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Electron-phonon effects on the photoacoustic response of gold core-silica shell nanoparticles : from the linear regime to nanocavitation

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Abstract

Coating gold nanostructures with a silica shell has been long considered for biomedical applications including photoacoustic imaging. Recent experimental and modeling investigations reported contradicting results concerning the effect of coating on the photoacoustic response of gold nanostructures. Enhanced photoacoustic response is generally attributed to facilitated heat transfer at gold/silica/water system. Here we examine the photoacoustic response of gold core-silica shell nanoparticles immersed in water using a combination of two-temperature model and hydrodynamic phase field simulations. Of particular interest here is the role of the interfacial coupling between gold electrons and silica shell phonons. We demonstrate that, as compared to uncoated nanoparticles, photoacoustic response is enhanced for very thin silica shells 5 nm and short laser pulses, but for thicker coatings the photoacoustic performance are generally deteriorated. We extend the study to the regime of nanocavitation and show that the generation of nanobubbles may also play a role in the enhanced acoustic response of core-shell nanoparticles. Our modeling effort may serve as guides for the optimization of the photoacoustic response of heterogeneous metal-dielectric nanoparticles.

I. INTRODUCTION

Gold nanoparticles are widely employed in photoacoustic imaging because of their strong ability to absorb light and the possibility to convert efficiently light in sound through expansion and heat transfer to the environment [1]. As compared with light scattering and ultrasound scattering, photoacoustic imaging combines the advantage of the sensitivity of gold nanostructures light absorption with the weak scattering of sound waves in biological media enabling signal propagation over centimeter length scales [2, 3]. At the core of this technique is the ability of metallic nanoparticles to convert light in heat, realizing controlled nanoscale sources of heat [4–6]. The nanoparticle resonance wavelength may be shifted to the near infrared region where tissue presents very low absorption [7].

Although bare gold nanostructures offer clear benefits for photoacoustic applications, they suffer from limitations which restrict their wide use in biological media. In particular, gold surfaces are not chemically stable in the presence of biomolecules [8]. Also, the interaction between a laser and gold nanoparticles may yield nanoparticle melting and reshaping [9, 10]. To overcome these limitations it has been long considered to coat gold nanostructures with a dielectric shell [11, 12]. Among the different materials, silica turns out to be a popular choice, because of its chemical inertia, biocompatibility and the wide range of possibilities to functionalize silica surfaces [8]. In addition, silica shell may enhance the nanoparticle stability and delay melting [13–15].

The photoacoustic response of silica coated nanoparticles has been investigated in the past decade by several groups [16–22]. Both experimental and modeling studies reported contradictory results concerning the enhancement of the photoacoustic signal of core-shell nanoparticles as compared with bare gold nanoparticles in water. In particular, Chen et al. reported a threefold increase of the photoacoustic response of silica-coated gold nanorods as compared with the uncoated nanorods [16]. This enhancement is thought not to originate from the change of the plasmonic absorption cross-section, but rather to facilitated heat transfer introduced by the silica shell. This interpretation is, at least qualitatively, consistent with time-resolved spectroscopy experiments demonstrating faster heat transfer for gold nanoparticles coated with thin silica shells and immersed in water as compared with bare gold nanoparticles [23]. Faster heat transfer is also found in two-temperature model simulations of heat transfer across gold nanoparticles embedded in very thin silica shell [24]. Facilitated

heat transfer is, in this case, ascribed to electron-phonon processes taking place at the interface between gold and the silica shell. The change of Kapitza resistance due to the presence of the silica shell plays also an important role in photoacoustic enhancement [16, 20].

Recent experimental and numerical works concluded, however, at a deterioration of the photoacoustic signal for coated gold nanostructures [21, 22]. These observations are consistent with earlier heat transfer dynamics studies from gold nanorods [25] showing heat transfer slowing down by silica shell. Further, numerical simulations by Pang et al. concluded that the Kapitza resistance has only a mild effect on the photoacoustic response [21].

The relative enhancement or deterioration of photoacoustic signal should be highly dependent on the shell thickness and also on the pulse duration pulse. Indeed, very thin silica shells and short pulse durations yield faster heat transfer to the environment [19, 24]. By the way contrast, it is clear that thick shells should slow down heat transfer because of the low thermal conductivity of silica, resulting in photoacoustic decrease [21, 25]. It is the purpose of this article to study numerically the transition between thin silica shells and thick ones for picosecond and nanosecond laser pulses.

Recent computational studies [19–21] predicted the photoacoustic response of silica coated nanoparticles by considering a single temperature field to describe heat transfer in these composite systems. This one temperature description is a fair approximation for nanosecond pulses, but at sub picosecond time scales, electron-phonon processes neglected in the one temperature description become important. Indeed, we recently showed the role played by electron-phonon processes on the heating kinetics of colloidal gold-core silica shell nanoparticles [24]. In the context of nanoscale thermal transport, several experimental studies investigated heat transport at metal/dielectric interfaces, at picosecond time scales. Recent transient thermoreflectance experiments probing heat transfer from a gold film to silicon or silica substrates [26–28] concluded on the existence of a direct electron-substrate energy transfer, resulting in an enhanced thermal boundary conductance [29]. This direct electron-phonon coupling energy channel has been predicted theoretically twenty years ago [30–33], although the exact nature of this coupling is still an open issue. One important consequence is that thermal transport at metal-non metal interfaces is enhanced when such electron-phonon conductance is present [29].

In this work, we compute theoretically the photoacoustic response of silica coated nanoparticles illuminated by short duration laser pulses by taking into account electron-

phonon processes inside the nanoparticles. To this end, we employ numerical simulations based on the combination of the two temperature model [34, 35] and phase field hydrodynamics simulations [36]. Two temperature model can capture the coupled evolution of the electronic and phonon temperatures in metallic systems following laser excitation. In addition, they have been shown to describe accurately the heat transfer kinetics down to nanoscale sizes and for subpicosecond time scales for moderate to strong excitation.

Another regime that we touch upon is the nanocavitation generation which occurs for strong laser pulses. It is known, indeed, that nanocavitation around illuminated gold nanoparticles yields enhanced photoacoustic response [37–40]. However, few studies have considered the effect of silica coating on nanocavitation and on the subsequent photoacoustic response [41]. Let us mention, however, recent time resolved spectroscopy experiments which concluded that coating delays the onset of cavitation [25], but these effects are not understood from a theoretical point of view. The remainder of this article is organized as follows. Section. II introduces the model. Numerical results are presented and discussed in Sec. III. A summary and perspectives are given in Sec. IV.

II. MODEL

Our model is a combination of the two-temperature model [34, 35] for the nanoparticle dynamics with a phase field description of the water dynamics. We first present the equations governing the thermal relaxation of the core-shell nanoparticle before introducing the equations supposed to ruling the thermal dynamics of water.

A. Nanoparticle

The system we investigate is a core-shell nanoparticle immersed in water and irradiated by a laser pulse, as represented in (Fig. 1.a). In all the following, we concentrate on a gold core-silica shell nanoparticle and gold nanoparticles for the sake of comparison. After pulsed illumination, thermal relaxation around the nanoparticle involves different channels, as summarized in Figure 1.b. The metal free electrons absorb instantaneously the laser energy, causing a rapid increase of the electronic temperature. This excess energy is then transferred to the silica shell by two different channels. The first channel is a direct coupling

between gold electrons and silica phonons and occurs at the core/shell interface through the electron-phonon thermal conductance σ_{es} . The second channel is an indirect coupling which involves electron-phonon energy exchange inside the gold core, quantified by the coupling factor G , and then phonon-phonon thermal coupling at the core/shell interface, quantified by the conductance σ_{ps} . With the heat diffusing in the shell, a thermal flux proportional to the phonon-water conductance σ_{sw} is induced across the shell/water interface, allowing the energy to diffuse in the infinite water reservoir. In the case of a bare gold nanoparticle, Fig. 1.c depicts the different energy channels. They involve, in particular, a thermal flux across the metal/water interface through the interfacial phonon-phonon conductance σ_{pw} .

For the core-shell nanoparticles, the evolution of the different temperatures is supposed to be governed by the following set of equations :

$$V_c c_e \frac{\partial T_e(t)}{\partial t} = -V_c G (T_e - T_p) - S_c \sigma_{\text{es}} (T_e - T_s(R_c, t)) + \mathcal{P}(t), \quad (1)$$

$$V_c c_p \frac{\partial T_p(t)}{\partial t} = V_c G (T_e - T_p) - S_c \sigma_{\text{ps}} (T_p - T_s(R_c, t)) \quad (2)$$

$$c_s \frac{\partial T_s(r, t)}{\partial t} = k_s \nabla^2 T_s, \quad (3)$$

Here, T_e , c_e denote the gold electronic temperature and heat capacity respectively; T_p and c_p denote the gold phonon temperature and heat capacity, T_s , c_s and k_s the silica temperature, heat capacity and thermal conductivity and T_w , c_w and k_w the water temperature, heat capacity and thermal conductivity. While r is the radial distance, R_c , S_c and V_c are the radius, surface and volume of the nanoparticle core. $R = R_c + d$, S and V are the same quantities for the entire nanoparticle, including the shell of thickness d , whose volume is $V_s = V - V_c$.

It is important to realize that, in the previous set of equations eq. 1 and eq. 2, we have assumed uniform temperatures for both the electronic and metal phonon degrees of freedom, as we have already shown that heat diffusion inside the metal core has little effect on the nanoparticle thermal relaxation following the laser excitation [24].

In the following, we consider for simplicity a square pulse characterized by the power : $\mathcal{P}(t) = \bar{P} \Theta(t_{\text{pul}} - t)$, with $\bar{P}$ the average laser power, Θ the Heaviside function and t_{pul} the pulse duration. The average power $\bar{P}$ is simply related to the laser fluence F and nanoparticle absorption cross-section $\sigma_{\text{abs}}(\lambda)$, through : $\bar{P} = \sigma_{\text{abs}}(\lambda) F / t_{\text{pul}}$, where σ_{abs} is described here

by Mie-theory [5, 42] for the spherical nanoparticles of interest here.

FIG. 1. Heat transfer from a core-shell nanoparticle and gold nanoparticle heated by a laser pulse. G is the coupling constant between electrons and phonons in the metal. σ_{es} , σ_{ps} , σ_{sw} and σ_{pw} are the interfacial conductances at the electron/silica, phonon/silica, silica/water and phonon/water interfaces respectively.

In addition to Eqs. (1)-(3) describing the temporal evolution of temperatures, the continuity of the heat flux across an interface implies the following boundary conditions at the core/shell interface $r = R_c$ and at the the shell/water interface $r = R_c + d$:

$$-k_s \nabla T_s(R_c, t) = \sigma_{es} (T_e - T_s(R_c, t)) + \sigma_{ps} (T_p - T_s(R_c, t)), \quad (4)$$

$$\begin{aligned} -k_s \nabla T_s(R, t) &= \sigma_{sw} (T_s(R, t) - T_w(R, t)) \\ &= -k_w \nabla T_w(R, t). \end{aligned} \quad (5)$$

Finally, as regards initial conditions, all the temperatures are assumed to be at room temperature T_0 .

The equations for the bare gold nanoparticle can be written in a similar manner and are

given here for the sake of completeness :

$$V_c c_e \frac{\partial T_e(t)}{\partial t} = -V_c G (T_e - T_p) + \mathcal{P}(t), \quad (6)$$

$$V_c c_p \frac{\partial T_p(t)}{\partial t} = V_c G (T_e - T_p) - S_c \sigma_{pw} (T_p - T_w(R_c, t)) \quad (7)$$

$$= -k_w \nabla T_w(R_c, t). \quad (8)$$

quantity	electron	phonon	silica
k (W m ⁻¹ K ⁻¹)	320.0	3.0	1.37
c (MJ m ⁻³ K ⁻¹)	0.0197	2.35	1.01

TABLE I. Thermal conductivity k and heat capacity c characterizing the different channels at $T_0 = 300$ K.

quantity	value	Reference
G (MW m ⁻³ K ⁻¹)	2.5×10^{10}	[43]
σ_{ps} (MW m ⁻² K ⁻¹)	141	[29]
σ_{sw} (MW m ⁻² K ⁻¹)	150	[44]
σ_{pw} (MW m ⁻² K ⁻¹)	139	[45, 46]

TABLE II. Electron-phonon coupling constant G and thermal boundary conductances.

We have listed in Tabs. I and II the parameters relevant for the gold-silica core-shell nanoparticles. If not otherwise mentioned, all properties are taken at a temperature $T_0 = 300$ K.

There are three quantities, however, for which it is essential that the temperature dependence is taken into account, namely the electronic heat capacity c_e , the interfacial electron-phonon conductance at the core/shell interface σ_{ep} and the coupling factor G . The interfacial electron-phonon conductance at the core/shell interface can be written as :

$$\sigma_{es} = A_{es} + B_{es} T_e \quad (9)$$

with the constant $A_{es} = 96.1 \text{ MW m}^{-2} \text{ K}^{-1}$ and $B_{es} = 0.18 \text{ MW m}^{-2} \text{ K}^{-2}$ [26]. For the temperature dependence of the electronic heat capacity and coupling factor, we use results of ab-initio calculations [43]. The resulting quantities are expressed using polynomial fits of the ab-initio calculations in the form described in the Appendix V.

B. Water dynamics

The dynamics of the fluid is described by a hydrodynamic phase field model based on the generic mass, momentum and energy conservation equations:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (10)$$

$$m\rho(\mathbf{r}) \left(\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} \right) = -\nabla \cdot (\mathbf{P} - \mathbf{D}), \quad (11)$$

$$m\rho(\mathbf{r})c_v(\mathbf{r}) \left(\frac{\partial T_w}{\partial t} + \mathbf{v} \cdot \nabla T_w \right) = -l(\mathbf{r})\nabla \cdot \mathbf{v} + \nabla \cdot (k_w(\mathbf{r})\nabla T_w) + \mathbf{D} : \nabla \mathbf{v}, \quad (12)$$

In these equations, $\rho(\mathbf{r})$ stands for the molecular density at a given position $\mathbf{r}$ outside the nanoparticle, $T_w(\mathbf{r})$ and $\mathbf{v}(\mathbf{r})$ are respectively the temperature and the velocity field inside the fluid. Due to the thermal gradient generated by the nanoparticles, properties like the thermal conductivity of the fluid $k_w(\mathbf{r})$, the specific heat $c_v(\mathbf{r})$ and the Clapeyron coefficient $l(\mathbf{r})$ have a spatial dependence that we emphasize in equation (12). m is the molecular mass and the two tensors $\mathbf{P}$ and $\mathbf{D}$ stand respectively for the pressure tensor and the dissipative stress tensor. The dissipative stress tensor takes the usual newtonian form:

$$D_{\alpha\beta} = \eta(\partial_\alpha v_\beta + \partial_\beta v_\alpha) + \left(\mu - \frac{2\eta}{3} \right) \nabla \cdot \mathbf{v} \delta_{\alpha\beta},$$

with η and μ the shear and bulk viscosities respectively, and $\delta_{\alpha\beta}$ is the Kronecker symbol. We shall assume here $\mu \simeq 5\eta/3$ [47], as it is the case for hard-sphere fluids. Since the viscosities may differ in the liquid and the vapor phases, we use a linear prescription for their local expression:

$$\eta(\mathbf{r}) = \eta_{\text{vap}} + \frac{\rho(\mathbf{r}) - \rho_{\text{vap}}}{\rho_{\text{liq}} - \rho_{\text{vap}}} (\eta_{\text{liq}} - \eta_{\text{vap}}),$$

where the subscripts “vap” and “liq” refer to the bulk values at 297 K referenced in Table III.

The same linear relationship with the density will be used for the thermophysical coefficients including the thermal conductivity λ and the specific heat c_v .

Due to the inhomogeneity of the system, and the possible formation of interfaces, the pressure tensor is not necessarily isotropic. A generic prescription for $\mathbf{P}$ is given by the Korteweg expression, that accounts for interfacial effects:

$$P_{\alpha\beta} = \left[P_{\text{bulk}} - w\rho\Delta\rho - \frac{w}{2}(\nabla\rho)^2 \right] \delta_{\alpha\beta} + w\partial_\alpha\rho\partial_\beta\rho,$$

Coefficient	Value at ρ_{liq}	Value at ρ_{vap}	Unit
λ	0.606	0.019	$\text{W m}^{-1}\text{K}^{-1}$
η	$8.98 \cdot 10^{-4}$	$9.9 \cdot 10^{-6}$	Pa s
c_v	4.13	1.44	$\text{kJ kg}^{-1}\text{K}^{-1}$

TABLE III. Thermophysical parameters for water at its saturation densities.

where P_{bulk} is the bulk pressure, that controls the phase behavior of the fluid, and serves to calculate the Clapeyron coefficient :

$$l = T_w \left(\frac{\partial P_{\text{bulk}}}{\partial T} \right)_{\rho}$$

w is a parameter related to the liquid-vapor interface thickness and controls the value of the surface tension. We set $w = 1.16 \cdot 10^{-20} \text{ J m}^5/\text{mol}^2$ to reproduce water surface tension at room temperature $\sigma_{LV} = 72 \cdot 10^{-3} \text{ J m}^{-2}$.

The equations (10-12) are quite generic and combined with the fluid equation of state, they form the basis of conventional diffuse interface approaches [48], that have been applied succesfully to describe boiling at the nanoscale [49, 50].

The specificity of the present approach is to describe the properties of water in a more quantitative way. To extend previous studies using the van der Waals thermodynamic model for the fluid [36, 40, 49–52], we shall make use of a better thermodynamic model specially designed for water: this model of Jeffery and Austin [53]. Although based on a van der Waals description, the model includes temperature dependences of the coefficients that have been adjusted to reproduce more accurately the thermodynamic properties of water, both on the liquid and the vapor side. Furthermore, the model contains low temperature corrections that permit to account for many specificities of water, like its maximal density around 3°C. These properties are due to the existence of hydrogen bonds that are absent in the generic van der Waals description. Thanks to this model we aim at a better quantitative description of the acoustic response of water following thermal exictation of the nanoparticle.

The model is constructed as follows: the bulk pressure is splitted in two contributions, a van der Waals like contribution P_{EOS} and the hydrogen bonds contribution P_{HB} [53]:

$$P_{\text{bulk}} = P_{\text{EOS}} + P_{\text{HB}},$$

with

$$\frac{P_{EOS}}{\rho R T_w} = 1 - \left(b^* + \frac{a_{vW}}{R T_w} \right) \rho + \frac{\alpha \rho}{1 - \lambda b(T_w) \rho}.$$

The function $b(T_w)$ takes the form:

$$b(T_w) = v_B \left\{ 0.2 \exp \left[-21.4 (T_w/T_B + 0.0445)^3 \right] - b_1 \exp (1.016 T_w/T_B) + b_2 \right\}.$$

Here, v_B and T_B are respectively the Boyle volume and temperature, and the constants appearing in these expressions are given by:

$$\begin{aligned} v_B &= 0.069405 \text{ nm}^3 & b_1 &= 0.25081 \\ T_B &= 1408.4 \text{ K} & b_2 &= 0.99859 \\ b^* &= 0.075117 \text{ nm}^3 & \lambda &= 0.3241 \\ \alpha &= 0.148874 \text{ nm}^3 \\ a_{vW} &= \frac{27 R^2 T_c^2}{64 P_c} = 1.5292 \text{ MPa nm}^6 \end{aligned}$$

Note that b_1 , b_2 and λ are dimensionless constants. Following [53], the hydrogen bond contribution is given by:

$$P_{HB} = -\rho^2 R T_w \frac{\partial f}{\partial \rho} \log \left[\frac{\Omega_0 + \Omega_{HB} \exp(-\epsilon_{HB}/R T_w)}{\Omega_0 + \Omega_{HB}} \right]$$

with:

$$f = \frac{1 + C_1}{\exp \left(\left(\frac{\rho - \rho_{HB}}{\sigma} \right)^2 \right) + C_1} \exp \left[-0.18 \left(\frac{T_w}{T_f} \right)^8 \right],$$

the fraction of hydrogen bonds in a dense state. The various constants entering in these expressions are given by [53]:

$$\begin{aligned} \Omega_0 &= \exp(-S_0/R) & \Omega_{HB} &= \exp(-S_{HB}/R) \\ S_0 &= -61.468 \text{ J/mol/K} & S_{HB} &= -5.128 \text{ J/mol/K} \\ \epsilon_{HB} &= -11.490 \text{ kJ/mol} \\ C_1 &= 0.7140 & \sigma &= 0.1687 \rho_{HB} \\ \rho_{HB} &= 28.2 \text{ nm}^{-3} & T_f &= 273.15 \text{ K} \end{aligned}$$

As previously mentionned, the temperature evolution of the fluid is coupled to that of the nanoparticle through the conductive flux at its surface (5). Note that our model neglects the nanoparticle expansion due to its heating. Indeed, we have observed that this expansion plays a minor role in the amplitude of the emitted pressure wave in the cavitation

regime [40]. Far away from the nanoparticle, perfectly match layers are implemented to avoid any reflection of the pressure waves generated by the sudden vapor generation, as detailed in [52]. We consider a spherically symmetric system that allows us to focus only on the radial component of the fields. The nanoparticles have a total radius ranging from 50 to 70 nm. The simulation cell, which is centered on the nanoparticle, has a size $L=6 \mu\text{ m}$. We use a space step of 0.2 nm and a maximum time step of $dt_{\text{max}} = 0.4 \text{ fs}$. Note that the initial thermal relaxation of the nanoparticle is much faster than the subsequent processes, in particular in the case of the 1 ps duration heating. To obtain a valid description of this relaxation, the time step is automatically reduced so that the maximum temperature variation in the particle during a time step is less than or equal to 0.1 K. A faster convergence of the code is obtained using a second order Runge-Kutta implementation of the conservation equations 1-3 and 10-12. The velocity field is calculated on a staggered grid, shifted from the main grid by half a lattice constant [52].

The radius of the metallic core of the particles is maintained at 50 nm and we focus our study on the effect of the thickness d of the silica shell. The effective absorption section of the particles therefore remains constant and is equal to $\sigma = 7.906 \cdot 10^{-15} \text{ m}^2$ at the plasmon resonance wavelength $\lambda = 530 \text{ nm}$.

III. RESULTS

In this section, we present the results for the photoacoustic response of core-shell nanoparticles immersed in water and compare to the case of bare gold nanoparticles. The nanoparticles are supposed to be irradiated by a laser pulse having a wavelength close to the plasmon resonance, $\lambda = 530 \text{ nm}$, and we consider two pulse durations, $t_p = 1 \text{ ps}$ and $t_p = 1 \text{ ns}$. In all the following, the gold core radius R_c is fixed at the value $R_c = 50 \text{ nm}$, so that the comparison between homogeneous gold nanoparticle and core-shell is made at a constant value of the absorption cross-section $\sigma_{\text{abs}}(\lambda)$. We will separate the case where the fluence is below the threshold for nanocavitation to the case where the fluence is above the threshold.

A. Below the nanocavitation threshold

We first consider the case of relatively low fluences F . In this regime, water in the vicinity of the nanoparticle is heated up at a maximal temperature below water spinodal temperature $T_s \simeq 550$ K, and no bubble formation occurs.

Figure 2 illustrates the pressure propagation in water for a short duration-picosecond-pulse. The waves are emitted at the nanoparticle surface and propagate over microns in water, the propagation being accompanied by dispersion. From the analysis of the position of the maximum wave position, one can infer an apparent sound velocity, whose value $c_w = 1524$ m/s is found to be close to the value of sound velocity in water under normal conditions. The wave amplitude decays spatially as r^α , with $\alpha = 1.57$, a value typical of laser-induced stress wave propagation [54, 55].

FIG. 2. Propagation of thermally-induced pressure waves away from the nanoparticle. Pressure profile at different times. The dashed lines indicate the pressure amplitude as it propagates in liquid water. Inset : Evolution of the maximum wave position as a function of time. The nanoparticle considered here is a gold core silica shell particle with a core radius $R_c = 50$ nm, a shell thickness $d = 5$ nm, the pulse duration $t_p = 1$ ps and the fluence $F = 77$ J/m².

The temporal evolution of the pressure in water at a distance $R = 500$ nm from the nanoparticle center is shown in Fig. 3. We choosed a distance $R = 500$ nm as it is a typical distance in a biological cell environment. Two different behaviours may be highlighted depending on the laser pulse duration. For a short pulse duration, core shell nanoparticles with a thin silica shell display the largest photoacoustic response. Core-shell nanoparticles having

FIG. 3. Temporal evolution of the pressure at a distance 500 nm from the nanoparticle surface, for a 1 ps pulse (left) and 1 ns pulse (right). For the two pulse durations, the laser fluence is $F = 77 \text{ J/m}^2$. Black lines correspond to a gold nanoparticle, while red, green and blue lines correspond to core-shell nanoparticles having respectively a shell thickness 5, 10 and 20 nm. Solid lines refer to the case with electron-phonon coupling at interfaces, while dashed lines correspond to the absence of electron-phonon coupling $\sigma_{\text{es}} = 0$. The gold core considered here has a radius $R_c = 50 \text{ nm}$.

a silica thickness larger than 10 nm display, however, a photoacoustic response lower than the corresponding bare nanoparticle. Also importantly, when the electron-phonon channel is switched off, the maximal pressure signal generated by core-shell nanoparticles, whatever the silica thickness, is lower than the signal corresponding to the homogeneous nanoparticle. This tends to conclude that electron-phonon processes taking place at the interface between gold and silica play a leading role in the enhancement of the photoacoustic response of core-shell nanoparticles.

For longer pulse durations, a slightly different scenario holds. First, the pressure signal has a longer duration, being of compressive nature before the end of the pulse and tensile after the pulse is switched off, as seen in Fig 3. Less expectedly, in the case of the nanosecond pulse duration, the homogeneous gold nanoparticle displays the higher photoacoustic response. Core-shell nanoparticles are characterized by a relatively lower response which decreases when the shell thickness increases. Again, we see in the nanosecond case, that electron-phonon coupling at the gold-silica interface have an influence on the amplitude of the photoacoustic response, and in the absence of this channel, the maximal pressure is

relatively smaller.

The fluence dependence of the maximal pressure at a distance $R = 500$ nm is represented

FIG. 4. Maximum of the pressure wave measured at a distance $R = 500$ nm from the nanoparticle center, for core-shell nanoparticles having different silica thicknesses, 5 nm (down triangles), 10 nm (diamonds) and 20 nm (up triangles) compared with bare gold nanoparticles (black circles). For core-shell nanoparticles, open symbols correspond to the case with electron-silica conductance σ_{es} , while filled symbols correspond to the case without electron-silica conductance $\sigma_{\text{es}} = 0$. Left : picosecond pulse duration. Right : nanosecond pulse duration. The gold core considered here has a radius $R_c = 50$ nm.

in Fig. 4. In this figure, we generalize the qualitative behaviour discussed before. First, for picosecond laser pulses, the maximal values of the pressure correspond to the core-shell nanoparticle having the thinnest silica shell, $d = 5$ nm. Core-shell nanoparticles having shell thickness larger than 10 nm display a photoacoustic response lower than the homogeneous gold nanoparticle. When the electron-phonon coupling at interface is switched off, however, the maximal pressure is always smaller for the core-shell nanoparticles in comparison with the homogeneous nanoparticle. Secondly, for the nanosecond pulse case, the bare gold nanoparticle displays the highest photoacoustic response. The maximal amplitude generated by core-shell nanoparticles is relatively lower and decreases for thick silica coating. In the nanosecond case also, the electron-phonon conductance σ_{es} contributes to enhance the photoacoustic response of core-shell nanoparticles, though its role is less critical as compared to the short pulse duration case.

FIG. 5. Temporal evolution of the electronic temperature (red curves), gold phonon temperature (black), silica temperature (purple) and surface water temperature (blue) for a gold-core silica shell nanoparticle having a silica thickness of 5 nm (solid curves) and a homogeneous gold nanoparticle (dashed curves). Left : case with electron -phonon coupling at interface. Right : without electron-phonon coupling σ_{es} . The green curves display the temporal evolution of the pressure at the nanoparticle surface. The pulse duration is $t_p = 1$ ps and the fluence is $F = 77$ J/m². The gold core considered here has a radius $R_c = 50$ nm.

To interpret the relatively high response of core-shell nanoparticles, we examined in Fig. 6 the temporal evolution of the different temperatures across the system. Apart from the electronic temperature T_e and the gold phonon temperature T_{core} , we considered also the silica and water temperatures at the position of the nanoparticle/water interface. Let us first concentrate on the case where the electron-phonon coupling at gold-silica interface is on. In this case, it is clear that electrons cool down faster in the core-shell nanoparticle as compared with the gold particle. This fast cooling is a direct consequence of the coupling between the metal electrons and the silica shell. Consequently, the silica shell is heated up on a 10 picosecond time scale and contributes to heat up water on the same short time scale. This fast heating is responsible for the peak pressure observed in water at short times, giving rise to the photoacoustic propagation in water. By the way of contrast, in the case of the homogeneous nanoparticle, liquid water is heated up on a much longer time scale. This is a result of the slow cooling kinetics of the electrons and the subsequent heating of the core phonons. Figure 5 shows that the relative low temperature level reached in water around the bare gold nanoparticle explains the fact that the photoacoustic response is of moderate

amplitude. The situation is different when the electron-phonon coupling is turned off as demonstrated in Fig. 6. In this latter case, the gold electrons cooling kinetics is the same for the bare nanoparticle and the core-shell nanoparticle. As a consequence, silica is heated up on longer time scales as compared to the case $\sigma_{es} \neq 0$. The direct coupling between the gold particle and water enables a relatively fast heating of the environment and the subsequent photoacoustic response. In the case of the core-shell nanoparticle, water is heated up on a longer time scale, due to the presence of the silica coating. The resulting maximal surface pressure is therefore lower, in qualitative agreement with the lower photoacoustic response.

FIG. 6. Temporal evolution of the electronic temperature T_e (left figures), the silica temperatures (middle) and the water temperature at the nanoparticle surface (right figures) for the gold nanoparticle (black lines) and the core-shell nanoparticles having shell thickness : 5 nm (red), 10 nm (green) and 20 nm (blue). Solid lines refer to the case with electron-phonon coupling at interfaces, while dashed lines correspond to the absence of electron-phonon coupling $\sigma_{es} = 0$. for the electronic temperatures T_e , we have zoomed the long time behaviour in the insets of the corresponding figures. The fluence is $F=77 \text{ J/m}^2$ and the gold core considered here have all a radius $R_c = 50 \text{ nm}$.

The effect of the silica shell thickness on water heating may be seen in fig. 6 for the two laser pulse durations. For the picosecond pulse case, the electronic temperature T_e is

maximal after 1 ps. The electron cooling occurs faster in the core-shell nanoparticles with electron-phonon interfacial coupling. Note that even in the absence of electron-phonon coupling, the electrons in the core-shell nanoparticles cool down faster than in the homogeneous particle, when the silica shell thickness is larger than 5 nm. The effect of σ_{es} may be clearly seen in the heating of the silica shells, as shown in the middle figure. Silica may be significantly heated up on a short ~ 10 ps time scale if the shell thickness is thin enough (5 nm). For thicker shells, silica is less heated up and the maximal temperature is reached on a longer time scale. This observation is related to the relatively low thermal conductivity of silica. The effect of the electron-phonon coupling is here again striking and plays a pivotal role in the silica heating kinetics. As a result, water in the vicinity of the nanoparticle may see its temperature raising on a 10 picosecond time scale, especially for 5 nm thick silica shells, noticeably faster than the water kinetics surrounding the gold nanoparticle. This effect disappears for thick silica shell or when the electron-phonon interfacial channel is turned off. In the nanosecond pulse case, the analysis of the different temperatures may shed some light in the behavior outlined before. Here again, despite the fact that the laser duration is longer, the electrons cool down faster in the core-shell nanoparticles even in the absence of electron-phonon coupling. Note that the maximal electronic temperature is attained at the end of the pulse, $t = 1$ ns. At this time, the silica temperature starts to decrease. Note that the electron-phonon conductance σ_{es} has less influence on the silica cooling kinetics on these time scales. This observation may be explained by the fact that, in the nanosecond time scale, the electrons maximal overheating ~ 300 K is one order of magnitude lower than the corresponding overheating reached in the picosecond time scale ~ 3000 K. As a consequence, core-shell nanoparticles heat up water less than homogeneous gold particles.

B. Nanocavitation regime

Here, we discuss the photoacoustic response displayed by the core-shell nanoparticles in the high fluence regime, where cavitation around the nanoparticles occurs. As shown in [36, 56], cavitation occurs when water temperature at a distance 1 nm from the nanoparticle surface reaches water spinodal temperature, around 550 K. Under these conditions, transient nanobubbles are generated and we already studied their dynamics elsewhere [40, 52]. Here, we concentrate on the effect of the silica shell thickness on the acoustic emission fol-

FIG. 7. Fluence threshold for nanocavitation as a function of the silica shell thickness. Vanishing shell thickness corresponds to the bare gold nanoparticle. Left : case with electron-silica conductance σ_{es} . Right : without electron-silica conductance $\sigma_{es} = 0$. Solid lines are guides to the eye. The gold core considered here has a radius $R_c = 50$ nm.

lowing the generation of a nanobubble.

Figure 7 shows the evolution of the cavitation fluence threshold with the silica shell thickness. It is seen that the cavitation threshold is higher for core-shell nanoparticles as compared with bare gold particles. The threshold increases with the shell thickness and is relatively higher for nanosecond pulses. Again, we can see the role of the interface electron-phonon processes, which tend to lower the cavitation threshold : in the absence of this channel, the threshold fluence is slightly enhanced, both for picosecond and nanosecond pulse durations. Next, we examine the photoacoustic response of the core-shell nanoparticles beyond cavitation, see Fig. 8. In the case of a picosecond pulse, we clearly see that still beyond cavitation threshold, the core shell nanoparticles with a thin silica shell display higher photoacoustic response as compared to the bare gold nanoparticle. Even core-shell nanoparticles with a thicker silica coating 10 nm may perform better than the bare gold nanoparticle at high fluences. This being said, we note that the interface electron-phonon conductance plays a leading role in the high values of the maximal pressure amplitude.

In the absence of this energy channel, the pressure wave amplitude emitted by core-shell nanoparticles decreases significantly. In the case of a nanosecond pulse, the situation is slightly different. As seen in Fig. 8, the cavitation fluence threshold is marked by a jump

FIG. 8. Same as Fig. 4 in the high fluence regime, where cavitation occurs. Left : picosecond pulse duration. Right : nanosecond pulse duration.

FIG. 9. Evolution of the maximum pressure as a function of the silica shell thickness, for different fluence levels. The case of a bare gold nanoparticle corresponds to a vanishing shell thickness. Left : picosecond pulse duration. Right : nanosecond pulse duration. Full symbols correspond to the case with electron-silica conductance σ_{es} , while open symbols correspond to the absence of electron-silica conductance. The gold core considered here has a radius $R_c = 50\text{nm}$.

of the pressure amplitude. Note that we already observed this behaviour in the case of the pressure emission around bare gold nanoparticles irradiated by nanosecond pulse [40]. Here, we can remark that the jump occurs for increasing fluence levels when the shell thickness increases. Noteworthy also is the fact that beyond the cavitation threshold, the pressure

amplitude seems to be weakly dependent on the shell thickness. Contrary to the low fluence regime, core shell nanoparticle may display relatively high photoacoustic response, especially for thin silica shells. The electron-phonon coupling at the interface plays a role here, though it has a least effect as compared to the picosecond pulse case.

Figure 9 summarizes our findings : for picosecond pulses, thin silica shells display the highest photoacoustic response, both in the low fluence and high fluence regimes. By contrast, in the case of nanosecond pulses, the presence of a silica shell tends to diminish the photoacoustic signal in the low fluence regime, below nanocavitation. Beyond cavitation, however, the photoacoustic signal is amplified and the generation of nanobubbles may help core-shell nanoparticles to emit relatively strong pressure waves.

IV. DISCUSSION AND CONCLUSION

In summary, we have investigated numerically the photoacoustic response of gold core-silica shell nanoparticles immersed in water and irradiated by a laser pulse having a wavelength close to the plasmon resonance of the nanoparticle. The acoustic response of water is described by a hydrodynamic phase field model which allows us to consider both the low fluence regime and the high fluence regime where nanocavitation may occur as a result of the nanoparticle strong heating.

We highlighted the major role played by the electron-phonon coupling between gold electrons and silica inside the core-shell nanoparticle. The existence of this energy channel has been recently evidenced experimentally by means of time resolved thermorefectance. The effect of this channel is particularly important when electrons and phonons are highly out of equilibrium, a situation occurring when the nanoparticle is irradiated by a short duration laser pulse. To preserve the benefit of the gold electron-silica phonon coupling one needs, however, to minimize the silica shell thickness in which large temperature gradients may set in as a result of the low thermal conductivity of silica. Following these qualitative conclusions, our numerical simulations show that core-shell nanoparticles having a shell thickness smaller than 10 nm and irradiated by picosecond laser pulse display a larger photoacoustic response as compared with bare gold nanoparticles having the same absorption cross-section. On the contrary, core shell nanoparticles with a thicker shell or core shell nanoparticles irradiated by a nanosecond laser pulse generally have a relatively low photoacoustic response

as compared with homogeneous gold nanoparticles.

These results are, at least qualitatively, consistent with earlier investigation of heat transfer across core-shell nanoparticles [23] which demonstrated better efficiency to transfer heat to their water environment as compared with gold nanoparticles. Our conclusions are also in line with other computational studies which concluded on the deterioration of the photoacoustic signal induced by the silica coating [20–22]. In particular, for nanosecond pulses we concluded that silica coating tends to diminish the photoacoustic signal unless nanocavitation occurs which is beneficial for thin silica shells.

This work may be extended in different directions. First, we considered here gold-silica core shell nanoparticles, but electron-phonon processes should take place in a wide array of metal/dielectric interfaces. Considering different core materials and coatings may help optimize the photothermal response of core shell nanoparticles. Modelling these effects calls for the determination of the electron-phonon conductance of different metal/dielectric interfaces using either time resolved thermorefectance or first principles calculations. Secondly, we concentrated in this article on gold silica nanospheres, but interfacial electron-phonon processes should obviously play a role for other geometries. Apart from silica coated nanorods, concentrated core-shell multilayers offer the promise to tune the photoacoustic conversion efficiency of heterogeneous nanoparticles [57, 58].

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V. APPENDIX

In this appendix, we give the expressions of the temperature dependent electron-phonon coupling constant and the electronic heat capacity.

$$G = \begin{cases} \sum_{j=0}^6 g_j T_{\text{inf}}^j, & \text{if } T_e \leq T_{\text{inf}} \\ \sum_{j=0}^6 g_j T_e^j, & \text{if } T_e \in [T_{\text{inf}}, T_{\text{sup}}] , \\ \sum_{j=0}^6 g_j T_{\text{sup}}^j, & \text{if } T_e \geq T_{\text{sup}} \end{cases} \quad (13)$$

$$c_e = \begin{cases} \sum_{j=0}^4 d_j T_e^j, & \text{if } T_e \leq T_{\text{inf}} \\ \sum_{j=0}^4 c_j T_e^j, & \text{if } T_e \in [T_{\text{inf}}, T_{\text{sup}}] , \\ \sum_{j=0}^4 c_j T_{\text{sup}}^j, & \text{if } T_e \geq T_{\text{sup}} \end{cases} \quad (14)$$

where $T_{\text{inf}} = 2700$ K and $T_{\text{sup}} = 20000$ K are two reference temperatures used for the polynomial fits. The parameters in equations 13-14 are given in Table IV.

Coefficient	Value	Unit
c_0	$7.31 \cdot 10^4$	$\text{Jm}^{-3}\text{K}^{-1}$
c_1	-79.7	$\text{Jm}^{-3}\text{K}^{-2}$
c_2	$5.38 \cdot 10^{-2}$	$\text{Jm}^{-3}\text{K}^{-3}$
c_3	$-3.52 \cdot 10^{-6}$	$\text{Jm}^{-3}\text{K}^{-4}$
c_4	$7.07 \cdot 10^{-11}$	$\text{Jm}^{-3}\text{K}^{-5}$
d_0	$3.59 \cdot 10^3$	$\text{Jm}^{-3}\text{K}^{-1}$
d_1	37.3	$\text{Jm}^{-3}\text{K}^{-2}$
d_2	$3.14 \cdot 10^{-2}$	$\text{Jm}^{-3}\text{K}^{-3}$
d_3	$-1.46 \cdot 10^{-5}$	$\text{Jm}^{-3}\text{K}^{-4}$
d_4	$2.61 \cdot 10^{-9}$	$\text{Jm}^{-3}\text{K}^{-5}$
g_0	$3.03 \cdot 10^{16}$	$\text{Wm}^{-3}\text{K}^{-1}$
g_1	$-4.98 \cdot 10^{12}$	$\text{Wm}^{-3}\text{K}^{-2}$
g_2	$-6.64 \cdot 10^8$	$\text{Wm}^{-3}\text{K}^{-3}$
g_3	$1.01 \cdot 10^6$	$\text{Wm}^{-3}\text{K}^{-4}$
g_4	$-1.35 \cdot 10^2$	$\text{Wm}^{-3}\text{K}^{-5}$
g_5	$6.84 \cdot 10^{-3}$	$\text{Wm}^{-3}\text{K}^{-6}$
g_6	$-1.23 \cdot 10^{-7}$	$\text{Wm}^{-3}\text{K}^{-7}$

TABLE IV. Coefficient appearing in the eqs. 13 and eq. 14.

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