New approximation for the effective energy of nonlinear conducting composites

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Approximations for the effective energy and, thus, effective conductivity of nonlinear, isotropic conducting dispersions are developed. This is accomplished by using the Ponte Castaneda variational principles [Philos. Trans. R. Soc. London Ser. A **340**, 1321 (1992)] and the Torquato approximation [J. Appl. Phys. **58**, 3790 (1985)] of the effective conductivity of corresponding linear composites. The results are obtained for dispersions with superconducting or insulating inclusions, and, more generally, for phases with a power-law energy. It is shown that the new approximations lie within the best available rigorous upper and lower bounds on the effective energy. © *1998 American Institute of Physics.* [S0021-8979(98)07913-4]

I. INTRODUCTION

This article considers the determination of the effective properties of nonlinear isotropic conducting composites made of two isotropic phases. The preponderance of previous work on estimating the effective conductivity of composites have treated cases in which the phases are linear conductors.[1–5] For linear, isotropic two-phase composites, Hashin and Shtrikman[2] found the best possible upper and lower bounds on the effective conductivity given only volume fraction information. By incorporating additional microstructural information, one can improve[1,3–5] upon the linear Hashin-Shtrikman bounds.

Bounding the effective properties of nonlinear composites is a much more difficult problem. Talbot and Willis[6] and Willis[7] suggested generalizations of the Hashin-Shtrikman variational method to include nonlinear composites. Talbot and Willis[8] used the new method to compute bounds on the effective properties of nonlinear heterogeneous dielectrics and compared them with self-consistent estimates. Ponte Castaneda[9,10] introduced a method that allows one to bound or approximate the effective properties of a nonlinear composite by using a bound or an approximation for the effective properties of a comparison composite with an identical microstructure but with linear constitutive relations.

The goal of the present article is to develop an approximation for the effective conductivity of nonlinear dispersions. This is done by applying an approach of Ponte Castaneda[9,10] that requires knowledge of the effective conductivity of a linear comparison material. Here we use an expression found for a linear material by Torquato.[11] This expression turns out to be useful in approximating the linear effective conductivity of dispersions.

The structure of the article is as follows: In Sec. II we introduce energy functions for the individual phases and the composite, and formulate a Dirichlet-type variational principle that describes the nonlinear conductor. In Sec. III we use the Ponte Castaneda[10] bounds on the effective properties of nonlinear composite conductors to derive general bounds on the effective energy of isotropic two-phase composites. Then we use the Torquato[11] approximation for the effective conductivity of a two-phase linear composite to approximate the effective energy of the composite made of two nonlinear conductors. In Sec. IV we study particular examples such as dispersions with superconducting or insulating inclusions, and two-phase composites with the phases characterized by a power-law dependence of the phase energy on the applied electrical field. In Sec. V, we make concluding remarks.

II. NONLINEAR CONDUCTORS: HOMOGENIZATION

Consider an isotropic conducting material and apply a constant electrical field $\mathbf{E}=-\nabla\varphi$, where φ is the electric potential. The energy dissipation in the isotropic material depends only on the magnitude E of the field $\mathbf{E}$ via the energy function $w(E)$. The current $\mathbf{J}$ is equal to the derivative of the energy with respect to the applied electrical field,

$$\mathbf{J}=\frac{\partial w(E)}{\partial \mathbf{E}}. \tag{1}$$

For a linear conductor, the energy is quadratic, $w(E)=\sigma E^2/2$, and the current is proportional to the applied field such that

$$\mathbf{J}=\sigma\mathbf{E}, \tag{2}$$

where the conductivity constant σ is independent of the applied field. For nonlinear media that we study here, the energy is not a quadratic function of the applied field. Correspondingly, relation (1) leads to Eq. (2), where the conductivity coefficient σ is a function of the applied field $\sigma=\sigma(\mathbf{E})$. This is precisely the case that we will study in this article.

Consider an isotropic composite made of N isotropic phases. We assume that the composite is periodic with Ω being the periodic cell, although all of the results can be easily proved in the random case as well assuming ergodicity of the microstructure. For such a composite, the local energy density function has the form

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$$W(\mathbf{x},E)=\sum_{i=1}^{N}\chi_i(\mathbf{x})w_i(E), \tag{3}$$

where $\mathbf{x}$ is the Cartesian coordinate of the point, and $\chi_i(\mathbf{x})$, $i=1,\ldots,N$ are the characteristic functions of the domains Ω_i occupied by the phase i, respectively. Here $w_i(E)$, $i=1,\ldots,N$ are the energy functions of the phases such that

$$w_i(E)\geqslant 0,\ \forall E,\ \ w_i(0)=0,\ \ i=1,\ldots,N. \tag{4}$$

We will assume that $w_i(E)$ $(i=1,\ldots,N)$ are continuous and convex functions of the field $\mathbf{E}$.

A homogenized system can be described[12,7] by the minimum energy principle that is analogous to the Dirichlet principle for a linear system. Specifically, the effective energy of the composite is given by

$$\hat{W}(\overline{\mathbf{E}})=\inf_{\substack{\mathbf{E}(\mathbf{x})\in\mathcal{E}_E\\ \langle\mathbf{E}(\mathbf{x})\rangle=\overline{\mathbf{E}}}}\langle W(\mathbf{x},E)\rangle, \tag{5}$$

where

$$\mathcal{E}_E=\{\mathbf{E}(\mathbf{x}):\mathbf{E}(\mathbf{x})\ \text{is}\ \Omega-\text{periodic},\quad \nabla\times\mathbf{E}(\mathbf{x})=0\}. \tag{6}$$

Here for any scalar or tensor variable $\mathbf{a}$, the angular brackets denote a volume average over the periodic cell or characteristic volume, i.e.,

$$\langle\mathbf{a}\rangle=\int_\Omega \mathbf{a}\,d\Omega \Big/ \int_\Omega d\Omega. \tag{7}$$

Our goal is to find bounds or approximations for the effective energy of Eq. (5).

III. BOUNDS AND APPROXIMATIONS ON THE EFFECTIVE ENERGY

Let us assume in addition that the functions $w_i(E)$ grow faster than quadratic functions of E. Specifically, we assume that

$$w_i(E)=f_i(r),\quad r=E^2,\quad f_i(r)\ \text{is convex},$$
$$i=1,\ldots,N. \tag{8}$$

For such a composite, Ponte Castaneda[10] proved a lower bound on the effective energy that we describe below. Let us introduce a linear comparison composite with a microstructure identical to the nonlinear composite, but made of isotropic phases with linear constitutive relations. Such a comparison composite can be described by the local conductivity function

$$\sigma^0(\mathbf{x})=\sum_{i=1}^{N}\chi_i(\mathbf{x})\sigma_i^0, \tag{9}$$

and has an effective energy

$$\hat{W}^0(\overline{\mathbf{E}})=\inf_{\substack{\mathbf{E}(\mathbf{x})\in\mathcal{E}_E\\ \langle\mathbf{E}(\mathbf{x})\rangle=\overline{\mathbf{E}}}}\left\langle\frac{1}{2}\sum_{i=1}^{N}\chi_i(\mathbf{x})\sigma_i^0E^2(\mathbf{x})\right\rangle. \tag{10}$$

Linear materials have been well-studied, and we will assume that we either have an approximation or a bound on the effective energy $\hat{W}^0(\overline{\mathbf{E}})$ of the linear material. Then the following Theorem holds:[10]

Theorem: The effective energy function $\hat{W}(\overline{\mathbf{E}})$ of the nonlinear conductor satisfies the inequality

$$\hat{W}(\overline{\mathbf{E}})\geqslant\max_{\sigma_i^0>0,\,i=1,\ldots,N}\left\{\hat{W}^0(\overline{\mathbf{E}})-\sum_{i=1}^{N}\phi_i v_i(\sigma_i^0)\right\}, \tag{11}$$

where $\hat{W}^0(\overline{\mathbf{E}})$ is the effective energy function of a linear comparison composite with phase conductivities σ_i^0, ϕ_i are the volume fractions of phases, and the functions $v_i(\sigma_i^0)$ are given by the relations

$$v_i(\sigma_i^0)=\sup_E\{w_i^0(E)-w_i(E)\},\quad i=1,\ldots,N. \tag{12}$$

Now we summarize an approach[10] concerning the evaluation of the bound of Eq. (11) for a specific form of the effective energy of the linear comparison material. In the rest of the paper, we study two-phase composites, i.e., $N=2$.

Let assume that the energy of the d-dimensional two-phase, linear comparison composite is approximated (or bounded) by the expression

$$\hat{W}^0(\overline{\mathbf{E}})=\tfrac{1}{2}\sigma_e^0\overline{E^2}, \tag{13}$$

where

$$\sigma_e^0=\phi_1\sigma_1^0+\phi_2\sigma_2^0-\frac{\phi_1\phi_2(\sigma_1^0-\sigma_2^0)^2}{\phi_2\sigma_1^0+\phi_1\sigma_2^0+(d-1)Y_0}. \tag{14}$$

Here Y_0 may be either constant or be a function of the type

$$Y_0=\zeta_1\sigma_1^0+\zeta_2\sigma_2^0-\frac{\zeta_1\zeta_2(\sigma_1^0-\sigma_2^0)^2}{\zeta_2\sigma_1^0+\zeta_1\sigma_2^0+Z_0/(d-1)} \tag{15}$$

with Z_0 being yet another constant. Many known bounds on the effective properties of two-phase linear composites can be presented in the forms of Eqs. (13)–(15). In particular, the arithmetic-mean upper bound (the Voigt bound) corresponds to $Y_0=\infty$. The harmonic-mean lower bound (the Reuss bound) corresponds to $Y_0=0$. The Hashin-Shtrikman[2] lower and upper bounds on the effective conductivity of the d-dimensional, two-phase conductor are given by Eq. (14), where $Y_0=\sigma_{\min}^0$ and $Y_0=\sigma_{\max}^0$, respectively ($\sigma_{\min}^0$ and $\sigma_{\max}^0$ are the minimal and maximal of the phase conductivities). The Beran[1] lower and upper three-point bounds are given by the expressions of Eqs. (14) and (15) with $Z_0=0$ and $Z_0=\infty$, respectively, and $\zeta_1=1-\zeta_2$ being the third-order geometrical parameters.[1,3,4] Finally, Milton's three-point bounds[3,4] are given by (14)-(15) where $Z_0=\sigma_{\min}^0$ for the lower bound for any d, $Z_0=\sigma_{\max}^0$ for the upper bound in two dimensions, and $Z_0=\infty$ for the upper bound if $d\geqslant 3$.

Torquato[11] derived an approximation for the effective

properties of the dispersions. Specifically, he showed that the effective conductivity of a d-dimensional dispersion (where phase 1 and phase 2 are the matrix and dispersed phases, respectively) is described with high accuracy by the formulas (14) and (15) where

$$Z_0 = B\sigma_1 \tag{16}$$

with the constant

$$B = (d-1)\frac{(d-1)-\zeta_2}{1-(d-1)\zeta_2} \tag{17}$$

independent of the phase properties. The Torquato approximation [Eqs. (14)–(17)] is accurate for a wide range of phase volume fractions and conductivities provided that the particles do not form large clusters.

Another advantage of the linear comparison material with the effective properties in Eqs. (14) and (15) is that the bound of Eq. (11) with the effective energy of the comparison material given by Eqs. (13)–(15) can be greatly simplified by using the procedure developed by Ponte Castaneda.[10] Specifically, this method yields the following approximation for the effective energy $\hat{W}(\overline{\mathbf{E}}) = \hat{w}(\overline{E})$ of nonlinear isotropic dispersions:

$$\hat{w}(\overline{E}) = \min_{\omega,\gamma}[\,\phi_2 w_2(\sqrt{(1+\phi_1\omega)^2 + (d-1)\phi_1\zeta_2\omega^2(1+\zeta_1\gamma)^2}\,\overline{E}) + \phi_1 w_1(\sqrt{(1-\phi_2\omega)^2 + (d-1)\phi_2\zeta_1\omega^2(1-\zeta_2\gamma)^2 + B\phi_2\zeta_1\zeta_2\omega^2\gamma^2}\,\overline{E})\,]. \tag{18}$$

Here we need to perform an optimization over only two scalar parameters $\omega \in (-\infty,\infty)$ and $\gamma \in (-\infty,\infty)$. This can be done either analytically (if the energy functions of the nonlinear phases are sufficiently simple), or numerically. One cannot proceed further without specifying the phase energy functions. We consider several specific examples below.

IV. EXAMPLES

In this section we will apply the formulas developed in the previous section to a number of specific examples. In particular, we consider superconducting inclusions, insulating inclusions, and cases with finite phase conductivities.

A. Superconducting inclusions

Let us assume that the dispersed phase 2 is a superconductor, i.e.,

$$w_2(E) = \begin{cases} 0, & \text{if} \quad E = 0; \\ \infty, & \text{if} \quad E \neq 0. \end{cases} \tag{19}$$

In such a case, the right-hand side of Eq. (18) is equal to infinity unless the argument of the function w_2 is equal to zero, i.e.,

$$\overline{E}\sqrt{(1+\phi_1\omega)^2 + (d-1)\phi_1\zeta_2\omega^2(1+\zeta_1\gamma)^2} = 0. \tag{20}$$

This defines the optimal values of the parameters ω and γ as

$$\omega = -1/\phi_1, \quad \gamma = -1/\zeta_1. \tag{21}$$

Then the energy of the composite is approximated by the expression

$$\hat{w}(\overline{E}) = \phi_1 w_1\left(\sqrt{\frac{\zeta_1 + (d-1)\phi_2 + B\phi_2\zeta_2}{\zeta_1\phi_1^2}}\,\overline{E}\right). \tag{22}$$

In particular, for a matrix made of a material with the power-law energy function

$$w_1(E) = \frac{1}{n}\sigma_1 E^n, \tag{23}$$

the effective energy is equal to

$$\hat{w}(\overline{E}) = \frac{1}{n}\sigma_e^{\sup}\overline{E}^n, \qquad \frac{\sigma_e^{\sup}}{\sigma_1} = \phi_1\left[\frac{\zeta_1 + (d-1)\phi_2 + B\phi_2\zeta_2}{\zeta_1\phi_1^2}\right]^{n/2}. \tag{24}$$

Figure 1 shows the dependence of the parameter $\sigma_e^{\sup}$ on the volume fraction of the dispersed phase 2 for a random equilibrium array of nonoverlapping spherical inclusions ($d=3$) for $n=2$ (linear material), $n=3$, and $n=5$. Such a

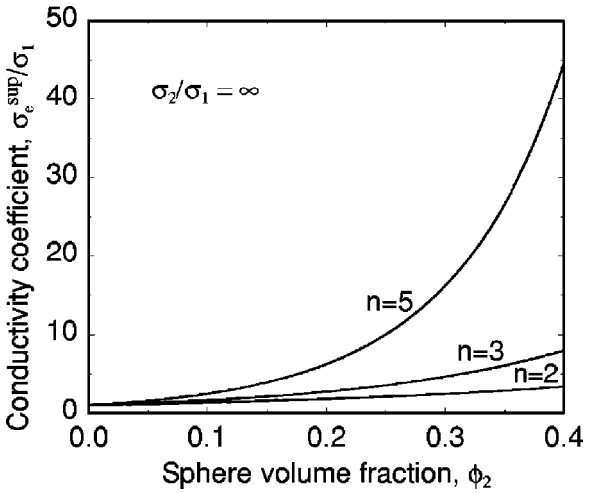

FIG. 1. Dimensionless conductivity coefficient $\sigma_e^{\sup}/\sigma_1$ vs the particle volume fraction ϕ_2 for random equilibrium arrays of spherical superconducting inclusions in a matrix with a power-law energy for several values of the exponent as obtained from Eq. (24).

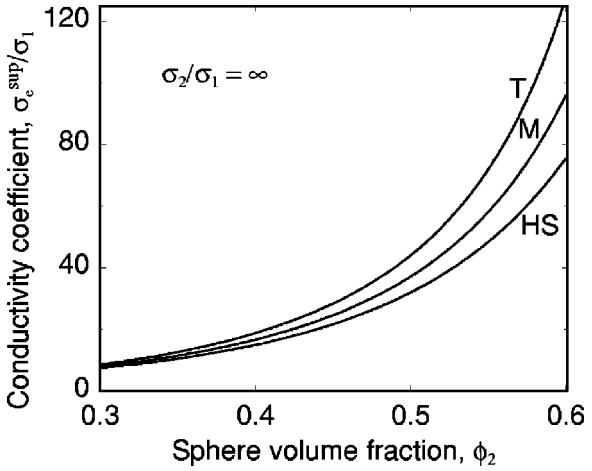

FIG. 2. Dimensionless conductivity coefficient $\sigma_e^{\sup}/\sigma_1$ vs the particle volume fraction ϕ_2 for random equilibrium arrays of spherical superconducting inclusions in a matrix with a quartic energy. Here T is the approximation obtained from Eq. (24) based on the Torquato (see Ref. 11) formula, M is the three-point lower bound based on the Milton (see Ref. 3) linear bound, and HS is the two-point bound based on the Hashin-Shtrikman (see Ref. 2) bound for the linear comparison material.

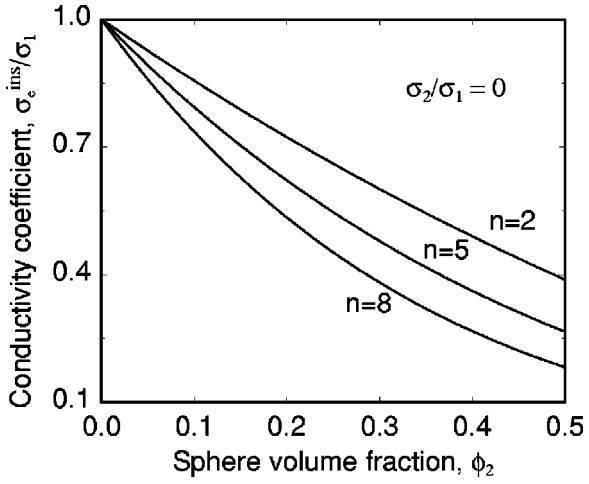

FIG. 3. Dependence of the dimensionless conductivity coefficient $\sigma_e^{\text{ins}}/\sigma_1$ vs the particle volume fraction ϕ_2 for random equilibrium arrays of spherical insulating inclusions in a matrix with a power-law energy for several values of the exponent as obtained from Eq. (30).

composite is isotropic by construction, and the geometrical parameter ζ_2 can be expressed as a function of the volume fraction as follows:[5]

$$\zeta_2 = 0.21068\phi_2 - 0.04693\phi_2^2. \tag{25}$$

It is noteworthy that dimensionless effective conductivity coefficient $\sigma_e^{\sup}/\sigma_1$ rapidly increases with the exponent n.

Figure 2 compares our new approximation with rigorous bounds for the power-law matrix material of Eq. (23) with $n=4$ and superconducting inclusions. One can see that the new approximation (curve T) lies above the lower three-point bound of Milton (curve M). For purposes of comparison, we also computed the lower Hashin-Shtrikman bound (curve HS). We see that the approximation based on the Torquato[11] formula satisfies rigorous two- and three-point bounds.

B. Insulating inclusions

Let us now evaluate the estimates of Eq. (18) on the effective energy of the composite of the same structure and matrix phase but with perfectly insulating inclusions when

$$w_2(E)=0, \quad \forall E. \tag{26}$$

In this case, the optimal values of the parameter ω and γ are those that minimize the argument

$$\sqrt{(1-\phi_2\omega)^2+(d-1)\phi_2\zeta_1\omega^2(1-\zeta_2\gamma)^2+B\phi_2\zeta_1\zeta_2\omega^2\gamma^2}\overline{E} \tag{27}$$

of the function $w_1(E)$ in Eq. (18). They are equal to

$$\omega=\frac{(d-1)\zeta_2+B}{(d-1)(\phi_2\zeta_2+B\zeta_1)+B\phi_2}, \quad \gamma=\frac{(d-1)}{(d-1)\zeta_2+B}. \tag{28}$$

Then the energy of the composite is approximated by the expression

$$\hat{w}(\overline{E})=\phi_1 w_1\left(\sqrt{\frac{(d-1)B\zeta_1}{(d-1)(\zeta_2\phi_2+B\zeta_1)+B\phi_2}}\overline{E}\right). \tag{29}$$

For a power-law matrix phase characterized by Eq. (23), the effective energy is given by

$$\hat{w}(\overline{E})=\frac{1}{n}\sigma_e^{\text{ins}}\overline{E^n}, \qquad \frac{\sigma_e^{\text{ins}}}{\sigma_1}=\phi_1\left[\frac{(d-1)B\zeta_1}{(d-1)(\zeta_2\phi_2+B\zeta_1)+B\phi_2}\right]^{n/2}. \tag{30}$$

Figure 3 illustrates the dependence of the coefficient σ_e^{ins} on the volume fraction of phase 2 for $n=2$, $n=5$, and $n=8$. Unlike the superconducting case, the dimensionless conductivity coefficient $\sigma_e^{\text{ins}}/\sigma_1$ decreases with the exponent n. We note also that it satisfies rigorous three-point upper bounds.

C. Two phases with a power-law energy

Now we turn our attention to the more general problem of a two-phase composite with finite phase conductivities. We evaluate the expressions (18) for the effective energy of a composite with phase energies given by

$$w_1(E)=\frac{1}{n}\sigma_1 E^n, \quad w_2(E)=\frac{1}{n}\sigma_2 E^n. \tag{31}$$

It is known that the effective energy has the same power-law behavior

$$\hat{w}(\overline{E})=\frac{1}{n}\sigma_e\overline{E^n}. \tag{32}$$

However, in this case, the optimal values of the parameters ω and γ cannot be found analytically and therefore we find them numerically.

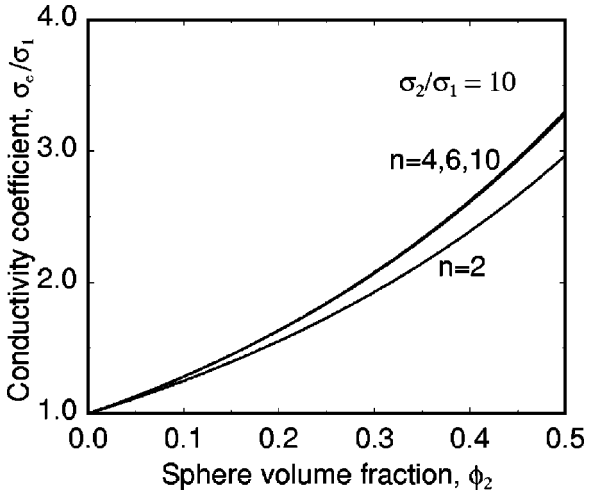

FIG. 4. Dimensionless conductivity coefficient σ_e/σ_1 vs the particle volume fraction ϕ_2 for random equilibrium arrays of spherical inclusions for materials with a power-law energy and $\sigma_2/\sigma_1=10$ for several values of the exponent as obtained from Eq. (18). Plots for $n=4$, 6, and 10 are indistinguishable on the scale of the figure.

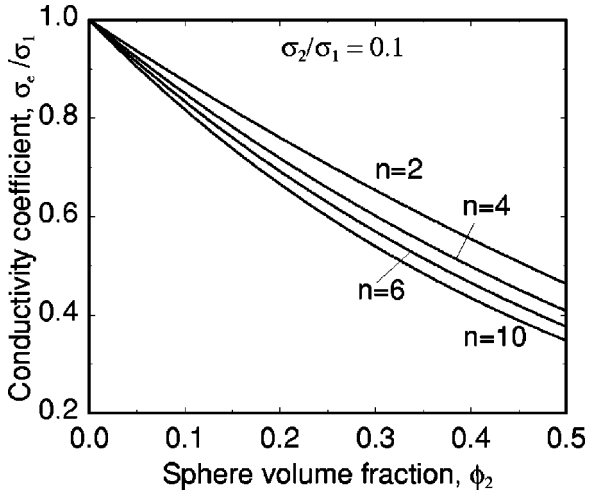

FIG. 5. Dimensionless conductivity coefficient σ_e/σ_1 vs the particle volume fraction ϕ_2 for random equilibrium arrays of spherical inclusions for materials with a power-law energy and $\sigma_2/\sigma_1=0.1$ for several values of the exponent as obtained from Eq. (18).

Figure 4 gives the dependence of the coefficient σ_e on the volume fraction of phase 2 for the phase contrast ratio

$$\sigma_2/\sigma_1=10 \tag{33}$$

and $n=2$, $n=4$, $n=6$, and $n=10$. Corresponding plots for the phase contrast ratio

$$\sigma_2/\sigma_1=0.1 \tag{34}$$

are shown in Fig. 5.

Similar to the limiting cases illustrated by Figs. 1 and 3, the dimensionless conductivity coefficient σ_e/σ_1 increases with the exponent n if the dispersed particles are more conducting than the matrix, and decreases with n if the conductivity of the dispersed particles is smaller than that of the matrix.

V. CONCLUSIONS

In this article we developed a new approximation for the effective conductivity of nonlinear isotropic dispersions. For power-law materials, the dimensionless conductivity coefficient σ_e/σ_1 increases with the exponent n if the dispersed particles are more conducting than the matrix, and decreases with n if the dispersed particles are less conducting than the matrix. For finite ratio of the phase properties, the dimensionless effective conductivity constant σ_e/σ_1 for conducting inclusions very weakly depends on the exponent n if $n \geqslant 4$ as can be seen in Fig. 4. For the cases considered, our approximation lies within the best available rigorous bounds on the effective energy.

ACKNOWLEDGMENTS

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