Photo-acoustic response of a single 430 nm gold particle: semi-analytical model and picosecond ultrasonics measurements

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Abstract. A semi-analytical model is developed to calculate the elastic response of a gold submicronic particle embedded in a silica thin film, following a subpicosecond optical excitation. Real and imaginary parts of the transient reflectivity are then derived, accounting for elasto-optic contribution in the particle and in the matrix, as well as particle and film surface motion. The major contribution comes from the particle surface displacement. Picosecond ultrasonics measurements in a reflection configuration on a single 430 nm diameter gold particle confirm the conclusions of the model and demonstrates the suitability of this technique to investigate the opto-acoustic response of such submicronic particles.

1. Introduction
A growing interest is shown in the study of elastical, mechanical and thermal properties of micrometric and nanometric structures, partly due to the possibility to design local opto-acoustic transducers with acoustic frequencies in the sub-THz range. Optical methods have turned out to be powerful for investigating the acoustical response of metal or semiconductor nanoparticles.[1, 2] Recently, van Dijk et al. reported on the ultrafast response of a single gold nanoparticle, avoiding an inhomogeneous broadening of the response due to measurements performed on an ensemble of particles.[3]

Up to now, pump-probe experiments were performed measuring the modification of the transmission of the particle. Here, we develop a semi-analytical model which predicts the transient reflectivity of the particle following a subpicosecond optical excitation. We then report on pump-probe experiments in a reflection configuration on a single gold particle of 430 nm diameter. We demonstrate that the major contribution to the transient reflectivity comes from the displacement of the particle-matrix interface.

2. Semi-analytical model
A gold spherical particle (radius $a$) embedded in a silica thin film is considered. The film is actually deposited onto the surface of a silica thick plate: in the following, we assume a semi-infinite medium, considering only the plane interface between thin film and air, located at a distance $d$ of the center of the particle. The geometry and the notation are defined in Fig. 1.
spherical coordinates. After a time Fourier Transform, this equation can be written:

\[ \partial_t^2 \phi - \frac{2}{r} \partial_r \phi - k_i^2 \phi = 0, \]  

(1)

where \( \phi \) is the Fourier Transform of \( \phi \). \( k_i = \omega / c_i \) is the longitudinal wavevector in the medium \( i \), characterized by a longitudinal sound velocity \( c_i \). For a gold particle embedded in a silica matrix, \( c_p = 3240 \text{ m.s}^{-1} \) and \( c_m = 5850 \text{ m.s}^{-1} \). [5, 6]

Solutions of Eq. (1) can be expressed with the help of spherical Bessel functions. In order to avoid a divergence at \( r = 0 \), the solution inside the particle is related to the spherical Bessel function of the first kind \( j_l \), with \( l \) the angular momentum. On the other hand, in the matrix, the radiation of the acoustical field far from the particle must vanish. This condition is satisfied by the spherical Bessel function of the third kind \( h_{l+1}^{(1)} \). [5] In both cases, the fundamental breathing mode corresponds to \( l = 0 \):

\[
\begin{align*}
\phi_p(r) &= A_p j_0(k_p r) \\
\tilde{u}_p(r) &= -A_k j_1(k_p r)
\end{align*}
\]

where \( A_p \) and \( A_m \) are two constants to be determined with the boundary conditions, which consist of the continuity of both displacement \( \tilde{u} \) and stress \( \tilde{\sigma} \) at the particle-matrix interface. These two conditions can be written \( \tilde{u}_m(a) = \tilde{u}_p(a) \) and \( \tilde{\sigma}_m(a) = \tilde{\sigma}_p(a) + \tilde{\sigma}^{th} \) where \( \tilde{\sigma}^{th} \) is the thermal stress generated by the pump pulse at the particle-matrix interface. In the following, we neglect the thermal diffusion and we assume an instantaneous optical excitation, leading to \( \tilde{\sigma}^{th} = -3B \alpha \eta_{abs} H_{\omega}/V C_l \), where \( B, \alpha, \) and \( C_l \) refer to the bulk elastic modulus, the linear dilatation coefficient and the heat capacity of gold, respectively. \( \eta_{abs} \) is the energy absorbed by the gold particle of volume \( V \) and \( H_{\omega} \) is the Fourier component at the circular frequency \( \omega \) of the Heaviside function.

The Fourier Transform \( \Delta \tilde{\sigma}/r_0 \) of the transient reflectivity of the particle for a given probe wavevector \( k \) is then calculated taking into account optical index changing in both the particle and the matrix, as well as particle and film surface displacements:[7]

\[
\frac{\Delta \tilde{\sigma}}{r_0} = -2 j k t_0^{-1} \int_0^a \frac{\partial}{\partial \eta} \tilde{\eta}_p(a - r') e^{2 j k n_p r'} dr' \\
+ \left[ e^{-2 j k n_a (r' - a)} + r_p^{+2} e^{2 j k n_a (r' - a)} \right] dr'.
\]
where $t_i$ and $r_i$ are respectively optical transmission and reflexion coefficients at interfaces ($i = p$: particle-matrix and $i = 1$ matrix-air interfaces). Exponents + and − refer to the propagation direction of the probe beam, respectively toward and outward the particle center. $\tilde{\eta}_{p,m}$ are the Fourier components of the strain and $\partial n/\partial \eta|_{p,m}$ are the photoelastic constants at the probe wavelength. At the equilibrium, $r_0 = r_0^+ \exp[2jkn_m(d - a)] + t_1^+ r_1^-$. An inverse Fourier Transform yields the temporal dynamics of $\Delta r/r_0$.

The particle and the film surface motion are taken into account by the first and second terms in Eq. (2), respectively. The elasto-optic contribution due to the interaction of the probe beam with the acoustical wavefronts propagating in the particle and in the matrix refer to the third and fourth term, respectively. Each contribution is indicated with a thick red line in Fig. 1.

The detection scheme used in picosecond ultrasonics experiments can be sensitive either in reflectometry to the real part of $\Delta r/r_0$ or in interferometry to its complex value.[7] In the following, we will therefore present the calculated dynamics of both $\text{Re}(\Delta r/r_0)$ and $\text{Im}(\Delta r/r_0)$.

Calculations are carried out for a 430 nm diameter gold particle embedded in a silica thin film, the fundamental breathing mode of this particle being at the same frequency as in experimental results presented below. The magnitude of the acoustical source is related to the energy absorbed by the particle. For a 395 nm pump wavelength, the Mie absorption cross-section of a 430 nm diameter gold sphere is about $1.5 \times 10^5 \text{ nm}^2$. Therefore, for a 7 pJ pump pulse and a 1 µm beam waist in the sample plane, one obtains $q_{\text{abs}} = 650 \text{ fJ}$. The calculated dynamics of the acoustical component of both the real $[\text{Re}(\Delta r/r_0)]$ and the imaginary part $[\text{Im}(\Delta r/r_0)]$ are displayed in Figs. 2(a) and 2(d), respectively.

![Figure 2](image_url)

**Figure 2.** (a) Dynamics of the acoustical component of $\text{Re}(\Delta r/r_0)$ for $d = 1400 \text{ nm}$. (b) Spectrum of the calculated signal displayed in (a). (c) Zoom on the first oscillations: $\text{Re}(\Delta r/r_0)$ (continuous line) and contribution of the first term of Eq. (2) (vertically shifted dashed line). (d) Dynamics of the acoustical component of $\text{Im}(\Delta r/r_0)$ for $d = 1400 \text{ nm}$. (e) Dynamics of $\text{Re}(\Delta r/r_0)$ measured on a single gold particle. (f) Spectrum of $\text{Re}(\Delta r/r_0)$. (g) Zoom on the first oscillations.

Acoustical vibrations of the particle result into strong oscillations in both $\text{Re}(\Delta r/r_0)$ and $\text{Im}(\Delta r/r_0)$, with a pronounced disymetry in the first hundreds of picoseconds [Fig. 2(c)]. For a given excitation, the magnitude of the imaginary part of $\Delta r/r_0$ is about five times greater than its real counterpart. The major contribution comes from the displacement of the particle-matrix interface, i.e. the first term in Eq. (2), displayed as a blue dashed line in Fig. 2(c). This dynamics is similar to the dynamics of the displacement previously calculated, as well as to the findings of Dufey and Fischer[8], who calculated the dynamics of the particle radius following a sudden excitation. Well defined peaks are present in the spectrum: the fundamental breathing
mode is at 7 GHz, while the two first harmonics are at 15 GHz and 23 GHz [cf. Fig. 2(b)].

3. Picosecond ultrasonics experiments
Experiments were performed with the usual picosecond ultrasonics setup.[9] A laser beam made of 100 fs pulses at 790 nm is splitted into two parts: the pump pulse (frequency doubled at 395 nm, 7pJ) and the probe pulse (790nm) are focused onto the sample through the same microscope objective (X50). The pump-probe cross-correlation in the focal plane is about 1 μm. A motorized delay line allow to create pump-probe delay up to 12 ns. The intensity of the reflected probe beam is then measured with a photodiode. The modulation of the pump beam amplitude at 330 kHz and the use of a lock-in amplified detection allow a sensitivity of about $10^{-7}$ for $\Delta r/r_0$. A reflection configuration was considered here, measuring the real part of $\Delta r/r_0$.[7] The fabrication method of submicron gold particles was the one proposed by Wang and Halas.[10] Spin-coating on a silica substrate was then used to spread these particles into a silica gel. A one day drying led to a few μm thin film.

Figure 2(e) presents the dynamics of $\text{Re}(\Delta r/r_0)$ resulting from the excitation of a single gold particle. The sharp peak at zero delay (ultrafast heating of the electron gas) and the slowly decaying background (thermal diffusion) are not predicted by the model previously detailed. However, strong oscillations with a disymetry in the first hundreds of picoseconds [cf. Fig. 2(g)] are clearly visible. The frequencies of the detected acoustical modes $[7.0 \pm 0.1 \text{ GHz, } 14.5 \pm 0.5 \text{ GHz and } 23.0 \pm 0.5 \text{ GHz, cf. Fig. 2(f)}]$ are in very good agreement with the frequencies predicted for the fundamental breathing mode of a 430 nm diameter gold particle and for its harmonics, as displayed in Fig. 2(b).

4. Conclusion
In conclusion, a semi-analytical model was developed to predict the transient reflectivity of a single submicronic gold particle embedded in a silica thin film, following a subpicosecond optical excitation. The major contribution of the displacement of the particle-matrix interface was confirmed with picosecond ultrasonics measurements in a reflection configuration on a single 430 nm diameter gold particle. Calculations have also showed that for a given excitation, the magnitude of $\text{Im}(\Delta r/r_0)$ is about 5 times the one of $\text{Re}(\Delta r/r_0)$. Pump-probe measurements in an interferometry configuration, which allows the determination of both $\text{Re}(\Delta r/r_0)$ and $\text{Im}(\Delta r/r_0)$[7], will lead to a higher sensitivity.

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References
[1] Verma P, Cordts W, Irmer G and Monecke J 1999 Phys. Rev. B 60 5778–5785
[2] Del Fatti N, Voisin C, Chevy F, Vallée F and Flytzanis C 1999 J. Chem. Phys. 110 11484–11487
[3] van Dijk M A, Lippitz M and Orrit M 2005 Phys. Rev. Lett. 95 267406
[4] Wright O B and Gusev V E 1996 Physica B 219-220 770 – 772
[5] Voisin C, Christofilos D, Fatti N D and Vallée F 2002 Physica B: Condensed Matter 316-317 89 – 94
[6] Love W F 1973 Phys. Rev. Lett. 31 822–825
[7] Perrin B, Bonello B, Jeannet J C and Romatet E 1996 Prog. Nat. Sci. 56 444
[8] Dufey F and Fischer S F 2007 J. Phys. Chem. C 111 3868–3872
[9] Thomsen C, Granh H T, Maris H J and Tauc J 1986 Phys. Rev. B 34 4129–4138
[10] Wang H and Halas N 2008 Adv. Mater. 20 820–825