Optical properties of closely packed nanoparticle films: spheroids and nanoshells

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Abstract
We have developed an effective medium theory for the optical properties of nanoparticle films by considering the exact local fields of spheroidal nanoparticles on a substrate. The model allows the calculation of reflectivity, transmission and absorption of nanoparticle films for a wide range of filling factors, nanoparticle aspect ratios and substrate dielectric characteristics. It is suitable for many applications as it can treat films of homogeneous or binary core-shell nanoparticles.

Keywords: aggregated thin films, nanoshells, optical properties

1. Introduction
Maxwell-Garnett [1] and David [2] were the first to develop practical theories of effective dielectric constants for media consisting of small (sub-wavelength) metal spheres and ellipsoids. In their approach, the application of an external field causes the metallic inclusions to become electrically polarized and so to generate their own local fields, which affect the dielectric properties of the host material. These models have proved to be very useful for calculating the optical properties of volume media containing a low density of metallic inclusions, but they are not applicable to high density volume media and planar granular films. Yamaguchi et al [3] developed a model suitable for discontinuous film on a substrate. This model (referred to as the Yamaguchi model throughout this work) takes into account the effects of the electrostatic dipole interaction between particles and their mirror images in the substrate, the polarization of the film itself, the variety of particle shapes and size effects within particles. Yamaguchi et al [3] developed a model suitable for discontinuous film on a substrate. This model (referred to as the Yamaguchi model throughout this work) takes into account the effects of the electrostatic dipole interaction between particles and their mirror images in the substrate, the polarization of the film itself, the variety of particle shapes and size effects within particles. It was extensively used in the analysis of experimental data from spectroscopic ellipsometry measurements on discontinuous metallic thin films and was found to give an adequate description of their optical properties [4–6]. However, as will be shown in this paper, the Yamaguchi model is valid only for low surface density monolayers, composed of spherical or near spherical nanoparticles. Many practically important situations, for instance high density films or films containing high aspect ratio particles or nanoshells, may not be treated within the Yamaguchi model.

In this work we develop a theory suitable for treating high surface density discontinuous thin films (monolayers). We improve the Yamaguchi model by replacing the dipole approximation for interactions between neighbouring particles and the substrate with a much more accurate expression accounting for the exact local fields of the spheroidal nanoparticles. This modification essentially removes the Yamaguchi model’s main problem, namely the appearance of unphysical negative values of the effective geometrical (depolarization) factor for high aspect ratio nanoparticles. Besides this, we extend the model to include binary nanoshell particles [7, 8] and illustrate the model by calculating the optical properties of binary gallium nanoshell films.

2. Overview of the Yamaguchi model
The film is regarded as a monolayer of small particles distributed on the surface of a transparent substrate with dielectric constant $\varepsilon_{\text{sub}}$, as shown in figure 1. The dipole moments, $P$ and $P'$, of each particle and its mirror image, induced by the electric field of the incident wave parallel to the substrate, point in opposite directions and are related to each other by the formula

$$P' = -\frac{\varepsilon_{\text{sub}} - \varepsilon_{\text{ext}}}{\varepsilon_{\text{sub}} + \varepsilon_{\text{ext}}} P$$

(1)

where $\varepsilon_{\text{ext}}$ is the dielectric constant of the medium surrounding the nanoparticles. The local field acting on each particle $E_{\text{loc}}$ is the sum of the external field $E_{\text{ext}}$ and additional fields $E_{\text{img}}$.


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neighbouring particles and the mirror images of those particles. The field $E_{\text{ext}}$ is given by

$$E_{\text{ext}} = E_{\text{ext}} + E_{\text{img}} + E_{\text{sub}}$$

where $h$ is the particle’s height. To calculate the contribution of the surrounding particles and their mirror images a spherical coordinate system is introduced with the origin at the centre of the nanoparticle. Given that the distance between neighbouring particles $r_j \gg h$, i.e. $\theta_j \equiv 0$, $P_j$ and $P_j'$ can be replaced with an effective dipole moment $P_j'$:

$$P_j' = P_j - P_j' = \frac{2\varepsilon_{\text{ext}}}{\varepsilon_{\text{sub}} + \varepsilon_{\text{ext}}} P_j.$$

The field $E_{\text{img}}$ is given by

$$E_{\text{img}} = -\frac{1}{4\pi\varepsilon_0\varepsilon_{\text{ext}}h^3} P' = \frac{1}{4\pi\varepsilon_0\varepsilon_{\text{ext}}h^3} \frac{\varepsilon_{\text{sub}} - \varepsilon_{\text{ext}}}{\varepsilon_{\text{sub}} + \varepsilon_{\text{ext}}} P.$$

where $\varepsilon_{\text{loc}}$ is the volume filling factor of the film, $q$ is the volume filling factor of the film, and $q = V/V^3$. Thus,

$$d_w = q h.$$

The dielectric constant $\varepsilon_{\text{eff}}$ of a plane-parallel film equivalent to a monolayer of small particles with the same shape, size and orientation is given by

$$\alpha = \frac{\varepsilon_{\text{int}} - \varepsilon_{\text{ext}}}{\varepsilon_{\text{ext}} + \frac{f}{f} (\varepsilon_{\text{int}} - \varepsilon_{\text{ext}})}$$

where

$$F = f + \varepsilon_{\text{ext}} \beta = f - \frac{\gamma^2}{24} \varepsilon_{\text{sub}} - \varepsilon_{\text{ext}}$$

is the effective geometrical factor of the particles and

$$f = \frac{\gamma^2}{2\sqrt{(\gamma^2 - 1)^3}} \left[ \frac{\pi}{2} - \frac{\sqrt{\gamma^2 - 1}}{\gamma^2} \arctan \left( \frac{1}{\sqrt{\gamma^2 - 1}} \right) \right].$$

Since that the tangential component of the electric field is conserved across the interface between two media, the microscopic field inside the film is simply equal to the incident field, i.e. $E = E_{\text{ext}}$. Taking this into account, equation (13) yields the following expression for the effective dielectric constant of the monolayer:

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{ext}} \left( q \frac{\varepsilon_{\text{int}} - \varepsilon_{\text{ext}}}{\varepsilon_{\text{ext}} + \frac{f}{f} (\varepsilon_{\text{int}} - \varepsilon_{\text{ext}})} + 1 \right).$$

3. Improvements to the Yamaguchi model

Despite all of the advantages provided by the discontinuous film theory of Yamaguchi and co-workers, their model has a number of limitations. One such limitations arises from the fact that the model was developed for $q \ll 1$, i.e. for cases where the separation between particles is large compared with their size. Furthermore, the model is only valid for monolayers composed of spherical or near spherical particles ($\lambda \equiv 1$). This becomes apparent if one considers the expression for the effective geometrical factor equation (14). For example, assuming $q = 0.01$, $\varepsilon_{\text{ext}} = 1$ and $\varepsilon_{\text{sub}} = 2.28$ (a typical value for a glass substrate), $F$ becomes negative for $\gamma > 3.25$ (figure 2). We believe that this is a major drawback of the
This limitation can be overcome by using the exact expression of the Yamaguchi model. Indeed, it means that for a metal particle under a non-zero applied field, the field produced by the image as determined by equation (3), $E_{\text{app}(\xi, \eta, \varsigma)} = -E_{\text{app}}(\xi > -c^2, -c^2 > \eta > -b^2, -b^2 > \varsigma > -a^2)$ (the surfaces $\xi = \eta = \varsigma = \text{constant}$ are confocal ellipsoids, $\eta = \varsigma = \text{constant}$ are hyperboloids of one sheet and $\xi = \text{constant}$ are hyperboloids of two sheets).

In the case when particles are oblate spheroids, i.e. $a = b > c$ (where $a = r$ is the radius and $2c = h$ is the height of the particles), the integral in equation (17) yields

$$\int_0^\infty \frac{dx}{\sqrt{(s + x^2)(s + (h/2)^2)}} = \frac{\pi}{2}[r^2 - (h/2)^2]^{3/2}$$

$$- \sqrt{\xi + (h/2)^2} \left[ \frac{\xi + (h/2)^2}{r^2 - (h/2)^2} \right]^{3/2} \arctan \left[ \frac{\xi + (h/2)^2}{\sqrt{r^2 - (h/2)^2}} \right].$$

In a Cartesian coordinate system with its origin at the centre of the spheroid and the $x$-axis parallel to the applied field ($\xi$-axis coinciding with the spheroid’s rotational axis), the expression for the potential of the applied field (18) is replaced with

$$\Phi_{\text{app}}(x, y, z) = -E_{\text{app}}x,$$  

while $\xi$ is expressed as

$$\xi = \frac{1}{2}(x^2 + y^2 + z^2 - (h/2)^2 - r^2)^2$$

$$- 4[x^2(h/2)^2 - r^2(z^2 - (h/2)^2)(x^2 + y^2)]^{1/2}$$

$$+ x^2 + y^2 + z^2 - (h/2)^2 - r^2).$$

Subsequently, the component of the spheroid’s own field parallel to the applied field (i.e. the $x$-component) is simply given by

$$E_x(x, y, z) = -\frac{\partial}{\partial x} \Delta \Phi(x, y, z).$$

For further calculations it is convenient to introduce $x' = x/r$, $y' = y/r$ and $z' = z/r$. Equations (20) and (21) are thus modified as follows:

$$\xi = r^2\xi' = r^2\frac{2}{3}((x'^2 + y'^2 + z'^2 - r^2 - 1)^2)$$

$$- 4[y'^2(1 - x'^2 - y'^2 - z'^2)]^{1/2}$$

$$+ x'^2 + y'^2 + z'^2 - r^2 - 1)$$

$$\Phi_{\text{app}}(x', y', z') = -E_{\text{app}}x'$$

where $r = 2r/h$ is the aspect ratio of the spheroid. Combining equations (17), (19), (23) and (24), and substituting the resulting expression for $\Delta \Phi$ into equation (22) one arrives at

$$E_x(x', y', z') = \alpha E_{\text{app}}A(x', y', z')$$
\[
A(x', y', z') = -\frac{1}{2(y'^2 - 1)} \left\{ \frac{\pi y^2}{2\sqrt{y'^2 - 1}} - \frac{\sqrt{y'^2 + 1}}{(\xi' + 1)} \right\} + \frac{y^2}{\sqrt{y'^2 - 1}} \arctan\left( \frac{\sqrt{y'^2 + 1}}{y'^2 - 1} \right) + \frac{x'\partial\xi'}{\partial x} \left[ \frac{\sqrt{y'^2 + 1}}{(\xi' + 1)^2} - \frac{y^2}{\sqrt{y'^2 + 1}(\xi' + 1)} \right]
\]  
(26)

and \(\partial\xi'/\partial x\) is determined by
\[
\frac{\partial\xi'}{\partial x} = r \frac{\partial\xi'}{\partial x'} = r x' \left[ 1 + [(x'^2 + y'^2 + z'^2 + y'^2 - 1) \right] \times [(x'^2 + y'^2 + z'^2 - y'^2 - 1)^2 - 4(y'^2 - 1 - x'^2 - y'^2 - z'^2)^{-1/2}] \right].
\]  
(27)

The set of equations (23), (25)–(27) describes the exact variation of the \(x\)-component of the spheroid’s own field in space, and shows that it corresponds to that of a point dipole only at very large distances \((x', y', z' \gg 1)\). Now, assuming \(E_{\text{sub}} = E_{\text{loc}}\), where \(E_{\text{loc}}\) is the local field acting on the particle as introduced in the section 2, equations (3) and (5) are replaced with
\[
E_{\text{avg}} = \frac{\alpha}{\epsilon_{\text{sub}} - \epsilon_{\text{ext}}} (A(0, 0, 2/\gamma) (28)
\]
\[
E_{\text{eff}} = \frac{\alpha E_{\text{loc}}}{\epsilon_{\text{sub}} + \epsilon_{\text{ext}}} \sum_{i,j} \left[ A(x'_i, y'_j, 0) - \frac{\epsilon_{\text{sub}} - \epsilon_{\text{ext}}}{\epsilon_{\text{sub}} + \epsilon_{\text{ext}}} A(x'_i, y'_j, 2/\gamma) \right] \]  
(29)

where \(x'_i = y'_j = n l/r = n (2/3)(\pi/q) \right)^{1/2}.\)  
(30)

Following the procedure described in section 2, and accounting for equations (28) and (29), we again obtain (16), where \(F\) is a modified effective geometrical factor of the form
\[
F = f - \frac{2}{\gamma} \sum_{i,j=2}^2 \sum_{j=2}^2 A \left( \frac{2\pi}{3q}, j \frac{2\pi}{3q}, 0 \right) - \frac{\epsilon_{\text{ext}}}{\epsilon_{\text{sub}} + \epsilon_{\text{ext}}} \sum_{i,j=2}^2 \sum_{j=2}^2 A \left( \frac{2\pi}{3q}, j \frac{2\pi}{3q}, 2/\gamma \right)- \frac{2\epsilon_{\text{ext}}}{\epsilon_{\text{ext}} + \epsilon_{\text{sub}}} 0.177 \frac{1}{\gamma} \frac{3q^2}{2\pi} \]  
(31)

where \(A(0, 0, 0) = 0.\)

Equation (31) accurately accounts for the interaction of a nanoparticle in the film with the rest of the film and with the mirror image of the film. The second term on the right-hand side of equation (31) accounts for contributions from the 24 nearest neighbors (as presented in figure 4). The third term describes the contribution from the images of these neighboring particles and the image of the central nanoparticle itself. The effect due to the rest of the monolayer/substrate system is calculated using the dipole field approximation and is described by the fourth term in equation (31). The existence of these different terms makes the model applicable even to closely packed particles with \(q \cong 1\). To illustrate this we present in figure 2 the effective geometrical factor as a function of aspect ratio for \(q = 0.01\) and 0.6: the model gives a physically acceptable dependence that approaches zero only at sufficiently large \(\gamma\).

\[\alpha' = \left[ \alpha_1 - \epsilon_{\text{sub}} \left( f_1 - \epsilon_{\text{sub}} \right) \right] \left[ \alpha_2 - \epsilon_{\text{ext}} \left( f_2 - \epsilon_{\text{ext}} \right) \right] \left[ \alpha_3 - \epsilon_{\text{int}} \left( f_3 - \epsilon_{\text{int}} \right) \right] \left[ \alpha_4 - \epsilon_{\text{int}} \left( f_4 - \epsilon_{\text{int}} \right) \right] \]  
(32)

where \(\alpha_1\) and \(\alpha_2\) are the dielectric constants of the spheroid’s core and shell respectively, \(f = f_3 + f_4\) is then determined by the effective dielectric constant \(\alpha'\) of the nanoparticle and \(\epsilon_{\text{int}}\) is the polarizability of the particle as defined by equation (12). The solution of this equation yields
\[
\epsilon_{\text{int}} = \epsilon_{\text{ext}} \frac{\alpha'(f_2 - 1) - 1}{\alpha' f_2 - 1}.
\]  
(33)

For the case of spherical or near spherical coated particles, i.e. when \(f_1 = f_2 = 1/3\), equation (32) is simplified to
\[
\alpha' = 3\left( \epsilon_{\text{ext}} - 2 \epsilon_{\text{int}} \right) (\epsilon_1 + 2\epsilon_2) + (1 - \Delta h/r)^3 (\epsilon_1 - \epsilon_2) (\epsilon_{\text{ext}} + 2\epsilon_2) \times \left[ (\epsilon_2 + 2\epsilon_{\text{ext}}) (\epsilon_1 + 2\epsilon_2) + 2(1 - \Delta h/r)^3 (\epsilon_2 - \epsilon_{\text{ext}}) (\epsilon_1 - \epsilon_2) \right]^{-1}
\]  
(34)

where \(\Delta h\) is the shell thickness, and \(\epsilon_{\text{int}}\) is given by
\[
\epsilon_{\text{int}} = \epsilon_{\text{ext}} \frac{3 - \alpha'}{3 - \alpha'}.\]
(35)
Thus, in order to calculate the effective dielectric constant $\varepsilon_{\text{eff}}$ of a monolayer composed of coated nanoparticles one simply needs to substitute equation (33) (or equation (35)) into (16) and assume $f = f_2$.

5. Reflectance, transmittance and absorption of a closely packed nanoparticle film

For the purposes of illustration we will use the model developed above to calculate the optical properties of a gallium binary nanoshell film as described in [12]. The particles are considered to be spheres of radius $r = 25\, \text{nm}$ distributed on the surface of the substrate with a mean separation $l = 100\, \text{nm}$. For the substrate we take a value of $\varepsilon_{\text{sub}} = 2.28$, and for the surrounding medium $\varepsilon_{\text{ext}} = 1$. The wavelength of the interrogating radiation $\lambda = 1310\, \text{nm}$. Once the effective dielectric constant $\varepsilon_{\text{eff}}$ can increase the reflectance and its reflectance and transmittance can be calculated using standard thin film formulae [13]:

$$ R = \left\{ A_1 \exp \left( \frac{4\pi n_2 h k_2}{\lambda} \right) + A_2 \exp \left( -\frac{4\pi n_2 h k_2}{\lambda} \right) + 2\sqrt{A_1 A_2} \cos \left( \phi_2 - \phi_1 - \frac{4\pi n_2 h n_2}{\lambda} \right) \right\} \times \left\{ A_1 \exp \left( -\frac{4\pi n_2 h k_2}{\lambda} \right) + A_2 \exp \left( \frac{4\pi n_2 h k_2}{\lambda} \right) + 2\sqrt{A_1 A_2} \cos \left( \phi_2 - \phi_1 + \frac{4\pi n_2 h n_2}{\lambda} \right) \right\}^{-1} \tag{36} $$

$$ T = \frac{n_3}{n_1} \left\{ B_1 B_2 \left\{ \exp \left( \frac{4\pi n_2 h k_2}{\lambda} \right) + A_1 A_2 \exp \left( -\frac{4\pi n_2 h k_2}{\lambda} \right) + 2\sqrt{A_1 A_2} \cos \left( \phi_2 - \phi_1 - \frac{4\pi n_2 h n_2}{\lambda} \right) \right\} \right\}^{-1} \tag{37} $$

where

$$ A_{1,2} = \frac{(n_{1,2} - n_3)^2 + (k_{1,2} - k_3)^2}{(n_{1,2} + n_3)^2 + (k_{1,2} + k_3)^2} \tag{38} $$

$$ B_{1,2} = 4 \frac{(n_{1,2})^2 + (k_{1,2})^2}{(n_{1,2} + n_3)^2 + (k_{1,2} + k_3)^2} \tag{39} $$

$$ \phi_{1,2} = \arctan \left( \frac{n_{1,2} k_{2,3} - n_{2,3} k_{1,2}}{n_{1,2} k_{2,3} + n_{2,3} k_{1,2}} \right) + \pi, \quad \text{if } (n_{1,2} k_{2,3} - n_{2,3} k_{1,2}) \geq 0 \quad \text{and} \quad [(n_{1,2})^2 - (n_{2,3})^2 + (k_{1,2})^2 - (k_3)^2] < 0; $$

$$ \phi_{1,2} = \arctan \left( \frac{n_{1,2} k_{2,3} - n_{2,3} k_{1,2}}{n_{1,2} k_{2,3} + n_{2,3} k_{1,2}} \right) - \pi, \quad \text{if } (n_{1,2} k_{2,3} - n_{2,3} k_{1,2}) < 0 \quad \text{and} \quad [(n_{1,2})^2 - (n_{2,3})^2 + (k_{1,2})^2 - (k_3)^2] > 0; $$

$$ \phi_{1,2} = \arctan \left( \frac{n_{1,2} k_{2,3} - n_{2,3} k_{1,2}}{n_{1,2} k_{2,3} + n_{2,3} k_{1,2}} \right) + 0, \quad \text{if } [(n_{1,2})^2 - (n_{2,3})^2 + (k_{1,2})^2 - (k_3)^2] \geq 0. \tag{40} $$

Here $n_1 - i k_1 = \sqrt{\varepsilon_{\text{sub}}}, n_2 - i k_2 = \sqrt{\varepsilon_{\text{eff}}}$ and $n_3 - i k_3 = \sqrt{\varepsilon_{\text{ext}}}$ are the refractive indices of the substrate, film and surrounding medium respectively.

Assuming that the gallium nanoparticles are covered with a shell in the liquid phase (as suggested in [12]), the effective dielectric constant of the monolayer, $\varepsilon_{\text{eff}}$, can be calculated for different shell thickness in the range $0 \leq \Delta h \leq r$. The dielectric constant of liquid gallium, $\varepsilon_2 = -115.3 - i98.4$, was taken from [14], while that of the solid phase (believed to be the $\gamma$- or $\delta$-phase), was assumed to have optical properties intermediate between those of the liquid and $\alpha$-phases, thus $\varepsilon_1 = -25.9 - i39.7$.

The calculated reflectance, transmittance and absorption of the gallium nanoparticle film as a function of shell thickness $\Delta h$ are presented in figure 5. It can be seen that a liquid gallium shell just a few nanometres thick can increase the reflectance of a solid nanoparticles by several percent. The transmittance also increases with increasing shell thickness but, in percentage terms, by a much smaller amount. The absorption drops by a factor of about two.

As another illustration, we will investigate the spectral dependence of the optical absorption cross-section of gallium nanoparticles with high aspect ratios distributed in a low-density monolayer ($q = 0.01$) on the surface of a silica substrate. The nanoparticles are considered as spheroids with $\gamma = 16$ having a binary core-shell structure: a solid core ($\gamma$- or $\delta$-phase) of the same aspect ratio as the entire spheroid is covered with a shell of the liquid metal (see the inset to figure 6). Due to the lack of information on the dielectric properties of gallium’s metastable phases the dielectric dispersion profile of the solid phase was modelled as a linear combination of those for liquid [14] and $\alpha$-gallium [15] with weight coefficients of 0.79 and 0.21 respectively. After calculating the polarizability of such nanoshells using equation (12), where $f$ is replaced with $F$, the absorption cross-section is simply given by [10]

$$ C_{\text{abs}} = V (2\pi \varepsilon_{\text{ext}}^{1/2}/\lambda) \text{Im}(\alpha). \tag{41} $$

In figure 6 we present the calculated absorption cross-section of the nanoshells as a function of wavelength for different values
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To further illustrate how the optical properties of the nanoparticle film are affected by its composition we can compare the spectral dependence of cross-sections for spherical and flattened ‘pancake’ nanoparticles in the solid phase with different values of \( q \). Figure 7 shows that the optical absorption resonance of the spherical nanoparticle is blue-shifted with respect to that of the flatter particles (a well known result) and with increasing volume filling factor both resonances become broader and shift towards longer wavelengths.

6. Conclusions

In conclusion, we have developed a significantly improved version of the Yamaguchi theory for the optical properties of aggregated metal films by considering the exact local fields of spheroidal nanoparticles and introducing a treatment of binary nanoshells.

References

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