Ultrafast x-ray scattering on nanoparticle dynamics

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Abstract. Pulsed X-ray scattering is used for the determination of structural dynamics of laser-irradiated gold particles. By combining several scattering methods such as powder scattering, small angle scattering and diffuse wide angle scattering it is possible to reconstruct the kinetics of structure evolution on several lengths scales and derive complementary information on the particles and their local environment. A generic structural phase diagram for the reaction as function of delay time after laser excitation and laser fluence can be constructed.

1. Introduction

Photothermal applications assisted by nanoparticles include diagnostics with antibody targeted nano-objects \cite{1}, thermal tissue treatment \cite{2} or membrane permeation by aid of laser excitation \cite{3}. On the structural level a manifold of reactions may occur to the nanoparticles and their local environment. Our research within the last years concentrated on resolving the structural dynamics with high time and atomic scale resolution. This leads to a detailed mechanistic insight into the reaction dynamics of nanoparticles, including lattice heating and melting \cite{4, 5}, non-thermal ablation \cite{6, 7, 8} or laser cavitation on the nanoscale \cite{9, 10}. By means of pulsed x-ray scattering \cite{11, 12, 13} of laser-excited samples on a 100 picosecond time scale it is even possible to resolve protein kinetics around ligated nanoparticles \cite{14}, which gives a hint on the impact of photothermolysis in a biological environment. Besides the pulse length effects the laser fluence plays a central role in the determination of a generic structural phase diagram. In contrast to molecular photo-excitation, where single photons are used to create an excited state, several photons are absorbed at a time. This leads finally to a direct correlation between lattice temperature and laser fluence.

In the following the technical basics of the investigation are described together with an overview of the observed reactions of photo-excited gold nanoparticles. This leads finally to a phase diagram in fluence and relaxation time comprising the sequence of reactions. Laser excitation of different classes of nanoparticles should show very similar reactions, in particular what concerns the thermal link between nanoparticles and solvent.

2. Pulsed X-ray scattering

The aim of time-resolved pump-probe methods in general is to (i) resolve intermediate states of the relaxation pathway, (ii) determine lifetimes of decay channels as indicators for energy levels and interaction channels between different elementary steps and (iii) determine the limits of linear excitation with possible transitions to non-linear phenomena at high excitation density.
Structural relaxations in particular can be addressed by probes that resolve multiple length scales from atomic rearrangements to microscale changes. Besides ultrafast electron diffraction and imaging [15, 16] pulsed x-ray scattering and spectroscopy [17, 18] are powerful methods for ultrafast structure determination. It is useful to recall two peculiarities of x-ray scattering when studying disordered samples, such as nanoparticles and suspensions or self-assemblies thereof. First, X-ray scattering is a weak process. A typical total cross section for a sub-millimeter sized liquid sample is in the order of $10^{-3}$. Therefore one task to perform pulsed X-ray experiments is to optimize the X-ray flux[19]. Second, scattering in disordered systems is a sum of all atomic correlations in the sample, be it the studied material, the solvent or the container. Despite the problem arising from the mixture of all these signals this can also be advantageous, considering that solute and solvent system interact by exchange of energy and material. This exchange can be determined.

The experimental setup therefore relies on a powerful, pulsed X-ray source and the means to determine small changes in scattering. The beamline ID09b at the European Synchrotron Radiation Facility uses an in-vacuum undulator with a quasi-monochromatic emission at 15-18 keV with some 5 % bandwidth. Laser excitation is done at low repetition rate with typically 1 kHz. This allows producing intense laser pulses, but reduces the duty cycle of the X-ray emission [20]. The X-ray pulse train is reduced to the 1 kHz rate by a rotating ultrasonic chopper wheel. In monochromatic mode (Si(111) channel-cut monochromator) about $10^{9}$ photons are delivered to the sample per second. In this mode small changes in the angular position of Bragg peaks allow for determining the lattice expansion of the particles, which, in turn, is a measure for the lattice temperature.

A higher flux can be used if bandwidth of the X-ray energy is relaxed by either using the full emission line or by introducing a multilayer monochromator of 2-3 % spectral width. Thereby $10^{11}$ photons per seconds can be used. Changes of disordered structure, such as atomic and molecular rearrangements in liquids or secondary structure in proteins have a broad signature in reciprocal space, which is not spoiled by the spectral bandwidth [21].

Highest sensitivity to tiny structural changes is achieved by a lock-in type of data acquisition. The sample is excited by a sequence of laser pulses, followed by delayed X-ray pulses that are synchronized in time. The scattering is accumulated on a 2D detector (CCD camera) and stored as single image. Afterwards the same acquisition is performed with laser pulses that follow the X-ray pulses. The latter image serves as reference for the non-excited sample, assuming that the excitation from a prior laser pulse has decayed. This is acceptable in our case, as after 1 ms energy has completely dissipated from the nanoscale environment. Additionally a fast pumping of the liquid completely exchanges the sample between two pulses. By repeating these images in a sequence a drift-free difference scattering distribution $\Delta S(Q)$ is derived.

3. Dynamics of laser-excited nanoparticle sols

A typical scattering distribution is displayed in figure 1 over a broad range of scattering vector Q. A gold sol of 36 nm particles has been pumped through a glass capillary and excited by femtosecond laser pulses at 400 nm. The first steps of excitation are well known: gold particles absorb light in the interband. The non-equilibrium electrons relax on a (sub-)picosecond time scale to heat the lattice within few picoseconds [22, 23]. Within the X-ray time resolution (100 ps) a well-defined, homogeneous temperature of the gold lattice can be assumed. The Bragg peaks are then shifted due to lattice expansion or disappear completely if the particles are molten. Melting was found to be faster than the 100-ps resolution [4]. As the particles are in contact to water, heat can flow into the liquid. This, however, is considerably slower and lasts for about 300 ps to 2 ns, depending on nanoparticle size [10]. The reason is that the interface between gold and water forms an acoustic impedance, the so-called interface resistance. This parameter mainly determines the time constant for cooling. The heat deposition into the nearby
water shell is substantial, which can raise the temperature to well above the critical temperature. A formation of vapor is the result. Careful analysis of the formation threshold for this process has revealed this as spinodal decomposition [5].

The vaporisation emanates as nanometric bubbles around the particles. In the small-angle-scattering (SAXS) region (A) a large change in scattering can be observed, which allows quantifying shape and size of the bubbles [9]. These bubbles undergo some expansion and recollapse within few nanoseconds, thereafter heat is dissipated into the environment. Not only the SAXS region is affected by the bubbles, but also $\Delta S$ at larger $Q$ (1-3 Å$^{-1}$). This is the region where the water structure factor has its maxima (C). A change here reflects the fact that the expansion of the bubbles results in a compression of the bulk water phase. The scattering is modeled by a pressure induced change $dS_p = dS/dp|_T \times \Delta p$ [24, 25]. $dS_p$ is in good agreement with the volume change due to bubble expansion.

In fact, this fast and local heating due to the heat release from the nanoparticles can be a tool for laser therapeutics of biological tissue, restricting the heat-affected zone strictly to the nanoscale [2]. With X-ray scattering the reaction of adsorbed proteins can be directly addressed. It has been seen that bovine serum albumin survives a temperature jump of 100 K without deterioration of the adsorption layer and of secondary structure (which would show up in region B). At the onset of bubble formation the proteins are ejected [14].

4. Generic phase diagram

Quantifying all the above findings, one can construct a ”phase diagram” for all observed structural relaxations (fig. 2). The thresholds and lifetimes of particle melting, bubble formation and particle destruction can be localized on a map of fluence versus delay after laser excitation. This phase diagram for gold particles (here the example of 36 nm particles) varies only weakly with nanoparticle size and laser pulse length. An additional pathway of restructuration forms by non-thermal ablation due to the high field strength of the laser pulse [6] when femtosecond laser pulses are used. This effect vanishes for pulses longer than 1 ps. Melting slightly above the melting threshold is followed by recrystallisation and unmodified particle shape. At higher fluence, nevertheless, particles are destroyed, possibly by evaporation or Coulomb explosion [26].

Laser pulses longer than the cooling time of the particles, in contrast, will lead to considerable dissipation of heat during the laser pulse. Therefore the thresholds for bubble formation and particle melting and the lifetimes will increase. Generally speaking, the fluence will be no longer a good measure for the reactions, but rather the peak flux of the laser.

In conclusion, pulsed X-ray scattering allows resolving a hierarchy of structural relaxations in nanoparticle sols. These relaxations include heating, cooling, bubble formation as well as
particle melting and non-thermal ablation. A "phase diagram" is constructed, which is useful as a general map of the timescales and fluence involved.

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