ESRF	**Experiment title:** Kinetics of nanoparticles during self-assembly	**Experiment number:** HS 4410
Beamline: ID01	**Date of experiment:** from: 25. 08. 2011 to: 30. 08. 2011	**Date of report:** 01. 09. 2011
Shifts: 15	**Local contact(s):** Peter Bösecke and Tobias Schulli	*Received at ESRF:*

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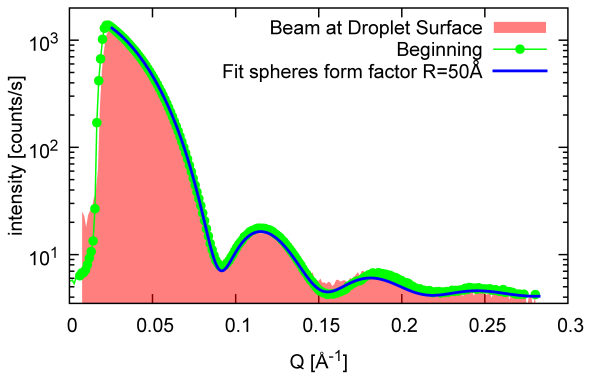
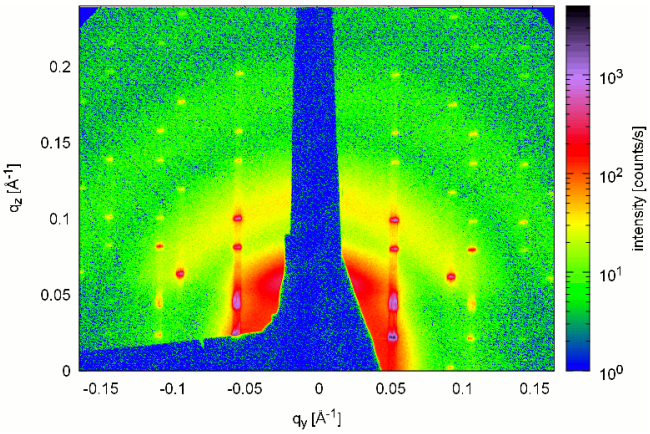
Report:
The goal of this beamtime was to investigate the ordering mechanism of magnetic nanoparticles during self organization in drop casting. Unfortunately the first 1.5 days could not be used as there were technical difficulties at the beamline concerning the vacuum system and detector readout.
After the problems had been solved a specific experimental vassal was installed, which allowed the controlled evaporation of toluene solvent for the nanoparticle deposition. Samples of nanocubes (≈10 nm edge length) and nanospheres (9.5 nm diameter) were investigated using different deposition conditions. After drop casting the particles on a silicon substrate the droplet was measured repeatedly in transmission at different heights above the silicon-toluene interface and in grazing incidence at 0.3 using a 20 μm focus. The evaporation speed was defined using different amounts of toluene reservoir and using a control valve. The current evaporation stage was monitored using a Keyence light band micrometer to measure the droplet height and a USB microscope to take images from the sample regularly.
From the transmission experiments no sign of order in the fluid could be found. As can be seen in figure 1, there is only a spherical form factor found at the beginning of the experiment (Green), which does not show a large change during evaporation until the droplet surface passes the beam (red area) at the same height. In the GISAXS experiments there was no sign of order during droplet evaporation, too.
After the droplet has collapsed (micro meter showed zero height and in the microscope image the droplet surface was not visible any more) the self organization started. The self organization occurred suddenly with already a large correlation length as can be

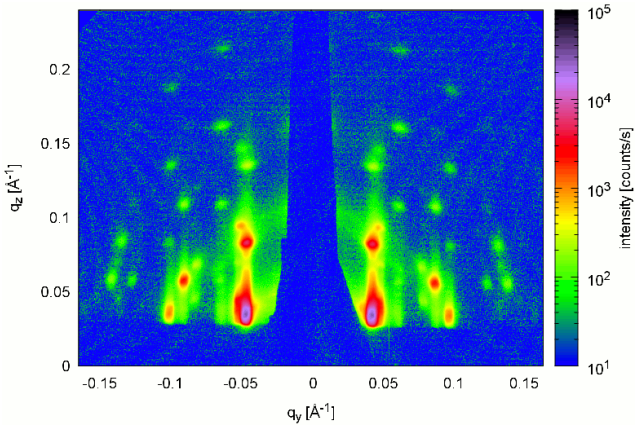
seen in the example of the nanocubes in figure 3, recorded less than 10 min after the first sign of order in an >12h experiment.
The nanospheres showed an even better order in the first stages of drying depicted in image 2. Further observation of the final stages of drying revealed a slow decrease of the form factor rings and increase in the spot intensities and sizes (fig. 4) as well as a change in the mesocrystal lattice constants most prominently visible in the difference plot shown in figure 5.
Despite a long drying time of several hours after the droplet has collapsed the structure formation was obviously not finished when the vessel was opened, as can be seen in the GISAXS image taken 5 min later (fig. 6).
Although these results are already remarkable, not all experiments could be finished due to the shortened beamtime. Observing the low evaporation rate experiments until the full dried samples would be of extraordinary interest.



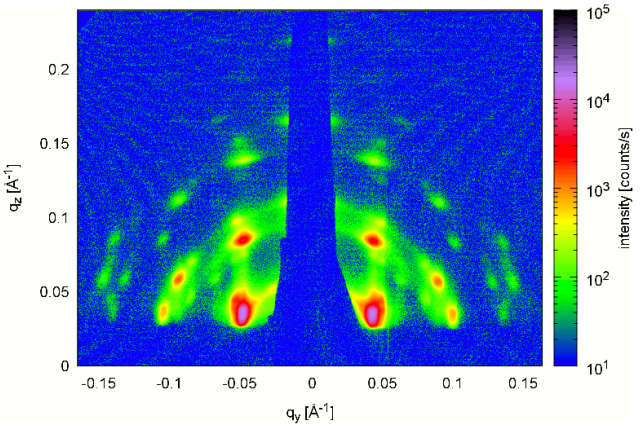
1: SAXS on spheres at h=100 μm



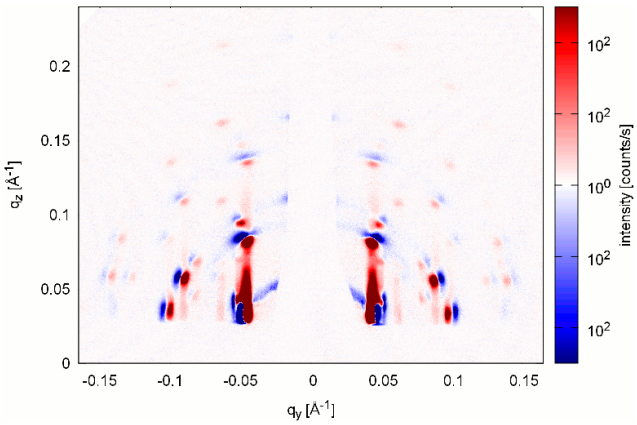
2: GISAXS on ordered spheres



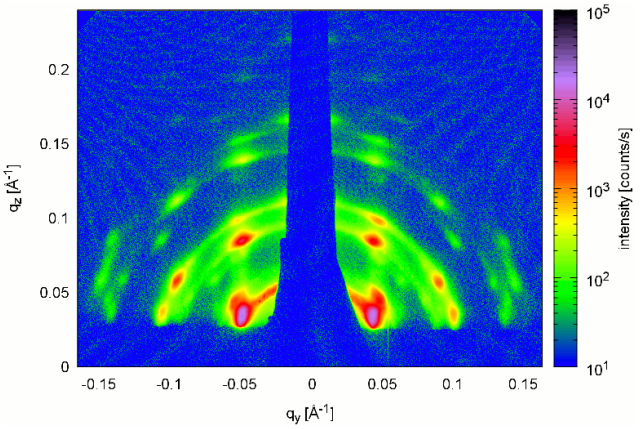
3: First stage of ordering of cubes



4: Later stage



5: Difference between fig. 3 and fig. 4



6: After opening vessel