Colloidal dynamics at the nanoscale studied with x-ray fluorescence correlation spectroscopy

Ch. Baumbach and Ch.G. Schroer

Institute of Structural Physics, Technische Universitaet Dresden, D-01062 Dresden, Germany

The aim of our experiments was to study the dynamics of gold nanoparticles suspended in water/glycerol mixtures with x-ray fluorescence correlation spectroscopy (XFCS) with unprecedented spatial resolution, providing direct insight into the dynamics on the nanoscale.
For our experiments we prepared several different suspension which included gold nanoparticles of different radii ranging from 10 nm up to 150 nm. Each sample only contained particles of one size. Each suspension was used either with only water or with a water/glycerol mixture. The gold concentrations in the samples was at about $1 \cdot 10^{-2}$wt%. The suspensions were held in glas capillaries with an inner diameter of 2 mm in the middle tapering down to 7μm at the tip.
Before the experiments we tested the fluoresence detector and the 2D-pixel detector (Pilatus 300K) to achieve temporal resolutions down to 10 ms. The present control software *accontrol* turned out to have a substantial time overhead during measurments of at least 50 ms. Therefore we used a python based script to reduce the overhead to about 2 ms. The setup for 15.25 keV of the previous beamtime was used. The focus size was $90 \times 90\text{nm}^2$.
We acquired several time series of a total of eight different samples each with a runtime of about 6 minutes. With the nanobeam we recorded both the fluorescence and diffraction patterns of the illuminated volume of the sample equalling to up to 30 000 data points per scan. At first we looked at the sum of the diffraction patterns of a single scan for the characteristic SAXS pattern caused by spherical particles. However, no such pattern was found so far. We suspect this is due to the very low signal-to-noise ratio (SNR) of the data for an entire time series.
Fig. 1 (a) shows at typical gold fluorescence intensity time-series binned to a temporal resolution of about 50 μs. The autocorrelation function of this time series is shown in fig 1 (b). Approximately 9 % of the observed variations are not explained by random variation. Of this 9 % about 3 % are related to changes in beam intensity and can be eliminated by normalization relative to the signal of a transmission diode. The remaining 6% in variation are attributed to the gold particles. This

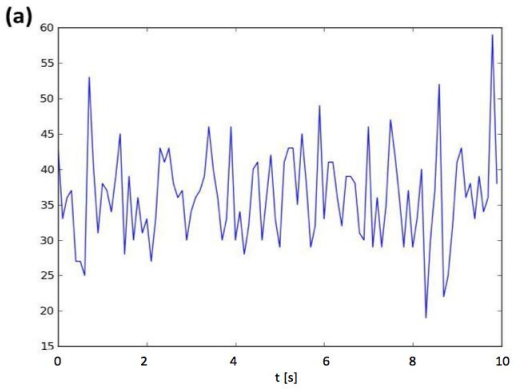

Figure 1: Variation of signal relative to random variation

indicates a SNR of only 6 %. We suspect that the SAXS signals of the gold particles are lost in the noise of the diffraction signal of the capillary and Compton scattering. This background can greatly be reduced by looking at the observed variance between diffraction images relative to the expected random variation as shown in fig 2. The spot in the center indicates that the beam

either moved, changed in intensity or that actual gold particles were passing through. Further out a diffraction ring is visible. The reciprocal distance of this ring is approx. 10 nm indicating the presence of gold particles of this size or larger. However, the manufacturing properties of these particles are supposed to lie close to a radius of 60 nm. The low signal to noise ratio complicates the interpretation of the fluorescence time series autocorrelation as the size of the particles and their distribution cannot be determined from the SAXS signal in a conventional way. We estimated that

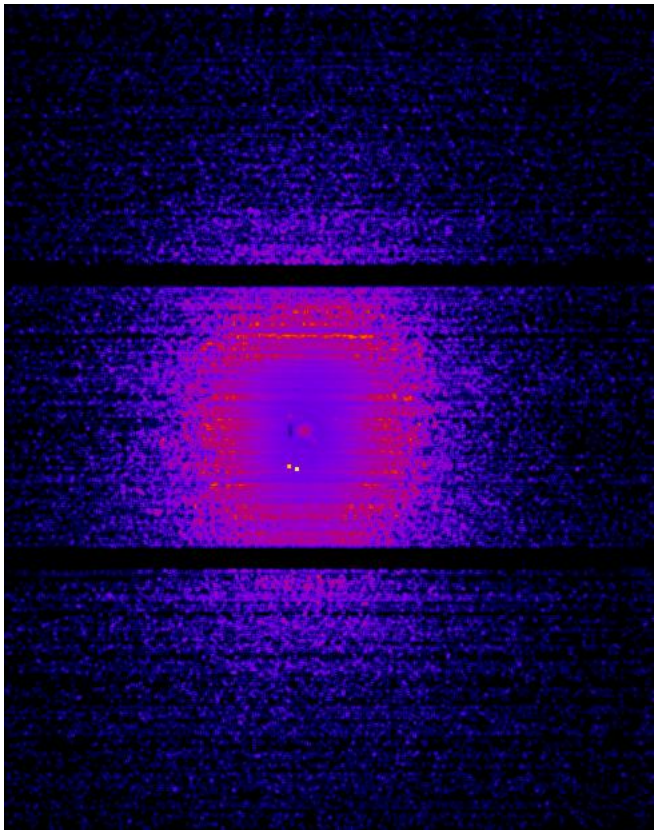

Figure 2: Gold fluorescence time-series of gold nano-particles in water (a) and the corresponding autocorrelation function (b).

only very rarely a particle actually crosses the center of the beam. We hope to improve the SNR by finding means to limit the analysis to temporal domains were a particle comes close to the center of the illumination. With a known particle size we could then calculate the diffusion constants for the different samples. These might give insights into possible deviations from Brownian motion at the nanoscale. The data analysis is still in progress.
In conclusion the experiments were successful as that we recorded time series of the gold fluorescence signals of nano particles in a spatial region equal to the beam size (approx. 90 x 90 nm^2) The first results of the analysis seem promising.