ESRF	**Experiment title:** Impulsive nanoparticle melting –The pulse length effect	**Experiment number**: SC2213
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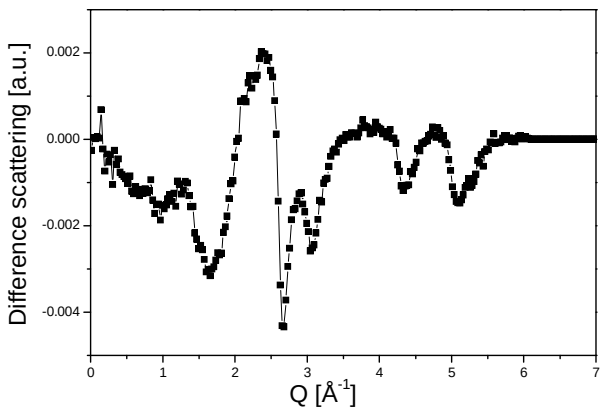
Report:

The aim of the present experiment was to address thermally induced structural modifications in proteins bound to gold nanoparticles. The nanoparticles act as laser light absorbers and heat sources. It is well understood, that with femtosecond or picosecond pulses particles can be heated to 1000 Kelvin within a few picoseconds. The heat is subsequently released within some 300 picoseconds for the particles investigated here (around 10-15 nm size).

The heat affected zone is very well known and extends only some 100 nm around the particles. If proteins are bound to the particle surface, they will experience a very rapid transient heat pulse. By using pulsed x-ray scattering the structural modifications are detected. Two different setups are relevant, one, where the detector is set to cover a large range in Q space (WAXS) and detects scattering from the liquid, the protein structure and the particle lattice. In a second setup the detector covers only the small ange scattering region (SAXS). Thereby structural modifications of the particle shape and the global density change around the nanoparticles are resolved [1].

As shown previously the water phase reacts on a short time scale with bubble formation at high laser fluence. This bubble formation is seen in WAXS by a change of the water structure factor, which is a broad double structure in the difference scattering (with and without laser), with a maximum located around Q=2.3 $Å^{-1}$ and two negative peaks around 1.7 and 2.8 $Å^{-1}$. The amplitude of this (Q independent) feature is proportional to the averaged pressure rise in the liquid [2]. Additionally a loss in the crystalline order of the gold particles may be observed, if their melting point is crossed. This is seen as negative peaks at the position of the powder rings (fig. 1). The information contained in the WAXS part allows to quantitatively establish the thermal dynamics including bubbe formation and particle melting threshold.



<u>Fig. 1:</u> Difference scattering pattern on the CCD after subtraction the dark state pattern from the excited state pattern of gold nanoparticles (14 nm) in aqueous suspension. The broad feature stems from the bubble induced density changes in water, while at distinct Q values a reduction due to the loss of powder scattering from the gold particles is seen at the (111), (200), (220) rings and so forth.The asymmetric shape is caused by the bandwidth of the undulator line in the polychromatic setup.

Additionally the bubble formation (or any density change around the particles) is visible in the SAXS region. The simulation of this part by typical form factors of spherical core shell systems allows to determine the buble size and to quantify the density changes [1, 3].
Within this beam time we have concentrated on the SAXS part for the detection of heat induced morphology changes in the protein covered particles. Gold particle suspensions (gold atomic concentration 2 mM) with adsorbed BSA layers were pumped through the laser xray interaction area and the changes in scattering cross section due to laser irradiation were recorded in a stroboscopic manner. The achieved signal-to-noise ratio was in the range below 10^{-4} for WAXS and 10^{-3} for SAXS (for 10 second exposures), which allows to detect very small changes. The parameter space of laser fluence and time delay was covered densely in order to detect fluence dependent changes both from the protein part and the buble nucleation part. As the laser fluence is converted into particle heating we can directly use the fluence scale as a measure for the maximal temperature in a shell around the particles. The corresponding heat transfer equations have been solved earlier [4, 5].
We had particular success in changing the sample system from a closed capillary to a free running laminar jet. Thereby the parasitic scattering is suppressed considerably. This allows to collect high quality data from limited amount of sample despite the (potentially) irreversible nature of the excitation and single shot exposure of the sample.
In particular we have derived a good understanding of the changes in the SAXS part. It is clear, that bubble nucleation and growth dynamics govern the first 2-3 ns delay. At later delays only the long lasting changes remain, which are essentially zero for the uncovered particles, while distinct changes still remain for the protein covered particles (see fig. 2).

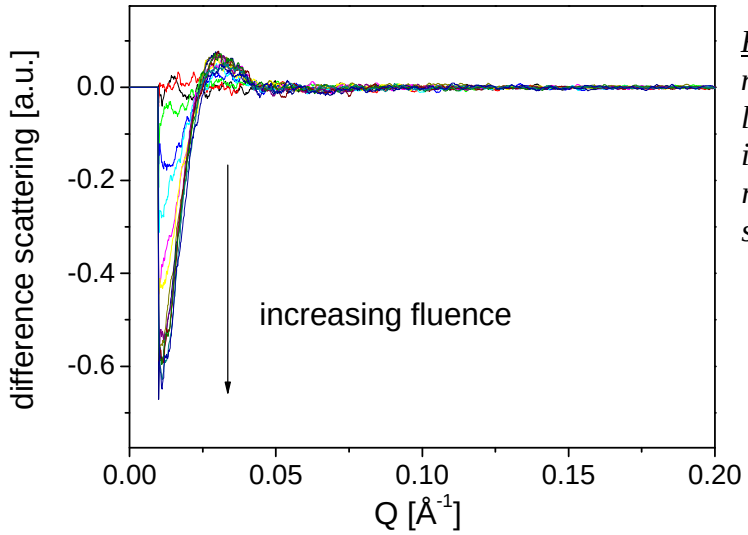


Fig. 2: Difference scattering in the SAXS region at a delay of 1 µs for a set of different laser fluences. The signal is rising in an intermediate fluence range. The signal shape remains Q independent, which assigns it as a stationary structure.

[1] A. Plech, V. Kotaidis, K. Istomin, M. Wulff: *Small angle pump-probe studies of photoexcited nanoparticles*, J. Synchr. Rad. 14 (2007) 288.

[2] A. Plech, V. Kotaidis, M. Lorenc, M. Wulff : *Thermal dynamics in laser excited metal nanoparticles*, Chem. Phys. Lett. **401**, (2005) 565.

[3] V. Kotaidis, A. Plech: *Cavitation dynamics on the nanoscale*, Appl. Phys. Lett., 84 (2005) 213102.

[4] A. Plech, et al.: *Laser-Induced heating and melting of gold nanoparticles studied by time-resolved x-ray scattering*, Phys. Rev. B 70 (2004) 195423.

[5] V. Kotaidis, C. Dahmen, G. von Plessen, F. Springer, A. Plech: *Excitation of nanoscale vapor bubbles at the surface of gold nanoparticles in water*, J. Chem. Phys., 124, (2006) 184702.