignment of the lamellar planes under shear parallel to the Couette cell walls. In the small q-range, still in the tangential geometry, the parasitic anisotropic contribution of the polycarbonate cell walls can be seen.

At a shear rate of $50 \text{ s}^{-1}$, the sample is in the MLV state, as can be followed by the viscosity evolution during the RheoSAXS experiment (figure 5). Both tangential and radial patterns give rise to completely isotropic signals. Because the intensity repartition of the peaks is unchanged, one can deduce that the POMs remain encapsulated within the onion membranes, otherwise, the first order Bragg peak will be the most intense, as in the case of the pure surfactant phase. Moreover, a broadening of the Bragg peaks is clearly detected. From the FWHM, an order of magnitude of the coherence length of the lamellar order of about 0.5 micrometers is deduced. Such an effect would not be detected using SANS because it requires sufficiently high resolution for the scattering q-vector. As derived from optical measurements under shear (see figure 5), a typical size for the MLVs is around 10 microns in radius, corresponding to about 1000 lamellar layers. This means that one MLV is formed of several coherent lamellar domains separated by defects rather than a perfect stacking of spherical curved multilayers. The RheoSAXS experiments also allow us to assign the change in the viscosity to the structural transition towards the MLV state.

Figure 4. SAXS patterns under shear of the lamellar phase of Brij30 (40 % vol. fraction) doped with POMs nanoparticles (4% vol. fraction in water).
3.1.2. Confinement of anisotropic nanoparticles. Lamellar phases of a non-ionic surfactant doped with anisotropic rod-like goethite (FeOOH iron oxide) particles were studied with shear rates up to 5000 s\(^{-1}\); the data suggest that the goethite particles embedded within the lamellar phase become strongly aligned at much lower shear rates than for a pure goethite solution alone. More precisely we observe that the goethite particles contained within the lamellar phase show strong alignment at a shear rate of 100 s\(^{-1}\), while a pure goethite phase exhibits no alignment at this shear rate; in order to achieve a comparable degree of alignment in the goethite alone, a much higher shear rate of around 5000 s\(^{-1}\) is required. This result proves that strong coupling between the host lamellar phase and the goethite nanoparticles is evident.

**Figure 5.** (a) Rheological curves for different doping concentrations (40% surfactant and 0-4% POMs vol. fractions) recorded during the RheoSAXS experiments. The lamellar—MLV transition under shear is confirmed by the optical texture in polarized light (b) and by the characteristic four-lobes SALS patterns (c).\(^{12}\)
3.2. Suspensions of disk-shaped clay particles
Suspensions of natural clays exhibit a wide range of rheological properties. In the case of beidellite swelling clays, the colloidal particles are very anisotropic, and can be approximated by a plate-like shape of average diameter 210 nm (polydispersity 40%) and thickness of 0.64 nm.

On increasing the concentration in water, this clay forms a birefringent nematic gel phase. Under shear flow, for shear rates larger than 100 s⁻¹, the 2D SAXS patterns (figure 6) in the tangential geometry exhibit a strong anisotropy that is more and more pronounced upon increasing the shear rate up to 2000 s⁻¹. At the same time, in the radial geometry (figure 6), almost no anisotropy is observed.

![Figure 6. Evolution of the SAXS pattern of a beidellite clay suspension (2.2 % vol. fraction in water) with shear rate in tangential geometry (grad v, Z) (left) and radial geometry (v, Z) (right).](image)

By combining the radial and tangential patterns, the complete 3D-orientation distribution for the normal of the plate-like particles can be obtained. As the anisotropy of the particles is very large, one can approximate the scattering of an individual particle (form factor contribution only) by an infinite line parallel to the normal to this particle. Because the scattering signal is confined at high shear rates along the velocity gradient direction (horizontal direction in the tangential geometry), the main orientation of the platelets under flow is the one with the normal parallel to the velocity gradient (orientation (1) in figure 7), as other orientations (2) and (3) are much less favoured.

The anisotropy of the SAXS pattern reveals the shear alignment of the particles. Moreover, even for small particle volume fractions (a few percent), strong modulations of the scattering associated with a structure factor contribution are observed like in Figure 6. This is in agreement with a stabilisation of this colloidal suspension by long-range electrostatic interactions.
4. Conclusions
Rheo-SAXS instruments in Couette shear cell geometry have been successfully implemented on the SWING beamline of the SOLEIL synchrotron. Such apparatus permits the simultaneous recording of rheological properties and structural information for strongly anisotropic complex fluids. This non-invasive technique is therefore an extremely useful aid to properly building the link between the orientational and microscopic structure of these materials and their macroscopic behaviour under flow. Two examples (doped lamellar phases and clay suspensions) of the first results obtained are given and illustrate the type of structural information that these instruments provide.

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