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Order and disorder in the microstructure of dielectrically nonlinear heterogeneous materials

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ABSTRACT

The paper deals with the electrical characterisation of dispersions of pseudo-oriented ellipsoids of revolution. We are thus dealing with mixtures of inclusions of arbitrary eccentricity and arbitrary non-random orientational distributions. The analysis ranges from parallel spheroidal inclusions to completely random oriented inclusions. A unified theory covers all the orientational distributions between the random and parallel cases. Each ellipsoidal inclusion is made from an isotropic nonlinear dielectric material described by means of the so-called Kerr nonlinear relation.

The electrical averaging inside the composite material is carried out by means of explicit results. We obtain closed form expressions for the macroscopic or equivalent dielectric properties of the overall composite materials. This study affirms that the nonlinear electrical behaviour of such a dispersion of pseudo-oriented particles is completely defined by two specific order parameters, which depends on the given angular distribution. The theory may be applied to characterise media with different shapes of the inclusions (i.e. spheres, cylinders or planar inhomogeneities) yielding a set of procedures describing several composite materials of great technological interest.

1. Introduction

In recent years, the characterisation of heterogeneous materials has attracted ever increasing interest. One central problem is the evaluation of the effective electric properties governing composite materials behaviour on the macroscopic scale. At present, it is well known that no universally applicable mixing formula exists that can give the effective properties of the heterogeneous materials as an average of the constituent properties. In fact, the details of the micro-geometry can play a crucial role in determining the overall properties, particularly when the crystalline grains have highly anisotropic behaviour. In the latter case there is a large difference in the properties of the constituent materials and nonlinearities cannot be neglected. Therefore, the elastic and electrical properties of composite materials are strongly microstructure dependent. The relationship between microstructure and properties may be used for designing and improving materials, or conversely, for interpreting experimental data in terms of micro-structural features. Ideally, the aim is to construct a theory that employs general micro-structural information to make accurate property predictions. Many theoretical formulas have been proposed to describe the behaviour of composite materials. A disadvantage of some approximated results is that they do not correspond to *a priori* known microstructure; these results may be interpreted and classified only by means of comparison with numerical or experimental data. A different class of theories is rigorously based on realistic microstructures. These are the classical Hashin–Shtrikman variational bounds [1,2], which provide an upper and lower bound for composite materials, and the expansions of Brown [3] and Torquato [4,5] which take into account the spatial correlation function of the phases.

Dispersions or suspensions of inclusions in a homogeneous matrix provide one example of heterogeneous materials. One of the first attempts to characterise electrical dispersions of spheres is that of Maxwell [6], who determined a famous formula for a strongly diluted suspension of spheres. A better model has been provided by the differential scheme, which derives from the mixture characterisation approach used by Bruggeman [7] and extensively described by Van Beek [8]. In this case, the relations are also valid for less diluted suspensions of spheres. To understand the effect of different shape of the inclusions, ellipsoidal shaped particles have been considered. The first attempt was made by Fricke [9,10]. In the current literature, Maxwell's relation for linear spheres [6,8], and Fricke's expressions for linear ellipsoids [9,10]

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belong to the so-called Maxwell–Garnett Effective Medium Theory [11,12]. Both cases are derived under the hypothesis of very low concentration of the linear dispersed component. A complete review of the Bruggeman (differential) theory for ellipsoidal inclusions can be found in Ref. [13].

In recent developments in material science, considerable attention has been devoted to electromagnetically nonlinear composite structures which find applications, for instance, in integrated optical devices such as optical switching and signal processing devices [14–16]. Intrinsic optical bistability has been extensively studied theoretically as well as experimentally with the help of mixture theory [17,18]. In all of these cases, a linear medium containing spherical or spheroidal inclusions has been considered. Recent progress in this field can be ascribed to Goncharenko et al. [19], who dealt with dielectrically linear and nonlinear spheroidal inclusions of geometric factors distributed probabilistically. Lakhtakia et al. studied size-dependent Bruggeman theory which considers the effective particle dimension for non dilute dispersions [20]. A wide survey of mixture theory applications has been made by Mackay [21] who analyzed the peculiar properties exhibited by metamaterials. Important results concerning dispersions of dielectrically nonlinear and graded parallel cylinders have been achieved by Wei et al. [22]. Our aim in this context is to extend previous work and to explore the importance of the orientational distribution and of the inclusion shape. To do so, we consider a dispersion of dielectrically nonlinear spheroidal particles (ellipsoids of revolution), pseudo-randomly oriented in a (dielectrically) linear matrix. We then develop a mathematical procedure to perform the needed averages of the electric quantities overall the possible orientations of the inclusions. This analysis leads to a nonlinear anisotropic constitutive equation connecting the macroscopic electric displacement to the macroscopic electric field. Particular attention is devoted to the analysis of the effects of the orientational distribution of the particles inside the composite material. The limiting cases of the present theory are represented by all the particles aligned with a given direction (perfect order) and all the particles randomly oriented (complete disorder). We take into account all the intermediate configurations between order and disorder with the aim of characterizing a material having its particles partially aligned. Fig. 1 shows some orientational distributions between the limiting cases described. To define the geometry, we consider an orthonormal reference frame, and we take the z-axis as the preferential direction of alignment. Each particle embedded in the matrix is not completely random in orientation. The orientation is described by the following statistical rule. The principal axis of each particle forms an angle ϑ with the z-axis. This angle follows a given probability density $f_\Theta(\vartheta)$ symmetrically distributed over 0–π. The symmetry of the density can be written as $f_\Theta(\vartheta) = f_\Theta(\pi - \vartheta)$. We assume that the orientation of each particle is statistically independent from the orientation of the other particles. If $f_\Theta(\vartheta) = (1/2)(\delta(\vartheta) + \delta(\vartheta - \pi))$ (where δ is the Dirac delta function) we have all the particles with $\vartheta = 0$ (or $\vartheta = \pi$, which corresponds to the same orientation) and, therefore all are oriented along the z-axis. If $f_\Theta(\vartheta) = \sin(\vartheta)/2$, then all the particles are in uniform random orientation in the space overall possible orientations. Any other symmetric statistical distribution $f_\Theta(\vartheta)$ defines a transversely isotropic (uniaxial) material with principal axis aligned with the z-axis. For example, if $f_\Theta(\vartheta) = \delta(\vartheta - \pi/2)$, then all the particles have their principal axes orthogonal to the z-axis. In the following sections, we develop a complete analysis of the combined effects of the shape (aspect ratio or eccentricity) of the particles and their state of order/disorder. This analysis allows us to evaluate the overall electric properties of the heterogeneous material. From the point of view of particle shape, the so-called depolarization factor L is the parameter that intervenes to characterise the medium. We verify that the state of order acts on the overall linear and nonlinear dielectric properties by means of two parameters defined as $C_2 = \langle\cos^2\vartheta\rangle$ and $C_4 = \langle\cos^4\vartheta\rangle$. These parameters correspond to the average values of $\cos^2\vartheta$ and $\cos^4\vartheta$, respectively, as computed by means of the density probability $f_\Theta(\vartheta)$. The results may be applied to describe the physical behaviour of heterogeneous materials starting from the knowledge of the physical properties of each medium composing the mixture, as well as of the structural properties of the mixture itself [i.e. shape of the inclusions and state of order of the orientations (L, C_2 and C_4)]. The results of this work have been derived under the electrostatic ($d/dt = 0$) assumption, but they also are valid in the low-frequency regime, as long as the wavelength parameter c/f is much larger than the largest dimension of the inclusions. The analysis performed in this work has immediate application to the field of liquid crystals. Our microstructure describes a material positionally disordered, but with partial orientational order which corresponds to a nematic phase in liquid crystals [23,24]. The level of ordering is reflected in the macroscopic properties. Some previous works have been developed in a way similar to this work but only from a dielectrically linear point of view [25–28]. The present work can therefore be considered a nonlinear extension of these previous papers.

2. Field perturbation due to single nonlinear ellipsoidal inclusions in a uniform field

Here we present a general solution to the problem of a nonlinear ellipsoidal particle embedded in a linear material. The theory is based on the following result derived for the linear case, which describes the behaviour of one electrically linear ellipsoidal particle of permittivity ε_2 in a linear homogeneous medium of

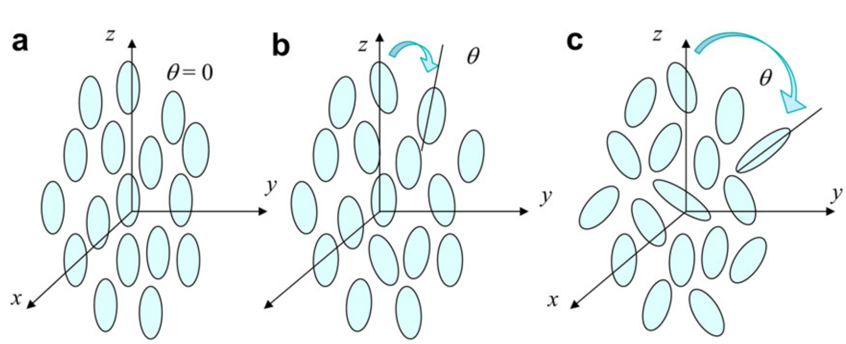

Fig. 1. Structure of a dispersion of pseudo-oriented ellipsoids. One can find some orientational distributions ranging from order to disorder. The two-phase material is described by the electric response of each phase, by the state of order and by the volume fraction of the inclusions.

permittivity ε_1. Let the axes of the ellipsoid be l_x, l_y and l_z (aligned with axes x, y, z of the ellipsoid reference frame), and let a uniform electric field $\vec{E}_0 = (E_{0x}, E_{0y}, E_{0z})$ be applied to the structure. Then, according to Stratton [29], the electric field $\vec{E}_s = (E_{sx}, E_{sy}, E_{sz})$ inside the ellipsoid is uniform and it can be expressed as follows:

$$E_{si} = \frac{E_{0i}}{1 + L_i(\varepsilon_2/\varepsilon_1 - 1)} \tag{1}$$

Here, and throughout the paper, the index i represents the x, y and z values. The expressions for the depolarization factors L_i in the case of a generally shaped ellipsoid can be found in the literature [13]. They can be expressed in terms of elliptic integrals. The condition $L_x + L_y + L_z = 1$ is always fulfilled.

Let's now generalize Eq. (1) to the case where a dielectrically nonlinear ellipsoid is embedded in the linear matrix. A nonlinear isotropic and homogeneous ellipsoid can be described from the electrical point of view by the constitutive equation $\vec{D} = \varepsilon(E)\vec{E}$ [30]. Here, $\vec{D}$ is the electric displacement inside the particle, $\vec{E}$ is the electric field and the function ε depends only on the modulus E of $\vec{E}$. This latter property accounts for the fact that the medium inside the ellipsoid is isotropic and homogeneous. The main result follows. The electric field inside the inclusion is uniform even in the nonlinear case and it may be calculated by means of the following system of equations:

$$E_{si} = \frac{E_{0i}}{1 + L_i[\varepsilon(E_s)/\varepsilon_1 - 1]}, \forall i \tag{2}$$

where, as before, $\vec{E}_0$ is a uniform electric field applied to the structure and $\vec{E}_s$, the unknown in the nonlinear system Eq. (2), is a uniform field as well. This property holds true for the following reason. If a solution to Eq. (2) exists, due to self-consistency, all the boundary conditions are fulfilled and the problem is completely analogous to its linear counterpart, treated by Stratton [29], provided that $\varepsilon_2 = \varepsilon(E_s)$.

In order to simplify the following analysis we will adopt ellipsoids of revolution. Thus we consider $l_x = l_y$ and we define the aspect ratio as $e = l_z/l_x = l_z/l_y$. The depolarization factors for ellipsoids of revolution may be computed in closed form as follows, and the results depend on the shape of the ellipsoid [13]. It is prolate (of ovary or elongated form) if $e > 1$ and oblate (of planetary or flattened form) if $e < 1$:

$$\begin{cases} L_x = L_y = \dfrac{e}{2}\displaystyle\int_0^{+\infty} \frac{d\xi}{(\xi+1)^2(\xi+e^2)^{1/2}} = \begin{cases} \dfrac{e}{4p^3}\left[2ep + \ln\dfrac{e-p}{e+p}\right] & \text{if} \quad e > 1 \\ \dfrac{e}{4q^3}\left[\pi - 2eq - 2\arctan\dfrac{e}{q}\right] & \text{if} \quad e < 1 \end{cases} \\ L_z = \dfrac{e}{2}\displaystyle\int_0^{+\infty} \frac{d\xi}{(\xi+1)(\xi+e^2)^{3/2}} = \begin{cases} \dfrac{1}{2p^3}\left[e\ln\dfrac{e+p}{e-p} - 2p\right] & \text{if} \quad e > 1 \\ \dfrac{1}{2q^3}\left[2q - e\pi + 2e\arctan\dfrac{e}{q}\right] & \text{if} \quad e < 1 \end{cases} \\ \text{where} \quad p = \sqrt{e^2 - 1} \quad \text{and} \quad q = \sqrt{1 - e^2} \end{cases} \tag{3}$$

The relation $2L_x + L_z = 1$ holds, and therefore we will consider $L = L_z$ as the main geometric parameter of the system. An interesting, related aspect shows up when one tries to solve the nonlinear Eq. (2) iteratively [31]. In order to solve for E_s, one starts with a given initial value E_s^0, and one uses the successive approximations described by the iteration rule:

$$E_{si}^{n+1} = \frac{E_{0i}}{1 + L_i\left[\varepsilon(\|\vec{E}_s^n\|)/\varepsilon_1 - 1\right]} \tag{4}$$

The following sufficient convergence criterion has been verified [31]. The iteration rule given by Eq. (4) is convergent to the exact internal electric field if the nonlinear material of the ellipsoid fulfils the condition $|(E/\varepsilon)\partial\varepsilon/\partial E| < 1$. In general, one can describe isotropic nonlinear dielectric materials by means of the so-called Kerr nonlinearity relation, often adopted in metamaterials study [21]:

$$\varepsilon(E) = \varepsilon_2 + \alpha E^2 \tag{5}$$

which assumes that ε_2 and α are constant. The Kerr nonlinearity can be *focusing* or *defocusing*, depending on whether $\alpha > 0$ or $\alpha < 0$ [32]. The convergence condition $|(E/\varepsilon)\partial\varepsilon/\partial E| < 1$ is always verified for a *defocusing* Kerr nonlinearity and is verified only if $E_s^2 < \varepsilon_2/\alpha$ (here E_s is the modulus of the actual electric field inside the inclusion) in case of a *focusing* nonlinearity [31].

3. Average electric field inside a single pseudo-random oriented inclusion

Now, our aim is to find an explicit version of Eq. (2), which is valid when the nonlinear permittivity is given by Eq. (5). To begin the analysis, we substitute Eq. (5), for the case of a single ellipsoid, in Eq. (2):

$$E_{si} = \frac{\varepsilon_1 E_{0i}}{\varepsilon_1 + L_i\left[\varepsilon_2 - \varepsilon_1 + \alpha\left(E_{sx}^2 + E_{sy}^2 + E_{sz}^2\right)\right]} \tag{6}$$

This is an algebraic system of degree nine with three unknowns, namely E_{sx}, E_{sy} and E_{sz} It might be hard, if not impossible, to solve analytically, but we are interested in just the first terms of a series expansion of the solution. To obtain it, we may adopt the *ansatz* $E_{si} = k_i E_{0i} + h_i E_{0i}^3$ and solve for k_i and h_i. Alternatively, we may use the iterative scheme given by Eq. (4), in literal form, adopting only the first iterations. For sake of brevity, we omit here the simple but long calculation, which leads to the solution:

$$E_{si} = \frac{\varepsilon_1 E_{0i}}{(1-L_i)\varepsilon_1 + L_i\varepsilon_2} - \frac{\alpha\varepsilon_1^3 L_i E_{0i}}{[(1-L_i)\varepsilon_1 + L_i\varepsilon_2]^2}\sum_j \frac{E_{0j}^2}{[(1-L_j)\varepsilon_1 + L_j\varepsilon_2]^2} + O\left(\left\|\vec{E}_0\right\|^4\right) \tag{7}$$

We observe that the first term represents the classic Lorentz field appearing in a dielectrically linear ellipsoidal inclusion. The second term is the first nonlinear contribution, which is directly proportional to the inclusion hyper-susceptibility α. To simplify the expressions, we henceforth use the notation $a_i = (1-L_i)\varepsilon_1 + L_i\varepsilon_2$. To derive the mixture behaviour, we need to calculate the electric field in a single nonlinear ellipsoidal inclusion that is arbitrarily oriented in space and embedded in a homogeneous medium having permittivity ε_1. In order to do this, we shall express Eq. (7) in the global framework of reference of the mixture. We define three unit vectors, indicating the principal directions of each ellipsoid in space: $\hat{n}_x, \hat{n}_y$ and $\hat{n}_z$. These correspond to the axes of the ellipsoid. By using Eq. (7), we may compute the electric field induced by a given external arbitrary uniform electric field inside the inclusion (henceforth we omit the additional higher-order terms):

$$\vec{E}_s = \left[\frac{\varepsilon_1 \vec{E}_0\cdot\hat{n}_i}{a_i} - \frac{\alpha\varepsilon_1^3 L_i \vec{E}_0\cdot\hat{n}_i}{a_i^2}\frac{\left(\vec{E}_0\cdot\hat{n}_j\right)\left(\vec{E}_0\cdot\hat{n}_j\right)}{a_j^2}\right]\hat{n}_i \tag{8}$$

We shall now average the above Eq. (8) overall the possible orientations of the particle. The expression for the internal electric field in Eq. (8) can be rewritten, component by component, as follows:

$$E_{sk} = \left[\frac{\varepsilon_1 E_{0l} n_{il}}{a_i} - \frac{\alpha\varepsilon_1^3 L_i E_{0l} n_{il}}{a_i^2}\frac{E_{0q} n_{jq} E_{0p} n_{jp}}{a_j^2}\right] n_{ik} \tag{9}$$

Here n_{jk} is the k-th component of the unit vector $\hat{n}_j$, $(j = x, y, z)$ and we have considered the implicit sums of i, j, l, q and p over 1, 2 and 3. For the following derivation, we are interested in the average value of the electric field $\vec{E}_s$ overall the possible orientations of the ellipsoid itself. We must then compute the following:

$$\langle E_{sk}\rangle = \frac{\varepsilon_1 E_{0l}\langle n_{il} n_{ik}\rangle}{a_i} - \frac{\alpha\varepsilon_1^3 L_i E_{0l} E_{0q} E_{0p}\langle n_{ik} n_{il} n_{jq} n_{jp}\rangle}{a_i^2 a_j^2} \tag{10}$$

We may use Euler angles representation $(\psi, \varphi$ and $\vartheta)$ to write down the explicit expressions for the components of the unit vectors $\hat{n}_x, \hat{n}_y$ and $\hat{n}_z$:

$$\begin{cases} \hat{n}_x = (\cos\psi\cos\varphi - \sin\psi\sin\varphi\cos\vartheta, -\cos\psi\sin\varphi - \sin\psi\cos\varphi\cos\vartheta, \sin\psi\sin\vartheta) \\ \hat{n}_y = (\sin\psi\cos\varphi + \cos\psi\sin\varphi\cos\vartheta, -\sin\psi\sin\varphi + \cos\psi\cos\varphi\cos\vartheta, -\cos\psi\sin\vartheta) \\ \hat{n}_z = (\sin\varphi\sin\vartheta, \sin\vartheta\cos\varphi, \cos\vartheta) \end{cases} \tag{11}$$

In order to obtain the average value of the electric field $\vec{E}_s$, we need to calculate the average value of the quantities defined in Eq. (10). This is done by the following integral over the Euler angles:

$$\langle E_{sk}\rangle = \frac{1}{4\pi^2}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi}\left[\frac{\varepsilon_1 E_{0l} n_{il} n_{ik}}{a_i} - \frac{\alpha\varepsilon_1^3 L_i E_{0l} E_{0q} E_{0p} n_{ik} n_{il} n_{jq} n_{jp}}{a_i^2 a_j^2}\right] \times \mathrm{d}\varphi\mathrm{d}\psi f_\Theta(\vartheta)\mathrm{d}\vartheta \tag{12}$$

In order to represent the above described orientation of the particles, the angles φ and ψ are uniformly distributed over the entire range $[0\ 2\pi]$ and the angle ϑ follows the given probability density $f_\Theta(\vartheta)$ over the range $[0\ \pi]$. So, by performing the integration described in Eq. (12) and by using Eq. (11), we find that the average value of E_{sk} depends on the two following parameters, defined by means of the density probability $f_\Theta(\vartheta)$:

$$C_2 = \int_0^{\pi}\cos^2\vartheta f_\Theta(\vartheta)\mathrm{d}\vartheta \tag{13}$$

$$C_4 = \int_0^{\pi}\cos^4\vartheta f_\Theta(\vartheta)\mathrm{d}\vartheta \tag{14}$$

These two parameters completely characterise the effects of the pseudo-orientation of the particles inside the medium. Some particular values follow. For the case of perfect order we have $f_\Theta(\vartheta) = (1/2)(\delta(\vartheta) + \delta(\vartheta - \pi))$ and the corresponding values are $C_2 = 1$ and $C_4 = 1$. Alternatively, for the case of complete disorder we have $f_\Theta(\vartheta) = \sin(\vartheta)/2$ and we obtain $C_2 = 1/3$ and $C_4 = 1/5$. Finally, when all the particles have their principal axes orthogonal to the z-axis, we have $f_\Theta(\vartheta) = \delta(\vartheta - \pi/2)$ and the values of the parameters are $C_2 = 0$ and $C_4 = 0$.

Because we are dealing with ellipsoids of revolution, in performing the integration of Eq. (12) we use the simplified notation $a_1 = a_2$ and $L_1 = L_2 = (1-L)/2$, $L_3 = L$. The factor L assumes some characteristic values that correspond to special shapes of the particles. For spheres $L = 1/3$; for cylinders $L = 0$; and for lamellae or penny shaped inclusions, $L = 1$. Summing up, we verified, after a very long but straightforward integration, that the following simple relation gives the final result of the averaging process:

$$\langle E_{sk}\rangle = \gamma_k E_{0k} - \alpha\mu_{kl} E_{0k} E_{0l}^2 \tag{15}$$

Here, summation on the index l is implied, and the parameters γ_k and μ_{kl} can be organized as follows:

$$\gamma = \begin{bmatrix}\gamma_1\\ \gamma_1\\ \gamma_3\end{bmatrix}; \mu = \begin{bmatrix}\mu_{11} & \mu_{11} & \mu_{13}\\ \mu_{11} & \mu_{11} & \mu_{13}\\ \mu_{31} & \mu_{31} & \mu_{33}\end{bmatrix} \tag{16}$$

The explicit results for the parameters γ_k are:

$$\gamma_1 = \frac{1}{2}\varepsilon_1\frac{a_1 + a_3}{a_1 a_3} + \frac{1}{2}\varepsilon_1\frac{a_3 - a_1}{a_1 a_3}C_2 \tag{17}$$

$$\gamma_3 = \varepsilon_1\frac{1}{a_1} + \varepsilon_1\frac{a_1 - a_3}{a_1 a_3}C_2 \tag{18}$$

Moreover, the explicit results for the parameters μ_{kl} are:

$$\begin{aligned}\mu_{11} = \frac{\varepsilon_1^3}{16 a_1^4 a_3^4}\Big\{ & a_1^2 a_3^2(1+L) + 3a_3^4(1-L) + 6La_1^4 \\ & + C_2\left[2a_1^2 a_3^2(1+L) + 2a_3^4(1-L) - 12La_1^4\right] \\ & + C_4\left[6La_1^4 - 3a_1^2 a_3^2(1+L) + 3a_3^4(1-L)\right]\Big\}\end{aligned} \tag{19}$$

$$\begin{aligned}\mu_{13} = \frac{\varepsilon_1^3}{16 a_1^4 a_3^4}\Big\{ & 8La_1^2 a_3^2 + 4a_3^4(1-L) + C_2\left[8a_3^4(1-L) + 24La_1^4\right. \\ & \left. - 4a_1^2 a_3^2(1+7L)\right] + C_4\left[12a_1^2 a_3^2(1+L) - 12a_3^4(1-L) - 24La_1^4\right]\Big\}\end{aligned} \tag{20}$$

$$\mu_{31}=\frac{\varepsilon_1^3}{4a_1^4a_3^4}\left\{a_1^2a_3^2(1-L)+a_3^4(1-L)+C_2\left[2a_3^4(1-L)+6La_1^4+2a_1^2a_3^2(L-2)\right]+C_4\left[3a_1^2a_3^2(1+L)-3a_3^4(1-L)-6La_1^4\right]\right\} \quad (21)$$

$$\mu_{33}=\frac{\varepsilon_1^3}{4a_1^4a_3^4}\left\{2a_3^4(1-L)+C_2\left[2a_1^2a_3^2(1+L)-4a_3^4(1-L)\right]+C_4\left[2a_3^4(1-L)-2a_1^2a_3^2(1+L)+4La_1^4\right]\right\} \quad (22)$$

This is a first analytical result which will play a crucial role in the theoretical development that follows. It is interesting to observe that if $a_1=a_3$ and $L=1/3$ (we are dealing with spherical inclusions), then the terms containing C_2 and C_4 completely disappear in Eqs. (17)–(22), as they must, because the orientation is not important for an isotropic spherical object.

4. Averaging process in a dilute mixture

From this point on, we analyse the dispersion of pseudo-oriented nonlinear ellipsoids. The permittivity of the inclusions is described by the isotropic nonlinear relation $\varepsilon(E)=\varepsilon_2+\alpha E^2$ [see Eq. (5)] and the linear matrix has permittivity ε_1. The overall electrical behaviour of the dispersion is expected to be anisotropic because of the pseudo random orientation of the particles. This is true because the z-axis has a special character induced by the partial alignment of the particles. Therefore, the equivalent electric constitutive equation can be expanded in series with respect to the averaged electric field components: $\langle D_k\rangle=\varepsilon_{kj}^{eq}\langle E_j\rangle+\chi_{kjil}^{eq}\langle E_j\rangle\langle E_i\rangle\langle E_l\rangle+\ldots$, where the coefficients $\varepsilon^{\mathrm{eq}}$ (the subscript eq denoting the *equivalent* character of the term) and χ^{eq} are tensors that depend on various parameters of the mixture such as the aspect ratio e of the ellipsoids, the volume fraction c of the included phase, the density probability $f_\Theta(\vartheta)$ describing the orientational distribution, the permittivities ε_1, ε_2 and the Kerr susceptibility α of the inclusions. The homogenisation procedure should provide the structure of the entries of the tensors $\varepsilon^{\mathrm{eq}}$ and χ^{eq} in terms of the mentioned parameters. In the technical literature, the coefficients α and χ^{eq} (the first nonlinear terms of the expanded constitutive equations for inclusions and mixture, respectively) are often called hyper-susceptibilities [21].

The main achievement of this work is the derivation of a closed form expression for the hyper-susceptibility ratio $\chi^{\mathrm{eq}}/\alpha$. These quantities are of interest inasmuch as they represent the amplification of the nonlinear behaviour of the composite material with respect to that of the inclusions. In particular, we are interested in the dependence of these parameters on the state of order/disorder of the system which is well described by the density probability$f_\Theta(\vartheta)$. In other words, we may write our results in terms of the order parameters C_2 and C_4. Moreover, we may describe the dependence of the hyper-susceptibility ratio $\chi^{\mathrm{eq}}/\alpha$ on the aspect ratio of the embedded particles, i.e. on the parameter e or L. The final expressions are derived under the assumption that the constitutive equation of the composite medium is of the form $\langle D_k\rangle=\varepsilon_{kj}^{eq}\langle E_j\rangle+\chi_{kjil}^{eq}\langle E_j\rangle\langle E_i\rangle\langle E_l\rangle$, which neglects higher-order terms. All the computations are carried out under the same hypothesis underlying the linear Maxwell–Garnett theory [12], that is, low concentration c of the dispersed phase. If we consider a mixture with a volume fraction $c\ll 1$ of pseudo-randomly oriented, dielectrically nonlinear ellipsoids embedded in a homogeneous matrix with permittivity ε_1, we thus can evaluate the average of the electric field over the space occupied by the mixture. It can be achieved via the following relationship:

$$\langle\vec{E}\rangle=c\langle\vec{E}_s\rangle+(1-c)\vec{E}_0 \quad (23)$$

This means that we do not take into account the interactions among the inclusions because of the very low concentration, i.e. each ellipsoid behaves as an isolated one. Once again, to derive Eq. (23), we assume an approximately uniform average electric field $\vec{E}_0$ in the space outside the inclusions. To evaluate the equivalent constitutive equation, we compute the average value of the displacement vector inside the random material. The region V is defined as the space occupied by the mixture, V_e as the region occupied by the inclusions, and V_o as the remaining space (so that $V=V_e\cup V_o$). The average value of $\vec{D}(\vec{r})=\varepsilon\vec{E}(\vec{r})$ is evaluated as follows ($\vec{D}$ and $\vec{E}$ represent the local fields, $\langle\vec{D}\rangle$ and $\langle\vec{E}\rangle$ their macroscopic counterparts):

$$\begin{aligned}\langle\vec{D}\rangle&=\frac{1}{|V|}\int_V\varepsilon\vec{E}(\vec{r})\mathrm{d}\vec{r}=\frac{1}{|V|}\varepsilon_1\int_{V_o}\vec{E}(\vec{r})\mathrm{d}\vec{r}+\frac{1}{|V|}\int_{V_e}\varepsilon\vec{E}(\vec{r})\mathrm{d}\vec{r}\\&=\frac{1}{|V|}\varepsilon_1\int_{V_o}\vec{E}(\vec{r})\mathrm{d}\vec{r}+\frac{1}{|V|}\varepsilon_1\int_{V_e}\vec{E}(\vec{r})\mathrm{d}\vec{r}\\&\quad+\frac{1}{|V|}\frac{|V_e|}{|V_e|}\int_{V_e}(\varepsilon-\varepsilon_1)\vec{E}(\vec{r})\mathrm{d}\vec{r}=\varepsilon_1\langle\vec{E}\rangle+c\langle[\varepsilon(E_s)-\varepsilon_1]\vec{E}_s\rangle\end{aligned} \quad (24)$$

Here $|V|$ is the measure of the region V. We note that the average value given by $\langle[\varepsilon(\|\vec{E}_s\|)-\varepsilon_1]\vec{E}_s\rangle$ is not available from the previous computations. We consider a single ellipsoidal nonlinear inclusion, and we search for the average value of the quantity $[\varepsilon(\|\vec{E}_s\|)-\varepsilon_1]\vec{E}_s$ overall the possible orientations of the particle. From Eq. (2) and Eq. (7) we obtain:

$$[\varepsilon(\|\vec{E}_s\|)-\varepsilon_1]E_{si}=\frac{\varepsilon_1}{L_i}(E_{0i}-E_{si})=\frac{\varepsilon_1}{L_i}\left[E_{0i}-\frac{\varepsilon_1E_{0i}}{a_i}+\frac{\alpha\varepsilon_1^3L_iE_{0i}}{a_i^2}\sum_j\frac{E_{0j}^2}{a_j^2}\right] \quad (25)$$

therefore, in vector notation:

$$[\varepsilon(\|\vec{E}_s\|)-\varepsilon_1]\vec{E}_s=\frac{\varepsilon_1}{L_i}\left[\vec{E}_0\cdot\hat{n}_i-\frac{\varepsilon_1\vec{E}_0\cdot\hat{n}_i}{a_i}+\frac{\alpha\varepsilon_1^3L_i\vec{E}_0\cdot\hat{n}_i}{a_i^2}\frac{\left(\vec{E}_0\cdot\hat{n}_j\right)\left(\vec{E}_0\cdot\hat{n}_j\right)}{a_j^2}\right]\hat{n}_i \quad (26)$$

By taking the k-th component in the global reference framework, we may write:

$$[\varepsilon(\|\vec{E}_s\|)-\varepsilon_1]E_{sk}=\frac{\varepsilon_1}{L_i}\left[E_{0l}n_{il}-\frac{\varepsilon_1E_{0l}n_{il}}{a_i}+\frac{\alpha\varepsilon_1^3L_iE_{0l}n_{il}}{a_i^2}\frac{E_{0q}n_{jq}E_{0p}n_{jp}}{a_j^2}\right]n_{ik} \quad (27)$$

and averaging, after some straightforward computation:

$$\langle D_{sk}-\varepsilon_1E_{sk}\rangle=\frac{\varepsilon_1(\varepsilon_2-\varepsilon_1)}{a_i}E_{0l}\langle n_{il}n_{ik}\rangle+\frac{\alpha\varepsilon_1^4E_{0l}}{a_i^2}\frac{E_{0q}E_{0p}}{a_j^2}\langle n_{il}n_{ik}n_{jq}n_{jp}\rangle \quad (28)$$

At this point, the explicit average value can be found by taking into consideration the expressions of the unit vectors $\hat{n}_x,\hat{n}_y$ and $\hat{n}_z$, given in Eq. (11), and performing the integration in a similar way to that shown in Eq. (12). The effects of the pseudo-orientation of the particles inside the medium are described, as before, by the order parameters C_2 and C_4. In performing the averaging in Eq. (28), we

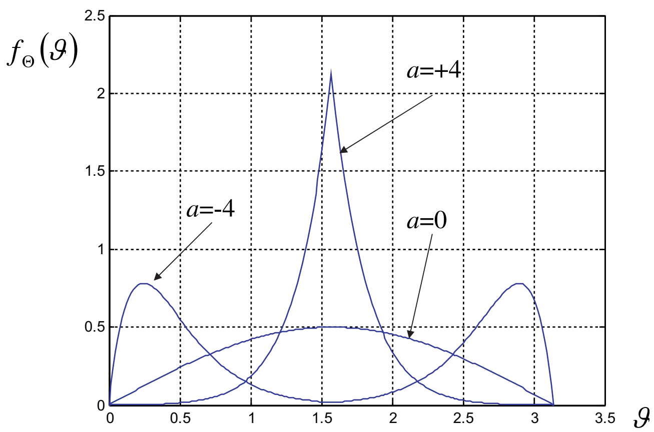

Fig. 2. Shape of the probability density defined in Eq. (40) in correspondence to three different values of the parameter a ($a=-4$, $a=0$ and $a=4$).

have again used the simplified notation $a_1 = a_2$ and $L_1 = L_2 = (1-L)/2$, $L_3 = L$. The final result for the quantity $\langle D_{sk} - \varepsilon_1 E_{sk}\rangle$ is therefore given by the following simple relation:

$$\langle D_{sk} - \varepsilon_1 E_{sk}\rangle = (\varepsilon_2 - \varepsilon_1)\gamma_k E_{0k} + \alpha\lambda_{kl} E_{0k} E_{0l}^2 \tag{29}$$

Here the sum over the index l is implied, and the parameters γ_k have been defined in Eqs. (16)–(18). Moreover, the parameters λ_{kl} can be arranged following the matrix notation:

$$\lambda = \begin{bmatrix} \lambda_{11} & \lambda_{11} & \lambda_{13} \\ \lambda_{11} & \lambda_{11} & \lambda_{13} \\ \lambda_{13} & \lambda_{13} & \lambda_{33} \end{bmatrix} \tag{30}$$

The explicit values of the relative entries have been calculated as follows:

$$\begin{aligned}\lambda_{11} = \frac{\varepsilon_1^4}{8a_1^4a_3^4}\Big\{&3a_1^4 + 2a_1^2a_2^3 + 3a_3^4 + C_2\left[4a_1^2a_3^2 + 2a_3^4 - 6a_1^4\right] \\ &+ C_4\left[3a_1^4 - 6a_1^2a_3^2 + 3a_3^4\right]\Big\}\end{aligned} \tag{31}$$

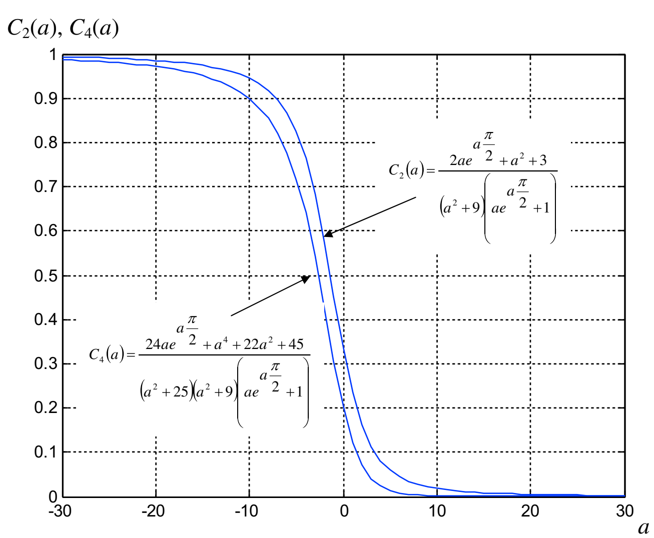

Fig. 3. Order parameters C_2 and C_4 versus the parameter a defining the probability density represented in Eq. (40) and plotted in Fig. 2.

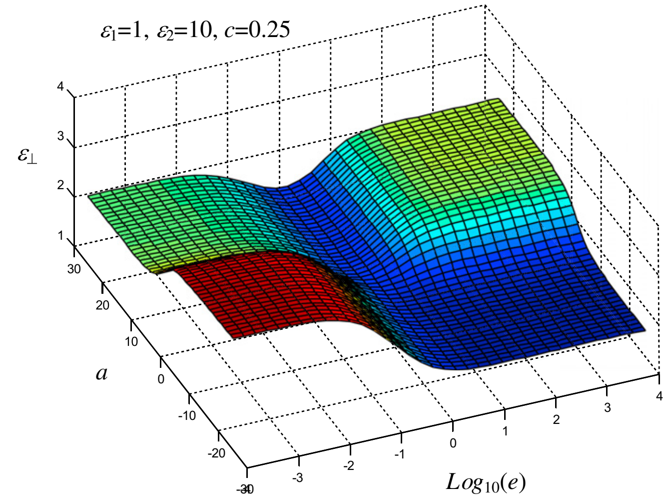

Fig. 4. Permittivity $\varepsilon_\perp$ versus a and $\mathrm{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 10$ and $c = 0.25$.

$$\begin{aligned}\lambda_{13} = \frac{\varepsilon_1^4}{8a_1^4a_3^4}\Big\{&4a_1^2a_3^2 + 4a_3^4 + C_2\left[8a_3^4 + 12a_1^4 - 20a_1^2a_3^2\right] \\ &+ C_4\left[24a_1^2a_3^2 - 12a_3^4 - 12a_1^4\right]\Big\}\end{aligned} \tag{32}$$

$$\lambda_{33} = \frac{\varepsilon_1^4}{2a_1^4a_3^4}\Big\{2a_3^4 + C_2\left[4a_1^2a_3^2 - 4a_3^4\right] + C_4\left[2a_3^4 + 2a_1^4 - 4a_1^2a_3^2\right]\Big\} \tag{33}$$

Once again, we observe that if $a_1 = a_3$ (we are dealing with spherical inclusions), then the terms containing C_2 and C_4 completely disappear in Eqs. (31)–(33), i.e. the orientation is not relevant for an isotropic spherical object. At this point, we have all the balance equations needed to describe the overall electrical behaviour of the pseudo-random dispersion. These relationships are summarised in Eq. (34). The first relation corresponds to Eq. (23) and yields the average electric field over the mixture volume in terms of the applied field and the average internal field (equation deduced under the hypothesis of low concentration). The second

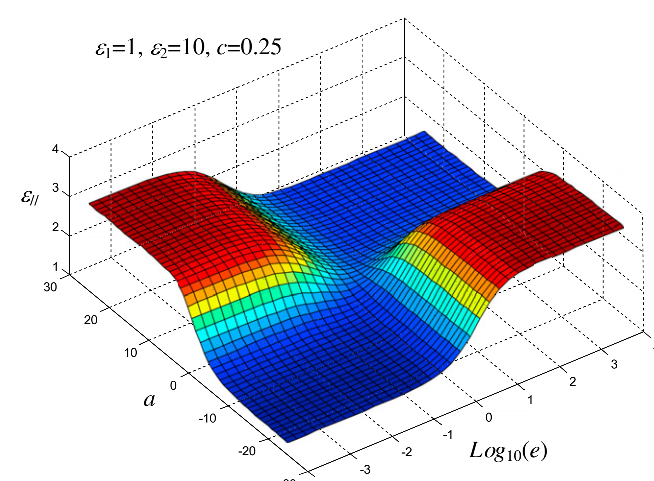

Fig. 5. Permittivity $\varepsilon_{//}$ versus a and $\mathrm{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 10$ and $c = 0.25$.

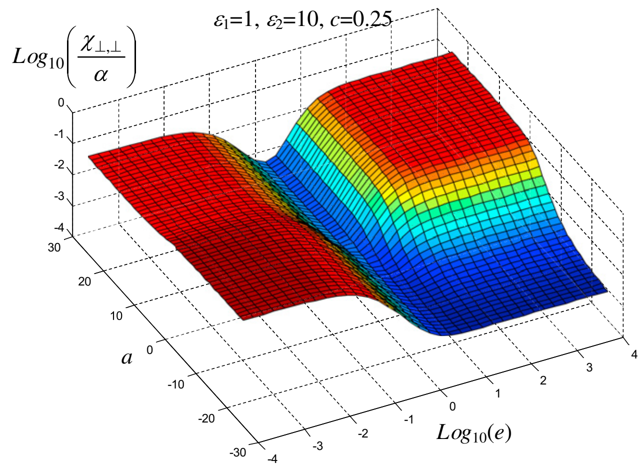

Fig. 6. Susceptibility amplification $\mathrm{Log}_{10}(\chi_{\perp,\perp}/\alpha)$ versus a and $\mathrm{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 10$ and $c = 0.25$.

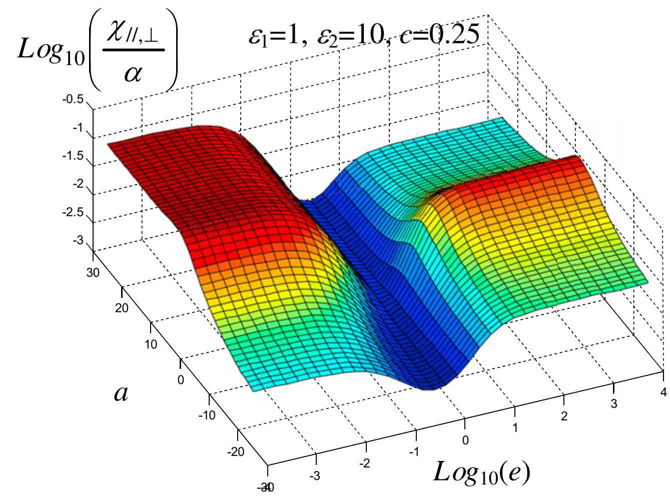

Fig. 8. Susceptibility amplification $\mathrm{Log}_{10}(\chi_{//,\perp}/\alpha)$ versus a and $\mathrm{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 10$ and $c = 0.25$.

relation is taken from Eq. (15) and gives the explicit value of the average electric field inside an inclusion. It accounts for just the first nonlinear terms. The third relation [see Eq. (24)] furnishes the average value of the displacement vector over the entire mixture volume (this formula is exact). Finally, the fourth equation is taken from Eq. (29) and gives the average value of the quantity $\langle D_{sk} - \varepsilon_1 E_{sk}\rangle$ in terms of the applied electric field (as before, it accounts just for the first nonlinear terms). The complete set of the balance equations follows:

$$\begin{cases} \langle E_k\rangle = c\langle E_{sk}\rangle + (1-c)E_{0k} \\ \langle E_{sk}\rangle = \gamma_k E_{0k} - \alpha\mu_{kl}E_{0k}E_{0l}^2 \\ \langle D_k\rangle = \varepsilon_1\langle E_k\rangle + c\langle D_{sk} - \varepsilon_1 E_{sk}\rangle \\ \langle D_{sk} - \varepsilon_1 E_{sk}\rangle = (\varepsilon_2 - \varepsilon_1)\gamma_k E_{0k} + \alpha\lambda_{kl}E_{0k}E_{0l}^2 \end{cases} \tag{34}$$

We may observe that the nonlinear terms, appearing in the second and in the fourth relations in Eq. (34), are simply proportional to the hyper-susceptibility parameter α of the inclusions. By substituting the second equation into the first, and the fourth relation in the third, we obtain a simpler system:

$$\begin{cases} \langle E_k\rangle = (1-c+c\gamma_k)E_{0k} - c\alpha\mu_{kl}E_{0k}E_{0l}^2 \\ \langle D_k\rangle = \varepsilon_1\langle E_k\rangle + c(\varepsilon_2-\varepsilon_1)\gamma_k E_{0k} + c\alpha\lambda_{kl}E_{0k}E_{0l}^2 \end{cases} \tag{35}$$

We have here three vector fields: the average electric field over the entire mixture, the average electric displacement, and the externally applied electric field. In order to determine the effective constitutive equation for the entire composite material, we should obtain a relationship among the components $\langle D_k\rangle$ and the components $\langle E_h\rangle$. We therefore have to eliminate the external field E_{0k} in Eq. (35). We thus need to solve the first relation in Eq. (35) with respect to E_{0k}. For our purposes, it is sufficient to obtain a series solution with two terms, and therefore we let $E_{0k} = g_k\langle E_k\rangle + m_{kl}\langle E_k\rangle\langle E_l\rangle^2$. We substitute the latter into the first relation in Eq. (35), and we solve for the unknown coefficients g_k and m_{kl}. The result is:

$$E_{0k} = \frac{\langle E_k\rangle}{1-c+c\gamma_k} + \frac{c\alpha\mu_{kl}\langle E_k\rangle\langle E_l\rangle^2}{(1-c+c\gamma_k)^2(1-c+c\gamma_l)^2} \tag{36}$$

The final achievement is obtained by substituting Eq. (36) in the second equation of system (35) and neglecting the powers of $\langle E_k\rangle$ greater than three:

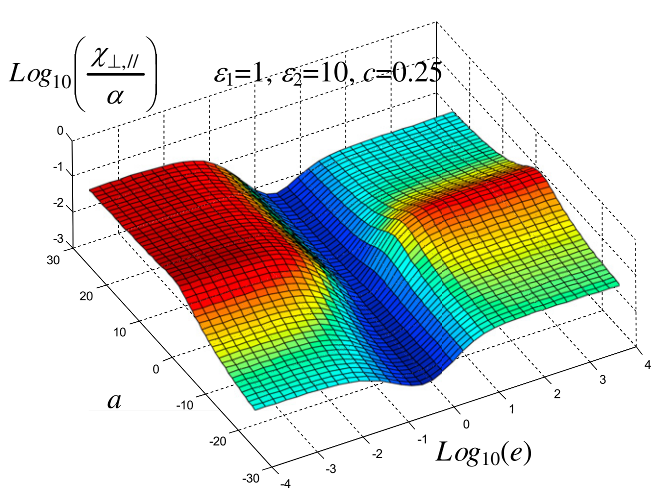

Fig. 7. Susceptibility amplification $\mathrm{Log}_{10}(\chi_{\perp,//}/\alpha)$ versus a and $\mathrm{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 10$ and $c = 0.25$.

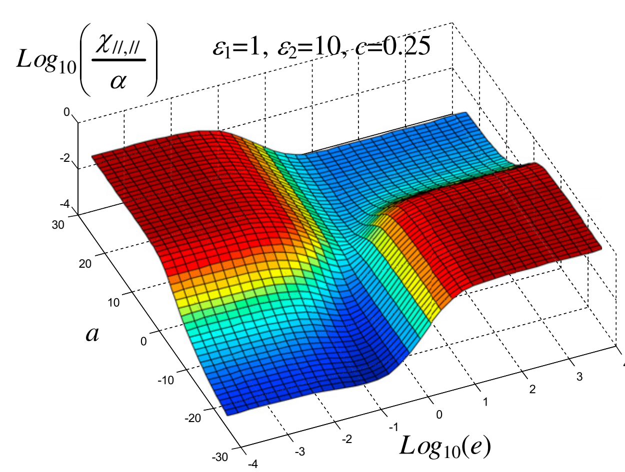

Fig. 9. Susceptibility amplification $\mathrm{Log}_{10}(\chi_{//,//}/\alpha)$ versus a and $Log_{10}\,(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 10$ and $c = 0.25$.

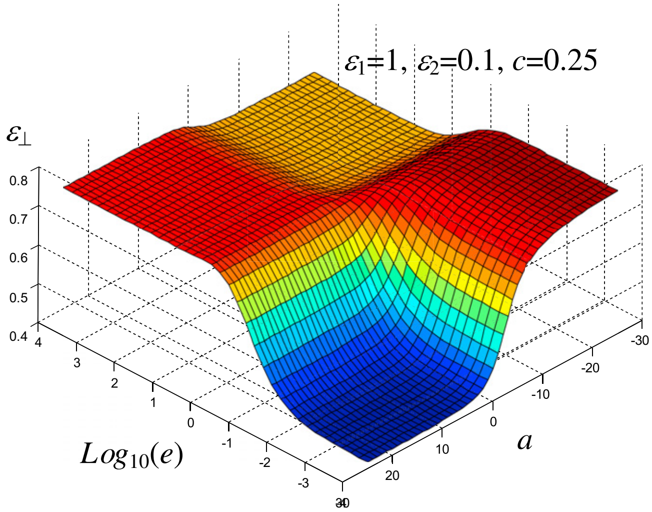

Fig. 10. Permittivity $\varepsilon_\perp$ versus a and $\text{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 0.1$ and $c = 0.25$.

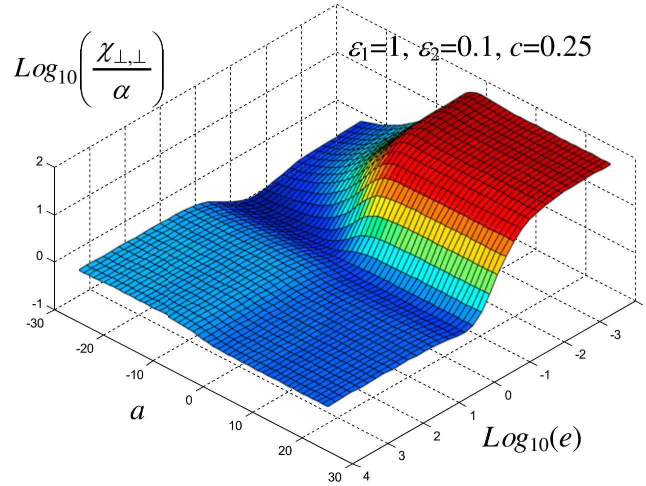

Fig. 12. Susceptibility amplification $\text{Log}_{10}(\chi_{\perp,\perp}/\alpha)$ versus a and $\text{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 0.1$ and $c = 0.25$.

$$\begin{aligned}\langle D_k \rangle &= \left[\varepsilon_1 + c(\varepsilon_2 - \varepsilon_1)\frac{\gamma_k}{1 - c + c\gamma_k}\right]\langle E_k \rangle \\ &\quad + \left[\alpha \frac{c^2(\varepsilon_2 - \varepsilon_1)\gamma_k \mu_{kl} + c\lambda_{kl}(1 - c + c\gamma_k)}{(1 - c + c\gamma_k)^2(1 - c + c\gamma_l)^2}\right]\langle E_k \rangle \langle E_l \rangle^2 \quad (37)\end{aligned}$$

Eq. (37) provides the first form of the constitutive equation of the overall dispersion. This result can be further simplified by defining the following quantities, which better describe the transversely isotropic (uniaxial) character of the composite material: $E_\perp^2 = \langle E_1 \rangle^2 + \langle E_2 \rangle^2, E_{//} = \langle E_3 \rangle, D_\perp^2 = \langle D_1 \rangle^2 + \langle D_2 \rangle^2$ and$D_{//} = \langle D_3 \rangle$. The symbol // indicates the components aligned with the principal axis (the z-axis) and the symbol $\perp$ indicates the components orthogonal to the principal axis. With such conventions, Eq. (37) may be rearranged as follows:

$$\begin{cases} D_\perp = E_\perp\left[\varepsilon_\perp + \chi_{\perp,\perp}E_\perp^2 + \chi_{\perp,//}E_{//}^2\right] \\ D_{//} = E_{//}\left[\varepsilon_{//} + \chi_{//,\perp}E_\perp^2 + \chi_{//,//}E_{//}^2\right] \end{cases} \quad (38)$$

The linear permittivities $\varepsilon_\perp$ and $\varepsilon_{//}$and the nonlinear hyper-susceptibilities $\chi_{\perp,\perp}$,$\chi_{\perp,//}$,$\chi_{//,\perp}$ and $\chi_{//,//}$ can be derived by comparing them with Eq. (37), and the relative explicit expressions are given below:

$$\begin{cases} \varepsilon_\perp = \varepsilon_1 + c(\varepsilon_2 - \varepsilon_1)\frac{\gamma_1}{1-c+c\gamma_1} \\ \varepsilon_{//} = \varepsilon_1 + c(\varepsilon_2 - \varepsilon_1)\frac{\gamma_3}{1-c+c\gamma_3} \end{cases} \begin{cases} \chi_{\perp,\perp} = \alpha\frac{c^2(\varepsilon_2-\varepsilon_1)\gamma_1\mu_{11}+c\lambda_{11}(1-c+c\gamma_1)}{(1-c+c\gamma_1)^4} \\ \chi_{\perp,//} = \alpha\frac{c^2(\varepsilon_2-\varepsilon_1)\gamma_1\mu_{13}+c\lambda_{13}(1-c+c\gamma_1)}{(1-c+c\gamma_1)^2(1-c+c\gamma_3)^2} \\ \chi_{//,\perp} = \alpha\frac{c^2(\varepsilon_2-\varepsilon_1)\gamma_3\mu_{31}+c\lambda_{13}(1-c+c\gamma_3)}{(1-c+c\gamma_1)^2(1-c+c\gamma_3)^2} \\ \chi_{//,//} = \alpha\frac{c^2(\varepsilon_2-\varepsilon_1)\gamma_3\mu_{33}+c\lambda_{33}(1-c+c\gamma_3)}{(1-c+c\gamma_3)^4} \end{cases} \quad (39)$$

All these quantities are the main parameters describing the nonlinear electrical behaviour of the overall dispersion. We may observe that the nonlinear susceptibilities $\chi_{\perp,\perp}$,$\chi_{\perp,//}$,$\chi_{//,\perp}$ and $\chi_{//,//}$ are proportional to the susceptibility α of the inclusions and depend on the factors γ_k, μ_{kl} and λ_{kl} defined in Eqs. (17)–(22) and Eqs. (31)–(33). Of note, and as expected, the results are explicitly written in terms of the depolarising factor $L_z = L$ of the inclusions, which depends directly on the aspect ratio e [see Eq. (3)], and in terms of the order parameters C_2 and C_4 that define the state of orientational

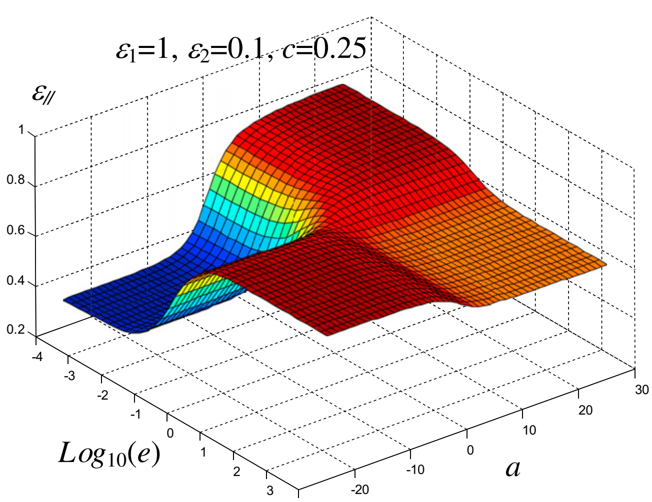

Fig. 11. Permittivity $\varepsilon_{//}$ versus a and $\text{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 0.1$ and $c = 0.25$.

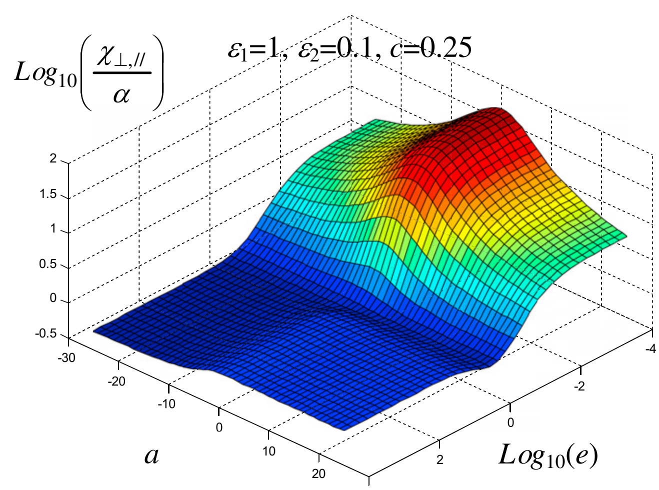

Fig. 13. Susceptibility amplification $\text{Log}_{10}(\chi_{\perp,//}/\alpha)$ versus a and $\text{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 0.1$ and $c = 0.25$.

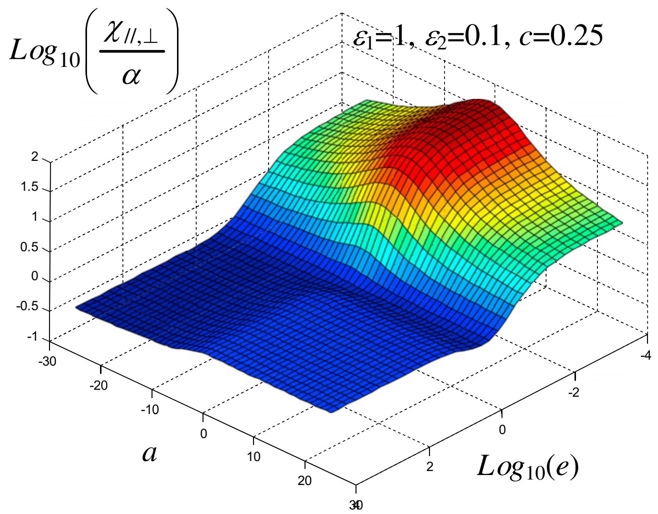

Fig. 14. Susceptibility amplification $\mathrm{Log}_{10}(\chi_{//,\perp}/\alpha)$ versus a and $\mathrm{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 0.1$ and $c = 0.25$.

order/disorder. The latter depends on the probability density $f_\Theta(\vartheta)$ (see Eqs. (13) and (14)). Finally, the particular cases of spherical inclusions ($a_1 = a_3$ and $L = 1/3$) and of ellipsoidal inclusions with isotropic distribution ($C_2 = 1/3$ and $C_4 = 1/5$) provide results in near perfect agreement with previous investigations [31].

5. Application example

In order to show some results of the previous procedure, we choose a particular probability density $f_\Theta(\vartheta)$ that depends on one parameter a. This probability density is particularly useful because, when the parameter a varies from $-\infty$ to $+\infty$, the orientational distribution of the inclusions assumes many interesting possibilities. More precisely, when $a \to -\infty$, we have the case of perfect order, and all the particles are aligned with the z-axis. When $a = 0$, we have the case of complete disorder (all the particles uniformly random oriented in the space), and when $a \to +\infty$ all the inclusions have their principal axes orthogonal to the z-axis. The expression of the normalised probability density over the range $[0, \pi]$ becomes:

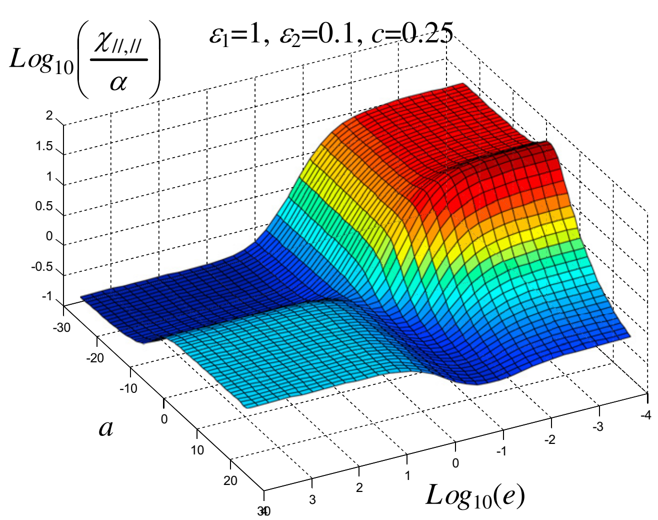

Fig. 15. Susceptibility amplification $\mathrm{Log}_{10}(\chi_{//,//}/\alpha)$ versus a and $\mathrm{Log}_{10}(e)$ for $\varepsilon_1 = 1$, $\varepsilon_2 = 0.1$ and $c = 0.25$.

$$f_\Theta(\vartheta) = \begin{cases} \dfrac{1}{2}\sin(\vartheta)\dfrac{(a^2+1)e^{a\vartheta}}{ae^{a\frac{\pi}{2}}+1} & \text{if } 0 \le \vartheta \le \dfrac{\pi}{2} \\ \dfrac{1}{2}\sin(\vartheta)\dfrac{(a^2+1)e^{a(\pi-\vartheta)}}{ae^{a\frac{\pi}{2}}+1} & \text{if } \dfrac{\pi}{2} < \vartheta \le \pi \end{cases} \quad (40)$$

This function is symmetrical with respect to $\vartheta = \pi/2$. If $a \to -\infty$ one can verify that $f_\Theta(\vartheta) = (1/2)(\delta(\vartheta) + \delta(\vartheta - \pi))$, where δ is the Dirac delta function (perfect order). If $a = 0$, we obtain $f_\Theta(\vartheta) = \sin(\vartheta)/2$(complete disorder). Finally, if $a \to +\infty$, it is possible to show that $f_\Theta(\vartheta) = \delta(\vartheta - \pi/2)$, and all the particles have their principal axes orthogonal to the z-axis. In Fig. 2, one can find the shape of this probability density corresponding to three different values of the parameter a ($a = -4$, $a = 0$ and $a = 4$). For negative values of a, one can observe that we obtain a bimodal density: for $a = 0$ we obtain the sinusoidally shaped function $f_\Theta(\vartheta) = \sin(\vartheta)/2$, and for positive value of a, we obtain unimodal behaviour. This probability density is particularly useful, because it allows calculation of the order parameters C_2 and C_4 in closed form:

$$C_2(a) = \int_0^\pi \cos^2\vartheta f_\Theta(\vartheta)\mathrm{d}\vartheta = \frac{1}{2}\frac{(a^2+1)}{ae^{a\frac{\pi}{2}}+1}\int_0^\pi \cos^2\vartheta \sin(\vartheta)e^{a\vartheta}\mathrm{d}\vartheta = \frac{2ae^{a\frac{\pi}{2}}+a^2+3}{(a^2+9)\left(ae^{a\frac{\pi}{2}}+1\right)} \quad (41)$$

$$C_4(a) = \int_0^\pi \cos^4\vartheta f_\Theta(\vartheta)\mathrm{d}\vartheta = \frac{1}{2}\frac{(a^2+1)}{ae^{a\frac{\pi}{2}}+1}\int_0^\pi \cos^4\vartheta \sin(\vartheta)e^{a\vartheta}\mathrm{d}\vartheta = \frac{24ae^{a\frac{\pi}{2}}+a^4+22a^2+45}{(a^2+25)(a^2+9)\left(ae^{a\frac{\pi}{2}}+1\right)} \quad (42)$$

The previous expressions yield the following special values: if $a \to -\infty$, we obtain $C_2 = C_4 = 1$; if $a = 0$ we get $C_2 = 1/3$ and $C_4 = 1/5$ and, finally, if $a \to +\infty$ we obtain $C_2 = C_4 = 0$ (Fig. 3). We have written a software code that implements the complete procedure summed up in Eq. (39) in order to obtain the macroscopic linear and nonlinear features of the composite material in terms of the aspect ratio e of the ellipsoids and of the parameter a controlling the state of order, as described above. A first series of results concerns the case where $\varepsilon_1 = 1$, $\varepsilon_2 = 10$ and $c = 0.25$. These are plotted in Figs. 4–9 versus a and $\mathrm{Log}_{10}(e)$. Specifically, Fig. 4 shows the permittivity $\varepsilon_\perp$, Fig. 5 the permittivity $\varepsilon_{//}$, Fig. 6 the susceptibility amplification $\mathrm{Log}_{10}(\chi_{\perp,\perp}/\alpha)$, Fig. 7 the susceptibility amplification $\mathrm{Log}_{10}(\chi_{\perp,//}/\alpha)$, Fig. 8 the susceptibility amplification $\mathrm{Log}_{10}(\chi_{//,\perp}/\alpha)$ and, finally, Fig. 9 shows the susceptibility amplification $\mathrm{Log}_{10}(\chi_{//,//}/\alpha)$. A second series of results, concerning the case where $\varepsilon_1 = 1$, $\varepsilon_2 = 0.1$ and $c = 0.25$, can be found in Figs. 10–15. As before, these cases are represented in terms of a and $\mathrm{Log}_{10}(e)$ and we have adopted the same order for the plots. We may compare the results obtained when $\varepsilon_2/\varepsilon_1 = 10$ and the results obtained when $\varepsilon_2/\varepsilon_1 = 1/10$. In both cases, as for the longitudinal and transversal permittivities, we may observe that the effect of the order/disorder shows opposite behaviour for prolate and oblate particles. Moreover, the complex behaviour of the susceptibility amplifications is inverted as we move from the case with $\varepsilon_2/\varepsilon_1 = 10$ to the case with $\varepsilon_2/\varepsilon_1 = 1/10$. The plots exhibit a very complex scenario for the macroscopic properties of the nonlinear material, that is strongly dependent on the state of order and on the geometric features of the embedded ellipsoids of revolution (prolate or oblate).

6. Conclusions

In this work we have analysed the nonlinear dielectric effects of the orientational order/disorder of non-spherical particles in composite or heterogeneous materials. As result of this analysis, we have found the correct definition of two order parameters (C_2 and C_4) in such a way as to predict the macroscopic electric properties as function of the state of microscopic order. In particular, we have found new explicit relationships that allow us to calculate the linear permittivity tensor and the nonlinear susceptibility tensor in terms of the shape of the embedded particles and the order parameters. We have outlined and applied a complete procedure which takes into account any given orientational distribution of ellipsoids in the matrix. The theory can find many applications to real physical situations ranging from technological aspects of composite materials to optical characterisation of nematic liquid crystals and to tissue modelling in biophysics.

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