



Experiment title: Can X-Ray Fluorescence Correlation Spectroscopy distinguish the dynamics of elementally different colloidal particles in suspension?	Experiment number: MI-755	
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Names and affiliations of applicants (* indicates experimentalists): Olaf Leupold*, Gerhard Grübel*, Stephan Roth*, Christian Schroer*, Wojciech Roseker*, Marcin Sikorski* Hasylab at DESY Notkestr. 85 D-22761 Hamburg Germany		

Report:

Photon-correlation spectroscopy (PCS), probing fluctuations in the scattered intensity to study particle dynamics in fluids is a well established technique both in the visible light regime [1] and using hard x-rays, X-ray photo correlation spectroscopy (XPCS) (see e.g. [2]). In scattering geometry it is important to have a coherent beam illuminating the sample, and to record the time fluctuations in the speckle pattern that are directly related to the dynamics of the scattering particles.

Another approach is to record the fluctuations in the fluorescence radiation, also quite frequently used with visible light [1], but there is only one example reported in literature for X-ray fluorescence correlation spectroscopy (XFCS) demonstrated in a pilot experiment by Wang et al. [3]. X-ray Fluorescence Correlation Spectroscopy does not require a coherent beam, instead the beam has to be strongly focused and the fluorescent intensity from a region around the focal point is probed. Time fluctuations in the fluorescent intensity reveal density fluctuations in the probe volume and by this the dynamics in the system. One of the interesting features of XFCS, which we wanted to exploit in this proposal, is the element sensitivity related to absorption edges, which can be selected by the tunability of synchrotron radiation.

In this pilot experiment we studied colloidal suspensions of Au nanoparticles with diameters ranging from 5 to 150 nm in water and water glycerol mixtures. The viscosity of the solvent was adjusted by choosing the water/glycerol mixing ratio and by controlling the temperature. The x-ray energy was 12 keV, which is just above the L3-edge of gold. The experimental setup is sketched in Fig. 1. For the XFCS measurements the monochromatic beam was focused by an arrangement of 78 compound refractive lenses made out of beryllium [4,5]. The theoretically expected size of the focal spot was about $9 \times 0.6 \mu\text{m}^2$ (hor. \times vert.). The fluorescence radiation was measured by an energy resolving detector, (**detector 2** in Fig. 1). For the SAXS measurements the Q-dependence of the scattered intensity was scanned via an avalanche photo diode (APD) (**detector 1**) providing the Q-resolution by the slit upstream the APD.

A typical SAXS pattern of a colloidal suspension of Au particles with nominal diameter of 100 nm is shown in Fig. 2. The fit curve yields an average particle size of 96 nm and a polydispersity of about 9 % in agreement with the specifications.

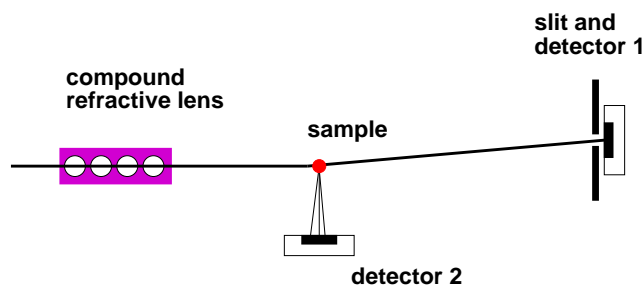


Fig. 1: Experimental scheme for XFCS and SAXS.

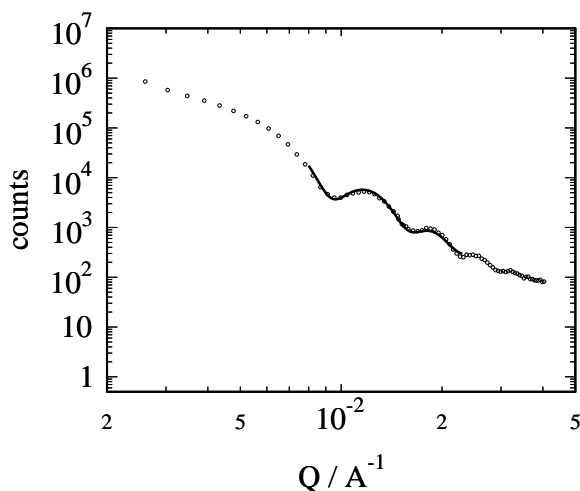


Fig. 2: SAXS pattern (circles) and fit curve (solid line) for 100 nm gold colloidal suspension.

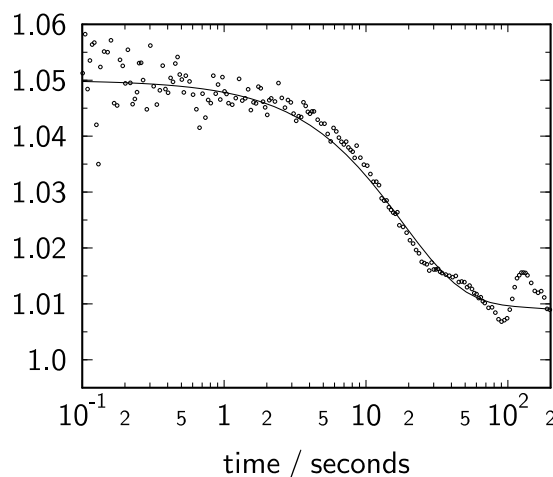


Fig. 3: Measured time correlation (circles) and fit curve (solid line) for 150 nm gold colloidal suspension (details see text).

The prerequisite for a reasonable contrast in the XFCS time correlation pattern is a small beam size. Despite of very careful alignment the beam focusing with well characterized compound refractive lenses was, however, poor. The size of the focal spot was as large as about $9 \times 6 \mu\text{m}^2$ (hor. \times vert.). This is not understood and needs further investigation. Nevertheless we took XFCS data on colloidal Au in mixed water/glycerol solvents. We got fluorescent count rates up to 1 kHz in the selected energy window. A typical XFCS correlation pattern is shown in Fig. 3 for gold particles of 150 nm in a 1:10 water/glycerol mixture. The particle concentration was 1.7×10^9 particles per ml water. A semiquantitative evaluation of the data assuming an exponential decay of the correlation function shows that there exists at least 1 characteristic decay time of about 20 seconds. We found this characteristic decay time in all samples containing nanoparticles of this size and assign it to sedimentation processes of the particles in suspension (in agreement with [3]).

References

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