Time-harmonic optical heating of plasmonic nanoparticles

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Under illumination at their plasmonic resonance wavelength, metal nanoparticles can turn into efficient nanosources of heat by light absorption. Heating a small volume makes it possible to achieve fast dynamics. In this paper, we investigate theoretically, numerically, and experimentally the temperature distribution of a plasmonic system generated by a modulated incoming light. In particular, we study the response in amplitude and phase of the temperature variations. The cases of single and multiple nanoparticles are both addressed. Many parameters are discussed such as the nature of the media (nanoparticle and surroundings), the size of the nanoparticle or of the plasmonic system, the nanoparticle interdistance, the frequency of the modulation, a possible finite surface thermal conductivity of the nanoparticles, and the dimensionality of the system. This work is also intended to determine how fast a plasmonic system is able to induce temperature variations in its surrounding medium.

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I. INTRODUCTION

Under illumination, a metal nanoparticle (NP) absorbs part of the incoming light, which turns it into an ideal nanosource of heat remotely controllable by light [1]. For this purpose, noble metals such as gold and silver are usually preferred since they feature enhanced optical absorption in the visible-infrared range due to plasmonic resonances. The use of metal NPs as nanosources of heat is now the approach of predilection to investigate thermal-induced processes at the nanoscale in areas of research such as nanochemistry [2], thermal biology [3], or for biomedical applications [4,5].

One of the main advantages of heating using plasmonic NPs is the ability to achieve fast dynamics, due to a reduced heated volume leading to a small thermal inertia [6]. Several works have reported studies on the thermal dynamic response of plasmonic NPs [7]. Most of them concern the dynamic within the NP itself and do not consider the temperature profile outside the NP [8-11], which is yet what matters for most applications. Other studies focused on the temperature dynamics outside the NP, in the surrounding medium, but mainly in a femtosecond to nanosecond pulsed-illumination regime [12-16]. However, slower time scales or modulated illuminations are not comprehensively investigated in the literature, in particular below 10⁵ Hz, which is yet the dynamics achieved in experiments based on the use of an optical chopper or an acoustooptic modulator. Our interest in studying the heating dynamics in plasmonics over this range of moderate frequencies stems from our current studies on microscale chemistry-related experiments where a thermal-induced reaction is generated by gold NPs heated by a modulated light. The delay between variations of product concentration and light modulation gives valuable information on the chemical reaction constants [17,18].

In this paper, we aim at giving a comprehensive description of the dynamic response of the temperature distribution created around plasmonic NPs under illumination. In a first part, we will start from the most simple case consisting of a single spherical metal nanoparticle. The resulting temperature modulation inside and outside the nanoparticle will be derived and discussed. In a second part, we increase the degree of complexity of the system by adding a surface thermal resistance to the nanoparticle. In a final part, we consider an assembly of nanoparticles in close proximity in order to investigate the role of thermal collective effects and of the dimensionality of the NP distribution. This final part is illustrated by experimental results performed on a twodimensional distribution of gold nanoparticles.

II. RESULTS AND DISCUSSION

Most notations used in this paper are gathered in Table I.

A. Single nanoparticle heating

To begin with, we shall study the heating dynamics of a *single* metal NP. For the sake of simplicity, and to obtain meaningful analytical close-form expressions, we consider the case of a *spherical* NP of radius R immersed in a uniform dielectric medium as represented in Fig. 1. The physical constants related to the most common media of interest are gathered in Table II. Due to central symmetry, all the physical quantities will be only dependent on the radial coordinate r.

In order to investigate how fast such a system can thermally respond subsequently to variations of the incoming light intensity, we shall study the time-harmonic regime at the angular frequency ω . As the thermal conductivity of gold is much larger than the one of the surrounding medium, one can consider the temperature as uniform *within* the NP [20]. The physical quantities of interest are thus the temperature field in the surrounding medium T(r,t) and the NP temperature $T_{\text{NP}}(t) = T(R,t)$. This equality stems from temperature continuity considerations at the NP interface. A temperature continuity between the surrounding medium and the NP assumes that no surface thermal resistivity exists at the metal/surroundings interface [12,21,22]. We will investigate the effect of the finite surface thermal conductivity in the next section.

We name

$$Q(t) = Q_0(1 + \cos\omega t) \tag{1}$$

TABLE I. Main notations used in this paper.

Name	Description	Dimension
r	Radial coordinate	m
t	Time	S
ω	Angular frequency of the light modulation	rad s^{-1}
f	Frequency of the light modulation	Hz
R	Nanoparticle radius	m
V	Nanoparticle volume	m ³
Т	Temperature in the surroundings	Κ
$T_{\rm NP}$	Temperature of the NP	Κ
Q	Power delivered by the NP	W
$\kappa_{\rm s}, \kappa_{\rm m}$	Thermal conductivities	$W m^{-1} K^{-1}$
$\rho_{\rm s}, \rho_{\rm m}$	Mass densities	$\rm kg \ m^{-3}$
$c_{\rm s}, c_{\rm m}$	Heat capacity	$J m^{-3} K^{-1}$
$a_{\rm s}, a_{\rm m}$	Thermal diffusivity	$\mathrm{m}^2~\mathrm{s}^{-1}$
k_{ω}	Complex thermal wave vector	m^{-1}
$\omega_{\rm s}, \omega_{\rm m}$	Angular frequency constants	rad s^{-1}
$ au, au_{s}$	Time constants	s
λ_{th}	Thermal wavelength	m
$\delta_{ m th}$	Thermal penetration length	m
$\ell_{\rm K}$	Kapitza length	m
g	Interface thermal conductivity	$W m^{-2} K^{-1}$
D	Size/diameter of the NP distribution	m
р	NP interdistance	m
$\mu, \xi, \xi_0,$	Dimensionless constants	1
$\lambda_{\mathrm{K}},\zeta_{2},\zeta_{3}$		

the heat power absorbed (or equivalently delivered) by the NP. The equations governing the temperature field read as [12]

$$\rho_{\rm s} c_{\rm s} \partial_t T(r,t) = \kappa_{\rm s} \frac{1}{r^2} \partial_r [r^2 \partial_r T(r,t)], \qquad (2)$$

$$V\rho_{\rm m}c_{\rm m}\frac{dT_{\rm NP}}{dt} = \kappa_{\rm s}\,4\pi\,R^2\partial_r T(R,t) + Q(t),\qquad(3)$$

where V is the volume of the NP. The subscript "s" refers to the surrounding medium while "m" refers to the metal of the NP. The first equation, valid outside the NP (r > R), is nothing but the heat diffusion equation. Note that this equation



FIG. 1. (Color online) Metal nanosphere (such as gold) immersed in a uniform dielectric medium (such as water) and illuminated using a modulated intensity.

TABLE II. Values of the physical constants associated to gold, water, and glass (values at approx. $25 \,^{\circ}$ C taken from Ref. [19]).

Name	Gold	Water	Glass	Unit
Thermal conductivity κ	317	0.60	1.39	
Specific-heat capacity ^a c	129	4187	840	
Mass density ρ	19.32	1.00	2.53	

^aAt constant pressure.

is not supposed to get affected by any thermal-induced fluid convection in most solvents [23]. The second equation is a statement of energy conservation. The excitation given by Eq. (1) is not purely harmonic. There is a constant offset, necessary to avoid unphysical negative values of heat power expected for a pure harmonic excitation $Q_0 \cos \omega t$. Thanks to the linearity of the equations, the problem can be divided into a static problem (led by the source term $Q_0 \cos \omega t$), whose solutions will add up.

The solution of the static problem is straightforward and reads as

$$T^{0}(r) = \frac{Q_{0}}{4\pi \kappa_{s} r} = T_{\rm NP}^{0} \frac{R}{r}, \quad r > R$$
(4)

$$T_{\rm NP}^0 = \frac{Q_0}{4\pi \,\kappa_{\rm s} R}.\tag{5}$$

The superscript "0" means $\omega = 0$ (static regime).

Regarding the time-harmonic problem, for which the excitation just reads as $Q(t) = Q_0 \cos \omega t$, one can use a complex formalism with the following notations for the three physical quantities introduced above:

$$Q^{\omega}(t) = Q_0 e^{-i\omega t}, \qquad (6)$$

$$T^{\omega}(r,t) = \bar{T} \,\frac{R}{r} e^{i(k_{\omega}r - \omega t)},\tag{7}$$

$$T_{\rm NP}^{\omega}(t) = \bar{T}_{\rm NP} e^{-i\omega t}.$$
(8)

 \overline{T}_{NP} and \overline{T} are the complex amplitudes of the temperatures inside and outside the NP, Q_0 is the amplitude of the heat power, that is supposed to be real and constant, and k_{ω} acts as a complex wave-vector amplitude. Note that the temperature continuity at the NP boundary implies $T_{NP}^{\omega}(t) = T^{\omega}(R,t)$ at any time t. It is also worth recasting Eqs. (2) and (3) using new meaningful physical constants:

$$\tau_{\rm s}\,\partial_t T(r,t) = \frac{R^2}{r^2}\,\partial_r [r^2 \partial_r T(r,t)],\tag{9}$$

$$\tau_{\rm m} \frac{dT_{\rm NP}}{dt} = R \,\partial_r T(R,t) + \frac{Q(t)}{4\pi \,\kappa \,R},\tag{10}$$

where two time constants have been introduced

$$\tau_{\rm s} = \omega_{\rm s}^{-1} = \frac{R^2 \,\rho_{\rm s} \,c_{\rm s}}{\kappa_{\rm s}} \,=\, \frac{R^2}{a_{\rm s}},\tag{11}$$

$$\tau_{\rm m} = \omega_{\rm m}^{-1} = \frac{R^2 \,\rho_{\rm m} c_{\rm m}}{3 \,\kappa_{\rm s}},$$
(12)

and where $a_s = \kappa_s / \rho_s c_s$ is the thermal diffusivity of the surroundings. We also defined ω_s and ω_m the two corresponding angular frequencies. Injecting Eq. (7) in (9) yields a dispersion relation that can be written in different forms:

$$k_{\omega}^2 R^2 = i \,\omega \,\tau_{\rm s},\tag{13}$$

$$k_{\omega} R = (1+i)\sqrt{\frac{\omega\,\tau_{\rm s}}{2}},\tag{14}$$

$$k_{\omega} = (1+i)\sqrt{\frac{\omega}{2\,a_{\rm s}}}.\tag{15}$$

The wave-vector amplitude k_{ω} is complex, which is characteristic of a diffusion problem. By developing the expression $\exp(ik_{\omega}r)$ using Eq. (15), one can evidence a thermal wave-length $\lambda_{\text{th}} = 2\pi/\text{Re}(k_{\omega})$:

$$\lambda_{\rm th} = 2\pi \sqrt{\frac{2\,a_{\rm s}}{\omega}} \tag{16}$$

and a thermal attenuation length (or thermal penetration length) defined by $\delta_{th} = 1/\text{Im}(k_{\omega})$:

$$\delta_{\rm th} = \sqrt{\frac{2\,a_{\rm s}}{\omega}}.\tag{17}$$

Consequently, in thermodynamics, any thermal wave is damped over a distance that is 2π shorter than the thermal wavelength, irrespectively of the nature of the surrounding medium and the frequency. In other words, a thermal wave is damped even before just one spatial oscillation. There is nothing to do against that and this is the reason why one usually never speaks about *thermal waves* in thermodynamics.

Injecting now the complex quantities (3), (7), and (2) in Eq. (10) yields

$$\bar{T}_{\rm NP} = \frac{Q_0}{4\pi \,\kappa_{\rm s} \,R \left(1 \,-\, i \,k_{\omega} \,R \,-\, i \,\omega \,\tau_{\rm m}\right)} \tag{18}$$

or, equivalently, using Eq. (14):

$$\bar{T}_{\rm NP} = \frac{Q_0}{4\pi \,\kappa_{\rm s} \,R \left[1 + (1 - i)\sqrt{\frac{\omega \tau_{\rm s}}{2}} - i \,\omega \,\tau_{\rm m}\right]}.$$
 (19)

Interestingly, three time scales are involved in the response of the NP temperature amplitude \bar{T}_{NP} , $\tau_{\omega} = 2\pi \omega^{-1}$, and the two time constants τ_s and τ_m defined by Eqs. (11) and (12). Here is some more insight into their significations. (i) τ_{ω} is nothing but the period of the oscillations of the excitation. (ii) $\tau_{\rm s}$ only involves the thermal characteristics of the surroundings. Indeed, it is the time scale associated to any thermal process occurring in a uniform medium over a domain of typical size R (irrespectively of the presence of a NP). (iii) $\tau_{\rm m}$ is the time scale of the thermal variations within the NP immersed in a surrounding medium of conductivity κ_s . Indeed, τ_m is proportional to $c_{\rm m}$, which represents the capacity of the metal to store thermal energy. The larger $c_{\rm m}$, the larger the stored heat energy is for a given NP temperature. Consequently, if $c_{\rm m}$ is too large, a heat exchange with the surroundings will not significantly vary the NP temperature, which will make any temperature variation last longer. In the limit case where $c_{\rm m}$ tends to infinity, the NP becomes a temperature reservoir that will no longer feature any temperature variation ($\tau_{\rm m} \rightarrow \infty$).

As the denominator of expression (18) features three terms, three different regimes associated to different time scales are conceivable, as a function of which term dominates. At sufficiently low frequency, the terms $k_{\omega}r$ and $\omega\tau_{\rm m}$ are much smaller than unity and thus negligible, which corresponds to the quasistatic regime: the temperature of the system will faithfully follow the variations of the laser intensity. Another regime appears as soon as $k_{\omega}R$ or $\omega\tau_{\rm m}$ becomes on the order of 1. In the case where $k_{\omega}R \sim 1$ first, the time scale is limited by the velocity of the energy diffusion in the liquid. In the other case where $\omega\tau_{\rm m} \sim 1$, the time scale is limited by the ability of the surrounding medium to rapidly affect the NP temperature. The relative significance of these two terms is given by the ratio

$$\frac{\omega \tau_{\rm m}}{\omega \tau_{\rm s}} = \frac{\rho_{\rm m} c_{\rm m}}{3 \, \rho_{\rm s} c_{\rm s}} = \frac{\mu}{3},\tag{20}$$

where we introduced the important dimensionless quantity

$$\mu = \frac{\rho_{\rm m} c_{\rm m}}{\rho_{\rm s} c_{\rm s}}.\tag{21}$$

This ratio is therefore only dependent on the nature of the media, not on the morphology. For gold and water, μ is very close to unity as it equals approximatively 0.60 at 25 °C. Interestingly, one has $\mu \approx 1$ for most metals in most dense media. Hence, the discussion and simulations conducted in this paper for gold nanoparticles in water can be qualitatively generalized for any plasmonic system. Since $\mu \approx 1$, the two terms $\omega \tau_s$ and $\omega \tau_m$ become significant in Eq. (19) from around the same frequency. This frequency can be estimated from the consideration $\omega \tau_s \sim 1$, which yields $R^2 \omega \sim a_s$. In other words, the quasistatic regime is lost as soon as the dimensionless number

$$\xi_0 = \frac{\omega R^2}{a_{\rm s}} = \omega \,\tau_{\rm s} = |k_\omega|^2 R^2 \tag{22}$$

is larger than unity. The subscript 0 means *single* NP. In this case, the response of the NP becomes delayed [because the denominator of expression (18) is no longer real], and reduced (because the denominator amplitude increases). In water, such a regime is achieved when

$$R^2 \omega \sim a_{\rm s} = 1.4 \times 10^{-7} \,{\rm m}^2 \,{\rm s}^{-1}.$$
 (23)

For even higher frequencies, the term $\omega \tau_m$ dominates in Eq. (19) as it scales as ω and not as $\sqrt{\omega}$. Using ξ_0 and μ , Eq. (18) can be recast in a simpler form

$$\bar{T}_{\rm NP} = \frac{T_{\rm NP}^0}{1 + (1-i)\sqrt{\xi_0/2} - i\,\mu\,\xi_0}.$$
 (24)

Consequently, despite the numerous parameters and physical constants that govern the system, the actual regime only depends on the two dimensionless parameters ξ_0 and μ .

Figures 2(a) and 2(b) represent the normalized amplitude $|\bar{T}_{\rm NP}/T_{\rm NP}^0|$ and phase $\arg(\bar{T}_{\rm NP})$ of the NP temperature, as a function of the parameter ξ_0 in the case of *gold* nanoparticles in *water*, i.e. $\mu = 0.60$ (solid lines). The information contained in these two graphs can be conveniently gathered within one single polar plot, as represented in Fig. 2(c). Various values of ξ_0 are indicated along the line shape. One can see that small values of ξ_0 indicate that the temperature variations faithfully



FIG. 2. (Color online) Numerical simulations. (a) Amplitude of the temperature modulation as a function of ξ_0 . (b) Phase shift of the temperature modulation as a function of ξ_0 . (c) (Solid line) Polar plot of the normalized complex amplitude $\bar{T}_{\rm NP}/T_{\rm NP}^0$ [see Eq. (18)] of a gold NP temperature immersed in water. (Dashed line) Polar plot of the same quantity discarding the correction term $\omega \tau_{\rm m}$. Circles indicate various values of ξ_0 .

follow the light modulation. For larger values of ξ_0 , a phase shift (between the temperature response and the excitation) along with a reduction of the amplitude of the oscillations is observed. Even though these trends are plotted as a function of the dimensionless parameter ξ_0 , they are not universal since \bar{T}_{NP} does not depend only on $\omega \tau_s = \xi_0$ but also on the nature of the nanoparticle *via* the term $\omega \tau_m$ [see Eq. (24)]. In addition to the actual line shape, another (dashed) line shape is plotted that corresponds to the response where the term $\omega \tau_m$ in Eq. (18) is discarded. This line shape is universal and does not depend on the nature of the media. Discarding this term markedly affects the response, according to the discussion of the former paragraph, except for low- ξ_0 values.

Note that the phase limit at high frequency (i.e., high ξ_0) tends toward $\pi/2$ because the term $i\omega\tau_m$ becomes dominant in Eq. (18). When this term is neglected, the limit is $\pi/4$



FIG. 3. (Color online) Evolution of the phase shift between the NP temperature oscillation and the light source modulation, as a function of the angular frequency ω , or equivalently as a function of the thermal attenuation length δ_{th} .

simply because the denominator in Eq. (24) is proportional to 1 - i instead of *i*. This single phase jump observed from 0 to $\pi/2$ is what is observed for *gold* nanoparticles in *water*. In the most general case involving any materials where μ could eventually be much smaller than unity, two successive jumps as a function of ω could occur, like what is schematized in Fig. 3. However, this does not occur in practice in nanoplasmonics as μ is always very close to unity for any standard metal/solvent association, as mentioned above. What has been represented in the particular case of gold in water in Fig. 2 is thus the general trend observed in nanoplasmonics.

As the range $[0,\omega_s]$ corresponds to the range where the temperature oscillation will not be delayed, τ_s turns out to be the minimum time scale of possible temperature variations using a single nanoparticle. In other words, variations faster (i.e., shorter) than τ_s will be damped. Using the results of our work and turning them into the temporal Fourier space makes it possible to answer the following question: How fast can the temperature can be varied in nanoplasmonics? This reasoning applies in any section of this paper.

Importantly, in nanoplasmonics, for reasonable angular frequencies and since NP sizes are supposed to remain below 1 μ m, the condition $\xi_0 \ll 1$ is usually fulfilled. Consequently, in most experiments using a continuous wave (cw) laser, eventually modulated in time using standard means, one can consider the NP temperature faithfully follows the variations of the laser intensity, which corresponds to the very right part of the polar plot, in Fig. 2(c).

Let us finally address the temperature *outside* the NP T(r,t). From Eqs. (2) and (18), it reads as

$$T(r,t) = \frac{Q_0}{4\pi \kappa_{\rm s} r} + \operatorname{Re}[T^{\omega}(r,t)], \qquad (25)$$

where

$$T^{\omega}(r,t) = \frac{Q_0}{4\pi \,\kappa_{\rm s} \,r} \,\left(\frac{e^{i\,k_{\omega}(r-R)-i\,\omega t}}{1-i\,k_{\omega}\,R-i\,\omega\,\tau_{\rm m}}\right). \tag{26}$$

For $\xi_0 \ll 1$, the usual case in nanoplasmonics as explained above, we end up with the familiar expression that is commonly used, for instance, in photothermal imaging [24,25]:

$$T(r,t) = \frac{Q_0}{4\pi \kappa_s r} \left[1 + e^{-(r-R)/\delta_{th}} \cos\left(\frac{2\pi}{\lambda_{th}}(r-R) - \omega t\right) \right].$$
(27)

B. Influence of an interface thermal resistance

We study in this section the dynamics of the temperature inside and outside a NP while taking into account an interface thermal conductivity g (power per unit surface and

temperature) or resistivity g^{-1} . A finite interface conductivity can be due to the presence of a molecular functionalization of the NP surface [12,21]. The direct consequence is the occurrence of a temperature discontinuity at the NP interface. As the inner and outer temperatures are different, their dynamics are no longer supposed to be identical.

In this context, it is useful to define the Kapitza length

$$\ell_{\rm K} = \frac{\kappa_{\rm s}}{g} \tag{28}$$

and the normalized Kapitza length

$$\lambda_{\rm K} = \ell_{\rm K}/R. \tag{29}$$

When $\lambda_K \gg 1$, a substantial temperature drop exists between the temperature inside and outside the NP, and the heat exchange is governed by the interface conductivity *g* and no longer by the surrounding conductivity κ_s . In Appendix A, we show that the complex NP temperature response becomes

$$\bar{T}_{\rm NP} = \frac{Q_0}{4\pi \,\kappa_{\rm s} \,R \left(\frac{1-i \,k_{\omega} R}{1+\lambda_{\rm K} (1-i \,k_{\omega} R)} - i \,\omega \,\tau_{\rm m}\right)}.\tag{30}$$

Note that Eq. (18) is retrieved from this equation for $\lambda_{\rm K} = 0$, as expected. For $\lambda_{\rm K} \gg 1$, this expression becomes

$$\bar{T}_{\rm NP} = \frac{Q_0}{4\pi \,\kappa_{\rm s} \,R \,\left(\lambda_{\rm K}^{-1} - \,i\,\omega\,\tau_{\rm m}\right)}.\tag{31}$$

When the interface thermal resistivity is significant, two regimes are thus expected: a low-frequency regime where $\lambda_{\rm K}^{-1}$ is dominant and where the NP temperature oscillates in phase with the excitation, and a high-frequency regime where $\omega \tau_{\rm m}$ dominates, where *g* no longer matters and where the temperature oscillates in quadrature.

The other physical quantity of interest is the temperature profile *outside* the NP given by Eq. (25) in the previous section, with this time

$$T^{\omega}(r,t) = \frac{T_{\rm NP}^0 e^{i \, k_{\omega} \, (r-R) - i \, \omega t}}{1 - i \, k_{\omega} \, R - i \, \omega \, \tau_{\rm m} [1 + \lambda_{\rm K} (1 - i k_{\omega} R)]}.$$
 (32)

Interestingly, unlike what is observed for the inner temperature T_{NP} , an interface resistivity only matters at high frequency for the temperature outside the NP. The high-frequency regime leads to

$$T^{\omega}(r,t) = -T_{\rm NP}^0 \, \frac{e^{i \, k_{\omega} (r-R) - i \, \omega t}}{\omega \, \tau_{\rm m} \ell_{\rm K} k_{\omega}}.$$
(33)

Since the argument of k_{ω} is $\pi/4$, the temperature at the vicinity of the NP oscillates therefore with a phase delay of $3\pi/4$ compared to the excitation Q(t).

Figure 4 presents numerical simulations of the temperature modulation for a single gold NP in water with interface thermal resistivity (solid lines, $\lambda_{\rm K} = 0.5$) and without interface thermal resistivity (dashed lines). Both the temperature modulations inside $(T_{\rm NP}^{\omega})$ and outside $[T^{\omega}(R)]$ the NP are plotted. The plotted temperatures are normalized by $Q_0/4\pi\kappa_{\rm s}R$. As $\lambda_{\rm K} \sim$ 1, the interface resistivity plays a significant role. High values of $\lambda_{\rm K}$ are rarely observed experimentally in nanoplasmonics. $\lambda_{\rm K} = 0.5$ corresponds for instance to a NP 24 nm in diameter and $g = 100 \,{\rm Wm}^{-2}{\rm K}^{-1}$. The important observation is that the temperature dynamics *outside* the NP is weakly affected by



FIG. 4. (Color online) Numerical simulations. (a) Normalized amplitude of the temperature modulation inside and outside the nanoparticle as a function of ξ_0 . (b) Phase delay of the temperature modulation. (c) Polar plot of the normalized temperature modulation.

an interface resistance. This turns out to be a general rule in nanoplasmonics. However, the temperature *inside* the NP can be markedly affected: At low frequency, it is already known that the temperature increase inside the NP is larger by a factor $1 + \lambda_{\rm K}$ compared with the temperature at the outer boundary of the NP (a temperature discontinuity occurs at the NP interface). This is what can be seen at low frequency in Fig. 4(a) where the line shape of normalized the temperature amplitude starts at 1.5. At higher frequency, Fig. 4(b) shows that a finite interface conductivity can increase the delay between the temperature modulation outside the NP and the modulation of the incoming power Q(t). We observe that the limiting phase shift is $3\pi/4$, as derived in the above paragraph. This value does not depend on the particular value of $\lambda_{\rm K}$, which means that actual limit is supposed to be $3\pi/4$ in any case since NPs always feature an interface conductivity, even very small. However, this regime may occur at very large frequencies if λ_{K} is small. Indeed, according to Eq. (33), if $\lambda_K \ll 1, \lambda_K$ starts playing a role when $\lambda_{\rm K} | k_{\omega} | R \ge 1$, i.e., when $\ell_{\rm K} \ge \delta_{\rm th}$. Consequently, to figure out whether an interface thermal conductivity can play a role in the temperature dynamics outside a NP, the Kapitza length $\ell_{\rm K}$



FIG. 5. (Color online) (a) Evolution of the phase shift between the inner NP temperature oscillation and the light source modulation, for large values of $\lambda_{\rm K}$, as a function of the angular frequency ω , or equivalently as a function of the thermal attenuation length $\delta_{\rm th}$. (b) Evolution of the phase shift of the *outer* NP temperature oscillation for small values of $\lambda_{\rm K}$. (c) Evolution of the phase shift of the *outer* NP temperature oscillation for large values of $\lambda_{\rm K}$.

has to be compared with the thermal attenuation length δ_{th} . Note that the relation $\delta_{\text{th}} \sim \ell_{\text{K}}$ amounts to writing

$$\omega \sim \frac{2g^2}{\rho_{\rm s} c_{\rm s} \kappa_{\rm s}} = \lambda_{\rm K}^{-2} \omega_{\rm s}. \tag{34}$$

Interestingly, this expression does not depend on the size of the particle. Consequently, no matter the size of the NP, if the interface resistance is not the dominant effect ($\lambda_{\rm K} \ll 1$), a limiting phase shift will occur but only for frequencies higher than the one given by Eq. (34). For $g = 100 \,{\rm Wm^{-2}K^{-1}}$ (which is a usual lower limit value), it yields $\omega \sim 10^{10}$ Hz. This angular frequency is very high, although a small value of g was chosen. In practice, the occurrence of the $3\pi/4$ regime at high frequency is therefore expected only when $\lambda_{\rm K}$ is not weak.

Figure 5 summarizes the successive regimes that have been discussed, as a function of the angular frequency ω , or equivalently as a function of the attenuation length δ_{th} . Both the temperature inside and outside the NP are represented. Note that the case $T_{\text{NP}}^{\omega}(0)$, $\lambda_{\text{K}} \ll 1$ (not represented in Fig. 5), corresponds to the chart displayed in Fig. 3.

C. Multiple nanoparticle heating

In this section, we consider the heat generation from an assembly of NPs. This is probably the most common situation since most of the experiments reporting photothermal effects of metal NPs for applications in nanochemistry, biosensing, or in medicine benefit from the collective effect of multiple NPs. To address this situation, we will consider a two-dimensional distribution of metal NPs in a uniform dielectric medium [see Fig. 6(a)].



FIG. 6. (Color online) (a) Gold nanospheres immersed in a uniform dielectric medium and illuminated using a modulated intensity at the angular frequency ω . (b), (c) Temperature distributions throughout periodic lattices of NPs in the steady state ($\omega = 0$). (b) Infinite lattice illuminated by a Gaussian beam (p = 150 nm, 2R = 15 nm, $D = 3 \mu$ m, P = 10 mW). (c) Finite-size square lattice of NPs, uniformly illuminated (p = 300 nm, 2R = 15 nm, $I = 5.7 \times 10^9$ Wm⁻²).

1. Theory of the steady state

Let us consider an assembly of *N* NPs. Under cw illumination, the temperature increase ΔT_j observed at the location of a NP $j \in [1, N]$ originates from two contributions [26]: the temperature increase generated by the NP itself, ΔT_j^s , and the temperature increase coming from the other N - 1 NPs, ΔT_j^{ext} :

$$\Delta T_j = \Delta T_j^{\rm s} + \Delta T_j^{\rm ext}.$$
(35)

If only a few NPs are dispersed here and there in the system, ΔT_j^s can be dominant and thermal cooperative effects can be neglected. However, when many NPs are gathered in close proximity, we usually observe $\Delta T_j^{\text{ext}} \gg \Delta T_j^s$. Figures 6(b) and 6(c) illustrate the two regimes. Figure 6(b) corresponds to the collective regime where ΔT^{ext} is dominant, while Fig. 6(c) corresponds to the thermal confinement regime where ΔT^s is dominant.

In order to easily predict the occurrence of one regime or another, a simple dimensionless number can be estimated, which reads as [26]

$$\zeta_2 = \frac{p^2}{3 D R},\tag{36}$$

where *p* is the average neighboring NP interdistance, *D* the typical size of the NP distribution, and *R* the typical NP radius. ζ_2 is an estimation of the order of magnitude of $\Delta T^s / \Delta T^{\text{ext}}$. The subscript 2 refers to the dimensionality of the NP distribution. If $\zeta_2 \ll 1$, cooperative effects dominate, $\Delta T_j^{\text{ext}} \gg \Delta T_j^s$, and the temperature of the NP *j* is ΔT_j^{ext} . If $\zeta_2 \gg 1$, the temperature distribution is confined around each NP and the NP temperatures can be estimated as if the NPs were alone: $\Delta T_j = \Delta T_j^s$.

2. Theory of the time-harmonic regime

The latter discussion was related to steady state. Let us now discuss the dynamic problem at the angular frequency ω . The case $\zeta_2 \gg 1$ amounts to considering the NPs individually. Hence, this situation refers to the previous section and will not be discussed hereinafter. In the current section, we will consider the collective regime ($\zeta_2 \ll 1$) characterized by a continuous and rather smooth temperature distribution throughout the NP distribution despite the nanometric size of the heat sources [such as in Fig. 6(b)]. From the results of the previous section, and in particular from Eqs. (2) and (18), one can define a Green's function G^{ω} of the problem such that $T^{\omega}(r,t) = Q_0 G^{\omega}(r,t)$ where

$$G^{\omega}(r,t) = \frac{1}{4\pi \kappa_{\rm s} r} \left(1 + \frac{e^{i k_{\omega} (r-R) - i\omega t}}{1 - i k_{\omega} R - i \omega \tau_{\rm m}} \right).$$
(37)

The real part of $Q_0 G^{\omega}(r,t)$ is basically the evolution of the temperature distribution around a spherical modulated source of heat $Q_0 (1 + \cos \omega t)$. When considering multiple NPs, each of them delivering a power Q_0 , the complex heat source density (HSD, power per unit area) reads as

$$q^{\omega}(\mathbf{r},t) = q_0(\mathbf{r})(1+e^{-i\omega t}), \qquad (38)$$

where
$$q_0(\mathbf{r}) = Q_0 \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j),$$
 (39)

where $\delta(\mathbf{r})$ is the two-dimensional Dirac distribution. The temperature increase anywhere in the system is then given by the convolution between this heat source density $q_0(\mathbf{r})$ with the Green's function (37), which yields

$$T^{\omega}(\mathbf{r},t) = \iint_{\mathcal{D}} G^{\omega}(|\mathbf{r}-\mathbf{r}'|,t)q_0(\mathbf{r}')d\mathbf{r}', \qquad (40)$$

$$T^{\omega}(\mathbf{r},t) = Q_0 \sum_{j=1}^{N} G^{\omega}(|\mathbf{r} - \mathbf{r}_j|, t).$$
(41)

Once again, this problem can be divided into a static problem and a harmonic problem. Anywhere in the system, the temperature reads as therefore

$$T^{\omega}(\mathbf{r},t) = T^{0}(\mathbf{r}) + \delta T^{\omega}(\mathbf{r})e^{-i[\omega t + \phi^{\omega}(\mathbf{r})]}.$$
 (42)

 T^0 corresponds to the temperature increase due to the static component $q_0(\mathbf{r})$ of the HSD. T^0 stands also for the time-average temperature distribution. δT^{ω} is the amplitude of

the temperature modulation due to the harmonic component $q_0(\mathbf{r}) \cos \omega t$ of the HSD profile. $\phi^{\omega}(\mathbf{r})$ is the phase shift between this temperature modulation and the light modulation at the location \mathbf{r} . Let us define two pertinent quantities: the normalized amplitude Δ^{ω} and the phase shift Φ^{ω} of the temperature oscillation *at the center* of the NP assembly:

$$\Delta^{\omega} = \delta T^{\omega}(\mathbf{0}) / T^{0}(\mathbf{0}), \tag{43}$$

$$\Phi^{\omega} = \phi^{\omega}(\mathbf{0}). \tag{44}$$

These quantities have the following properties: $\Delta^{\omega \to 0} = 1$ (the amplitude of temperature modulation is maximum) and $\Phi^{\omega \to 0} = 0$ (the temperature variations follow in phase the heat delivery).

Figure 7 presents numerical simulations of Δ^{ω} and Φ^{ω} , for a circular illuminated array of diameter D, as a function of D and $f = 2\pi/\omega$ in water, for metal NPs with a radius of R = 14 nm and an interdistance p = 72 nm. These maps are convenient to retrieve the properties of the temperature response at a glance, in the case of a watery environment. Interestingly, in the case of a collective thermal regime ($\zeta_2 \ll 1$), which is the most common case, these maps are not dependent on the particular morphology of the NP lattice (R and p). These maps can thus be used for any system, as long as it is immersed in water, or in a medium with the same thermal diffusivity a_s . The slanted lines present on both images reveal that the problem is invariant for a given $f D^2$ value. More precisely, the problem is invariant by transformation at constant

$$\xi = \frac{\omega D^2}{4a_{\rm s}} \tag{45}$$

similarly with Eq. (22) where the NP radius *R* is here replaced by the radius D/2 of the NP distribution. Figures 7(c) and 7(d) represent Δ^{ω} and Φ^{ω} as a function of the dimensionless parameter ξ . These two line shapes can be gathered in a single polar plot, as represented in Fig. 7(e). In Figs. 7(a) and 7(b), a clear transition is observed, represented by the slanted line in the middle of the maps. It corresponds to the region where $\xi \sim 1$. Such an observation reveals that the characteristic time scale of the problem is

$$\tau = \frac{D^2}{4a_{\rm s}}.\tag{46}$$

For $\xi \ll 1$, i.e., when the system is small or when the modulation is slow, the temperature at the center of the system follows in phase and in amplitude the heat delivery. The temperature at the center of the system oscillates around T^0 , between 0 and $2T^0$. However, when $\xi > 1$, i.e., when the system is big or when the modulation is too fast, one can observe the appearance of a phase shift of $\pi/4$, along with a reduction of the temperature modulation amplitude. A delayed regime occurs. Note that ξ can be recast as

$$\xi = \frac{D^2}{2\delta_{\rm th}^2}.\tag{47}$$

For high frequencies, the thermal attenuation length δ_{th} is large and weakens when increasing the frequency. Another point of view is thus to consider that the transition to the delayed regime occurs when the thermal attenuation length becomes on the order of the size of the heat source distribution.



FIG. 7. (Color online) (a) Normalized temperature amplitude Δ^{ω} at the center of the NP assembly as a function of the frequency f and the diameter D of the heat source. (b) Phase shift Φ^{ω} of the temperature at the center of the NP assembly as a function of the frequency f and the diameter of the heat source. In (a) and (b), the linear map on the left corresponds to the limit case where D is so small that only one NP is illuminated. (c) Δ^{ω} as a function of ξ . (d) Φ^{ω} as a function of ξ . The dashed line corresponds to the approximation where $\omega \tau_{\rm m}$ and $\omega \tau_{\rm s}$ are discarded in the Green's function. (e) Phase diagram of the modulated temperature at the center of the system $\Delta^{\omega} e^{i\Phi^{\omega}}$ as a function of the parameter $\xi = \omega D^2/4a_{\rm s}$.

For even higher values of ξ , one can see in Fig. 7(d) that the phase shift further increases above $\pi/4$, and even diverges, which is characterized by the line shape in the polar plot of Fig. 7(e) that very locally coils up around the origin. This divergence of the phase shift is visible also in Fig. 7(b) by looking more carefully at the top of the map: one can notice that the slanted symmetry is broken for high values of the frequency f. The phase shift increases above $\pi/4$ and becomes independent on the beam diameter D. Such a regime occurs when δ_{th} further shrinks and becomes on the order of the NP interdistance p. This divergence of the phase shift at high frequency is therefore inherent to the discrete nature of the heat source density. In this regime, the thermal wave no longer propagates from one particle to another [see the discussion on thermal waves after Eq. (16)] and the NPs can be considered to be isolated regarding their temperature modulation. This is why the response of the system becomes independent on the beam diameter. However, in this regime, the amplitude of the temperature oscillations around each NP will be rather insignificant since much smaller than the average temperature increase of the system ($\Delta^{\omega} \ll 1$).

Note that the term $\omega \tau_m$ in the expression of the Green's function (37) appears as an unnecessary correction. Discarding this term does not change anything in the results displayed in Fig. 7. As a consequence, the only time scale that plays a role is τ_s , and the Green's function can be simplified accordingly. Then, unlike what was stated in the single-NP case, when using multiple NPs one can easily reach a delay in the temperature response.

An interesting feature that deserves attention is the plateau at $\pi/4$ observed in Fig. 7(d) for $\xi \gg 1$. To explain the origin of this particular value, let us consider the low-frequency approximation consisting in discarding the terms $k_{\omega}R$ and $\omega\tau_{\rm m}$ in the denominator of the Green's function (37). Let us consider also a uniform heat source density q_0 , discarding its discrete nature, over a circular area of diameter *D* much larger than the attenuation length δ_{th} ($\xi \gg 1$). With these approximations, one can derive a simple close-form expression of the complex amplitude of the temperature by convolution between the simplified Green's function and the continuous heat source density:

$$\bar{T}^{\omega}(0) = \int_0^\infty q_0 \frac{e^{ik_{\omega}r}}{4\pi\kappa_{\rm s}r} 2\pi r \, dr, \tag{48}$$

$$\bar{T}^{\omega}(0) = i \, \frac{q_0}{2\kappa_{\rm s} k_{\omega}}.\tag{49}$$

As $\arg(k_{\omega}) = \pi/4$, one naturally obtains $\arg[\bar{T}^{\omega}(0)] = \pi/4$. The origin of this particular limit value of the phase arises thus from the complex nature of the wave-vector amplitude k_{ω} . However, the dimensionality of the system plays also an important role. Indeed, let us consider a hypothetical *three-dimensional* distribution of heat sources (i.e., a spherical volume instead of a circular area). The calculation of $\bar{T}^{\omega}(0)$ would be rather

$$\bar{T}^{\omega}(0) = \int_0^\infty q_0 \frac{e^{ik_\omega r}}{4\pi\kappa_{\rm s} r} 4\pi r^2 dr, \qquad (50)$$

$$\bar{T}^{\omega}(0) = -\frac{q_0}{\kappa_{\rm s} k_{\omega}^2} \tag{51}$$

with q_0 a power per unit volume (instead of area). For a three-dimensional heat source distribution, the phase shift at high frequencies is thus $\pi/2$, instead of $\pi/4$ in two dimensions. The dimensionality of the heat source is thus an important parameter to determine the thermal dynamic response of a system. Close-form expressions of Δ^{ω} and Φ^{ω} as a function of ξ can be determined with the approximations mentioned above. These expressions are derived and given in Appendix B. Note that for a three-dimensional system, the occurrence of cooperative effects is governed by the



FIG. 8. (Color online) (a) Evolution of the phase shift between the temperature oscillation at the center of the NP array and the light source modulation, as a function of the angular frequency ω , or equivalently as a function of the thermal attenuation length δ_{th} . (b) Same plot in the case of a three-dimensional distribution of NPs.







The different regimes that can occur as a function of the angular frequency ω and the attenuation length are summarized in Fig. 8.

3. Experimental measurements

In order to support the theoretical development and the results of the numerical simulations described above, we have conducted experimental measurements aimed at measuring Δ^{ω} and Φ^{ω} for a given plasmonic system. We have chosen to consider the case of a quasihexagonal array of spherical gold NPs made by bloc copolymer micellar lithography. Such a technique produces an even distribution of spherical and identical NPs firmly attached onto the substrate. The average NP radius is R = 14 nm and the average NP interdistance is p = 72 nm. The NP distribution was heated using a uniform



FIG. 9. (Color online) (a) Experimental setup. (b) Scanning electron microscope image of the gold nanoparticle sample made by block copolymer lithography. (c) Schematic of the illumination conditions at the sample location.

FIG. 10. (Color online) Experimental results. (a) Amplitude of the temperature modulation. (b) Phase shift of the temperature modulation. (c) Polar plot of the temperature modulation. Solid lines: theory. Circles: measurements.

light beam of diameter $D = 30.0 \,\mu\text{m}$ at $\lambda = 532 \,\text{nm}$ (matching the NP plasmon resonance wavelength), which was modulated using an acoustooptic modulator (AOM, see Fig. 9). The temperature variations were probed using a laser beam at 632 nm (chosen to be out of the plasmon resonance) and a thermal lens effect: when the temperature of the medium surrounding the NPs increases, it creates a decrease of its refractive index acting as a local thermal lens that contributes to distort the wavefront of the probe beam [28,29]. By aperture clipping along the detection beam path, this wavefront distortion induces variations of the intensity measured by a photodiode. Another photodiode (not represented in the schematic) was used to follow the modulation of the heating laser beam intensity, as a reference. The signals from both photodiodes were sent to a lock-in amplifier (Ametek, 7280 DSP, Signal recovery) to measure the thermal response of the system in terms of amplitude and phase. The results are plotted in Fig. 10, along with numerical simulations, evidencing a good agreement.

4. Spatiotemporal evolution

So far, we mainly focused on the response of the system around the center of the NP distribution, which is usually what matters in experimental investigations. However, we will shortly explain to what extent some nonuniformity of the amplitude and phase can be expected in such a problem.

Figure 11 plots the profiles of the normalized temperature Re[$T^{\omega}(\mathbf{r},t)/T^{0}(\mathbf{r})$], the modulated temperature component Re[$(T^{\omega}(\mathbf{r},t) - T^{0}(\mathbf{r}))/T^{0}(\mathbf{r})$], and its phase arg[$T^{\omega}(\mathbf{r},t)$] throughout the NP distribution for various values of ξ . For each graph of the two first lines, four temperature profiles are plotted corresponding to four different and evenly distributed times *t* during a period of modulation. For low- ξ values, one can see that the temperature oscillates in phase with the excitation. This is the quasistatic regime. For larger values of ξ , the amplitude of the temperature oscillation weakens and for very large values of ξ , the modulation is so fast that the system no longer follows and reaches a steady state corresponding to a constant HSD $q_0(r)$. When increasing ξ , one can naturally observe an increase of the phase shift, up to the expected value $\pi/4$, as evidenced in the first section. Interestingly, this phase shift of $\pi/4$ is uniform over the location of the heat sources. This effect comes from the fact that the phase at each location of the system does not receive any contribution from sources further than δ_{th} . Each location of the system does not "see" further than δ_{th} , which creates this spatial invariance throughout the source distribution, far from the boundaries of the NP distribution.

III. CONCLUSION

To summarize, we have characterized the thermal response of a plasmonic system under time-harmonic illumination. Focus has been put on the response in *amplitude* and *phase* of the temperature evolution of the system. For the sake of comprehensiveness, we investigated both single and multiple nanoparticle illuminations.

In the case of a single nanoparticle illumination, as $\mu \sim 1$ in nanoplasmonics, a $\pi/2$ delayed regime is expected to occur when the radius *R* of the nanoparticle and the angular frequency ω are such that $R^2 \omega \gg a_w$ where a_w is the thermal diffusivity of the surroundings. This condition is, however, rarely fulfilled in nanoplasmonics ($R < 1 \mu$ m) for frequencies below 10 MHz.



FIG. 11. (Color online) Temperature profile across the heated area for different values of ξ varying from 10⁻² to 10³. In each case, different temperature profiles are plotted corresponding to four different times t_0, t_1, t_2, t_3 over the time period, such that $t_j = j/4 \times 2\pi/\omega$.

When a metal/surroundings interface resistivity is taken into account, the inner and outer temperatures of the nanoparticle are no longer supposed to be identical, and may feature a different dynamics. In particular, while the limit phase shift at high frequency remains $\pi/2$ for the inner temperature oscillation, it becomes $3\pi/4$ for the temperature oscillation in the surrounding medium at the vicinity of the nanoparticle.

When multiple NPs are gathered in close proximity, the occurrence of a delayed regime no longer necessitates very high frequencies or large nanoparticles, and can be easily observed experimentally. A first delayed regime occurs when the condition $D^2\omega > a_w$ is fulfilled where *D* is the typical size of the nanoparticle distribution. Interestingly, the associated phase shift depends on the dimensionality of the system. While a phase shift of $\pi/4$ is expected for a two-dimensional distribution of NPs, a phase shift of $\pi/2$ is expected for a three-dimensional distribution. A second regime at higher frequency occurs when $p^2\omega > a_w$ where *p* is the typical NP interdistance and is characterized by a divergent phase shift.

This work is typically intended to be useful when plasmonic systems are illuminated using a light source modulated by an optical chopper or an acoustooptic modulator, which is a common situation encountered for instance in photothermal imaging [24,25,30].

Apart from describing the physics of time-harmonic heating in nanoplasmonics, this work is also intended to provide all the information needed to answer the recurring question in nanoplasmonics: how fast temperature can be varied using light illumination of plasmonic nanoparticles. Indeed, for each angular frequency ω characterizing the transition from an inphase regime to a delayed regime derived in this work, $2\pi\omega^{-1}$ turns out to be the shorter time scale of possible temperature variations in a given plasmonic system.

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APPENDIX A: CALCULATION OF THE COMPLEX AMPLITUDE OF THE TEMPERATURE RESPONSE OF A SINGLE NANOPARTICLE FEATURING A FINITE SURFACE THERMAL CONDUCTIVITY

In this appendix, the system under study is a metal sphere immersed in a uniform medium. The sphere features a surface thermal conductivity g. To conduct the calculations, we consider that this finite conductivity is due to a thin and uniform layer of thickness ε covering the nanoparticle. In this case, it features a thermal conductivity $\kappa_1 = \varepsilon g$. This system is schematized in Fig. 12.

The equations governing the dynamics of this system are

$$\rho_{\rm s} \, c_{\rm s} \, \partial_t T(r,t) = \kappa_{\rm s} \frac{1}{r^2} \partial_r [r^2 \partial_r T(r,t)], \tag{A1}$$

$$V\rho_{\rm m}c_{\rm m}\frac{dT_{\rm NP}}{dt} = \kappa_{\rm s} 4\pi \ R^2 \partial_r T(R,t) + \ Q(t), \qquad (A2)$$

$$\kappa_1 \partial_r T_1(R + \varepsilon, t) = \kappa_s \partial_r T(R + \varepsilon, t).$$
(A3)



FIG. 12. (Color online) Temperature profile as a function of the radial coordinate r.

As ε is small, one can assume $T_1(r,t)$ to be linear, and the temperature continuity implies

$$T_1(r,t) = \frac{\Delta T(t)}{\varepsilon}(r-R) + T_{\rm NP}(t), \qquad (A4)$$

where
$$\Delta T(t) = T(R + \varepsilon, t) - T_{\text{NP}}(t).$$
 (A5)

Let us define the complex notations

V

$$Q^{\omega}(t) = Q_0 e^{-i\omega t}, \qquad (A6)$$

$$T_{\rm NP}^{\omega}(t) = \bar{T}_{\rm NP} \, e^{-i\,\omega t},\tag{A7}$$

$$T_1^{\omega}(r,t) = \frac{\Delta \bar{T} e^{-i\omega t}}{\varepsilon} (r-R) + \bar{T}_{\rm NP} e^{-i\omega t}, \qquad (A8)$$

$$T^{\omega}(r,t) = \bar{T} \, \frac{R+\varepsilon}{r} e^{i(k_{\omega}r-\omega t)}.$$
 (A9)

First, by injecting Eqs. (A7) and (A8) in Eq. (A2) and using the limit $\varepsilon \rightarrow 0$, one obtains

$$-V\rho_{\rm m} c_{\rm m} i\omega \bar{T}_{\rm NP} = 4\pi R^2 g e^{ik_{\omega}R} \Delta \bar{T} + Q_0. \qquad (A10)$$

Second, by injecting Eqs. (A8) and (A9) in Eq. (A3) and using the limit $\varepsilon \to 0$, one obtains

$$g\Delta \bar{T} = \frac{\kappa_2}{R} \bar{T} e^{ik_\omega R} (ik_\omega R - 1).$$
(A11)

Equations (A5), (A10), and (A11) form a system of three linear equations with three unknowns that are \overline{T} , \overline{T}_{NP} , and $\Delta \overline{T}$. The solutions read as

$$\bar{T}_{\rm NP} = \frac{Q_0}{4\pi \kappa_{\rm s} R \left(\frac{1-ik_{\omega} R}{1+\lambda_{\rm K}(1-ik_{\omega} R)} - i \omega \tau_{\rm m}\right)},$$
$$\bar{T} = \frac{e^{-ik_{\omega} R}}{1-ik_{\omega} R - i \omega \tau_{\rm m}[1+\lambda_{\rm K}(1-ik_{\omega} R)]}.$$

From these expressions, the amplitude and phase response of the temperature inside and outside the nanoparticle can be easily estimated.

APPENDIX B: CALCULATION OF THE COMPLEX AMPLITUDE OF THE TEMPERATURE RESPONSE AT THE CENTER OF A UNIFORM HEAT SOURCE DISTRIBUTION WITH CENTRAL SYMMETRY

1. Two-dimensional case

Consider a circular and uniform two-dimensional heat source density, oscillating over time at the angular frequency ω . In cylindrical coordinates, the oscillating component of the heat source density reads as

$$q(r,\theta,z,t) = q_0 \cos \omega t \tag{B1}$$

for z = 0 and r < D/2. q = 0 elsewhere. q_0 is here a power per unit area. Using a complex notation

$$q^{\omega}(r,\theta,z,t) = q_0 e^{-i\omega t} \tag{B2}$$

and the Green's function

$$G^{\omega}(r,\theta,z,t) = \frac{e^{i\kappa_{\omega}r - i\omega t}}{4\pi\kappa\sqrt{r^2 + z^2}},$$
(B3)

one can calculate the complex amplitude of the temperature modulation at the center of the system:

$$\bar{T}(t) = \int_0^{D/2} \int_0^{2\pi} G^{\omega}(r,\theta,0,t) q_0 r \, d\theta \, dr, \qquad (B4)$$

$$\bar{T}(t) = \frac{q_0}{2i\kappa k_\omega} (e^{ik_\omega D/2} - 1)e^{-i\omega t}.$$
 (B5)

From this expression, the amplitude and phase response of the temperature can be easily derived, keeping in mind that k_{ω} is complex [see Eq. (15)].

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2. Three-dimensional case

Consider a spherical and uniform heat source density, oscillating over time at the angular frequency ω . In spherical coordinates, the oscillating component of the heat source density reads as

$$q(r,t) = q_0 \cos \omega t \tag{B6}$$

for r < D/2. q = 0 elsewhere. q_0 is here a power per unit volume. Using a complex notation

$$q^{\omega}(r,t) = q_0 e^{-i\omega t} \tag{B7}$$

and the Green's function

$$G^{\omega}(r,t) = \frac{e^{ik_{\omega}r - i\omega t}}{4\pi\kappa r}$$
(B8)

one can calculate the complex amplitude of the temperature modulation at the center of the sphere:

$$\bar{T}(t) = \int_0^{D/2} G^{\omega}(r,t) q_0 4\pi r^2 dr,$$
 (B9)

$$\bar{T}(t) = \frac{q_0}{k_\omega^2 \kappa} \left[e^{ik_\omega D/2} \left(1 - i\frac{Dk_\omega}{2} \right) - 1 \right] e^{-i\omega t}.$$
 (B10)

From this expression, the amplitude and phase response of the temperature can be easily derived, keeping in mind that k_{ω} is complex [see Eq. (15)].

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