Effective-medium theory of nonlinear ellipsoidal composites

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We develop an effective-medium theory for nonlinear, ellipsoidal particles embedded in a host medium. Specifically, we treat spheroidal-shaped particles and give results for oriented and random configurations of the particles. We discuss metallic particles embedded in a linear dielectric medium and examine the enhancement of their nonlinear response at the surface-plasmon resonances.

I. INTRODUCTION

There are many physical phenomena in composite media that can be described by an effective-medium theory. Examples include the dielectric behavior of heterogeneous systems,[1] the electronic conductivity of polycrystalline on inhomogeneous metals,[2-4] and particle diffusion in disordered media.[5] Recently, interest has turned to the nonlinear response of these media, with interesting experimental results indicating a large enhancement (10^6-10^8) of the effective nonlinearity.[6,7] This enhancement is consistent with the effective-medium theory calculations presented by those authors using the surface-plasmon resonance of the metal particles. The effective nonlinearity has been examined in an electrical transport problem and the same surface-plasmon resonance was found to dominate the results.[8]

Agarwal and Dutta Gupta[9] have recently examined the foundations of the effective-medium theory for nonlinear optical effects using a T-matrix approach. Stroud and Hui[8] have developed a variational approach to the nonlinear conductivity problem, but there is, of course, a strong analogy between their work and the nonlinear optical problem. The results of these papers are valid only for spherical particle shapes.

When ellipsoidal particles are used, one essential property is retained from the spherical particle case; namely, the electric field inside the ellipsoid is constant. There are, however, important changes in the formulation that need to be made when the particle shapes are ellipsoidal. This has already been noted in the linear regime where the effective-medium dielectric constant has been calculated.[1] The induced polarization direction in the ellipsoid is not generally parallel to the applied field; as a consequence, the scattered radiation is anisotropic as the direction of the driving field is changed. Furthermore, the magnitude of the induced polarization also varies with the direction of the driving field.

Metal particles are a special example of this phenomenon. There are surface-plasmon resonances determined by the dielectric properties of the metal particle and the medium in which it is embedded.

In this paper we provide results for spheroidal-shaped particles and perform the calculations in inhomogeneous media where the particles have a special distribution of their orientation. For instance, if the particles are oriented parallel to one another, then the effective dielectric tensor will be anisotropic. This can be probed by polarization effects in the reflected and transmitted light, and in the conjugate wave in a four-wave-mixing experiment.[7]

In Sec. II, we develop the formalism in which our results are derived. The results for nonlinear spheroidal-shaped particles in a linear or nonlinear medium are presented in Sec. III. We also calculate the nonlinear susceptibility appropriate for a four-wave-mixing experiment. In Sec. IV we take the special case of spherical particles in order to compare our results directly with those from recent publications. Section V is devoted to our conclusions.

II. FORMALISM

The inhomogeneous medium is characterized by a dielectric tensor $\underline{\epsilon}(\mathbf{x})$ which is a function of frequency and the electromagnetic field as well as being a random function of position. In the present problem, the material is composed of nonspherical grains which have a volume fraction f in the medium and a particular orientational distribution. The grains have a dielectric function

$$\underline{\epsilon}_m = \underline{\epsilon}_m + \underline{\Delta}\epsilon_m(\mathbf{E}_m)\ , \tag{1}$$

where $\underline{\epsilon}_m$ is the linear dielectric tensor and $\underline{\Delta}\epsilon_m(\mathbf{E}_m)$ is a field-dependent contribution to the dielectric constant. The value of the field in the medium $\mathbf{E}_m$ depends on the dielectric constant of the surrounding material and the orientation of the grain.

Similarly, the host material is considered to be a material with a dielectric function

$$\underline{\epsilon}_h = \epsilon_h + \underline{\Delta}\epsilon_h(\mathbf{E}_h)\ . \tag{2}$$

The terms in Eq. (2) are similarly interpreted and $\mathbf{E}_h$ is the value of the electric field in the host material.

The distribution of these dielectric materials has a factor that refers to their translational position and a factor that refers to the orientation of the ellipsoidal grain; let this factor be the angles $\boldsymbol{\theta}=(\theta_1,\theta_2,\theta_3)$, which give the orientation of the grain with respect to the space-fixed coordinates. The dielectric function has the following distribution of values for volume fraction f and volume fraction $(1-f)$, respectively:

$$\underline{\epsilon}(\mathbf{x})=\begin{cases}\underline{\epsilon}_m(\boldsymbol{\theta})\\ \underline{\epsilon}_h(\boldsymbol{\theta})\ .\end{cases} \tag{3}$$

This distribution does not incorporate correlations between the grains that would exist at high-volume fractions. The orientation of these grains is accounted for by averaging over a distribution of angles $\boldsymbol{\theta}$. Various cases will be discussed in Sec. III.

We restrict our discussion of the effective-medium theory to the quasistatic case, when $d/\lambda \ll 1$; d is a characteristic size of the grain and λ is the wavelength of light in that grain. In this limit, the electromagnetic field equations can be approximated by the static equations

$$\begin{aligned}&\nabla\cdot\underline{\epsilon}(\mathbf{x})\cdot\mathbf{E}=0\ ,\\ &\nabla\times\mathbf{E}=0\ .\end{aligned} \tag{4}$$

From the latter equation, we use the scalar potential to solve for the electric field inside the medium and Eqs. (4) are reduced to

$$\nabla\cdot\underline{\epsilon}\cdot\nabla\phi=0\ . \tag{5}$$

We introduce the dielectric tensor $\underline{\epsilon}_0$ which depends on the electric field in the average medium. Since we impose the boundary conditions of a uniform applied field, consistent with the quasistatic limit, $\underline{\epsilon}_0$ does not have a spatial variation. The dielectric function matrix is now

$$\underline{\epsilon}(\mathbf{x})=\underline{\epsilon}_0+\delta\underline{\epsilon}(\mathbf{x})\ , \tag{6}$$

and Eq. (5) becomes

$$\nabla\cdot\underline{\epsilon}_0\cdot\nabla\phi+\nabla\cdot\delta\underline{\epsilon}(\mathbf{x})\cdot\nabla\phi=0\ . \tag{7}$$

The Green function for the background medium satisfies the equation

$$\nabla\cdot\underline{\epsilon}_0\cdot\nabla g=-\delta(\mathbf{x}-\mathbf{x}_0)\ . \tag{8}$$

The solution of Eq. (8) for an infinite medium is

$$g(\mathbf{x},\mathbf{x}_0)=\frac{1}{4\pi\sqrt{\det(\underline{\epsilon}_0)}}\times\left[\frac{(x-x_0)^2}{\epsilon_{x0}}+\frac{(y-y_0)^2}{\epsilon_{y0}}+\frac{(z-z_0)^2}{\epsilon_{z0}}\right]^{-1/2} \tag{9}$$

where ϵ_{i0}, $i=x$, y, and z are the principal values of the dielectric tensor $\underline{\epsilon}_0$. The formal solution of Eq. (7) is

$$\phi(\mathbf{x})=\phi_0(\mathbf{x})-\int_v d^3x'g(\mathbf{x},\mathbf{x}')\nabla'\cdot\delta\underline{\epsilon}(\mathbf{x}')\cdot\nabla'\phi(\mathbf{x}')\ . \tag{10}$$

Here $\phi_0(\mathbf{x})$ is the solution of Laplace's equation with the appropriate boundary conditions. The electric field is

$$\mathbf{E}=\mathbf{E}_0+\int_v d^3x'\underline{G}(\mathbf{x},\mathbf{x}')\cdot\underline{\delta\epsilon}(\mathbf{x}')\cdot\mathbf{E}(\mathbf{x}')\ , \tag{11}$$

where we have integrated by parts and the dyadic Green function is defined as

$$G_{ij}(\mathbf{x},\mathbf{x}')=\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j'}g(\mathbf{x},\mathbf{x}')\ . \tag{12}$$

$\mathbf{E}_0$ is the field at the boundary of the volume.

Equation (11) is reexpressed by defining a susceptibility tensor $\chi(\mathbf{x}')$:

$$\mathbf{E}=\mathbf{E}_0+\int_v d^3x'\underline{G}(\mathbf{x},\mathbf{x}')\cdot\chi(\mathbf{x}')\cdot\mathbf{E}_0\ ; \tag{13}$$

then we find the following:

$$\chi(\mathbf{x})=\delta\underline{\epsilon}(\mathbf{x})\cdot\left[\underline{I}+\int_v d^3x'\underline{G}(\mathbf{x},\mathbf{x}')\cdot\underline{\chi}(\mathbf{x}')\right]\ , \tag{14}$$

where $\underline{I}$ is the identity matrix.

In the effective-medium theory, the random medium is replaced by a homogeneous, averaged medium, except for a small volume v_e, which has a distribution of dielectric functions according to Eq. (3). The volume v_e has an ellipsoidal shape; outside the ellipsoid, the medium has the background dielectric tensor $\underline{\epsilon}_0$. According to this approximation, the integral in Eq. (14) has the form

$$\int_v d^3x'\underline{G}(\mathbf{x},\mathbf{x}')\cdot\underline{\chi}(\mathbf{x}')\simeq\int_{v-v_e}d^3x'\underline{G}(\mathbf{x},\mathbf{x}')\cdot\langle\underline{\chi}(\mathbf{x}')\rangle+\int_{v_e}d^3x'\underline{G}(\mathbf{x},\mathbf{x}')\cdot\underline{\chi}(\mathbf{x}')\ . \tag{15}$$

For ellipsoids, the field inside is uniform and $\underline{\chi}(\mathbf{x}')$ will be independent of position. The field inside the medium is not equal to the applied field $\mathbf{E}_0$, nor is it parallel to the applied field. The expression to evaluate $\langle\underline{\chi}(\mathbf{x})\rangle$ is deduced using Eqs. (14) and (15). The result is

$$\langle\underline{\chi}(\mathbf{x})\rangle=\langle[\underline{I}-\delta\underline{\epsilon}(\mathbf{x})\cdot\underline{\Gamma}]^{-1}\cdot\delta\underline{\epsilon}(x)\cdot[\underline{I}-\underline{\Gamma}\cdot\langle\underline{\chi}(\mathbf{x})\rangle]\rangle\ , \tag{16}$$

where the depolarization tensor Γ can be calculated after integrating by parts

$$\Gamma_{ij}=\oint_{S(v_e)}d\mathbf{S}'\cdot\hat{\mathbf{e}}_i\frac{\partial}{\partial x_j}g(\mathbf{x},\mathbf{x}')\ . \tag{17}$$

$\hat{\mathbf{e}}_i$ is the unit vector along the ith axis. $\underline{\chi}(\mathbf{x})$ is equivalent to the T matrix;[4] the average displacement field is

$$\langle\mathbf{D}\rangle=\underline{\epsilon}_0\cdot\langle\mathbf{E}\rangle+\langle\delta\epsilon\cdot\mathbf{E}\rangle\ ; \tag{18}$$

by the definition of χ, the last term is $\langle\underline{\chi}\rangle\cdot\mathbf{E}_0$. This can be written using Eq. (18) as

$$\langle\underline{\chi}\rangle\cdot\mathbf{E}_0=\langle\underline{\chi}\rangle(\underline{I}+\langle\underline{G}\cdot\underline{\chi}\rangle)^{-1}\cdot\langle\mathbf{E}\rangle\ . \tag{19}$$

The relation between the average electric field and the average displacement field is

$$\langle\mathbf{D}\rangle=[\underline{\epsilon}_0+\langle\underline{\chi}\rangle\cdot(\underline{I}+\langle\underline{G}\cdot\underline{\chi}\rangle)^{-1}]\cdot\langle\mathbf{E}\rangle\ . \tag{20}$$

The effective dielectric tensor for the medium is

$$\overline{\underline{\epsilon}}=\underline{\epsilon}_0+\langle\underline{\chi}\rangle\cdot(\underline{I}+\langle\underline{G}\cdot\underline{\chi}\rangle)^{-1}\ . \tag{21}$$

A self-consistency condition is imposed on Eq. (21), namely,

$$\langle \underline{\chi} \rangle = 0 \ . \tag{22}$$

This is interpreted as the requirement that averaging over the embedded volume element will result in an effective homogeneous medium with dielectric function $\underline{\bar{\epsilon}} = \underline{\epsilon}_0$ where no scattering occurs. The task of finding $\underline{\bar{\epsilon}}$ is now reduced to calculating Eq. (22). This is done for several cases in Sec. III and spherical particles in Sec. IV.

III. RESULTS

In this section we treat two situations that exemplify the novel features of applying effective-medium theory to nonlinear media. The main difficulty in the application of the theory is that the functional form of $\underline{\bar{\epsilon}}$ is unknown, but it can be determined in special cases when the particles are oriented. In these cases, the polarization of the field with respect to the particle axes is important and can result in qualitative as well as quantitative differences in the results.

A. Oriented spheroids

We choose spheroidal-shaped particles for convenience. In Appendix A, the Green function and depolarization tensor are calculated for spheroidal-shaped particles.

When the particles have their axes parallel to one another, the effective medium will be anisotropic. Of course, for small concentrations this anisotropy is small and proportional to the volume fraction. Nevertheless, even a small anisotropy can have a measurable effect on the polarization of the electromagnetic field.

Orienting the particles has another important consequence for our development of the effective-medium theory. The dielectric functions in Eqs. (1) and (2) would all experience the same local-field amplitudes. The local field inside the metal particles is

$$\mathbf{E}_m = \underline{\gamma}^m \cdot \mathbf{E}_0 \ , \tag{23}$$

where $\underline{\gamma}^m$ is a diagonal matrix when the principal axes of the spheroid are used and

$$\underline{\gamma}^m = [\underline{I} + \underline{\Gamma} \cdot (\underline{\epsilon}_m - \underline{\bar{\epsilon}})]^{-1} \ . \tag{24}$$

In an anisotropic medium Γ has the scaling discussed in Appendix A. Similar results hold when the particle embedded in the effective medium is the dielectric host, the evaluation of $\mathbf{E}_h$ requires the replacement of $\underline{\epsilon}_m$ with $\underline{\epsilon}_h$.

The self-consistency condition derived in Appendix B can be evaluated for small concentrations by expanding in the concentration

$$\begin{aligned} \bar{\epsilon}_x &\simeq \epsilon_h + f\Delta\epsilon_x \ , \\ \bar{\epsilon}_z &\simeq \epsilon_h + f\Delta\epsilon_z \ . \end{aligned} \tag{25}$$

The corrections are

$$\Delta\epsilon_x = \frac{(\epsilon_m - \epsilon_h)}{1 + (\epsilon_m - \epsilon_h)\Gamma_{xx}^h} \ ,$$

and

$$\Delta\epsilon_z = \frac{\epsilon_m - \epsilon_h)}{1 + (\epsilon_m - \epsilon_h)\Gamma_{zz}^h} \ . \tag{26}$$

The factors Γ_{xx}^h and Γ_{zz}^h are given by Eqs. (A7) and (A8) with $\epsilon = \epsilon_h$.

All the dielectric constants may be field dependent. For instance, if we choose Kerr media in Eqs. (1) and (2), $\Delta\epsilon_m = \chi_m^{(3)}|\mathbf{E}_m|^2$, $\Delta\epsilon_h = \chi_h^{(3)}|\mathbf{E}_h|^2$ and $\Delta\epsilon_h = \chi_h^{(3)}|\mathbf{E}_h|^2$, the effective medium is not merely a Kerr medium. In the limit where f is small, $\mathbf{E}_h \simeq \mathbf{E}_0$ and

$$\mathbf{E}_m \simeq \frac{(\hat{e}_x E_{0x} + \hat{e}_y E_{0y})}{1 + \Gamma_{xx}(\epsilon_{mL} + \chi_m^{(3)}|\mathbf{E}_m|^2 - \epsilon_{hL} - \chi_h^{(3)}|\mathbf{E}_h|^2)} + \frac{\hat{e}_z E_{0z}}{1 + \Gamma_{zz}(\epsilon_{mL} + \chi_m^{(3)}|\mathbf{E}_m|^2 - \epsilon_{hL} - \chi_h^{(3)}|\mathbf{E}_h|^2)} \ . \tag{27}$$

Equation (27) can have multiple solutions for $|\mathbf{E}_m|$ with $|\mathbf{E}_h|$ held constant. This leads to a bistable behavior that is controlled by the surface-plasmon resonances in the denominators of Eq. (27). This has been analyzed in detail for spheres in a previous publication.[10] The sharpest resonances occur when the applied field is lined up along one of the principal axes of the ellipsoid.

B. Randomly oriented spheroids

The averaging of Eq. (B1) over random orientations results in an effective-medium dielectric function that is isotropic, but an essential complication arises in the nonlinear media because the local fields in Eq. (23) change for different orientations of the ellipsoid. This effect must be included in the averages.

We cannot obtain a simple closed-form expression for $\bar{\epsilon}$ as we did in Eq. (26); however, we can expand the effective-medium dielectric function in powers of applied field

$$\bar{\epsilon} = \bar{\epsilon}_L + \bar{\chi}^{(3)}|\mathbf{E}_0|^2 + O(|\mathbf{E}_0|^4) \ . \tag{28}$$

The linear coefficient $\bar{\epsilon}_L$ and the effective nonlinear Kerr coefficient $\bar{\chi}^{(3)}$ are solved by using the self-consistency condition in Eq. (B1) in Appendix B. The coordinates for Γ are expressed in axes that are fixed to the spheroid. The average over all orientations is carried out by projecting the tensor onto space-fixed axes along the direction of the applied field $\hat{e}_0\mathbf{E}_0/|\mathbf{E}_0|$. The linear contribution to the dielectric function has the expression

$$\frac{2}{3}\left[\frac{f(\bar{\epsilon}_L - \bar{\epsilon}_{mL})}{(1-\Gamma_{xx})\bar{\epsilon}_L + \Gamma_{xx}\epsilon_{mL}} + \frac{(1-f)(\bar{\epsilon}_L - \bar{\epsilon}_{hL})}{(1-\Gamma_{xx})\bar{\epsilon}_L + \Gamma_{xx}\epsilon_{hL}}\right] + \tfrac{1}{3}[\Gamma_{xx} \to \Gamma_{zz}] = 0 \ . \tag{29}$$

For the nonlinear contribution the expression

$$\bar{\chi}^{(3)}\left[\frac{2}{3}\left[\frac{f\epsilon_{mL}}{(1-\Gamma_{xx}\bar{\epsilon}_L+\Gamma_{xx}\epsilon_{mL})^2}+\frac{(1-f)\epsilon_{hL}}{(1-\Gamma_{xx}\bar{\epsilon}_L+\Gamma_{xx}\epsilon_{hL})^2}\right]+\frac{1}{3}[\Gamma_{xx}\to\Gamma_{zz}]\right]$$
$$=\chi_m^{(3)}f\left[\left(\tfrac{4}{15}|\gamma_{xx}^m|^2+\tfrac{1}{15}|\gamma_{zz}^m|^2\right)\frac{2\epsilon_{mL}}{[(1-\Gamma_{xx})\bar{\epsilon}_L+\Gamma_{xx}\epsilon_{mL}]^2}+\left(\tfrac{3}{15}|\gamma_{zz}^m|^2+\tfrac{2}{15}|\gamma_{xx}^m|^2\right)\frac{\bar{\epsilon}_L}{[(1-\Gamma_{zz})\bar{\epsilon}_L+\Gamma_{zz}\epsilon_{mL}]^2}\right]$$
$$+\chi_h^{(3)}(1-f)\{\underline{\gamma}^m\to\underline{\gamma}^h,\epsilon_{mL}\to\epsilon_{hL}\}\ . \tag{30}$$

The matrix $\underline{\gamma}^m$ is given in Eq. (24) using $\underline{\epsilon}_{mL}$ and $\underline{\epsilon}_L$ only and $\underline{\gamma}^h$ is formed by again replacing $\underline{\epsilon}_{mL}$ with $\underline{\epsilon}_{hL}$.

In the small concentration limit, for $\chi_h^{(3)}=0$ and spherical particles, we recover the results of previous researchers.[7,9,10] The case where $\chi_m^{(3)}=0$ and $\chi_h^{(3)}\neq 0$ has no significant enhancement of the effective nonlinearity at small concentrations.

IV. SPHERICAL PARTICLES

The connection of our results to previous work can be made by examining spherical particles in the low-concentration limit $f\ll 1$. In this case, the expressions in Eqs. (25) and (26) become identical: $\bar{\epsilon}_x=\bar{\epsilon}_z$ and $\Delta\epsilon_z=\Delta\epsilon_z$. The depolarization tensor components are

$$\Gamma_{xx}^h=\Gamma_{zz}^h=\frac{1}{3\epsilon_h}\ . \tag{31}$$

To make the connection with Agarwal and Dutta Gupta[9] we assume that the metal particles form a Kerr medium

$$\epsilon_m=\epsilon_{mL}+\chi_m^{(3)}u_L\ , \tag{32}$$

where we define the symbol with the amplitude of the local field in the metal $u_L=|E_m|^2$. The dielectric function in Eq. (26) is

$$\Delta\epsilon=\frac{3\epsilon_h(\epsilon_m-\epsilon_h)}{2\epsilon_h+\epsilon_m}=\gamma^m(\epsilon_m-\epsilon_h)\ . \tag{33}$$

The last equality defines the enhancement factor for spherical grains γ^m.

the dielectric function can be expanded as a power series in the parameter u_L

$$\bar{\epsilon}=\bar{\epsilon}_L+\chi_L^{(3)}u_L+\chi_L^{(5)}u_L^2+\cdots\ . \tag{34}$$

We would like to express ϵ as a power series in the applied field. Using Eq. (23),

$$E_0=\frac{E_L}{\gamma^m}\ , \tag{35}$$

we define the linear enhancement factor

$$\gamma_L^m=\frac{3\epsilon_h}{2\epsilon_h+\epsilon_{mL}}\ , \tag{36}$$

then the applied field is related to the local field by

$$E_0=\frac{E_L}{\gamma_L^m}\left[1+\frac{\gamma_L^m\chi_m^{(3)}}{3\epsilon_h}u_L\right]\ . \tag{37}$$

Equation (34) is expressed as a series in $|E_0|^2$

$$\bar{\epsilon}=\bar{\epsilon}_L+\bar{\chi}^{(3)}|E_0|^2+\bar{\chi}^{(5)}|E_0|^4+\cdots\ . \tag{38}$$

From Eqs. (32) and (33) we find

$$\chi_L^{(3)}=f(\gamma_L^m)^2\chi_m^{(3)}\ ,$$
$$\chi_L^{(5)}=-a\chi_L^{(3)}\ ,$$

and, in general,

$$\chi_L^{(2n+1)}=(-a)^{n-1}\chi_L^{(3)} \tag{39}$$

is here

$$a=\frac{\gamma_L^m\chi_m^{(3)}}{3\epsilon_h}\ . \tag{40}$$

From Eq. (37) we express u_L as a power series in $|E_0|^2$; we substitute the power series into Eq. (34) and identify the first three coefficients in Eq. (38) as

$$\bar{\chi}^{(3)}=f\chi_m^{(3)}|\gamma_L^m|^2(\gamma^m)^2\ ,$$
$$\bar{\chi}^{(5)}=-(a+a^*)|\gamma_L^m|^4\chi_L^{(3)}+|\gamma_L^m|^2\chi_L^{(5)}\ ,$$

and

$$\bar{\chi}^{(7)}=|\gamma_L^m|^6[(2a^2+2a^{*2}+3aa^*)\chi_L^{(3)}-2(a+a^*)\chi_L^{(5)}+\chi_L^{(7)}]\ . \tag{41}$$

The first two coefficients are identical to those given by Agarwal and Dutta Gupta.[9] The last one was not provided in their paper. Moreover, by continuing this procedure additional coefficients are derived in a straightforward fashion.

V. CONCLUSIONS

The effective-medium theory for ellipsoidal particles embedded in a host dielectric allows for a nonlinear response of the ellipsoidal shapes and incorporates new features that are not available when spherical particles are used.

First, the magnitude of the local field in the particles is affected by the shape of the particles through the depolarization tensor. The use of metallic ellipsoidal particles can exhibit this property in a particularly dramatic fashion. Ellipsoidal particles have several surface-plasmon resonances determined by the ratio of major and minor axes. Near one of these surface-plasmon resonances, the enhancement can be several orders of magnitude, the maximum enhancement depending inversely on the imaginary part of the metal's complex dielectric constant. By designing the particle shape, the surface-plasmon resonance can be chosen to be at a frequency where this imaginary contribution is minimized.

Second, there is an effective birefringence in the medium when the ellipsoidal particles are oriented. Unpolarized light propagating through this medium will be polarized by the different absorption characteristics of the orthogonal polarizations.

The effective-medium theory, yielding significantly enhanced optical nonlinearities, is especially important for four-wave-mixing experiments, which are proportional to $\bar{\chi}^{(3)}$ squared. As Eq. (30) reveals, the surface-plasmon resonances are raised to the fourth power. For this reason, the frequency response of the conjugate signed in these experiments is a much more sensitive probe of the particle shape than say the determination of the linear absorption. The surface-plasmon resonances will be accentuated in the conjugate signal to the eighth power.[11]

At high concentrations, there are several new problems which need to be addressed. The particles will be close enough that dipole-dipole interactions need to be included. The fields outside the ellipsoidal particles are concentrated at the tips and can lead to enhancement of the host medium nonlinearity. Furthermore, the positions of the particles will be correlated at high concentrations and this effect has not been accounted for in the present formulation.

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APPENDIX A: SPHEROIDAL DEPOLARIZATION TENSOR

The depolarization tensor in Eq. (16) is defined by the volume integral

$$\Gamma_{ij}=\int_{v_e} d^3x'\hat{\mathbf{e}}_i\cdot\underline{G}\cdot\hat{\mathbf{e}}_j \; . \tag{A1}$$

The divergence theorem can be used to express this quantity as the surface integral given in Eq. (17). We will use the latter result to calculate the components of Γ. First, we calculate them for a prolate spheroid in an isotropic medium and then we generalize the results to anisotropic media. The results for oblate spheroids are reported for completeness without derivation.

1. Isotropic media

For an isotropic medium, the Green function is given by Eq. (9) with $\epsilon_x=\epsilon_y=\epsilon_z=\epsilon$. This Green function needs to be expressed in prolate-spheroidal coordinates. We choose the foci of the ellipses at $(0,0\pm a/2)$; the distance of the foci from the point (x,y,z) is

$$r_\pm=[x^2+y^2+(z\mp a/2)^2]^{1/2} \; .$$

With these definitions the prolate-spheroidal coordinates are[12]

$$\zeta=\frac{r_+ + r_-}{a}, \quad \eta=\frac{r_- - r_+}{a} \; ,$$

and

$$\phi=\tan^{-1}(x/y) \; . \tag{A2}$$

The Cartesian coordinates are

$$\begin{aligned} x&=\frac{a}{2}[(\zeta^2-1)(1-\eta^2)]^{1/2}\cos\phi \; , \\ y&=\frac{a}{2}[(\zeta^2-1)(1-\eta^2)]^{1/2}\sin\phi \; , \\ z&=\frac{a}{2}\zeta\eta \; . \end{aligned} \tag{A3}$$

The solutions of Laplace's equation for the coordinates η are the associate Legendre polynomials $P_n^m(\eta)$ with $|\eta|\le 1$. The solutions for ϕ are the trigonometric functions $\cos m\phi$ and $\sin m\phi$. The range of values for ζ is $|\zeta|\ge 1$; the solutions of the separated differential equation are $P_n^m(\zeta)$ and $Q_n^m(\zeta)$, where $Q_n^m(\zeta)$ are the associated Legendre functions of the second kind. In these coordinates the Green function is

$$\begin{aligned} g(\mathbf{x},\mathbf{x}')&=\frac{1}{4\pi\epsilon|\mathbf{x}-\mathbf{x}'|} \\ &=\frac{1}{2\pi a\epsilon}\sum_{n=0}^{\infty}(2n+1)\sum_{m=0}^{n}\delta_m i^m\left[\frac{(n-m)!}{(n+m)!}\right]^2 \\ &\quad\times\cos[m(\phi-\phi')]P_n^m(\eta') \\ &\quad\times P_n^m(\eta)P_n^m(\zeta_<)P_n^m(\zeta_>) \; , \end{aligned}$$

where

$$\zeta_<=\min(\zeta',\zeta), \quad \zeta_>=\max(\zeta',\zeta) \; . \tag{A4}$$

δ_m is called Neumann's factor: $\delta_0=1$; otherwise, $\delta_m=2$.

For the $i=x$, $j=x$ component of the depolarization tensor, we have

$$\Gamma_{xx}=\frac{\partial}{\partial x}\int_{S(V_e)} d\mathbf{S}'\cdot\hat{\mathbf{e}}_x g(\mathbf{x},\mathbf{x}') \; . \tag{A5}$$

The surface of the ellipsoid is defined by a value ζ' and ζ_1, the surface element is $d\mathbf{S}'=h_\eta h_\phi d\eta' d\phi'\hat{\mathbf{e}}_\zeta$; where h_η and h_ϕ are the coordinates' scale factors. The integral in Eq. (A5) is

$$\Gamma_{xx}=\frac{\partial}{\partial x}\left[\frac{a}{2}\right]^2\int_{-1}^{1}d\eta'\int_0^{2\pi}d\phi'\zeta_1(\zeta_1^2-1)^{1/2}(1-\eta^2)^{1/2} \times\cos\phi' g(\mathbf{x},\mathbf{x}') \tag{A6}$$

The integration over ϕ' gives only the $m=1$ term from the sum in Eq. (A4). Similarly, the integral over η' vanishes, except for the term $n=1$. The integral is a linear function of x and Γ_{xx} is a constant with the value

$$\Gamma_{xx}=\frac{\zeta_1(\zeta_1^2-1)}{2\epsilon}\left[\frac{\zeta_1}{\zeta_1^2-1}-\frac{1}{2}\ln\left[\frac{\zeta_1+1}{\zeta_1-1}\right]\right] \; . \tag{A7a}$$

By symmetry $\Gamma_{yy}=\Gamma_{xx}$ and Eq. (8) lead to the identity

$$\Gamma_{zz}=\frac{1}{\epsilon}-2\Gamma_{xx}=\frac{(\zeta_1^2-1)}{\epsilon}\left[\frac{1}{2}\zeta_1\ln\left[\frac{\zeta_1+1}{\zeta_1-1}\right]-1\right] . \tag{A7b}$$

ζ_1 is related to the ratio of minor axis to major axis r by $\zeta_1=(1-r^2)^{-1/2}$.

For the oblate spheroids a similar calculation gives[1]

$$\Gamma_{xx}=\frac{r}{2\epsilon(1-r^2)}\left[\frac{A\cos(r)}{(1-r^2)^{1/2}}-r\right] , \tag{A8a}$$

and

$$\Gamma_{zz}=\frac{1}{\epsilon(1-r^2)}\left[1-\frac{r}{(1-r^2)^{1/2}}A\cos(r)\right] , \tag{A8b}$$

where r is the ratio of minor to major axes.

2. Anisotropic media

For anisotropic media, we need only scale the coordinates to obtain the result. Let $\epsilon_x=\epsilon_y$, and scale the coordinates $\tilde{x}=x/\sqrt{\epsilon_x}$, $\tilde{y}=y/\sqrt{\epsilon_y}$, and $\tilde{z}=z/\sqrt{\epsilon_z}$. The Green function in Eq. (9) is identical of Eq. (A4) with $\epsilon=\epsilon_x\sqrt{\epsilon_z}$. the solution of the problem in the scaled coordinates proceeds exactly as we have outlined above with the results given in Eqs. (A7)–(A9). However, the ratio of major to minor axes is $\tilde{r}=r\sqrt{\epsilon_z/\epsilon_x}$ for oblate ellipsoids and $\tilde{r}=r\sqrt{\epsilon_z/\epsilon_x}$ for oblate ellipsoids. To obtain the unscaled depolarization tensor components from the scaled ones, use the identity

$$\Gamma_{ii}=\frac{\det(\underline{\epsilon})}{\epsilon_i}\tilde{\Gamma}_{ii} , \tag{A9}$$

where the tilde denotes the scaled result.

APPENDIX B: EXPRESSIONS FOR THE SELF-CONSISTENCY CONDITION

In an anisotropic effective medium with dielectric functions $\bar{\epsilon}_x$ and $\bar{\epsilon}_z$, the results of Eq. (22) are evaluated from Eq. (16). We assume the host and microparticle media to be isotropic with volume fractions $(1-f)$ and f, respectively.

The self-consistency condition matrix form is

$$\langle f[\underline{I}+\underline{\Gamma}\cdot(\underline{\epsilon}_m-\underline{\bar{\epsilon}})]^{-1}(\underline{\epsilon}_m-\underline{\bar{\epsilon}}) +(1-f)[\underline{I}+\underline{\Gamma}\cdot(\underline{\epsilon}_h-\underline{\bar{\epsilon}})]^{-1}(\underline{\epsilon}_h-\underline{\bar{\epsilon}})\rangle_\Omega=\underline{0} , \tag{B1}$$

where the outside average is over the orientations of the spheroid with respect to the applied field. The dielectric functions $\underline{\epsilon}_m$ and $\underline{\epsilon}_h$ depend on the orientation of the particle through their dependence on the internal local field.

When the particles are oriented parallel to one another, the orientational average in Eq. (B1) gives the equations

$$\frac{f(\epsilon_m-\bar{\epsilon}_x)}{1+(\epsilon_m-\bar{\epsilon}_x)\Gamma_{xx}}+\frac{(1-f)(\epsilon_h-\bar{\epsilon}_x)}{1+(\epsilon_h-\bar{\epsilon}_x)\Gamma_{xx}}=0$$

and

$$\frac{f(\epsilon_m-\bar{\epsilon}_z)}{1+(\epsilon_m-\bar{\epsilon}_z)\Gamma_{zz}}+\frac{(1-f)(\epsilon_h-\bar{\epsilon}_z)}{1+(\epsilon_h-\bar{\epsilon}_z)\Gamma_{zz}}=0 . \tag{B2}$$

These equations must be simultaneously solved since Γ_{xx} and Γ_{zz}, see Appendix A, contain nonlinear combinations of $\bar{\epsilon}_x$ and $\bar{\epsilon}_z$.

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