

## Paradoxes in laser heating of plasmonic nanoparticles

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*New Journal of Physics* **14** (2012) 093022 (14pp)

Received 21 June 2012

Published 13 September 2012

Online at <http://www.njp.org/>

doi:10.1088/1367-2630/14/9/093022

**Abstract.** We study the problem of the laser heating of plasmonic nanoparticles and demonstrate that, in sharp contrast to the common belief, a particle with a small dissipative constant absorbs much more energy than the particle with a large value of this constant. Even higher effective absorption may be achieved for core-shell nanoparticles. Our analysis uses the exact Mie solutions, and optimization of the input energy is performed at a fixed fluence with respect to the particle size, wavelength and duration of the laser pulse. We introduce a new quantity, *the effective absorption coefficient* of a particle, which allows one to compare quantitatively the light absorption by nanoparticles with that of

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a bulk material. We describe a range of parameters where a *giant absorption enhancement* can be observed and give practical examples of metals whose optical properties vary from weak (potassium) to strong (platinum) dissipation.

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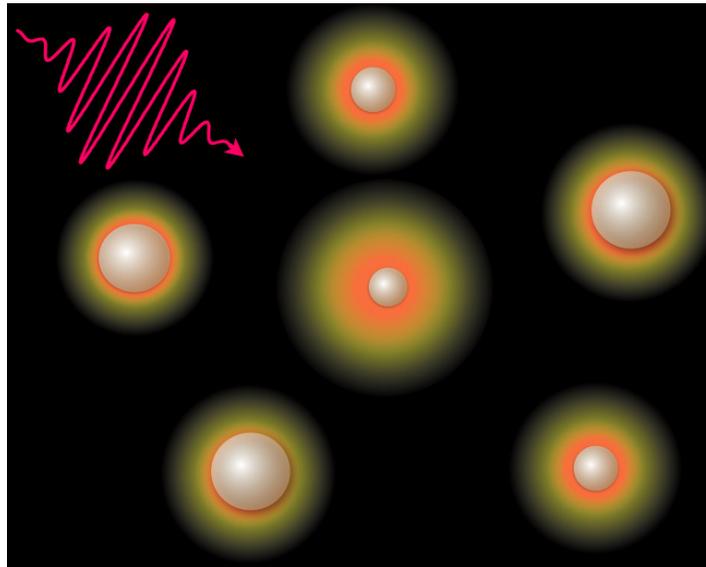
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## 1. Introduction

Absorption of light by small plasmonic nanoparticles is a key effect for numerous applications of nanostructures in data storage technology, nanotechnology, chemistry, biophysics and bioengineering. The absorption characteristics depend on the material of the particle and its shape. It is relevant to mention the absorption enhancement in amorphous silicon nanocone arrays [1]. The properties of such black silicon are useful for a wide range of commercial devices. In recent years, the problem of laser heating of plasmonic nanoparticles has attracted much attention (see, e.g., [2–11] and references therein). A similar problem appears in astrophysics with thermal noise in interstellar dust where temperature fluctuations for small particles of interstellar dust may be about 1000 K [12].

The problem of the effective absorption of light by particles stimulated a great deal of research and posed many non-trivial questions. In one of his famous papers, see [13], Bohren tried to answer the question: ‘how can a particle absorb more than the light incident on it?’. He was puzzled by the fact that the absorption cross section may be larger than the geometrical cross section of the same particle. The answer was quite simple: since the light is an electromagnetic wave, a small particle can disturb the flow of electromagnetic energy in its neighborhood and act as a funnel. In this paper, we refine this question and ask: ‘can a particle with a small dissipative constant absorb more than one with a large value of this constant?’. By doing a systematic analysis, we demonstrate that the answer is: ‘yes, it can’; namely, counter-intuitively, in the vicinity of the localized surface plasmon resonances the maximal absorption is achieved at a certain *small* value of the dissipative constant of the particle. This effect might have a large impact on the laser heating and related phenomena.

In this paper, we discuss the problem of optimization of the energy input of a laser pulse into a nanoparticle. Our study gives rise to a number of paradoxical, counter-intuitive conclusions, which shed new light on this important problem. The structure of the paper is as follows: first, we discuss the origin of the mentioned paradoxes; then, we perform a general analysis of the optimization problem based on the exact Mie solution [14]; next, we present the results of the optimization for six cases of nanoparticles made of different materials; and then study the effect of heat diffusion from a particle to a host medium (figure 1). Finally, in section 5 we summarize the obtained results and conclude.



**Figure 1.** Schematic diagram of laser heating of nanoparticles embedded in a transparent host medium. For short laser pulses, the heated layers of the medium in the vicinity of the nanoparticles are thin, and the corresponding energy losses may be neglected.

## 2. Absorption enhancement

Dissipation of energy is given by divergence of the Poynting vector (see, e.g., section 80 in the book [15]). For non-magnetic media with  $\mu = 1$ , this value is proportional to the imaginary part of complex dielectric permittivity,  $\text{Im } \epsilon$ . Therefore, it seems that, in order to increase the energy release at the particle, one has to increase the value  $\text{Im } \epsilon$  for the particle's material: the larger the  $\text{Im } \epsilon$ , the larger the energy release. However, this simple reasoning does not take into account the concentration of the electromagnetic energy in the particle due to diffraction. Meanwhile, close to the frequencies of the plasmon (polariton) resonances, i.e. the frequencies of the eigenmodes of electromagnetic oscillations in the particle regarded as a resonator, this concentration may be very large. Bearing in mind that the amplitude of the oscillations at the resonant points *decreases* with an increase of  $\text{Im } \epsilon$ , one arrives at the conclusion that the problem of optimization of the energy release of a nanoparticle irradiated by a laser beam is not so straightforward, and requires a more accurate investigation.

To be specific, let us consider the laser heating of a thermally isolated spherical particle. From the energy balance, neglecting heat diffusion, one can write a linear relation for the conversion of light energy (laser fluence  $\Phi$  ( $\text{J cm}^{-2}$ )) into the density of the internal absorbed energy  $\mathcal{E}$  ( $\text{J cm}^{-3}$ ) of a material [16]:

$$\mathcal{E} = \frac{3}{4} \frac{Q_{\text{abs}}}{R} \Phi. \quad (1)$$

Here  $R$  is the particle radius and  $Q_{\text{abs}}$  is the so-called absorption efficiency [14] (the absorption cross section  $\sigma_{\text{abs}}$  normalized over the geometrical cross section,  $Q_{\text{abs}} = \sigma_{\text{abs}}/\pi R^2$ ). Employing the exact Mie solution for the scattering of a plane electromagnetic wave by a spherical particle,

this quantity can be written as follows:

$$Q_{\text{abs}} = Q_{\text{ext}} - Q_{\text{sca}}, \quad Q_{\text{ext}} = \frac{2}{q^2} \sum_{\ell=1}^{\infty} (2\ell + 1) \text{Re}(a_{\ell} + b_{\ell}), \quad Q_{\text{sca}} = \frac{2}{q^2} \sum_{\ell=1}^{\infty} (2\ell + 1) \{|a_{\ell}|^2 + |b_{\ell}|^2\},$$

where  $q$  is the so-called size parameter. In the case of a particle placed in vacuum,  $q = kR = \omega R/c = 2\pi R/\lambda$ . Here  $k$ ,  $\omega$  and  $\lambda$  stand for the light wavenumber, frequency and wavelength, respectively. For nanoparticles at the optical frequencies, we have  $q \ll 1$ . The scattering amplitudes  $a_{\ell}$  (electric) and  $b_{\ell}$  (magnetic) are defined by the Mie formulae

$$a_{\ell} = \frac{F_{\ell}^{(a)}}{F_{\ell}^{(a)} + iG_{\ell}^{(a)}}, \quad b_{\ell} = \frac{F_{\ell}^{(b)}}{F_{\ell}^{(b)} + iG_{\ell}^{(b)}}, \quad (2)$$

and quantities  $F_{\ell}^{(a,b)}$  and  $G_{\ell}^{(a,b)}$  are expressed in terms of the Bessel and Neumann functions [14].

Under the validity of the Rayleigh approximation [14, 15], the dominant absorption efficiency is given by the dipole mode

$$Q_{\text{abs}} = q \frac{12 \epsilon''}{(\epsilon' + 2)^2 + \epsilon''^2}, \quad (3)$$

where  $\epsilon' = \text{Re } \epsilon$  and  $\epsilon'' = \text{Im } \epsilon$ .

As follows from equation (3), the absorption efficiency has a singularity when  $\epsilon' \rightarrow -2$  and  $\epsilon'' \rightarrow 0$ . Specifically, at  $\epsilon' \rightarrow -2$ ,  $\epsilon'' \rightarrow 0$  the efficiency does not have a definite limit, and may have any value depending on the shape of a trajectory along which one approaches the point  $\epsilon' = -2$ ,  $\epsilon'' = 0$  on the  $(\epsilon', \epsilon'')$  plane.

To see that, we assume that the trajectory is described by the expression  $\epsilon' + 2 = B(\epsilon'')^{\theta}$ , where  $B$  and  $\theta$  are constants. Then,  $Q_{\text{abs}}$  diverges at  $\epsilon'' \rightarrow 0$  and  $\theta > 1/2$ , vanishes at  $\theta < 1/2$  and may be equal to any value (depending of the value of  $B$ ) at  $\theta = 1/2$ .

Singularity of  $Q_{\text{abs}}$  at  $\epsilon' = -2$ ,  $\epsilon'' \rightarrow 0$  may bring about a paradoxical conclusion opposite to the naïve one mentioned above (the larger the  $\epsilon''$ , the larger the absorption), namely that non-dissipating plasmonic nanoparticles with  $\epsilon'' = 0$  exhibit the most efficient heating [2, 6]. However, this conclusion is erroneous too. The problem is that in the vicinity of the plasmon resonances for weakly dissipating materials the Rayleigh scattering is replaced by the anomalous scattering [17], whose analysis requires the study of the complete Mie solution [14] (see also [18, 19]). Such a study is performed below.

To begin we note that the dimension of the quantity

$$\alpha_{\text{eff}} = \frac{3Q_{\text{abs}}}{4R}$$

in equation (1) is ( $1 \text{ cm}^{-1}$ ). Therefore, this quantity may play the role of an effective absorption coefficient for a particle. To understand whether the particle has any advantage in the light absorption relative to the same material in a bulk, it is convenient to compare  $\alpha_{\text{eff}}$  with the absorption coefficient of the latter. The absorption coefficient  $\alpha$ , describing the spatial decay of the Poynting vector at the normal light incidence on a surface of a semi-infinite medium with complex dielectric permittivity  $\epsilon$ , is given by the expression

$$\alpha = 2k \text{Im} \sqrt{\epsilon} \equiv 2\kappa k, \quad (4)$$

where  $\kappa$  is the imaginary part of the refractive index of the medium,  $\sqrt{\epsilon} = n + i\kappa$ .

For a majority of metals in the optical range,  $\alpha \approx 10^5\text{--}10^6 \text{ cm}^{-1}$  [16]. However, if we try to use this expression for  $\alpha$  to define a characteristic scale for the energy release in a medium, we

face a paradox once more. The paradox is seen clearly if we consider a medium with  $\text{Re } \epsilon < 0$  and  $\text{Im } \epsilon = 0$ . Such a medium is non-dissipating, so the energy release there should be zero and obviously does not have any characteristic scale. On the other hand, equation (4) in this case provides quite a finite value of  $\alpha$ .

The paradox is resolved easily if we recollect that only a part of the incident fluence is absorbed, while the other part is reflected. Taking into account this fact, one should conclude that, an analogue of equation (1) for the semi-infinite medium in the immediate vicinity of its boundary reads as

$$\mathcal{E} = \mathcal{A}\alpha\Phi, \quad (5)$$

where  $\mathcal{A}$  stands for absorptivity. In the aforementioned case ( $\text{Re } \epsilon < 0$  and  $\text{Im } \epsilon = 0$ ) the particle does not absorb any radiation,  $\mathcal{A} = 0$ , and no energy is released in the medium, indeed. If a plane electromagnetic wave propagating in a vacuum is incident on a medium with complex refractive index  $n + i\kappa$ , the absorptivity is given by the following well-known expression:

$$\mathcal{A} = \frac{4n}{(n+1)^2 + \kappa^2}. \quad (6)$$

In practical cases,  $\mathcal{A}$  depends also on the quality of the surface, the way it was treated, etc. All these effects may be incorporated into the developed analysis if required. To this end, phenomenological (experimental) values of  $\mathcal{A}$  should be employed instead of equation (6).

To compare quantitatively the light absorption by the particle and the same bulk material, it is convenient to introduce the net absorption enhancement factor

$$\beta_{\text{eff}} = \frac{\beta}{\mathcal{A}}, \quad \beta = \frac{\alpha_{\text{eff}}}{\alpha}, \quad (7)$$

where  $\mathcal{A}$  is defined either by equation (6) or by an experimental value. Since  $0 \leq \mathcal{A} \leq 1$ , the quantity  $\beta$  presents the *minimal* value of the absorption enhancement. The condition  $\beta_{\text{eff}} \geq \beta \gg 1$  means that the nanoparticle absorbs light much more efficiently than the corresponding bulk material. To distinguish the role of partial resonances, we introduce also the partial enhancement factors  $\beta_{\text{eff}}^{(\ell)}$  and  $\beta^{(\ell)}$  with replacement in the definition of  $\alpha_{\text{eff}}$  in equation (7),  $Q_{\text{abs}} \rightarrow Q_{\text{abs}}^{(\ell)}$ , where the partial absorption efficiencies  $Q_{\text{abs}}^{(\ell)}$  read as

$$Q_{\text{abs}}^{(\ell)} = Q_{\text{ext}}^{(\ell)} - Q_{\text{sca}}^{(\ell)}, \quad Q_{\text{ext}}^{(\ell)} = \frac{2}{q^2}(2\ell+1)\text{Re}(a_\ell + b_\ell), \quad Q_{\text{sca}}^{(\ell)} = \frac{2}{q^2}(2\ell+1)(|a_\ell|^2 + |b_\ell|^2).$$

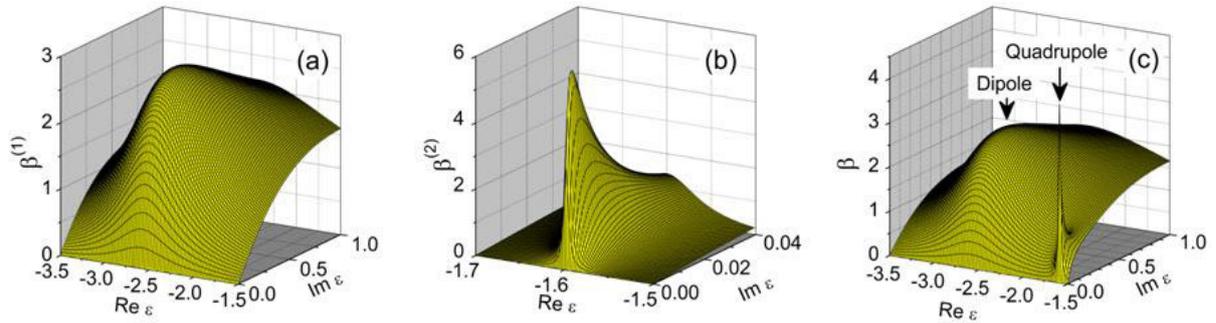
Examples of the dipole ( $\ell = 1$ ) and quadrupole ( $\ell = 2$ ) plasmon resonances in absorption are shown in figure 2 for the size parameter  $q = 0.5$ . From this figure, one can easily find the corresponding values of the real and imaginary parts of dielectric permittivity  $\epsilon$  for each partial resonance.

Similar maxima exist in the absorption efficiencies  $Q_{\text{abs}}^{(\ell)}(\epsilon)$  for all orders of the resonances. For small size parameter  $q \ll 1$ , they follow trajectories of the surface plasmon resonances given by an approximate formulae [20]:

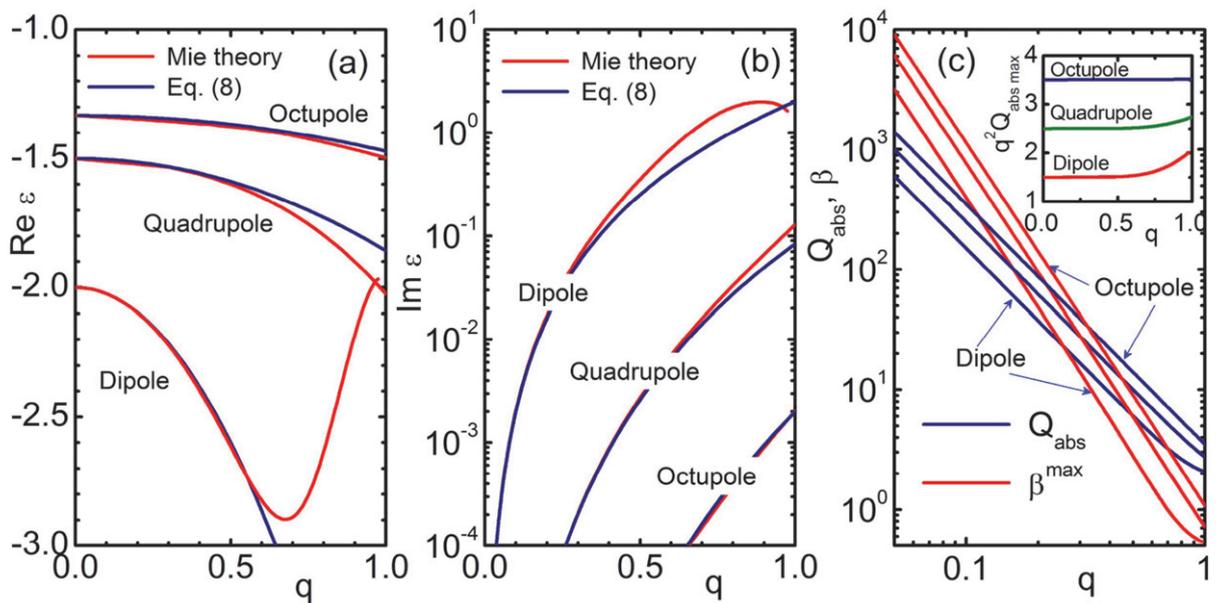
$$\text{Re } \epsilon \approx - \left[ \frac{\ell+1}{\ell} + q^2 \frac{2(2\ell+1)(\ell+1)}{\ell^2(2\ell-1)(2\ell+3)} \right], \quad \text{Im } \epsilon \approx q^{2\ell+1} \frac{\ell+1}{[\ell(2\ell-1)!!]^2}. \quad (8)$$

The corresponding maximal value of  $Q_{\text{abs}}^{(\ell)}$  at  $q \ll 1$  is [20]

$$Q_{\text{abs max}}^{(\ell)} = \frac{1}{q^2} \left( \ell + \frac{1}{2} \right). \quad (9)$$

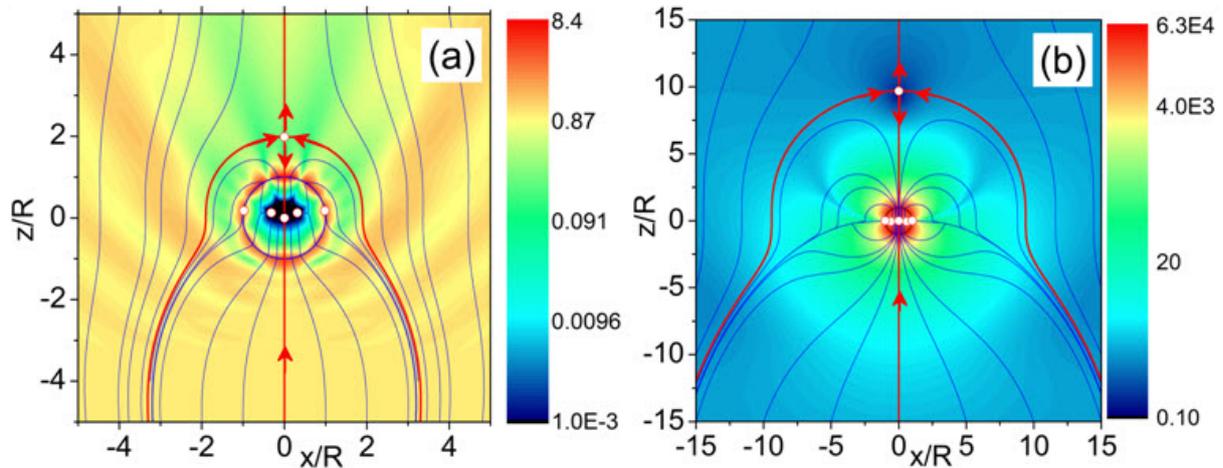


**Figure 2.** Absorption enhancement  $\beta^{(1)}$  (a),  $\beta^{(2)}$ (b) and total  $\beta$  (c) for the size parameter  $q = 0.5$ . Calculations are performed in accord with the complete Mie solution for a particle irradiated in a vacuum.



**Figure 3.** Values of dielectric permittivity corresponding to the maximal absorption of a nanoparticle irradiated by a plane electromagnetic wave in a vacuum versus the size parameter, according to equation (8) and calculated from the complete Mie solution:  $\text{Re } \epsilon(q)$  (a) and  $\text{Im } \epsilon(q)$  (b). Maximal values of  $Q_{\text{abs}}$  and the ratio  $\alpha_{\text{eff}}/\alpha = \beta$  along the optimal material parameters (c). The inset in panel (c) illustrates the variation of the coefficient  $q^2 Q_{\text{abs max}}^{(\ell)}$  at the maximal absorption versus the size parameter.

In figure 3, we present the trajectories of these maxima according to the complete Mie solution. Equations (8) and (9) agree excellently with the exact solution up to the size parameter  $q \approx 0.5$ . In figure 3(c) one can see that  $Q_{\text{abs max}}^{(\ell)} \propto q^{-2}$ , in agreement with equation (9), and  $\beta \propto q^{-3}$ , in agreement with equations (7) and (9). Deviations of the coefficients from the values defined by equation (8) with an increase in the size parameter are shown in the inset of figure 3(c). Naturally, for larger values of the size parameter, we approach the absorptivity of a bulk



**Figure 4.** The Poynting vector distribution in the  $xz$  plane for the maximal absorption in the vicinity of the dipole resonance for particles irradiated in a vacuum. The plane, linearly polarized incident wave propagates along the  $z$ -axis with the vector  $\mathbf{E}$  lying in the  $xz$  plane. The size parameter  $q = 0.5$  (a) and  $q = 0.1$  (b). For the corresponding values of dielectric permittivity, see figures 3(a) and (b). Color density plots present the modulus of the Poynting vector  $|\mathbf{S}|^2$  (in log scale). The Poynting vector lines are blue. The surface of the particle is marked with a black circle. Inside the particle  $\text{div } \mathbf{S} < 0$ ; outside the particle, in free space  $\text{div } \mathbf{S} = 0$ . Red lines in the plots designate separatrices illustrating *the funnel effect* [13]. Red circles indicate singular points, namely one saddle point above the particle, two singular points on the particle surface and a few stable nodes inside the particles, which correspond to the positions of ‘absorption attractors’. Note the difference in the scales of panels (a) and (b).

material. At the same time, for small values of the size parameter, it is possible to obtain a huge enhancement in the absorption, e.g. by three or four orders of magnitude, compared to the absorption of a bulk material (see figure 3(c)). This allows us to term the effect of absorption enhancement for weakly dissipating plasmonic nanoparticles as the *anomalous light absorption*.

The physical grounds for the absorption enhancement near the surface plasmon resonances are related to an increase in the effective cross section of the nanoparticle, which may greatly exceed its geometrical cross section  $\pi R^2$ . The latter can be clearly seen from the Poynting vector distribution [13, 21–23]. To illustrate the difference in the Poynting vector distributions at the maximal absorption for ‘small’ and ‘large’ particles, in figure 4 we show the corresponding plots for the dipole resonance. Outside the particle in a vacuum  $\text{div } \mathbf{S} = 0$ , while inside the absorbing particle  $\text{div } \mathbf{S} < 0$ . It allows us to select the whole energy flux into two distinct parts. The Poynting vector lines that penetrate the particle *and end inside it* belong to one group, and those that bypass the particle *and continue to infinity* belong to the other group. The two groups are separated by separatrices marked in red in figure 4. A part of the energy flux of the first group results in the *funnel effect*—when the particle acts as an attractor collecting light from a large area and delivering it to the particle. As a result, the effective absorption area  $\pi R_{\text{eff}}^2$  becomes much larger than the geometric cross section. The smaller the particle the more pronounced the effect. In the discussed example  $(R_{\text{eff}}/R)^2 \approx 10$  at  $q = 0.5$  (figure 4(a)), while at  $q = 0.1$  it is about 300 (figure 4(b)).

These results have a simple explanation, namely, owing to the diffractive limit, the maximal diameter of the ‘funnel’ inlet cannot exceed  $\lambda$ . Then, taking into account that, if  $\ell$  is not too large,  $q$  is the only small parameter in the problem, and that at  $q \ll 1$  all the three partial resonant cross sections  $\sigma_{\text{ext max}}^{(\ell)}$ ,  $\sigma_{\text{sca max}}^{(\ell)}$  and  $\sigma_{\text{abs max}}^{(\ell)}$  approach certain finite,  $q$ -independent limits [17–20], we arrive at the conclusion that the three quantities should be of the same order of magnitude:  $\sigma_{\text{ext max}}^{(\ell)} \sim \sigma_{\text{sca max}}^{(\ell)} \sim \sigma_{\text{abs max}}^{(\ell)} \sim \pi \lambda^2/4$ . It brings about the following estimates:

$$Q_{\text{ext max}}^{(\ell)} \sim Q_{\text{sca max}}^{(\ell)} \sim Q_{\text{abs max}}^{(\ell)} \sim (R_{\text{eff}}/R)^2 \sim (\pi/q)^2,$$

which agree with the results discussed in the preceding paragraph, see also equation (11) below and the corresponding expressions in [17–20].

It has been shown above that under the Rayleigh approximation for  $Q_{\text{abs}}$ , the point  $\epsilon' = -2$ ,  $\epsilon'' = 0$  is singular. It is interesting to elucidate the actual behavior of  $Q_{\text{abs}}(\epsilon', \epsilon'')$  in the vicinity of this point as well as in the vicinity of the maximum of the anomalous absorption based upon the exact Mie solution. Then, a problem about the lineshape for the discussed resonant absorption arises. A general analytical expression for this lineshape has been obtained in a recent publication of one of the authors [20]. It has been shown therein that the lineshape of  $Q_{\text{abs}}(\epsilon', \epsilon'')$  in the region of anomalous absorption is described by the following universal function:

$$\frac{q^2 Q_{\text{abs}}}{2(2\ell + 1)} = \frac{\zeta}{(1 + \zeta)^2 + \xi^2}, \quad (10)$$

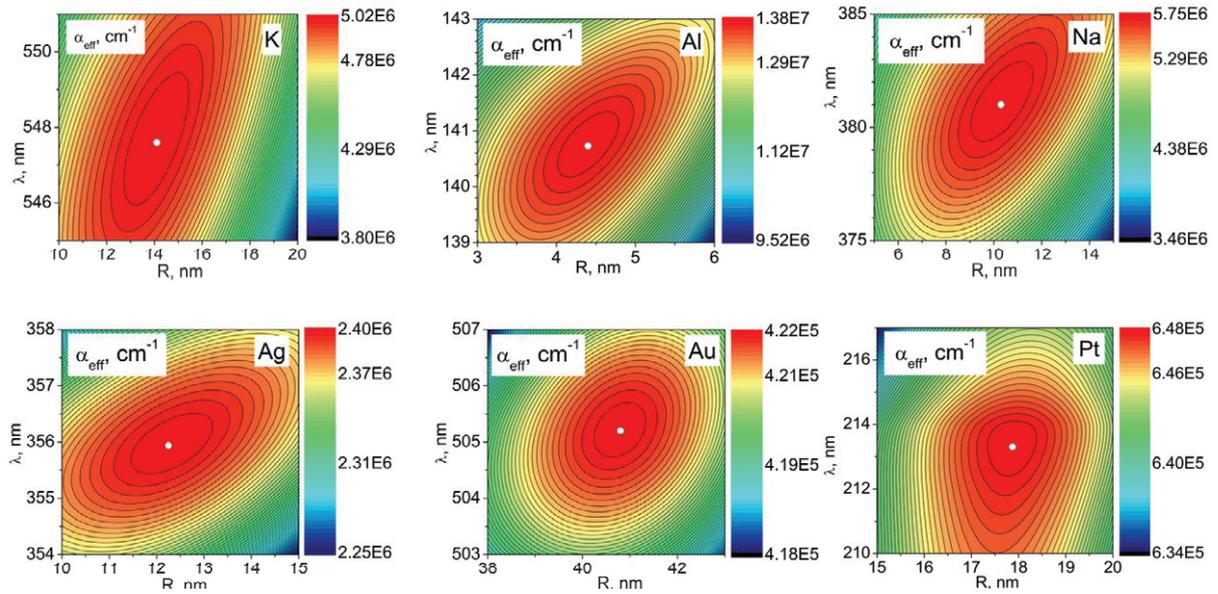
regardless of the order of the resonance (i.e. the value of  $\ell$ ). Here  $\xi = \Delta^{(\ell)} \epsilon' / f_\ell(q)$ ,  $\zeta = \epsilon'' / f_\ell(q)$  and  $\Delta^{(\ell)} \epsilon'$  stand for departure of  $\epsilon$  from its resonant value, defined by equation (8).

Although shapes of the cross sections of the surface defined by equation (10) by the planes  $\xi = \text{const}$  and  $\zeta = \text{const}$  are substantially different, in the vicinity of the maximum the surface is reduced to the paraboloid of revolution:

$$\frac{q^2 Q_{\text{abs}}}{2(2\ell + 1)} = \frac{1}{4} - \frac{r^2}{16}.$$

Here  $r^2 = \xi^2 + (\Delta\zeta)^2$  and  $\Delta\zeta$  denotes a deviation of  $\zeta$  from the value  $\zeta = 1$ , where the latter corresponds to the maximum of  $Q_{\text{abs}}$ . Regarding the behavior of  $Q_{\text{abs}}$  at  $\epsilon'' \rightarrow 0$ , it is seen straightforwardly that in this limit  $Q_{\text{abs}}$  is a linear function of  $\epsilon''$  at any fixed  $\epsilon'$ .

Completing this section, let us discuss a seeming analogy between the light scattering of a particle with  $\epsilon'' \rightarrow 0$  and light reflection by an ‘ideal’ conductor, whose conductivity  $\sigma$  tends to infinity. It seems that an analogy does exist: at  $\sigma \rightarrow \infty$   $\epsilon \simeq i\epsilon'' = i4\pi\sigma/\omega \rightarrow \infty$ , hence  $n = \kappa = \sqrt{\epsilon''/2} \rightarrow \infty$  and  $\mathcal{A} \rightarrow 0$ , see equation (6). It means that the ideal conductor reflects 100% of incident light and does not absorb any. A particle with  $\epsilon'' = 0$  just scatters incident light and does not absorb it too. However, the analogy is seeming indeed. Firstly, note that these two cases correspond to the opposite limits, since in our case  $\epsilon$  is almost purely real with a small imaginary part. Secondly, the skin-layer  $\delta = 1/\alpha$  for the ideal conductor vanishing ( $\delta \sim c/\sqrt{\sigma\omega} \rightarrow 0$  at  $\sigma \rightarrow \infty$ ). In contrast, in our case the field penetrates the entire particle, see figure 5, and all the phenomena discussed above are based upon this effect. The list of differences may be extended. These differences bring about different physics. Thus, in fact, the two phenomena are dissimilar. The analogy between them is forced and may give rise to erroneous conclusions.



**Figure 5.** Contour plots for the effective absorption coefficients of different nanoparticles irradiated in a vacuum.

### 3. Optimization

It is clear that the discussed huge enhancement in absorption is attractive for many applications. At the same time, in order to obtain this enhancement, one needs an extremely small value of  $\text{Im } \epsilon$ ; for example, for the dipole resonance at  $q = 0.1$  the corresponding value of  $\text{Im } \epsilon \approx 10^{-3}$ , see figure 3(c). The importance of weak dissipation for plasmonic materials was emphasized in many papers, and some ideas to create weakly dissipating plasmonic materials were suggested (see, for example, [24]). To understand to what extent this reasoning may be applied to natural materials, we performed numerical calculations for six metals: potassium, aluminum, sodium, silver, gold and platinum, whose properties cover a vast range from weak dissipation at the optical frequencies (potassium) to strong dissipation (platinum). For these calculations, we use the optical properties of the materials from Palik's book [25], which are approximated with the help of the Drude formula:

$$\epsilon = \epsilon' + i\epsilon'' = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2} \left( 1 - i\frac{\gamma}{\omega} \right), \quad (11)$$

where  $\omega_p$  and  $\gamma$  stand for the plasma and collision frequencies, respectively. Equation (11) can be applied to any material provided the plasma and collision frequencies are functions of  $\omega$ . These functions are calculated at every point in the table [25] with polynomial interpolation between the points. The effect of the nanoparticle size was taken into account with the help of renormalization of the corresponding collision frequency of free electrons,  $\gamma = \gamma_\infty + v_F/R$ , where  $\gamma_\infty$  is the collision frequency for a bulk material (at a given  $\omega$ ) and  $v_F$  is the Fermi velocity of electrons [26]. The diffraction problem is treated within the framework of the complete Mie solution. For practical materials, we are more interested in the values of the effective absorption coefficient  $\alpha_{\text{eff}}$  rather than in dimensionless parameters  $\beta$  or  $\beta_{\text{eff}}$ . Examples of such calculations are summarized in table 1. The second column  $\lambda_0$ , nm, shows the wavelength where the

**Table 1.** Values of the parameters maximizing the absorption of nanoparticles made of different metals irradiated by a plane electromagnetic wave in a vacuum.

Metal	$\lambda_0$ , nm	$\text{Im } \epsilon(\lambda_0)$	Fermi velocity, $v_F$ , cm s <sup>-1</sup>	Optimal $R$ , nm	Optimal $\lambda$ , nm	$\alpha_{\text{eff}}^{\text{max}}$ , cm <sup>-1</sup>	$\alpha$ , cm <sup>-1</sup> (bulk)	$\mathcal{A}(\lambda_{\text{optimal}})$	$\beta_{\text{eff}}$
K	542	0.138	$0.86 \times 10^8$	14.1	547.6	$5.02 \times 10^6$	$3.29 \times 10^5$	0.063	242
Al	138.8	0.16	$2.02 \times 10^8$	4.4	140.7	$1.38 \times 10^7$	$1.29 \times 10^6$	0.073	147
Na	377	0.178	$1.07 \times 10^8$	10.3	381	$5.75 \times 10^6$	$4.74 \times 10^5$	0.080	151
Ag	354	0.6	$1.39 \times 10^8$	12.2	356	$2.40 \times 10^6$	$5.2 \times 10^5$	0.240	19.2
Au	485	3.97	$1.39 \times 10^8$	40.8	505.2	$4.22 \times 10^5$	$4.83 \times 10^5$	0.578	1.51
Pt	276	5.64	$1.45 \times 10^8$	17.9	213.3	$6.48 \times 10^5$	$9.1 \times 10^5$	0.576	1.24

infinitesimal particle ( $q \rightarrow 0$ ) has the dipole plasmon resonance:  $\text{Re } \epsilon = -2$ . The third column indicates  $\text{Im } \epsilon(\lambda_0)$ . This column allows one to distinguish the weakly dissipating materials with  $\text{Im } \epsilon(\lambda_0) \ll 1$  from strongly dissipating with  $\text{Im } \epsilon(\lambda_0)$  of the order of unity, or larger than that. The values of the Fermi velocity were taken from [27]. The next three columns summarize the results of calculations of the maximal effective absorption according to the complete Mie solution. We present also the absorption coefficient of the corresponding bulk materials at the wavelengths of the maximal effective absorption of the nanoparticles and the parameter  $\beta_{\text{eff}}$  for the corresponding absorption enhancement with  $\mathcal{A}$  calculated in accord with equation (6). As one can see, for weakly dissipating metals (K, Al, Na), it is possible to obtain enhancement in absorption by more than two orders of magnitude. For strongly dissipating materials (Au and Pt), the effective absorption coefficient  $\alpha_{\text{eff}}$  is even below the absorption coefficient for the bulk material. For Ag with ‘intermediate’ dissipation the ratio  $\alpha_{\text{eff}}/\alpha \approx 4.6$ . Nonetheless, the net enhancement factor  $\beta_{\text{eff}}$  for Ag is about 20, owing to a small value of absorptivity for the bulk material. Examples of distributions of the efficient absorption coefficient for a number of metals in the vicinity of the optimal parameters are shown in figure 5. The dependences  $\alpha_{\text{eff}}(R, \lambda)$  for the other metals are similar. Note that while for weakly dissipating materials the wavelengths, maximizing the absorption and scattering efficiencies, practically coincide with each other [20] (the difference between them for potassium is less than 1 nm), there exists a pronounced mismatch between the two quantities for strongly dissipating materials. Thus, for gold the mismatch is equal to 15 nm.

Note also that for the ‘ideal’ optimization, when  $\epsilon'$  and  $\epsilon''$  may be regarded as two independent tuning parameters,  $\alpha_{\text{eff}}$  increases monotonically with an increase of the order of resonance  $\ell$ , at least as long as the particle may be regarded as small, see equation (9) and figure 3. In fact, for the discussed real metals, when instead of  $\epsilon'$  and  $\epsilon''$  the actual tuning parameter is  $\omega$  the absolute maximum of  $\alpha_{\text{eff}}$  corresponds to the dipole mode ( $\ell = 1$ ).

Bearing in mind that for a thermally isolated particle  $\mathcal{E} = C\rho T$ , where  $C$  stands for the specific heat and  $\rho$  is the density, it is easy to estimate the fluence  $\Phi$  which is required to achieve a desired temperature rise, e.g.  $T = 100$  K. It is clear that weakly dissipating particles need a smaller fluence than strongly dissipating particles. For instance, to heat a potassium particle to the same temperature as a gold particle, we need almost 50 times smaller fluence. Further enhancement of absorption can be achieved for weakly dissipating particles embedded in transparent media. For example, for K in a KCl host medium at the optimal parameters

( $R = 13.5$  nm and  $\lambda = 738.6$  nm) the effective absorption can reach  $6.91 \times 10^6$  cm<sup>-1</sup>. It is about 40% larger than that for the same particle in a vacuum and 20 times larger than the absorption coefficient for a bulk material. However, the largest increase in the effective absorption coefficient may be obtained for a core-shell particle with the optimized core radius, shell radius and incident wavelength. For K particle inside a KCl shell in a vacuum, it is possible to reach the effective absorption coefficient  $2.05 \times 10^7$  cm<sup>-1</sup>. Such optimized core-shell structures may be very attractive for biomedical and other applications.

#### 4. Heat transfer

When a nanoparticle is heated inside a host medium, it is important to select a suitable pulse duration for the heating. To this end, one should solve the heat-transfer equation. In our recent paper [28], this problem was inspected for a broad range of different parameters. However, for a majority of typical cases one can neglect the temperature gradient within the particle and consider a homogeneous particle temperature rise  $T_p(t)$ . In this case, the problem of the laser heating is simplified. For example, we discuss the spherically symmetric problem for a particle embedded in some medium with heat diffusivity  $\chi$ . We consider a non-absorbing (transparent) medium, which is heated by heat diffusion from the particle solely. The solution of the heat diffusion equation (see, e.g., [29]) yields

$$T_p(t) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} T_p(s) e^{st} ds, \quad (12)$$

where  $T_p(s)$  is the Laplace image

$$T_p(s) = \frac{3}{4} \frac{I(s) Q_{\text{abs}} R}{C \rho R^2 s + 3\kappa_m (1 + R\sqrt{s/\chi})}. \quad (13)$$

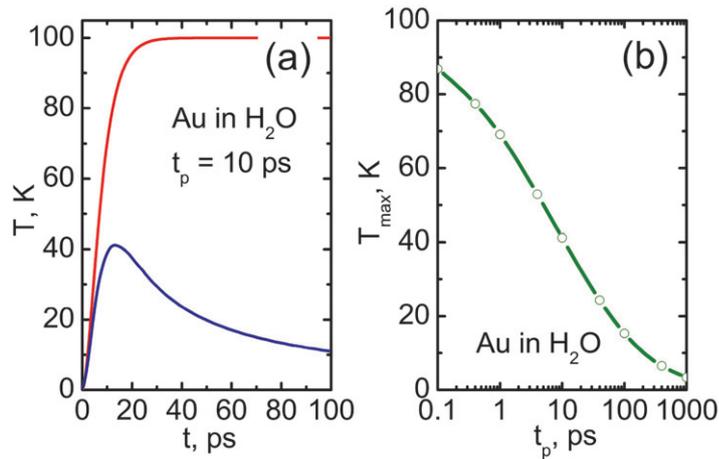
Here  $\kappa_m$  stands for the thermal conductivity of the host medium and  $I(s)$  is the Laplace image of the laser beam intensity  $I(t)$  (W cm<sup>-2</sup>). For example, for a smooth laser pulse with  $I(t) = (t/t_\ell^2) \Phi \exp(-t/t_\ell)$ ,  $t \geq 0$  [30], one obtains

$$I(s) = \Phi \frac{1}{(1 + st_\ell)^2}. \quad (14)$$

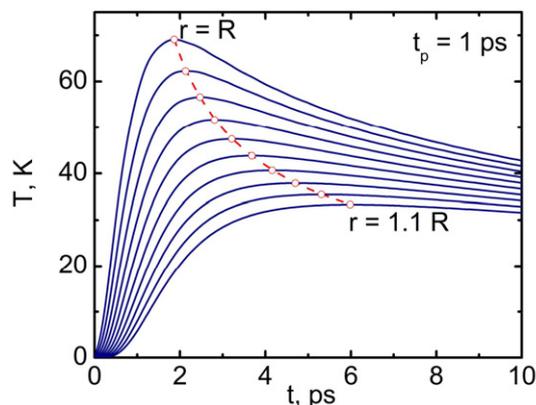
The parameter  $t_\ell$  in equation (14) is related to the pulse duration  $t_p$  (full-width at half-maximum) as follows:  $t_\ell = t_p/2.446$ . The corresponding temperature rise of the nanoparticle may be found from equations (12)–(14) by numerical integration. In figure 6, we show an example of these calculations for the temperature rise of a gold particle heated by a smooth laser pulse. It is a typical setup for biomedical applications [31]. We can see that heat transfer to the environment suppresses the temperature rise dramatically. To reach temperatures comparable with that for thermally isolated particles, one needs very short laser pulses.

In biomedical applications, it is important to localize the heating area of a host medium in the immediate vicinity of the nanoparticle. When the particle temperature rise  $T_p(t)$  is known, the temperature rise distribution in the surrounding medium is given by the following expression [29]:

$$T(r, t) = \frac{2}{\sqrt{\pi}} \frac{R}{r} \int_{\frac{r-R}{2\sqrt{\chi t}}}^{\infty} T_p \left( t - \frac{(r-R)^2}{4\chi\mu^2} \right) e^{-\mu^2} d\mu, \quad r \geq R. \quad (15)$$



**Figure 6.** Temperature rise for a gold nanoparticle ( $R = 21.5$  nm) in water, which corresponds to the parameters for the maximal effective absorption by a laser pulse with  $t_p = 10$  ps and fluence  $\Phi = 236.7 \mu\text{J cm}^{-2}$  (a). The red line presents the temperature rise for the thermally isolated particle. The maximal temperature rise of the particle heated by fluence  $\Phi = 236.7 \mu\text{J cm}^{-2}$  versus pulse durations  $t_p$  (b).



**Figure 7.** Temperature rise for a gold nanoparticle ( $R = 21.5$  nm) in water; a laser pulse with  $t_p = 1$  ps and fluence  $\Phi = 236.7 \mu\text{J cm}^{-2}$ . Different curves correspond to different distances  $r$ , monotonically varying from  $r = R$  to  $1.1R$ . It is seen that the maximal heating decreases sharply with a small increase in  $r$ .

Some results of the calculations of the temperature rise profile described by equations (12)–(15) are shown in figure 7.

The huge increase in the effective absorption for a weakly dissipating plasmonic particle in a shell permits us to deliver the laser energy through a thick layer of biological tissue without significant heating of the tissue itself. In the optical range of the spectrum, the absorption coefficient for different tissues varies from  $\alpha_{\text{tissue}} = 10$  to  $100 \text{ cm}^{-1}$  [32]. This is by a few orders of magnitude smaller than the effective absorption coefficient which can be reached for weakly

dissipating plasmonic particles. This permits us to administrate considerable heating of weakly dissipating nanoparticles situated in the tissue in the depth range from 1 mm to 1 cm, depending on the  $\alpha_{\text{tissue}}$  value, without damage of the tissue by a laser beam.

The heating may be enhanced considerably if it is produced by an aggregate of nanoparticles. If the characteristic distance between the particles in the aggregate is sufficiently long, one may consider the heating effect produced individually by each particle. However, the problem becomes more complicated when the particles are placed sufficiently close to each other. In this case, the temperature distribution depends on the number of particles within the cluster [33] and effects related to overlap of thermal fields produced in the host medium by each individual particle [34–36]. Another idea to enhance the heating may be based on the black-hole effect for touching spherical particles [37].

## 5. Conclusions

Thus, we have obtained a counter-intuitive result that the largest effective absorption coefficient can be achieved for weakly dissipating plasmonic nanoparticles, in spite of the fact that the conversion of the light energy into the internal absorbed energy is proportional to the dissipation parameter  $\text{Im } \epsilon$ . Our calculations based on the exact Mie solution have revealed that weakly dissipating plasmonic nanoparticles may exhibit *giant absorption enhancement* growing proportionally to the inverse cube of the particle size. For example, at the size parameter  $q = 0.1$  and optimized values of other parameters of the problem, one can achieve an effective absorption three orders of magnitude larger than that for bulk samples. For natural materials, the full optimization of absorption cannot be performed because of a fixed dependence of complex  $\epsilon(\omega)$  for every given material, which does not allow us to employ  $\text{Re } \epsilon$  and  $\text{Im } \epsilon$  as independent tuning parameters. Nonetheless, for nanoparticles made of weakly dissipating metals, the effective absorption coefficient may exceed that for the same bulk materials by two orders of magnitude. It permits us to use efficient heating of nanoparticles embedded in a host medium, e.g. in liquids or solids. To minimize heat diffusion, very short laser pulses (in typical cases shorter than 10 ps) should be employed. We note that, for the sake of simplicity, in this paper most calculations have been performed for a particle irradiated in a vacuum. The calculations can be easily extended to the case when a particle is embedded in a transparent medium with a purely real refractive index  $n_m$ . To this end, we should just take into account a complex refractive index of the particle as the relative index, namely  $n \rightarrow n/n_m$ . We believe that our results may be useful in optimizing many experiments on laser heating of nanoparticles, and will stimulate further experimental studies of this important effect.

## Acknowledgments

BL acknowledge funding provided by the SERC Agency of Science, Technology and Research (A\*STAR) Superlens Program (project no. 092 154 0099) and the DSI Core Project on Nanoparticles. This work was supported by the Australian Research Council through Future Fellowship and Discovery programs and by the Russian Foundation for Basic Research through grant no. 12-02-00391-a.

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