

# Time-resolved X-ray microscopy of nanoparticle aggregates under oscillatory shear

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Of all the current detection techniques with nanometre resolution, only X-ray microscopy allows imaging of nanoparticles in suspension. Can it also be used to investigate structural dynamics? When studying the response to mechanical stimuli, the challenge lies in its application with a precision comparable with the spatial resolution. In the first shear experiments performed in an X-ray microscope, this has been accomplished by inserting a piezo actuator driven shear cell into the focal plane of a scanning transmission X-ray microscope. Thus shear-induced re-organization of magnetite nanoparticle aggregates could be demonstrated in suspension. As X-ray microscopy proves suitable for studying structural change, new prospects open up in physics at small length scales.

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## 1. Introduction

A number of experimental methods and devices have been developed for space- and time-resolved investigation of the structural response to mechanical shear, electric fields, temperature and so on in a variety of tunable environments. So far our knowledge on structure in materials composed of nanometre-sized entities is largely based on electron microscopy and scattering methods. Since the former requires frozen or dried samples and the latter average over large sample volumes, no information on structural changes in solution, the native environment for most nanoparticle systems, can be obtained.

Scanning transmission X-ray microscopes (STXMs) focus a highly monochromatic synchrotron X-ray beam with the help of Fresnel zone plates. Imaging of the sample is provided by scanning the focal spot over the sample and measuring the transmission point by point. STXMs offer the possibility to resolve individual particles of a wide variety of chemical compositions and sizes down to a few tens of nanometres, *i.e.* one order of magnitude below those resolved by laser-scanning confocal microscopes. Contrast in STXM derives either from the spatial dependence of electron density or from element-specific resonances at absorption edges. High-quality Fresnel zone plates provide lateral resolution below 35 nm (Chao *et al.*, 2005). Individual particles of a wide variety of chemical compositions (Araki *et al.*, 2006) have been resolved at that resolution. The depth of focus in STXM extends over a few micrometres, hence both bulk structure and interface effects can be analyzed, either in transmission or tomography images, as performed in biological samples such as fossil embryos (Donoghue *et al.*, 2006). STXM has been combined with external magnetic fields (Van Waeyenberge *et al.*, 2006). Yet the main advantage of X-ray microscopy is that it can be carried out in liquid media, as demonstrated by the detection of intracellular flow using

contrast-rich nanoparticles (Le Gros *et al.*, 2005). Since particle behaviour in solution is strongly influenced by solvent properties, STXM, unlike electron microscopy and scattering methods, offers the hitherto unique possibility to observe structures while modulating solvent-mediated interactions (Van Waeyenberge *et al.*, 2006).

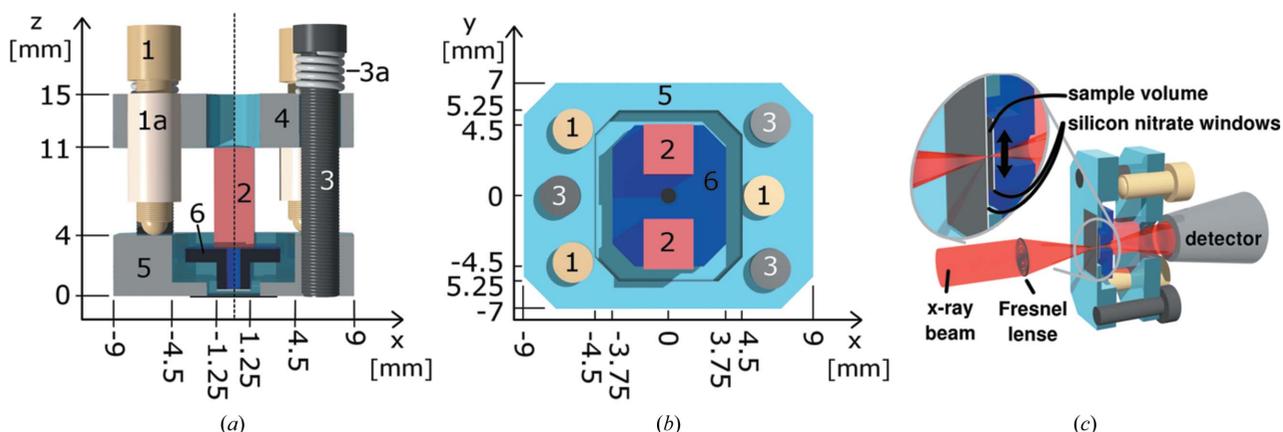
The time required for image acquisition still poses a serious hindrance for the investigation of dynamical processes such as re-organization, in particular because of radiation-induced damage to the sample. Especially in polymer melts, X-ray irradiation causes changes in the chemical structure and cross-linking (Coffey *et al.*, 2002). Moreover, any external manipulation has to be applied with an accuracy at least matching that of the imaging device. Thus, simultaneous imaging and stimulation at nanometre resolution remains a technical challenge.

## 2. Method and results

To explore whether real-time analysis of structural change can be performed using present-day X-ray microscopy, we constructed a shear cell (Fig. 1), to be inserted into the focal plane of the STXM at the Paul Scherrer Institute (Villigen, Switzerland). To prevent it from interfering with the optical components of the microscope, *i.e.* Fresnel zone plates, pinhole and the detector, the size of our shear cell amounted to 14 × 18 × 20 mm. The sample cell, with a total volume of 10 µl, contained a window consisting of two silicon nitride membranes spaced at about 5–10 µm, the regular sample thickness in this device. The oscillatory scanning motion of the sample could be controlled with nanometre precision. Shear was applied by moving the detector-side cell wall perpendicular to the X-ray beam using a piezo actuator with a maximal displacement of ±2.5 µm.

As a model system, we chose a suspension of 50 nm-sized magnetite particles (Auernhammer *et al.*, 2006) with attractive effective interactions. Brownian motion and inertia effects were

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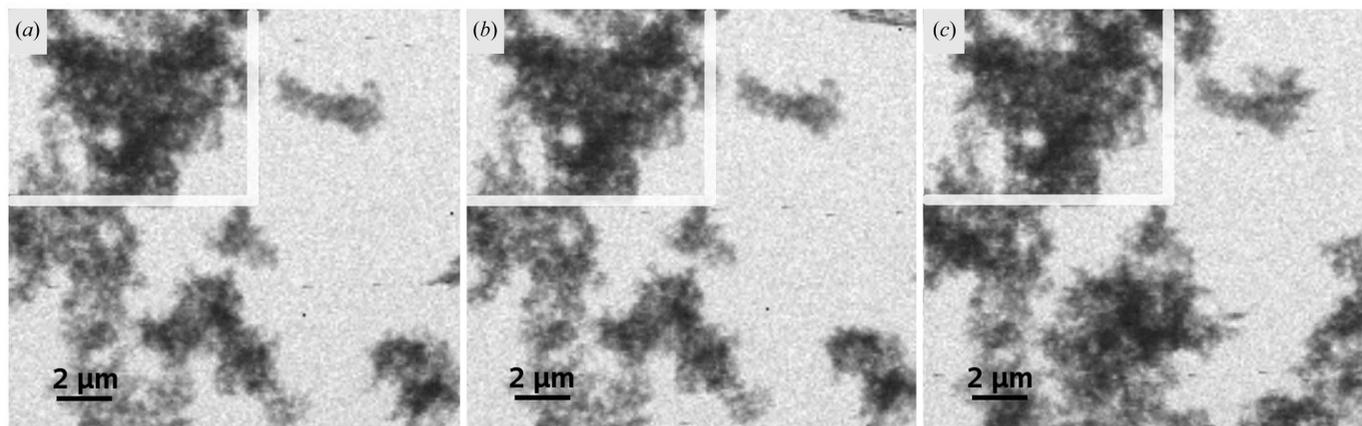


**Figure 1** Sketches of the shear cell in coordinate systems with the  $z$ -axis along the X-ray beam, with  $z = 0$  being the sample plane. In (a) a vertical cut through the cell illustrates the design principle, where the dashed line indicates the path of the X-ray beam. The outer part of the shear cell (1, 3, 4, 5) consists of a base plate (4) which holds the front plate (5) via three micrometre screws (1, diameter 2.5 mm, purchased from Owis, Staufen, Germany). The guiding nuts (1a) for the micrometre screws are glued into the base plate with two-component adhesive. Both parts are screwed together with three screws (3, diameter 2.5 mm). Springs (3a) between these screws and the base plate allow the force on the micrometre screws to be controlled. In the inner part of the shear cell (2, 6) two piezo shear actuators (2, purchased from PI Ceramic, Lederhose, Germany) are situated which provide movement of the inner front plate (6) along the  $x$ -axis with an amplitude of maximum  $\pm 2.5 \mu\text{m}$ . The  $\text{Si}_3\text{N}_4$  membrane windows are glued onto the outer (5) and inner (6) front plate with wax. (b) A cut perpendicular to the beam direction, showing the positioning of the micrometre screws (1), the piezo actuators (2), the outer (5) and inner front plate (6). The black dot shows the hole for the X-ray beam. (c) Position of the shear cell (sample thickness 5–10  $\mu\text{m}$ ) in the optical path of the X-ray microscope. Shear is induced by moving one of the two silicon nitride window membranes (inset).

slowed down by dispersing the particles in a polydimethylsiloxane (PDMS) melt ( $MW_{\text{PDMS}} \approx 18 \text{ kg mol}^{-1}$ ). The particles are known to aggregate and form a space-filling structure at a volume fraction as low as 1% (Auernhammer *et al.*, 2006). Images of a sample containing about 0.5 vol% magnetite particles (dark) embedded in PDMS (light) are shown in Fig. 2. The electron density contrast proved sufficient to allow measurements far away from all absorption edges of the matrix material. At the chosen energy (1000 eV), the dominating contrast mechanism is off-resonant absorption. Thus, high photon energy and low intensities strongly reduced irreversible cross-linking of the polymer matrix.

The particles formed loosely packed aggregates (Fig. 2a) whose size varied between several hundred nanometres and a few micrometres. As a transmission method, X-ray microscopy reflects the superposition of particles by the greyscale of the image. This implies that the more particles lie along the path of the X-ray beam the darker the pixel appears. To create a well defined reference point, we

cross-linked the upper left-hand corner of the sample (white outline in Fig. 2) with an X-ray dose approximately two orders of magnitude larger than used for imaging. With STXM being a scanning method, acquisition takes approximately 2 min per image. To investigate rearrangements of particles owing to Brownian motion, an image was recorded after 12 min (Fig. 2b), showing hardly any changes. Next we sheared the sample at 200 Hz for 10 s with 2  $\mu\text{m}$  amplitude. Whereas the cross-linked upper left-hand corner remained almost unchanged, pronounced shear-induced rearrangements of the clusters were visible in the rest of the sample (Fig. 2c). Several clusters broke up, others deformed or combined. Particles moved by several micrometres. Even after more than ten scans, rearrangement, partial disintegration and growth of aggregates were still observed, indicating that no substantial changes of particle–particle and particle–matrix interactions were induced at the time and energies required. The strong magnetic interaction between particles (exceeding at least ten times the thermal energy) obviously prevented rearrangement at



**Figure 2** X-ray microscope images recorded at 1000 eV showing aggregates of 50 nm-sized magnetite particles in a liquid polydimethylsiloxane matrix (a), repeated after 12 min (b), and their reorganization after shear (c). After loading the sample this sample area has already been scanned six times beforehand, demonstrating that even after several scans no significant cross-linking could be detected, *i.e.* the PDMS matrix is still liquid-like. The area marked in white has been cross-linked prior to the experiment and serves as a reference region.

rest as well as complete disintegration during shear. The particles moved while shear was applied and relaxed back to a steady state after discontinuation of shear.

### 3. Conclusion

With these experiments we have shown that it is possible to apply shear to a sample with accuracy and reproducibility comparable with that of X-ray microscopy. By working off-resonant we strongly reduced irreversible cross-linking of the polymer matrix, permitting the time evolution of particle clusters to be investigated. Shear-induced reorganization of aggregates of particles a few tens of nanometres in size could be demonstrated by X-ray microscopy even at high shear rates. The successful combination of shear experiments with X-ray microscopy is encouraging since length scales of tens of nanometres become accessible to optical techniques. This opens new perspectives in studying soft-matter dynamics. It may soon be possible to quantitatively analyze stimulation-induced changes during the entire stimulation process.

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