ESRF	**Experiment title:** **Investigation of Alpha-Beta Relaxation of Nano Particles Trapped in a Network of Smart Wormlike Micelles with XPCS and XSVS**	**Experiment number**: SC 4824
Beamline: ID10	**Date of experiment**: from: 04/04/2018 to: 10/04/2018	**Date of report**: 08/08/2018
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With proposal 78982 we aimed to study the dynamics of nano particles (NP) trapped in a network of entangled wormlike micelles formed by cetyltrimethylammonium bromide (CTAB) [1] and trans-ortho-methoxycinnamic acid (OMCA) [2] in aqueous solution. The photosensitivity of the cinnamic acid turns the fluid into a photorheological liquid, whose viscoelastic properties can be altered by UV-illumination [3]; for example, the shear viscosity can be tuned over several orders of magnitude.

Data measured in a previous experiment at ID10 (SC 4553) indicated that the micelles exhibit complex dynamical properties accessible through the correlation functions of silicon tracer particles measured with X-Ray photon correlation spectroscopy (XPCS) and X-Ray speckle visibility spectroscopy (XSVS) [4]. The correlation functions showed a decreasing non-ergodicity plateau indicative of a second relaxation process happening on time scales faster than a milli second and out of reach with the available setup at that time.

During experiment SC4824 we could use the Eiger 500k detector which allowed for measuring speckle patterns with repetition rates up to 22kHz and delay times in the micro second regime. This detector made it possible to capture dynamics from micro seconds up to hundreds of seconds. Thereby, we were able to acquire data on both relaxation processes as a function of momentum transfer and UV illumination time (Figure 1).

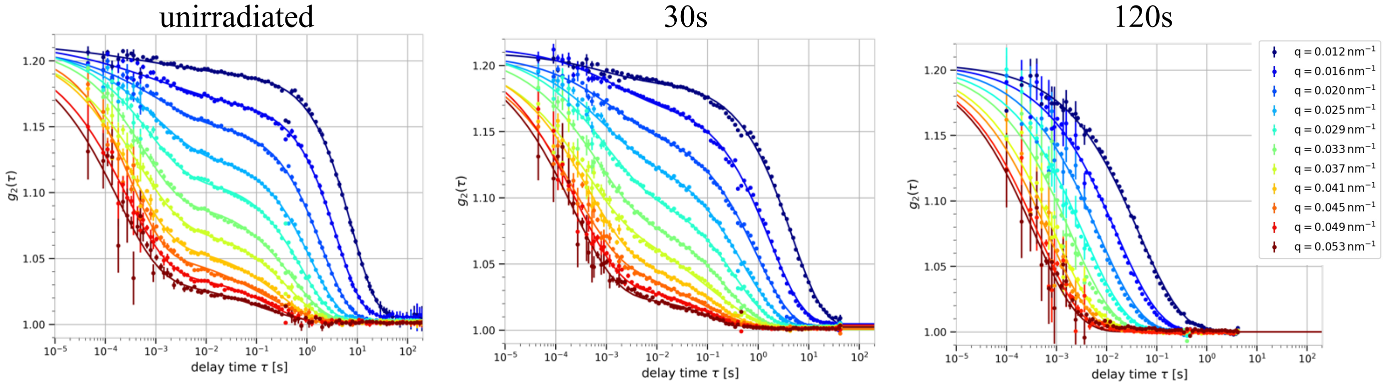

Figure 1: Correlation functions of 100nm Silica spheres trapped in a network of OMCA-CTAB micelles (concentration 50mM:50mM). For each of the three plots 70 time series had to be measured to acquire reasonable statistics. The samples were illuminated by a UV lamp for up to 120s in a 2mm thick capillary.

The setup at ID10EH2 was used in the small angle scattering geometry with the Eiger 500k detector being placed behind an evacuated 5m long flight tube, increasing the spatial resolution and the speckle size while decreasing parasitic air scattering of the X-Rays. The sample was filled in 2mm capillaries, which provided a sufficiently large scattering volume. Monochromatic X-Rays with an energy of 8keV were impinging on a 10μm x 10μm area on the sample providing the necessary coherence to measure speckle patterns. The samples were illuminated with UV light in the preparation lab of ID10 with a Hg arc light source.

We measured correlation functions of a static vycor glass and Silica particles in water and glycerol as reference samples before switching to the OMCA-CTAB micelles. These measurements were crucial especially for the later XSVS measurements which above all rely on the characterization of the detector and its ability to measure the photon distribution in the low intensity limit as well as the maximum contrast. Since the OMCA-CTAB micelles are easily damaged by the X-Rays, we characterized beam induced effects to the sample and found that with an attenuation factor of 100 the sample could stand the beam for at least 50 seconds (Figure 2). The corresponding dose was the upper limit a spot on the sample was exposed to before moving the beam to a fresh sample position.

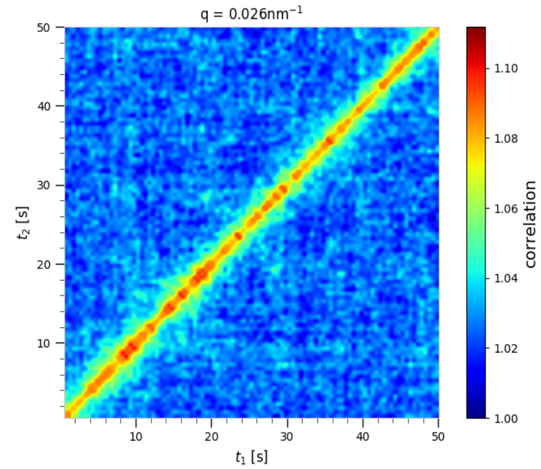

Figure 2: Two time correlation function measured with an unirradiated OMCA-CTAB sample with 100nm NP. The incoming intensity was attenuated by a factor of hundred.

Owing to the high repetition rate of the Eiger detector, the entire correlation function of the sample could be measured from micro seconds to hundreds of seconds (Figure 1). Micelle concentration and particle size were adjusted such that both relaxation modes were clearly distinguishable over a wide range of momentum transfers. The particle density was varied to optimize the scattering signal while keeping the influence on the network as low as possible. Illuminating the samples with UV radiation has a large impact on the dynamical properties in particular on the slow relaxation mode, while the fast relaxation is almost not affected. Following the model of glassy systems, the fast process describes the local motion of NP trapped in the network while the slow one reflects the long range network diffusion. The network decomposition induced by UV illumination weekens the network bondings, which allows faster diffusion of NP and decreases the shear viscosity. On the other hand, the local motion of particles is not affected by the long-range network structure and, therefore, the fast relaxation remains unaffacted after UV illumination. The time constants of the slow relaxation continuously decrease as a function of UV-illumination time. After 120 seconds the network has been completely decomposed and the second relaxation mode is not visible anymore.

Keeping the radition dose per spot small and using short exposure times in combination with a weak scattering signal from the sample made this experiment extremely challenging. At the same time, good statistics of the correlation functions were required in order to get quantitative results over a wide range of momentum transfers. Therefore, about 70 time series with different exposure times had to be measured on different spots on the sample to calculate each correlation function showed in Figure 1, which rendered the experiment also very time consuming.

A huge drawback and a factor that took a lot of time during the experiment was the instability of the detector. The Eiger 500k was crashing randomly without any explainable reason during the entire beamtime and had to be restarted manually by opening the hutch, unplugging and plugging the power plug of the detector and restarting the detector control software on the beamline computer. A more stable integration of the Eiger detector into the ID10 beamline environment would have made the experiment even more successful.

References

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