Effective permittivity for resonant plasmonic nanoparticle systems via dressed polarizability

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Abstract: We present an effective medium theory for resonant plasmonic nanoparticle systems. By utilizing the notion of dressed polarizability to describe dipolar particle interactions, we show that even highly concentrated, resonant plasmonic particles can be correctly described by the effective medium theory. The effective permittivity tensor of a nanoparticle monolayer is found explicitly and the resulting absorbance spectrum is shown to agree with rigorous numerical results from the FDTD model. The effective theory based on dressed polarizability provides a powerful tool to tailor resonant optical behaviors and design diverse plasmonic devices.

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References and links
1. Introduction

Plasmon resonant metal nanoparticles have been widely employed as building blocks of diverse nano-optical applications, such as surface enhanced Raman spectroscopies [1,2], optical nanocircuits [3], photovoltaic devices [4] and nanoparticle-based transmission lines [5]. Recent advances in nanofabrication techniques have made it easy to construct complex nanostructures such as dimers and one or two dimensional arrays using plasmonic nanoparticles as components [6,7]. When particles are close, coupling between nearby particles affects the local plasmon resonance behavior of single particles and subsequently the overall optical property of the complex structures they are involved in. The generalized Mie theory provides a rigorous framework for the description of interacting nanoparticle systems whose complexity prohibits an intuitive physical understanding [8]. Other theoretical approaches have been proposed for more simplistic descriptions. In particular, the plasmon hybridization method has successfully explained interactions between plasmon modes in a coupled cluster of particles such as dimers by using an analogy with quantum systems [9,10]. The Maxwell-Garnet (MG) effective medium theory provides a simple model for calculating the macroscopic optical properties of materials with a dilute inclusion of spherical nanoparticles [11,12]. It takes into account the dipolar interaction between particles through the averaged Lorentz local field. Unlike plasmon hybridization methods, the MG theory is not valid near the plasmonic resonances of metal particles [13]. Together with other restrictions on the MG theory, such as the small particle size and the low concentration, this off-resonant restriction discourages the use of the MG effective medium approach for resonant plasmonic particle systems.

In this paper, we resolve this problem by showing that even highly concentrated, resonant plasmonic particles can be correctly described by an effective medium theory by using a more elaborate treatment of the dipolar interaction between nearby particles. We utilize the notion of dressed polarizability [14,15] and present a simple yet reasonably accurate description of the dipolar particle interaction as well as the macroscopic optical properties. A monolayer of nanoparticles is taken as an exemplary system and the dressed polarizability is evaluated explicitly. This results in an effective permittivity of the monolayer modifying the MG theory and gives absorbance spectrums that agree nicely with the more rigorous Finite Difference Time Domain (FDTD) results.

2. The dressed polarizability

In the quasi-static limit, scattered light by a single spherical nanoparticle is described by the electric field of a point dipole located at the center of a sphere of radius $a$. The dipole moment $p$ of the point dipole, which is the volume integral of polarization $P$, is induced by the incident electric field $E_0$ such that

$$p = \frac{\varepsilon - 1}{\varepsilon + 2} a^3 E_0 = \alpha_0 E_0,$$

where $\alpha_0$ is the polarizability of the sphere and $\varepsilon$ is the relative permittivity. The polarization $P$ is proportional to the internal electric field inside the sphere, which is constant in the quasi-static limit. For a fine sized particle, dynamical effects come into play through changing the local field and subsequently the polarizability $\alpha_0$ with a perturbative correctional factor [16,17]. In addition to the dynamical effect, nearby particles also change the constant internal field, as depicted in Fig. 1. Figure 1(a) shows the intensity profile and electric field vector map calculated using the Finite Difference Time Domain (FDTD) method. The vector map clearly shows that the internal electric field is significantly enhanced by nearby particles while its spatial distribution remains approximately constant. This
enhances the particle dipole moment \( \mathbf{p} \). The ‘dressed polarizability’ is defined as the ratio between the enhanced dipole moment and the incident field. Figure 1(c) illustrates two different situations of dressed polarizability where nearby particles either enhance or quench the internal field depending on the location.

Fig. 1. (a) the field intensity profile (left) and the vector field plot (right) of a monolayer with a lattice constant of 23 nm at 537 nm resonant wavelength, and (b) the field intensity profile (left) and the vector field plot (right) of a single non-interacting particle at the same wavelength. (c) Schematic of plasmonic interaction between metallic nanoparticles which enhance or quench polarization of each particle, and (d) the bare polarizability (blue line) and the dressed polarizability (red) normalized by the cubic of the particle radius, \( a^3 \).

In order to evaluate the dressed polarizability, we first note that the dipole moments of interacting particles are not solely induced by the incident field \( \mathbf{E}_0 \), but by the local field \( \mathbf{E}_{\text{loc}} \) at the particle location which is a superposition of the field \( \mathbf{E}_0 \) and the fields generated by dipole moments of other particles. For simplicity, we assume that the particles are of spherical shape and form a lattice so that all particles have the same dipole moment \( \mathbf{p} \). Then the local field \( \mathbf{E}_{\text{loc}} \) is given by

\[
\mathbf{E}_{\text{loc}} = \mathbf{E}_0 + G \mathbf{p}, \tag{2}
\]

where \( G \) is the coupling coefficient determined by the geometrical configuration of particles. The dipole moment \( \mathbf{p} \) is induced by the local field \( \mathbf{E}_{\text{loc}} \) so that

\[
\mathbf{p} = \alpha_0 \mathbf{E}_{\text{loc}} = \alpha_0 (\mathbf{E}_0 + G \mathbf{p}) = (1 - \alpha_0 G)^{-1} \alpha_0 \mathbf{E}_0. \tag{3}
\]

From this, we obtain the dressed polarizability and the dressed internal field \( \mathbf{E}_{\text{int,d}} \),

\[
\alpha_d = (1 - \alpha_0 G)^{-1} \alpha_0 \equiv \gamma \alpha_0, \tag{4}
\]

\[
\mathbf{E}_{\text{int,d}} = \left(1 - \frac{\alpha_0}{\alpha^3}\right) \gamma \mathbf{E}_0, \tag{5}
\]

where \( \gamma = (1 - \alpha_0 G)^{-1} \) is the dressing factor and we assume that the dressed internal field is constant.
3. Derivation of the coupling coefficient $G$

In the following, we focus on a monolayer configuration as a test system. Identical particles of radius $a$ and relative permittivity $\varepsilon$ form a two dimensional rectangular array with the lattice constants $d_y$ and $d_z$, which are smaller than the wavelength $\lambda$ of the incident light. For this monolayer, the coupling coefficient $G$ can be found by a direct evaluation of the retarded dipolar field resulting from the neighboring particles.

Here, we evaluate the coupling coefficient $G$ defined through Eq. (2) by considering only nearest neighboring spheres. The dipole moment $p = (4\pi/3)a^3P$ is the volume integral of polarization $P$ which is assumed to be a constant vector oriented along the $z$-direction inside all spheres. Since the local field $E_{loc}$ is the superposition of the incident field $E_0$ oriented along the $z$-direction and the depolarization field generated by nearby induced dipoles and also the self-generated dynamical field, we can obtain the $Gp$ - term by evaluating these depolarization fields explicitly. We calculate the depolarization field at the origin $O$ in Fig. 2. generated by a dielectric sphere of radius $a$ centered at $O'$ which is located at $r_s = (r_0, \theta_0, \phi_0)$. As components perpendicular to $P$ cancel on integration due to symmetry, we need to integrate only the parallel component of the depolarization field generated by a dipole moment $dp(r) = PdV$. Expanding the retarded dipolar field up to the second order in $k$, the parallel component is given by [16]

$$dE_{d,\parallel} = \left[ \frac{1}{r^3}(3\cos^2 \theta - 1) + \frac{k^2}{2r} \left( \cos^2 \theta + 1 \right) \right] PdV,$$

where $(r, \theta, \phi)$ specifies the location of the volume element. To facilitate the integration, we introduce a spherical coordinate system $(r', \theta', \phi')$ whose origin is located at the center of the sphere at $r_s = (r_0, \theta_0, \phi_0)$. Two coordinate systems are related by

$$r(r', \theta', \phi') = \sqrt{x^2 + y^2 + z^2} = \sqrt{r'^2 + r_0^2 - 2r'r_0\cos\gamma},$$

Fig. 2. Original spherical coordinate system $(r, \theta, \phi)$ centered at $O$ and the spherical coordinate system $(r', \theta', \phi')$ centered at $O'$ shifted from $O$ by $r_s = (r_0, \theta_0, \phi_0)$.
\[ \theta(r', \theta', \phi') = \cos^{-1}\left( \frac{z}{r} \right) = \cos^{-1}\left( \frac{r' \cos \theta' + r_0 \cos \theta_0}{r} \right), \]  
(8)

\[ \phi(r', \theta', \phi') = \tan^{-1}\left( \frac{y}{x} \right) = \tan^{-1}\left( \frac{r' \sin \theta' \sin \phi' + r_0 \sin \theta_0 \sin \phi_0}{r' \sin \theta' \cos \phi' + r_0 \sin \theta_0 \cos \phi_0} \right). \]  
(9)

where \( \gamma \) is the angle between the vector \( r_0 \) and the position vector \( r' \) in frame \( O' \). It satisfies

\[ \cos \gamma = \cos(\phi' - \phi_0) \sin \theta' \sin \theta_0 + \cos \theta \cos \theta_0. \]  
(10)

In order to derive the depolarization field of a monolayer, we consider only neighboring spheres and perform the integration separately for the enhanced and quenched arrangements in Fig. 1.

3.1 Enhanced arrangement

Consider a monolayer of spheres forming a rectangular lattice in the yz-plane with lattice constants \( d_y \) and \( d_z \). As depicted in Fig. 1, neighboring spheres aligned along the polarization direction enhances depolarization. Specifically, spheres located at \( r_0 = (r_0 = d_y, \theta_0 = 0) \) and \( r_0 = (r_0 = d_y, \theta_0 = \pi) \) enhance the parallel component of the depolarization field while perpendicular components cancel on integration due to the symmetric configuration. For \( r_0 = (d_y, 0) \), the corresponding coordinate transformation simplifies to

\[ r(r', \theta') = \sqrt{r'^2 + d_z^2 + 2r_0 \cos \theta'}, \]  
(11)

and \( \phi = \phi' \). Integrating the \( k \)-independent term in Eq. (6), we obtain

\[ P \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \frac{1}{r(r', \theta')} \left[ 3 \cos^2 \theta(r', \theta') - 1 \right] r'^2 \sin \theta' dr' d\theta' d\phi' = \frac{8 \pi}{3} \left( \frac{a}{d_z} \right)^3 P, \]  
(13)

whereas integration of the \( k \)-dependent term in Eq. (6) yields

\[ P \int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \frac{k^2}{2r(r', \theta')} \left[ \cos^2 \theta(r', \theta') + 1 \right] r'^2 \sin \theta' dr' d\theta' d\phi' = \frac{4 \pi}{15} \left( \frac{a}{d_z} \right)^3 (5d_z^2 - a^2) k^2 P. \]  
(14)

The other sphere located at \( (d_y, -\pi) \) gives the same contribution due to the symmetric configuration. Summing all these contributions, the depolarization field for the enhanced arrangement is given by

\[ \mathbf{E}_d^{\text{enhanced}} = \frac{2}{d_z} \left( \frac{a}{d_z} \right)^3 \left[ \frac{8 \pi}{3} \left( \frac{a}{d_z} \right)^3 \left( 5d_z^2 - a^2 \right) k^2 \right] P. \]  
(15)
In Eq. (15), the $k$-independent static term which gives dominant contribution in Eq. (15) has positive sign, and it, consequently, enhances the depolarization fields of particles with the enhanced arrangement.

### 3.2 Quenched arrangement

Spheres located at \( \mathbf{r}_s = \left( d_s, \frac{\pi}{2}, \frac{\pi}{2} \right) \) and \( \left( d_s, -\frac{\pi}{2}, -\frac{\pi}{2} \right) \) quench the depolarization field. In order to handle the \( \phi \)-dependence of the integrand, we use the following addition theorem:

\[
\frac{1}{r(r', \theta', \phi')} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} d^{2l+1}_l Y_{l}^{m} (\theta_0, \phi_0) Y_{l}^{m} (\theta', \phi').
\]  

Then, integration of the $k$-independent term in Eq. (6) yields

\[
P[\left. \int_{0}^{\pi} \int_{0}^{2\pi} \frac{1}{r(r', \theta', \phi')} \left[ 3 \cos^2 \theta (r', \theta') - 1 \right] r'^2 \sin \theta' dr' d\theta' d\phi' \right] \approx -\frac{4\pi}{3} \left( \frac{a}{d_s} \right)^3 P + \frac{4\pi}{5} \left( \frac{a}{d_s} \right)^5 + O\left( \left( \frac{a}{d_s} \right)^7 \right).
\]  

Likewise, integration of the $k$-dependent term yields

\[
P[\left. \int_{0}^{\pi} \int_{0}^{2\pi} \frac{k^2}{2r(r', \theta')} \left[ \cos^2 \theta (r', \theta') + 1 \right] r'^2 \sin \theta' dr' d\theta' d\phi' \right] \approx \frac{2\pi}{15} \left( \frac{a}{d_s} \right)^3 (5d_s^2 + a^2) k^2 P + O\left( \left( \frac{a}{d_s} \right)^7 k a^2 \right).
\]  

Perpendicular components once again cancel on integration. Summing all contributions except for the negligible higher-order terms, we have the depolarization field for the quenched arrangement,

\[
E_{\text{quenched}} = 2 \left( \frac{a}{d_s} \right)^3 \left[ \frac{4\pi}{3} \left( -1 + \frac{2}{5} \left( \frac{a}{d_s} \right)^2 \right) + \frac{1}{10} (5d_s^2 + a^2) \right] P.
\]  

In Eq. (19), the $k$-independent static terms have negative sign, and then it quenches the depolarization fields of particles with the quenched arrangement.

### 3.3 Self depolarization

Due to the effect of finite size, a sphere experiences self-generated depolarization field which is given by [16]

\[
E_{\text{self}} = -\frac{4\pi}{3} (1 - k^2 a^2) \mathbf{P}.
\]  

The static part of $E_{\text{self}}$ has been already used up in determining the polarizability $\alpha_0$. Only the $k$-dependent dynamical part contributes to the depolarization when we consider the modification of polarizability $\alpha_0$.

### 3.4 Total depolarization for the nanoparticle monolayer

Finally, combining all these effects together, the depolarization field is given by
\[
E_{layer} = E_{\text{enhanced}} + E_{\text{quenched}} + E_{\text{eff}}
\]

\[
= \frac{4\pi}{3} \left[ k^2 a^2 + 2 \left( \frac{a^3}{d_z} \right)^3 \left( 2 + \frac{k^2}{5} (5d_z^2 - a^2) \right) - \left( \frac{a}{d_z} \right)^3 \left( 1 - \frac{k^2}{10} (5d_z^2 + a^2) \right) + \frac{3}{5} \left( \frac{a^3}{d_z} \right)^3 \right] \mathbf{P},
\] (21)

From the relation \( E_{layer} = G \mathbf{p} = G(4\pi / 3)a \mathbf{P} \), we obtain the coupling coefficient \( G \), explicitly with the incident electric field oriented along the x-direction is given by

\[
a' G = k^2 a^2 + 2 \left( \frac{a^3}{d_z} \right)^3 \left[ 2 + \frac{k^2}{5} (5d_z^2 - a^2) \right] - \left( \frac{a}{d_z} \right)^3 \left[ 1 - \frac{k^2}{10} (5d_z^2 + a^2) \right] + \frac{3}{5} \left( \frac{a^3}{d_z} \right)^3,
\] (22)

where \( k = 2\pi / \lambda \) is a wavenumber and radiative corrections are kept up to the second order in \( k \).

4. Effective permittivity via dressed polarizability

Consider a monolayer of spheres forming a rectangular lattice in the xy-plane with lattice constants \( d_x \) and \( d_y \). Using the dressed internal field of Eq. (5) and the coupling coefficient of Eq. (22), we define the effective permittivity as the ratio between the averaged \( E \) and \( D \) fields,

\[
\epsilon_{\text{eff}} = \frac{\langle D \rangle}{\langle E \rangle} = \frac{f \varepsilon_{\text{int},d}(\lambda, a, d) + (1 - f) \varepsilon_0}{f \varepsilon_{\text{int},d}(\lambda, a, d) + (1 - f) \varepsilon_0} = \frac{1 + 2f + (f - 1)a^2 G_j \varepsilon + 2 - 2f + (1 - f)a^2 G_j \varepsilon}{1 - f + (f - 1)a^2 G_j \varepsilon + 2 + f + (1 - f)a^2 G_j \varepsilon},
\] (23)

where \( f \) is the filling factor defined by \( f = 4\pi a^3 / 3 \overline{d}^3 \) and \( \overline{d} \) is the geometrical mean of the lattice constants \( d_x \) and \( d_y \) (\( \overline{d} = \sqrt{d_x d_y} \)). As there is no unique definition of the filling factor as a volume density applicable to a two dimensional single layer of particles, here we assume that the single isotropic layer is part of a three dimensional cubic lattice sharing the same filling factor. For anisotropic lattices, we take the average lattice constant \( \overline{d} = \sqrt{d_x d_y} \) for the third lattice constant in three dimensional lattices. The other diagonal component of the effective permittivity tensor, \( \epsilon_{\text{eff}} \), for the incident electric field oriented along the y-direction, can be simply obtained by interchanging \( x \) and \( y \) in the above equation. This modifies the Maxwell-Garnet effective medium theory with an anisotropic inclusion of particle interactions.

Our modification provides a successful effective medium theory for resonant plasmonic nanoparticle systems. To demonstrate this, we calculated the absorbance spectrum of gold nanoparticle monolayers using the Fresnel equation for a slab with effective permittivity \( \epsilon_{\text{eff}} \) and compared our result with the rigorous FDTD results. Figure 3 shows a contour map of calculated results for the absorbance spectrum of gold nanoparticle in square lattice monolayers. While keeping the particle size constant (\( a = 10 \) nm), we varied the lattice constants \( d_x = d_y = d \) from 20 nm (the touching limit) to 30 nm. The permittivity of gold is modeled through the Drude-critical point model [18,19] by fitting the experimental data of Johnson and Christry [20]. The contour map shows that plasmonic resonance become stronger and the peak is red-shifted as the gap decreases. Figures 3(b), 3(c) and 3(d) specifically compare absorbance spectra with the predictions of the MG theory and FDTD calculations. There is an excellent agreement between our model and the FDTD result while the MG theory fails to predict the absorbance spectra near resonance. The peak absorbance depicted in
Figs. 3(b), 3(c) and 3(d) show the margin of deviation of 2%, 14% and 9% respectively which result from the neglect of higher order pole excitations and interactions with other neighboring particles. The agreement ceases to exist near the touching limit due to the quantum tunneling which comes into play below sub nanometer the gap size and also at the touching limit where the layer becomes conductive. In Figs. 3(b), 3(c) and 3(d), the MG theory not only underestimates the magnitude it also fails to produce the red-shift behavior of the resonance peaks while our model shows the agreement. We were also able to confirm that dipolar interaction between nearby particles does indeed control the resonant behavior of dense plasmonic nanoparticle systems.

Equipped with the ability to predict resonance behaviors, our effective medium model provides a wonderful opportunity for tailoring optical response in dense plasmonic systems. Figure 4 describes the effective refractive index \( \tilde{n}_{\text{eff}} = \sqrt{\tilde{\varepsilon}_{\text{eff}}} = n_{\text{eff}} + ik_{\text{eff}} \) of a homogenized gold nanoparticle monolayer. It shows characteristically different spectral behaviors depending on wavelength. In the central resonant region, both the real and imaginary part of the refractive indices become significantly enhanced. Near resonance, the real and imaginary part of the refractive indices are sensitively influenced by the lattice constant \( d \). The maximum values of \( n_{\text{eff}} \) and \( k_{\text{eff}} \) show a 3.5-fold and 12-fold increase, respectively, with corresponding peak shifts from 545 nm to 596 nm and from 514 nm to 564 nm when the lattice constant \( d \) decreases by only 10 nm. In contrast, in the off-resonant long wavelength region the imaginary part becomes nearly zero, this implies that nanoparticle systems are transparent in this region despite of their extremely high density. This is also shown in the absorbance spectrum plotted in Fig. 3. In the off-resonant short wavelength region, the
imaginary part becomes relatively large this is clearly shown in the figure of merit behavior in Fig. 4(c).

![Figure 4](image)

Fig. 4. Effective indices: (a) real part of effective refractive index $n_{\text{eff}}$, (b) imaginary part of effective refractive index $k_{\text{eff}}$ and (c) figure of merit (FOM) which is defined by

$$FOM = \frac{n_{\text{eff}}}{k_{\text{eff}}}.$$

If particles form a non-square type rectangular lattice ($d_x \neq d_y$), the effective medium possesses anisotropic permittivity ($\varepsilon_{\text{eff}}^x \neq \varepsilon_{\text{eff}}^y$). This is in sharp contrast to MG theory which is used to explain the properties of dilute, small, randomly placed spheres utilizing only the overall particle filling factor $f$. Figure 5 compares absorbance spectrum for three different cases of rectangular layers: enhanced ($d_y < d_x$), isotropic ($d_y = d_x$) and quenched ($d_y > d_x$) layer. The filling factor is fixed to a constant value, $f = 0.24$, as such the MG theory predicts the same spectrum for all three cases. We also note that the isotropic and quenched layers agree quite well with the FDTD results while the enhanced layer case shows deviation in the off-resonant short wave length region. This is due to the neglect of higher-order excitations including the quadrupolar interaction, which become dominant factors between close particles of relatively large size as pointed out in earlier literatures [14,15,21].

![Figure 5](image)

Fig. 5. Absorbance spectrum for (a) the enhanced monolayer with $d_y = 23.6$ nm, $d_x = 28.6$ nm (red line), (b) the isotropic monolayer $d_y = d_x = 26$ nm (black), and (c) the quenched monolayer $d_y = 28.6$ nm, $d_x = 23.6$ nm (blue). The enhanced and quenched monolayers have an anisotropic arrangement of gold nanoparticles of radius 10 nm along the x, y direction, but they have an identical filling factor $f = 0.24$ because the geometric mean of their interparticle distances $\bar{d}$ is constant for each monolayer at 26 nm. These anisotropic absorbance characteristics cannot be obtained via the Maxwell-Garnett effective medium theory.
4. Conclusion

In this paper, we showed that the dipolar interaction among plasmonic nanoparticles can be efficiently modeled in terms of the dressed polarizability. The effective medium theory utilizing dressed polarizability provided a successful description for the monolayer system of resonant plasmonic particles. Our approach is not restricted to the monolayer configuration but it can be readily generalized to other periodic configurations such as bi-layers or 3-dimensional lattices that possess a symmetric distribution of induced dipole moments for each particles. Generalization to randomly distributed nanoparticle systems can be also made in terms of the averaged depolarization field $\langle E_d \rangle$ and the averaged lattice constant $\langle d \rangle$. As an effective medium theory for resonant plasmonic particles, the proposed model provides abundant information useful for tailoring optical properties including the shift of resonance frequency and the change in resonance strength via controlling the geometry of the system. The proposed model can be also an efficient tool to design diverse plasmonic devices such as Raman spectroscopies, optical nanocircuits, photovoltaic devices and nanoparticle-based transmission lines.

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