

X-Ray Fluorescence Correlation Spectroscopy – a Tool to Study Element Specific Dynamics

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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 [1] and the hard X-ray regime [2]. In (visible light) PCS or (X-ray) XPCS it is important to have a coherent beam illuminating the sample, and to record the temporal 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, quite frequently used with visible light [1], and recently also reported for X-rays (X-ray fluorescence correlation spectroscopy, XFCS) 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 number fluctuations in the probe volume and by this the dynamics in the system. One of the interesting features of XFCS is the element sensitivity related to absorption edges, which can be selected by the tunability of synchrotron radiation. In this study we employed compound refractive lenses (CRL) [4, 5] in order to create a micrometer sized focal spot for the XFCS experiment.

In this experiment we studied suspensions of colloidal 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 absorption edge of gold.

The experiment was performed at the ID10C station (Troika beamline) at the ESRF. The experimental setup is sketched in Fig. 1. A pair of mirrors suppresses higher harmonics from two U27 undulators. The Si(111) channel cut monochromator yields an energy resolution of $\approx 10^{-4}$ at 12 keV. For the XFCS measurements the monochromatic beam was focused by an arrangement of 75 compound refractive lenses made out of beryllium [4, 5] located at 580 mm from the sample. The size of the focal spot was about $9 \times 6 \mu\text{m}^2$ (FWHM, hor. \times vert.). The fluorescence radiation was measured in the horizontal plane by an energy resolving detector. We used a silicon drift diode (Ketek AXAS) with an active area of 10 mm^2 and a nominal energy resolution of about 150 eV at 6 keV. Samples were measured in glass capillaries of 1 mm diameter installed in an evacuated sample chamber, in order to reduce parasitic scattering. The energy window of a single channel analyzer (SCA) was carefully adjusted to the 9.7 keV Au L_{α} fluorescence line. The SCA-signal was used to record the intensity autocorrelation function of the Au fluorescence radiation employing a hardware correlator (Flex01D-08). There was a small background resulting from the low energy shoulder of the 12 keV incident beam.

The XFCS data were taken on colloidal Au in several water/glycerol solvents. The fluorescent count rates reached up to 1 kHz in the selected energy window. A typical XFCS correlation functions is shown in Fig. 2 for gold particles of 150 nm diameter in a 1:10 water/glycerol mixture. The particle concentration was 1.7×10^9 particles per ml water.

The XFCS correlation function $g(t)$ is given by [3]:

$$g(t) = 1 + \langle N \rangle^{-1} (1 + t/\tau_d)^{-1} \times \exp \{-t^2/[\tau_s^2(1 + t/\tau_d)]\} \quad (1)$$

where $\langle N \rangle$ is the average number of particles in the scattering volume, which is determined by the concentration, the thickness of the capillary and the cross section of the focused beam.

τ_d and τ_s , respectively, are the characteristic time constants for translational diffusive motion and sedimentation. The fit curve using eq. 1 and the results of the fit are also shown in Fig. 2.

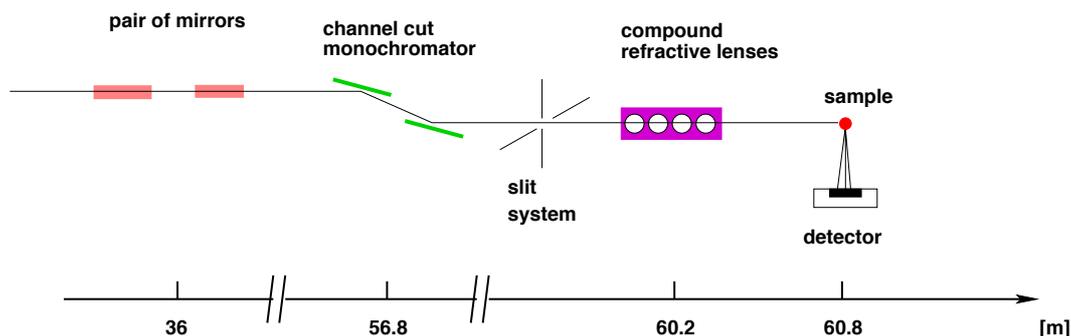


Figure 1: Experimental setup for XFCS (top view). A pair of vertically deflecting mirrors is followed by a horizontally deflecting Si (1 1 1) channel cut monochromator. A slit system and a set of compound refracting lenses (CRLs) provides the μm sized beam. The energy resolving silicon drift diode records fluorescence radiation in the horizontal plane.

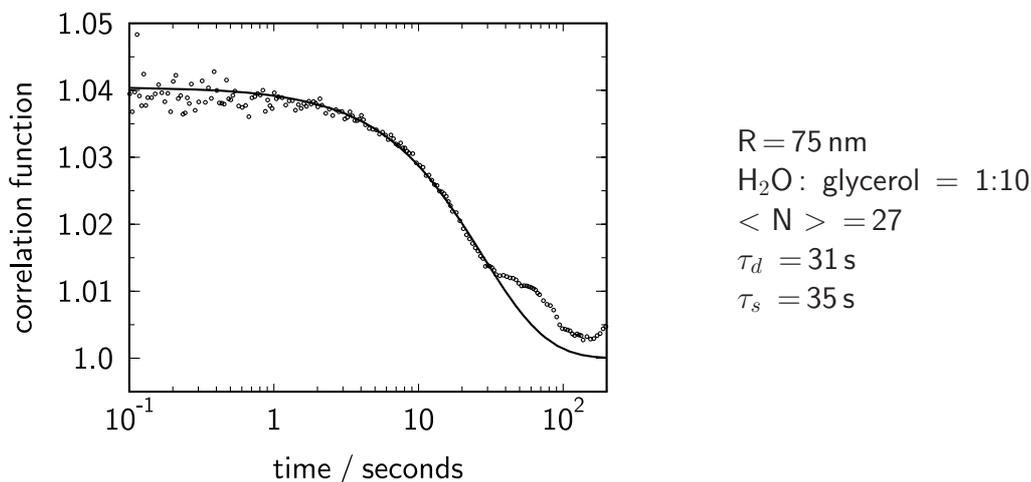


Figure 2: Measured time correlation function (circles) and fit curve (solid lines) for a 150 nm colloidal gold suspension with a water/glycerol ratio of the solvent of 1:10.

A more detailed evaluation was presented at the SAS2006 conference and will be published elsewhere [6].

References

- [1] B.J. Berne, and R. Pecora, *Dynamic Light Scattering*, John Wiley & Sons, New York (1976))
- [2] G. Grübel, and F. Zontone, *J. of Alloys and Compounds* **362**(2004),3 (and references therein)
- [3] J. Wang et al. *Phys. Rev. Lett.* **80** (1998), 1110.
- [4] B. Lengeler et al. *J. Synchrotron Radiation* **9**(2002), 119
- [5] A. Snigirev et al. *Nature (London)* **384** (1996), 49
- [6] O. Leupold et al., *J. of Appl. Cryst.*, (2006), submitted