ESRF	**Experiment title:** The earliest steps in particle genesis during pulsed laser ablation in liquid (PLAL)	**Experiment number**: MA3821
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Report:

During laser ablation of noble metals into liquid medium nanoparticles are created and ejected in a volume of about 3x3x2 mm^3. This material is confined by the formation of a highly dynamic cavitation bubble. We have earlier established that particles can be detected inside the bubble and being released after bubble collapse on a time scale of tens of microseconds [1,2]. The particle population is typically seen as small, primary particles (being 10-15 nm in diameter for noble metals as silver or gold) and secondary, larger particles from 20 to 100 nm. The latter are meant to originate partly from an agglomeration step induced by the confinement of the cavitation bubble [3,4]. Related to that, we could show that size quenching is possible through addition of minute amounts of electrolytes or larger organic molecules to the water [5]. This is thought to be related to surface passivation of primary particles that reduces irreversible particle aggregation. The quenching effect could already be detected within the first bubble in the vapor phase. On the other hand, theoretical investigation raised suspicion that some of the larger particles might emanate very early during the phase explosion of the laser-irradiated target [6]. So far, time resolution was limited. Therefore we aimed for a probe extension to shorter time scales for the characterization of the nanoparticles.

Experimental setup:

A water-flow chamber is mounted on the diffractometer of the ID09 time-resolved beamline. The beamline picosecond laser irradiates the target inside the chamber at 1 kHz, while the pulsed X-ray beam probes the scattering from an area close to the target to detect emerging nanoparticles. Particle sizes are accessed by small angle scattering (SAXS) with a 60 cm sample-detector distance, while the crystallinity is probed by wide-angle scattering (WAXS) with a 120 mm distance.

Results:

In SAXS we could see the population of nanoparticles rising with the growth of the cavitation bubble, while the WAXS gave information on both the particle crystallinity and the thermodynamic state of the water phase. The latter is inferred from the shape of the liquid scattering peak and is sensitive on pressure changes due to bubble expansion. Interestingly, the initial shock wave emission with a velocity faster the speed of sound in water is clearly detected, adding to the picture of reactions during ablation. Figure 1 shows representative difference maps of scattering (at a defined delay after laser excitation compared to before excitation).

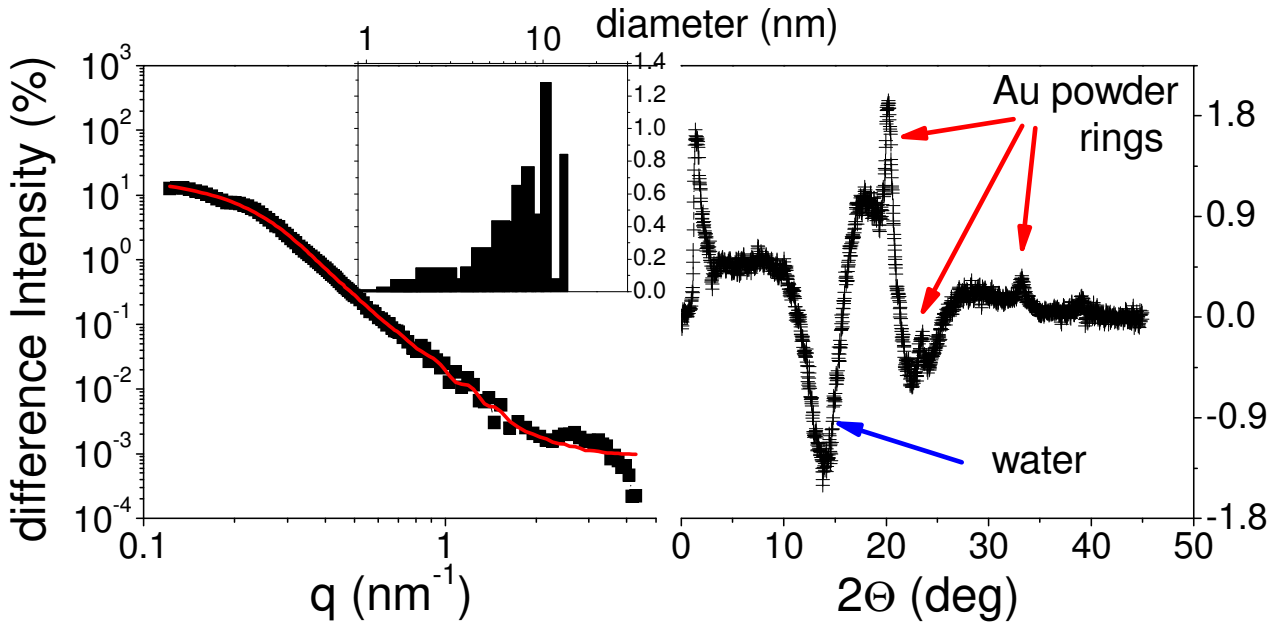

Fig. 1: Difference scattering distributions at a 10 µs delay after laser impinging the target at a 0.2 mm distance from the surface in SAXS (left) and WAXS (right). The line in SAXS shows a fit with a free size distribution of nanoparticles with a reverse-Monte-Carlo optimization. The size hitogram is displayed in the inset. The Finite difference signal in WAXS is composed of difference scattering of the compressed water phase and emerging powder peaks of the gold nanoparticles.

Conclusions

We could resolve the temporal behaviour of laser-produced nanoparticles in liquid solution at very early time points while the cavitation bubble is just forming. Thus a quantitative modeling of particle density and sizes as compared to proposed models can be performed. Analysis is ongoing.

References:

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