Thermodynamics of nanosecond nanobubble formation at laser-excited metal nanoparticles

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Abstract. The nonlinear thermal behavior of laser-heated gold nanoparticles in aqueous suspension is determined by time-resolved optical spectroscopy and x-ray scattering. The nanoparticles can be excited transiently to high lattice temperatures owing to their large absorption cross-section and slow heat dissipation to the surrounding. A consequence is the observation of lattice expansion, changed optical transmission, vapor bubble formation or particle melting. The heat transfer equations are solved for two limiting cases of heat pulses shorter and longer than the characteristic cooling time. The results of pulsed excitation with femtosecond and nanosecond lasers are explained by the theoretical prediction, and the bubble formation is interpreted by a spinodal decomposition at the particle–liquid interface. It is shown that both the laser spectroscopy and x-ray scattering results agree qualitatively and quantitatively, underlining the validity of the comprehensive model.
1. Introduction

The interaction of light with metal nanoparticles shows a number of nonlinearities that are interesting both from the fundamental point of view and in view of applications. The nonlinearities are related to a strong non-equilibrium excitation of the electron gas followed by lattice excitation. Femtosecond pulses lead to heating of the electron gas within hundreds of femtoseconds, followed by coupling to the lattice within a few picoseconds [1]–[4]. The transfer into the surrounding medium, such as water, is two orders of magnitude slower. This remarkable localization of energy within the particle is the starting point for a nonlinear threshold process, explosive boiling adjacent to the particles. As the heat is localized for some nanoseconds close to the nanoparticles, the spinodal temperature of the water can easily be surpassed and leads to homogeneous nucleation of vapor and the formation of nanometric bubbles.

At the same time, metal nanoparticles have been employed to be conjugated with organic molecules, such as proteins or DNA, which opens up the possibility to selectively label tissues with specific interactions, such as antibody–antigen reactions. Biomedical applications of these targeted particles employing the boiling process seek to take advantage of the very localized energy deposition in order to restrict mutilating effects on tissue to a small volume range [5]–[10]. Both the high temperature close to the nanoparticles and the shear forces due to bubble explosion are considered as stimuli for the mutilation. Vapor bubbles can also aid diagnostics, for instance during imaging, as they may act as scattering centers for the probe. A prerequisite for the study of the various biological effects is a deep understanding of the bubble formation process and thermal dynamics of the nanoparticle suspension system. Both thermal dynamics and the nonlinear process caused by the bubble formation have earlier been studied by applying femtosecond or nanosecond excitation and probing by optical absorption spectroscopy [5], [11]–[20] and visible light scattering [21, 22] respectively. But only time-resolved x-ray scattering helped us to resolve the quantitative picture of the bubble nucleation threshold [23] and bubble dynamics [24, 25]. Although this method gives direct structural information with high time resolution and identification of particle state [26, 27],

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solvent dynamics [28] or adsorbed layers [29], it is a complicated method, difficult to use in applied problems.

Consequently, the aim of the present work is to compare the bubble formation process in gold nanoparticle suspensions using x-rays as a structural probe for visible light spectroscopy. The two relevant cases of excitation with femtosecond and nanosecond pulses will be investigated. Whereas for femtosecond excitation the time scales of the different subsystems are completely separated, energy input and dissipation occur at the same time during nanosecond excitation. The approach of exciting with nanosecond pulses and probing by visible light is closer to applications, as they are readily available in biological nanophotothermolysis studies. It will be shown that the phenomenology does not differ qualitatively for both cases, which is underlined by a fully quantitative prediction of the kinetics through solving the heat transfer equations.

In particular, the calculated threshold is well reproduced, which is at variance with earlier confusing results [18, 22] that questioned the general understanding of this process.

2. Methods

For a comprehensive description of the thermal dynamics on the nanoscale, a number of ingredients have to be established.

Firstly, an adequate sample system has to be defined, which allows us, to great precision, to correlate the real structure behavior with the idealized description. Gold nanoparticles are particularly suited for this approach, because procedures exist to produce batches of high uniformity and shape definition. Here we use quasi-spherical particles in aqueous solution. Gold nanoparticles have been produced by the classical Turkevich method [30, 31] with some modifications allowing for higher concentration of gold particles and for size definition by changing educt concentrations [32, 33]. The particles are quite spherical and of defined size dispersion. The particle suspensions with size from 8 to 36 nm can be synthesized from a 2 mM gold ion solution and fully quantitative transformation into particles [34]. The size dispersion is typically about 13% rms. Larger particles tend to deviate more from spherical shape and the highest monomer concentration would be 1.6 mM. The size dispersion as determined by small angle x-ray scattering (SAXS) amounts to 15–18% rms (which includes the deviation from spherical shape). Some caution should be taken for particles larger than 70–80 nm, where the aspect ratio of the ellipsoids can amount to up to 1.6. Some of the nanosecond excitation experiments presented here utilize commercial gold particle suspensions (BB International), which have excellent sphericity and size dispersion (typically 8%).

2.1. Laser excitation and absorption cross-section

Secondly, the interaction with (intense) light fields has to be quantified. Gold particles, apart from being inert in ambient conditions, are excellent tools due to their marked optical properties. The most important information in the optical extinction spectra is the intense absorption line due to the excitation of a surface plasmon resonance (SPR), which, in a dipole approximation of the oscillating conduction electrons, can be written as

\[
\sigma_{\text{ext}} = \frac{9 V \epsilon_m^{3/2} \cdot \omega \epsilon_2(\omega)}{c \cdot (\epsilon_1(\omega) + 2\epsilon_m)^2 + \epsilon_2(\omega)^2},
\]

(1)
with the spherical particle volume $V$, speed of light $c$, the light frequency $\omega$ and the dielectric constant $\epsilon_m$ of the surrounding medium. The functions $\epsilon_1$ and $\epsilon_2$ describe the real and imaginary parts of the dielectric function of the particle material. The resonance is expected when the denominator of equation (1) becomes small, i.e. near $\epsilon_2(\omega) = -2\epsilon_m$. A full description according to the Mie theory includes multipole expansion in a spherical symmetry, which adds the size dependence of the SPR [35, 36]. This dependence is an extremely useful tool for determining the sizes by pure optical methods and the optical response to structural changes [37]–[39]. The code for the Mie calculations is also available as free software\textsuperscript{3} including the modeling of the concentric dielectric environment around the particles [40].

On the basis of the Mie calculations, one can predict the extinction changes of gold nanoparticles due to a modification in the medium, such as the heating of the water phase or bubble formation. An example is shown in figure 1. The change in the refractive index of water, respectively vapor, is reflected by the damping and blue shift of the SPR. Large vapor bubbles are seen directly due to their scattering contribution to extinction. The extinction will serve as a tool for the detection of the reaction in the medium following rapid heating.

The shape of the SPR is also modified by heterogeneous broadening [2, 41, 42] due to size and shape dispersion. This turns out to be problematic when trying to determine quantitatively the absorbed laser energy in the particles.

To overcome this problem, a laser wavelength far from the SPR was used for the synthesized particles with broader size dispersion. Wavelengths at either about 400 nm (frequency-doubled Ti–Sa femtosecond laser) or 355 nm (frequency-tripled Nd–YAG nanosecond laser) allowed us to target the interband absorption. The commercial particles of better size definition were also excited close to the SPR peak, suffering less from inhomogeneous broadening. Extinction at the interband absorption is roughly proportional to the particle volume for smaller particles, which reduces the effect of size dispersion greatly.

\textsuperscript{3} By P Laven, available at: http://www.philiplaven.com/mieplot.htm (2005).
Figure 2. Measured extinction cross-section of citrate synthesized gold particles as a function of diameter at 400 nm. The sizes have been in part determined by dynamic light scattering (crosses) and by the calibration of the plasmon resonance wavelength (squares) by SEM and SAXS [33]. The lines are calculations of the Mie extinction and absorption cross-sections using bulk gold parameters. The dotted line is the scaled particle volume. Right-hand side: TEM image of 29 nm gold particles together with a size histogram.

We have made a comparison between the calculated extinction at 400 nm and the measured extinction of a suspension of given particle size and concentration. The curve is shown in figure 2 and shows in general a good correlation. In particular, the relation with particle volume is shown (dashed line, scaled). A closer inspection, however, reveals an absolute reduction of the measured cross-sections with the Mie calculation by some 20%, which is not easy to interpret. The reason could be some calibration problem of the particle number, but also residual non-sphericity, in particular for larger particles. For the calculations, we have used the measured extinction rather than the theoretical Mie values [27]. A representative transmission electron microscopy (TEM) image of 29 nm particles is shown in figure 2 together with a size histogram showing a dispersion of 17%.

2.2. Description of heat transfer

The next point to quantify is the calculation of the heat transfer. The first simplification to be made here is that pure diffusive heat transport is assumed within one phase. Radiative heat transport is not considered either, which can easily be shown to be negligible for the time scales of nanoseconds and temperature rise of about 100–500 °C.

A number of approaches exist for solving the thermal transport equations, partly inspired by engineering demands [43] and partly by pure scaling arguments [44]. A complication of the

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4 This may be questionable for length scales below the mean free path of phonons. The mean free path amounts to some 1–2 nm in the liquid and modifications due to this effect shall be neglected.
description apart from the non-integrability of the differential heat equation
\[ \rho c \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + Q(t) \] (2)

(with temperature \( T \), heat capacity \( c \), density \( \rho \), heat conduction \( \kappa \) and deposited heat \( Q(t) \)) is the fact that two mechanisms of heat transfer have to be considered, the transport across the particle–water interface \([26]\) and the diffusive heat transport within the water phase \([12, 45]\). Often the interface transport, also named Kapitza resistance, is considered to be faster than transport in the medium (water). However, on the nanoscale this is not necessarily true. The critical thermal interface resistance (TIR) \( G_c \) of equal contributions of both effects \([46]\) can be defined by comparing the thermal diffusivity to the mismatch in sound velocity between the particle and the medium. This mismatch is the source of reduced energy transport across the interface:
\[ G_c = 3 \kappa \left( \frac{c_l \rho_l}{c_p \rho_p} \right)^2 \frac{1}{3 \cdot c_p \rho_p} \cdot \frac{1}{R} \] (3)

with the heat diffusivity \( \kappa = K/(\rho c_l) \) \((K, \rho_p, c_p \text{ and } c_l \text{ denoting the diffusion coefficient in the water phase, the densities of the liquid and the particle and the sound velocities in the particle and water})\). For the currently considered gold particles in the range of radii \( a \) from 5 to 50 nm, the critical interface conductivity is in the range of 60–600 MW\( (\text{m} \cdot \text{K})^{-1} \), which turns out to be of the same order as the previously observed TIR \([13]\). Figure 3 shows examples of the temperature rise in the water phase close to the interface at the given temperature of the particles for the different conditions discussed here.

Also, in general, the temperatures of the electron gas, particle lattice and surrounding represent systems of coupled differential equations. The first pair of the electron gas and lattice is described by the so-called ‘two-temperature model’, which is important when using the electron–phonon coupling within the particle \([47, 48]\). An extension of this model accounts also for the coupling to the surrounding medium, as demonstrated in \([49]\). As has been shown, a separation of time scales is possible if (i) the heating of the particle (duration of the laser pulse, respectively electron–phonon coupling) is much faster than the heat conduction to the medium or (ii) the heating is slower than the cooling of the particle via the particle–medium interface. Then a system of two coupled heat equations for the particle and medium temperatures is given, thereby assuming that the temperature distribution within the particle is constant due to a much higher conductivity in gold than in the medium, while the temperature in the medium is allowed to vary spatially:
\[ M c_p \left( \frac{d}{dt} (T_p(t) - T_0) \right) - Q(t) + 4 \pi R^2 G \cdot (T_p(t) - T_f(r = R, t)) = 0, \] (4)
\[ \frac{\partial}{\partial r} T_f(r, t) \bigg|_{r=R} + G/K \cdot (T_p(t) - T_f(r, t)) = 0. \] (5)

The term \( Q(t) \) denotes the time-dependent heat input into the particle by a long laser pulse. In the case of femtosecond heating pulses, this expression is neglected, while the initial temperature \( T_0 \) of the particle is set to the temperature directly after laser excitation and phonon equilibration.

(i) The limiting case for short pulses

We shall regard excitation conditions in the ultrafast case for spherical symmetry and separation of time scales, which allows us to solve the coupled equations in the Laplace

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Figure 3. The maximum temperature reached at the adjacent water layer as a function of particle size in the limit of short pulses (open squares for 60 MW \((\text{m}^2 \cdot \text{K})^{-1}\) and full squares for 120 MW \((\text{m}^2 \cdot \text{K})^{-1}\)) and in the limit of long pulses evaluated at 3 ns (full black line for 60 MW \((\text{m}^2 \cdot \text{K})^{-1}\) and dashed red line for 120 MW \((\text{m}^2 \cdot \text{K})^{-1}\)). The initial particle temperature rise is set to 900 K.

Space:

\[
\frac{\partial}{\partial r} T_f(r, s) \bigg|_{r=R} + \frac{G}{K} \cdot (T_p(s) - T_f(r, s)) = 0,
\]

where \(s\) denotes the time-conjugated variable in the Laplace domain. \(T_0\) is the initial temperature of the nanoparticle with radius \(R\), mass \(M\) and specific heat \(c_p\). \(T_f(r, t)\) is the temperature of the surrounding fluid with thermal conductivity \(K\), density \(\rho\) and specific heat \(c_l\). The temperature \(T_p\) of the particle at time \(t\) after the excitation is obtained by inverse Laplace transformation as

\[
T_p(t) = \frac{2k R^2 g^2 T_0}{\pi} \int_0^\infty \frac{\exp(-\kappa u^2 t/R^2) u^2 du}{(u^2(1+Rg) - k R g)^2 + (u^3 - k R g u)^2}.
\]

The abbreviations \(k = 4\pi R^3 \rho c_l/(M c_p)\) and \(g = G/K\) are used for the sake of compactness. The integral is solved numerically using material constants for gold and water from the literature \([27, 51, 52]^{5}\). We are, in particular, interested in the water temperature at the particle interface, which is important for vapor nucleation. The temperature in the water phase can be computed by

\[
T_f(r) \bigg|_{r>R} = \frac{2a}{r \sqrt{\pi}} \int_{(r-a)/2}\^\infty T_f \left( r = a, t - \frac{(r-a)^2}{4\kappa \mu^2} \right) e^{-\mu^2} d\mu.
\]

\(^{5}\) In particular, the values for the heat capacity of gold \(c_p = 23.81 \text{ J} (\text{K} \cdot \text{mol})^{-1}\), of water \(c_l = 75.3 \text{ J} (\text{K} \cdot \text{mol})^{-1}\) and the heat conduction of water \(\kappa = 0.597 \text{ W} (\text{m} \cdot \text{K})^{-1}\) are used.
The limiting case for long pulses

In the case of pulses that are long compared to the heat transfer times, equations (4) will be solved accordingly by taking into account the source term \( Q \), which in the simplest case can be a step function. The temperature distribution in and around the particle is then evaluated for \( t = \tau_{\text{laser}} \), which is the duration of the laser pulse. The corresponding Laplace formulation is then given by adding \( Q/s \) in the first equation of (6).

A solution of the equations for \( T_p(s) \) and a backtransform into the time domain yields an expression for the temperatures inside the particle and in the medium adjacent to the particle interface [53]:

\[
T_p(t) = \frac{Q(1 + R_g)}{4\pi R^2 K_g} + \frac{1}{2\pi^2 K} \int_0^\infty \frac{\exp(-K u^2 t/R^2)}{(u^2(1 + R_g) - k R_g)^2 + (u^3 - k R_g u)^2} du, \tag{10}
\]

\[
T_i(r = R, t) = \frac{M c_p}{4\pi R G} \frac{d}{dt} T_p(t) + T_p(t) - \frac{Q}{4\pi R^2 G}. \tag{11}
\]

The equation was derived to calculate the continuous wave heating of nanoparticles by a laser [54], but it may also serve to mimic a sufficiently long laser pulse of duration \( \tau_n \) when evaluating equation (11) at \( t = \tau_n \).

2.3. Bubble dynamics

The equations for heat transfer within the last paragraphs are not explicitly temperature dependent. The reached temperatures scale linearly with the energy deposition by the laser, but otherwise the temporal behavior is identical. Corrections to this generic solution are introduced by the temperature-dependent material constants, such as thermal diffusivity or heat capacity of water. These are not considered here, as they constitute second order effects not harming the total picture. However, the situation changes abruptly when the water temperature reaches the liquid–gas phase transition. Evaporation sets in, which changes the heat transfer completely. Heterogeneous nucleation of bubbles has been seen on laser-excited melanosomes [15]. This nucleation starts above the boiling point at an overheating of some 40 K for long laser pulses [17]. With shorter excitation and dependent on the nanoparticle material, stronger overheating of up to 140 K has been observed. The principal limit will be spinodal temperature of water, where the liquid phase becomes unstable. After nucleation the heat transfer is reduced strongly, decoupling the particle from the medium [23]. The formed bubble is initially in a non-equilibrium state at high pressure and temperature. It subsequently expands and dissipates energy by means of pressure and temperature to the medium. A collapse of the bubbles is expected, described by the Rayleigh–Plesset equation [55, 56], which is a general equation of the non-equilibrium hydrodynamics of gas bubbles in a dense medium. The description has been shown to be valid in different phenomena, such as in explosive boiling experiments (in wire [57, 58] or laser heating [15, 59]) and for pressure-driven bubbles (such as in sonoluminescence [60, 61]):

\[
\rho \left( R \ddot{R} + \frac{3}{2} \dot{R}^2 \right) = p_i, \text{eq} \cdot \left( \frac{R_0}{R} \right)^{3 \kappa} - p_{\text{ext}} - \frac{2\sigma}{R} - \frac{3\mu \dot{R}}{R}. \tag{12}
\]

A bubble with radius \( R \) within a liquid of density \( \rho \) reacts to a non-equilibrium of pressures outside the bubble (\( p_{\text{ext}} \)) and inside the bubble. The term \( p_i, \text{eq} \) denotes the pressure evolution inside the bubble for dynamically varying radius. The polytropic exponent \( \kappa \) defines whether
the expansion/compression is adiabatic ($\kappa \leq 1.66$) or isothermal ($\kappa = 1$). The Laplace pressure containing the surface tension $\sigma$ adds an additional external pressure, whereas the (bulk) viscosity $\mu$ represents a friction force to the bubble motion and is responsible for the damping of the oscillation. The function $R(t)$ is solved numerically with given boundary conditions of $R|_{t=0}$ and $R_{\text{max}}$ as the maximum bubble size.

2.4. Pulsed x-ray scattering

The phenomena described here occur on the nanometer scale, which demands experimental methods with high resolution power if direct structure information is to be obtained. X-ray scattering methods provide these tools and allow us to resolve particle and bubble morphology with high spatial resolution. Therefore, we employed SAXS for the determination of bubble sizes. At the same time, x-ray powder scattering resolves the lattice motion of the nanoparticles, which can serve as a local thermometer for the particles. The shift of the powder scattering to lower angles due to thermal expansion encodes the lattice temperature via the expansion coefficient [27].

Another aspect of the solution scattering proved useful for the analysis of the bubble kinetics. The signal from the liquid scattering is sensitive to water molecule correlations [62, 63]. Upon a change of temperature and pressure, the correlations change and thus the distribution of x-ray scattering changes. This change is widely temperature independent and can be expressed by generic second order susceptibilities [24], [64]–[67]. The pressure derivative $dS/dp_T$ [24] is shown in figure 4 on top of the measured difference curve. An important aspect in the present case is that the average (scalar) change of the liquid structure factor can be related to the average volume change in the water medium due to expanding vapor bubbles. It has been shown that the SAXS and liquid scattering determinations of bubble sizes are in good agreement, which forms a valuable tool for correlating the bubble threshold with the particle temperature via the lattice expansion and melting [25, 28]. A composite difference scattering plot over a large scattering vector interval for 36 nm gold particles is shown in figure 4, which contains all the observables.

In practice the experiment was performed at the European Synchrotron Radiation Facility at the time-resolved beam line ID09b, where 100 ps x-ray pulses in conjunction with a synchronized laser source are available. A brief sketch is depicted in figure 5. An amplified Ti(Sa) laser at 1 kHz is frequency doubled and synchronized with the synchrotron emission. The x-ray pulse repetition rate is adjusted to the same frequency by a pulse selector (rotating chopper). The x-ray focus size is 0.1 mm, while the laser is focused by means of a 500 mm lens to a 0.22 mm spot size. The laser fluence was determined with a thermal power meter (Coherent) through a knife edge scan assuming a Gaussian spatial profile. Both pulses overlap on the sample, which was prepared as a jet in a thin-walled capillary. Thereby an exchange of liquid volume is achieved from shot to shot in order not to accumulate damage. The scattering is recorded on a charge coupled device (CCD) camera with a phosphor screen (MarCCD, respectively Frelon). The laser–x-ray delay can be freely adjusted with 5 ps steps. Scattering from $10^3$ to $3 \times 10^4$ pulses is accumulated on the CCD before reading the image. Details of the setup and analysis methods are given elsewhere [68, 69]. The rotationally symmetric scattering distribution was evaluated by azimuthal averaging to derive the scattering distribution $S(Q)$ with $Q = (4\pi/\lambda) \cdot \sin(2\theta/2)$ being the scattering vector. The wavelength was centered around 0.8267 Å with a $1.4 \times 10^{-4}$ bandwidth for the gold powder scattering and $2.6 \times 10^{-2}$...
Figure 4. Left: transient scattering difference \( Q \times \Delta S(Q, \tau = 650 \text{ ps}) \) (black circles) in a wide \( Q \) range from the SAXS region to wide angle scattering at a laser fluence of 138 J m\(^{-2}\) for 36 nm particles. The oscillations at low \( Q \) are due to vapor bubble formation, while at large \( Q \) the signal from compressed liquid water is visible, intercepted by the loss in powder scattering due to particle melting. A corresponding response of pure water is shown for comparison (blue line, shifted for clarity). The red line includes a simulation of the mesoscopic density changes around the particles (in SAXS) and the static difference function for pressurized pure water at large \( Q \) [24]. Right: the shift in the (111) powder reflection from non-excited (black squares) to excitation with 90 J m\(^{-2}\) (red bullets) and 160 J m\(^{-2}\) (open circles) together with Lorentzian peak fits.

Analysis of the small angle scattering is performed by simulating concentric density profiles of spherical geometry around the particles, including the bubble shell [25]. The shift of the powder rings can be derived from Lorentzian fits to the peak, mainly the (111) reflection. By relating the peak shift to the lattice expansion coefficient, the lattice temperature is derived. The change in liquid scattering is fitted in amplitude by the generic function \( dS/dP|_T \) [66, 70] and absolute scaling of scattering intensities. This function is the pure response of bulk water to a change of pressure. By using the equation of state the bubble volume can be derived [24].

2.5. Transient optical spectroscopy

While x-ray scattering is an excellent method for the nanoscale structure determination, it is located at a large-scale facility installation, which is not readily available for daily experiments. Laser spectroscopy, on the other hand, has been used extensively for nanoparticle spectroscopy and recording of dynamics. The structural information is in many cases indirect, but by a proper modeling of the optical response good insights into the structure formation can be obtained. Ultrafast laser spectroscopy has been used to probe picosecond dynamics, typically electronic relaxations and ultrafast particle vibrations [39, 71, 72]. The determination of particle melting...
or bubble formation has often not been possible unambiguously. The simplest approach, at least on the nanosecond scale, is to probe directly the spectral response with a fast detector and an oscilloscope, making use of the high sensitivity of the plasmon resonance to changes in the temperature or dielectric medium.

Examples of Mie calculations of the extinction spectra of gold nanoparticle suspensions are shown in figure 6. The temperature increase of the water phase causes a weakening and slight blue shift of the resonance, which is very weak at 100 °C (see also figure 1) but can be drastic if the water phase is close to the critical temperature or even replaced by vapor (calculations of the optical properties at 300 °C are taken from [73, 74]). In the vapor case the resonator strength is strongly damped through the decoupling of the SPR from the dielectric environment.
Figure 6. Calculated extinction of a nanoparticle suspension at room temperature, at 300 °C and of isolated gold particles in vapor (left). On the right the extinction differences from the ambient case are shown. The lines mark the positions of the laser lines used for probing.

In practical terms, we have set up two configurations for the optical probing of the particle excitation. One is a single shot method of a steady liquid, which allows us to use several probe colors at the same time (figure 5(B)). The optical density at 532 nm was about 1 (for a 10 mm cuvette), which meant that the pump fluence within the overlap (∼1 mm) of pump and probe lasers was only slowly varying. The pump laser was not focused in order to achieve a homogeneous illumination across the probe lasers. A 10 ns Nd:YAG laser pulse was used, which was frequency doubled. This setup served to observe the general spectral behavior in a semi-quantitative way. A better control over the fluence and the exposed volume can be achieved by a perpendicular setup (part A) of figure 5. The pump laser, a frequency-tripled Nd:YAG laser (Continuum) with 3 ns pulse length, was collimated to a line focus across a capillary that enclosed the flowing gold hydrosol. Perpendicular to that, a probe laser beam (cw laser at either 532 nm (Nd:YAG, Pusch Optoelectronics) or 632 nm (He(He) laser)) crossed the laser excited volume. In order not to add the effects from immobilized particles on the capillary wall, the pump laser was restricted by a slit in the direction of the probe laser, while the probe laser was focused down to 40 µm far below the capillary diameter (0.3 mm), in order not to touch the entrance part of the pump laser. This ensured a probing with spatially constant laser excitation fluence and allowed us to derive the fluence quantitatively.

The capillaries were commercial round x-ray capillaries (Hilgenberg) with 10 µm wall thickness sealed into a flow system to refresh the liquid within the excited volume for each pump pulse. In order not to distort the probe beam focusing, the capillary was immersed into a water filled square cuvette, which prevents cylinder focussing and reduced reflections.

Probing for the multi-wavelength setup was done with fast photodiodes (FND 100Q, EG&G) and a digital storage oscilloscope (1 GHz). Single shots were recorded with a set of solid-state lasers (Oxxius, Coherent Innova and a conventional laser diode for 405, 488, 635 and 660 nm, respectively). The time lag between shots was several seconds in order to allow complete relaxation of the sample. For the crossed beam setup, a 10 Hz repetition rate was used on a photodiode (Thorlabs). Every single shot was stored independently together with the signal.
Figure 7. Transient extinction change of a nanoparticle suspension of 80 nm diameter by four collinear multicolor laser probe beams excited with a single 10 ns laser pulse at 532 nm at a fluence of (A) 300 J m$^{-2}$ and (B) 450 J m$^{-2}$. 

from a pickup photodiode (energy meter, Becker and Hickl PDI-400) for the recording of pump pulse intensity. This allowed us to sort the data afterwards as a function of pump intensity before averaging and thus circumvent intensity fluctuations of the pump pulses.

Typical traces of the multi-wavelength probe are shown in figure 7 at two different pulse energies for 80 nm particles. The extinction decreases after the laser pulse arrival (300 J m$^{-2}$) in accordance with the calculated reduction at particle heating, respectively bubble formation. An immediate observation is also that the sensitivity is highest for wavelengths close to the plasmon resonance. One particular point should, however, be highlighted. At 488 nm, a very slight increase of the extinction is observed a short time after excitation (arrow on the left side). This small effect is indeed predicted in the calculation in figure 6 as an indicator of the blue shift of the resonance as the refractive index of liquid water is reduced due to the increased temperature.

The resonance is damped after the vapor formation sets in, thus reducing the extinction also for the 488 nm trace. Therefore at 300 J m$^{-2}$ the fluence was sufficient to drive the system above the bubble formation threshold. At even higher fluence the vapor bubbles grow large enough to contribute to extinction by their scattering power. The extinction can again increase (arrow on the right side). The sensitivity here is highest at lower wavelength, which is already predicted by the bubble extinction curves in figure 1. In the results section, we will concentrate on the discussion of the perpendicular setup in order to understand the bubble formation process. At 532 nm probe wavelength the sensitivity is highest to detect the first signatures of bubble formation.
3. Results and discussion

The main goal of the following discussion of the x-ray results is to verify the calculations of heat transfer. Some of the data have been published before and will be critically reviewed. As already mentioned the femtosecond laser and x-ray experiment have the advantage that the femtosecond excitation provides perfect confinement during the excitation, separated time scales for the relaxation and sensitivity to the nanometric to atomic scale. The theoretical concept is therefore clear. Compared to that, the most common case of optical light probing is more ambiguous. The results of the x-ray experiment can therefore serve to gain confidence about the approach, which reduces the number of uncertainties when investigating the optical experiment. Indeed the next paragraph shows that there is excellent agreement between the data and calculation.

3.1. Femtosecond excitation

X-ray scattering provides several levels of structural information, which are separated in reciprocal space. The particle lattice is accessible via Bragg scattering (powder rings), which is a good indicator of the lattice expansion and thus particle lattice temperature. We have good indications that for sufficiently large particles (≃60 nm) the expansion coefficient does not differ strongly from bulk and that the energy balance of laser fluence versus lattice expansion is understood quantitatively [23, 27, 75]. Consequently, the heat transfer equations can be compared to the observed decay of the lattice expansion after the initial heating by femtosecond laser pulses. In figure 8, the measured expansion transients have been overlaid on the corresponding cooling curves as calculated by equation (8). The maximum temperature in the calculation has been scaled in amplitude, using the fact that the cooling calculations are not inherently dependent on the absolute strength of excitation or temperature.

The only parameter to adapt is the value of the interface conductivity, which has been set to the prior found value of 105 MW m$^{-2}$. Although for the smaller particles the scattering of the values is considerable (due to the error in the analysis of weak powder scattering) the agreement in time scales is still very good for all three particle sizes. This result is assuming regular heat transfer. The effects of temperature variable heat conduction, e.g. in the water phase, may add slight corrections to the scenario. Bubble formation is not yet included and indeed the excitation fluence was kept below the values needed for bubble nucleation [23, 28].

Bubble formation can be seen by three effects, namely the breakdown of heat transfer at longer time scales [27], the appearance of additional (weak) changes in the water scattering cross-section [24] and, most prominently, the appearance of modifications to the small angle cross-section (see figure 4). The two latter methods can be quantified in terms of bubble size and bubble morphology. The change in the small angle scattering signal allows detailed modeling of the bubbles with their size, density profile and interface sharpness [25]. These results serve as proofs that the bubble is indeed well defined with spherical shape, centered around the nanoparticles and developing a sharp interface already for the very early bubbles. However, a disadvantage of the SAXS data is that when the size dispersion of the bubbles increases, in particular during the collapse phase, the determination of the density profile around the gold particles will be dominated by ensemble effects, which precludes an in-depth study of the collapse phase. This collapse, meanwhile, is very interesting in terms of the hydrodynamics of nanoscale oscillating bubbles. Apart from the subtle difference in the interpretation of SAXS
Figure 8. Lattice temperature transients of different-sized gold particles as determined by the lattice expansion in time-resolved x-ray scattering. The lines on the top of the scatter data are the results from the calculation of the cooling equation (8). The temperature change of the adjacent water layer is taken from the heat transfer calculation (lower blue lines: bold for 100 nm, dashed for 36 nm and dotted for 14 nm). The data for 36 and 100 nm are taken from [23] and [27].

and liquid scattering, both methods deliver comparable data during the growth stage of the bubbles.

Figure 9 shows an example of bubble size evolution around two different particle sizes (9 and 36 nm diameter) at a laser fluence way above the bubble formation threshold derived via the liquid scattering change. A lifetime of the bubble around the small particle of 400 ps compares to a lifetime of 1.7 ns for the larger particles. Both can be well modeled with the Rayleigh–Plesset equation when only the final bubble size is varied to fit the measurement. The detailed evaluation for the 9 nm particles is described in [25]. The calculation suggests adiabatic dynamics for the obtained polytropic exponent. This is a reasonable assumption, considering the ultrafast motion of the bubbles. The predicted bubble collapse is followed by several rebounds, which, however, cannot be observed here due to the temporal dephasing of the bubble ensemble of slightly different sizes. This calculation also returns the pressure evolution within the bubbles, seen in the upper part of the figure. It starts with some 30 MPa at early times, which decays upon bubble expansion, to finally produce a spike of high pressure during collapse. The height of this spike depends critically on the damping and also sphericity of the bubbles, which remains to be detected directly. Investigations of sonoluminescence suggest extreme compression ratios with 500 MPa pressures for macroscopically (10 µm) collapsing bubbles [76].

Consequently, pulsed x-ray scattering allows for precise determination of the particle morphology, including possible shape modification and melting of the particles [77] and the bubble formation processes at nanometer length scale directly. Nevertheless, it represents a specialized technique not readily available for every investigation. The high temporal and size resolutions will also come to a limit when the sample heterogeneity reduces the accessible information about the level of individual particles. Here, scalar methods may be competitive.
3.2. Nanosecond excitation

Laser absorption spectroscopy [78] or scattering [22, 79] is one possible scalar method, as the measured quantity has no momentum and therefore spatial resolution. The scalar property of the sample, transmission or scattering, is indirectly sensitive to the nanoscale processes via the interaction cross-section in a non-trivial way as sketched in section 2.5. For the analysis of the energy scale of the excitation we concentrate on the early signals right within or right after the pump laser pulse.

At these time delays the highest signals are seen and should be most sensitive for the lower fluences and small bubbles. Consequently, this analysis procedure allows us to achieve the lowest possible detection limit for the nucleation process. In a typical experiment, a large number of time traces with variable laser fluence are averaged, bundled by similar fluence values. In figure 10, the right side, such an extinction change $\epsilon(\Phi)/\epsilon(0)_{t=5\text{ ns}}$ is shown as a function of laser fluence. It is a typical curve for larger particles, where the initial bleaching is well developed. A calculation of the extinction as a function of bubble size is drawn on the left side. The interpretation assumes that the extinction first drops at increasing fluence (increasing maximal bubble size) due to the decoupling of the SPR from the dielectric surrounding. The calculation shows that this occurs within the first 20 nm of bubble shell thickness to reach a minimum at about 70 nm bubble diameter. At larger laser fluence, the bubble increases in size and enhances scattering as a positive contribution to the extinction. For even larger bubbles the initial structure of the particle will not matter any more and the extinction will strongly increase. This prediction is indeed found in the measurement when assuming that the maximum bubble
radius should scale with the laser fluence above the nucleation threshold. Two lines (apart from the zero line) are drawn in figure 10, the right side: a dashed line, which marks the maximum possible extinction change without vapor formation, and the lower (red) line, which gives the minimum extinction value at a developed bubble. The nucleation threshold is therefore located at the crossing of the dashed line (arrow) where indeed a steep change of the extinction starts.

The measured extinction function versus laser fluence can also be inverted to yield the bubble size when using the calculated relation between the size and extinction change. Unfortunately, the observed minimum extinction does not reach the absolute values of the predicted reduction of extinction (solid red line). This might stem from a slight overestimation of particle density together with macroscopic transmission losses (thermal lensing in one direction). Therefore, we stretched the vertical scale slightly to match the predicted magnitude (the error in bubble size should be small, as the curve still possesses a zero crossing, where bubble scattering equals the extinction loss at the SPR). Both branches of positive and negative slope have been inverted independently. Indeed a smooth curve is obtained in figure 11(A). At the vanishing slope of the calibration curve the inversion of the data is certainly worst, but a consistent picture of the bubble sizes can be achieved. Quite a similar picture to the femtosecond excitation is observed (figure 11(B)), where for larger particles a sublinear increase of bubble size with fluence is also observed. A rough estimation of the amount of deposited energy in a bubble of given size would scale with the bubble volume, i.e. with an exponent of 1/3 with size. Consequently, a power law behavior should be expected if a constant fraction of the energy is deposited in bubbles of comparable thermodynamic parameters.

We observe an exponent of about 0.45, which is higher than 1/3. It may be explained by a larger amount of dissipated energy for smaller bubbles due to better heat conduction in the early phase of the bubble formation. On the other hand, optical limitation, i.e. a change of the absorption coefficient already during the laser irradiation, would result in the opposite, namely that energy is less efficiently absorbed by the particle for higher fluences, where bubble formation is more rapid.
Figure 11. (A) Maximum bubble radius of around 60 nm particles excited at 355 nm with nanosecond pulses as determined by inverting the transmission change from figure 10 with the calculated change. Data around 800 are discontinuous because of the vanishing slope of the calculated relation. (B) Maximum bubble size of 36 nm particles excited at 400 nm with femtosecond pulses directly determined by SAXS.

3.3. Comparison of fluence behavior with calculations

Finally, the above measurement of the optical extinction change and semi-quantitative determination of bubble sizes allows us to verify the nucleation threshold for bubble formation. First of all, in the femtosecond experiment with the x-ray probe the nucleation thresholds have been determined with high sensitivity. The results have been reported in [23]. The general observation that nucleation is only observed far above the boiling point of water is confirmed also by optical measurements of larger objects, including gold particles [15, 17]. The estimation of the threshold is best compatible with a spinodal process, where explosive evaporation sets in once the temperature of the water shell around the particles surpasses the kinetic barrier for nucleation (spinodal line) [80]. Indeed the data shown in figure 12 are explained by a nucleation temperature of 85% of the critical temperature of water [23].

For the nanosecond case a similar derivation of the nucleation threshold can be done. Here we do not have a direct measure of the particle temperature, but rather rely on the calculation of the temperature rise according to the model explained in section 2.2. This connects laser fluence to particle temperature and also water temperature close to the particle surface.

The threshold fluence in the optical experiments is then derived by the intersection of the measured extinction change with the calculated value for liquid water at high temperature (shown in figure 10 as a dashed horizontal line). One should, however, keep in mind that the level of transmission change can only be given with precaution for water temperatures above the boiling point. During the excitation, one cannot assume an isobaric situation around the particles, so that the equation of state of the water shell is difficult to calculate [81]. Within these limitations, the agreement between the calculation of a spinodal process and the derived thresholds in figure 13 is fair, given that other groups have found discrepancies of two orders of magnitude.

The measured threshold in figure 13 is in agreement with the prediction of a spinodal process, in particular for larger particle sizes. The small deviation at larger fluence may be attributed to systematic errors in determining the threshold in the optical probing. In general the
Figure 12. Bubble formation threshold as a function of particle diameter for femtosecond laser excitation and x-ray probing. The dashed line stands for a threshold estimation at 85% of the critical temperature of water. The data points are taken from [23].

Figure 13. Bubble formation threshold as a function of particle diameter for nanosecond laser excitation. The red symbols denote probing with 633 nm light. The full line represents the calculated threshold for a spinodal decomposition analogous to the femtosecond case. The femtosecond threshold is also shown as a line with squares.

agreement here is satisfactory. An interesting deviation is seen consistently for small particles for both probe wavelengths. The 18 nm particles seem to nucleate at clearly lower fluence than expected. Although no indications were found, one might speculate that particle clustering could lower the threshold already if the heat affected zones of individual particles start to overlap. At these distances a change of the extinction due to plasmon coupling may not yet occur. Indeed as the atom concentration in the used samples is constant the particle number density is highest for the smallest particles. We believe that elastic effects, such as negative pressure [81], should matter more for the larger particles due to the smaller divergence of the pressure wave.
On the other hand, small particles melt at lower temperature, which may also be seen as a plasmon bleaching and may compete with the interpretation at decoupling of the SPR from the water phase. A quantitative analysis, however, shows that with a temperature drop across the interface to 42% of the particle temperature for 10 nm diameter particles, this temperature should be at about 660 K above room temperature at the spinodal point of water, which is still below the size-dependent melting point. The melting point depression should matter below 7–8 nm diameter \[82\], which is smaller than the measured particle sizes. Surface melting might also contribute to SPR damping \[39, 83\], which is, meanwhile, highly questionable to happen on ultrafast time scales.

4. Conclusions

The bubble formation process in gold nanoparticle suspensions has been studied with both femtosecond and nanosecond laser excitations. By probing the nanoscale structural changes with pulsed x-rays the structure evolution of the particles as well as the surrounding vapor layer can be directly resolved and the threshold for formation determined. The temperature close to the particles suggests that this process is a homogeneous nucleation process, crossing the spinodal line of water. Qualitatively the same behavior is found for the nanosecond excitation, where the threshold fluence also corresponds to a prediction of spinodal decomposition. The solution of the heat transport equation taking into account the TIR is a particularly useful tool.

We would like to state that optical absorption spectroscopy is, in general, capable of resolving the main steps of structure formation, such as SPR bleaching due to decoupling of the particle from the liquid and enhanced scattering of light if the bubbles approach the optical wavelength.

Comparing the absolute threshold for femtosecond and nanosecond excitation, one may find it surprising that they differ only by a factor of 2 for medium-size particles and even less for the larger particles. This behavior is, nevertheless, easily explained by the length scale of heat diffusion within the water phase. While the deposition of energy within the nanoparticles completes within picoseconds, the transfer across the interface and the bulk diffusion are much slower. The transport of heat away from the nanoparticles proceeds within more than 1 ns for 36 nm diameter \[23\]. Therefore within this time the heat accumulates within a narrow region of some 50 nm, still available for reaching temperatures close to the spinodal line. While the laser fluence is the adequate parameter that defines heating in the limit of short pulses, in general for long pulses the peak intensity is more adequate. Here there is only this factor of 2 difference; thus the fluence is still a meaningful parameter for the (few) nanoseconds case.

As a consequence, it is now clear that the time scale of heat diffusion is relevant for judging the bubble formation as a function of pulse length. Highest efficiency for bubble formation will be expected as long as the laser pulse remains around this nanosecond limit. Judging the action of laser heating in applications such as phototherapy or diagnostics can indeed be done in a quantitative manner as the thermal model is shown to be very reliable.

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