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Citation: J. Appl. Phys. 114, 164102 (2013); doi: 10.1063/1.4826616
View online: http://dx.doi.org/10.1063/1.4826616
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v114/i16
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JOURNAL OF APPLIED PHYSICS **114**, 164102 (2013)

Effective medium approximations for anisotropic composites with arbitrary component orientation

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(Received 14 September 2013; accepted 7 October 2013; published online 23 October 2013)

A Maxwell Garnett approximation (MGA) and a symmetric effective medium approximation (SEMA) are derived for anisotropic composites of host-inclusion and symmetric-grains morphologies, respectively, with ellipsoidal grains of arbitrary intrinsic, shape and orientation anisotropies. The effect of anisotropy on the effective dielectric tensor is illustrated in both cases. The MGA shows negative and non-monotonic off-diagonal elements for geometries where the host and inclusions are not mutually aligned. The SEMA leads to an anisotropy-dependent nonlinear behaviour of the conductivity as a function of volume fraction above a percolation threshold of conductor-insulator composites, in contrast to the well-known linear behaviour of the isotropic effective medium model. The percolation threshold obtained for composites of aligned ellipsoids is isotropic and independent of the ellipsoids aspect ratio. Thus, the common identification of the percolation threshold with the depolarization factors of the grains is unjustified and a description of anisotropic percolation requires explicit anisotropic geometric characteristics. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4826616]

I. INTRODUCTION

The Maxwell Garnett approximation[1] (MGA), also known as the Clausius-Mossotti approximation, and the Bruggeman symmetric effective medium approximation[2] (SEMA) are the most widely used methods for calculating the bulk dielectric properties of inhomogeneous materials.[3–8] The MGA is useful when one of the components can be considered as a host in which inclusions of the other components are embedded, whereas the SEMA is more appropriate to microgeometries where the grains of the various components are symmetrically distributed, with no clear matrix component. These approximations are based on an exact calculation of the field inside a single spherical or ellipsoidal inclusion embedded in a uniform host (the host component in the MGA, or the effective medium in the SEMA), and an approximate treatment of the dipole field induced in the host by the different inclusions, which results in a uniform field inside all the inclusions. The MGA estimates the macroscopic response of the composite by summing the average effect of this dipole field. In the SEMA, the effective medium properties are determined self-consistently by demanding that the average effect of the dipole field vanishes.[3,4] Both approximations have been extensively used for studying the properties of isotropic two-component mixtures, in which the components are isotropic materials with scalar dielectric coefficients and the components grains are assumed to be spherical. Simple generalizations have been formulated for isotropic mixtures including randomly oriented ellipsoidal grains, with dielectric coefficients that are either scalar or tensors with principal axes aligned with those of the ellipsoids.[5,9–11] Numerical studies of randomly oriented arbitrarily shaped inclusions in mixtures of isotropic components have also been analysed based on these generalizations.[12] Polycrystalline aggregates of a single anisotropic component, where the inhomogeneity arises from the random local dielectric tensor orientation throughout the system, have also been treated by a similar extension of the SEMA.[13,14] These generalizations consider mixtures in which the anisotropy is local and the grains are randomly oriented, thus leading to an isotropic composite.

Applications of the MGA and SEMA to macroscopically anisotropic composites are much less common. Most of them consider suspensions of parallel ellipsoids in an isotropic host and just apply three MGA expressions, one for each of the principal axes of the inclusions, with the corresponding depolarization factors, to calculate the three principal components of the effective dielectric tensor.[5,11] Such MGA expressions have also been applied to interpret results of numerical calculations of the depolarization factors of arbitrarily shaped inclusions.[15] SEMA versions of this approach abound in the literature[15–20] and are extensively used for comparison with experimental results, although they are obviously inconsistent since they ignore the anisotropy of the effective medium in parallel ellipsoid composites. More general versions of the MGA treat suspensions of spheres with anisotropic intrinsic dielectric tensors[21] and suspensions of ellipsoids of isotropic materials[22,23] with various orientation distributions in isotropic hosts. The macroscopic anisotropy in these cases is determined by the details of the orientation distributions. Rigorous bounds on the dielectric tensor of composites of arbitrarily oriented spheroids in an isotropic host have also been formulated, in terms of geometric n-point correlation functions.[24,25]

Studies of composites where the host component (in the MGA) or the effective medium (in the SEMA) is anisotropic, require a solution of the electrostatic problem of a spherical or ellipsoidal inclusion in a uniform anisotropic medium.

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This solution is relatively recent and not widely known, thus such treatments of anisotropic host composites are rare. Stroud[13] was the first to derive an implicit solution, based on a Green's function approach, for the effective conductivity tensor of materials consisting of crystallites of arbitrary shape and orientational symmetry. He applied this solution to derive the above mentioned SEMA result for an isotropic polycrystalline medium of anisotropic crystallites and a similar result for a polycrystalline metal in the presence of magnetic field. Diaz-Guilera and Tremblay[26] applied this formalism to uniaxial mixtures of parallel spheroids, with principal axes that coincide with the axes of their conductivity tensor, and an isotropic conductor. They first noted that when the composite itself is anisotropic, the SEMA leads to a system of coupled equations (two equations in the uniaxial case they considered) for the elements of the effective conductivity tensor. Lakhtakia *et al.*[27] used an alternative Green's function derivation to find the polarizability of a sphere, with a uniaxial dielectric tensor, embedded in an aligned uniaxial host, and applied it to obtain an MGA and an EMA for uniaxial composite media of such spheres. The EMA they obtained is essentially identical to that of Diaz-Guilera and Tremblay.[26] A different approach, based on a coordinate transformation that converts the anisotropic host into an isotropic one, was introduced by Sihvola.[28] It was used to explicitly solve the electrostatic problem of a sphere, or ellipsoid, in an anisotropic host and formulate an MGA for mixtures where such inclusions are aligned with the principal axes of the host.[5,28] The same transformation was used by Milton to find the effective dielectric tensor of assemblages of stretched confocal coated ellipsoids.[14]

In this paper, we use the coordinate transformation method to obtain general MGA and SEMA expressions for composites of anisotropic hosts and ellipsoidal inclusions with arbitrary intrinsic and orientation anisotropy. Such a general treatment of anisotropy is necessary for estimating the properties of a wide variety of novel composite materials, from columnar thin films[20] to metamaterials with liquid crystalline components[29] or components with indefinite permeability tensors.[30] We illustrate the effects of anisotropy on the effective dielectric tensor in both approximations. The rest of the paper is organized as follows: The solution of the electrostatic problem of an ellipsoid in a uniform anisotropic medium is revisited in Sec. II, and an explicit expression is derived for its polarizability at arbitrary orientation and intrinsic dielectric tensor. The MGA for suspensions of anisotropic inclusions in an anisotropic host is introduced in Sec. III, and a few specific examples are studied. In Sec. IV, we introduce the SEMA for anisotropic composites of ellipsoidal grains with general intrinsic and orientation anisotropy and apply it to study the properties of anisotropic percolating conductor-insulator mixtures. Finally, a brief conclusion is included in Sec. V.

II. AN ELLIPSOIDAL INCLUSION IN AN ANISOTROPIC HOST

Consider a parallel plate condenser whose plates are large enough so that edge effects can be neglected. The condenser is filled by a homogeneous anisotropic medium with a tensor dielectric constant

$$\tilde{\epsilon}_h = \begin{pmatrix} \epsilon_x & 0 & 0 \\ 0 & \epsilon_y & 0 \\ 0 & 0 & \epsilon_z \end{pmatrix}. \tag{1}$$

A single ellipsoidal inclusion, arbitrarily oriented relative to the principal axes of $\tilde{\epsilon}_h$, is embedded in this host. Its surface is described by the general expression

$$\mathbf{X}^{\mathbf{T}} R^T(\theta,\phi) A^{-1} R(\theta,\phi)\mathbf{X} = 1, \tag{2}$$

where $\mathbf{X} = (x,\ y,\ z)$, R is a rotation matrix defined by the angles θ and ϕ and

$$A = \begin{pmatrix} a^2 & 0 & 0 \\ 0 & b^2 & 0 \\ 0 & 0 & c^2 \end{pmatrix}$$

is the principal axes matrix of the ellipsoid. A voltage is applied between the condenser plates such that the volume averaged field in the system is E_0. The electrostatics of the problem is defined by the static Maxwell equation $\nabla \cdot \mathbf{D} = \nabla \cdot \left(\tilde{\epsilon}(r)E(r)\right) = 0$, which leads to

$$\begin{aligned} \nabla \cdot \left(\tilde{\epsilon}_h E(r)\right) = 0 \quad & \text{in the host} \\ \nabla \cdot \left(\tilde{\epsilon}_{in} E(r)\right) = 0 \quad & \text{in the inclusion,} \end{aligned} \tag{3}$$

where $\tilde{\epsilon}_{in}$ is the inclusion dielectric tensor. The solution of these equations for an isotropic host, where $\tilde{\epsilon}_h$ is a scalar and $\tilde{\epsilon}_{in}$ is an arbitrary dielectric tensor, is well-known.[31] The anisotropic host equations (3) can be transformed into equivalent equations with an isotropic host using the coordinate transformation[5,28]

$$(x,y,z) \to \left(\sqrt{\frac{\epsilon_z}{\epsilon_x}}x, \sqrt{\frac{\epsilon_z}{\epsilon_y}}y, z\right) = (x_t, y_t, z_t). \tag{4}$$

This leads to

$$\begin{aligned} \nabla_t \cdot \left(\epsilon_z E_t(r_t)\right) = 0 \quad & \text{in the host} \\ \nabla_t \cdot \left(\tilde{\epsilon}_{in,t} E_t(r_t)\right) = 0 \quad & \text{in the inclusion,} \end{aligned} \tag{5}$$

where $\nabla_t = \sqrt{\frac{\tilde{\epsilon}_h}{\epsilon_z}}\nabla$ is the gradient in the (x_t, y_t, z_t) coordinate system and

$$E_t = \sqrt{\frac{\tilde{\epsilon}_h}{\epsilon_z}}E \quad \text{and} \quad \tilde{\epsilon}_{in,t} = \epsilon_z \tilde{\epsilon}_h^{-\frac{1}{2}} \tilde{\epsilon}_{in} \tilde{\epsilon}_h^{-\frac{1}{2}} \tag{6}$$

are the electric field and the inclusion dielectric tensor in this system. The shape of the ellipsoid (2) is also transformed into

$$\mathbf{X}_t^T R^T(\theta_t,\phi_t) A_t^{-1} R(\theta_t,\phi_t)\mathbf{X}_t = 1, \tag{7}$$

where $\mathbf{X}_t = (x_t, y_t, z_t)$, the rotation angles θ_t and ϕ_t are generally different from θ and ϕ and

$$A_t = \begin{pmatrix} a_t^2 & 0 & 0 \\ 0 & b_t^2 & 0 \\ 0 & 0 & c_t^2 \end{pmatrix}$$

is the principal axes matrix of the transformed ellipsoid. In the simple case of parallel ellipsoidal inclusions aligned with the principal axes of $\tilde{\epsilon}_h$, $\theta = \phi = 0$, the transformed ellipsoid is also aligned in the same direction and its principal axes are $a_t = \sqrt{\frac{\epsilon_z}{\epsilon_x}}a$, $b_t = \sqrt{\frac{\epsilon_z}{\epsilon_y}}b$ and $c_t = c$. In general, the orientation of the transformed ellipsoid differs from the initial orientation and its principal axes have to be extracted directly from Eq. (7).

Following the coordinate transformation (4), we have in Eq. (5) an ellipsoid embedded in a homogeneous isotropic host with a dielectric constant ϵ_z. In this case, the electric field $E_{in,t}$ and the displacement field $D_{in,t} = \tilde{\epsilon}_{in,t}E_{in,t}$ inside the inclusion are uniform and satisfy the exact relation[31]

$$\epsilon_z E_{in,t} + \tilde{d}_t(D_{in,t} - \epsilon_z E_{in,t}) = \epsilon_z E_{0,t}, \tag{8}$$

where $\tilde{d}_t$ is the depolarization tensor of the transformed ellipsoid. The elements of $\tilde{d}_t$ in the directions of the ellipsoid principal axes are given by

$$d_\zeta = \frac{1}{2}a_t b_t c_t \int_0^\infty \frac{ds}{(s+\zeta^2)\sqrt{(s+a_t^2)(s+b_t^2)(s+c_t^2)}},$$

for $\zeta = a_t$, b_t and c_t. Substituting in Eq. (8), the transformed fields and inclusion dielectric tensor from Eq. (6), we find

$$E_{in} = \left[\tilde{\epsilon}_h + \tilde{\epsilon}_h^{\frac{1}{2}}\tilde{d}_t\tilde{\epsilon}_h^{-\frac{1}{2}}\tilde{\epsilon}_{in} - \tilde{\epsilon}_h^{\frac{1}{2}}\tilde{d}_t\tilde{\epsilon}_h^{\frac{1}{2}}\right]^{-1}\tilde{\epsilon}_h E_0 = \tilde{\kappa}E_0. \tag{9}$$

This relation between the uniform field E_{in} inside the ellipsoid and the applied field E_0 depends on $\tilde{d}_t$, the depolarization tensor of the *transformed* ellipsoid (7). The dipole moment of the inclusion is

$$p_{in} = V_{in}\frac{D_{in} - \tilde{\epsilon}_h E_{in}}{4\pi} = \frac{V_{in}}{4\pi}\tilde{\alpha}E_0, \tag{10}$$

where V_{in} is the volume of the ellipsoid and

$$\tilde{\alpha} = (\tilde{\epsilon}_{in} - \tilde{\epsilon}_h)\tilde{\kappa} \tag{11}$$

is its polarizability tensor. In cases where the inclusion is a sphere, or an ellipsoid aligned with the principal axes of $\tilde{\epsilon}_h$, $\tilde{d}_t$ and $\tilde{\epsilon}_h$ commute and Eq. (11) is reduced into

$$\tilde{\alpha} = (\tilde{\epsilon}_{in} - \tilde{\epsilon}_h)[\tilde{\epsilon}_h + \tilde{d}_t(\tilde{\epsilon}_{in} - \tilde{\epsilon}_h)]^{-1}\tilde{\epsilon}_h. \tag{12}$$

The solution for this specific case was previously obtained by Sihvola (Equation (5.92) in Ref. 5). If $\tilde{\epsilon}_h$ is reduced to a scalar then $\tilde{d}_t$ is replaced by the ordinary depolarization tensor of the inclusion, without the transformation (4). This leads to the well known result for an inclusion in an isotropic host.[31]

III. THE LOCAL FIELD AND THE MAXWELL GARNETT APPROXIMATION

Consider a medium containing a few ellipsoidal inclusions, randomly distributed in an anisotropic host, sufficiently far apart for their mutual interactions to be negligible. The volume averaged polarization in the medium is

$$\langle P\rangle = \frac{1}{V}\sum_{\{in\}} p_{in} = \frac{f}{4\pi}\langle\tilde{\alpha}\rangle_R E_0, \tag{13}$$

where f is the volume fraction of the inclusions and $\langle\rangle_R$ denotes an average over the orientations of the ellipsoidal inclusions and the dielectric tensors inside them. The bulk effective dielectric tensor can be defined by the ratio between the volume averaged displacement field $D_0 = \langle D\rangle$ and the volume averaged electric field E_0

$$D_0 = \tilde{\epsilon}_h E_0 + 4\pi\langle P\rangle = (\tilde{\epsilon}_h + f\langle\tilde{\alpha}\rangle_R)E_0 = \tilde{\epsilon}_e E_0. \tag{14}$$

The bulk effective dielectric tensor is therefore

$$\tilde{\epsilon}_e = \tilde{\epsilon}_h + f\langle\tilde{\alpha}\rangle_R. \tag{15}$$

This result, ignoring the interaction between the different inclusions, is usually called the dilute limit.

The electrostatic interaction between the inclusions is negligible only in mixtures where their volume fraction is very small. In all other cases, this interaction should be taken into account when calculating the dielectric properties of the system. This is most easily done in the MGA, where the average field acting on each inclusion is considered to be not the applied field E_0, but the well-known Lorentz local field.[3] Using this correction, the dipolar interaction between the inclusions is taken into account in an averaged way. A simple method to calculate this correction, usually referred to as the excluded volume approach, was proposed by Bragg and Pippard.[3,32] The average field acting on an inclusion, in a mixture that is not too dense, is the average field in the host medium E_{ex}. Substituting E_{ex} for E_0 in Eq. (9), we find that the field inside an inclusion satisfies the relation $E_{in} = \tilde{\kappa}E_{ex}$. The averaged field over the entire system, inside and outside the inclusions, must still be E_0. Therefore, the average fields in the host and in the inclusions satisfy the simple relation

$$f\langle E_{in}\rangle + (1-f)E_{ex} = E_0, \tag{16}$$

where the angular brackets denote a volume average inside the inclusions. Solving this relation for E_{ex} we find

$$E_{ex} = [(1-f)I + f\langle\tilde{\kappa}\rangle_R]^{-1}E_0, \tag{17}$$

where I is the 3×3 identity matrix. This result can again be used with Eq. (14) and $\langle P\rangle = \frac{f}{4\pi}\langle\tilde{\alpha}\rangle_R E_{ex}$ to calculate the volume averaged polarization and the bulk effective dielectric tensor

$$\tilde{\epsilon}_e = \tilde{\epsilon}_h + f\langle\tilde{\alpha}\rangle_R[(1-f)I + f\langle\tilde{\kappa}\rangle_R]^{-1}. \tag{18}$$

This is the MGA result for mixtures of anisotropic inclusions in an anisotropic host. It is valid for any orientation distribution of the ellipsoids and the dielectric tensor inside them relative to the dielectric tensor of the host. If the dielectric tensor of the inclusions and their geometric principal axes are aligned with the principal dielectric axes of the host, then $\tilde{\epsilon}_{in}$, $\tilde{d}_t$ and $\tilde{\epsilon}_h$ all commute and this result reduces to

$$\tilde{\epsilon}_e = \tilde{\epsilon}_h + f\tilde{\epsilon}_h(\tilde{\epsilon}_{in} - \tilde{\epsilon}_h)[\tilde{\epsilon}_h + (1-f)\tilde{d}_t(\tilde{\epsilon}_{in} - \tilde{\epsilon}_h)]^{-1}. \quad (19)$$

Sihvola obtained this result for this case (Equation (5.95) in Ref. 5), using a different treatment of the average field in the host. If $\tilde{\epsilon}_h$ is a scalar, Eq. (18) reduces to the MGA for anisotropic inclusions in an isotropic host.[21,22]

Applying the MGA of Eq. (18), care must be taken that $\tilde{d}_t$ is the depolarization tensor of the transformed inclusion (7), not of the real one (2). Consider a composite with parallel prolate spheroidal inclusions, with principal axes (1,1,2) aligned at 45° to the z-axis on the xz-plane (i.e., rotated by 45° around the y-axis, see medium-size smooth spheroid in Fig. 1(a)). The shape and orientation of the transformed ellipsoid (7) depend on $\tilde{\epsilon}_h$. Fig. 1(a) shows two such ellipsoids, one for $\epsilon_x = 15$, $\epsilon_y = 14$, and $\epsilon_z = 1$ (the smaller netted ellipsoid) and another for $\epsilon_x = 1$, $\epsilon_y = 14$, and $\epsilon_z = 15$ (the larger dotted ellipsoid). It is clear that both transformed ellipsoids are very different from the original in shape and orientation, in particular, they are not spheroids but general ellipsoids. The depolarization tensors of these ellipsoids are used in evaluating the MGA effective dielectric tensor (18). The orientation and shape of the transformed ellipsoids change with the orientation of the spheroidal inclusion. This is demonstrated in Fig. 1(b), where the same spheroid is shown, but now aligned at 20° to the z-axis, with its transformed ellipsoids in the same two hosts. Therefore, in mixtures of identical ellipsoids that are not parallel, the transformed ellipsoids vary in shape, and the averaging in Eq. (18) should be performed both over the orientation distribution of the inclusions and the corresponding distribution of depolarization tensors $\tilde{d}_t$.

Results of the MGA for the composites of Fig. 1(a) (spheroids aligned at 45° in each of the two hosts discussed above) are shown in Fig. 2. The component inside the inclusions is itself anisotropic, and the alignment of its dielectric tensor affects the effective dielectric tensor of the mixture. In the examples of Fig. 2 the dielectric tensor of the inclusion component is

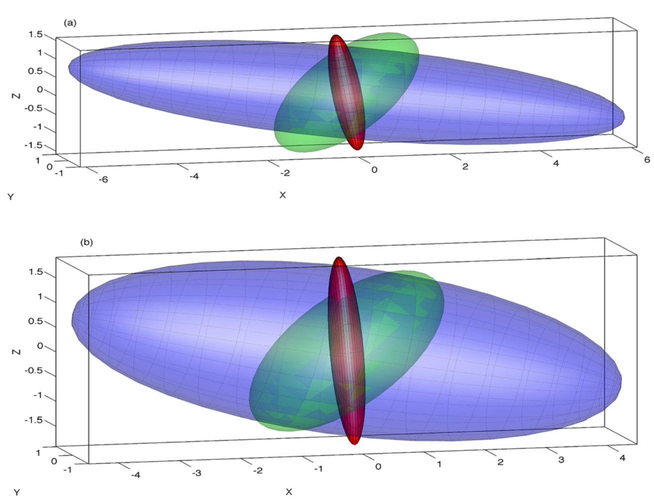

FIG. 1. A prolate spheroid oriented at 45° (a) or at 20° (b) to the z-axis (medium smooth green surface) and its corresponding transformed ellipsoids, for $\epsilon_x = 15$, $\epsilon_y = 14$, and $\epsilon_z = 1$ (small netted red ellipsoids) and for $\epsilon_x = 1$, $\epsilon_y = 14$, and $\epsilon_z = 15$ (larger dotted blue ellipsoids).

$$\tilde{\epsilon}_{in} = \begin{pmatrix} 6 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 7 \end{pmatrix}. \quad (20)$$

For each of the anisotropic hosts of Fig. 1, we consider two different orientations of $\tilde{\epsilon}_{in}$ inside the inclusions. In the first case, $\tilde{\epsilon}_{in}$ is aligned with $\tilde{\epsilon}_h$ and its representation in the (x, y, z) coordinate system is given by Eq. (20). In the other case, it is aligned with the shape of the ellipsoidal inclusions (rotated by 45°) and its representation in the (x, y, z) coordinate system is

$$\tilde{\epsilon}_{in} = \begin{pmatrix} 6.5 & 0 & 0.5 \\ 0 & 3 & 0 \\ 0.5 & 0 & 6.5 \end{pmatrix}. \quad (21)$$

In both cases, the diagonal elements of $\tilde{\epsilon}_e$ vary monotonically, as a function of the inclusions volume fraction, between the corresponding elements of the host and the inclusion component. The off-diagonal elements are not monotonic, and are negative in different ranges of f, due to the mis-orientations of $\tilde{\epsilon}_h$, $\tilde{\epsilon}_{in}$ and $\tilde{d}_t$. This behaviour is more pronounced when $\tilde{\epsilon}_h$ and $\tilde{\epsilon}_{in}$ are aligned (Figs. 2(c) and 2(d)), where the range of negative off-diagonal terms extends over all concentrations, except $f = 0$ and 1.

IV. A SYMMETRIC EFFECTIVE MEDIUM APPROXIMATION

The SEMA models composites in which the grains of the various components are randomly and symmetrically distributed, so that none of the components is identifiable as a host in which the others are preferentially embedded.[2,3] It becomes exact in a hierarchical geometry where spherical grains of two components play symmetrical geometric roles.[14,33] In this approximation, all the material outside a given ellipsoidal grain produces a homogeneous medium. The effective properties of this medium are calculated by imposing the self-consistency condition that the average polarization induced in the medium by all the grains vanishes. Applying this condition to a composite with grain polarizabilities given by Eq. (11), we find

$$\left\langle (\tilde{\epsilon}_{in} - \tilde{\epsilon}_e)\left[\tilde{\epsilon}_e + \tilde{\epsilon}_e^{\frac{1}{2}}\tilde{d}_t\tilde{\epsilon}_e^{-\frac{1}{2}}\tilde{\epsilon}_{in} - \tilde{\epsilon}_e^{\frac{1}{2}}\tilde{d}_t\tilde{\epsilon}_e^{\frac{1}{2}}\right]^{-1}\right\rangle = 0. \quad (22)$$

It should be noted that since, in this approximation, the anisotropic host is the effective medium itself, the depolarization tensors $\tilde{d}_t$ in Eq. (22) depend implicitly on elements of the effective dielectric tensor that determine the shape and orientation of the transformed ellipsoidal grains, via Eqs. (4) and (7). Thus, in the general case, where the dielectric tensors of the components and their grains are not mutually aligned, the self-consistency condition (22) leads to a system of six coupled equations for the different elements of $\tilde{\epsilon}_e$. It should also be noted that, in this general case, the orientation of $\tilde{\epsilon}_e$ is not known *a priory* but varies as a function of the volume fractions of the components. Therefore, the transformation (4) would be performed at a different orientation, which has to be deduced self-consistently, at each

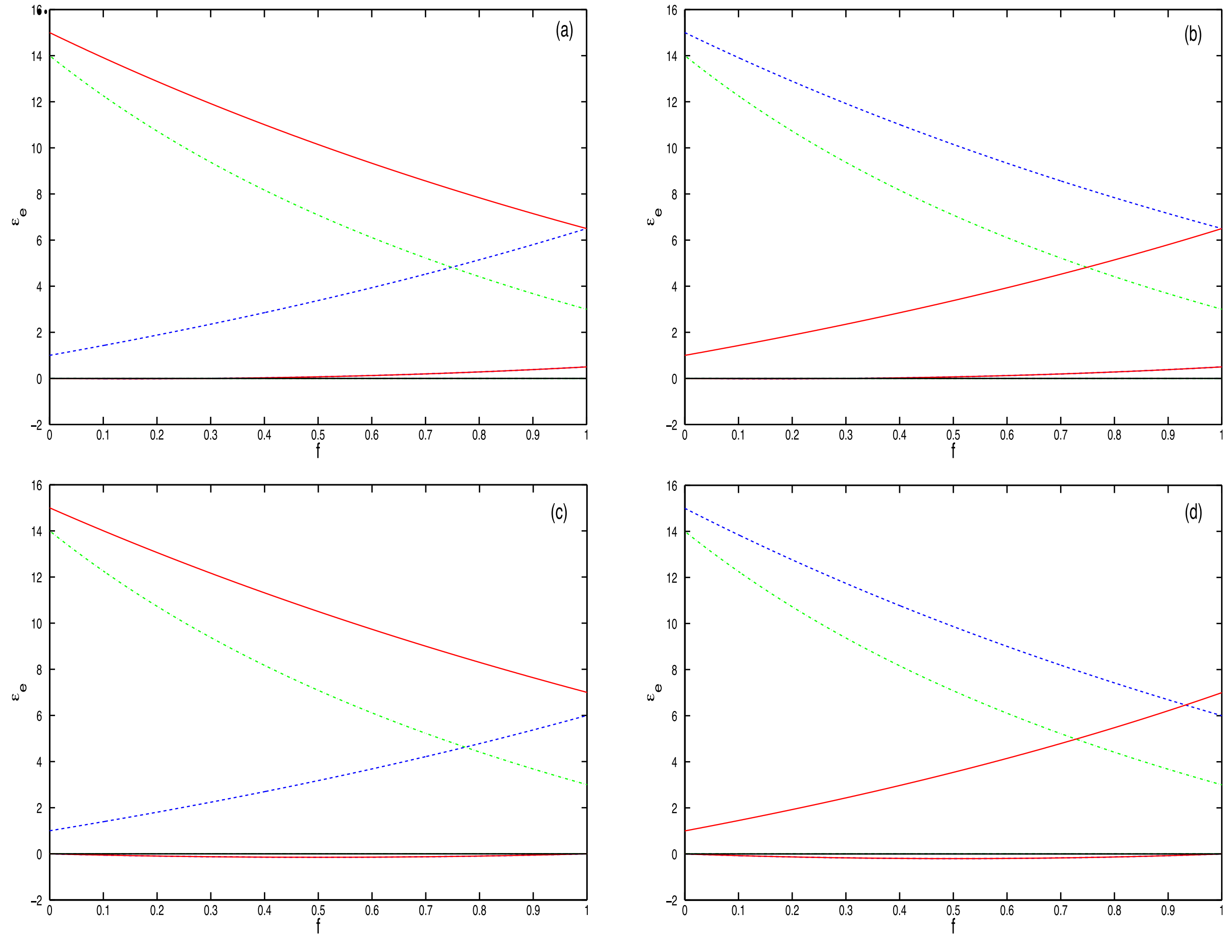

FIG. 2. The MGA effective dielectric tensor elements for the composites of Fig. 1(a), as a function of the inclusions volume fraction f. In (a) and (b) the dielectric tensor of the inclusions $\tilde{\epsilon}_{in}$ is aligned with their geometric principal axes. In (c) and (d) it is aligned with the dielectric tensor of the host. In (a) and (c) the host has $\epsilon_x = 1$, $\epsilon_y = 14$, and $\epsilon_z = 15$. In (b) and (d) it is $\epsilon_x = 15$, $\epsilon_y = 14$, and $\epsilon_z = 1$. In each plot the upper three curves are the diagonal elements of $\tilde{\epsilon}_e : \tilde{\epsilon}_{e,x}$ (dashed, blue), $\tilde{\epsilon}_{e,y}$ (dashed-dotted, green) and $\tilde{\epsilon}_{e,z}$ (solid, red). The lower curve is $\tilde{\epsilon}_{e,xz}$ (solid, red), the other off-diagonal elements are identically zero.

composition. If the dielectric tensors of the components and their grains are all aligned, i.e., the dielectric tensors and the characteristic matrices of the ellipsoids are all diagonal in the same coordinate system, then the transformed ellipsoids and the effective dielectric tensor are also aligned and we get

$$f(\tilde{\epsilon}_1 - \tilde{\epsilon}_e)[\tilde{\epsilon}_e + \tilde{d}_{t,1}(\tilde{\epsilon}_1 - \tilde{\epsilon}_e)]^{-1} + (1-f)(\tilde{\epsilon}_2 - \tilde{\epsilon}_e)[\tilde{\epsilon}_e + \tilde{d}_{t,2}(\tilde{\epsilon}_2 - \tilde{\epsilon}_e)]^{-1} = 0. \quad (23)$$

Here, we only have to solve three coupled equations for the three diagonal elements of $\tilde{\epsilon}_e$. An example of the SEMA of Eq. (23) for a composite with components

$$\tilde{\epsilon}_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 14 & 0 \\ 0 & 0 & 15 \end{pmatrix} \quad \text{and} \quad \tilde{\epsilon}_2 = \begin{pmatrix} 6 & 0 & 0 \\ 0 & 3 & 0 \\ 0 & 0 & 7 \end{pmatrix} \quad (24)$$

is shown in Fig. 3, for three cases of spherical, prolate and oblate spheroids. While the elements of $\tilde{\epsilon}_e$ are, as expected, the same at $f = 0$, 1 in all cases, their variation with f depends on the shape of the grains. Also shown for comparison are the elements of $\tilde{\epsilon}_e$ for spherical grains that were not calculated self-consistently with anisotropy dependent $\tilde{d}_t$ but assumed to have constant depolarization factors of 1/3. The differences in this example are apparent but not large. They increase with increasing anisotropy, as the differences between the grains real and transformed shapes become more pronounced.

A. Percolation in conductor-insulator composites

One of the appealing features of the SEMA is that it is the simplest approximation that shows a non-trivial

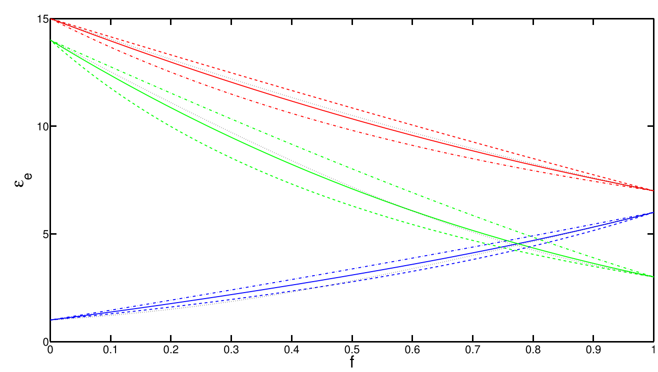

FIG. 3. The SEMA effective dielectric tensor elements of two component composites with aligned component dielectric tensors $\epsilon_x = 1$, $\epsilon_y = 14$, $\epsilon_z = 15$, and $\epsilon_x = 6$, $\epsilon_y = 3$, $\epsilon_z = 7$, and spherical grains (solid lines), prolate spheroids with $c/a = 5$ (dashed lines) and oblate spheroids with $a/c = 5$ (dashed-dotted lines). The dots denote the results for spheres with a constant depolarization factor 1/3.

percolation threshold for the effective conductivity of conductor-insulator composites, where $\sigma_1/\sigma_2 = 0$. For isotropic composites with spherical grains, the percolation threshold is $f_c = 1/3$, the depolarization factor of a sphere, and the dependence of the effective conductivity on composition above percolation is linear,[3,4,11] $\sigma_e \propto (f - f_c)$. In isotropic mixtures of randomly oriented ellipsoids, f_c is their smallest depolarization factor, which decreases as the aspect ratio of the ellipsoids increases.[3,9] To look at the percolation characteristics of the SEMA for anisotropic composites, we rewrite Eq. (23) for conductivities, with two components

$$\tilde{\sigma}_1 = 0 \quad \text{and} \quad \tilde{\sigma}_2 = \begin{pmatrix} \sigma_x & 0 & 0 \\ 0 & \sigma_y & 0 \\ 0 & 0 & \sigma_z \end{pmatrix}. \tag{25}$$

Assuming that the grains of both components are spheres or parallel ellipsoids with the same aspect ratio, and that the conductivity tensor $\tilde{\sigma}_2$ in all component 2 grains is aligned with their principal axes, this gives a set of three coupled equations for the elements of $\tilde{\sigma}_e$

$$\tilde{\sigma}_{e,i} = \sigma_i \frac{f - d_{t,i}}{1 - d_{t,i}}, \tag{26}$$

where $i = x, y, z$. If $\sigma_x = \sigma_y$ and the grains are spheroids then $\tilde{\sigma}_e$ is uniaxial and the transformed grains are also spheroids with depolarization factors[31]

$$d_{t,z} = \begin{cases} \dfrac{1+e^2}{e^3}(e - \arctan e) & \text{for oblate spheroids} \\ \dfrac{1-e^2}{2e^3}\left(\log\dfrac{1+e}{1-e} - 2e\right) & \text{for prolate spheroids,} \end{cases} \tag{27}$$

where their eccentricity is

$$e = \begin{cases} \left(\dfrac{\sigma_{e,z}}{\sigma_{e,x}}\left(\dfrac{a}{c}\right)^2 - 1\right)^{\frac{1}{2}} & \text{for oblate spheroids} \\ \left(1 - \dfrac{\sigma_{e,z}}{\sigma_{e,x}}\left(\dfrac{a}{c}\right)^2\right)^{\frac{1}{2}} & \text{for prolate spheroids,} \end{cases}$$

and $d_{t,x} = (1 - d_{t,z})/2$.

Examples of the effective conductivities of Eq. (26) for a uniaxial composite ($\sigma_x = \sigma_y = 1$, $\sigma_z > 1$) of spherical and spheroidal grains of different aspect ratios are shown in Figures 4 and 5. Two features are immediately apparent: (1) The percolation threshold is $f_c = 1/3$ for both $\sigma_{e,z}$ and $\sigma_{e,x}$, independent of the aspect ratio of the grains. (2) The behaviour of $\sigma_{e,z}$ and $\sigma_{e,x}$ above the percolation threshold is nonlinear and depends on the aspect ratio of the grains. In some cases they even cross each other at some $f > f_c$. At these crossing points, the different microscopic anisotropies of the grain shapes and the components conductivity tensor exactly cancel such that the composite is macroscopically isotropic. In Figures 4 and 5, $\sigma_z > 1$ and the crossing points appear for oblate spheroids. For $\sigma_z < 1$ they would appear for prolate spheroids.

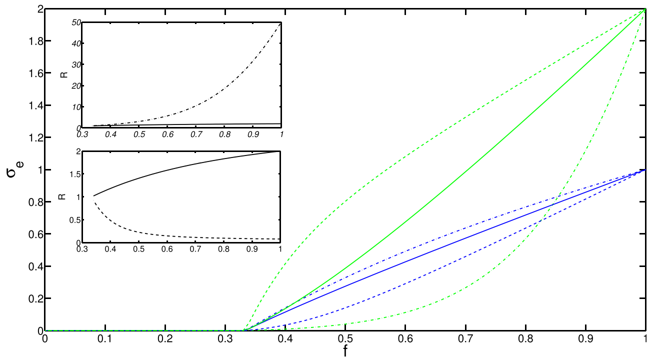

FIG. 4. The SEMA conductivity tensor elements $\sigma_{e,z}$ (upper, green curves) and $\sigma_{e,x}$ (lower, blue curves) of a conductor-insulator composite with $\sigma_x = \sigma_y = 1$ and $\sigma_z = 2$ for spherical grains (solid lines), prolate spheroids with $c/a = 5$ (dashed lines) and oblate spheroids with $a/c = 5$ (dashed-dotted lines). The insets show the convergence of the aspect ratio of the transformed grains, $R = \frac{\sigma_{e,z}}{\sigma_{e,x}}\left(\frac{a}{c}\right)^2$, to 1 at $f_c = 1/3$.

Similar examples for biaxial conductor-insulator composites ($\sigma_x = 1$, $\sigma_y = 2$ and $\sigma_z = 5$) with two different types of ellipsoidal inclusions are shown in Fig. 6. The percolation threshold for the three effective conductivity tensor elements is again $f_c = 1/3$, for both types of grains. The behaviour above the percolation threshold is nonlinear and depends on the shape of the grains. In the case where the large axis of the grains is also the axis of smaller conductivity (circle marked lines in Fig. 6) the elements of σ_e cross each other, leading to three values of f where the composite is macroscopically uniaxial.

The independence of f_c of the shape of the grains is very peculiar and stands in contrast to our intuition regarding the anisotropy of the percolation in composites with parallel elongated grains. It seems clear that in this case the percolation threshold in the direction of the long grain dimension should be lower than in the perpendicular direction. This intuition is obviously correct, but is not reproduced by the electrostatics of spheroids in anisotropic hosts. As f approaches $f_c = 1/3$, the coupling of Eq. (26) causes a convergence to 1 of the effective aspect ratios of the transformed inclusions (as shown in the insets of Figures 4 and 6). The transformed grains become more spherical, leading to an

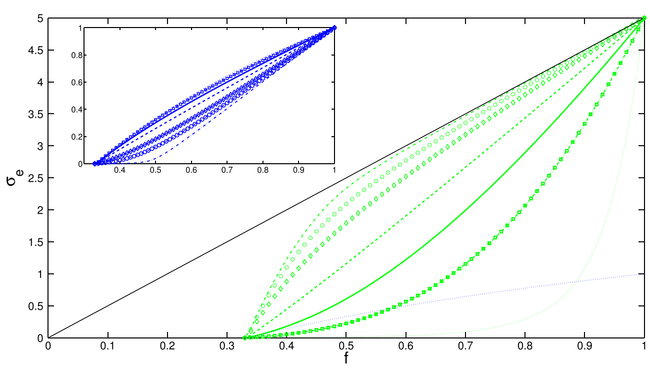

FIG. 5. The SEMA $\sigma_{e,z}$ of a conductor-insulator composite with $\sigma_x = \sigma_y = 1$ and $\sigma_z = 5$ for spherical grains (solid line), prolate spheroids with $c/a = 2$ (dash), $c/a = 5$ (diamonds), $c/a = 10$ (circles) and $c/a = 30$ (dashed-dotted) and oblate spheroids with $c/a = 0.5$ (squares) and $c/a = 0.1$ (dots). The inset shows $\sigma_{e,x}$ for the same cases. $\sigma_{e,x}$ for $c/a = 0.1$ (dots) is also shown in the main figure.

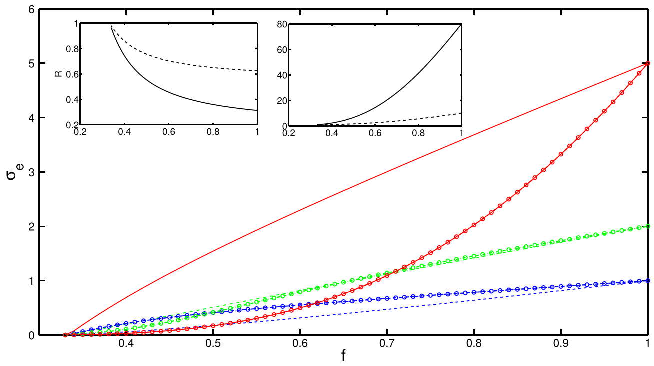

FIG. 6. The SEMA effective conductivity elements of biaxial composites with $\sigma_x = 1$, $\sigma_y = 2$, $\sigma_z = 5$ and ellipsoidal inclusions, $a = 4$, $b = 2$ and $c = 1$ (circle marked curves and right inset), or $a = 1$, $b = 2$ and $c = 4$ (unmarked curves and left inset). $\sigma_{e,z}$ is shown in solid lines, $\sigma_{e,y}$ in dashed-dotted lines and $\sigma_{e,x}$ in dashed lines. The insets show the convergence of the aspect ratios of the transformed grains, $R_x = \frac{\sigma_{e,z}}{\sigma_{e,x}}\left(\frac{a}{c}\right)^2$ (solid lines) and $R_y = \frac{\sigma_{e,z}}{\sigma_{e,y}}\left(\frac{b}{c}\right)^2$ (dashed lines), to 1 at $f_c = 1/3$.

isotropic percolation threshold as in the isotropic SEMA for spherical grains.[3,4] This effect is sharper at larger aspect ratios, as it becomes more difficult for the electrostatics to compensate for the anisotropic shape of the grains by increasing the $\sigma_{e,z}/\sigma_{e,x}$ and the $\sigma_{e,z}/\sigma_{e,y}$ ratios. At infinite aspect ratios the compensation is no longer possible and the SEMA reduces to the limit of parallel cylinders, where $\sigma_{e,z} = f\sigma_z$. This is demonstrated in Fig. 5, where the $\sigma_{e,z}$ curve above f_c becomes more concave for larger prolate aspect ratios, as it approaches the linear $f\sigma_z$ limit.

V. CONCLUSION

In this paper, we present a Maxwell Garnett approximation (MGA) and a symmetric effective medium approximation (SEMA) for anisotropic composites with ellipsoidal grains of arbitrary intrinsic, shape and orientation anisotropy. The derivation is based on a transformation of the electrostatic problem of an anisotropic host into an equivalent problem of an isotropic host with differently shaped and oriented inclusions. Averaging the polarization of these transformed inclusions produces the approximations for the effective properties of the composite. The importance of the transformed inclusions, although already noted in previous works,[5,27,28] has not been widely recognized. Thus, inconsistent formulas that ignore the anisotropy of the effective medium, by considering the polarization of the geometric inclusions instead of the transformed ones, are still commonly used.[18–20] These inconsistent formulas may lead to errors in the interpretation of experimental data on highly anisotropic inhomogeneous media. They should thus be replaced by the MGA or SEMA presented in this paper, when applied to a wide variety of novel anisotropic composites and metamaterials.[20,29,30]

We demonstrated the effect of anisotropy on the effective dielectric tensor in both approximations. In the MGA, it leads in some cases to negative and non-monotonic off-diagonal elements of the effective dielectric tensor, due to the misalignment of the host and the inclusions. In the SEMA, the anisotropy leads to a nonlinear variation of the effective conductivity at concentrations above the percolation threshold of anisotropic conductor-insulator composites, in contrast to the well-known linearity of the isotropic effective medium model. This nonlinear behaviour is anisotropy-dependent, thus conductor-insulator mixtures with different anisotropies would exhibit various nonlinearities above the percolation transition. In addition, the percolation threshold obtained for composites of aligned ellipsoids is isotropic and independent of their aspect ratio. For isotropic composites with spherical grains the percolation threshold in the well-known isotropic SEMA is $f_c = 1/3$. In mixtures of randomly oriented ellipsoids, this value decreases with increasing aspect ratio of the ellipsoids and is characterized by the smallest depolarization factor of the ellipsoids.[3,9,34] Similarly, in composites of aligned ellipsoids, the percolation threshold is obtained in the direction most favorable for contact and has been related to the corresponding depolarization factor.[7] The values of the percolation threshold obtained in numerical studies of various percolating systems are very sensitive to details of the microgeometry and are usually different from the depolarization factors of the inclusions, but the qualitative trend of decreasing threshold with increasing aspect ratio of the grains is preserved (see e.g., Refs. 7, 35, and references therein). The isotropy of the percolation in the anisotropic SEMA, we presented here, demonstrates that the common identification of the percolation threshold with the depolarization factors of the grains, although qualitatively appealing, is unjustified. It should serve to emphasize the distinction between percolation, which is a geometric phenomenon, and the polarization defined by the depolarization factors, which is an electrostatic property. Therefore, a description of anisotropic percolation is not achieved within a self-consistent effective medium approximation but should include explicit anisotropic microgeometric characteristics.

ACKNOWLEDGMENTS

We thank G. W. Milton for useful discussions. O.L. thanks the Department of Mathematics of the University of Utah for its hospitality. E.C. was partially supported by NSF Grant No. CMG-0934721.

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