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From Mie to Fresnel through effective medium approximation with multipole contributions

Abhinav Malasi[1], **Ramki Kalyanaraman**[1,2] **and Hernando Garcia**[3]

[1] Dept. of Chemical and Biomolecular Engineering, University of Tennessee Knoxville, TN, USA
[2] Dept. of Materials Science and Engineering, University of Tennessee Knoxville, TN, USA
[3] Dept. of Physics, Southern Illinois University, Edwardsville, IL, USA

E-mail: hgarcia@siue.edu

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Abstract

The Mie theory gives the exact solution to scattering from spherical particles while the Fresnel theory provides the solution to optical behavior of multilayer thin film structures. Often, the bridge between the two theories to explain the behavior of materials such as nanoparticles in a host dielectric matrix, is done by effective medium approximation (EMA) models which exclusively rely on the dipolar response of the scattering objects. Here, we present a way to capture multipole effects using EMA. The effective complex dielectric function of the composite is derived using the Clausius–Mossotti relation and the multipole coefficients of the approximate Mie theory. The optical density (OD) of the dielectric slab is then calculated using the Fresnel approach. We have applied the resulting equation to predict the particle size dependent dipole and quadrupole behavior for spherical Ag nanoparticles embedded in glass matrix. This dielectric function contains the relevant properties of EMA and at the same time predicts the multipole contributions present in the single particle Mie model.

Keywords: nanoparticles, quadrupole, mie, fresnel, size dependence, plasmon, effective medium

(Some figures may appear in colour only in the online journal)

1. Introduction

Materials with heterogeneity in structure and composition and which show useful optical properties are all around us. From the perspective of advanced technologies, heterogeneous materials made from nanoscale components that scatter light resonantly, such as by plasmonic effects, are finding use in many different fields, including for ultrasensitive biological and chemical sensing by plasmonics [1–3], for tailored light scattering to improve solar cell efficiency [4, 5], and for coupling of plasmonics with magnetic Kerr effect for various applications [6–9]. The design of such materials and the predictions or evaluation of their optical performance, such as by knowledge of the dielectric function, and scattering and absorption cross-sections, can be achieved either through a complete solution of Maxwell's equations or by approximate solutions via effective medium approximations (EMA). The benefit of the former is a highly accurate quantitative picture of the electromagnetic fields but at the expense of less physical insight and large computational expense [10]. In contrast, EMA models can provide a fast and easy route to obtaining the central physical behaviors of complicated heterostructure systems as shown by several studies [11–18].

The fundamental models used to calculate plasmonic properties of scattering objects, such as metal inclusions, are those given by Rayleigh [19] and Mie [20]. The Rayleigh solution predicts the optical behavior correctly for inclusions much smaller then the incident wavelength [19], where the field inside the inclusion is uniform. The optical response from a metal inclusion of arbitrary size in an otherwise homogeneous and transparent media was solved by Mie [20]. The Mie solution uses the variation of field inside the

inclusions which are large or comparable to the wavelength of incident light, thus predicting more accurately the plasmonic behavior for large inclusions. Recently, Lukyanchuk *et al* [21] showed that the Rayleigh approach deviates for materials having low dissipation rate, and in this case, the light scattered by a small spherical particle can be explained by Mie theory. The exact solution to the Maxwell equations are approximated in accordance with the size parameter being much less than the incident wavelength. This model predicts the multipole resonances appropriately, a feature that becomes increasingly important as the particle size increases [22–24]. However, these models only give accurate information on the behavior of scattering and absorption dependence on wavelength of incident light for a *single* particle system.

Many approaches to incorporate scattering and absorption to describe heterogeneous systems by an effective dielectric function (ε_{eff}) have been done in the past. For example, Foldy [25] proposed that the incident and scattering wave combined to form a wave that travels uniformly in the composite without scattering and having a different group velocity from that of incident wave. This wave experiences reflection and refraction as well as showing coherent scattering. In the analysis he provided an expression for the group velocity and the wave vector, but not a formal definition of ε_{eff}. In the work by Lewin [26], an expression for the dielectric function of a composite was found using Fresnel formulas for the reflection and transmission coefficients and using the first term of the coefficient for the scattering wave from the Mie formalism. Further, he showed that the permittivity of the system has volumetric dependence but not the particle size dependence. Lax [27], on the other hand, used tools from scattering theory to define a propagation constant in accordance with the optical theorem, but no expression was derived. An approach similar to the one that we are proposing in this work, was taken by Doyle [28]. Doyle calculated the polarizability of a small metal particle using the scattering coefficients from Mie theory and combined the Clausius–Mossotti (CM) equation to obtain an effective dielectric constant and in this way succeeded in introducing size-dependence in an effective dielectric function. Dungey and Bohren [29] refined the calculation by incorporating the coupled dipole approximation with the polarizability expression calculated by Doyle [28]. This new method gave results that were comparable with the experimental extinction data. It is worth mentioning here that in Dungey and Bohren's approach only extinction and scattering coefficients were calculated and there is no definition of a effective dielectric function of the system. The current status is that existing theories either ignore one or more important parameters, such as size dependence and influence of the higher order multipoles, or do not explicitly discuss the effective dielectric function of the system, and in the event they do incorporate all effects, remain computationally expensive.

Therefore, the primary motivation of this work is to be able to come up with an EMA approach to predict the optical behavior of heterogeneous materials in which inclusions, such as nanoparticles can have size-dependent optical responses. In other words, we have attempted to bridge the Fresnel technique with the Mie solution, which includes size-dependent behaviors, via an EMA approach, as depicted in figure 1. Currently, this bridging is done using the Maxwell–Garnett (MG) [30], approach in which the inclusion size is much smaller then the wavelength. As a result, only dipolar effcts are observable in the MG approach, and the multi-polar effects often necessary to capture the size dependence, are lacking. In our work, the bridging was successfully achieved by defining the polarizability in terms of the approximate Mie solution which contains higher order multipole terms which are not present in MG theory. We assumed that the induced field inside the particle is uniform and the particles are non-interacting with each other. This resulting model, which contained the higher order plasmon modes, accurately predicted the size dependent behavior of metal particles embedded in a dielectric over a wide particle size range, while being computationally less challenging.

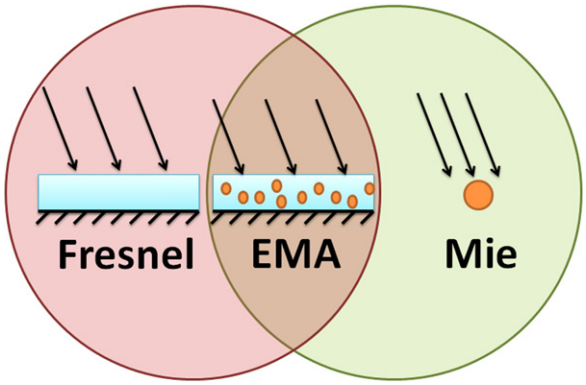

Figure 1. Schematic figure illustrating the primary motivation of this manuscript, which is to bridge EMA, Mie and Fresnel theories, i.e. incorporate size-dependent optical behaviors originating from multi-polar modes of the inclusions within EMA approaches.

The content of this manuscript is divided as follows. In Section II, we outline the theory and derive the main equation for the effective dielectric constant. We show that for the case of Ag nanoparticles embedded in glass matrix, the equation obeys causality. In section III, we calculate the optical density (OD) and compare it with typical approaches like the MG, Gans and Happel (GH), and Mie theories and also compare the predicted results with the experimental data. In section 4, we discuss the limitations of the model and provide conclusions in section 5.

2. Theory

The most familiar form of EMA is the CM approximation where the system is described by an effective dielectric function ε_{eff} given by

$$\frac{\varepsilon_{\text{eff}}(\omega)}{\varepsilon_{\text{h}}(\omega)} = 1 + \frac{\frac{n\alpha}{\varepsilon_o}}{1 - \frac{n\alpha}{3\varepsilon_o}} \tag{1}$$

where, n is the microscopic volume density of the number of

spheres in the system, α is the particle polarizability and ε_h is the dielectric constant of the host. If only the dipole contribution is taken into account, the polarizability is given by

$$\alpha(\omega) = 4\pi\varepsilon_o r^3 \frac{\varepsilon_i(\omega) - \varepsilon_h(\omega)}{\varepsilon_i(\omega) + 2\varepsilon_h(\omega)} \tag{2}$$

where ε_i is the dielectric constant of the inclusion and r is its radius.

On substituting equation (2) in equation (1), one gets the widely used MG approximation [30]. The CM approximation in the EMA is a consequence of considering that the randomly distributed dipoles and the induced dipole moment can be approximated as the mean induced dipole moment given by [31]

$$p_j = \frac{P\left(R_j\right)}{n\left(R_j\right)} \tag{3}$$

where $P\left(R_j\right)$ is the macroscopic polarization of the system at location R_j and $n\left(R_j\right)$ is the macroscopic density of the metal spheres at location R_j. If this approximation is used then the CM relation is rigorous.

As mentioned earlier, as the particle radius increases, quadrupole and higher order multipole contribution becomes important [21, 24], and the question arises as to how to incorporate these effects into EMA theories. Here, we propose to use the CM equation in conjunction with Mie's solution. This will contain all the multipole contributions to the particle polarizability, thereby giving a multipole EMA for the dielectric function of a composite, such as nanoparticles embedded in a host medium. This will also provide us with a fundamental binary mixing rule that can be used consistently to obtain the effective dielectric constant of multicomponent systems, as done in [13].

There are several key aspects of EMA theories. The key fundamental definition of an effective dielectric function is that the local field effect should contribute to the total Hamiltonian of the system but should not by any means alter the causal nature of the material. Also, as the inclusion concentration tends to zero the behavior of the effective dielectric function should tend asymptotically to the dielectric function of the host, which obeys causality, and it must therefore be true that the effective dielectric function should follow the Kramers–Kronig relation [32].

The second and more deeper aspect of EMA is that for particles for which $d/\lambda \geqslant 10^{-2}$, light scattering becomes dominant and an EMA becomes irrelevant. When this happens the system, according to the generalized view, cannot be described by an effective dielectric function, it does not follow the laws of geometrical optics, and neither can it be described by the Fresnel equation [33]. But this aspect is more controversial, because if one performed a Gedanken experiment where a black box that contained the material is subjected to the excitation by an electromagnetic optical field, then the main question will be: is the spectral distribution of the input electromagnetic field collected at the output affected entirely by scattering or due to absorption? If we assume that the system follows Beer–Lambert law then the output intensity can be expressed as

$$I = I_o e^{-\phi d} \tag{4}$$

where ϕ is the absorption coefficient and d is the medium thickness. The absorption coefficient can be related to the imaginary part of an 'effective dielectric' constant, and then, assuming that the system is causal, the real part of this effective dielectric function can be calculated. In fact one can go further to say that the system can be described by an effective dielectric constant that incorporates multipole expansion of Mie's solution and at the same time can be used for multilayer systems in a Fresnel-type approach as follows. The OD predicted by Mie, is given by

$$\mathrm{OD} = \log\left(\left(1 - R_{\mathrm{eff}}\right)^2 e^{\sigma_{\mathrm{ext}}\rho d}\right) \tag{5}$$

where, ρ is the particle density, σ_{ext} is the extinction coefficient, d is the sample thickness and R_{eff} is the reflection losses coming from the walls where the sample is contained. On the other hand, the OD predicted by EMA is given by

$$\mathrm{OD} = \log\left(\left(1 - R_{\mathrm{eff}}\right)^2 e^{\phi d}\right) \tag{6}$$

where, the absorption coefficient is given by

$$\phi = \frac{2\pi}{\lambda\, Re\left(\sqrt{\varepsilon_{\mathrm{eff}}}\right)} Im\left(\varepsilon_{\mathrm{eff}}\right) \tag{7}$$

and the reflection coefficient by

$$R_{\mathrm{eff}} = \frac{\left[\left(Re\left(\sqrt{\varepsilon_{\mathrm{eff}}} - 1\right)\right)^2 + \left(Im\left(\sqrt{\varepsilon_{\mathrm{eff}}}\right)\right)^2\right]}{\left[\left(Re\left(\sqrt{\varepsilon_{\mathrm{eff}}} + 1\right)\right)^2 + \left(Im\left(\sqrt{\varepsilon_{\mathrm{eff}}}\right)\right)^2\right]} \tag{8}$$

It is worth mentioning that the above equation can easily be extended to the case of oblique incidence and the results show perfect agreement with the Mie approach.

The suggestion we make here is that if both the equations predict the same spectral behavior then one must accept that the system can be described by an effective dielectric via Mie theory (that includes multipole expansions) and at the same time be applicable for multilayer systems in a Fresnel type approach.

To bridge the Mie, Fresnel and EMA, an effective polarizability is required which will contain the multipole expansion terms of the Mie theory. This can then be used in conjunction with CM to get the OD of the relevant system. To achieve this, the concept of an effective polarizability was used in the context of the CM equation by Barrera *et al* [34]. They were able to include local-field fluctuations in a system consisting of small spheres embedded in a dielectric medium and expressed the bare polarizability used in the CM equation by an effective polarizability. This polarizability is given by an algebraic equation that depends on the polarizability of the inclusion, the volume fraction and on the two particle distribution function [34]. It was also shown that the use of an effective polarizability can account for the effects of

radiation-reaction, which is necessary for scattering. Further it was shown that on expansion of the effective polarizability, the first term accounted for the absorption while the second term accounted for scattering [35]. Our central hypothesis is therefore based on the main idea of a Gedanken experiment (the uncertainty in distinguishing between scattering and absorption when one only knows the input and output of the field) and on the idea that an effective polarization can be defined such that it may be able to contain terms responsible for absorption and scattering [35] with the extinction cross-section given as:

$$\sigma_{\text{ext}} = \frac{k}{\varepsilon_o} Im\left(\alpha_{\text{eff}}\right) \tag{9}$$

where, $k = \frac{2\pi n_d}{\lambda}$, n_d is the refractive index of the medium and λ is the wavelength of light. As we show, while using σ_{ext} does the job adequately, using the absorption cross section instead of the extinction cross-section fails in two aspects; first, it does not obey causality because it ignores scattering, and second, it does not predict the same output as Mie theory [36].

To obtain the expression for the effective dielectric function we use the definition of the extinction cross section given by equation (9), where, for the Mie solution, the extinction coefficient can be expressed as:

$$\sigma_{\text{ext}} = \frac{2\pi r^2}{q^2} Re\left\{\sum_{l=1}\left(2\,l+1\right)\left({}^{e}a_l + {}^{m}b_l\right)\right\} \tag{10}$$

where, a and b correspond to the Mie coefficients and are given in terms of the Ricaty–Bessel cylindrical functions, and e and m correspond to the electric and magnetic multipole contributions, respectively. The l corresponds to the order of the contribution such that $l = 1$ is the dipole, while $l = 2$ corresponds to the quadrupole. The quadrupole contribution has a strong dependency on particle size and become important as the particle size increases. If z is a complex number then it is easy to say that

$$Re\left(z\right) = Im\left(iz\right) \tag{11}$$

Using the above relation, the extinction coefficient can be expressed as

$$\sigma_{\text{ext}} = \frac{2\pi r^2}{q^2} Im\left\{\sum_{l=1} i\left(2\,l+1\right)\left({}^{e}a_l + {}^{m}b_l\right)\right\} \tag{12}$$

On comparing equations (9) and (12) the polarizability is given by:

$$\alpha = \frac{2\pi r^3 \varepsilon_o}{q^3}\left\{\sum_{l=1} i\left(2\,l+1\right)\left({}^{e}a_l + {}^{m}b_l\right)\right\} \tag{13}$$

and using this expression, the effective dielectric function in the CM equation can be written as:

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{h}} - \frac{\frac{3f\varepsilon_h}{2q^3} Im\left\{\sum_{l=1} i\left(2\,l+1\right)\left({}^{e}a_l + {}^{m}b_l\right)\right\}}{1 + \frac{f}{2q^3} Im\left\{\sum_{l=1} i\left(2\,l+1\right)\left({}^{e}a_l + {}^{m}b_l\right)\right\}} \tag{14}$$

where, f is the volume fraction of the inclusion, and q is the size parameter defined below. In the cases where the particle radius is much smaller than the wavelength of the electromagnetic wave or that the size parameter q satisfies $q = \frac{2\pi r n_h}{\lambda} \ll 1$, then by using the power expansion of the cylindrical function (using terms of the leading order), it can be found that for the electric and magnetic dipole and quadrupole terms [21]:

$${}^{e}a_l = \frac{\Re_l^e}{\Re_l^e + i\Im_l^e} \tag{15}$$

$${}^{m}b_l = \frac{\Re_l^m}{\Re_l^m + i\Im_l^m} \tag{16}$$

where

$$\Re_l^e \approx q^{2\,l+1}\frac{\left(l+1\right)}{\left[\left(2\,l+1\right)!!\right]^2} n^l\left(n^2-1\right) \tag{17}$$

$$\Im_l^e \approx n^l \frac{l}{2\,l+1} \times\left[n^2 + \frac{l+1}{l} - \frac{q^2}{2}\left(n^2-1\right)\left(\frac{n^2}{2\,l+3} + \frac{l+1}{l\left(2\,l-1\right)}\right)\right] \tag{18}$$

$$\Re_l^m \approx -\frac{nq^2}{2\,l+1}\Re_l^e \tag{19}$$

$$\Im_l^m \approx -n^{l+1}\left[1 + \frac{1-n^2}{2\left(2\,l+1\right)}q^2\right] \tag{20}$$

and $n = \frac{\varepsilon_i(\omega)}{\varepsilon_h}$. Finally the effective dielectric function can be expressed as

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{h}} - 3f\varepsilon_{\text{h}} \times \frac{3\left({}^{e}a_1 + {}^{m}b_1\right) + 5\left({}^{e}a_2 + {}^{m}b_2\right)}{2iq^3 + f\left(3\left({}^{e}a_1 + {}^{m}b_1\right) + 5\left({}^{e}a_2 + {}^{m}b_2\right)\right)} \tag{21}$$

It is interesting to note that in the above equation when q is set to zero, the MG approximation is recovered. The above expression lacks symmetry in the sense that when $f = 1$, the dielectric function of the mixture is not equal to the dielectric function of the inclusion, and this asymmetry prevents it from being used as a bound. As mentioned earlier, this equation must obey causality. Therefore we have first calculated the real part of the dielectric function using the imaginary part predicted by the above equation for Ag nanoparticles (in a glass matrix). We have used the experimental values for the dielectric constant of Ag nanoparticles, suitably corrected for the modification of the relaxation time due to the small particle radius, as explained below. The, method employed here is based on the approach of Bachrach and Brown [37], and is called the subtracted Kramers–Kronig relation, which can be derived assuming that one has an independent experimental point given by:

$$Re\left(\varepsilon\left(\omega_1\right)\right) = \frac{2}{\pi}P\int_0^{\infty}\frac{\omega'\,Im\left(\varepsilon\left(\omega_1\right)\right)}{\omega'^2 - \omega_1^2}\mathrm{d}\omega' \tag{22}$$

where ω_1 is a reference frequency. By subtracting this

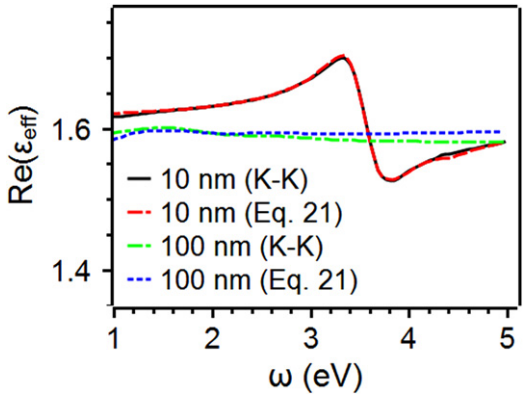

Figure 2. Real part of the effective dielectric function for two different particle sizes, as predicted by K–K relation and by our theory result, equation (21).

equation from the general form of the Kramer–Kronig relation we obtain the following relations:

$$\begin{aligned} Re\left(\varepsilon(\omega)-\varepsilon(\omega_1)\right) &= \frac{2}{\pi}P\int_0^\infty \frac{\omega'\, Im\left(\varepsilon(\omega')\right)}{\omega'^2-\omega^2}\mathrm{d}\omega' \\ &\quad -\frac{2}{\pi}P\int_0^\infty \frac{\omega'\, Im\left(\varepsilon(\omega')\right)}{\omega'^2-\omega_1^2}\mathrm{d}\omega' \\ &= \frac{2}{\pi}P\int_0^\infty \frac{\omega'\, Im\left(\varepsilon(\omega')\right)\left(\omega^2-\omega_1^2\right)}{\left(\omega'^2-\omega^2\right)\left(\omega'^2-\omega_1^2\right)}\mathrm{d}\omega' \\ &= \frac{2}{\pi}\left(\omega^2-\omega_1^2\right)P \\ &\quad \times\int_0^\infty \frac{\omega'\, Im\left(\varepsilon(\omega')\right)}{\left(\omega'^2-\omega^2\right)\left(\omega'^2-\omega_1^2\right)}\mathrm{d}\omega' \end{aligned} \tag{23}$$

where, $\varepsilon(\omega)$ is the complex dielectric function and $\varepsilon(\omega_1)$ is a known value of the real part of the dielectric function. The P stands for the principal value of the integral. This equation is easier to implement and converges more rapidly than the standard Kramers–Kronig relation. It is used to reduce errors that are introduced in evaluating the integral over the whole range of frequencies when, experimentally, only a finite range of frequencies are accessible. The anchor or reference point in our calculation is given by a value calculated using equation (21). Using the effective dielectric function of the system in the above equation for particles of radius 10 and 100 nm, and a volume fraction $f = 0.01$, we calculated the real part of the dielectric function and compared it with the results predicted by the theory, as shown in figure 2. The result is remarkably good taking into account the fact that most of the values for the dielectric function of Ag above 4 eV and below 1 eV are extrapolated as a piecewise polynomial.

3. Results

In figure 3 we show the OD as a function of wavelength, for the case of 10 and 100 nm radius Ag, respectively, using the most common approaches (MG, GH, and Mie theories) as

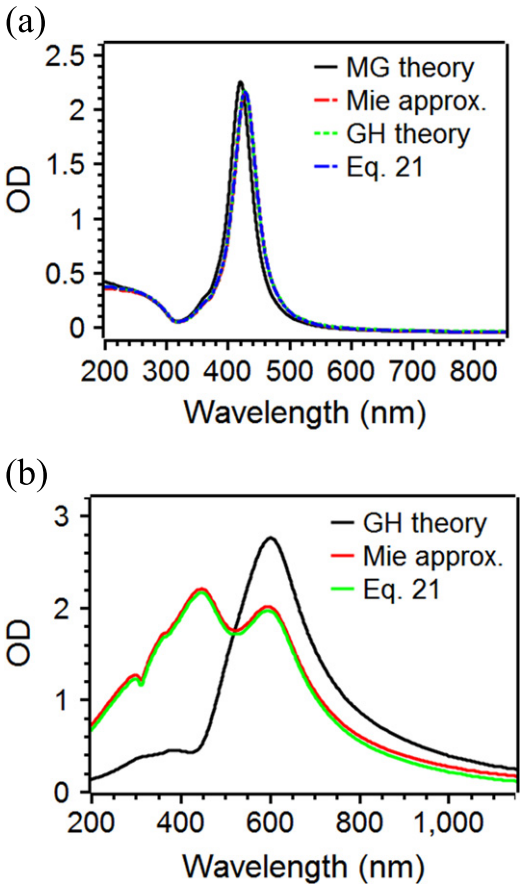

Figure 3. OD for (a) 10 nm and (b) 100 nm radius Ag nanoparticles embedded in glass matrix. The plots were calculated using the MG (MG), Gans-Happel (GH), and approximate Mie theories, as well as by our new theory, equation (21).

well as equation (21) for a volume fraction of $f = 0.01$ in glass. The dielectric function used in the calculation was corrected for the electron collision with the surface, which, in general, changes the scattering contribution from phonons, impurities, and defects with respect to the electron relaxation time. This correction can be incorporated in the analysis using the following expression [38]:

$$\begin{aligned} \varepsilon(\omega, r) &= \varepsilon_{\mathrm{bulk}}(\omega) \\ &\quad + \omega_p^2\left(\frac{1}{\omega^2+\Gamma_\infty^{-2}}-\frac{1}{\omega^2+\Gamma(r)^2}\right) \\ &\quad + i\frac{\omega_p^2}{\omega}\left(\frac{\Gamma(r)}{\omega^2+\Gamma(r)^2}-\frac{\Gamma_\infty^{-1}}{\omega^2+\Gamma_\infty^{-2}}\right) \end{aligned} \tag{24}$$

In the above equation ω_p is the electron plasma frequency, Γ_∞ is the electron conductivity relaxation time, and Γ_r is given by

$$\Gamma(r) = \frac{1}{\Gamma_\infty} + A\frac{v_\mathrm{F}}{r} \tag{25}$$

where, v_F is the Fermi velocity, and A is a constant of the O (1), and for spheres, $A \approx 1$ [39]. The refractive index for Ag was obtained from [40], while the additional information for

Ag to be used in the subsequent calculations was taken from [41], including ω_P of 9.6 eV, Γ_∞ of 2.89×10^{-14} s and the v_F of 1.39×10^6m s^{-1}.

To compare the results, it was necessary to ensure consistency of the particle radius r with the volume fraction and volume density of particles (ρ), which was estimated for $f = 0.01$ to be:

$$r = \sqrt[3]{\frac{3f}{4\pi\rho}} \tag{26}$$

for values of $\rho = 2387\mu\text{m}^{-3}$ for the 10 nm radius and $\rho = 2.387\mu\text{m}^{-3}$ for the 100 nm radius particles.

In an attempt to incorporate the full Mie theory in an EMA scheme and obtain an effective dielectric function, GH [42] incorporated electric dipole and quadrupole as well as magnetic dipole and quadrupole contributions in a single expression, using the full Mie coefficients. In figure 3, we have compared their results with predictions of the OD using the MG approach, GH result, approximate Mie solution from [21], and our equation (21) for the two different particle sizes. It is quite evident that our result gives remarkably similar results to the Mie, and GH approaches. From figure 3(b), it can be seen that equation (21) predicts the quadrupole and dipole more accurately than predicted by GH approach. The GH approach does not predict the absorbance in accordance with the Mie theory and shows a highly damped behavior for the quadrupole mode. The results of figure 3 indicate that the effective dielectric function in our model, given by equation (21), is quite accurate and its use within the EMA model accurately predicts higher order plasmonic modes for various particle sizes.

In figure 4 we have compared the OD of experimental data extracted from [38] for a composite made from Ag clusters embedded in a glass matrix. The clusters have an average size centered around 40 nm, but their volume fraction and the medium thickness was not provided. We have utilized equation (21) to obtain a theoretical prediction based on a best fit to the experimental data. The free parameters in the fit were the particle radius, the volume fraction, and the thickness of the composite. In figure 4, the equation (21) result is for an average radius of 42.31 nm, with a volume fraction of 0.003046 in a glass matrix of dielectric function equal to 2.0, propagating through a composite of thickness 6.83 μm. We have also included the results from the various other theories, including Mie, GH, and MG. The MG theory curve (scaled by a factor of 0.5) only predicts the dipole peak contribution of the system and is way off from the experimental value. While the Mie and GH theory predict the dipole peak accurately, the quadrupole peak is only predicted by Mie. More interestingly, the prediction of our equation (21) overlays the Mie result very well. In addition, our theory is in excellent agreement with experiment, despite incomplete information on details of the material provided in [38].

In figure 5(a), we show the resonance wavelength for the dipole and the quadrupole as a function of particle radius calculated using equation (21) for the system studied in figure 4. We observed that the red shift of the quadrupole resonance is less dramatic as compared to the dipole resonance. In figure 5(b), the OD curves for Ag nanoparticles embedded in glass matrix of different average size are compared to show that our model can easily capture the plasmon modes and can also show the changing intensity of the plasmon mode as a function of size.

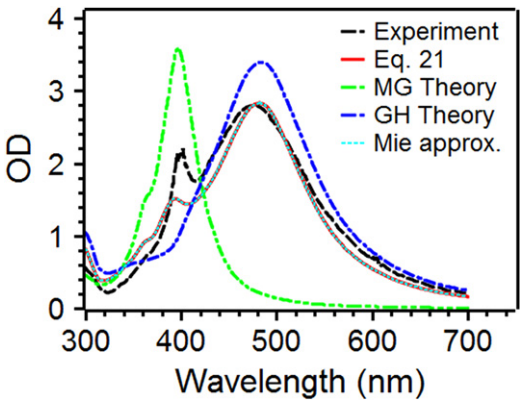

Figure 4. Comparison of our theoretical prediction based on equation (21) (solid red curve) to the experimental measurement (dashed black curve) of OD of nanoparticles of Ag with average size of 40 nm embedded in a glass matrix (experimental data was taken from [38]). Results of the MG theory (green dashed curve, scaled by a factor of 0.5), GH (dark blue dashed curve), and Mie (light blue dashed curve) theories are also shown. Our new EMA theory result of equation (21) overlays the Mie theory result very well, while predicting both the dipole and quadrupole peaks.

4. Limitations of the model

The first limitation of the model is its inability to predict the phenomenon of percolation threshold that is common in effective medium theories of the Bruggeman type [43], and in extended MG approximations [44, 45]. This is due to the fact that in our present case the role of the inclusion and the role of the host are not symmetric. In other words, the complementary mixture that results in the exchange of the host and the inclusion and at the same time exchanging their volume fraction is not possible in our model. In our opinion, it is not a major limitation in the sense that the model was derived in the spirit of low volume fraction. What we would like to focus now is on identifying the criteria for the applicability of equation (21), which is given in detail by Mackay and Lakhtakia [46] where they studied the applicability of Lewin's homogenization formula. They raised three objections to the applicability of a homogenization theory.

(a) *The inclusion should be small relative to the wavelength in the host material as well as in the inclusion material*. In this regard we believe that this restriction must be implemented with caution because the theory resides in incorporating higher multipole terms in the expression, and the higher resonance is what we are after. In the particular approximation that we used in the paper, we retained up to the quadrupole term, but we can include more terms in the

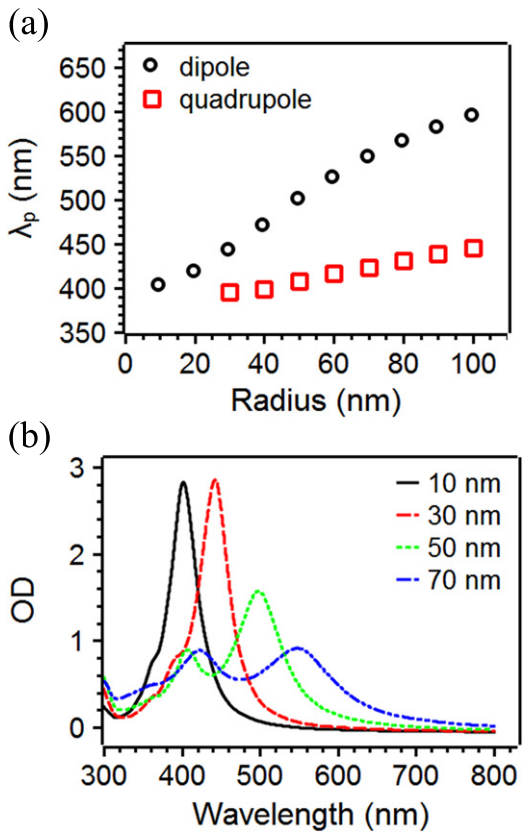

Figure 5. (a) The resonance wavelength of the dipole (open circles) and quadrupole (open squares) excitation of Ag nanoparticles embedded in glass as a function of the particle radius calculated using equation (21). (b) Plot of the absorption curves generated for Ag nanoparticles of different radius embedded in glass matrix.

expression and reproduce the multipole resonances pointed out by this restriction. This restriction is already implemented in Mie's approximation.

(b) *If the conditions* $Re\{\varepsilon_i\}\, Re\{\varepsilon_h\} \ll 0$ *and* $Im\{\varepsilon_i\} \ll Re\{\varepsilon_i\}$ *are satisfied, then it is inappropriate for arbitrary values of the volume fraction*. This is more demanding because it can easily be satisfied by typical noble metals used commonly in plasmonic applications. However, we have argued that the strong resonances that appear as a function of volume fraction tend to happen in the large inclusion concentration and for large negative values of the dielectric function. In fact for typical values of Ag, these resonance tend to appear in volume fraction greater than 0.5.

(c) *The restriction on the volume fraction is related to the size parameter q of the model*. As was mentioned earlier, the phenomenon of percolation can be predicted by the Bruggeman formalism where the inclusion and the host are on equal footing. This is not the case in our present work. One interesting aspect of the equation (21), is that if the second term in the denominator is ignored, we recovered Foldy's result. This is achieved by assuming that the propagation constant in its formulation can be identified to be related to an effective dielectric function of the mixture and the extinction cross section is given by Mie's result. Phenomenologically we have found that the agreement with Mie's results at normal incidence is correlated to the size parameter and the volume fraction such that

$$\frac{f}{q^3} = \left(\frac{\lambda}{n}\right)^3 \frac{\rho}{6\pi^2} < 1$$

Or using the density of modes on an electromagnetic wave in k-space given by [47]:

$$\rho_k = \frac{8\pi n^3}{3\lambda^3}$$

Then the restriction can be written as

$$\frac{\rho}{\rho_k} < 2\pi$$

This condition implies that the volume occupied by one particle in the host must be smaller by the volume occupied by the mode of the electromagnetic field in k-space. This restriction will determine the particle density which in turn will determine the volume fraction and the particle radius through equation (26). The estimated values for particles of the order of 20 nm at $\lambda \approx 800$ nm have volume fraction of the order of $f = 0.02$, while for particle of 80 nm radius at $\lambda \approx 800$ nm the volume fraction is of the order of $f = 0.2$. Of course, the restriction of percolation must be take into account such that in general $f < 0.3$.

5. Conclusion

We have developed a simple approach to express Mie's multipole expansion within EMA theories. This theory captures the physical behavior of the plasmon resonance as a function of size and adequately describes the quadrupole resonance. The derived result can be easily applied to multicomponent system analysis [48] and can potentially be used in conjunction with other EMA approaches [32, 33, 49] for analysis of reflection and transmission in nanostructured systems. Future work will be aimed at utilizing this approach to investigate the optical transmission and reflection from metal multicomponent systems.

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