An effective-medium approach to the optical properties of heterogeneous materials with nonlinear properties

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Abstract. We have derived an analytic approach, based on the hypothesis of the effective-medium theory, to evaluate the effective dielectric magnitudes, including the effective third order nonlinear optical susceptibility $\chi^{(3)}$, of a heterogeneous two-component medium in which one of the components (the host matrix or the embedded particle respectively) presents nonlinear behaviour. Our formulation allows us to solve the full nonlinear problem in the whole range of concentrations without treating the nonlinear effects as a small perturbation to the linear behaviour. Therefore, it can be considered as an upper limit of the commonly used low-field nonlinear approximations for heterogeneous materials. Under certain conditions, these composites can exhibit a bistable regime that the present theory properly describes in wide ranges of the concentration, shape, wavelength, dielectric contants and intrinsic nonlinear optical susceptibility of the nonlinear component as well as in terms of the intensity of the external electric field. The present approach has been used to calculate the nonlinear optical response of Cu–Al$_2$O$_3$ nanocomposites.

1. Introduction

The precise evaluation of the effective properties of heterogeneous materials is an open question. In the case of the long-wavelength approximation, the formulation of the problem notably simplifies to a Laplace equation which, once solved with appropriate boundary conditions, provides all the electrical properties of a composite material. Although there is not a general solution procedure of the Laplace equation, several formulations have been developed to give an approximate solution for linear media (for a recent revision see [1]). However, in the case when at least one of the components of the heterogeneous medium has a non-negligible nonlinear behaviour, the conventional linear formulations are not valid. There have been some previous theoretical studies treating the problem of linking the effective macroscopic properties with the nonlinear microscopic properties of

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one of the components of the heterogeneous material. The simplest models for describing these kinds of material, the Maxwell-Garnett theory [2] or the Mie theory [3], use the high-dilution approximation in order to calculate the optical effective properties. More general approaches based on a more accurate calculation of the effective dielectric constant of a heterogeneous medium with one of the components nonlinear have been developed by several workers [4–9]. In these formulations, several of the following approximations have been taken into account in order to calculate the effective nonlinear magnitudes:

(i) Quasistatic or low-field approximation, that is, the nonlinear part of the dielectric constant is much smaller than the leading linear term;
(ii) Very low concentration of one of the components;
(iii) The complex third-order nonlinear optical susceptibility of the nonlinear component is assumed to be purely real.

However, in a real composite these hypothesis are very restrictive for the following reasons:

(i) It is hard to establish conditions under which the regime of external applied power verifies that the nonlinear term is only a small perturbation of the linear term. This condition is usually satisfied in the neighbourhood of the plasmon wavelength.
(ii) It is difficult to prepare highly diluted and monodisperse composites.
(iii) The nonlinear component always has a complex (real and imaginary) coefficient $\chi^{(3)}$ [10] corresponding to the Kerr effect.

Therefore, a more general theory, valid for a wide range of conditions, would be necessary in order to check the range of applicability of the existing low field and low concentration nonlinear theories.

One of the most remarkable features of heterogeneous materials, in which at least one of the components is optically nonlinear, is the optical bistability. This effect has attracted much interest in the last few years owing to its many potential applications in optical devices such as optical transistors, high-speed optical information-processing devices and optical switches [11–13]. Optical bistability has been found experimentally in aerosols [3] and layered linear-nonlinear materials [14]. Also, the optical response, including bistability, has been analytically solved in the general case of nonlinear dielectric films [15, 16]. Several workers have predicted the appearance of optical bistability in insulator–metal mixtures in which one of the components is a nonlinear material [2–7], [9–12] where optical bistability is found in the neighbourhood of the plasmon frequency corresponding to the metallic particle [4]. At this frequency any small perturbation in $\varepsilon_p$ induces large variations in the effective dielectric constant. However, the perturbative approximations are unable to predict the optical behaviour of the material composite in the case of high metallic concentrations (larger than 1–10%) [2, 17, 18] or outside the plasmon frequency.

Moreover, it could be easily checked that, at frequencies close to the plasmon resonance, the low-concentration approximation is hard to satisfy. This is due to the poor convergence of the $f$-power expansion of any effective dielectric constant theory in the plasmon frequency. Therefore, only a generalized theory, valid for arbitrary values of concentration and electric fields, could properly describe the nonlinear optical response of heterogeneous materials.
In the present study we have developed a long-wavelength (compared with the particle size) non-perturbative effective-medium approach that allows us to calculate the optical properties of heterogeneous bicomponent materials in which at least one of the components exhibits nonlinear properties. The geometry of the particle is taken into account by introducing a percolation threshold parameter whose value can be derived from our model equations as a function of the particle shapes [19]. Moreover, the bistability regions can be calculated as a function of the frequency, particle shape and concentration, percolation threshold, external electric field, etc.

Although we shall illustrate our general formulation with a binary composite where one of the components is nonlinear, the present approach can be extended to multicomponent composites with two or more nonlinear components.

2. Theory

2.1. Effective dielectric constant in nonlinear composites

For simplicity we consider that an heterogeneous material is composed of a binary mixture of particles, labelled \( m \) and \( p \), much smaller than the wavelength. This is equivalent to assuming that we have inclusions \( p \) of a certain shape distributed in a matrix \( m \) in such a way that between \( p \) particles appear holes filled with matrix particles. Generally, both components \( m \) and \( p \) could exhibit nonlinear behaviour:

\[
D_m = \varepsilon_0 (\varepsilon_{m0} + \chi_m^{(3)} |E_m|^2) E_m
\]

\[
D_p = \varepsilon_0 (\varepsilon_{p0} + \chi_p^{(3)} |E_p|^2) E_p,
\]

where the magnitudes \( \varepsilon_0, \varepsilon_{m0}, \varepsilon_{p0} \) and \( \chi_m^{(3)} \), \( \chi_p^{(3)} \) are the dielectric constant of free space, the complex relative dielectric constant of the matrix and the inclusion particles at low field intensities and their complex third order nonlinear susceptibilities respectively. All these magnitudes are scalars since both components \( m \) and \( p \) are assumed to be isotropic. Moreover, \( |E_m| \) and \( |E_p| \) are the moduli of the particles’ internal electric fields. In the case when both components are nonlinear, it is customary to define the effective dielectric constants as follows:

\[
\varepsilon_p = \varepsilon_{p0} + \chi_p^{(3)} |E_p|^2
\]

\[
\varepsilon_m = \varepsilon_{m0} + \chi_m^{(3)} |E_m|^2.
\]

Equations (2) and (3) only account for the first and second terms of the power series of the dielectric constants \( \varepsilon_p \) and \( \varepsilon_m \) as a function of the microscopic electric field. Equations (2) and (3) only consider the so-called Kerr-like nonlinearity which is valid only when \( \chi_p^{(3)} |E_p|^2 \) and \( \chi_m^{(3)} |E_m|^2 \) are equal to or less than \( \varepsilon_{p0} \) and \( \varepsilon_{m0} \) respectively. These restrictions, which only apply for microscopic fields, hold in a reasonably wide range of applied power densities. For power densities leading to internal electric fields such that \( |E_p|^2 \) and/or \( |E_m|^2 \) are larger than \( \varepsilon_{p0}/\chi_p^{(3)} \) and/or \( \varepsilon_{m0}/\chi_m^{(3)} \) respectively, higher-order terms should be considered in equations (2) and (3). Although the Kerr-like approximation is valid for moderate microscopic fields, it will induce large macroscopic (effective) nonlinear optical properties in the composite material. We have estimated that, for the power density range covered...
in our calculations, that is $10^{-3} \leq I_0 \leq 300$ (see figures), the cubic nonlinearity is sufficient since we found $\varepsilon_{p0} \approx \chi_p^{(3)} |\mathbf{E}_p|^2$.

For simplicity, we consider that all the particles of each component of the composite have the same shape (ellipsoidal or spherical) and when we have ellipsoids, their principal axes coincide with the morphological axes. Moreover, we assume that all the particles, both $p$ and $m$, have their morphological axis perpendicular to the normal of the surface interface of the heterogeneous material. We also consider an $s$-polarized incident light beam so that the electric field is parallel to the composite surface. It has been recently reported that preferential orientation of elongated isotropic ellipsoids could induce a slight anisotropy in the composite (with its optical axis parallel to the normal of the surface) [20].

However, it should be noted that the $s$ component of the polarization will propagate in the medium through the ordinary ray and it will not be affected by any possible anisotropy [21].

In this paper we shall only consider the case of one of the materials, that of type $p$, having a large nonlinear susceptibility. Additionally, we use an effective-medium theory (EMT) so that the average electric field $(\mathbf{E}^{ex})$ outside the particles is constant and homogeneous. Under these conditions, it is possible to relate the average of the particles’ internal electric field $(\mathbf{E})_{p,m}$ to the average external field $(\mathbf{E}^{ex})$ through the general expression [22, 23]

$$\langle \mathbf{E} \rangle_{j,p,m} = \frac{\varepsilon_{jk,p,m}^{ex}}{(1 - L_{jk,p,m}) + L_{jk,p,m} \varepsilon_{jk,p,m}^{ex}} \langle \mathbf{E}^{ex} \rangle_{j,p,m},$$

where $\varepsilon_{jk,p,m}^{ex}$ is the $jk$th component of the dielectric constant tensor outside the $p$ and/or $m$ particles, $L_{jk,p,m}$ is the $jk$th component of the depolarization factor tensor, $\langle \mathbf{E} \rangle_{j,p,m}$ stands for the $jth$ component of a particle internal electric field $\mathbf{E}_{p,m}$ in the frame of the particle’s morphological axis, and $\varepsilon_{jk,p,m}$ is the $jth$ component of the dielectric constant tensor of the material particle (inclusion or matrix). The effective-medium approximation states that $\varepsilon_{jk,p,m}^{ex} = L_{jk,p,m}^{ex} = \langle \varepsilon \rangle_{jk}^{ex}$ and $\langle \mathbf{E}^{ex} \rangle_{j,p} = \langle \mathbf{E}^{ex} \rangle_{j,m} = \langle \mathbf{E}^{ex} \rangle$. This approximation is valid when the spatial fluctuations of the electric field inside the embedded particles are small. The latter fails when the concentration of particles is close to the percolation threshold so that the effective-medium approximation has limited applicability in this case. However, it should be added that, for concentrations both above and below the percolation threshold, the effective-medium approximation works reasonably well. We shall assume that the external radiation is $s$ polarized so that the external applied field $E_0$ is parallel to the surface interface of the heterogeneous sample; then it is equal to the average electric field in the neighbourhood of particles $p$ and/or $m$, that is $E_0 = \langle \mathbf{E}^{ex} \rangle$ and $\langle \varepsilon \rangle^{ex} = \langle \varepsilon \rangle$. Therefore, in the reference system of the spheroids and taking into account that the material particles are isotropic ($\varepsilon_{jk,p,m} = \varepsilon_{p,m}$) we have that, for the case of the $p$ particles,

$$\langle \mathbf{E} \rangle_{z,p} = \frac{\varepsilon}{(1 - L_{zz,p}) \varepsilon + L_{zz,p} \varepsilon_p} E_0,$$

where the $z$ axis corresponds to the morphological axis of the spheroids. A similar expression can be derived for $m$ particles.

In the case of nonlinear particles, the combination of the material equation (1) with equations (2) and (3) leads to
where, for clarity, we shall drop hereafter the tensorial subscript so that $L_{zz; p} = L_p$ and $L_{zz; m} = L_m$.

From equation (6) it is clear that the nonlinear increment of $\varepsilon_p$, that is $\Delta \varepsilon_p$, defined below, is proportional to $\chi_p^{(3)}$, being the real proportionality constant. Therefore,

$$\Delta \varepsilon_p = \varepsilon_p - \varepsilon_{p0} = \frac{\langle \varepsilon \rangle E_0}{(1 - L_p)\langle \varepsilon \rangle + L_p\varepsilon_p} |E_0|^2 \chi_p^{(3)}.$$

The above expression implies that, as will be shown below, the complex phase of $\chi_p^{(3)}$ is identical with that of $\chi_p^{(3)}$. The real and imaginary parts of $\Delta \varepsilon_p$ and $\chi_p^{(3)}$ are hereafter defined as

$$\Delta \varepsilon_p = \Delta \varepsilon_p' + i \Delta \varepsilon_p'', \quad \chi_p^{(3)} = \chi_p^{(3)'} + i\chi_p^{(3)''},$$

so that

$$\Delta \varepsilon_p = \Delta \varepsilon_p' \left( 1 + i \frac{\Delta \varepsilon_p''}{\Delta \varepsilon_p} \right), \quad \chi_p^{(3)} = \chi_p^{(3)'} \left( 1 + i \frac{\chi_p^{(3)''}}{\chi_p^{(3)'}} \right).$$

By defining the new variables

$$x = \Delta \varepsilon_p', \quad \tan \phi_p = \frac{\Delta \varepsilon_p''}{\Delta \varepsilon_p}, \quad \Psi = 1 + i \tan \phi_p,$$

we have

$$\Delta \varepsilon_p = x \Psi.$$

Therefore, as a consequence of equation (7), we obtain

$$\frac{\Delta \varepsilon_p''}{\Delta \varepsilon_p'} = \frac{\chi_p^{(3)''}}{\chi_p^{(3)'}} = \tan \phi_p;$$

this latter expression states that $\tan \phi_p$ is the phase of both the complex magnitudes $\Delta \varepsilon_p$ and $\chi_p^{(3)}$.

By taking into account equations (6)–(12), we have the following equation in $x$:

$$x = \frac{|\langle \varepsilon \rangle(x)|^2}{|(1 - L_p)\langle \varepsilon \rangle + L_p\varepsilon_p(x)|^2} I_E \chi_p^{(3)'},$$

where $I_E = |E_0|^2$.

The former expression is a cubic-like equations in $x$ whose coefficients depend on several parameters and on $\langle \varepsilon \rangle(x)$. After rearranging terms in equation (13), we obtain

$$F(x) = a_1 x^3 + b_1 x^2 + c_1 x + d_1 = 0,$$

where the coefficients $a_1(x)$, $b_1(x)$, $c_1(x)$ and $d_1$ are all real and given by
\begin{equation}
a_1(x) = \frac{L_p^2(1 + \tan^2 \phi_p)}{\langle \varepsilon(x) \rangle^2},
\end{equation}
(15)

\begin{equation}
b_1(x) = \frac{2L_p \Re \left[ \left( (1 - L_p) \langle \varepsilon(x) \rangle + L_p \varepsilon_{p0} \right) (1 - i \tan \phi_p) \right]}{\langle \varepsilon(x) \rangle^2},
\end{equation}
(16)

\begin{equation}
c_1(x) = \left( 1 - L_p \right) + L_p \frac{\varepsilon_{p0}}{\varepsilon(x)} \right)^2,
\end{equation}
(17)

\begin{equation}
d_1 = -I_E \chi^{(3)}.\end{equation}
(18)

Equation (13) relates the increment \( x \) of the real part of the dielectric constant of the \( p \) component to the effective dielectric constant \( \langle \varepsilon \rangle \), which is a function of \( \varepsilon_p(x) \). The relationship between these can be calculated by an effective-medium approximation. For simplicity, we have used the Bruggeman–Landauer [24, 25] formulation slightly modified in order to distinguish the two different shapes of the particles \( p \) and \( m \) of the composite.

Therefore, the effective medium equation for the effective dielectric constant of a binary composite becomes,
\begin{equation}
(1 - f) \frac{\varepsilon_m - \langle \varepsilon \rangle(x)}{(1 - L_m)\langle \varepsilon \rangle(x) + L_m \varepsilon_m} + f \frac{\varepsilon_p(x) - \langle \varepsilon \rangle(x)}{(1 - L_p)\langle \varepsilon \rangle(x) + L_p \varepsilon_p(x)} = 0,
\end{equation}
(19)

where \( f \) is the volume concentration or filling factor of the component \( p \).

After some rearrangement in equation (19) we reach a second-order algebraic equation for \( \langle \varepsilon \rangle \) of the form
\begin{equation}
b_2 \langle \varepsilon \rangle^2 + c_2 \langle \varepsilon \rangle + d_2 = 0,
\end{equation}
(20)

where the coefficients \( b_2, c_2 \) and \( d_2 \) are given by the expressions
\begin{equation}
b_2 = (1 - f)(1 - L_p) + f(1 - L_m),
\end{equation}
(21)

\begin{equation}
c_2 = \varepsilon_p(x)[L_p(1 - f) - f(1 - L_m)] + \varepsilon_m[fL_m - (1 - f)(1 - L_p)],
\end{equation}
(22)

\begin{equation}
d_2 = -\varepsilon_m \varepsilon_p(x)[(1 - f)L_p + fL_m].
\end{equation}
(23)

In the present formulation, all the effective macroscopic properties such as the index of refraction, reflectance or absorbance of heterogeneous materials are derived from a system of two nonlinear (sixth-degree) expressions given by equations (13) and (19).

At this point, it is worth introducing a new magnitude, specific to nonlinear heterogeneous systems. In fact, because these materials present a nonlinear behaviour, an effective third-order optical susceptibility \( \langle \chi^{(3)} \rangle \) can be defined and is given by [10]
\begin{equation}
\langle \chi^{(3)} \rangle = \frac{\langle \varepsilon \rangle - \langle \varepsilon \rangle_{E_0=0}}{|E_0|^2}.
\end{equation}
(24)

This magnitude, in the limit of low applied field, high dilution \( f \ll 1 \), where the Maxwell-Garnett theory [2, 27, 28] is satisfied) and spherical particles becomes [10, 29]
\begin{equation}
\langle \chi^{(3)} \rangle = f \mu^2 |\mu|^2 \chi^{(3)} \quad \text{with} \quad \mu = \frac{3\varepsilon_m}{2\varepsilon_m + \varepsilon_{p0}}.
\end{equation}
(25)
Equation (25), which is nowadays widely used, notably differs from the exact general definition (equation (24)) even at low concentrations \( f \geq 0.01 \).

### 2.2. Analytic solutions in the limit cases

Equation (19) predicts a percolative transition for \( \varepsilon \) at a threshold concentration \( f_c \) when \( \varepsilon_p \gg \varepsilon_m \). This condition may be satisfied in the case of very high applied density powers, so that it is worth describing the asymptotic behaviour of the present EMT for that condition. Applying \( \varepsilon_p \gg \varepsilon_m \) to equation (19) we have that

\[
\text{if } \varepsilon_p \gg \varepsilon_m, \langle \varepsilon \rangle = \frac{\varepsilon_m[(1-f)L_p] - fL_m - (1-f)L_p}{(1-L_m) - L_p(1-f)},
\]

\[
\text{if } \varepsilon_p, \langle \varepsilon \rangle \gg \varepsilon_m \Rightarrow \langle \varepsilon \rangle = \frac{\varepsilon_p(L_p(1-f) - f(1-L_m))}{(1-L_p)(1-f) - f(1-L_m)}.
\]

Equation (26) diverges when

\[
f = f_c = \frac{L_p}{1 + L_p - L_m}.
\]

On the contrary, equation (27) tends to zero when \( f = f_c \). It is important to stress that \( f_c \) represents a concentration of \( p \) particles at which the average dielectric constant of the heterogeneous mixture suddenly changes. Therefore, the link between the concept of percolation threshold and the morphological description of inclusion and matrix particles is established by equation (28). Moreover, since \( L_p \) can be approximately estimated from the shape determined by electron microscopy, another way of viewing equation (28) is by considering it as a relationship between the percolation threshold \( f_c \) and the specific way that the matrix particles pack around the inclusion particles; different inclusion arrangements would produce different shapes for the spaces in between, which are filled by the matrix particles [19]. The link between \( L_m \) and \( f_c \) is given by

\[
L_m = 1 + L_p - \frac{L_p}{f_c}.
\]

By using equation (29), equations (26) and (27) can be rewritten as a function of \( f_c \) as follows:

\[
f < f_c \Rightarrow \varepsilon_p \gg \varepsilon_m, \langle \varepsilon \rangle \Rightarrow \langle \varepsilon \rangle = \frac{\varepsilon_m[L_p(f_c - L_p)]}{L_p(f_c - f)},
\]

\[
f > f_c \Rightarrow \varepsilon_p, \langle \varepsilon \rangle \gg \varepsilon_m \Rightarrow \langle \varepsilon \rangle = \frac{\varepsilon_p}{L_p[f_c(1-L_p) + f(L_p - f_c)]},
\]

which, in the particular case of a spherical shape \( (L_p = L_m = \frac{1}{2} \) and \( f_c = \frac{1}{3} \)), reduce to

\[
f < f_c = \frac{1}{3} \Rightarrow \varepsilon_p \gg \varepsilon_m, \langle \varepsilon \rangle \Rightarrow \langle \varepsilon \rangle = \frac{\varepsilon_m}{3}(f_c - f)^{-1},
\]

\[
f > f_c = \frac{1}{3} \Rightarrow \varepsilon_p, \langle \varepsilon \rangle \gg \varepsilon_m \Rightarrow \langle \varepsilon \rangle = \frac{3\varepsilon_p}{2}(f - f_c).
\]

We now want to estimate the dependence of \( \langle \varepsilon \rangle \) and \( \varepsilon_p \) versus the power density in the range of high and very high powers. We assume that at high powers \( \varepsilon_p \gg \varepsilon_m \). In this case, using equations (6), (30) and (31) we have
linear optical behaviour is given by $f$ and the volume concentration of the inclusions. The values obtained for the non-linear component reach the percolation threshold. Below $f$, the effective dielectric constant and the power density needed to achieve the nonlinear dielectric constant $h$ introducing equations (30), (31), (34) and (35) into equation (24). We find that $f$ independent of the applied power density. In the case of higher concentrations, the composite material exhibits a percolative transition from a linear optical response $f < f_c$ to a nonlinear optical response $f > f_c$. Thus, studying the evolution of $\varepsilon_p$ and $\langle \varepsilon \rangle$ as functions of different experimental parameters.

The above analytical expressions for $\varepsilon_p$ and $\langle \varepsilon \rangle$ must be understood as the asymptotic behaviour of the effective dielectric constant at high power densities. Thus, studying the evolution of $\varepsilon_p$ and $\langle \varepsilon \rangle$ in this regime (high power) it could be possible to measure $\chi_p^{(3)}$ experimentally as a function of the applied power density and the volume concentration of the inclusions. The values obtained for $\langle \varepsilon \rangle$, both below and above $f_c$, indicate that $\langle \varepsilon \rangle$ exhibits a transition when the concentration of the nonlinear component reaches the percolation threshold. Below $f_c$, the effective nonlinear dielectric constant $\langle \varepsilon \rangle$ saturates for high values of applied fields. However, once the concentration of the nonlinear component is higher than $f_c$, the heterogeneous medium behaves as a Kerr-like medium in the range of large applied electric fields.

We can also estimate the behaviour of $\langle \chi^{(3)} \rangle$ in the limit of high powers by introducing equations (30), (31), (34) and (35) into equation (24). We find that $\langle \chi^{(3)} \rangle$ tends to 0 if $f < \frac{1}{2}$ and that $\langle \chi^{(3)} \rangle$ tends to a constant if $f > \frac{1}{2}$. Therefore, when $I_E \to \infty$, the composite material exhibits a percolative transition from a linear optical behaviour ($f < \frac{1}{2}$) to a nonlinear optical response ($f > \frac{1}{2}$).

Thus, equations (26)–(31) together with equations (34) and (35) can be very useful for determining the trend of both $\varepsilon_p$ and $\langle \varepsilon \rangle$ as functions of different experimental parameters.

2.3. General numerical approximation for $\langle \varepsilon \rangle$

The aim of this section is to provide a guide about how to determine numerically the dependence of the effective dielectric constant with the applied power density by using the analytical expressions previously introduced. The common procedure to perform nonlinear experiments is to apply a strong external power to a composite and to measure the optical effective properties. However, we have found out that, in order to obtain the input–output curves, it is easier to proceed in the opposite way, that is to obtain values of the applied density power as a function of the nonlinear dielectric constant. Therefore, the increment $x$ of the real part of $\varepsilon_p$, is taken as an independent variable that allows us to calculate first the effective dielectric constant and then the power density needed to achieve the previously fixed values of $x$. This procedure, which is based on equation (14) is a
cubic polynomial in \( x \) with non-constant coefficients, which truly becomes a sixth-degree polynomial such as
\[
I_E^{(3)'} = [a_1 x^2 + b_1(x)x + c_1(x)]x,
\]
or, in a concise form,
\[
I_E = \frac{F(x, I_E = 0)}{\chi_p^{(3)'}},
\]  \( \text{(37)} \)

2.4. Conditions for the bistability of \( \langle \varepsilon \rangle \)

One of the most remarkable features of composites with nonlinear components is that, under certain conditions, theoretical models predict that they can exhibit bistable behaviour [2, 4, 5]. However, the predicted bistability ranges are specific to the EMT considered in each approximation. Thus, we have considered that it could be convenient to study optical bistability within the framework of a more general formalism. This formalism, based on the geometrical interpretation of equation (13), allows us to determine the range of bistability of a nonlinear composite independently of the EMT used. Our procedure takes into account that the solution of equation (13) can be seen as the cut of a straight line \( y = x \) with the function \( y = F(x) \) (see figure 1 later). This procedure has already been used by Arnold et al. [3] in the case of a highly diluted nonlinear aerosol. In the case of a bistable solution of equation (13) the line \( y = x \) cuts the function \( y = F(x) \) at three points. Thus, it is evident that the bistability domain is limited by the condition that the straight line cuts the function \( y = F(x) \) twice. This implies that, at one of these intersection points, the function \( F(x) \) must have a slope equal to 1:
\[
\left. \frac{dF(x)}{dx} \right|_{x=x_l} = \frac{F(x_l)}{x_l}. \]  \( \text{(38)} \)

In this section we shall analyse equation (38) in order to find the solutions. The function \( F(x) \) is given by equation (13) as
\[
F(x) = \left. \frac{|\langle \varepsilon \rangle(x)|^2 I_E^{(3)'} \chi_x}{|\left(1 - L_p\langle \varepsilon \rangle \frac{x}{L} + L_p\varepsilon_{p0}(x) + L_p x\varepsilon_{p0}'\right)|^2}. \]  \( \text{(39)} \)

After some algebra we can rewrite equation (39) so that we have a Lorentzian-like function \( F(x) \) of the form
\[
F(x) = \frac{n_0^2 I_E^{(3)'} \chi_x}{(x - x_p)^2 + \gamma^2}, \]  \( \text{(40)} \)
where
\[
n_0^2 = \frac{|\langle \varepsilon \rangle(x)|^2}{L_p^2(1 + \tan^2 \phi_p)}, \]  \( \text{(41)} \)
\[
\gamma^2 = \frac{1}{L_p^2(1 + \tan^2 \phi_p)} \left( |(1 - L_p\langle \varepsilon \rangle + L_p\varepsilon_{p0})^2| \frac{1}{1 + \tan^2 \phi_p} + |(1 - L_p\langle \varepsilon \rangle + L_p\varepsilon_{p0})^2| \tan^2 \phi_p \frac{1}{1 + \tan^2 \phi_p} \right.
\]  \( \text{(42)} \)

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and
\[ x_p = -\frac{(1 - L_p)\langle \varepsilon \rangle' + L_p\varepsilon'_p + \tan \phi_p [(1 - L_p)\langle \varepsilon \rangle'' + L_p\varepsilon''_p]}{L_p(1 + \tan^2 \phi_p)}, \tag{43} \]

where \( \gamma \) is the half-width at half-maximum and \( x_p \) is the position of the maximum of the Lorentzian-like function.

Equation (43) defines the condition for the surface plasmon resonance (SPR) since, when \( x = x_p \), the denominator of the function \( F(x) \) minimizes. For a linear medium, \( x = 0 \) and the former SPR condition \( x = x_p = 0 \) is only satisfied at a single frequency. However, in the case of a nonlinear medium, it is plausible to find that \( x_p \geq 0 \) in a certain frequency range. Therefore, one can expect that the SPR conditions will be verified in this frequency range but at different power densities (obtained after solving equation (13)) for each frequency. It should be pointed out that the commonly used quasistatic approximations implies that \( \Delta \varepsilon_p \ll \varepsilon_p \), and this condition is only valid to study the bistable behaviour when \( x_p = 0 \). However, when \( x_p \neq 0 \), then \( \Delta \varepsilon_p \) is of the order of magnitude of \( \varepsilon_p \) so that any possible bistability study must be carried out with a non-quasistatic approximation [4].

It should also be noted that the plasmon condition depends on the shape of the particle and on the real and imaginary parts of the dielectric constant (\( \varepsilon_{\text{ph}} \)) of the particle, on the value of the complex average dielectric constant and on \( \tan \phi_p \).

Equations (41)–(43) determine the parameters of equation (40). In general, \( n_0 \), \( \gamma \) and \( x_p \) depend on \( x \): this occurs in a complicated way because of the dependence in the effective dielectric constant and then on \( x \). However, in the case of a mixture of a transparent matrix with highly diluted small metallic particles (\( f \ll 1 \); and \( \varepsilon_p' < 0 \), \( \varepsilon_p'' > 0 \) and \( |\varepsilon_p''| \approx |\varepsilon_p'| \) the following conditions are fulfilled:
\[ |\langle \varepsilon \rangle' | \ll |\langle \varepsilon \rangle| \approx |\langle \varepsilon \rangle|, \quad |\langle \varepsilon \rangle'' | \ll \varepsilon_p' \tag{44} \]

In addition, \( |\langle \varepsilon \rangle| \) can be considered as nearly \( x \) independent. In fact, we have checked that, in high-metal-dilution conditions, \( |\langle \varepsilon \rangle| \) only varies a maximum of 10\% above its constant value when \( x \approx x_p \). This implies that \( n_0 \) and \( x_p \) can be considered as constant parameters. Also, although \( \langle \varepsilon \rangle'' \) cannot be considered as \( x \) independent, this value can be neglected in \( (1 - L_p)\langle \varepsilon \rangle'' + L_p\varepsilon''_p \approx \varepsilon''_p \), since \( \langle \varepsilon \rangle'' \ll \varepsilon_p'' \) according to equation (44). The latter condition allows us to consider the parameter \( \gamma \) as approximately \( x \) independent.

Above the limits of our approximation (44), the variation in \( \langle \varepsilon \rangle \) as a function of \( x \) begins to play an important role in the behaviour of the parameters of \( F(x) \). This induces an additional broadening of \( F(x) \). A general treatment of the bistability problem, without any of the approximations made above, requires a deep knowledge of the dependence of \( \langle \varepsilon \rangle \) with \( x \) in the neighbourhood of the SPR. This subject is outside the scope of the present work and it is sufficiently complex to warrant development in a separate contribution.

Equations (42) and (43) are notably simplified if we assume that the third-order nonlinear optical susceptibility is mainly controlled by its real part, \( \chi_p^{(3)} \ll \chi_p^{(3)} \), which implies that \( \tan \phi_p \rightarrow 0 \). Then we have
\[ x_p \approx -\varepsilon'_p \left[ \frac{1 - L_p}{L_p} \langle \varepsilon \rangle' + \tan \phi_p \left( \frac{1 - L_p}{L_p} \langle \varepsilon \rangle'' + \varepsilon''_p \right) \right], \tag{45} \]

and
The latter equation becomes even simpler when we deal with a transparent matrix in the regime of high metal dilution where the following relationship holds: \( \langle \varepsilon \rangle' \gg \langle \varepsilon \rangle'' \approx 0 \), and then \( \langle \varepsilon \rangle'' \) can be neglected when compared with \( \langle \varepsilon \rangle' \). Thus, \( \gamma^2 \) becomes

\[
\gamma^2 \approx \varepsilon''_{p0} + 2 \tan \phi_p (x_p + \varepsilon''_{p0} \tan \phi_p) \tag{47}
\]

and \( x_p \) becomes

\[
x_p \approx -\varepsilon'_{p0} - \left( \frac{1 - L_p}{L_p} \langle \varepsilon \rangle' + \varepsilon''_{p0} \tan \phi_p \right). \tag{48}
\]

Therefore, after the above approximations, equation (13) becomes

\[
x = F(x) \approx \frac{\eta_0^2 I_E \chi_p^{(3)}}{(x - x_p)^2 + \gamma^2}. \tag{49}
\]

At this point we can retrieve the geometrical interpretation of the bistability criteria represented by equation (38) applied on the approximation given by equation (49). In this case, the solutions of equation (49) can be described as the cut of a straight line, with slope \( 1/I_0 \), where \( I_0 = I_E \chi_p^{(3)} \). This line intersects the curve \( F(x) \) at three points (hexagons) defining the three solutions \( (x_1, x_2, x_3) \) of equation (49) in a bistability regime.

The application of condition (38) on equation (49) allows us to obtain the bistability criterion

\[
\frac{2(x_l - x_p)}{(x_l - x_p)^2 + \gamma^2} = \frac{1}{x_l}, \tag{50}
\]

which, after some algebra, leads to a quadratic equation in \( x \) given by

\[
-3x_l^2 + 4x_p x_l - (x_p^2 + \gamma^2) = 0, \tag{51}
\]

whose solution is given by

\[
x_l = \frac{2x_p \pm (x_p^2 - 3\gamma^2)^{1/2}}{3}. \tag{52}
\]

Thus, the bound values \( x_l \) of the bistability region, depend on the values of \( \gamma \).

When \( \gamma = x_p/3^{1/2} \), we find that \( x_l = 2x_p/3 \), which determines the maximum value of \( \gamma \) for which bistability is allowed.

When \( \gamma \to 0 \), we have the widest \( x \) range of bistability:

\[
x_l \approx \frac{2}{3} x_p ± \frac{1}{3} x_p \left( 1 - \frac{3\gamma^2}{2x_p^2} \right), \quad x_{l1} \approx x_p \left( 1 - \frac{\gamma^2}{2x_p^2} \right), \quad x_{l2} \approx x_p \left( 1 + \frac{\gamma^2}{2x_p^2} \right). \tag{53}
\]

Therefore, we can derive from equation (49) the bounds of the bistability region expected for very low filling factors:
Following the above geometrical criteria, we can determine the upper and lower bounds of the wavelength interval for which bistability most probably exists. In order to have the broadest bistability region it is necessary that the interval $x_{l2} - x_{l1}$ is as large as possible. From equation (52) this interval can be estimated as

$$x_{l2} - x_{l1} = \frac{3}{2}(x_p^2 - 3\gamma^2)^{1/2}. \quad (57)$$

It can be easily proved that the above interval is a maximum when $\gamma$ takes its minimum value. Considering equations (46) and (47), this minimum value of $\gamma$ can be found if the wavelength of the experiment is shifted to the minimum value of $\varepsilon_{pl0}(\lambda)$ or $\tan \phi_p < 0$. Previous work, restricted by the initial quasistatic hypothesis $\Delta \varepsilon_p \ll \varepsilon_p$, has attempted to find bistability features in a spectral area close to the SPR corresponding to the linear regime ($I_0 \approx 0$). However, after our result, we
think that it is better to increase this spectral area from the SPR wavelength up to the wavelength that minimizes $\varepsilon_{\rho 0}(\lambda)$.

If we had assumed above that the third-order nonlinear optical susceptibility was driven by its imaginary part ($\tan \phi_p \to \infty$, i.e. $\chi_p^{(3)} \to 0$) instead of by its real component (so that $\tan \phi_p \to 0$), we would have found that

$$x_p = -\left( \frac{1}{L_p} \left[ (1 - L_p) \langle \varepsilon \rangle'' + L_p \varepsilon_{\rho 0}'' \right] \right), \quad (58)$$

which, since $\langle \varepsilon \rangle''$, $L_p$ and $\varepsilon_{\rho 0}''$ are always positive, locate the centre of the Lorentzian-like function $F(x)$ on the negative $x$ axis; therefore, this makes it impossible to find a bistability region according to the above-mentioned criteria.

3. Results and discussion

In this section we present the results of calculations based on the previously presented formalism applied to a real system. It is assumed that the particles of each component have the same ellipsoidal shape different from the shape of the other component. In order to make a comparison with a real experimental system, we have chosen the copper–alumina (Cu–Al$_2$O$_3$) binary system where Cu nanocrystals are the embedded particles (component $p$) in an Al$_2$O$_3$ matrix (component $m$). This kind of nanocomposite can be synthesized by several procedures [30]. The linear optical properties of these substances are well known and appear in [28, 31, 32] (some representative values are as follows: Cu, $\varepsilon(590\text{ nm}) = -7.65 + i2.61$, $\varepsilon(610\text{ nm}) = -9.44 + i1.92$, $\varepsilon(650\text{ nm}) = -13.21 + i1.57$ and $\varepsilon(800\text{ nm}) = -25.72 + i2.69$, Al$_2$O$_3$: $\varepsilon = 3.1738$). We have not considered any particle size dependence of the linear dielectric constants of Cu and Al$_2$O$_3$. On the other hand, the nonlinear optical properties of nanocomposites formed by metal or semiconductor nanocrystals embedded in dielectric hosts have been intensively studied for the last two decades because these materials might become a very interesting alternative for the development of optical switching devices in waveguides [11, 33]. In particular, Cu–Al$_2$O$_3$ nanocomposites exhibit strong third-order nonlinear optical susceptibilities [29] whose values are expected to increase in importance as the nanocrystal size decreases [29]. Our approach is illustrated for two different metal concentrations, $f = 0.01$ and $f = 0.1$, as a representation of the high- and moderate-dilution regimes. The optical properties of the lowest concentration may be approximated by the Maxwell-Garnett theory [34] but the latter needs a full EMT treatment. In addition, the dependence of the effective dielectric constant on the particle shape and on the value and phase of the nonlinear optical susceptibility has been estimated.

The structure of equations (36) and (37) allows us to represent all the calculated magnitudes as a function of the adimensional power density $I_0 = I_{E\chi_p^{(3)}}$. Some of the presented calculations reflect variations in effective optical properties with the adimensional power density $I_0$ at a fixed wavelength. We have chosen the wavelength $\lambda = 650\text{ nm}$ corresponding to the minimum of $\text{Im}[n(\lambda)]$. This is the condition obtained from equations (47) and (57) in order to have the broadest interval of bistability in the Cu–Al$_2$O$_3$ system. In this section we shall discuss the results concerning the cases for one nonlinear medium and the variation in $n(\lambda)$ with different power densities respectively.
In order to understand the nonlinear behaviour of composites, plots of several effective optical magnitudes of the composite versus the applied power density $I_0$ have been calculated from equations (15)–(18), (19) and (36). In figure 2 we have plotted the real and imaginary parts of the effective index of refraction for metal concentration $f = 0.01$ (figures 2(a) and (b)) and $f = 0.1$ (figures 2(c) and (d)). On each graph we have used three different configurations for the composite (see table 1 for details). Curves $a$ are for composites with spherical metallic particles with negative values of the imaginary part of the nonlinear susceptibility $\chi^{(3)}_p < 0$, curves $b$ refer to spherical metallic particles with $\chi^{(3)}_p = 0$ and curves $c$ correspond

![Figure 2](image_url)

Figure 2. Real part $\text{Re}(n)$ and imaginary part $\text{Im}(n)$ of the index of refraction, $n$ as a function of $I_0$ for $\lambda = 650\text{nm}$ and for the conditions in table 1: (a) $\text{Re}(n)$ for $f = 0.01$; (b) $\text{Im}(n)$ for $f = 0.01$; (c) $\text{Re}(n)$ for $f = 0.1$; (d) $\text{Im}(n)$ for $f = 0.1$.

In order to understand the nonlinear behaviour of composites, plots of several effective optical magnitudes of the composite versus the applied power density $I_0$ have been calculated from equations (15)–(18), (19) and (36). In figure 2 we have plotted the real and imaginary parts of the effective index of refraction for metal concentration $f = 0.01$ (figures 2(a) and (b)) and $f = 0.1$ (figures 2(c) and (d)). On each graph we have used three different configurations for the composite (see table 1 for details). Curves $a$ are for composites with spherical metallic particles with negative values of the imaginary part of the nonlinear susceptibility $\chi^{(3)}_p < 0$, curves $b$ refer to spherical metallic particles with $\chi^{(3)}_p = 0$ and curves $c$ correspond

Table 1. Conditions for which the present approach has been implemented in the cases of a composite with one nonlinear medium.

<table>
<thead>
<tr>
<th>Curve</th>
<th>$L_0$</th>
<th>$L_m$</th>
<th>$\tan \phi_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.3333</td>
<td>0.3333</td>
<td>-0.1</td>
</tr>
<tr>
<td>b</td>
<td>0.3333</td>
<td>0.3333</td>
<td>0</td>
</tr>
<tr>
<td>c</td>
<td>1.0</td>
<td>0.3333</td>
<td>0</td>
</tr>
</tbody>
</table>
to cylindrical-like metallic particles with $\chi_p^{(3)\prime\prime} = 0$. In these three cases we have considered the insulator particles as spherical. The evolutions of $\text{Re}(n)$ versus $I_0$ for $f = 0.01$ are similar for the three composites considered. Bistability loops are always found. In curves $a$ and $b$ this loop appears between $I_0 = 0.1$ and $I_0 = 1$, being larger in the first case, whereas for cylindrical particles (curve $c$) the bistability range is wider but placed at higher power $I_0 \approx 10$. The imaginary part of the index of refraction presents different additional features. As in the former case, curves $a$ and $b$ present similar bistability behaviours at low $I_0$. However, in the case of curve $a$ it displays a sharp reduction at power density values close to 10. This is an unphysical feature of the model due to the assumption that $\text{Im}(\chi_p^{(3)}) < 0$, which is valid only for low power densities [10]. However, in the range of high power densities, this hypothesis does not have a physical meaning above a critical value $I_{Ec} = \text{Im}(\varepsilon_{p0})/\text{Im}(\chi_p^{(3)})$, where the imaginary part of the dielectric constant becomes negative and that breaks the causality principle.

The most noticeable feature of curve $c$ in figure 2(b), corresponding to prolate spheroids, is the large bistability interval, as can be seen in the corresponding curve of figure 2(a) owing to the low value of $\langle \varepsilon \rangle^{(\prime\prime)}$ in the linear regime (see equations (46) and (57)).

Figures 2(c) and (d) represent the evolutions of the effective refraction index versus the power density for composites with a metallic particle concentration $f = 0.1$. In the case in figure 2(c), there are several differences from figure 2(a). It can be seen that $\text{Re}(n)$ decreases with increasing applied power for curves $a$ and $b$ until a minimum is reached at values of $I_0$ ranging from 1 to 10. This behaviour is opposed to that observed when $f = 0.01$ and is somehow surprising because the common behaviour of a homogeneous nonlinear material is to increase the index of refraction continuously with increasing applied power. At this concentration, the loops due to bistability disappear in the calculations based on assuming spherical metallic particles, and only a small domain of bistability remains in curve $a$ around $I_0 = 2$. Furthermore, curves $c$ look very similar in figures 2(a) and (c). This suggests that, in order to obtain a large bistability domain, better results will be obtained with metallic particles of an elongated ellipsoidal geometry.

It is clear that the bistability range may change notably depending on several features of the composites (particle shape, concentration, imaginary part of the nonlinear susceptibility, etc). Following the arguments given in section 2.4, we now want to illustrate a simple method, based on the graphic representation of function $F(x)$, which makes it possible to determine the domain of bistability of a composite. Although some parts of the discussion below refer to high dilution conditions ($f \ll 1$), the basic principles, namely equations (38) and (39), are totally general and can be used to determine the domain of bistability graphically. On the other hand, the conclusions obtained, that is the widest bistability range in the case of minimum values of $\varepsilon_{p0}$ and/or $\tan \phi_p < 0$ and no possible bistability when $\chi_p^{(3)\prime\prime} > 0$, can be qualitatively applied for composites with high metal concentrations.

Curves $a$–$c$ in figures 3 and 4 give the functions $F(x)$ corresponding to the power curves plotted in figures 2(a) to (d). It can be seen that, in the case of high dilution $f = 0.01$ (figure 3), the curves present the aspect of narrow Lorentzians, especially in the case of cylindrical-like particles (curve $c$). In this case, the height of its $F(x)$ curve is not very large, a fact that indicates that large values of density
power are required to obtain a bistability behaviour. For higher concentrations $f = 0.1$ (figure 4), only curve $c$ preserves a Lorentzian-like aspect. In curves $a$ and $b$, the dependence (through $\varepsilon_p$) of the effective dielectric constant with $x$ notably broadens and introduces asymmetry into $F(x)$. However, under these conditions, the graphical criterion showed in figure 1 is still valid and can be used to investigate the optical properties of these composites.
We have seen that the nonlinear properties of composite materials may be notably different from those of their individual components. This can be evaluated by a study of the dependence of the effective value of the nonlinear optical susceptibility, previously defined in equation (24), versus the external applied power. In a nonlinear homogeneous material (neglecting the high-power terms) \(\langle \chi^{(3)} \rangle\) is power density independent by definition. However, this fact is not satisfied in a heterogeneous material owing to the interaction of different types of materials through the effective medium approximation. Figure 5(a) represents the evolution of \(S = |\langle \chi^{(3)} \rangle/\chi^{(3)}_p|\) as a function of the power density for the six previously considered nanocomposites in figure 2. The magnitude \(S\) is indeed proportional to the four-wave-mixing signal [28]. Most of the curves in figure 5(a) present three different regions. In the linear regime, which corresponds to low power densities, \(\langle \chi^{(3)} \rangle\) appears to be constant in a wide range of values of \(I_0\). Once the power density reaches a critical value, a very large increase in the effective nonlinear optical susceptibility appears; this is associated in several cases with bistability. Finally, when the power further increases, \(\langle \chi^{(3)} \rangle\) tends to zero following a \(I_0^1\) power law. This behaviour is similar to that of liquid crystals [14] the nonlinear response of which saturates at a certain power density. However, in a realistic case, the nonlinear part of the matrix susceptibility can no longer be neglected. Thus, at very high power densities, it is expected that \(\langle \chi^{(3)} \rangle\) will take values close to \(\chi^{(3)}_m\).

Another noticeable effect is that, as the concentration \(f\) of embedded particles increases, there is a shift in \(S\) towards higher power densities (see figure 5(a)). Moreover, the observed bistable behaviour for the case of embedded particles of ellipsoidal shape at \(f = 0.1\) (curve \(c\)) remains similar to that at \(f = 0.01\) (curve \(c\)) although shifted towards higher density powers.

We have plotted in figure 5(b) a comparison between the values of \(S\) from the low-field low-\(f\) approach [35] (dotted curve \(a\)) given by equation (25) where \(\varepsilon_{p0}\) has been substituted by \(\varepsilon_p\) (equation (6) with \(\varepsilon = \varepsilon_m\)), the values of \(S\) obtained following the high dilution \((f \ll 1)\) Maxwell-Garnett approximation (broken curve \(b\)) [2] and the values of \(S\) derived from equations (13), (19) and (24) of the present nonlinear EMT (solid curve \(c\)) valid for any value of the filling factor and of the applied electric field. The Maxwell-Garnett \(S\) values are derived when substituting \(\varepsilon\) by \(\varepsilon_m\) in equations (6) and (13), and solving afterwards the cubic equation (14). Figure 5(b) shows that, when \(f = 0.001\) and \(I_0 \rightarrow 0\), \(S\) becomes nearly power independent and almost the same for the three considered cases in curves \(a-c\). At higher values of \(I_0\), our theory (curve \(c\)) and the Maxwell-Garnett approach (curve \(b\)) are, as expected, nearly identical; however, the low-field low-\(f\) approximation (curve \(a\)) overestimates the values of \(S\) given by curves \(b\) and \(c\) except at very high \(I_0\) where all of them converge to zero since at such high powers \(\langle \chi^{(3)} \rangle\) tends to \(\chi^{(3)}_m = 0\) (the matrix Al\(_2\)O\(_3\) is a linear material). When \(f = 0.1\), both the Maxwell-Garnett values of \(S\) (curve \(b\)) and the low-field low-\(f\) estimation of \(S\) (curve \(a\)) fail to follow the present theory even at low powers. In the range of \(I_0\) between 0.7 and 20, the approximations in curves \(a\) and \(b\) overestimate the present theory by one to more than two orders of magnitude. Therefore, as can be seen from figure 5(b), the Maxwell-Garnett and the low-field low-\(f\) approximations are only valid for \(f = 0.001\) while at \(f = 0.1\) they fail to reproduce the values of \(S\) obtained from our theory. Moreover, figure 5(b) shows that, in general, curves \(a\) and \(b\) overestimate the interval of powers where bistability can exist.
One of the advantages of using a strong nonlinear approximation is the fact that optical bistability can be accurately found at arbitrary wavelengths other than the linear plasmon wavelength. In this sense, we have estimated the range of bistability of Cu–Al2O3 nanocomposites from equations (38)–(39) as shown in figure 6. It has been assumed that \( L_m = \frac{1}{3} \) and \( \tan \phi_m = 0 \), and we have checked the bistability of the composite as a function of the concentration \( f \) and depolarization factor \( L_p \) of the Cu nanoparticles at four different wavelengths (590, 610, 650 and 800 nm). The lines in figure 6 represent the boundary, at a definite wavelength, between the bistability and non-bistability regimes, the upper part being the bistability domain. As an example, at 800 nm, bistability is predicted for \( L_p = 0.4 \) and \( f = 0.5 \) while it is not expected for \( L_p = 0.3 \) and \( f = 0.15 \). As a general conclusion one can conclude that, the larger \( L_p \), the easier it is to find bistability in a metal–insulator composite.

It is worth pointing out that outside the plasmon frequency the low-concentration approximations give acceptable values of optical variables in the quasistatic approximation even at concentration \( f \ll 0.1 \). In fact, it is usually accepted that for this range of concentrations the average dielectric constant is nearly linear with \( f \) [8, 10, 19]. However, in the case of a plasmon resonance, the second order of the \( f \)-power expansion of \( \langle \varepsilon \rangle \) diverges. This implies that, in a
realistic insulator–metal composite, the low-concentration approximations are valid only in a very small range of \( f \) values.

In the following we have studied the dependence of the index of refraction dispersion relationship, \( n(\lambda) \), on different values of the power density. Because optical ellipsometry is a relatively widespread experimental technique for determining \( n(\lambda) \), any possible dependence of this magnitude on the power density could be easily checked. In figure 7, we have plotted a series of spectra \( \text{Im}[n(\lambda)] \) for several values of the applied power density. For the considered case, the concentration of spherical metal (Cu) particles was very low \( (f = 0.01) \), and the optical nonlinear susceptibility of the metal was assumed to be purely real \( (\chi^{(3)}_\rho = \chi^{(3)}_p) \).

The matrix (Al\(_2\)O\(_3\)) was assumed to be a linear material composed of spherical particles. The adimensional applied power density \( I_0 = I_E\chi^{(3)}_p \) ranged from \( 10^{-3} \) to \( 10^2 \). All represented curves in figure 7 show a clear maximum corresponding to the SPR. For low values of \( I_0 \), such a maximum is centred around 590 nm as is usually observed [29, 30] in Cu–Al\(_2\)O\(_3\) composites. However, when the applied power exceeds a critical value, which in this case is \( I_0 = 0.1 \), the SPR shifts towards higher wavelengths. The dependence of the SPR wavelength on the applied power density \( I_0 \) appears in the inset of figure 7. In addition, the position of the SPR peak reaches its maximum value at \( \lambda = 650 \text{ nm} \), which coincides with the minimum value of \( \text{Im}(\varepsilon_\rho) \).

In figure 8, we have represented the same spectra as in figure 7, but assuming a metallic particle concentration \( f = 0.1 \), that is ten times that in the former case. The most marked difference from the spectra shown in figure 7 is the large broadening of the SPR peaks. This is commonly found in composites with a high absorbing component content [34]. Moreover, for the same power densities as used in figure 7, the SPR peak is shifted about 50 nm towards higher wavelengths.
Figure 7. Imaginary part (Im(\(\eta\))) of the index of refraction as a function of the wavelength \(\lambda\) for \(f = 0.01\), \(L_p = L_m = \frac{1}{3}\), \(\tan \phi_p = \chi_p^{(3)}/\chi_p^{(3)} = 0\) and different values of \(I_0\) ranging from \(10^{-3}\) to \(10^2\). The inset represents the SPR wavelength of the metal as a function of the applied power density.

Figure 8. The same as figure 7 but for \(f = 0.1\).
Finally, we have included, in figure 9, two spectra calculated in the case of cylindrical-like ($L_p = 1$) metallic particles with $f = 0.1$. In the linear case ($I_0 = 0$), the SPR appears as a shoulder around 550 nm. However, when the applied power is as high as $I_0 = 10$, the calculated spectrum presents a SPR at 570 nm and the spectrum exhibits a bistability regime between 610 and 750 nm.

4. Conclusions

The present study can be useful to determine the optimum experimental conditions for observing bistable behaviour in composite materials with at least one nonlinear component, although the present approach can also be applied to composites with two or more components presenting nonlinear optical behaviour.

We have shown that, as opposed to what happens in homogeneous nonlinear materials, the effective third order nonlinear optical susceptibility of composites with one nonlinear component exhibit a clear dependence with the applied power density. Moreover, we also found that the SPR wavelength depends on the applied power density and that, at high power densities, the composite has a bistability response.

The present approach can also be employed for evaluating effective dielectric magnitudes (index of refraction, electrical conductivity, reflectance and absorbance) in a range of parameters where conventional EMT approaches fail owing to the importance of the nonlinear effects. Therefore, the results presented in this work can be used as a useful tool for the design of new optical switching devices.

Figure 9. The same as figure 7 but for $f = 0.1$ and $L_p = 1$ and for two representative values of the applied power density: curve $a$, $I_0 = 10^{-3}$; curve $b$, $I_0 = 10$. 
based on the enhanced nonlinear optical response of nanocomposites such as Cu–Al₂O₃, Cu–SiO₂, Au–SiO₂ or Au–TiO₂.

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