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Thermal Kinetics of Gold Nanosphere under a Burst of Femtosecond Laser †

Selma Mediene * and Assia Rachida Senoudi

Physics Department, Theoretical Physics Laboratory, Tlemcen University, Tlemcen 13000, Algeria; arsenoudi@gmail.com

* Correspondence: selma.mediene@univ-tlemcen.dz

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Abstract: Thermal dynamics of spherical gold nanoparticle under a femtosecond laser burst irradiation at 550 nm wavelength, 100-fs pulse duration and F = 1 J/m² laser fluence are investigated numerically. Unique spherical gold nanoparticle immersed in water is heated by a single pulse laser and then after by a number of sub-pulses. The two-temperature model is used to describe the energy-exchange dynamics of gold nanoparticle, in addition to Fourier's law and to the relation between the thermal conductivity of the water and the temperature. Our results show that the irradiation of a gold nanoparticle by a femtosecond laser burst with a separation time between sub-pulses less than the thermal relaxation time leads to a fast heat accumulation which enhance the temperatures of the electron, the phonon and the water near the gold nanoparticle surface.

Keywords: femtosecond laser; gold nanoparticle; thermal accumulation; two-temperature model

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1. Introduction

The interaction of metallic nanoparticles with intense light fields is an appealing field of science. In particular, gold nanoparticles (AuNps) because of their potential applications to nonlinear optics, [1], solar energy [2] chemical sensing [3] and in nano-medicine spherical AuNps are widely used as photothermal drug delivery or in hyperthermia cancer therapy [4,5] due to their relative ease of fabrication, non-toxicity, ease of binding to antibodies, and due to their excellent thermal, optical, chemical, and biological properties. These unique and amazing properties are due to the localized surface plasmon resonance effect (LSPR) defined by collective oscillations of free electrons of AuNp surface when irradiated by a laser field at a specific wavelength. AuNps are characterized by their high absorption cross-section and neglected scattering [6] at visible or infrared frequencies (depending on the size and the shape of the AuNp). Optical cross-sections can be calculated according to the Mie diffusion theory for the spherical shape [7]. Computer calculation of optical cross-sections of AuNp can be performed using a FORTRAN code [8].

In hyperthermia, free electrons absorb the laser energy due to the inverse bremsstralung, they are relaxed through electron-electron scattering over time of 100 fs up to 1 ps, then lattice starts to heat as a result of electron-phonon scattering until its thermal equilibrium reached in several ten of ps, and then the heat is transferred from particle into surrounding medium through phonon-phonon coupling, in few ns [9], the thermalization phase is very short. The electron and the lattice subsystems can be characterized by their temperatures (T_e, T_L) computed using the two-temperature diffusion model (TTM) [10–15]. In the TTM, we included the energy dissipation due to the heat conduction through the AuNp/water interface. The deposition of radiation energy is generally non-uniform throughout the particle volume, however for the case where $2\pi R/\lambda < 1$ (R is the radius of the AuNp and λ is the wavelength of incident light), we assumed that the laser energy

deposed on the AuNp is uniform throughout its volume [13], this simplify the problem where temperatures are only in relation to time.

In this work, we performed numerical simulations to study the heat accumulation due by a femtosecond laser burst. Single 40 nm diameter spherical AuNp, immersed in water is heated first by one single Gaussian 100-fs pulse and $F = 1$ J/m^2 laser fluence (fixed in the numerical simulation), then after by a sequency of sub-pulses having different separation time. The separation time is modified for studying the heat accumulation in the AuNp. We computed the temporal evolution of the electrons gas, the gold lattice and the water near the AuNp surface temperatures; for one pulse and for five sub-pulses per burst. The obtained results show that the irradiation of the AuNp by a femtosecond laser burst with a separation time less than the thermal relaxation time, enhances the electron, phonon and AuNp/water interface temperatures without increasing the laser energy.

2. Materials and Methods

The TTM as shown in Equation (1) is composed by two equations, the first one describes the thermal energy transfer from the electron gas to the lattice and the second one describes the transfer from the lattice to the surrounding water:

$$\begin{cases} C_e \dfrac{dT_e(t)}{dt} = -g(T_e(t) - T_L(t)) + S(t) \\ C_L \dfrac{dT_L(t)}{dt} = g(T_e(t) - T_L(t)) - Q_C \end{cases} \quad (1)$$

T is the temperature, C is the heat capacity per unit of volume which depends on T, where e and L denote electron and lattice, respectively; $S(t)$ represents the laser energy deposition into the electron subsystem of the AuNp per unit of time (t) and per unit of volume; The electron-phonon coupling factor g describes the energy exchange from the electrons to the lattice through electron–phonon scattering and it can be expressed as [10] by $g = g_0 (A_e/B_L(Te + T_L) + 1)$ with $g_0 = 2.2\ 10^{16}$ Wm^{-3} K^{-1}, the coupling factor at room temperature, $A_e = 1.2\ 10^7$ K^{-2} s^{-1} and $B_L = 1.23\ 10^{11}$ K^{-1} s^{-1} are material constants.

The expression of S(t) [14] is given as follows:

$$S(t) = \frac{C_{abs} \times P(t)}{V_P} \quad (2)$$

Table 1. Parameters used in numerical computation.

Parameter	Value	Ref.
AuNp		
Electron heat capacity, C_e (Jm^{-3} K^{-1})	$C_e = 70 \times T_e$	[12]
Lattice heat capacity, C_L (Jm^{-3} K^{-1})	$C_L = \rho_{gold} \times (109.707T_L - 3.4 \times 10^{-4}{T_L}^2 + 5.\times 10^{-7}{T_L}^3 - 3.93 \times 10^{-10}{T_L}^4 + 1.17 \times 10^{-13}{T_L}^5)$	[11]
Density, ρ_{gold} (Kg m^{-3})	$\rho_{gold} = 1.93 \times 10^4$	[12]
Gold melting temperature, T_m (K)	1337	[5,11]
Water		
Critical temperature, T_{Cr} (K)	647	[5,11]
Boiling temperature, T_b (K)	3130	[5,11]
Cavitation threshold T_{cav} (K)	573	
Thermal conductance at the gold/water interface, G (wm^{-2} K^{-1})	$G = 105 \times 10^6$	[5]
Thermal conductivity, k_∞ at T = 300 K (Wm^{-1} K^{-1})	0.61	[5]

C_{abs} is the optical absorption efficiency, V_p is the AuNp volume and $P(t)$ is the intensity of the pulsed laser.

Equation (3) describes *P(t)* having a Gaussian distribution, for multi-pulse irradiation [14], with N the number of sub-pulses per burst, t_{sep} the separation time between two consecutives sub-pulses, F is the laser fluence and τ_p is the pulse duration,

$$P(t) = \sum_{j=1}^{N} \frac{2\sqrt{ln\,2}}{\sqrt{\pi}} \frac{F}{\tau_P} exp\left(-4ln2\left(t - 2\tau_P - (j-1)t_{sep}\right)^2 / {\tau_P}^2\right) \quad (3)$$

In Equation (1), the rate of the heat conduction loss from the AuNp to its surroundings per unit of volume (Q_C) can be computed according to Fourier's law [13] as:

$$Q_C = \frac{S_p}{R} \int_{T_\infty}^{T_s} k(T)dT \quad (4)$$

T_s is the temperature at AuNp/water interface, $k(T)$ is the thermal conductivity of the water and S_p is the surface area of the spherical AuNp. The dependence of the thermal conductivity of the external medium temperature is given as a power law temperature function: $k(T) = k\infty(T/T\infty)^b$ in which $k\infty$ represents the thermal conductivity of the surrounding medium at $T\infty$ = 300 K. For water, the parameter b = 1 as reported in [13]. The integration of Equation (4) leads to:

$$Q_C = 2\pi R k_\infty T_\infty \left(\left(\frac{T_L(t)}{T_\infty}\right)^2 - 1\right) \quad (5)$$

The temperature at the AuNp/water interface T_{ws} [10] can be expressed as:

$$T_{ws}(t) = T_L(t) - \frac{Q_C}{G\,S_p} \quad (6)$$

G is the interface thermal conductivity that describes the energy transfer from the particle to the water. Phase transitions are not included in the model because of the low value chosen for the fluence laser.

We performed a Fortran code based on the fourth-order Runge-Kutta algorithm [16], with the initial conditions, T_e (t = 0) = T_L (t = 0) = 300 K, for solving the coupled equations in TTM and computing T_{ws}.

3. Results and Discussion

Figure 1 shows the optical cross-sections of the AuNp embedded in water, The exctinction, the absoprtion and the scattering as a function of wavelength, computed by Mie Code. As seen at LSPR λ = 524 nm, the high absorption cross-section (C_{abs} = 3623.83 nm^2) is reported and a weak scattering.

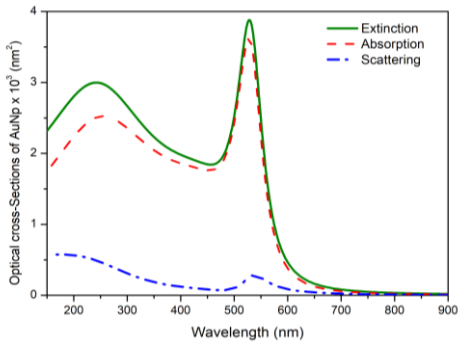


Figure 1. Optical cross-sections upon wavelengths of incident light calculated using Mie theory for the 40 nm diameter AuNp embedded in water.

We report in Figure 2, the thermal response of the electron gas, the gold lattice, and the water near AuNp surface, when a 40 nm diameter AuNp is heated by one single femtosecond pulse laser (N = 1 in Equation (3)) and cooled in water, the pulse duration is τ_p =

100 fs and the laser fluence is F = 1 J/m². The step time in simulation is of 10^{-2} ps. This figure illustrates clearly the ultra-fast process of electrons compared to phonons. The temperature T_e increases to reach the temperature of 1800 K at 300 fs. The electronic thermal relaxation causes an increase in T_L = 340 K at approximately 50 ps. As T_L increases the temperature jump at the interface, due to the heat loss from the particle surface to the water, the temperature T_{ws} of the latter begins to increase to reach its maximum value T_{ws} = 326 K. The cooling time of the AuNp in the water is of average 3 ns.

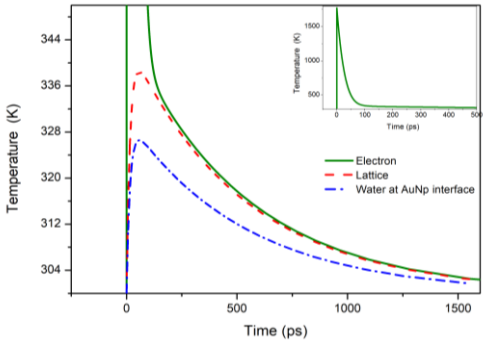
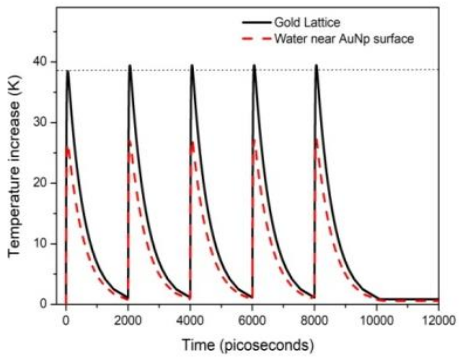
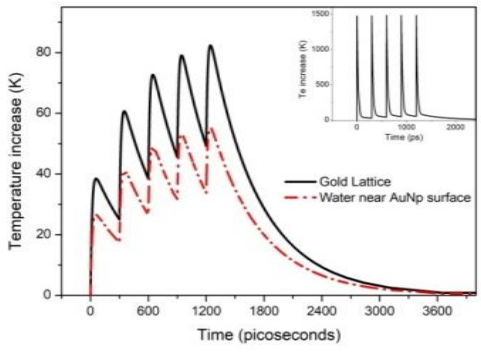


Figure 2. Temporal evolution of T_e, T_L and T_{ws} of 40 nm diameter AuNp heated by one single femtosecond pulse and cooled in water. τ_p = 100 fs and F= 1 J/m². In inset, temporal evolution of electron temperature.

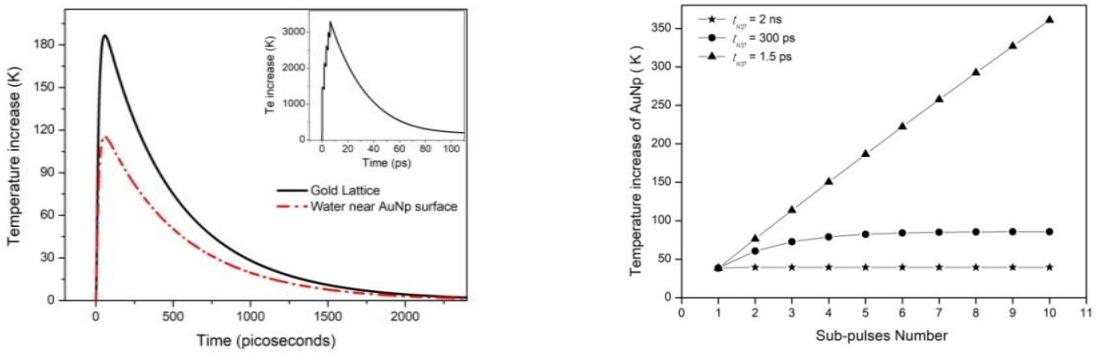
Figure 3 shows the temporal evolution of the temperatures T_e, T_L and T_{ws} during the irradiation by N = 5 sub-pulses at 1 J/m²; In Figure 3a, the separation time between sub-pulses is fixed to t_{sep} = 2 ns (0.5 GHz) that is much longer than the electron relaxation time which is smaller than 1 ps and the electron-phonon coupling time which is of average 50 ps as reported in [12], the thermal relaxation of AuNp occurs before the coming of the next sub-pulse. The effect of the multi-pulses on the heat accumulation is not particularly observable since for the second sub-pulse only an increase of 1 K in T_L and 0.5 K in T_{ws}; No effect for the next sub-pulses. Our conclusion is similar to that of Lutfellin et al. [5] where no heat accumulation was observed for laser having τ_p = 10 ns and t_{sep} = 10 ns. The authors in ref. [11] studied the heating of gold nanorod irradiated by 80 pulses of τ_p = 280 fs and t_{sep} = 12.5 ns they found that the accumulation effect is not pronounced with temperature rise of 3 K for the first few pulses.



(**a**)



(**b**)



(**c**) (**d**)

Figure 3. Temperature increases for 5 sub-pulses with a duration time 100 fs and a fluence of 1 J/m^2. Separation time between sub-pulses is of (**a**) 2 ns, (**b**) 300 ps and (**c**) 1.5 ps. The curves in (**d**) depict the increment of maximal temperature of AuNp as function of the number of sub-pulses for the different separation times.

Figure 3b reports the results for t_{sep} = 300 ps (1/3 MHz). The repetition rate is fixed much longer than the time of the electrons relaxation which occurs before the coming of the next sub-pulse, that why in the Figure 3b in inset, the maximum of T_e seems the same; the thermal accumulation is observed in the lattice and the AuNp /water interface with maximal temperature of T_L = 85 K (rate of increase of 17 K/sub-pulse) and T_{ws} = 55 K (5.5 K/sub-pulse). Ali et al. in ref. [15] resolved the TTM in addition of the heat diffusion equation for hollow gold nanoshells irradiated by N = 5 sub-pulses of τ_p = 5 ns and separated by 21 ns, they noticed a temperature rise of 0.5 K/sub-pulse because of the separation time is smaller than the total relaxation time of the AuNp.

In Figure 3c, t_{sep} = 1.5 ps (2/3 MHz) which is much less than the transfer time of the thermal energy to the lattice. Fast thermal accumulation was observed, where the electrons have sufficient time to accumulate all the energy and to transfer it, only once to the phonons and the environment respectively. The increase of the maximal temperature of T_L = 190 K (38 K/sub-pulse) and T_{ws} = 110 K (22 K/sub-pulse). The curves in Figure 3d can indicate the threshold sub-pulses to avoid the melting point (T_m) of AuNp, the boiling temperature (T_b), the critical temperature (T_{Cr}), and the cavitation threshold of water (T_{cav}).

4. Conclusions

In this work, we investigated the energy exchange dynamics in the spherical AuNp heated by a femtosecond laser burst. The results founded show that a sequency of sub-pulses adequately separated by a time less than the thermal relaxation is sufficient to produce a fast heat accumulation in the AuNp temperature as well the external temperature near the interface, without having to increase the laser energy. This accumulation process could be a good way to control the heat needed to damage cancer cells.

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