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Conductivities of heterogeneous media with graded anisotropic constituents

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Two methods are presented to predict the effective conductivities of heterogeneous media containing discretely suspended particles. The particles have either graded anisotropy or a graded anisotropic interphase. A differential replacement procedure based on an energy equivalency condition is presented first to replace the graded anisotropic constituents by equivalent homogeneous isotropic particles. This allows many approximate schemes to be used to predict the effective conductivities of the heterogeneous media containing graded anisotropic constituents from the conductivity of the equivalent homogeneous particles. Next, the optimized upper and lower bounds on the effective conductivities of these heterogeneous media are presented by introducing comparison materials. It is shown that the DRP predictions are within these bounds for the considered media. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2222078]

I. INTRODUCTION

The prediction of the effective physical properties of heterogeneous media, such as their dielectric constants, thermal or electric conductivities, and effective elastic constants, has a long history because of its great scientific and engineering significance. It has attracted the attention of many luminaries including Maxwell, Rayleigh, and Einstein.[1–3] Many approaches and predictive schemes have been proposed and summarized in articles and textbooks.[4–13] Recently, the effective conductivities of graded heterogeneous media have been receiving a lot of attention[14–18] due to the increasing interest in functionally graded materials (FGMs) which have many engineering applications.[19] Many graded materials, such as biological cells, also exist in nature.[20] It is also known that physical anisotropy is widespread in these graded materials. For example, the human head is sometimes modeled as a sphere covered with a few layers of different anisotropic conductivities in electroencephalography.[21] There are many heterogeneous materials with dielectric anisotropy such as liquid crystal droplets,[22] cell membranes with mobile charges,[23] and polycrystal aggregates.[11] The effect of the radial dielectric anisotropy on light scattering in small nematic spheres has also been reported.[24]

Some researchers have predicted the effective dielectric response of heterogeneous media containing graded anisotropic particles using the anisotropic differential effective dipole approximation (ADEDA).[14,25–27] In this approximation, an equivalent homogeneous particle that induces the same dipole moment as the original graded particle is used to replace the latter.[25–27] Zhong *et al.*[28] and Shen and Li[29] developed a differential replacement method to predict the effective elastic moduli of composites containing fibers/spheres with an inhomogeneous interphase. Among the approximate schemes for predicting the effective properties of heterogeneous media, the schemes that bound the possible range of the effective properties are of fundamental importance. Appropriate bounds can be used to assess a particular predictive scheme, and they can also constitute an accurate prediction of the effective properties when the bounds fall in a sufficiently narrow range. The well-known Hashin-Shtrikman bounds[12] are applicable to a heterogeneous medium in which each constituent phase has a definite conductivity and a definite volume fraction. Therefore, generally, they cannot be applied to heterogeneous media with graded constituents. Recently, Wang *et al.*[30] gave the bounds on the effective conductivities of heterogeneous media containing discretely suspended particles with a graded interphase or graded particles by introducing comparison materials with microstructures different from those of the graded heterogeneous media. However, these bounds were deduced under the assumption that the graded constituents exhibit an isotropic response.

In this paper, we present two methods to predict the effective conductivities of heterogeneous media containing either graded anisotropic interphases or graded anisotropic particles. A differential replacement procedure based on an energy equivalency condition is first presented. In this procedure, the particles with a graded anisotropic interphase or the graded anisotropic particles are replaced by equivalent isotropic and homogeneous particles. This allows many known schemes to be used to predict the effective conductivity of the heterogeneous medium from the conductivity of the equivalent homogeneous particles. We then present the bounds on the effective conductivities of heterogeneous media comprising continuous matrices and discretely suspended graded anisotropic particles or graded anisotropic interphases

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by introducing comparison materials with microstructures different from those of the heterogeneous media under consideration.

II. DIFFERENTIAL REPLACEMENT PROCEDURE

Hashin and Shtrikman pointed out that the problems of predicting the effective magnetic permeability, dielectric constant, electric conductivity, heat conductivity, and diffusivity of heterogeneous media are mathematically analogous.[12] Thus, we consider the steady-state electric conduction problems in two kinds of heterogeneous medium. The first kind consists of a continuous, isotropic, and homogeneous matrix and homogeneous but anisotropic spherical particles where a graded and radially anisotropic interphase exists between a particle and the matrix. The second consists of a continuous, isotropic, and homogeneous matrix and discretely suspended graded spherical particles which have a radially anisotropic conductivity profile. By radial anisotropy it is meant that the conductivity of the spherical particle or the interphase in the radial direction is different from that in the tangential direction.[21,31] For both kinds of graded heterogeneous medium under consideration, we use the spherical coordinate system (r,θ,φ) for convenience with the origin of coordinates at the center of a spherical particle. The graded and radially anisotropic spherical particle or the graded and radially anisotropic interphase has the following conductivity profile:

$$\boldsymbol{\sigma}_k(r) = \sigma_{rrk}(r)\mathbf{e}_r \otimes \mathbf{e}_r + \sigma_{\theta\theta k}(r)(\mathbf{e}_\theta \otimes \mathbf{e}_\theta + \mathbf{e}_\varphi \otimes \mathbf{e}_\varphi) \quad (k = P,I), \tag{1}$$

where $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_\varphi$ are the *local* unit base vectors in the spherical coordinate system. Here, and in the following, the subscripts $k=P,I$ denote the particle and the interphase, respectively. The matrix is isotropic, and its conductivity is denoted by $\boldsymbol{\sigma}_M=\sigma_M\mathbf{I}$. Therefore, when the radially anisotropic particles or the particles with a radially anisotropic interphase are randomly distributed, the effective conductivity of the heterogeneous medium will still be isotropic.

For each of the above two kinds of heterogeneous medium, let $\mathbf{J}(\mathbf{x})$ denote the local flux at position $\mathbf{x}$, and $\mathbf{E}(\mathbf{x})$ denote the local field intensity. Under the steady-state condition with no source, the conservation of energy requires that $\mathbf{J}(\mathbf{x})$ be divergence-free, i.e., $\nabla\cdot\mathbf{J}(\mathbf{x})=0$. The intensity field $\mathbf{E}(\mathbf{x})$ is taken to be irrotational, i.e., $\nabla\times\mathbf{E}(\mathbf{x})=0$, where $\mathbf{E}(\mathbf{x})=-\nabla\Phi(\mathbf{x})$ and $\Phi(\mathbf{x})$ is the potential field. The linear constitutive relation between $\mathbf{J}(\mathbf{x})$ and $\mathbf{E}(\mathbf{x})$ is $\mathbf{J}(\mathbf{x})=\boldsymbol{\sigma}(\mathbf{x})\cdot\mathbf{E}(\mathbf{x})$ or $\mathbf{E}(\mathbf{x})=\boldsymbol{\rho}(\mathbf{x})\cdot\mathbf{J}(\mathbf{x})$, where $\boldsymbol{\sigma}(\mathbf{x})$ and $\boldsymbol{\rho}(\mathbf{x})$ are the second-order conductivity and resistivity tensors, respectively, and they are reciprocal. The energy dissipated per unit volume in a material is a non-negative quantity proportional to the inner product of the intensity field and flux field,[15] i.e., $w(\mathbf{x})=\frac{1}{2}\mathbf{E}(\mathbf{x})\cdot\mathbf{J}(\mathbf{x})=\frac{1}{2}\mathbf{E}(\mathbf{x})\cdot\boldsymbol{\sigma}(\mathbf{x})\cdot\mathbf{E}(\mathbf{x})\geqslant 0$ [or $w(\mathbf{x})=\frac{1}{2}\mathbf{E}(\mathbf{x})\cdot\mathbf{J}(\mathbf{x})=\frac{1}{2}\mathbf{J}(\mathbf{x})\cdot\boldsymbol{\rho}(\mathbf{x})\cdot\mathbf{J}(\mathbf{x})\geqslant 0$].

To reveal the effect of the graded constituents on the effective conductivity of the graded heterogeneous medium [Fig. 1(a)], we first present below a differential replacement procedure (DRP) based on an energy equivalency condition, which replaces a graded particle or a homogeneous particle together with the graded interphase by an equivalent homogeneous and isotropic particle.

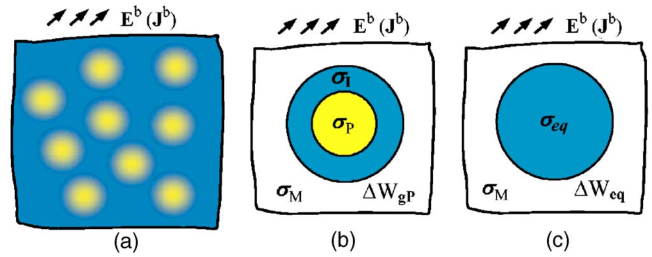

FIG. 1. (Color online) A heterogeneous medium with a continuous matrix and discrete homogeneous particles with a graded interphase or discrete graded particles (a), a particle with a graded anisotropic interphase (b), and a homogeneous equivalent isotropic particle (c).

A. Replacement procedure

Consider a single isotropic particle of a radius r_P with a radially anisotropic but homogeneous (nongraded) interphase (exterior radius r_I) embedded in an infinite homogeneous medium (matrix) with the isotropic conductivity σ_M [Fig. 1(b)]. The remote intensity (flux) is $\mathbf{E}^b$ ($\mathbf{J}^b$), and the conductivities of the particle and the interphase are $\boldsymbol{\sigma}_P$ and $\boldsymbol{\sigma}_I$, respectively. For brevity, here and everywhere in this paper, all length scales are regarded as being normalized by the radius r_P of the spherical particles. Thus, $\mathbf{x}$ denotes the normalized position vector of a material point and r denotes the normalized distance of a material point from the center of the spherical particle. Assume that the remote intensity field is $\mathbf{E}^b=E_z^b\mathbf{e}_z$ along the z axis, where $\mathbf{e}_z$ is the unit vector along the z axis. The local potential in the isotropic particle is

$$\Phi_P = F_P r\cos\theta \quad \text{for } 0 < r \leqslant r_P, \tag{2}$$

and that in the anisotropic interphase is

$$\Phi_I = \left(F_I r^\tau + \frac{G_I}{r^{\tau+1}}\right)\cos\theta \quad \text{for } r_P \leqslant r \leqslant r_I, \tag{3}$$

where $\tau=\frac{1}{2}(-1+\sqrt{1+8\sigma_{\theta\theta I}/\sigma_{rrI}})$. In the isotropic matrix,

$$\Phi_M = \left(F_M r + \frac{G_M}{r^2}\right)\cos\theta \quad \text{for } r \geqslant r_I, \tag{4}$$

where F_P, F_I, G_I, F_M, and G_M are unknown constants to be determined from the continuity conditions of the local potentials and the normal components of the flux at the two interfaces $r=r_P$ and $r=r_I$, and the prescribed remote condition.

Generally, when a particle with an interphase is embedded in the infinite medium, there will be a change ΔW_{gP} [Fig. 1(b)] in the energy of the medium compared with the energy of the homogeneous medium under the same intensity (flux). Now, we replace the particle along with the interphase by an equivalent homogeneous particle with isotropic conductivity $\sigma_{\rm eq}$ [the radius of the equivalent particle is the same as the outer radius of the interphase, Fig. 1(c)]. The unknown conductivity $\sigma_{\rm eq}$ is determined by requiring that the change $\Delta W_{\rm eq}$ in the energy induced by embedding the equivalent particle in the matrix be equal to the change ΔW_{gP} induced by the original particle together with its interphase, i.e.,

$\Delta W_{gP}=\Delta W_{\rm eq}$. From the local fields in Eqs. (2)–(4), and the interface and boundary conditions, the energy change ΔW_{gP} in Fig. 1(b) is

$$\Delta W_{gP} = -\frac{3G_M\sigma_M}{2r_I^3}V_{\rm eq}E_z^b, \tag{5}$$

where $V_{\rm eq}$ is the volume of the original particle together with its interphase [Fig. 1(b)], and the constant G_M is given by

$$G_M = -\frac{r_I^3E_z^b[(\sigma_M-\tau\sigma_{rrI})(\sigma_P+\tau_1\sigma_{rrI})+c_P^{(1+2\tau)/3}(\tau\sigma_{\rho\rho I}-\sigma_P)(\sigma_M+\tau_1\sigma_{rrI})]}{c_P^{(1+2\tau)/3}(\tau\sigma_{rrI}-\sigma_P)(2\sigma_M-\tau_1\sigma_{rrI})+(\sigma_P+\tau_1\sigma_{rrI})(2\sigma_M+\tau\sigma_{rrI})}, \tag{6}$$

where $\tau_1=\tau+1$, $c_P=r_P^3/r_I^3$. The energy change $\Delta W_{\rm eq}$ in Fig. 1(c) is

$$\Delta W_{\rm eq} = \frac{3\sigma_M(\sigma_M-\sigma_{\rm eq})}{2(2\sigma_M+\sigma_{\rm eq})}V_{\rm eq}(E_z^b)^2. \tag{7}$$

From the energy equivalency condition, $\Delta W_{gP}=\Delta W_{\rm eq}$, $\sigma_{\rm eq}$ works out to be

$$\sigma_{\rm eq} = \sigma_{rrI}\frac{[\tau+\tau_1c_P^{(1+2\tau)/3}]\sigma_P+\tau\tau_1[1-c_P^{(1+2\tau)/3}]\sigma_{rrI}}{[1-c_P^{(1+2\tau)/3}]\sigma_P+[\tau_1+\tau c_P^{(1+2\tau)/3}]\sigma_{rrI}}. \tag{8}$$

For a multilayered anisotropic interphase, the replacement procedure is repeated as many times as the number of layers, beginning from the innermost layer and ending with the outermost.

B. Differential replacement procedure (DRP)

The replacement procedure described above can be extended to the case of a graded anisotropic interphase or a graded anisotropic particle by a limiting process. Let $\sigma_{\rm eq}(r)$ be the conductivity of a sphere with radius r. Now cover it with a thin and homogeneous coating of thickness dr and conductivity $\boldsymbol{\sigma}_I(r+\alpha dr)$, given by Eq. (1), where α is an arbitrary fraction, i.e., $\alpha\in[0,1]$. Then, the conductivity of the composite sphere of radius $r+dr$, denoted by $\sigma_{\rm eq}(r+dr)$, can be obtained using Eq. (8) for a two-phase material, i.e.,

$$\sigma_{\rm eq}(r+dr) = \sigma_{rrI}(r+\alpha dr)\frac{[\tau+\tau_1c_P^{(1+2\tau)/3}]\sigma_{\rm eq}(r)+\tau\tau_1[1-c_P^{(1+2\tau)/3}]\sigma_{rrI}(r+\alpha dr)}{[1-c_P^{(1+2\tau)/3}]\sigma_{\rm eq}(r)+[\tau_1+\tau c_P^{(1+2\tau)/3}]\sigma_{rrI}(r+\alpha dr)}, \tag{9}$$

where $c_P[c_P=r^3/(r+dr)^3]$ is the volume fraction of the sphere with radius $r\in[r_P,r_I]$ in the composite sphere with radius $r+dr$. Now let dr approach zero. This gives the governing differential equation in terms of $\sigma_{\rm eq}(r)$ for a graded anisotropic interphase

$$\frac{d\sigma_{\rm eq}(r)}{dr} = -\frac{(\sigma_{\rm eq}-\tau\sigma_{rrI})(\sigma_{\rm eq}+\tau_1\sigma_{rrI})}{r\sigma_{rrI}}, \quad \sigma_{rrI}|_{(r=r_P)}=\sigma_P. \tag{10}$$

For an isotropic interphase, $\sigma_{rrI}=\sigma_{\theta\theta I}=\sigma_I$, Eq. (10) reduces to

$$\frac{d\sigma_{\rm eq}(r)}{dr} = -\frac{(\sigma_{\rm eq}-\sigma_I)(\sigma_{\rm eq}+2\sigma_I)}{r\sigma_I}, \quad \sigma_I|_{(r=r_P)}=\sigma_P. \tag{11}$$

To solve a graded anisotropic particle without an interphase, we start with an infinitesimal isotropic spherical core with conductivity $\sigma(0)$. Then following the above procedure for the graded anisotropic interphase, we obtain the governing equation in terms of $\sigma_{\rm eq}(r)$,

$$\frac{d\sigma_{\rm eq}(r)}{dr} = -\frac{(\sigma_{\rm eq}-\beta\sigma_{rrP})(\sigma_{\rm eq}+\beta_1\sigma_{rrP})}{r\sigma_{rrP}}, \quad \sigma_{rrP}|_{(r=0^+)} = \sigma(0), \tag{12}$$

where $\beta=\frac{1}{2}(-1+\sqrt{1+8\sigma_{\theta\theta P}/\sigma_{rrP}})$, $\beta_1=\beta+1$. For the isotropic case, Eq. (12) reduces to

$$\frac{d\sigma_{\rm eq}(r)}{dr} = -\frac{(\sigma_{\rm eq}-\sigma_P)(\sigma_{\rm eq}+2\sigma_P)}{r\sigma_P}, \quad \sigma_P|_{(r=0^+)}=\sigma(0). \tag{13}$$

The differential equations in Eqs. (10)–(13) are nothing but the Tartar formulas, which were obtained for assemblages of spheres with varying radial and tangential conductivities.(11) It is noted that Dong *et al.*,[26] Gao *et al.*,[27] Yu and Gu[32] obtained the dielectric constants of graded anisotropic spherical particles by the ADEDA and the differential effective multipole moment approximation (DEMMA); the governing equation of the dielectric constants obtained by the dipole moment equivalency condition is the same as that in Eq. (12) obtained by the energy equivalency condition. Shen and Li[29] predicted the effective elastic moduli of composites containing fibers/spheres with a graded interphase using the elastic energy equivalency condition, which is the counter-

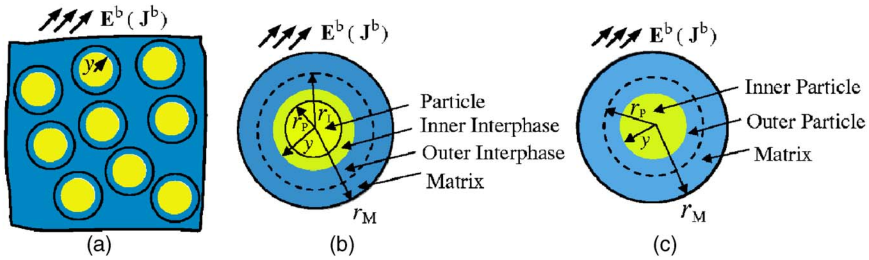

FIG. 2. (Color online) The comparison material with a continuous matrix and discrete homogeneous (nongraded) particles (a); CSA configurations for calculating the average quantities $\langle \mathbf{E}^0 \cdot \Delta\sigma \cdot \mathbf{E}^0 \rangle$, $\langle \mathbf{J}_0 \cdot \Delta\rho \cdot \mathbf{J}_0 \rangle$, and $\bar{\sigma}^0$ of the comparison materials for the heterogeneous medium with a graded interphase (b) and with graded particles (c).

part of the present conduction problem; they found that their elastic moduli agreed very well with those obtained by the finite element method.

Equations (10)–(13) for the graded anisotropic interphase and the graded anisotropic particle can be applied to arbitrary conductivity profiles. Using the conductivity σ_{eq} of the equivalent homogeneous particle and the available predictive schemes, e.g., the composite sphere assemblage (CSA) model,[11,12] or the generalized self-consistent method (GSCM),[33–35] etc., the effective conductivity of a heterogeneous medium containing homogeneous and isotropic particles with a graded anisotropic interphase or graded anisotropic particles can be obtained. In this paper, we use the CSA model[11,12] to predict the effective conductivity $\bar{\sigma}$ of the composite, i.e.,

$$\bar{\sigma} = \frac{\sigma_M[(1+2f_{eq})\sigma_{eq} + 2(1-f_{eq})\sigma_M]}{(1-f_{eq})\sigma_{eq} + (2+f_{eq})\sigma_M}, \quad (14)$$

where σ_{eq} is given by Eqs. (10) and (11) for a graded anisotropic interphase and Eqs. (12) and (13) for a graded anisotropic particle. f_{eq} denotes the volume fraction of the equivalent homogeneous particles in the heterogeneous medium.

In the foregoing we described the DRP to estimate the effective conductivities of heterogeneous media containing graded anisotropic interphases or graded anisotropic particles. In the following, we will obtain optimized bounds on the effective conductivities of these heterogeneous media.

III. THEORY OF OPTIMIZED BOUNDS

Wang *et al.*[30] presented a theory to obtain the optimized bounds on the effective conductivities of heterogeneous media containing graded isotropic interphases or graded isotropic particles by introducing comparison materials with microstructures different from those of the considered heterogeneous media. They used the GSCM scheme to evaluate the field quantities needed in obtaining the bounds. In this paper, we will generalize the theory of Wang *et al.*[30] to obtain the bounds on the effective conductivities of heterogeneous media containing homogeneous but anisotropic spherical particles with a graded anisotropic interphase or containing graded anisotropic spherical particles without an interphase. However, the field quantities needed for obtaining the bounds will be evaluated by the CSA scheme.

A. Theory of upper and lower bounds

As will be made clear below, the comparison materials for both kinds of heterogeneous medium under consideration consist of a continuous and homogeneous matrix and discrete homogeneous (nongraded) particles, and the exterior boundary of a representative volume element (RVE) of the comparison materials is the same as that of the real materials [Fig. 2(a)]. The conductivity and resistivity tensors at a point $\mathbf{x}$ in the comparison material are denoted by $\boldsymbol{\sigma}^0(\mathbf{x})$ and $\boldsymbol{\rho}_0(\mathbf{x})$ [Fig. 2(a)], respectively.

The exterior boundaries S of the RVEs of the real [Fig. 1(a)] and comparison materials [Fig. 2(a)] are subjected to the following boundary condition:

$$\Phi|_S = -\mathbf{E}^b \cdot \mathbf{x}. \quad (15)$$

According to the theory of Wang *et al.*,[30] the upper bound on the effective conductivity of a real composite containing graded constituents can be obtained from the following inequality:

$$\mathbf{E}^b \cdot (\bar{\boldsymbol{\sigma}} - \bar{\boldsymbol{\sigma}}^0) \cdot \mathbf{E}^b \leqslant \langle \mathbf{E}^0 \cdot \Delta\boldsymbol{\sigma} \cdot \mathbf{E}^0 \rangle, \quad (16)$$

where $\langle \cdot \rangle$ denotes the volume average of the corresponding quantity, $\mathbf{E}^0(\mathbf{x})$ is the intensity in the comparison material under $\mathbf{E}^b$, $\Delta\boldsymbol{\sigma} = \boldsymbol{\sigma} - \boldsymbol{\sigma}^0$, and $\boldsymbol{\sigma}$ and $\boldsymbol{\sigma}^0$ are the conductivity tensors of the real and the comparison materials, respectively, and $\bar{\boldsymbol{\sigma}}$ and $\bar{\boldsymbol{\sigma}}^0$ are the effective conductivity tensors of the real and the comparison materials, respectively. From Eq. (16), it is seen that the upper bound on the effective conductivity of the real material can be obtained once $\mathbf{E}^0$ and $\bar{\boldsymbol{\sigma}}^0$ for the comparison material with the homogeneous constituents under the constant intensity vector $\mathbf{E}^b$ are known.

If, on the other hand, the exterior boundaries S of the RVEs of the real and comparison materials in Figs. 1(a) and 2(a) are subjected to the following boundary condition:

$$\mathbf{J}|_S = \mathbf{J}^b, \quad (17)$$

then the lower bound on the effective conductivity can be obtained from the following inequality:[30]

$$\mathbf{J}^b \cdot (\bar{\boldsymbol{\rho}} - \bar{\boldsymbol{\rho}}_0) \cdot \mathbf{J}^b \leqslant \langle \mathbf{J}_0 \cdot \Delta\boldsymbol{\rho} \cdot \mathbf{J}_0 \rangle, \quad (18)$$

where $\mathbf{J}_0(\mathbf{x})$ is the flux in the comparison material, $\Delta\boldsymbol{\rho} = \boldsymbol{\rho} - \boldsymbol{\rho}_0$, and $\boldsymbol{\rho}$ and $\boldsymbol{\rho}_0$ are the resistivity tensors of the real and the comparison materials, respectively, and $\bar{\boldsymbol{\rho}}$ and $\bar{\boldsymbol{\rho}}_0$ are the effective resistivity tensors of the real and the comparison materials, respectively. The lower bound on the effective conductivity of the real material can be obtained once $\mathbf{J}_0$ and $\bar{\boldsymbol{\sigma}}^0$ for the comparison material with the homogeneous constituents under the constant flux vector $\mathbf{J}^b$ are known.

B. Comparison materials and CSA configuration

Let r_P denote the radii of the spherical particles in a heterogeneous medium containing discretely suspended homogeneous spherical particles with a graded anisotropic interphase or graded spherical particles without an interphase. In the first kind of heterogeneous medium, the conductivity of the graded anisotropic interphase is assumed to vary in the radial direction. The outer radius of the graded interphase is denoted by r_I, as shown in Fig. 2(b). For this kind of heterogenous medium, as in the work of Wang *et al.*,[30] we introduce a comparison material which consists of a homogeneous matrix and homogeneous particles. The conductivities of the matrix and particles in the comparison material are chosen to be the same as those of the particles and the matrix of the real material. However, in the comparison material, the interphase region is divided into two concentric subregions, designated as the inner and outer parts. The conductivity of the inner part is chosen to be the same as that of the particle, $\boldsymbol{\sigma}^0=\boldsymbol{\sigma}_P$ $(r_P \leqslant r \leqslant y, r_P \equiv 1)$, and that of the outer part to be as that of the matrix, $\boldsymbol{\sigma}^0=\boldsymbol{\sigma}_M$ $(y \leqslant r \leqslant r_I)$ [Fig. 2(b)]. The comparison material so constructed is a two-phase heterogeneous medium consisting of the homogeneous isotropic matrix and homogeneous anisotropic particles, as shown in Fig. 2(a). The local intensity $\mathbf{E}^0(\mathbf{x})$ and flux $\mathbf{J}_0(\mathbf{x})$ in this two-phase heterogeneous medium, which are needed in the calculations of the bounds in Eqs. (16) and (18), are calculated using the CSA configuration in Fig. 2(b).

In the second kind of heterogeneous medium, the conductivity of the particles is assumed to vary in the radial direction. The comparison material is constructed in the following way. A graded particle of radius r_P is divided into two concentric parts, namely, the inner part with radius y and the outer part with radius r_P. The conductivity of the inner part can be chosen to be an arbitrary constant. In the calculations to follow, it is chosen to be a constant which is equal to the conductivity either at the center of the original graded particle or at the dividing line $r=y$. The conductivity of the outer part, which is actually a spherical shell surrounding the inner particle, is chosen to be that of the matrix of the real material [Fig. 2(c)].

Therefore, both comparison materials are a two-phase heterogeneous medium consisting of a homogeneous matrix and homogeneous spherical particles, as shown in Fig. 2(a). In order to derive the bounds from the inequalities in Eqs. (16) and (18), we need to calculate the fields $\mathbf{E}^0(\mathbf{x})$, $\mathbf{J}_0(\mathbf{x})$, and $\bar{\boldsymbol{\sigma}}^0$ in these two-phase comparison materials. Many approximate schemes can be used to evaluate $\mathbf{E}^0(\mathbf{x})$, $\mathbf{J}_0(\mathbf{x})$, and $\bar{\boldsymbol{\sigma}}^0$ for the comparison material, and different schemes produce different approximations of $\langle \mathbf{E}^0 \cdot \Delta\boldsymbol{\sigma} \cdot \mathbf{E}^0 \rangle$ $(\langle \mathbf{J}_0 \cdot \Delta\boldsymbol{\rho} \cdot \mathbf{J}_0 \rangle)$ and $\bar{\boldsymbol{\sigma}}^0$. In this paper, we will use the CSA model[11,12] to evaluate $\langle \mathbf{E}^0 \cdot \Delta\boldsymbol{\sigma} \cdot \mathbf{E}^0 \rangle$ $(\langle \mathbf{J}_0 \cdot \Delta\boldsymbol{\rho} \cdot \mathbf{J}_0 \rangle)$ and $\bar{\boldsymbol{\sigma}}^0$ of the comparison materials.

The CSA scheme is based on an anisotropic but homogeneous spherical particle (radius $r=y$) with an isotropic matrix shell (radius $r=r_M$) subjected to the intensity $\mathbf{E}^b$ or flux $\mathbf{J}^b$ [Fig. 2(b) or 2(c)] on its outer surface. The local potential in the anisotropic particle is given by

$$\Phi_P = F_P r^{\beta} \cos\theta \quad \text{at } 0 < r \leqslant r_P. \tag{19}$$

The local potential in the matrix is given by Eq. (4). The constants F_M, G_M, and F_P in Eqs. (4) and (19) are determined by the boundary and interface conditions for the CSA configuration, namely, the continuity conditions of the local potential and the normal components of the flux at $r=y$, and the boundary condition

$$\begin{cases} \Phi_P = \Phi_M, \ J_r^P = J_r^M & \text{at } r = y \\ \Phi_M = -E_z^b r \cos\theta & \text{at } r = r_M. \end{cases} \tag{20}$$

Thus the effective conductivity $\bar{\sigma}^0$ of the comparison material can be determined,

$$\bar{\sigma}^0 = \frac{\sigma_M[(1+2f_P)\beta\sigma_{rrP} + 2(1-f_P)\sigma_M]}{(1-f_P)\beta\sigma_{rrP} + (2+f_P)\sigma_M}, \tag{21}$$

where $f_P=(y/r_M)^3$ is the volume fraction of the homogeneous particle in the comparison materials. Hashin and Shtrikman[12] gave the effective conductivity of a heterogeneous medium containing isotropic particles using the CSA model. For isotropic particles $\beta=1$, Eq. (21) reduces to their result. The local intensity fields $\mathbf{E}_P^0$ and $\mathbf{E}_M^0$ in the anisotropic particle (with radius $r=y$) and in the matrix (with outer radius $r=r_M$) under $\mathbf{E}^b=E_z^b\mathbf{e}_z$ are, respectively,

$$\mathbf{E}_P^0 = \frac{3y^{(1-\beta)}\sin 2\theta(\beta-1)\sigma_M}{2H^0 r^{(1-\beta)}} E_z^b(\cos\varphi\mathbf{e}_x + \sin\varphi\mathbf{e}_y) + \frac{3y^{(1-\beta)}\sigma_M}{H^0 r^{(1-\beta)}} E_z^b(\beta\cos^2\theta + \sin^2\theta)\mathbf{e}_z, \tag{22}$$

$$\mathbf{E}_M^0 = \frac{3y^3(\beta\sigma_{rrP}-\sigma_M)\sin 2\theta}{2H^0 r^3} E_z^b(\cos\varphi\mathbf{e}_x + \sin\varphi\mathbf{e}_y) + \frac{E_z^b}{H^0}\left[\beta\sigma_{rrP} + 2\sigma_M + \frac{(1+3\cos 2\theta)y^3}{2r^3} \times (\beta\sigma_{rrP}-\sigma_M)\right]\mathbf{e}_z, \tag{23}$$

where $H^0=(1-f_P)\beta\sigma_{rrP}+(2+f_P)\sigma_M$, $\mathbf{e}_x$, $\mathbf{e}_y$, and $\mathbf{e}_z$ are the unit base vectors of the Cartesian coordinate system, and $r(y \leqslant r \leqslant r_M)$ is the radial distance from the origin.

Likewise, the local flux fields $\mathbf{J}_0^P$ and $\mathbf{J}_0^M$ in the anisotropic particle (with radius $r=y$) and in the matrix (with outer radius $r=r_M$) under $\mathbf{J}^b=J_z^b\mathbf{e}_z$ are, respectively,

$$\mathbf{J}_0^P = \frac{3y^{(1-\beta)}\sin 2\theta(\beta\sigma_{rrP}-\sigma_{\theta\theta P})}{2H_0 r^{(1-\beta)}} J_z^b(\cos\varphi\mathbf{e}_x + \sin\varphi\mathbf{e}_y) + \frac{3y^{(1-\beta)}}{H_0 r^{(1-\beta)}} J_z^b(\beta\cos^2\theta\sigma_{rrP} + \sin^2\theta\sigma_{\theta\theta P})\mathbf{e}_z, \tag{24}$$

$$\mathbf{J}_0^M = \frac{3y^3(\beta\sigma_{rrP}-\sigma_M)\sin 2\theta}{2H_0 r^3} J_z^b(\cos\varphi\mathbf{e}_x + \sin\varphi\mathbf{e}_y) + \frac{J_z^b}{H_0}\left[\beta\sigma_{rrP} + 2\sigma_M + \frac{(1+3\cos 2\theta)y^3}{2r^3} \times (\beta\sigma_{rrP}-\sigma_M)\right]\mathbf{e}_z, \tag{25}$$

where $H_0=(1+2f_P)\beta\sigma_{rrP}+2(1-f_P)\sigma_M$.

Equations (16) and (21)–(23) give the upper bound on the effective conductivities of the graded heterogeneous media, whereas Eqs. (18), (21), (24), and (25) give the lower bound. As these bounds depend on the variable y, they can be optimized with respect to y. In the following, we shall calculate the bounds and the DRP predictions for some particular material compositions.

IV. APPLICATION OF DRP AND BOUNDS TO GRADED INTERPHASE

The effective conductivity of the heterogeneous medium containing homogeneous particles with a graded anisotropic interphase is bounded from above by Eq. (16),

$$\bar{\sigma} \leqslant \bar{\sigma}^0 + B_I(y), \tag{26}$$

in which

$$\begin{aligned} B_I(y) &= \frac{f_I}{(\mathbf{E}^b \cdot \mathbf{E}^b)} \langle \mathbf{E}^0 \cdot \Delta\boldsymbol{\sigma} \cdot \mathbf{E}^0 \rangle_I \\ &= \frac{1}{(\mathbf{E}^b \cdot \mathbf{E}^b)} \{ f_{IP} \langle \mathbf{E}_P^0 \cdot \Delta\boldsymbol{\sigma} \cdot \mathbf{E}_P^0 \rangle_{IP} \\ &\quad + f_{IM} \langle \mathbf{E}_M^0 \cdot \Delta\boldsymbol{\sigma} \cdot \mathbf{E}_M^0 \rangle_{IM} \}. \end{aligned} \tag{27}$$

Here, $f_I=(r_I^3-r_P^3)/r_M^3$ is the volume fraction of the graded interphase in the real materials, $f_{IP}=(y^3-r_P^3)/r_M^3$ and $f_{IM}=(r_I^3-y^3)/r_M^3$. $\langle\cdot\rangle_I$ denotes the volume average over the entire interphase ($r_P \leqslant r \leqslant r_I$), $\langle\cdot\rangle_{IP}$ denotes the volume average over the inner interphase ($r_P \leqslant r \leqslant y$), and $\langle\cdot\rangle_{IM}$ denotes the volume average over the outer interphase ($y \leqslant r \leqslant r_I$). $\bar{\sigma}^0$, B_I, $\mathbf{E}_P^0$, and $\mathbf{E}_M^0$ are all functions of y, and $\bar{\sigma}^0$, $\mathbf{E}_P^0$, and $\mathbf{E}_M^0$ are given in Eqs. (21)–(23). Let the parameter y vary between r_P and r_I to give the minimum value of the quantity on the right side of Eq. (26), then the optimized upper bound $\bar{\sigma}^{\text{upp}}$ on $\bar{\sigma}$ can be obtained

$$\bar{\sigma}^{\text{upp}} = \min_{(r_P \leqslant y \leqslant r_I)} \{ \bar{\sigma}^0(y) + B_I(y) \}. \tag{28}$$

The lower bound can be obtained from Eq. (18),

$$\bar{\sigma} \geqslant \frac{1}{\bar{\rho}_0 + B_I'(y)}, \tag{29}$$

in which

$$\begin{aligned} B_I'(y) &= \frac{f_I}{(\mathbf{J}^b \cdot \mathbf{J}^b)} \langle \mathbf{J}_0 \cdot \Delta\boldsymbol{\rho} \cdot \mathbf{J}_0 \rangle_I \\ &= \frac{1}{(\mathbf{J}^b \cdot \mathbf{J}^b)} \{ f_{IP} \langle \mathbf{J}_0^P \cdot \Delta\boldsymbol{\rho} \cdot \mathbf{J}_0^P \rangle_{IP} \\ &\quad + f_{IM} \langle \mathbf{J}_0^M \cdot \Delta\boldsymbol{\rho} \cdot \mathbf{J}_0^M \rangle_{IM} \}. \end{aligned} \tag{30}$$

In Eqs. (29) and (30), $\bar{\rho}_0$ ($\bar{\rho}_0=1/\bar{\sigma}^0$), $\mathbf{J}_0^P$, $\mathbf{J}_0^M$, and B_I' are all functions of y, and $\bar{\sigma}^0$, $\mathbf{J}_0^P$, and $\mathbf{J}_0^M$ are given in Eqs. (21), (24), and (25). Let the parameter y vary between r_P and r_I to give the maximum of the quantity on the right side of Eq. (29), then we can get the optimized lower bound $\bar{\sigma}_{\text{low}}$ on $\bar{\sigma}$,

$$\bar{\sigma}_{\text{low}} = \max_{(r_P \leqslant y \leqslant r_I)} \left\{ \frac{\bar{\sigma}^0(y)}{1 + \bar{\sigma}^0(y) B_I'(y)} \right\}. \tag{31}$$

We now compare the optimized bounds and the DRP prediction of the normalized effective conductivity $\bar{\sigma}/\sigma_M$ of a heterogeneous medium containing isotropic homogeneous particles with a graded anisotropic interphase. The physical and geometrical parameters for the heterogeneous medium are chosen as follows: the conductivity of the particles is higher than that of the matrix ($\sigma_P=5\sigma_M$); the conductivity profile of the interphase follows a simple power law, $\sigma_{rrI}=5\sigma_M r^2$, $\sigma_{\theta\theta I}=5\sigma_M r^Q$, where Q is a power exponent; the ratio of the interphase thickness to the radius of the particles is $t=0.1$. The bounds and the DRP prediction of the normalized effective conductivity $\bar{\sigma}/\sigma_M$ of this medium are shown in Fig. 3 as functions of power exponent Q. It is seen that the DRP prediction always lies within the optimized upper and lower bounds.

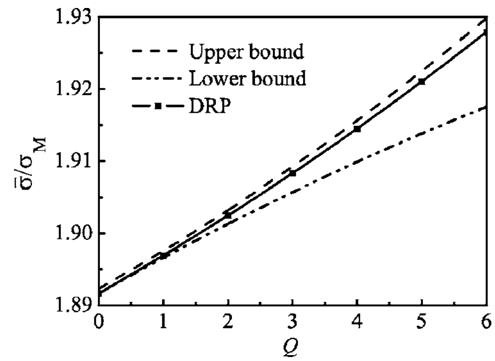

FIG. 3. Bounds and DRP prediction of the normalized effective conductivity $\bar{\sigma}/\sigma_M$ of a heterogeneous medium containing spherical isotropic particles with a graded anisotropic interphase ($\sigma_P=5\sigma_M$, $\sigma_{rrI}=5\sigma_M r^2$, $\sigma_{\theta\theta I}=5\sigma_M r^Q$, $f_R=0.3$, where f_R is the volume fraction of the particles in the medium).

V. APPLICATION OF DRP AND BOUNDS TO GRADED PARTICLES

The effective conductivity of a heterogeneous medium containing graded anisotropic particles can be bounded by Eq. (16),

$$\bar{\sigma} \leqslant \bar{\sigma}^0 + B_P(y), \tag{32}$$

in which

$$\begin{aligned} B_P(y) &= \frac{f_R}{(\mathbf{E}^b \cdot \mathbf{E}^b)} \langle \mathbf{E}^0 \cdot \Delta\boldsymbol{\sigma} \cdot \mathbf{E}^0 \rangle_P \\ &= \frac{1}{(\mathbf{E}^b \cdot \mathbf{E}^b)} \{ f_{PP} \langle \mathbf{E}_P^0 \cdot \Delta\boldsymbol{\sigma} \cdot \mathbf{E}_P^0 \rangle_{PP} \\ &\quad + f_{PM} \langle \mathbf{E}_M^0 \cdot \Delta\boldsymbol{\sigma} \cdot \mathbf{E}_M^0 \rangle_{PM} \}. \end{aligned} \tag{33}$$

Here, $f_R=r_P^3/r_M^3$ is the volume fraction of the particles in the real materials, $f_{PP}=y^3/r_M^3$, and $f_{PM}=(r_P^3-y^3)/r_M^3$. $\langle\cdot\rangle_P$ denotes the volume average over the particle ($0 \leqslant r \leqslant r_P$), $\langle\cdot\rangle_{PP}$ denotes the volume average over the inner part of the particle ($0 \leqslant r \leqslant y$), and $\langle\cdot\rangle_{PM}$ denotes the volume average over the outer part of the particle ($y \leqslant r \leqslant r_P$). In this case, $\bar{\sigma}^0$ and $\mathbf{E}^0$ are all functions of y, and $\bar{\sigma}^0$, $\mathbf{E}_P^0$, and $\mathbf{E}_M^0$ are given in Eqs. (21)–(23). Let y vary between 0 and r_P to give the minimum of the quantity on the right side of Eq. (32), then the upper bound $\bar{\sigma}^{\text{upp}}$ on $\bar{\sigma}$ is obtained,

$$\bar{\sigma}^{\text{upp}} = \min_{(0 \leqslant y \leqslant r_P)} \{ \bar{\sigma}^0(y) + B_P(y) \}. \tag{34}$$

The lower bound can be obtained from the inequality

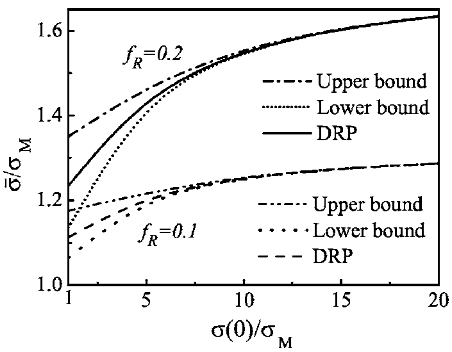

FIG. 4. Bounds and DRP prediction of the normalized effective conductivity $\bar{\sigma}/\sigma_M$ of a heterogeneous medium containing graded anisotropic spherical particles with a linear conductivity profile $\sigma_{rrP}(r)=\sigma(0)+gr$, $\sigma_{\theta\theta P}(r)=\sigma(0)+hr$ $(g=\sigma_M, h=3\sigma_M)$.

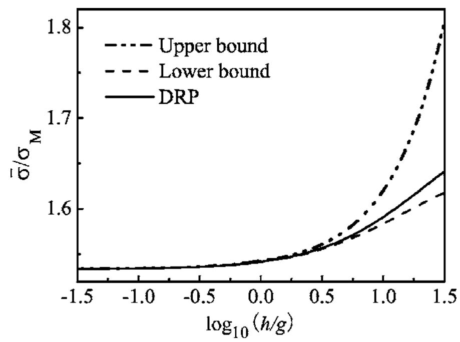

FIG. 5. Bounds and DRP prediction of the normalized effective conductivity $\bar{\sigma}/\sigma_M$ of a heterogeneous medium containing graded anisotropic spherical particles with a linear conductivity profile $\sigma_{rrP}(r)=\sigma(0)+gr$, $\sigma_{\theta\theta P}(r)=\sigma(0)+hr$ $(\sigma(0)=10\sigma_M, g=\sigma_M, f_R=0.2)$.

$$\bar{\sigma} \geqslant \frac{1}{\bar{\rho}_0 + B'_P(y)}, \tag{35}$$

in which

$$\begin{aligned} B'_P(y) &= \frac{f_R}{(\mathbf{J}^b \cdot \mathbf{J}^b)} \langle \mathbf{J}_0 \cdot \Delta\boldsymbol{\rho} \cdot \mathbf{J}_0 \rangle_P \\ &= \frac{1}{(\mathbf{J}^b \cdot \mathbf{J}^b)} \{ f_{PP} \langle \mathbf{J}_0^P \cdot \Delta\boldsymbol{\rho} \cdot \mathbf{J}_0^P \rangle_{PP} \\ &\quad + f_{PM} \langle \mathbf{J}_0^M \cdot \Delta\boldsymbol{\rho} \cdot \mathbf{J}_0^M \rangle_{PM} \}. \end{aligned} \tag{36}$$

In Eqs. (35) and (36), $\bar{\rho}_0$ $(\bar{\rho}_0 = 1/\bar{\sigma}^0)$, $\mathbf{J}_0$, and $\bar{\sigma}^0$ are all functions of y, and $\bar{\sigma}^0$, $\mathbf{J}_0^P$, and $\mathbf{J}_0^M$ are given in Eqs. (21), (24), and (25). Let y vary between 0 and r_P to give the maximum of the quantity on the right side of Eq. (35), then the lower bound $\bar{\sigma}_{\text{low}}$ on $\bar{\sigma}$ is obtained,

$$\bar{\sigma}_{\text{low}} = \max_{(0 \leqslant y \leqslant r_P)} \left\{ \frac{\bar{\sigma}^0(y)}{1 + \bar{\sigma}^0(y) B'_P(y)} \right\}. \tag{37}$$

We compare the bounds and the DRP prediction of the normalized effective conductivity $\bar{\sigma}/\sigma_M$ of a heterogeneous medium containing graded anisotropic spherical particles with a linear conductivity profile $\sigma_{rrP}(r)=\sigma(0)+gr$, $\sigma_{\theta\theta P}(r)=\sigma(0)+hr$, where $\sigma(0)$, g, and h are constants. Figure 4 shows the variation of the normalized effective conductivity $\bar{\sigma}/\sigma_M$ with $\sigma(0)/\sigma_M$ for two values of f_R. It is seen that the DRP prediction always lies within the optimized upper and lower bounds, and the three curves are indistinguishable when $\sigma(0)/\sigma_M > 10$. The normalized effective conductivity $\bar{\sigma}/\sigma_M$ as a function of $\log_{10}(h/g)$ is shown in Fig. 5. The DRP prediction also lies within the optimized upper and lower bounds, and the three curves are indistinguishable when $\log_{10}(h/g) < 0.25$.

VI. CONCLUSIONS

In this paper, we introduced comparison materials with homogeneous constituents to derive the optimized upper and lower bounds on the effective conductivities of heterogeneous media containing homogeneous but anisotropic particles with a graded anisotropic interphase or graded anisotropic particles. The effective conductivities of these heterogeneous media were also predicted using a differential replacement procedure (DRP). It is shown the DRP predictions are within the appropriate bounds for the considered materials. Therefore, the DRP can be regarded as a simple predictive scheme with good accuracy. Although the studies in this paper are for graded heterogeneous media with linear properties, the results can be useful in the study of the effective constitutive relations of nonlinear heterogeneous media following the theoretical framework based on the concept of *linear comparison materials*, as demonstrated, for example, in the work of Ponte Castañeda.10

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