Light-induced structural phase behaviour of metal nanoparticle materials

A Plech\textsuperscript{1}, V Kotaidis\textsuperscript{1}, M Wulff\textsuperscript{2}, C Dahmen\textsuperscript{3}, G von Plessen\textsuperscript{3}

\textsuperscript{1}Fachbereich Physik der Universität Konstanz, Universitätsstr. 10, D-78457 Konstanz, EU
\textsuperscript{2}ESRF, BP 220, F-38043 Grenoble, EU
\textsuperscript{3}I. Physikalisches Institut, RWTH Aachen, D-52056 Aachen, EU

E-mail: anton.plech@uni-konstanz.de

Abstract. We have investigated the structural dynamics of gold nanoparticles induced by femtosecond light excitation. Structure evolution in both embedded particles (glass matrix or liquid water suspension) and quasi-free particles adsorbed on a solid surface is analyzed. By use of stroboscopic laser pump-x-ray probe techniques the structural relaxations have been resolved on the 100 ps time scale at the European Synchrotron Radiation Facility. Several methods including powder scattering, liquid scattering and small angle scattering serve to resolve microscopic and mesoscopic length scales of the composite system. The thermal response includes the heating, lattice melting, explosive solvent evaporation and solvent cooling subsequent to the laser flash excitation. Nonthermal effects are observed with femtosecond excitation. They are attributed to ablation from the particle and particle explosion at strong nonequilibrium conditions. The observations can form a complete picture of the energy dissipation and phase transitions involved in nanoscale composites.

1. Introduction
Optical properties of nanoparticles and nanoparticle composites including nonlinear optical response are widely studied and well understood [1, 2]. Optical excitations in metal nanoparticles include the response of the conduction electron system, especially the plasmon resonance, which provides a channel for ultrafast energy transduction. While it is known, that ultrafast and strong nonequilibrium excitation induces important structural relaxations, less information is available on this aspect, where studies have concentrated on the electron phonon coupling and vibrational properties due to size confinement, mostly studied by laser pump-probe spectroscopy [3, 4, 5, 6]. An attempt to resolve the melting process has been reported, where the shape transformation served as indicator for the lattice melting [7]. By use of x-ray scattering methods, the structural relaxations in condensed matter, and in particular in nanoscale systems are directly accessible. We have reported the ultrafast heating of silver and gold particles [8, 9], the determination of lattice temperatures and melting in gold sols [10] and the reaction of the water medium upon the energy flow [11].

2. Materials and methods
The time resolved scattering experiments on the nanoparticle composites have been performed at the beam port ID09B at the ESRF [12]. A femtosecond regenerative Ti:Sapphire amplifier system (Coherent MIRA, Spectra Physics Hurricane) has been synchro-locked to the radio frequency of
the electron storage ring. Thus the emission of laser pulses is time locked to the pulse train of emitted x-rays from the storage ring. A 235 pole undulator of 17 mm period produces intense x-ray pulses at a center wavelength of 15 keV. They either pass through a channel-cut silicon monochromator in order to achieve an energy resolution of $1.4 \times 10^{-4}$ or are guided directly to the sample after further opening the undulator gap and optimizing heat load, spectral purity and achievable momentum transfer [13].

The matching of the x-ray repetition frequencies to the laser firing at 986 Hz is achieved by a mechanical chopper, which is synchronized to a fixed electron pulse in the ring. The delay between laser and x-ray pulses can be varied in steps of 5 ps over a millisecond range. The electronic jitter is much smaller than the x-ray pulse length of 80-110 ps (16 bunch mode). The calibration of coinciding laser and x-ray pulses (delay $\tau = 0$) is done by the onset of photo signals as seen in the inset of figure 1, to a precision better than 20 ps. This setup allows one to apply pump-probes schemes as known from femtosecond spectroscopy except that a two dimensional x-ray detector can be used to record the reciprocal space at atomic scale resolution.

The laser power is controlled by a combination of a $\lambda/2$ retarder and a Glan laser prism and calibrated with a laser power meter (Coherent). The 150 fs pulses at 800nm from the regenerative amplifier are frequency-doubled to 400 nm and used for sample excitation.

Gold nanoparticles have been synthesized by the well known citrate method [14]. We control the sizes of the particles by varying the relative concentrations of gold ions with respect to the citrate reductant, which serves also as stabilizer. The size distribution is found to be within 12 % - 18 % depending on particle size and calibrated by SEM, SAXS measurements and optical extinction spectra. The sols have a rather high gold concentration (0.8 - 1.2 mM) and can be directly used for the photo excitation studies, when pumped through a 300 $\mu$m borosilicate capillary and illuminated by coaxial x-ray and laser pulses. They have also been adsorbed onto a solid surface of float glass in submonolayer coverage. This technique uses the established electrostatic self-assembly processes, as developed for aqueous polyelectrolyte adsorption [15]. As final step a thin layer of waterglass (sodium waterglass, Roth Chemicals) can be spin coated on top followed by an annealing step at 200 $^\circ$C. This results in a solid glassy layer of roughly 20 $\mu$m, in which the particles are embedded.

For the powder scattering from the particle lattice a series of images at various delays are collected. A careful normalization and subtraction of the background is necessary, the powder scattering distributed in Debye-Scherrer rings, is usually within a 1-10 % range of the background. The resulting peaks are fitted by appropriate functions, typically single or multiple Lorentz functions. The peak positions (mainly of the (111) reflection) serve to derive the lattice parameter. Integrated intensity and peak width are important for the determination of lattice strain and melting.

SAXS and liquid scattering are recorded with the polychromatic x-ray pulses at different sample-detector distances (630 mm and 60 mm). As the relative photoinduced signal in these measurements is extremely weak ($10^{-4}$ to $10^{-2}$) compared to the background (scattering from the capillary, liquid and air) a set of interleaved exposures has to be taken, where once the x-ray pulse arrives before the laser pulse (serves as unperturbed reference) and at variable delay after laser excitation. The CCD images are then subtracted from each other after proper normalization to remove drifts, corrected for polarization, space angle intensity and integrated azimutally to derive the difference photosignal $\Delta S(Q, \tau)$ where $Q = 4\pi/\lambda \cdot \sin(2\Theta/2)$ denotes the scattering vector as calculated from the scattering angle $2\Theta$ [16].

3. Linear response of the nanoparticles composites: Heat dissipation, melting and water evaporation
The phonon excitation from a heated electron gas as modeled by the two temperature model of the coupled electron and phonon gas is a relatively fast step, which occurs within 2-5ps [17, 18, 2].
With our standard setup it cannot be resolved in time. The shortest available pulses (at low bunch current in the storage ring) of 75 ps FWHM still show a resolution limited rise of the lattice parameter after laser excitation [19].

After the initial fast heating of the lattice a relaxation appears that strongly depends on size and contact medium of the particles. In general the cooling times scale with the ratio of volume to surface of the particles, i.e. with the radius, by an interplay between stored energy and cooling efficiency [20, 5]. Therefore particles on a free surface show very long relaxation times up to 13 ns, seen in figure 1 a) for 102 nm particles, in comparison to 35 nm particles with 750 ps. Covering these particles by a glass layer drastically reduces the cooling time as is expected for the increased thermal contact area (850 ps for 85 nm particles).

A quantitative calculation is possible, when taking two mechanisms of heat resistance into account, the finite conductance across the interface particle-medium and the heat diffusivity in the bulk medium. Silver particles in glass have shown a predominance of the interface conductance $G$, probably because of the nonideal physical contact, with $G = 190 MW/m^2/K$ [8], whereas for gold particles in water the diffusivity in the water phase is more important, with $G = 105 MW/m^2/K$ [10]. The fits are presented in figure 1 (b) for two particles sizes.

![Figure 1](image.png)

**Figure 1.** Lattice expansion for gold particles on a glass surface (a) and in water (b) as function of laser-x-ray delay together with simulations (a: exponential decays, b: see text). Particles on the surface were 35 nm (○), 102 nm (●) and 85 nm diameter, the latter covered by a glassy layer (+). Particles in water were 100 nm (●) and 52 nm (△) diameter. The inset shows the rise of the signal at short delays for the 102 nm particles with a fitted error function together with its derivative, a Gaussian of 45 ps FWHM.

This energy relaxation can be regarded as a general description, which is to first approximation not explicitly temperature dependent. The dynamics change completely when discontinuities of the condensed phase, such as phase transitions, are involved. One transition is the liquid vapor transition of water in the case of gold suspensions. It has been found that structural transients in the water phase occur at high excitation density [21, 11]. At the same time the heat transfer collapses at a threshold value of the excitation density and the cooling rate of the particles is reduced [22].

The structural transients in the water phase indicate a bulk compression that is caused by the formation of vapor bubbles close to the particles, which grow and then vanish on the nanosecond time scale. The vapor formation is not caused by normal boiling, but by explosive evaporation close to the water spinodal temperature [23] due to the large heating rate that locally exceeds $6 \cdot 10^{12} K/s$. 
Figure 2. Liquid scattering changes of the water phase after laser excitation as function of scattering vector \( \mathbf{Q} \). The laser power was 5 times the melting threshold. From bottom to top: 50 ps, 250 ps, 1 ns, 5 ns, 2 \( \mu \)s compared to the static differential \( \frac{dS}{dp} \bigg| T \) (+) with equal modulations. The marks indicate dips caused by Bragg scattering disappearance. The inset shows the amplitude of the signal as function of delay.

Secondly the excitation kinetics can be intercepted by the melting transition of the crystalline particles, as evidenced by the vanishing of the Bragg scattering [10]. It is found that after a cooling step the particles partially recrystallize. Yet the melting transition is in agreement with the cooling times (Figure 3). In addition the existence of supercooled liquid particles in the solution, as evidenced by the melting transition of the Bragg scattering [10]. It is found that after a cooling step the particles partially recrystallize. However the melting transition is in agreement with the cooling times (Figure 3).

Figure 3. Profile of the Bragg scattering of the gold (111) reflection of 100 nm particles in water for different delays. a and b: no laser (–), 14.4 mW (+), 29 mW (–); c: 14.4 mW (+), 29 mW (–), 79.5 mW (–), 170 mW (–).

For different delays a and b: no laser (+). The laser power was 5 times the melting threshold. The inset shows the expansion shortly after the excitation for these rather large particles. The observation shows expansion shortly after the excitation for these rather large particles. The inset shows the expansion shortly after the excitation for these rather large particles.
Nonthermal behaviour - lattice motion and fission

The above effects are explained by continuum theory and not primarily confinement effects. The size enters only as scaling argument via the transit times of mechanical (sound) and thermal (heat diffusivity) relaxations. Structural changes unique to the nanoscale are observed as well. Earlier optical studies have evidenced the presence of nonthermal motion that can be regarded as particles shape vibrations [3, 4]. The majority of all observations have focussed only on the lowest order symmetrical motion, the spherical expansion and compression mode of round particles. X-ray scattering is sensitive to the vibrations [9], but presently the temporal resolution does not allow to resolve the typical periods (5 - 50 ps within the present size range [25]). Still the nonthermal contribution to lattice excitation is visible through the strain induced by the vibrations and visualized by the Bragg profile distortion. We believe that for short delays (4 - 25 ps) within the present size range [25] the nonthermal contribution to lattice excitation is visible through the strain induced by the vibrations and visualized by the Bragg profile distortion. X-ray scattering is sensitive to the vibrations [9], but presently the temporal resolution does not allow to resolve the typical periods (5 - 50 ps within the present size range [25]).

Another consequence of the ultrafast excitation is the possibility of material transport by nonthermal motion that can be regarded as particles shape vibrations [3]. The majority of all observations have focussed only on the lowest order symmetrical motion, the spherical expansion and compression mode of round particles. X-ray scattering is sensitive to the vibrations [9], but presently the temporal resolution does not allow to resolve the typical periods (5 - 50 ps within the present size range [25]). Still the nonthermal contribution to lattice excitation is visible through the strain induced by the vibrations and visualized by the Bragg profile distortion. X-ray scattering is sensitive to the vibrations [9], but presently the temporal resolution does not allow to resolve the typical periods (5 - 50 ps within the present size range [25]).

Another consequence of the ultrafast excitation is the possibility of material transport by nonthermal motion that can be regarded as particles shape vibrations [3]. The majority of all observations have focussed only on the lowest order symmetrical motion, the spherical expansion and compression mode of round particles. X-ray scattering is sensitive to the vibrations [9], but presently the temporal resolution does not allow to resolve the typical periods (5 - 50 ps within the present size range [25]). Still the nonthermal contribution to lattice excitation is visible through the strain induced by the vibrations and visualized by the Bragg profile distortion. X-ray scattering is sensitive to the vibrations [9], but presently the temporal resolution does not allow to resolve the typical periods (5 - 50 ps within the present size range [25]).
vanishes completely at the melting point. The supported particles however show a very narrow interval of linear expansion, above which no further expansion is recorded. This is accompanied by the nearly complete loss of scattering intensity. The particles have lost their crystallinity and probably their shape as well. An indication is the SAXS signal from the debris appearing at low Q in figure 2. The destruction of the particles forms a serious limitation for applications, which rely on reversible processes. It can, on the other hand, be an interesting mechanism for controlled manipulation and structuring of nanoscale material. The quantitative understanding of the interplay of energetic relaxations and structural response is important for nanophotonic materials applications.

**Acknowledgments**

Discussions and help from M. Lorenc, H. Stark, J. Boneberg and P. Leiderer are acknowledged. The work is supported by the ESRF, DFG and the Center for Junior Research Fellows Konstanz.

5. **References**

[1] Kreibig U and Vollmer M 1995 *Optical Properties of Metal Clusters* (Berlin: Springer)

[2] Lisk S and El-Sayed M A 2000 *Int. Reviews in Phys. Chem.* 19 409 and references therein.

[3] Del Fatti N, Voisin C, Chevè F, Vallée F and Flytzanis C 1999 *J. Chem. Phys.* 110 11484; Voisin C, del Fatti N, Christofilos D and Vallée F 2001 *J. Phys. Chem.* 105 2264

[4] Hodak J H, Henglein A and Hartland G V 1999 *J. Chem. Phys.* 111 8613

[5] Hu M and Hartland G V 2002 *J. Phys. Chem.* B 106 7029

[6] Hartland G V, Hu M and Sader J E 2003 *J. Phys. Chem.* B 107 7472

[7] Link S and El-Sayed M A 2001 *J. Chem. Phys.* 114 2362

[8] Plech A, Wulf M, Kuerbitz S, Berg K-J, Berg G, Graener H, Grézillon S, Kaempfe M, Feldmann J and von Plessen G 2003 *Europhys. Lett.* 61 762

[9] Plech A, Grézillon S, von Plessen G, Scheidt K and Naylor G 2004 *Chem. Phys.* 295 55

[10] Plech A, Kotaidis V, Grézillon S, Dahmen C and von Plessen G 2004 *Phys. Rev.* B 70 195423

[11] Plech A, Kotaidis V, Lorenz M and Wulf M 2005 *Chem. Phys. Lett.* 401 565

[12] Schotte F, Techert S, Anfinrud P A, Stajer V, Moffat K and Wulf M 2002 in: *Third-Generation Hard X-ray Synchrotron Radiation Sources, ed. D. Mills* (New York: John Wiley & Sons)

[13] Wulf M, Plech A, Eybert L, Randler R, Schotte F and Anfinrud P A 2002 *Faraday Disc.* 122 13

[14] Turkevich J, Stevenson P C and Hillier J 1951 *Discuss. Faraday Soc.* 11 55; Enüstün B V and Turkevich J 1963 *J. Am. Chem. Soc.* 85 3317

[15] Decher G 1997 *Science* 277 5330

[16] Plech A, Wulf M, Bratos S, Mirloup F, Vuilleumier R, Schotte F and Anfinrud P A 2004 *Phys. Rev. Lett.* 92 125505

[17] Bigot J Y, Merle J C, Cregut O, and Daunois A 1995 *Phys. Rev. Lett.* 75 4702

[18] Perner M, Bost P, Lemmer U, von Plessen G, Feldmann J, Becker U, Mennig M, Schmitt M and Schmidt H 1997 *Phys. Rev. Lett.* 78 2192

[19] The resolution limit is however smaller than the pulse length, as long as the excited state (expanded lattice) differs from the ground state in Q space. In that case at nominal delay τ = 0 only half of the x-ray pulse probes the excited state, which encompasses half of the pulse duration. In our case the signal rise time, as modeled by an error function is as short as 45 ps (see inset in figure 1). Normal 16 bunch operation with 4-7 mA bunch current would still allow to resolve 80 ps for 110 ps pulses.

[20] Wilson O M, Hu X, Cahill D G, and Braun P V 2002 *Phys. Rev.* B 66 224301

[21] Hu M, Petrova H and Hartland G V 2004 *Chem. Phys. Lett.* 391 220

[22] Kotaidis V, Dahmen C, von Plessen G, Springer F and Plech A 2005 *submitted*

[23] Debenedetti P G 1996 *Metastable liquids: concepts and principles* (Princeton: Princeton Univ. Press)

[24] Buffat P and Borel J P 1976 *Phys. Rev.* A 13 2287

[25] Sader J E, Hartland G V, and Mulvaney P 2002 *J. Phys. Chem.* B 106 1399-1402