Plasmon resonance and heat generation model in nanostructures

Xiaoping Fang † Youjun Deng ‡ Jing Li §

Abstract

In this paper, we investigate the photothermal effects of the plasmon resonance. Metal nanoparticles efficiently generate heat in the presence of electromagnetic radiation. The process is strongly enhanced when a fixed frequency of the incident wave illuminate on nanoparticles such that plasmon resonance happen. We shall introduce the electromagnetic radiation model and show exactly how and when the plasmon resonance happen. We then construct the heat generation and transfer model and derive the heat effect induced by plasmon resonance. Finally, we consider the heat generation under plasmon resonance in a concentric nanoshell structure.

Mathematics subject classification (MSC2000): 35Q60, 35C20
Keywords: photothermal effect, plasmon resonance, nanoparticle, Maxwell equation, concentric nanoshell

1 Introduction

There has been a great deal of interest in recent years in the study of physical property - heat generation by Nanoparticles (NPs) under optical illumination. The optical properties of NPs, including both semiconductor [15] and metal nanocrystals [7], have been studied intensively. When the NPs are illuminated by an incident wave with special frequency, the plasmon resonance can be excited with a strong field enhancement inside and around the NPs. Such effect has a wide range of potential applications in such as near-field microscopy [5, 6], signal amplification, molecular recognition [12], nano-lithography [16], etc. Heat is generated when imaginary part of the property of the NP does not vanish. The heating effect becomes especially strong under the plasmon resonance conditions when the energy of incident photons is close to the plasmon frequency of the NP. The heat can be used for melting the surrounding matrix like ice and polymer [8, 14, 21], as well as for cancer diagnosis and therapy [10, 11, 13, 22].
To mathematically explain the plasmon resonance of NPs and the heat generated by plasmon resonance, there are two models to be considered. Firstly, the Maxwell system is introduced to explain the process of plasmon resonance. We shall give the exact mathematical theory on how the plasmon resonance happen when the NPs is illuminated by electromagnetic wave. We show the asymptotic expansion of electromagnetic fields perturbed by small inclusions derived in [2, 4]. The first order expansion is quite important to see the innate of the inclusion. It can be used for the size estimation of the small inclusion and more importantly, it gives us a way to see through when the plasm on resonance happens if the inclusions (NPs), such as gold (Au) NPs and Silver (Ag) NPs, have negative real part in the parameters. We show that when the electric permittivity of the NP is such that a contrast parameter becomes the eigenvalue of an integral operator, plasmon resonance happen. We then analyze the heat generation and transfer process by strictly deduction. Finally, a typical nanostructure of concentric nanoshell is considered and we show exactly how is the plasmon resonance excited by incident light.

The organization of this paper is as follows. In section 2, we introduce some preliminary works concerning the electromagnetic field model. We present the far field expansion of the electromagnetic field perturbed by the nanoparticles. In the case that the nanoparticles are sphere shaped, we show exactly how the plasmon resonance happen when Drude model is applied. In section 3, the heat generation and transferring model is considered. The heat transferring is explicit shown for sphere nanoparticle. Finally, in section 4, we consider a special concentric nanoshell structure. The strict mathematical proof is given concerning the plasmon resonance. To our knowledge, it is the first time to show exactly the plasmon resonance in this concentric nanoshell structure.

2 Plasmon resonance model

Let $D$ be the nanoparticle situated in $\mathbb{R}^3$ with $C^{1,\eta}$ boundary for some $\eta > 0$, and let $(\epsilon_0, \mu_0)$ be the pair of electromagnetic parameters (permittivity and permeability) of the matrix $(\mathbb{R}^3 \setminus D)$ and $(\epsilon_1, \mu_1)$ be that of the nanoparticle. Then the permittivity and permeability distributions are given by

$$
\begin{align*}
\epsilon &= \epsilon_0 \chi(\mathbb{R}^3 \setminus D) + \epsilon_1 \chi(D) \quad \text{and} \quad \mu = \mu_0 \chi(\mathbb{R}^3 \setminus D) + \mu_1 \chi(D),
\end{align*}
$$

where $\chi$ denotes the characteristic function. In the sequel, we set $k_1 = \omega \sqrt{\epsilon_1 \mu_1}$ and $k_0 = \omega \sqrt{\epsilon_0 \mu_0}$. Suppose the nanoparticle $D$ is illuminated by a given incident plane wave with the electric and magnetic fields $(E^{in}, H^{in})$, which is the solution to the Maxwell equations

$$
\begin{align*}
\nabla \times E^{in} &= i \omega \mu_0 H^{in} & \text{in } \mathbb{R}^3, \\
\nabla \times H^{in} &= -i \omega \epsilon_0 E^{in} & \text{in } \mathbb{R}^3,
\end{align*}
$$

where $i = \sqrt{-1}$. We can treat the nanoparticle $D$ as a scatterer in front of the incident wave. The total fields denoted by $(E, H)$, is the solution to the following Maxwell equations:

$$
\begin{align*}
\nabla \times E &= i \omega \mu H & \text{in } \mathbb{R}^3 \setminus \partial D, \\
\nabla \times H &= -i \omega \epsilon E & \text{in } \mathbb{R}^3 \setminus \partial D, \\
\left[ \nu \times E \right] &= \left[ \nu \times H \right] &= 0 & \text{on } \partial D,
\end{align*}
$$

subject to the Silver-Müller radiation condition:

$$
\lim_{|x| \to \infty} |x| (\sqrt{\mu} (H - H^{in}) \times \hat{x} - \sqrt{\epsilon} (E - E^{in})) = 0,
$$

2
where $\hat{x} = x/|x|$. Here, $[\nu \times E]$ and $[\nu \times H]$ denote the jump of $\nu \times E$ and $\nu \times H$ along $\partial D$, namely,

$$
[\nu \times E] = (\nu \times E)|_{\partial D}^+ - (\nu \times E)|_{\partial D}^-, \quad [\nu \times H] = (\nu \times H)|_{\partial D}^+ - (\nu \times H)|_{\partial D}^-,
$$

where $|_{\partial D}^+$ means the limit to the outside of $\partial D$ and $|_{\partial D}^-$ means the limit to the inside of $\partial D$.

In what follows, we recall the analytic solution to (2.1). Firstly, for $k > 0$, the fundamental solution $\Gamma_k$ to the Helmholtz operator $(\Delta + k^2)$ in $\mathbb{R}^3$ is

$$
\Gamma_k(x) = -\frac{e^{ik|x|}}{4\pi|x|}. \quad (2.2)
$$

To proceed, we introduce some vector functional space and some important integrals. Let $\nabla_{\partial D}$ denote the surface divergence. Denote by $L^2_T(\partial D) := \{ \varphi \in L^2(\partial D)^3, \nu \cdot \varphi = 0 \}$ the tangential vector space. We introduce the function spaces

$$
TH(\text{div}, \partial D) := \left\{ \varphi \in L^2_T(\partial D) : \nabla_{\partial D} \cdot \varphi \in L^2(\partial D) \right\},
$$

$$
TH(\text{curl}, \partial D) := \left\{ \varphi \in L^2_T(\partial D) : \nabla_{\partial D} \cdot (\varphi \times \nu) \in L^2(\partial D) \right\},
$$

equipped with the norms

$$
\|\varphi\|_{TH(\text{div}, \partial D)} = \|\varphi\|_{L^2(\partial D)} + \|\nabla_{\partial D} \cdot \varphi\|_{L^2(\partial D)},
$$

$$
\|\varphi\|_{TH(\text{curl}, \partial D)} = \|\varphi\|_{L^2(\partial D)} + \|\nabla_{\partial D} \cdot (\varphi \times \nu)\|_{L^2(\partial D)}.
$$

For a density $\phi \in TH(\text{div}, \partial D)$, we define the single layer potential associated with the fundamental solutions $\Gamma_k$ given in (2.2) by

$$
S^k_D[\phi](x) := \int_{\partial D} \Gamma_k(x - y) \phi(y) ds(y), \quad x \in \mathbb{R}^3.
$$

For a scalar density contained in $L^2(\partial D)$, the single layer potential is defined by the same way. We also define boundary integral operators

$$
L^k_D[\phi](x) := (\nu \times (k^2 S^k_D[\phi] + \nabla S^k_D[\nabla_{\partial D} \cdot \phi]))(x),
$$

$$
M^k_D[\phi](x) := \text{p.v.} \int_{\partial D} \nu(x) \cdot (\nabla_x \times (\Gamma_k(x - y) \phi(y))) ds(y), \quad x \in \partial D.
$$

There admits the following jump formula on the boundary of $D$

$$
[\nu \times \nabla \times S^k_D[\phi]]_{\pm} = (\mp \frac{I}{2} + M^k_D)[\phi]. \quad (2.3)
$$

Then the solution to (2.1) can be represented as the following

$$
E(x) = \begin{cases} 
E'(x) + \mu_0 \nabla \times S^h_D[\phi](x) + \nabla \times \nabla \times S^h_D[\psi](x), & x \in \mathbb{R}^3 \setminus \mathcal{T}, \\
\mu_1 \nabla \times S^h_D[\phi](x) + \nabla \times \nabla \times S^h_D[\psi](x), & x \in D,
\end{cases} \quad (2.4)
$$
and
\[ H(x) = -\frac{i}{\omega \mu} (\nabla \times E)(x), \quad x \in \mathbb{R}^3 \setminus \partial D, \]
where the pair \((\phi, \psi) \in TH(\text{div}, \partial D) \times TH(\text{div}, \partial D)\) is the unique solution to
\[
\begin{bmatrix}
\mathcal{M}_1 & \mathcal{L}_D^{k_1} - \mathcal{L}_D^{k_0} \\
\mathcal{L}_D^{k_1} - \mathcal{L}_D^{k_0} & \mathcal{M}_2
\end{bmatrix}
\begin{bmatrix}
\phi \\
\psi
\end{bmatrix}
= \begin{bmatrix}
\nu \times E^{in} \\
i \omega \nu \times H^{in}
\end{bmatrix} \bigg|_{\partial D}. \tag{2.5}
\]
where
\[ \mathcal{M}_1 := \frac{\mu_1 + \mu_0}{2} I + \mu_1 \mathcal{M}_D^{k_1} - \mu_0 \mathcal{M}_D^{k_0}, \quad \mathcal{M}_2 := \left( \frac{k_1^2}{2 \mu_1} + \frac{k_0^2}{2 \mu_0} \right) I + \frac{k_1^2}{\mu_1} \mathcal{M}_D^{k_1} - \frac{k_0^2}{\mu_0} \mathcal{M}_D^{k_0}. \]

Denote by \(\lambda_\epsilon\) and \(\lambda_\mu\) the electric permittivity and magnetic permeability contrasts:
\[
\lambda_\epsilon = \frac{\epsilon_1 + \epsilon_0}{2 (\epsilon_1 - \epsilon_0)} \quad \text{and} \quad \lambda_\mu = \frac{\mu_1 + \mu_0}{2 (\mu_1 - \mu_0)}. \tag{2.6}
\]
We point out that if \(\lambda_\epsilon\) and \(\lambda_\mu\) are greater than \(1/2\), or the permittivity and permeability are all positive numbers, then the invertibility of the system of equations (2.5) on \(TH(\text{div}, \partial D) \times TH(\text{div}, \partial D)\) was proved in [20].

### 2.1 Drude model

In what follows, we consider the physical process on the plasmon resonance when the nanoparticle \(D\) is illuminated by the incident wave. According to the Drude model the electric permittivity of the nanoparticle \(D\) behaviors as a function of the angular frequency \(\omega\), or exactly (see e.g. [18])
\[
\epsilon_1 = \epsilon(\omega) = \epsilon_0 \left(1 - \frac{\omega_p^2}{\omega(\omega + i \tau)}\right) \tag{2.7}
\]
where \(\omega_p\) is the plasma frequency of the bulk material and \(\tau\) is the width of the resonance. Let \(D = \delta B + z\), where \(B\) is a \(C^{1,\eta}\) domain containing the origin. For a scalar density \(\phi \in L^2(\partial B)\), define the well-known Neumann-Poincaré operator by
\[
K_B^*[\phi](x) := \text{p.v.} \int_{\partial B} \frac{\partial \Gamma}{\partial \nu(x)}(x - y) \phi(y) \, ds(y), \tag{2.8}
\]
where \(\partial / \partial \nu\) denotes the normal derivative and p.v. denotes the Cauchy principal value. Denote by \(G(x, z)\) the matrix valued function (Dyadic Green function)
\[
G(x, z) = \epsilon_0 \Gamma_{k_0}(x - z) I + \frac{1}{k_0^2} \nabla_{x} \Gamma_{k_0}(x - z)
\]
then there holds the following far field expansion for the electric field

**Theorem 2.1 (Theorem 3.8 in [2])** Define the polarization tensors
\[
M^c := \int_{\partial B} \tilde{y}(\lambda_\epsilon I - K_B^*)^{-1}[\nu] ds(\tilde{y}) \quad \text{and} \quad M^h := \int_{\partial B} \tilde{y}(\lambda_\mu I - K_B^*)^{-1}[\nu] ds(\tilde{y}) \tag{2.9}
\]
then there holds the following far field expansion

\[
\mathbf{E}(x) - \mathbf{E}_m^0(x) = -\delta^3 \omega^2 \mu_0 G(x, z) M^r \mathbf{E}^m(z) - \delta^3 \frac{i \omega \mu_0}{\epsilon_0} \nabla \times G(x, z) M^h \mathbf{H}^m(z) + O(\delta^4).
\]

(2.10)

Since the eigenvalue of Neumann-Poincaré operator \( K_B^* \) lies in the span \((-1/2, 1/2)\) (cf. [3]), polarization tensors \( M^r \) and \( M^h \) are well-defined if the material parameters are all positive. However, if the parameters of the NP are not positive numbers then polarization tensors may not be well-defined since \( \lambda, I - K_B^* \lambda \) and \( \lambda, I - K_B^* \lambda \) may not be invertible in this case. It is also shown in [2] that when the electric and magnetic properties of the NPs meet that their real parts make \( \lambda_e \) or \( \lambda_m \) be the eigenvalue of \( K_B^* \), the plasmon resonance happens. We shall see when the parameters obey the Drude and the angular frequency of the incident wave is well chosen, the plasmon resonance is excited.

### 2.2 Sphere nanoparticles

We shall consider that the nanoparticle \( D \) is a sphere shaped inclusion. Suppose the radius of NP is \( r_{NP} \). The electric permittivity of \( D \) obeys the Drude model (2.7). We mention that the wavelength, denoted by \( \lambda \), of the incident wave is much larger than the radius of the NP, i.e., \( \lambda \gg r_{NP} \). Suppose the incident electric field is uniformly distributed, \( \mathbf{E}_m^0 = \mathbf{E}_0 \), where \( \mathbf{E}_0 \) is a constant vector representing the amplitude of the incoming light. Due to the symmetric property of \( D \), we suppose the electric potentials, denoted by \( u \), inside and outside \( D \) have the form

\[
u = \left\{ \begin{array}{ll}
\mathbf{E}_0 \cdot \mathbf{x} + \frac{\mathbf{E}_0 \cdot \mathbf{x}}{|\mathbf{x}|^3} & \mathbf{x} \in \mathbb{R}^3 \setminus D, \\
\mathbf{E}_2 \cdot \mathbf{x} & \mathbf{x} \in D.
\end{array} \right.
\]

The scattering part \( \mathbf{E}_1 \cdot \mathbf{x}/|\mathbf{x}|^3 \) decays fast as the light travels far away. By introducing the spherical harmonic functions \( Y_1^{m}(\theta, \varphi) \), \( m = -1, 0, 1, 1 \), we actually have

\[
\mathbf{E}_0 \cdot \mathbf{x} = r \sum_{m=-1}^{1} a_{0m} Y_1^m, \quad \mathbf{E}_1 \cdot \mathbf{x}/|\mathbf{x}|^3 = r^{-2} \sum_{m=-1}^{1} a_{1m} Y_2^m, \quad \mathbf{E}_2 \cdot \mathbf{x} = r \sum_{m=-1}^{1} a_{2m} Y_1^m
\]

where the coefficients \( a_{jm}, j = 0, 1, 2 \) can be determined by transmission conditions, namely

\[
ar_{NP} \sum_{m=-1}^{1} a_{0m} Y_1^m + r_{NP}^2 \sum_{m=-1}^{1} a_{1m} Y_2^m = r_{NP} \sum_{m=-1}^{1} a_{2m} Y_1^m,
\]

\[
\epsilon_0 \sum_{m=-1}^{1} a_{0m} Y_1^m - 2 \epsilon_0^2 \sum_{m=-1}^{1} a_{1m} Y_2^m = \epsilon_1 \sum_{m=-1}^{1} a_{2m} Y_1^m.
\]

By solving the above equations we have

\[
a_{2m} = \frac{3 \epsilon_0}{2 \epsilon_0 + \epsilon_1} a_{0m}, \quad \text{and} \quad a_{1m} = \frac{\epsilon_0 - \epsilon_1}{2 \epsilon_0 + \epsilon_1} \frac{1}{r_{NP}^2} a_{0m}.
\]

Thus there holds the following relation

\[
\mathbf{E}_2 = \frac{3 \epsilon_0}{2 \epsilon_0 + \epsilon_1} \mathbf{E}_0, \quad \text{and} \quad \mathbf{E}_1 = \frac{\epsilon_0 - \epsilon_1}{2 \epsilon_0 + \epsilon_1} r_{NP}^2 \mathbf{E}_0.
\]
The energy of the NP, denoted by $E$, after the incident light ($E_0$) illumination reads

$$E = \int_D |E_2|^2 dx = \left| \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_1} \right|^2 \int_D |E_0|^2 dx. \quad (2.11)$$

In what follows, we show how does the plasmon resonance happen when the electric permittivity of NP obeys the Drude model. Mathematically, we give the definition on when does the plasmon resonance happen.

**Definition 2.2** Let $\epsilon_1$ satisfy (2.7). We call the plasmon resonance happen if the energy of the NP induced by the illumination of the incident light blows up in the following way

$$\lim_{\tau \to 0} \tau E = \infty.$$ 

Based on the Definition 2.2 and (2.11) we can easily get the following result

**Theorem 2.3** Let $\lambda$ and $v$ be the wavelength and speed of the incident light, respectively. If $\lambda = \frac{2\pi v}{\sqrt{3} \omega_p}$, then the plasmon resonance happen.

**Proof.** The angular frequency $\omega$ is given by

$$\omega = \frac{2\pi v}{\lambda} = \frac{\sqrt{3}}{3} \omega_p.$$ 

A direct calculation by using (2.7) gives

$$\epsilon_1 = \left(1 - \frac{\omega_p^2}{\omega^2 + \tau^2}\right) \epsilon_0 + i \frac{\omega_p \tau}{\omega(\omega^2 + \tau^2)} \epsilon_0 = -2\epsilon_0 + i \frac{3\sqrt{3} \tau}{\omega_p} \epsilon_0 + O(\tau^2).$$

Then by (2.11) the energy can be estimated by

$$E = \left| \frac{3\epsilon_0}{i \frac{3\sqrt{3} \tau}{\omega_p} \epsilon_0 + O(\tau^2)} \right|^2 \int_D |E_0|^2 dx = \frac{\sqrt{3}}{3} \omega_p^2 \tau^{-2} \int_D |E_0|^2 dx + O(\tau^{-1}).$$

We thus have

$$\lim_{\tau \to 0} \tau E = \infty$$

and plasmon resonance happens. \(\square\)

We mention that in the lossless Drude mode case ($\tau = 0$), the permittivity $\epsilon_1$ turns to such that $\lambda$, is the eigenvalue of the Neumann-Poincaré operator $K_D$. To explain this, we first present a lemma which gives the eigenvalue of $K_D^*$ with respect to eigenfunctions $Y_{1m}$ when $D$ is a sphere.

**Lemma 2.4** (cf. [1]) Let $B_0$ be a ball with radius $r_0$ then we have

$$K_{B_0}^*[Y_{1m}](x) = \frac{1}{6} Y_{1m}, \quad |x| = r = r_0, \quad m = -1, 0, 1.$$ 

We thus come to the conclusion since in the lossless Drude mode $\epsilon_1 = -2\epsilon_0$, and

$$\lambda_\epsilon = \frac{\epsilon_1 + \epsilon_0}{2(\epsilon_1 - \epsilon_0)} = \frac{1}{6}$$

which is exactly the eigenvalue of $K_D$ when the incident light is uniformly distributed.
3 Heat generation and transfer

In this section, we consider the heat generated by NPs under plasmon resonance. Heat transfer in a system with NPs is described by the usual heat transfer equation

$$\rho(x)c(x)\frac{\partial T(x,t)}{\partial t} = \nabla(\sigma(x)\nabla T(x,t)) + Q(x,t)$$ (3.1)

where $T(x,t)$ is the temperature, $\rho(x)$, $c(x)$ and $\sigma(x)$ are the mass density, specific heat, and thermal conductivity, respectively. $Q(x,t)$ is the heat intensity which represents an energy source coming from light dissipation in NPs. It is shown in [9] that $Q(x,t)$ relates to the electric field by

$$Q(x,t) = \frac{1}{8\pi}\omega^{3}\Im m(\epsilon_{1})|E_{2}|^{2}$$

where $\Im m(\epsilon_{1})$ means the imaginary part of the electric permittivity $\epsilon_{1}$, given by Drude model and $E_{2}$ has been calculated in the last section. Thus we get

$$Q(x,t) = \frac{1}{8\pi}\omega^{3}\Im m(\epsilon_{1})\frac{3\epsilon_{0}}{2\epsilon_{0} + \epsilon_{1}}|E_{0}|^{2}.$$ 

Heat transfers through the NP requires quite few time. We thus consider the steady state of this process. Denote by $\sigma_{0}$ and $\sigma_{NP}$ the thermal conductivities outside and inside the NP, respectively. Then in the steady state, we have

$$\begin{cases}
\sigma_{NP}\Delta T + Q = 0 & x \in D, \\
\sigma_{0}\Delta T = 0 & x \in \mathbb{R}^{3}\setminus D.
\end{cases}$$

Since the heat source is generated from the center of the NP, it spreads uniformly in every direction due to the uniform thermal diffusion properties of the NP and the matrix. It also decays to nothing as $|x| \to 0$. We suppose the temperature inside and outside the NP has the form

$$T = \begin{cases}
A - \frac{2|\mathbf{x}|^{2}}{6\sigma_{NP}} & x \in D, \\
B/|\mathbf{x}| & x \in \mathbb{R}^{3}\setminus D.
\end{cases}$$

By using the transmission conditions we thus have

$$A = \frac{2\sigma_{0} + \sigma_{NP}}{6\sigma_{0}\sigma_{NP}}Qr_{NP}^{2}, \quad B = \frac{r_{NP}Q}{3\sigma_{0}}.$$

Denote by $V_{NP}$ the volume of the NP then temperature distribution outside the NP is given by

$$T = \frac{r_{NP}^{3}Q}{3\sigma_{0}r} = \frac{V_{NP}Q}{4\pi\sigma_{0}} \frac{1}{r}, \quad r = |\mathbf{x}| > r_{NP}$$

which is in accordance with [9]. It is seen that the heating effect becomes especially strong under the plasmon resonance conditions since $Q$ is greatly increased under plasmon resonance.
4 Concentric nanoshell

In this section, we investigate the plasmonic properties of a concentric nanoshell. The plasmon hybridization model has been used to explain the properties of nanoshell, a tunable plasmonic nanoparticle consisting of a dielectric (silica) core and a metallic (Au or Ag) shell. Fig. 1 gives an example of concentric nanoshell with two layers of metal NPs. This concentric nanoshell consists of alternating layers of dielectric and metal, essentially a nanoshell enclosed within another nanoshell, inspiring its alternative name of nanomatryushka (cf. [17]). We shall show how does the plasmon resonance happen in this kind of structure. We can also see how sensitive does the inner and outer radius of the shell layer influence the plasmon resonance.

From the analysis in the last sections, we should only consider the system in the influence of the electric field. Suppose once again that the incident wave is uniformly distributed with amplitude \( E_0 \). Define

\[
A_1 := \{ r \leq r_1 \}, \quad A_j := \{ r_j < r \leq r_{j+1} \}, \quad j = 1, 2, 3, \quad A_5 := \{ r > r_4 \}.
\]

By the symmetric properties of the concentric nanoshell, we suppose the total electric potential \( u \) has the form

\[
\begin{align*}
\begin{cases}
E_1 \cdot x = r \sum_{m=-1}^{1} a_{1m} Y_1^m, & x \in A_1, \\
E_{j1} \cdot x + E_{j2} \cdot x / |x|^3 = r \sum_{m=-1}^{1} a_{jm} Y_1^m + r^{-2} \sum_{m=-1}^{1} b_{jm} Y_1^m, & x \in A_j, \quad j = 2, 3, 4, \\
E_0 \cdot x + E_5 \cdot x / |x|^3 = r \sum_{m=-1}^{1} a_{0m} Y_1^m + r^{-2} \sum_{m=-1}^{1} b_{5m} Y_1^m, & x \in A_5.
\end{cases}
\end{align*}
\]

The transmission conditions on the interface \( \{ r = r_j \}, j = 1, 2, 3, 4 \) are given by

\[
\begin{align*}
a_{j+1m} r_j + b_{j+1m} r_j^{-2} &= a_{jm} r_j + b_{jm} r_j^{-2}, \\
\epsilon_{j+1} (a_{j+1m} - 2b_{j+1m} r_j^{-3}) &= \epsilon_j (a_{jm} - 2b_{jm} r_j^{-3}).
\end{align*}
\]
where we set $b_{1m} = 0$ and $a_{5m} = a_{0m}$, $m = -1, 0, 1$. By setting
\[
\lambda_j = \frac{2\epsilon_{j+1} + \epsilon_j}{\epsilon_{j+1} - \epsilon_j}, \quad j = 1, 2, 3, 4
\]
and some basic arrangements to the equations given by transmission conditions, we get
\[
\lambda_1(a_{2m} - a_{1m}) - \sum_{j=2}^{4} (a_{j+1m} - a_{jm}) = -a_{0m}
\]
\[
-2(a_{2m} - a_{1m})\left(\frac{r_1}{r_2}\right)^3 - \lambda_2(a_{3m} - a_{2m}) + \sum_{j=3}^{4} (a_{j+1m} - a_{jm}) = a_{0m}
\]
\[
2 \sum_{j=1}^{2} (a_{j+1m} - a_{jm})\left(\frac{r_1}{r_2}\right)^3 + \lambda_3(a_{4m} - a_{3m}) - (a_{5m} - a_{4m}) = -a_{0m}
\]
\[
-2 \sum_{j=1}^{3} (a_{j+1m} - a_{jm})\left(\frac{r_1}{r_4}\right)^3 - \lambda_4(a_{5m} - a_{4m}) = a_{0m}
\]
Define the matrix $P$ and $\Upsilon_n$ by
\[
P := \begin{bmatrix}
\lambda_1 & -1 & -1 & -1 \\
-2(r_1/r_2)^3 & -\lambda_2 & 1 & 1 \\
2(r_1/r_3)^3 & 2(r_2/r_3)^3 & \lambda_3 & -1 \\
-2(r_1/r_4)^3 & -2(r_2/r_4)^3 & -2(r_3/r_4)^3 & -\lambda_4
\end{bmatrix}
\]
\[
\Upsilon := \begin{bmatrix}
\frac{r_1^3}{\lambda_1^3} & 0 & 0 & 0 \\
0 & \frac{r_2^3}{\lambda_2^3} & 0 & 0 \\
0 & 0 & \frac{r_3^3}{\lambda_3^3} & 0 \\
0 & 0 & 0 & \frac{r_4^3}{\lambda_4^3}
\end{bmatrix}.
\]
Then there holds
\[
b_m = a_{0m}\Xi (P^{-1} - \Upsilon e)
\]
where $b_m := (b_{2m}, b_{3m}, b_{4m}, b_{5m})^T$, $e := (1, -1, 1, -1)^T$ and
\[
\Xi = \begin{bmatrix}
1 & 0 & 0 & 0 \\
1 & 1 & 0 & 0 \\
1 & 1 & 1 & 0 \\
1 & 1 & 1 & 1
\end{bmatrix}.
\]
We also have
\[
a_m = a_{0m}(-\Xi^T P^{-1} e + e_4)
\]
where $a_m := (a_{1m}, a_{2m}, a_{3m}, a_{4m})^T$ and $e_4 := (1, 1, 1, 1)^T$. What we concern is the energy generated in the metal shells. By the analysis before, we have in mind that in plasmon resonance mode, the energy blows up if the imaginary part of material property of the metal particles goes to zero. To simplify the analysis, in what follows we suppose that the material properties of the dielectric core are fixed and $\epsilon_1 = \epsilon_3 = \epsilon_5$. Let $\epsilon_s = \epsilon_2 = \epsilon_4$. Then we have
\[
\lambda_1 = \lambda_3 = 1 - \lambda_2 = 1 - \lambda_4 = \frac{2\epsilon_s + \epsilon_1}{\epsilon_s - \epsilon_1}
\]
Under these assumptions, we have $P = \lambda_1 I - K$, where $I$ is the identity matrix and $K$ has the form
\[
K = \begin{bmatrix}
0 & 1 & 1 & 1 \\
2(r_1/r_2)^3 & 1 & -1 & -1 \\
-2(r_1/r_3)^3 & -2(r_2/r_3)^3 & 0 & 1 \\
2(r_1/r_4)^3 & 2(r_2/r_4)^3 & 2(r_3/r_4)^3 & 1
\end{bmatrix}
\]
Judging from (4.4) and (4.5), we set the determinant of $P$, or $\lambda_1 I - K$, to be zero and we have the equation

$$0 = \lambda_1^4 - 2\lambda_1^3 + \left(-2r_3^2 r_2^3 + 2r_1^3 r_3^3 - 2r_1^3 r_4^3 + 2r_2^3 r_4^3 - 2r_3^3 r_4^3 + 1\right)\lambda_1^3 + \left(2r_1^3 r_2^3 - 2r_1^3 r_4^3 + 2r_2^3 r_4^3 - 2r_3^3 r_4^3 + 2r_3^3 r_4^3\right)\lambda_1 + 4r_3^3 r_4^3$$

(4.7)

which is a forth order equation with respect to $\lambda_1$. It is easy to see that the solution are exactly the eigenvalues of the matrix $K$. We can actually solve the forth order equation explicitly by using some tools like matlab, etc. It can be seen that all the four roots of the equation are real. However, we shall not discuss the reason here why all solutions should be real but the reader who is interested may consult any book concerning the theory of algebra equations (see, e.g., [19]). We also see in this equation that the solution only depends on the ratios of the radii. Table 1 lists the solutions to four different kinds of ratios.

| $r_1 : r_2 : r_3 : r_4$ | $\lambda_1$ | $\epsilon_s / \epsilon_1$ | $r_1 : r_2 : r_3 : r_4$ | $\lambda_1$ | $\epsilon_s / \epsilon_1$ |
|-------------------------|-------------|--------------------------|-------------------------|-------------|--------------------------|
| 4 : 5 : 9 : 10           | -0.5915     | -0.1576                  | 3 : 4 : 7 : 8           | 1.5013      | -0.0624                  |
|                         | -0.8550     | -0.0508                  |                         | 1.8237      | -0.0264                  |
|                         | 1.8550      | -19.6878                 |                         | 1.8327      | 16.0206                  |
| 5 : 6 : 11 : 12         | -0.6546     | -0.1301                  | -0.3787                 | -0.2612     |
|                         | -0.8771     | -0.0427                  | -0.7702                 | -0.0830     |
|                         | 1.8771      | -23.4024                 | 1.7702                  | 12.0547     |

The following theorem gives exactly how the plasmon resonance happen in this concentric nanoshell structure.

**Theorem 4.1** Suppose $\epsilon_1 = \epsilon_3 = \epsilon_5$. Let $\epsilon_s = \epsilon_2 = \epsilon_4$. If the angular frequency $\omega$ of the incident light is chosen such that

$$\lim_{\tau \to 0} \epsilon_s(\omega) = \epsilon^*(\omega)$$

and there exists a vector $v_1^* \in \mathbb{R}^4$ such that

$$P(\epsilon^*)v_1^* = 0, \quad |v_1^*| = 1 \quad and \quad v_1^* \cdot e \neq 0$$

then the plasmon resonance happen in concentric nanoshell.

**Proof.** By the assumptions and Drude model we have

$$\epsilon_s(\omega) = \epsilon^* + i\tau \frac{\omega_p}{\omega^3} + O(\tau^2).$$

We then have

$$\lambda_1(\epsilon_s) = \lambda_1(\epsilon^*) + i\tau \frac{\omega_p}{\omega^3}\left(-2\epsilon^* + \epsilon_1 + \frac{1}{\epsilon^* - \epsilon_1}\right) + O(\tau^2).$$
We also have that $\lambda_1(\epsilon^*)$ is one eigenvalue of $K$, with corresponding eigenvector $\mathbf{v}_1^\ast$. Furthermore,

$$ P(\epsilon_s) = P(\epsilon^*) + i\tau \frac{\omega_p}{\omega_0} \left( -(2\epsilon^* + \epsilon_1) + \frac{1}{\epsilon_1 - \epsilon_i} \right) I + O(r^2)I $$

In the following we let $b := b^2 \left( -(2\epsilon^* + \epsilon_1) + \frac{1}{\epsilon_1 - \epsilon_i} \right)$. By the assumptions we have

$$ P(\epsilon_s) \mathbf{v}_1^\ast = (i\tau b + O(r^2)) \mathbf{v}_1^\ast $$

and thus

$$ P(\epsilon_s)^{-1} \mathbf{v}_1^\ast = (-i\tau^{-1}b^{-1} + O(1)) \mathbf{v}_1^\ast. $$

Next, we calculate the energy generated in the metal shell. Denote by $\mathcal{E}$ the energy generated in the metal shell then we have

$$ \mathcal{E} = \int_{A_2} \left| \sum_{m=-1}^{1} \left( r a_{2m} Y_1^m + r^{-2} b_{2m} Y_1^m \right) \right|^2 dx + \int_{A_4} \left| \sum_{m=-1}^{1} \left( r a_{4m} Y_1^m + r^{-2} b_{4m} Y_1^m \right) \right|^2 dx $$

By using the orthogonality of the spherical harmonic functions $Y_1^m$, (4.4) and (4.5) we have

$$ \mathcal{E} = \frac{r_3^2 - r_1^2}{3} \sum_{m=-1}^{1} |a_{2m}|^2 + \frac{r_3^2 - r_1^2}{3} \sum_{m=-1}^{1} |a_{4m}|^2 - \frac{r_2^5 - r_1^5}{5} \sum_{m=-1}^{1} |b_{2m}|^2 - \frac{r_4^5 - r_3^5}{5} \sum_{m=-1}^{1} |b_{4m}|^2 $$

where the four functions which depend on $\epsilon_s$, i.e., $f_1(\epsilon_s)$, $f_2(\epsilon_s)$, $f_3(\epsilon_s)$, $f_4(\epsilon_s)$ have the form

$$ f_1(\epsilon_s) := -(0, 1, 1, 1) P(\epsilon_s)^{-1} \mathbf{e} + 1, \quad f_2(\epsilon_s) := -(0, 0, 0, 1) P(\epsilon_s)^{-1} \mathbf{e} + 1 $$

$$ f_3(\epsilon_s) := (1, 0, 0, 0) \mathbf{Y} P(\epsilon_s)^{-1} \mathbf{e}, \quad f_4(\epsilon_s) := (1, 1, 1, 0) \mathbf{Y} P(\epsilon_s)^{-1} \mathbf{e}. $$

Define

$$ F = \begin{bmatrix} 0 & -1 & -1 & -1 \\ 0 & 0 & 0 & -1 \\ r_1^3 & 0 & 0 & 0 \\ r_1^3 & r_2^3 & r_3^3 & 0 \end{bmatrix} $$

then $(f_1(\epsilon_s), f_2(\epsilon_s), f_3(\epsilon_s), f_4(\epsilon_s))^T = FP(\epsilon_s)^{-1} \mathbf{e} + (1, 1, 0, 0)^T$. Since we have $\det(F) = r_1^3(r_2^3 - r_3^3) \neq 0$, with out loss of generality we suppose $(1, 0, 0, 0) \mathbf{Y} \mathbf{v}_1^\ast \neq 0$. Since all the four terms in the expression of $\mathcal{E}$ are positive terms, we only analyze the term which contains $f_3(\epsilon_s)$ (otherwise, if $(0, 1, 1, 1) \mathbf{v}_1^\ast \neq 0$ then we consider $f_1(\epsilon_s)$ and so on). Let $\mathbf{v}_1^\ast, \mathbf{v}_2^\ast, \mathbf{v}_3^\ast$ and $\mathbf{v}_4^\ast$ be the eigenvectors of $K$ and $\lambda_1(\epsilon^*), \lambda_2^*, \lambda_3^*, \lambda_4^*$ be the corresponding eigenvalues. Then $\mathbf{e} = \mathbf{v}_1^\ast \cdot \mathbf{v}_1^\ast + \mathbf{v}_2^\ast \cdot \mathbf{v}_2^\ast + \mathbf{v}_3^\ast \cdot \mathbf{v}_3^\ast + \mathbf{v}_4^\ast \cdot \mathbf{v}_4^\ast$. Direct calculations give

$$ P(\epsilon_s)^{-1} \mathbf{e} = (\lambda_1(\epsilon_s) - \lambda_2^*)(\mathbf{v}_1^\ast \cdot \mathbf{v}_1^\ast) + \sum_{j=2}^{4} (\lambda_1(\epsilon_s) - \lambda_j^*)^{-1} \mathbf{v}_j^\ast \cdot \mathbf{v}_j^\ast $$

$$ = -i\tau^{-1}b^{-1} \mathbf{v}_1^\ast \cdot \mathbf{v}_1^\ast + O(1). $$

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Thus we have
\[
\tau \left| f_3(\epsilon_\kappa) \right|^2 = \tau \left|-i\tau^{-1}b^{-1}(1,0,0,0)\Upsilon e \cdot \nu_1^* + O(1) \right|^2 = \tau^{-1}b^{-2}(1,0,0,0)\Upsilon \nu_1^* e \cdot \nu_1^* + O(1).
\]
By the assumptions \((1,0,0,0)\Upsilon \nu_1^* \neq 0\) and \(e \cdot \nu_1^* \neq 0\) we finally have
\[
\lim_{\tau \to 0} \tau \mathcal{E} = \infty
\]
which completes the proof by using Definition 2.2.

We make a short remark here. We have seen in Table 1 that there are four possible frequencies, according to Drude model, of incident waves which can be used to excite the plasmon resonance. The concentric nanoshell structure, in the mean time, only contains two metal shells. Thus if the number of metal shells and dielectric cores is increasing, more different frequencies of incident lights can be absorbed and turned to a large amount of heat. The photothermal effects can be used for a variety of imaging and therapeutic applications.

5 Conclusions

We studied the heat generation and transferring model in the presence of plasmon resonance when the NPs are illuminated by incident waves. For a electromagnetic wave illumination, the first order expansion in terms of polarization tensors was presented, and the key point for inducing plasmon resonance emerged. We showed strictly how the plasmon resonance happen when the nanoparticle is sphere shaped and obeys the Drude model. We investigated the heat generation and transferring for spherical nanoparticle. The photothermal effect is greatly enhanced under plasmon resonance. For a concentric nanoshell structure, we proved that the plasmon resonance happen when the frequency of the incident waves is well chosen. Future works will be focused on the interaction of the nanoparticles under plasmon resonance which is not only a very important physical problem but also a great mathematical problem.

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