Effective conductivity of anisotropic two-phase composite media

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We derive a new perturbation expansion for the effective conductivity tensor σ_e of a macroscopically anisotropic d-dimensional two-phase composite of arbitrary microstructure. The nth-order tensor coefficients $A_n^{(i)}$ of the expansion (termed n-point microstructural parameters) are given explicitly in terms of integrals over the set of n-point probability functions (associated with the ith phase) which statistically characterize the microstructure. Macroscopic anisotropy arises out of some asymmetry in the microstructure, i.e., due to statistical anisotropy (e.g., a distribution of oriented, nonspherical inclusions in a matrix, layered media, such as sandstones and laminates, etc.). General and useful properties of the n-point microstructural parameters are established, and contact is made with the formal results of Milton. We then derive rigorous nth-order bounds on σ_e (from our perturbation expansion) that depend upon the n-point parameters $A_n^{(i)}$ for $n=1$, 2, 3, and 4. This is the first time that such bounds (for $n>1$) have been explicitly given in terms of the $A_n^{(i)}$.

I. INTRODUCTION

The problem of relating the macroscopic properties of a material to its microstructure is a classical one in physics. The determination of the effective electrical conductivity tensor σ_e of a random d-dimensional two-phase composite medium is the focus of this article. For reasons of mathematical analogy, the results of this study translate immediately into equivalent results for the effective thermal conductivity, dielectric constant, diffusion coefficient, and magnetic permeability tensors of such composites.

For macroscopically isotropic two-phase composites (i.e., $\sigma_e=\sigma_e U$), considerable advances in predicting σ_e have been made since the pioneering paper of Brown[1] in which it was shown that σ_e depends upon an infinite set of correlation functions that statistically characterize the composite. Rigorous techniques employed to attack this problem include bounding methods,[2–7] cluster expansions,[8] and perturbation expansions;[9] see also the recent review article by Torquato.[10]

The determination of the conductivity tensor σ_e for the more complicated case of a macroscopically anisotropic composite (e.g., oriented nonspherical inclusions, layered media, etc.) has been less extensively studied. Hori[11] developed perturbation expansions and bounds for σ_e. These results, however, have some undesirable features as described below. Willis[12] derived bounds on σ_e for composites containing aligned, ellipsoidal inclusions which depend upon the microstructure via the shape of the inclusions and volume fraction only. More recent work includes the development of Hashin-Shtrikman–type bounds by Kohn and Milton[13] and the mathematically rigorous and elegant continued-fractions approach to bounds of Milton;[14] see also references contained therein.

In this study we derive a new perturbation expansion for the conductivity tensor σ_e of a macroscopically anisotropic d-dimensional two-phase composite of arbitrary microstructure. The nth-order tensor coefficients $A_n^{(i)}$ of the expansion (termed n-point microstructural parameters) are given explicitly in terms of the set of n-point probability functions $S_1^{(i)},\ldots,S_n^{(i)}$ of the medium. The quantity $S_n^{(i)}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$ gives the probability of finding n points at positions $\mathbf{r}_1,\ldots,\mathbf{r}_n$, respectively, simultaneously in phase i ($i=1,2$). General and useful properties of the n-point microstructural parameters are established and contact is made with the formal results of Milton. We then derive rigorous nth-order bounds on σ_e that depend upon the n-point parameters $A_n^{(i)}$ for $n=1$, 2, 3, and 4. This is the first time that such bounds (for $n>1$) have been explicitly given in terms of the $A_n^{(i)}$.

II. PERTURBATION EXPANSION OF σ_e FOR ARBITRARY DIMENSIONALITY

Consider deriving a perturbation expansion for the effective electrical conductivity tensor σ_e of a random two-phase d-dimensional composite medium which is macroscopically homogeneous but anisotropic. The method we use to obtain such an expansion follows one given by Torquato[9] for d-dimensional isotropic composites which generalizes an approach due to Brown[1] for three-dimensional (3D) isotropic media. The composite medium is a domain of space D of d-dimensional volume V which is subdivided into two phases: one phase D_1, characterized by volume fraction ϕ_1 and isotropic conductivity σ_1, and another phase D_2, characterized by a volume fraction ϕ_2 and isotropic conductivity σ_2. The lo-

cal conductivity at position $\mathbf{r}$ is given by the scalar function

$$\sigma(\mathbf{r})=\sigma_j+(\sigma_i-\sigma_j)I^{(i)}(\mathbf{r}),\quad i\neq j\ , \tag{2.1}$$

where the characteristic function of phase i is

$$I^{(i)}(\mathbf{r})=\begin{cases}1, & \mathbf{r}\in D_i\\ 0, & \text{otherwise}\ .\end{cases} \tag{2.2}$$

As indicated above, each phase is isotropic and hence macroscopic anisotropy arises out of some asymmetry in the microstructure, i.e., due to statistical anisotropy (e.g., a distribution of oriented nonspherical inclusions in a matrix, layered media, such as sandstones and laminates, etc.).

We take the sample, for purposes of generality, to be a d-dimensional ellipsoid of finite size and shape. Consider subjecting it to the time-independent applied electric field $\mathbf{E}_0(\mathbf{r})$. The solution of Maxwell's electrostatic equations for this situation may be formally expressed as an integral equation using the Green's function for the Maxwell electric field $\mathbf{E}(\mathbf{r})$:[9]

$$\mathbf{E}_L(\mathbf{r})=\mathbf{E}_0(\mathbf{r})+\int_\delta d\mathbf{r}'\mathsf{T}^{(j)}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{P}(\mathbf{r}')\ , \tag{2.3}$$

where the "Lorentz electric field" $\mathbf{E}_L(\mathbf{r})$ is related to the Maxwell field by

$$\mathbf{E}_L(\mathbf{r})=\left[1+\frac{[\sigma(\mathbf{r})-\sigma_j]}{\sigma_j d}\right]\mathbf{E}(\mathbf{r}) \tag{2.4}$$

and $\mathbf{P}(\mathbf{r})$ is the induced polarization field (relative to the medium in the absence of material i) given by

$$\mathbf{P}(\mathbf{r})=\frac{[\sigma(\mathbf{r})-\sigma_j]}{2(d-1)\pi}\mathbf{E}(\mathbf{r})\ . \tag{2.5}$$

Moreover,

$$\mathsf{T}^{(j)}(\mathbf{r})\equiv\frac{1}{\sigma_j}\mathsf{t}=\frac{d\,\mathbf{r}\,\mathbf{r}-r^2\mathsf{U}}{\sigma_j r^{d+2}}\ , \tag{2.6}$$

appearing in Eq. (2.3), is the dipole-dipole interaction tensor, where $r=|\mathbf{r}|$ and U is the unit dyadic. The subscript δ on the integral of Eq. (2.3) (which is to be integrated over the sample volume V) indicates that it is carried out with the exclusion of an infinitesimally small d-dimensional sphere centered at $\mathbf{r}$. Combining Eqs. (2.4) and (2.5) gives

$$\mathbf{P}(\mathbf{r})=\frac{\sigma_j d}{2(d-1)\pi}\left[\frac{\sigma(\mathbf{r})-\sigma_j}{\sigma(\mathbf{r})+(d-1)\sigma_j}\right]\mathbf{E}_L(\mathbf{r})$$

$$=\frac{\sigma_j d}{2(d-1)\pi}\beta_{ij}I^{(i)}(\mathbf{r})\mathbf{E}_L(\mathbf{r}),\quad i\neq j\ , \tag{2.7}$$

where

$$\beta_{ij}=\frac{\sigma_i-\sigma_j}{\sigma_i+(d-1)\sigma_j} \tag{2.8}$$

is a parameter bounded by $-(d-1)^{-1}\leq\beta_{ij}\leq 1$ and, apart from a trivial constant, is equal to the dipole polarizability of a d-dimensional sphere of conductivity σ_i embedded in a matrix of conductivity σ_j. The second line of Eq. (2.7) results when Eq. (2.1) is substituted into the first line.

The effective conductivity $\boldsymbol{\sigma}_e$ of the composite medium, a symmetric second-rank tensor, is defined through the averaged relation

$$\langle\mathbf{P}(\mathbf{r})\rangle=\frac{\sigma_j d}{2(d-1)\pi}[\boldsymbol{\sigma}_e+(d-1)\sigma_j\mathsf{U}]^{-1}$$

$$\times(\boldsymbol{\sigma}_e-\sigma_j\mathsf{U})\langle\mathbf{E}_L(\mathbf{r})\rangle\ , \tag{2.9}$$

where angular brackets denote an ensemble average. This definition of $\boldsymbol{\sigma}_e$ is equivalent to the one derived from $\langle\sigma(\mathbf{r})\mathbf{E}(\mathbf{r})\rangle=\boldsymbol{\sigma}_e\cdot\langle\mathbf{E}(\mathbf{r})\rangle$, i.e., the averaged form of Ohm's law.

Following Torquato,[9] an integral equation for the local polarization $\mathbf{P}(\mathbf{r})$ is obtained by combining Eqs. (2.3) and (2.7). The integral equation is solved for $\mathbf{P}(\mathbf{r})$ by successive substitutions, resulting in an expansion in powers of β_{ij}, which formally may be expressed as an operator acting on the applied field $\mathbf{E}_0(\mathbf{r})$. This relation between $\mathbf{P}(\mathbf{r})$ and $\mathbf{E}_0(\mathbf{r})$ is then averaged. As is well known from electrostatics, relations between average fields [such as $\langle\mathbf{P}(\mathbf{r})\rangle$] and $\mathbf{E}_0(\mathbf{r})$ are dependent upon the shape of the sample. Accordingly, one inverts the series for $\langle\mathbf{P}(\mathbf{r})\rangle$ in terms of $\mathbf{E}_0(\mathbf{r})$ and then eliminates $\mathbf{E}_0(\mathbf{r})$ using the average of Eq. (2.3). This resulting relation between $\langle\mathbf{P}(\mathbf{r})\rangle$ and $\langle\mathbf{E}_L(\mathbf{r})\rangle$ is localized, i.e., independent of the shape of the sample and hence involves absolutely convergent integrals. Thus one may pass to the limit of an infinite volume without any ambiguity and obtain from this localized relation, which defines $\boldsymbol{\sigma}_e$ [Eq. (2.9)], a perturbation expansion for $\boldsymbol{\sigma}_e$ of macroscopically anisotropic two-phase media of arbitrary microstructure.

The expansion which results after employing this methodology is given by

$$(\beta_{ij}\phi_i)^2(\boldsymbol{\sigma}_e-\sigma_j\mathsf{U})^{-1}[\boldsymbol{\sigma}_e+(d-1)\sigma_j\mathsf{U}]$$

$$=\phi_i\beta_{ij}\mathsf{U}-\sum_{n=2}^{\infty}\mathsf{A}_n^{(i)}\beta_{ij}^n,\quad i\neq j\ , \tag{2.10}$$

where the tensor coefficients $\mathsf{A}_n^{(i)}$ are integrals over a set of n-point probability functions associated with the phase i: for $n=2$,

$$\mathsf{A}_2^{(i)}=\frac{d}{2\pi(d-1)}\int_\delta d\mathbf{r}\,\mathsf{t}(\mathbf{r})[S_2^{(i)}(\mathbf{r})-\phi_i^2] \tag{2.11a}$$

and for $n\geq 3$,

$$\mathsf{A}_n^{(i)}=(-1)^n\phi_i^{2-n}\left[\frac{d}{2\pi(d-1)}\right]^{n-1}$$

$$\times\int\int\cdots\int d\mathbf{r}_2 d\mathbf{r}_3\cdots d\mathbf{r}_n$$

$$\times\mathsf{t}(1,2)\cdot\mathsf{t}(2,3)\cdots\mathsf{t}(n-1,n)$$

$$\times C_n^{(i)}(1,2,\ldots,n)\ , \tag{2.11b}$$

where scaled tensors $\mathsf{t}(i,j)$ [defined by (2.6)] stand for $\mathsf{t}(\mathbf{r}_i-\mathbf{r}_j)$ and $C_n^{(i)}$ is the determinant[9] given by

$$C_n^{(i)}=\begin{vmatrix} S_2^{(i)}(1,2) & S_1^{(i)}(2) & 0 & \cdots & 0 & 0 \\ S_3^{(i)}(1,2,3) & S_2^{(i)}(2,3) & S_1^{(i)}(3) & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \cdots & \vdots & \vdots \\ S_{n-1}^{(i)}(1,\ldots,n-1) & S_{n-2}^{(i)}(2,\ldots,n-1) & S_{n-3}^{(i)}(3,\ldots,n-1) & \cdots & S_2^{(i)}(n-2,n-1) & S_1^{(i)}(n-1) \\ S_n^{(i)}(1,\ldots,n) & S_{n-1}^{(i)}(2,\ldots,n) & S_{n-2}^{(i)}(3,\ldots,n) & \cdots & S_3^{(i)}(n-2,n-1,n) & S_2^{(i)}(n-1,n) \end{vmatrix} . \tag{2.12}$$

Here the n-point probability function[15]

$$S_n^{(i)}(1,2,\ldots,n)=S_n^{(i)}(\mathbf{r}_{12},\mathbf{r}_{23},\ldots,\mathbf{r}_{1n}) \equiv\langle I^{(i)}(\mathbf{r}_1)I^{(i)}(\mathbf{r}_2)\cdots I^{(i)}(\mathbf{r}_n)\rangle \tag{2.13}$$

gives the probability of finding n points with positions $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n$ all in phase i. In (2.13) we have used the fact that the medium is statistically anisotropic but homogeneous, i.e., the $S_n^{(i)}$ depend upon the relative displacements $\mathbf{r}_{ij}=\mathbf{r}_j-\mathbf{r}_i$.

Clearly, the one-point function $S_1^{(i)}$ is simply the volume fraction of phase i, i.e., ϕ_i. Since the quantity within the brackets of (2.11a) and the determinant $C_n^{(i)}$ identically vanish at the boundary of the sample, because of the asymptotic properties of the $S_n^{(i)}$ (see Ref. 15), the integrals in (2.11) are shape independent, and hence any convenient shape (such as a sphere for $d=3$ or circular disk for $d=2$) may be employed for the (infinite) domain of integration. Moreover, the limiting process of excluding an infinitesimally small cavity about $\mathbf{r}_{ij}=0$ in the integrals (2.11b) is no longer necessary since $C_n^{(i)}$ again is identically zero for such values. We refer to the symmetric tensor coefficients $\mathsf{A}_n^{(i)}$ [given by (2.11)], which depend upon the set $S_1^{(i)},\ldots S_n^{(i)}$, as n-point microstructural parameters or integrals. The n-point tensors $\mathsf{A}_n^{(i)}$ ($n=2,3,\ldots$) generally will not possess common principal axes. This implies that for general media the principal axes of the macroscopic conductivity tensor $\boldsymbol{\sigma}_e$ will rotate as the phase conductivity ratio changes, such as composites with chirality, i.e., composites with some degree of left- or right-handed asymmetry.[13] Nonetheless, there exists a large class of media which has the symmetry required for all the $\mathsf{A}_n^{(i)}$ to possess common principal axes (e.g., a random distribution of oriented, identical ellipsoids or cylinders in a matrix); in such instances n-point tensor multiplication is commutative. Note that the lowest-order parameter, $\mathsf{A}_2^{(i)}$, depends upon the two-point correlation function. This is to be contrasted with the isotropic result in which the lowest-order parameter is the three-point parameter, i.e., $\mathsf{A}_2^{(i)}=0$.[9]

Perturbation expansion (2.10) for the anisotropic effective conductivity tensor $\boldsymbol{\sigma}_e$ of d-dimensional two-phase composites is new. It actually represents two series expansions, one for $i=1$ and $j=2$, and the other for $i=2$ and $j=1$. It is useful at this point to compare it to another perturbation expansion obtained by Hori.[11] First, Hori derived his series expression using a different approach and expansion parameter. Second, the coefficients of his expansion depend upon derivatives of the n-point correlation functions. In practice, one measures the correlation functions themselves, not their derivatives. One can, by integration by parts, reexpress Hori's integrals in terms of the correlation functions but such a procedure is already tedious for the analogous *isotropic* three-point parameter;[16,17] it becomes progressively harder to carry this out as the order of the n-point parameter increases. Our expansion enjoys the advantage of possessing coefficients $\mathsf{A}_n^{(i)}$ given by (2.11) which depend upon the correlation functions themselves. Third, unlike the n-point integrals $\mathsf{A}_n^{(i)}$, defined by (2.11), the corresponding integrals of Hori are generally conditionally convergent, i.e., they depend upon the shape of the macroscopic sample.

For some subsequent calculations it will be convenient to use the expansion of the effective conductivity tensor in powers of $\delta_{ij}=(\sigma_i-\sigma_j)/\sigma_j$. (Note that δ_{ij} is not the Kronecker delta.) Employing (2.10) we find through fourth order that

$$\frac{\boldsymbol{\sigma}_e}{\sigma_j}=\mathsf{U}+\mathsf{a}_1^{(i)}\delta_{ij}+\mathsf{a}_2^{(i)}\delta_{ij}^2+\mathsf{a}_3^{(i)}\delta_{ij}^3 +\mathsf{a}_4^{(i)}\delta_{ij}^4+O(\delta_{ij}^5),\quad i\neq j\ , \tag{2.14}$$

where

$$\mathsf{a}_1^{(i)}=\phi_i\mathsf{U}\ , \tag{2.15}$$

$$\mathsf{a}_2^{(i)}=\frac{1}{d}(\mathsf{A}_2^{(i)}-\phi_i\phi_j\mathsf{U})\ , \tag{2.16}$$

$$\mathsf{a}_3^{(i)}=\frac{1}{d^2}\left[\phi_j^2\phi_i\left[\mathsf{U}-\frac{\mathsf{A}_2^{(i)}}{\phi_i\phi_j}\right]^2+\mathsf{A}_3^{(i)}\right]\ , \tag{2.17}$$

and

$$\mathsf{a}_4^{(i)}=\frac{1}{d^3}\left[-\phi_i\phi_j^3\left[\mathsf{U}-\frac{1}{\phi_i\phi_j}\mathsf{A}_2^{(i)}\right]^3 -\phi_j\left[\mathsf{U}-\frac{1}{\phi_i\phi_j}\mathsf{A}_2^{(i)}\right]\cdot\mathsf{A}_3^{(i)} -\phi_j\mathsf{A}_3^{(i)}\cdot\left[\mathsf{U}-\frac{1}{\phi_i\phi_j}\mathsf{A}_2^{(i)}\right] -\mathsf{A}_3^{(i)}+\mathsf{A}_4^{(i)}\right]\ . \tag{2.18}$$

III. GENERAL PROPERTIES OF THE n-POINT MICROSTRUCTURAL PARAMETERS

Here we shall establish some general and useful properties of the n-point microstructural parameters $\mathsf{A}_n^{(i)}$. First,

we describe a general procedure which enables one to establish the relations between the n-point tensors in different phases and explicitly give these relations for $n=2$, 3, and 4. Second, we study some general tensor properties of the $\mathsf{A}_n^{(i)}$. Last, we examine those microstructures (isotropic or anisotropic) which produce macroscopic isotropy. In subsections A and B, we make contact with the formal results of Milton.[14]

A. Relations between the microstructural parameters in different phases

The n-point microstructural parameters associated with phases 1 and 2 are related to one another, i.e., $\mathsf{A}_n^{(1)}$ and $\mathsf{A}_n^{(2)}$ are dependent upon one another. To obtain the relations between the microstructural parameters, one first writes, using Eq. (2.10), two different perturbation series for σ_e, one with the phase 1 as the host material ($j=1$) and the other with the phase 2 as the host material ($j=2$), i.e., one obtains series such as (2.14). The fact that σ_e is invariant to such an interchange of the phases means that the $\mathsf{A}_n^{(1)}$ are related to the $\mathsf{A}_n^{(2)}$. For $n=2$, one very quickly obtains that

$$\mathsf{A}_2^{(1)}=\mathsf{A}_2^{(2)} . \tag{3.1}$$

After considerable algebra, one also finds that

$$\mathsf{A}_3^{(1)}+\mathsf{A}_3^{(2)}=(d-1)\phi_1\phi_2\mathsf{U}-(d-2)\mathsf{A}_2^{(1)} -\frac{1}{\phi_1\phi_2}\mathsf{A}_2^{(1)}\cdot\mathsf{A}_2^{(1)} , \tag{3.2}$$

and

$$\mathsf{A}_4^{(1)}-\mathsf{A}_4^{(2)}=(d-2)(\mathsf{A}_3^{(2)}-\mathsf{A}_3^{(1)})+\frac{1}{\phi_1\phi_2}\mathsf{A}_2^{(1)}\cdot\mathsf{A}_3^{(2)} -\frac{1}{\phi_1\phi_2}\mathsf{A}_3^{(1)}\cdot\mathsf{A}_2^{(1)} . \tag{3.3}$$

By employing the method described above, one may obtain similar relations for higher-order microstructural parameters. However, as remarked in Sec. IV on bounds, the determination of n-point probability functions, and hence the $\mathsf{A}_n^{(i)}$, for $n\geq 5$ is presently very difficult (either theoretically or experimentally) for general microstructures. Thus the three relations given above are the only ones of practical value.

Note that relations (3.1)–(3.3) are the anisotropic counterparts of the relations between the n-point parameters derived by Torquato[9] for the isotropic case (see discussion at the end of this section). Since the two-point parameters [according to Eq. (3.1)] are equal, we shall henceforth (in most cases) refer to them as simply A_2 without the superscript.

Milton[14] has employed the mathematically elegant formalism of continued fractions to obtain bounds on σ_e for multiphase composites. His treatment leads to a sequence of matrices which he refers to as weights $\mathsf{W}_n^{(i)}$ ($n=0,1,2,\ldots$) and normalization factors N_n ($n=1,2,3,\ldots$).[18] The weights and normalization factors formally depend upon the microgeometry. However, he does not express these matrices explicitly in terms of integrals over the n-point correlation functions. The $\mathsf{W}_n^{(i)}$ and N_n are, in fact, related to the $\mathsf{A}_n^{(i)}$ given here. One of the contributions of this paper will be to explicitly express lower-order $\mathsf{W}_n^{(i)}$ and N_n in terms of our n-point tensors $\mathsf{A}_n^{(i)}$ and thus explicitly express the former in terms of integrals involving the $S_n^{(i)}$. It turns out that the weights $\mathsf{W}_n^{(i)}$ depend upon the set $\phi_1,\mathsf{A}_2^{(i)},\mathsf{A}_3^{(i)},\ldots,\mathsf{A}_{2n+1}^{(i)}$ (and hence upon the set $S_2^{(i)},S_3^{(i)},\ldots,S_{2n+1}^{(i)}$) and the normalizations $\mathsf{N}_n^{(i)}$ depend upon the set $\phi_1,\mathsf{A}_2^{(i)},\mathsf{A}_3^{(i)},\ldots,\mathsf{A}_{2n}^{(i)}$ (and hence upon the set $S_2^{(i)},S_3^{(i)},\ldots,S_{2n}^{(i)}$. In other words, $\mathsf{W}_n^{(i)}$ and N_n depend upon the sets of the n-point parameters up to the odd-point parameter $\mathsf{A}_{2n+1}^{(i)}$ and even-point parameter $\mathsf{A}_{2n}^{(i)}$, respectively. Working in Hilbert spaces enabled Milton to deduce properties and relations involving the $\mathsf{W}_n^{(i)}$ and N_n without having to explicitly know the integral forms involving the correlation functions $S_n^{(i)}$. One such relation concerns the weights, which are given by

$$\sum_i \mathsf{W}_n^{(i)}=\mathsf{U}, \quad n\geq 0 . \tag{3.4}$$

Note that $\mathsf{W}_0^{(i)}$ trivially involves the volume fraction through the relation $\mathsf{W}_0^{(i)}=\phi_i\mathsf{U}$.

Of the relations (3.1)–(3.3) that we have derived, only (3.2) can be put in the form of (3.4). If we define the tensors

$$\mathsf{M}=(d-1)\phi_1\phi_2\mathsf{U}-(d-2)\mathsf{A}_2-\frac{1}{\phi_1\phi_2}\mathsf{A}_2\cdot\mathsf{A}_2 , \tag{3.5}$$

and

$$\zeta_i=\mathsf{M}^{-1/2}\mathsf{A}_3^{(i)}\mathsf{M}^{-1/2} , \tag{3.6}$$

and substitute into (3.2), we find

$$\zeta_1+\zeta_2=\mathsf{U} . \tag{3.7}$$

Thus, comparing (3.4) and (3.7) leads one to obtain the identification

$$\mathsf{W}_1^{(i)}=\zeta_i . \tag{3.8}$$

However, in order to complete the proof that $\mathsf{W}_1^{(i)}=\zeta_i$, one must show that ζ_i is positive semidefinite, as will be done shortly. Note that the analogues of (3.1) and (3.3) in terms of normalization factors and weights can be obtained using Milton's formalism.

B. Tensor properties

1. *Arbitrary dimensionality*

We now shall study some general tensor properties of the lower-order microstructural parameters. Along the way, we shall make the connection between $\mathsf{A}_2^{(i)}$, $\mathsf{A}_3^{(i)}$, and $\mathsf{A}_4^{(i)}$ and Milton's tensors N_1, $\mathsf{W}_1^{(i)}$, and N_2, and directly verify, for $n=1$, the tensor properties

$$\mathsf{W}_n^{(i)}\geq 0 \quad (n=0,1,\ldots) , \tag{3.9a}$$

$$\mathsf{N}_n\geq 0 \quad (n=1,2,\ldots) , \tag{3.9b}$$

which Milton obtained. By (3.9) we mean that both the weights and normalization factors are positive

semidefinite. As noted earlier, his weights and normalization factors are not given explicitly in terms of the microstructure, nonetheless, in the general and powerful formalism he employs, relations (3.9a) and (3.9b) arise naturally as constraints on the matrices.

Consider the perturbation expansion of σ_e in powers of δ_{ij}, i.e., expansion (2.14). Taking the second derivative of this expression with respect to σ_j and comparing to the iterative scheme of Milton gives

$$\mathsf{N}_1=-\mathsf{U}+d\left[\mathsf{U}-\frac{1}{\phi_1\phi_2}\mathsf{A}_2\right]^{-1} . \tag{3.10}$$

Milton has shown that N_1 has the additional property

$$\mathrm{tr}(\mathsf{U}+\mathsf{N}_1)^{-1}=1 . \tag{3.11}$$

Equation (3.11) can be shown very easily in our case by writing

$$(\mathsf{U}+\mathsf{N}_1)^{-1}=\frac{1}{d}\left[\mathsf{U}-\frac{1}{\phi_1\phi_2}\mathsf{A}_2\right] , \tag{3.12}$$

and by noting that $\mathrm{tr}(\mathsf{U})=d$ and $\mathrm{tr}(\mathsf{A}_2)=0$. The latter trace condition follows from Eq. (2.11a) showing the direct relationship of $\mathsf{A}_2^{(i)}$ to the traceless tensor $\mathsf{t}(\mathbf{r})$, Eq. (2.6).

Next, we consider bounding the elements of A_2 and explicitly proving the positive semidefiniteness of N_1. In order to do so, we introduce the intermediate quantity

$$\mathsf{A}_2^*=\frac{1}{2(d-1)\pi}\int_\delta d\mathbf{r}\,\nabla\left[\frac{1}{r}\right]\nabla\left[\frac{S_2(r)-\phi_2^2}{\phi_1\phi_2}\right] . \tag{3.13}$$

We refer to A_2^* as the "depolarization factor" tensor for reasons given in Sec. IV. Integrating (3.13) by parts and using (3.12) yields

$$\mathsf{A}_2^*=\frac{1}{d}\left[\mathsf{U}-\frac{1}{\phi_1\phi_2}\mathsf{A}_2\right]=(\mathsf{U}+\mathsf{N}_1)^{-1} . \tag{3.14}$$

Note that A_2^* is just the left-hand side of (3.12). That the depolarization factor tensor A_2^* is a symmetric matrix follows because A_2 is symmetric. From (3.11) and (3.14), one directly finds that $\mathrm{tr}(\mathsf{A}_2^*)=1$. Now using the method Torquato[16] employed to show the positivity property of the three-point parameter in the isotropic case, we may write the diagonalized form of A_2^* [denoted by $(A_2^*)_{ii}$] as

$$\begin{aligned}(A_2^*)_{ii}&=\frac{1}{4(d-1)^2\pi^2\phi_1\phi_2}\left[\int_\delta d\mathbf{r}\,\nabla\left[\frac{1}{r}\right]\frac{\partial I(\mathbf{r})}{\partial r_i}\right]^2\\ &\geq 0 \quad \text{(no sum implied)}\\ &=\frac{1}{d}\left[1-\frac{1}{\phi_1\phi_2}(A_2)_{ii}\right]\geq 0 ,\end{aligned} \tag{3.15}$$

where $I(\mathbf{r})$ is the characteristic function of either phase 1 or 2 [cf. (2.2)] and $(A_2)_{ii}$ denotes the diagonal elements of the diagonalized form of A_2. The second line of (3.15) follows from (3.14). Since $\mathrm{tr}(\mathsf{A}_2^*)=1$ and $(A_2^*)_{ii}\geq 0$, we also have the upper bound $(A_2^*)_{ii}\leq 1$. In summary,

$$0\leq(A_2^*)_{ii}\leq 1 . \tag{3.16}$$

This implies the bounds

$$-(d-1)\phi_1\phi_2\leq(A_2)_{ii}\leq\phi_1\phi_2 . \tag{3.17}$$

There are microgeometries which attain the extreme limits of (3.16) and (3.17). For example, for needle-shaped inclusions of infinitesimal cross section oriented along the third principal axis (see discussion in Sec. IV), we have

$$\begin{aligned}&(A_2^*)_{11}=(A_2^*)_{22}=\tfrac{1}{2},\quad (A_2^*)_{33}=0 ,\\ &(A_2)_{11}=(A_2)_{22}=\frac{-\phi_1\phi_2}{2},\quad (A_2)_{33}=\phi_1\phi_2 .\end{aligned} \tag{3.18}$$

For disk-shaped plates of infinitesimal thickness oriented such that the third principal axis is perpendicular to the plate (see discussion in Sec. IV), we have

$$\begin{aligned}&(A_2^*)_{11}=(A_2^*)_{22}=0,\quad (A_2^*)_{33}=1 ,\\ &(A_2)_{11}=(A_2)_{22}=\phi_1\phi_2,\quad (A_2)_{33}=-2\phi_1\phi_2 .\end{aligned} \tag{3.19}$$

In passing, we note that for spherical inclusions,

$$\begin{aligned}&(A_2^*)_{11}=(A_2^*)_{22}=(A_2^*)_{33}=\tfrac{1}{3} ,\\ &(A_2)_{ii}=0 \quad \text{for all } i .\end{aligned} \tag{3.20}$$

Two-dimensional analogues of Eqs. (3.18) and (3.20) are given in Sec. IV.

From Eq. (3.10), the diagonalized form of N_1 is given as

$$(N_1)_{ii}=\frac{(d-1)\phi_1\phi_2+(A_2)_{ii}}{\phi_1\phi_2-(A_2)_{ii}} . \tag{3.21}$$

Combining the upper bound of (3.17) and (3.21), one finally obtains that

$$(N_1)_{ii}\geq 0 , \tag{3.22}$$

and thus N_1 is positive semidefinite in the principal-axis frame. Since N_1 in any other reference frame is a real symmetric matrix, and thus is diagonalized with some unitary matrix, it is easy to show that N_1 is positive semidefinite in any reference frame. This proves relation (3.9b) for $n=1$. We note that the denominator in Eq. (3.21) may become zero, and thus the possibility of an infinity in some or all of the elements of N_1 is not ruled out.

Next we turn our attention to the tensor $\mathsf{A}_3^{(i)}$ and the weight tensor $\mathsf{W}_1^{(i)}$. First, it may be noted that in terms of the normalization tensor N_1, the tensor M of Eq. (3.5) may be written as

$$\mathsf{M}=d^2\phi_1\phi_2\mathsf{N}_1(\mathsf{N}_1+\mathsf{U})^{-2} , \tag{3.23}$$

so that

$$\mathsf{W}_1^{(i)}=\frac{1}{d^2\phi_1\phi_2}\mathsf{N}_1^{-1/2}(\mathsf{N}_1+\mathsf{U})\mathsf{A}_3^{(i)}(\mathsf{N}_1+\mathsf{U})\mathsf{N}_1^{-1/2} . \tag{3.24}$$

Here we have made use of (3.6) and (3.8). Relation (3.24) could also have been obtained in a manner similar to that used to relate $\mathsf{A}_2^{(i)}$ and N_1 [cf. Eq. (3.10) and the discussion above it].

Consider now studying the positivity properties of the tensors $A_3^{(i)}$. Because of the upper bound of (3.17), the ith diagonal element of the diagonalized form of M [Eq. (3.5)] may be written as

$$M_{ii} \geq [(d-1)\phi_1\phi_2 - (d-2)\phi_1\phi_2 - \phi_1\phi_2] \tag{3.25}$$

or

$$M_{ii} \geq 0 \ . \tag{3.26}$$

Equation (3.26) implies that M is positive semidefinite. The condition $\mathrm{tr}(A_2)=0$ implies that M can never be the null tensor, unless the volume fraction ϕ_i is trivially equal to zero.

Again, if we use the method of Torquato[16] (the details of which are not given here), $A_3^{(i)}$ can be written in quadratic form, thus we find that

$$A_3^{(i)} \geq 0 \ . \tag{3.27}$$

Combination of (3.26) and (3.27) yields

$$W_1^{(i)} \geq 0 \ , \tag{3.28}$$

which proves expression (3.9a) for $n=1$.

Following the same procedure as was employed to get (3.10), we find after considerable algebra that

$$(N_2+U)^{-1} = -d\phi_1\phi_2 N_1 (N_1+U)^{-2} \times (A_4^{(2)} - A_3^{(2)})(A_3^{(1)}A_3^{(2)})^{-1} - N_1(N_1+U)^{-1}A_3^{(2)}(A_3^{(1)})^{-1} \ . \tag{3.29}$$

Equation (3.29), unlike the previous relations, is restricted to media in which the n-point tensors possess common principal axes. As noted in Sec. II, this still represents a large class of anisotropic media. Note that N_2 could also have been expressed in terms of $A_4^{(1)}$ via the relation (3.2). We shall not explicitly study the positivity properties of $A_4^{(i)}$ or N_2 since the algebra involved is quite tedious.

2. *Two-dimensional composites*

In two dimensions some special properties hold for the n-point microstructural parameters $A_n^{(i)}$. In particular, we shall show that all the odd-point parameters $A_{2n+1}^{(i)}$ are scalar multipliers of the unit tensor and all the even-point parameters $A_{2n}^{(i)}$ are traceless. Implications of these results with respect to the properties of the weights and normalization factors are then discussed.

First, consider the three-point tensor $A_3^{(i)}$. From (2.11b), it is seen that this tensor involves the product of two t tensors in the integrand. This product is given by

$$\mathbf{t}(1,2)\cdot\mathbf{t}(2,3) = \frac{1}{r_{12}^2 r_{23}^2} \begin{bmatrix} \cos 2\theta_1 & \sin 2\theta_1 \\ \sin 2\theta_1 & -\cos 2\theta_1 \end{bmatrix} \begin{bmatrix} \cos 2\theta_3 & \sin 2\theta_3 \\ \sin 2\theta_3 & -\cos 2\theta_3 \end{bmatrix} = \frac{1}{r_{12}^2 r_{23}^2} \begin{bmatrix} \cos 2(\theta_1-\theta_3) & \sin 2(\theta_1-\theta_3) \\ \sin 2(\theta_1-\theta_3) & \cos 2(\theta_1-\theta_3) \end{bmatrix} . \tag{3.30}$$

Here θ_1 and θ_3 are the angles which the vectors $\mathbf{r}_{12}$ and $\mathbf{r}_{23}$, respectively, make with the horizontal axis. Now, in the principal-axes frame, the off-diagonal terms give integrated values of zero. But the diagonal terms will give identical results. So $A_3^{(i)}$ is a scalar multiplier of the unit tensor: $A_3^{(i)} = A_3^{(i)}U$. in fact, we can assert the general property that any odd-point parameter $A_{2n+1}^{(i)}$ (in 2D) is proportional to the unit tensor:

$$A_{2n+1}^{(i)} = A_{2n+1}^{(i)}U \ . \tag{3.31}$$

Result (3.31) follows because the integrand of this parameter contains the product of an even number ($2n$) of t tensors. When these tensors are multiplied in pairs, one obtains a product of n tensors of the type (3.30) which when integrated yields a tensor whose diagonal elements are equal. Interestingly, directionality in the effective property does not enter through the odd-point parameters but must enter through the even-point parameters.

Milton[14] has shown that the weight tensors have precisely the same property as the odd-point parameters, namely,

$$W_n^{(i)} = W_n^{(i)}U \ . \tag{3.32}$$

We can explicitly prove (3.32) for $n=1$ by writing the weight tensor as

$$W_1^{(i)} = (\phi_1\phi_2 U - \frac{1}{\phi_1\phi_2}A_2\cdot A_2)^{-1/2} A_3^{(i)} \times \left(\phi_1\phi_2 U - \frac{1}{\phi_1\phi_2}A_2\cdot A_2\right)^{-1/2} . \tag{3.33}$$

Here we have employed (3.5), (3.6), and (3.8). In the principal-axes frame of A_2, we can write

$$A_2\cdot A_2 = \begin{bmatrix} q & 0 \\ 0 & -q \end{bmatrix} \begin{bmatrix} q & 0 \\ 0 & -q \end{bmatrix} = q^2 U \ ,$$

where q is some scalar quantity. Using this result in conjunction with (3.31) and (3.33) yields

$$W_1^{(i)} = W_1^{(i)}U \ ,$$

which proves (3.32) for $n=1$. Now since the weights $W_n^{(i)}$ are proportional to the parameters $A_{2n+1}^{(i)}$ (through leading order), it is plausible that the weights themselves are scalar multiplies of the unit tensor for any n; this, howev-

er, will not be proved here since one must have the explicit expressions relating $W_n^{(i)}$ to the set $A_2^{(i)}, \ldots, A_{2n+1}^{(i)}$ for all n.

Now consider the even-point parameters $A_{2n}^{(i)}$. From (2.11b) it is observed that $A_{2n}^{(i)}$ involves a product of an odd number of t tensors $[t(1,2)\cdots t(2n-1,2n)]$. Performing all the integrations except over position 2 and employing the same reasoning used to prove (3.31), we can write

$$A_{2n}^{(i)} \propto \int d\mathbf{r}\, t(\mathbf{r}) \cdot f_{2n-1}(\mathbf{r}) U ,$$

where $f_{2n-1}(\mathbf{r})$ is some arbitrary scalar function of $\mathbf{r}$ which results after integrating over positions $3, \ldots, 2n$. Because t is traceless, then we have

$$\mathrm{tr}(A_{2n}^{(i)}) = 0 \quad (n = 1,2, \ldots) . \tag{3.34}$$

For macroscopically isotropic media, result (3.34) implies that all the even-point parameters are identically zero, i.e., $A_{2n}^{(i)} = \mathbf{0}$.

Property (3.34) implies an interesting property of the normalization factors. Consider first the first normalization N_1. Since A_2 is traceless, then in the principal-axes frame it will be diagonal with $(A_2)_{11} = -(A_2)_{22}$. Looking at the elements of N_1 as given in (3.21) for $d = 2$, it is clear that

$$\det N_1 = \frac{\phi_1\phi_2 + (A_2)_{11}}{\phi_1\phi_2 - (A_2)_{11}} \cdot \frac{\phi_1\phi_2 + (A_2)_{22}}{\phi_1\phi_2 - (A_2)_{22}} = 1 .$$

This equation states that the first normalization factor has unit determinant. Using (3.29), (3.31), and (3.34), we can similarly show that

$$\det N_2 = 1 .$$

In fact, Milton[14] has shown that $\det N_n = 1$ for any n. This general result arises quite naturally in his formalism. From the above discussion, it is seen that the traceless condition on the even-point parameters $A_{2n}^{(i)}$ implies that the N_n have unit determinant for any n and vice versa.

C. Isotropic limit

We remark now on the situations in which macroscopic anisotropy degenerates into isotropy. The simplest case is that of statistically isotropic media, i.e., materials characterized by correlation functions $S_n^{(i)}$ which depend only upon the relative distances between the points. For such media, for example, $S_2^{(i)}(\mathbf{r}) = S_2^{(i)}(r)$ depends only upon the distance $r \equiv |\mathbf{r}|$. Examples of such composites include distributions of inclusions with hyperspherical symmetry (spheres or circular disks) and asymmetric objects which are placed randomly and with random orientation. Note that since

$$A_2 \propto \int_\delta d\mathbf{r}\, t(\mathbf{r})[S_2^{(i)}(\mathbf{r}) - \phi_i^2] \tag{3.35}$$

and

$$\int_\delta d\mathbf{r}\, t(\mathbf{r}) = \mathbf{0} ,$$

the two-point parameter vanishes, i.e.,

$$A_2 = \mathbf{0} , \tag{3.36}$$

if the two-point probability function depends only upon the scalar r. This is exactly the reason the perturbation series in the macroscopically isotropic case[9] starts from $n = 3$, and not from $n = 2$ as in the present case. For microstructures which possess rotational invariance, it is straightforward to show that the n-point tensors for $n \geq 3$ become isotropic, i.e.,

$$A_n^{(i)} = A_n^{(i)} U, \quad n \geq 3 \tag{3.37}$$

and hence

$$\sigma_e = \sigma_e U , \tag{3.38}$$

thus recovering the isotropic perturbation expansion of Torquato (1985).

Macroscopic isotropy can also be achieved for certain statistically anisotropic materials. (Macroscopic anisotropy necessarily implies statistical anisotropy, however.) We will explicitly consider $d = 2$ and 3, respectively. In two dimensions, the tensor $t(\mathbf{r})$, $\mathbf{r} = (r,\theta)$, is proportional to the tensor

$$\begin{bmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{bmatrix} . \tag{3.39}$$

Thus, if $S_2^{(i)}(r,\theta)$ has a fourfold rotation axis and is invariansst the transformation

$$\theta \rightarrow (90° - \theta) , \tag{3.40}$$

i.e., a reflection symmetry about the $\theta = 45°$ line, then the integral in (3.35) is zero and isotropy is achieved. For example, composites consisting of a random but statistically isotropic distribution of circles, circular inclusions centered on a square lattice, and oriented but randomly or periodically arranged squares possess such symmetry. In more general situations where the fourfold axis is not present, if $S_2(r,\theta)$ has reflection symmetry in each quadrant about the diagonal which bisects it, then $A_2^{(i)} = 0$. This seems to be the fundamental symmetry required for macroscopic isotropy in the 2D case. Using this property, one can show, for example, that for circular inclusions on a regular hexagonal lattice, by rotating the principal axes of the lattice by 15°, one goes to a set of axes in which reflection symmetry holds in each quadrant. Thus the bulk property for this lattice will be isotropic, and hence this set of axes is identified to be the principal axes for the macroscopic system. For any regular $2n$-sided polygon lattice ($n \geq 2$), by rotating the principal axes of the lattice by an angle $\alpha = \pi/4n$, we can show that macroscopic isotropy is achieved. For microstructures consisting of, for example, oriented, nonspherical inclusions (such as ellipses, rectangles, etc.) either randomly or periodically arranged, or of oriented laminates, the effective property is anisotropic.

In three dimensions, the tensor $t(\mathbf{r})$, $\mathbf{r} = (r,\theta,\phi)$, is proportional to

$$\begin{bmatrix} 3\sin^2\theta\cos^2 - 1 & * & * \\ * & 3\sin^2\theta\sin^2\phi - 1 & * \\ * & * & 3\cos^2\theta - 1 \end{bmatrix} , \tag{3.41}$$

where we have not written the off-diagonal terms. Now, if each octant looks identical in the principal-axes frame and if the transformation

$$\phi \rightarrow 90° - \phi, \quad \theta = \theta \tag{3.42}$$

makes $S_2^{(i)}(\mathbf{r})$ invariant, then it is easily shown that two of the diagonal elements of $\mathsf{A}_2[(A_2)_{11}=(A_2)_{22}]$ are identical. Now, if the symmetry (3.42) (i.e., 45°-reflection symmetry) holds in any plane formed by any two principal axes, then all the diagonal elements of A_2 are identical. Hence, the traceless property of A_2 ensures that $\mathsf{A}_2=\mathbf{0}$. In three dimensions, composites consisting of a random but statistically isotropic distribution of spheres, spheres centered on cubic lattices, and oriented but randomly or periodically arranged cubes possess such symmetry, for example. Even in more general situations where cubic symmetry is absent, and each octant does not look identical in the principal-axes frame, if $S_2(\mathbf{r})$ is invariansst reflection about diagonal planes which contain the third axis and bisect each quadrant of the xy plane (for any arbitrary choice of the third axis), the two-point parameter vanishes. For microstructures consisting of, for example, oriented, nonspherical inclusions (such as ellipsoids, parallelopipeds, rods, etc.) either randomly or periodically arranged, or of oriented laminates, the effective property is anisotropic. As is clear from the argument above, the symmetry of $S_2(\mathbf{r})$ discussed above holds true in any dimension.

Finally, we prove that the condition $\mathsf{A}_2=\mathbf{0}$ is sufficient for the effective property to be isotropic. This is proved by showing that the symmetries which make $\mathsf{A}_2=\mathbf{0}$ also make $\mathsf{A}_n^{(i)}$ $(n \geq 3)$ isotropic. Consider the case $n=3$ first. Employing (2.11b) it is easy to see that the three-point parameter can be rewritten in terms of the symmetric integral operator

$$\Gamma[\cdot] = \int d\mathbf{r}' t(\mathbf{r}-\mathbf{r}')[\cdot] \tag{3.43}$$

as

$$\mathsf{A}_3^{(i)} \propto \Gamma \cdot \Gamma \mathsf{C}_3^{(i)} , \tag{3.44}$$

where $C_3^{(i)}$ is the determinant given by (2.12). Now if $S_2^{(i)}$ and $S_3^{(i)}$ both possess reflection symmetry in the 1-2 plane of the principal-axes frame, then $\Gamma_{11}=\Gamma_{22}$, and hence $(A_3)_{11}=(A_3)_{22}$. If this symmetry holds in any plane formed by any two principal axes, then all the diagonal elements of $\mathsf{A}_3^{(i)}$ are identical and thus

$$\mathsf{A}_3^{(i)} = A_3^{(i)} \mathsf{U} . \tag{3.45}$$

The tensor $\mathsf{A}_4^{(i)}$ involves the product of another such integral operator [cf. (3.43)]. Hence, under the above symmetry in all the planes, the four-point tensor must also be isotropic, and by induction for any $n \geq 3$,

$$\mathsf{A}_n^{(i)} = A_n^{(i)} \mathsf{U} . \tag{3.46}$$

In passing we remark that when the effective conductivity tensor is isotropic, we have

$$\mathsf{A}_3^{(i)} = (d-1)\phi_1\phi_2\zeta_i \mathsf{U} \tag{3.47}$$

and

$$\mathsf{A}_4^{(i)} = (d-1)\phi_1\phi_2\gamma_i \mathsf{U} . \tag{3.48}$$

In such instances, relations (3.2) and (3.3) reduce to

$$\zeta_1 + \zeta_2 = 1 , \tag{3.49}$$

$$\gamma_1 - \gamma_2 = (d-2)(\zeta_2 - \zeta_1) . \tag{3.50}$$

These results were first obtained by Torquato[9] for macroscopically isotropic composites[19] [however, relation (3.49) was obtained earlier by Torquato[16] and Milton[17]].

IV. BOUNDS ON THE EFFECTIVE CONDUCTIVITY TENSOR

Until recently, knowledge of lower-order n-point probability functions (i.e., $S_1^{(i)}$, $S_2^{(i)}$, $S_3^{(i)}$, and $S_4^{(i)}$) even for macroscopically isotropic media has been virtually nonexistent, either theoretically or experimentally.[20] In the last several years considerable advances have been made along these lines both theoretically[15,21] and experimentally,[22] and as a result, effective property relations which depend upon such information have been computed.[7,9,22,23] It appears, however, that the determination of the $S_n^{(i)}$ for $n \geq 5$ of arbitrary media is beyond presently available technology. Thus series representations of σ_e such as (2.10) cannot be exactly summed. Rigorous methods to estimate σ_e must necessarily involve limited microstructural information.

Here we obtain rigorous upper and lower bounds on σ_e. Bounds on effective properties are useful since (i) they may be used to test the merits of a theory or computer experiment; (ii) as successively more microstructural information is included, the bounds become progressively narrower; and (iii) one of the bounds can typically provide a good estimate of the effective property, for a wide range of volume fractions, even when the reciprocal bound diverges from it.[10]

In order to derive the bounds we shall make use of a key observation made by Kohn and Milton,[13] namely, that the scalar effective conductivity σ_e is a Stieltjes function. Certain Padé approximants of Stieltjes functions are known to form converging upper and lower bounds on the function.[24] Kohn and Milton[13] noted that particular Padé approximants of the expansion of the scalar conductivity σ_e in powers of $\delta_{ij}=(\sigma_i-\sigma_j)/\sigma_j$ yielded his nth-order bounds for isotropic media.[5] The even $2m$-order bounds on the scaled conductivity σ_e/σ_j are obtained by forming the $[m,m]$ Padé approximant of the perturbation expansion for σ_e/σ_j in powers of δ_{ij}, whereas the odd $(2m+1)$-order upper and lower bounds are derived by forming the $[m+1,m]$ Padé approximant of the expansion for σ_e/σ_j in powers of δ_{ij} and the $[m,m+1]$ Padé approximant of the expansion for σ_e/σ_i in powers of δ_{ij}, respectively.

Heretofore, the connection between Padé approximants of perturbation series and bounds has only been established for the isotropic case. Here we shall establish such a connection for the anisotropic conductivity up through fourth-order bounds. Consider first the case of anisotropic conductivity in which all of the n-point mi-

crostructural tensors possess the same principal axes, i.e., they all commute. As noted earlier, this constitutes a large class of d-dimensional anisotropic two-phase media, e.g., random distributions of oriented nonspherical inclusions. When such symmetry is present, the aforementioned Padé approximant methodology used to obtain isotropic bounds extends directly to this anisotropic case. Specifically, in the principal-axes frame, the problem reduces to solving d-independent scalar problems, i.e., obtaining the Padé approximants (as described above for the isotropic instance) for each principal direction. More generally, one is interested in determining whether the Padé approximant technique can be extended to anisotropic media in which the n-point parameters do not possess the same principal axes (see discussion of Sec. II). For this general situation we propose that the Padé approximant of the perturbation expansion of scaled conductivity tensor (either $\boldsymbol{\sigma}_e/\sigma_j$ or $\boldsymbol{\sigma}_e/\sigma_i$) in powers of δ_{ij} be of the form

$$\tfrac{1}{2}\mathsf{A}\mathsf{B}^{-1}+\tfrac{1}{2}(\mathsf{A}\mathsf{B}^{-1})^T ,$$

since $\boldsymbol{\sigma}_e$ is a symmetric tensor. Here A and B represent polynomials of degree n and m, respectively, in δ_{ij} with tensor coefficients; superscript T denotes the transpose. The symmetric form given above then is the $[n,m]$ Padé approximant for the general anisotropic case. We shall explicitly show that the [0,1], [1,0], [1,1], [2,1], [1,2], and [2,2] Padé approximants of the anisotropic analogue of the particular perturbation series described above for the isotropic case lead to anisotropic generalizations of the isotropic first-, second-, third-, and fourth-order bounds. Although this suggests that such a procedure to obtain bounds may be extended to derive fifth- and higher-order bounds, it is not altogether clear that this will be the case. It should be noted that the first- and second-order bounds are trivial cases in the following sense: first-order bounds will only involve the tensor $\mathsf{a}_1^{(i)}$ which is just proportional to the unit dyadic U and the second-order bounds will involve $\mathsf{a}_1^{(i)}$ and $\mathsf{a}_2^{(i)}$ which always commute. Third- and higher-order bounds will involve symmetric tensor coefficients which generally do not commute.

We shall use this Padé approximant prescription in conjunction with series (2.14) to derive first-, second-, third-, and fourth-order bounds for the tensor problem. By definition, nth-order bounds depend upon the set $S_1^{(i)},\ldots,S_n^{(i)}$. In what follows, we will employ the shorthand notation

$$\begin{aligned}
&\langle\sigma\rangle=\sigma_1\phi_1+\sigma_2\phi_2 ,\\
&\langle\tilde{\sigma}\rangle=\sigma_1\phi_2+\sigma_2\phi_1 ,\\
&\langle\boldsymbol{\sigma}\rangle_\xi=\sigma_1\xi_1+\sigma_2\xi_2 ,\\
&\langle\boldsymbol{\sigma}\rangle_\xi=\sigma_1\xi_2+\sigma_2\xi_1 ,
\end{aligned} \tag{4.1}$$

where ξ_i is defined by (3.6). Moreover, we let $\boldsymbol{\sigma}_e^{(nL)}$ and $\boldsymbol{\sigma}_e^{(nU)}$ denote nth-order lower and upper bounds, respectively.

A. First-order bounds

Forming the [0,1] and [1,0] Padé approximants of the series described above yields, respectively, the first-order lower and upper bounds:

$$\boldsymbol{\sigma}_e^{(1L)}=\frac{\sigma_1\sigma_2}{\langle\tilde{\sigma}\rangle}\mathsf{U} , \tag{4.2}$$

$$\boldsymbol{\sigma}_e^{(1U)}=\langle\sigma\rangle\mathsf{U} . \tag{4.3}$$

Recall that odd $(2m+1)$-order upper and lower bounds are derived from the $[m+1,m]$ Padé approximant of the expansion for $\boldsymbol{\sigma}_e/\sigma_j$ in powers of δ_{ij} [Eq. (2.14)] and the $[m,m+1]$ Padé approximant of the series for $\boldsymbol{\sigma}_e/\sigma_i$ in powers of δ_{ij}. Equations (4.2) and (4.3), which represent the harmonic and arithmetic means of the local conductivity, respectively, were first derived by Wiener[25] in the isotropic context. They are exactly attained for parallel slab geometries: (4.2) being the case in which the applied field is directed perpendicular to the slabs—the law of "series resistances"—and (4.3) being the case in which $\mathbf{E}_0$ is directed along the slabs—the law of "parallel resistances."

B. Second-order bounds

When we take the [1,1] Padé approximant of the series (2.14), we obtain the expression

$$\frac{\boldsymbol{\sigma}_e^{(2)}}{\sigma_j}=\left[\mathsf{U}+\left[\phi_i\mathsf{U}-\frac{1}{\phi_i}\mathsf{a}_2^{(i)}\right]\delta_{ij}\right]\times\left[\mathsf{U}-\frac{1}{\phi_i}\mathsf{a}_2^{(i)}\delta_{ij}\right]^{-1} . \tag{4.4}$$

Here $\mathsf{a}_2^{(i)}$ is given by Eq. (2.16). Equation (4.4) for $\sigma_2\geq\sigma_1$ (as described below) gives a lower bound $\boldsymbol{\sigma}_e^{(2L)}$ for $j=1$ and $i=2$ and an upper bound $\boldsymbol{\sigma}_e^{(2U)}$ for $j=2$ and $i=1$. These second-order bounds explicitly given in terms of ϕ_i and A_2 are new (although bounds of this type are implicit in the work of Willis[12] for the 3D case only). We can write these second-order bounds in terms of the first normalization tensor using (2.16) and (3.10) as follows:

$$\frac{\boldsymbol{\sigma}_e^{(2)}}{\sigma_j}=(\sigma_i\mathsf{U}+\langle\sigma\rangle\mathsf{N}_1)\cdot(\langle\tilde{\sigma}\rangle\mathsf{U}+\sigma_j\mathsf{N}_1)^{-1} . \tag{4.5}$$

It should be noted that these bounds are identical to the anisotropic Hashin-Shtrikman variational bounds that one may obtain by employing the scheme outlined by Milton.[14] Our bounds are explicitly given in terms of $S_2^{(i)}$, however. Hence, the [1,1] Padé approximants are indeed rigorous bounds.

The bounds (4.4) or (4.5) are exactly realized for a variety of model composites,[4,5] one of which consists of inclusions of "singly coated" ellipsoids in d dimensions. The inner core and the outer concentric shell make up the two phases and depending on this composition either the upper or the lower bound becomes the exact effective conductivity. These ellipsoids are all oriented in the same direction, but since they have to fill up the whole space, they appear in continuously varying sizes such

that the ratios of their principal axes remain fixed. Bounds (4.4) and (4.5) are generalizations of second-order Hashin-Shtrikman bounds and reduce to the latter in the macroscopic isotropic limit, i.e., when $\mathsf{A}_2=\mathbf{0}$.

Willis[12] explicitly derived anisotropic second-order bounds, using the Hashin-Shtrikman variational principle, for the special case of 3D media consisting of oriented ellipsoids in a matrix. For this special geometry, if we take phases 1 and 2 to be the matrix and included phases, respectively, we can relate his P tensor to our two-point tensors as follows:

$$\mathsf{P}=\frac{1}{\sigma_1}\mathsf{A}_2^*=\frac{1}{3\sigma_1}\left[\mathsf{U}-\frac{1}{\phi_1\phi_2}\mathsf{A}_2\right], \tag{4.6}$$

where A_2 is given by (2.11a) and A_2^* is given by (3.13) or (3.14). He shows that P for this geometry is simply a constant tensor depending only upon the shape of the ellipsoid, and explicitly obtains an expression for an ellipsoid of circular cross section in one plane and an elliptical cross section in the other two planes. In fact, P is trivially related to the well-known depolarization factor tensor for an ellipsoid[26] (although Willis himself does not explicitly note this) which turns out to be exactly A_2^*, (3.13) or (3.14). In two dimensions, A_2^* would just correspond to the depolarization factor tensor for an ellipse. For 2D and 3D ellipsoids, we respectively have the elliptic integrals[26]

$$(A_2^*)_{ii}=\frac{a_1a_2}{2}\int_0^\infty\frac{dt}{(t+a_i)[(t+a_1^2)(t+a_2^2)]^{1/2}}, \tag{4.7}$$

$$(A_2^*)_{ii}=\frac{a_1a_2a_3}{2}\times\int_0^\infty\frac{dt}{(t+a_i)[(t+a_1^2)(t+a_2^2)(t+a_3^2)]^{1/2}}, \tag{4.8}$$

where the a_i are the semiaxes of the ellipsoids. (Note that Willis considered the specific case of $a_1=a_2$ with a_3 arbitrary.) For the 3D cases of needle-, disk-, and spherical-shaped inclusions, we have given the diagonal elements of both A_2^* and A_2 in Eqs. (3.18), (3.19), and (3.20), respectively. For 2D needles oriented along the second principal axis, (4.7) gives

$$\begin{aligned}&(A_2^*)_{11}=1,\quad (A_2^*)_{22}=0,\\ &(A_2)_{11}=-\phi_1\phi_2,\quad (A_2)_{22}=\phi_1\phi_2.\end{aligned} \tag{4.9}$$

For circles, $a_1=a_2$ and (4.7) easily yields

$$\begin{aligned}&(A_2^*)_{11}=(A_2^*)_{22}=\tfrac{1}{2},\\ &(A_2)_{11}=(A_2)_{22}=0.\end{aligned} \tag{4.10}$$

For microstructures other than oriented ellipsoids, the depolarization factor tensor will not be as simple as (4.7) or (4.8), but rather will depend upon $S_2(r)$ in a nontrivial manner. Thus bounds (4.4) or (4.5) are generalizations of Willis' bounds for arbitrary microgeometries.

It should be noted that the second-order bounds (4.4) or (4.5) are exact to first order in the volume fraction ϕ_2 for the case of composites composed of inclusions (phase 2) distributed throughout a matrix (phase 1). Hence, for oriented but identical ellipsoids, the second-order bounds in conjunction with the depolarization factor tensors, (4.7) and (4.8), give the exact dilute results of Polder and Van Santen.[26] Of course, the bounds do not give exact results beyond first order in ϕ_2.

We close this discussion on second-order bounds by making two simple observations. If the depolarization factor tensor becomes zero for some of the principal-axes directions, i.e.,

$$(A_2^*)_{kk}=0,$$

then

$$(A_2)_{kk}=\phi_1\phi_2,$$

and hence from (4.4) we find that

$$(\sigma_e^{(2U)})_{kk}=\langle\sigma\rangle,$$

which is exactly the first-order upper bound (4.3). This is not unexpected since this corresponds to a geometry of either infinitely long needles or parallel slabs for which the depolarization is zero in the direction along the needles or slabs. Furthermore, if all but one of the diagonal elements of $\underline{A}_2$ are equal to $\phi_1\phi_2$, then because $\underline{A}_2$ is traceless,

$$(A_2)_{zz}=-(d-1)\phi_1\phi_2$$

in the remaining z direction. Substituting this result into the lower bound (4.4), we find

$$(\sigma_e^{(2L)})_{zz}=\frac{\sigma_1\sigma_2}{\langle\tilde{\sigma}\rangle}\mathsf{U},$$

which is just the first-order lower bound. Again, this is not surprising since it corresponds to the conductivity for parallel slabs perpendicular to the slabs.

C. Third-order bounds

By following the aforementioned prescription for odd-order bounds, the [1,2] Padé approximant (third-order lower bound) is obtained as

$$\left[\frac{\sigma_e^{(3L)}}{\sigma_2}\right]^{-1}=(1+\phi_1\delta_{21})\mathsf{U}+\delta_{21}^2\mathsf{c}_2\cdot[(1-\phi_1\delta_{21})\mathsf{c}_2+(\mathsf{b}_3+\phi_1\mathsf{b}_2)\delta_{21}]^{-1}\cdot\mathsf{c}_2, \tag{4.11}$$

where

$$\mathsf{b}_2=\phi_1\mathsf{U}+\mathsf{a}_2^{(1)}, \tag{4.12}$$

$$\mathsf{c}_2=\phi_1^2\mathsf{U}-\mathsf{b}_2, \tag{4.13}$$

and

$$\mathsf{b}_3=-(\phi_1\mathsf{U}+2\mathsf{a}_2^{(1)}+\mathsf{a}_3^{(1)}). \tag{4.14}$$

The [2,1] Padé approximant (third-order upper bound) is given by

$$\frac{\sigma_e^{(3U)}}{\sigma_1} = (1+\phi_2\delta_{21})\mathsf{U} + \delta_{21}^2 \mathsf{a}_2^{(2)}\cdot(\mathsf{a}_2^{(2)}-\mathsf{a}_3^{(2)}\delta_{21})^{-1}\cdot\mathsf{a}_2^{(2)} , \tag{4.15}$$

where $\mathsf{a}_2^{(2)}$ and $\mathsf{a}_3^{(3)}$ are given by Eqs. (2.16) and (2.17), respectively.

We claim that (4.11) and (4.15) are bounds since we have shown that they are precisely equal to the rigorous third-order lower and upper bounds that are obtained from the variational principles of minimum potential energy and minimum complementary energy,[3] respectively. This derivation will not be given here, however. The third-order bounds presented here in terms of our two- and three-point parameters are entirely new. We note that for isotropic media, these bounds reduce to the well-known Beran[3,16,17] and Silnutzer[17,27] bounds for $d=3$ and 2, respectively. In terms of the normalization tensor N_1 and the weight tensors ζ_i, these bounds may be written as

$$\sigma_e^{(3L)} = [\langle\sigma\rangle\mathsf{U}+\mathsf{N}_1^{-1/2}\langle\tilde{\sigma}\rangle_\zeta\mathsf{N}_1^{-1/2}]\cdot\left[\mathsf{U}+\frac{\langle\tilde{\sigma}\rangle}{\sigma_1\sigma_2}\mathsf{N}_1^{-1/2}\langle\tilde{\sigma}\rangle_\zeta\mathsf{N}_1^{-1/2}\right]^{-1} , \tag{4.16}$$

and

$$\sigma_e^{(3U)} = [\sigma_1\sigma_2\mathsf{U}+\langle\sigma\rangle\mathsf{N}_1^{1/2}\langle\sigma\rangle_\zeta\mathsf{N}_1^{1/2}]\cdot[\langle\tilde{\sigma}\rangle\mathsf{U}+\mathsf{N}_1^{1/2}\langle\sigma\rangle_\zeta\mathsf{N}_1^{1/2}]^{-1} . \tag{4.17}$$

We found that the third-order bounds we obtained by applying Milton's scheme[14] are identical to the third-order bounds presented here.

D. Fourth-order bounds

Finally by taking the [2,2] Padé approximants of series (2.14), we can obtain fourth-order bounds as

$$\frac{\sigma_e^{(4)}}{\sigma_j} = \tfrac{1}{2}\mathsf{A}\mathsf{B}^{-1}+\tfrac{1}{2}(\mathsf{A}\mathsf{B}^{-1})^T , \tag{4.18}$$

where

$$\mathsf{A} = \mathsf{U}+\mathsf{p}_1^{(i)}\delta_{ij}+\mathsf{p}_2^{(i)}\delta_{ij}^2 , \tag{4.19}$$

$$\mathsf{B} = (\mathsf{U}+\mathsf{q}_1^{(i)}\delta_{ij}+\mathsf{q}_2^{(i)}\delta_{ij}^2)^{-1} , \tag{4.20}$$

$$\mathsf{p}_1^{(i)} = \phi_i\mathsf{U}+\mathsf{q}_1^{(i)} , \tag{4.21}$$

$$\mathsf{p}_2^{(i)} = \mathsf{a}_2^{(i)}-\phi_i^{-1}\mathsf{a}_3^{(i)}+(\phi_i\mathsf{U}-\phi_i^{-1}\mathsf{a}_2^{(i)})\cdot\mathsf{q}_1^{(i)} , \tag{4.22}$$

$$\mathsf{q}_1^{(i)} = (\mathsf{a}_2^{(i)}\cdot\mathsf{a}_2^{(i)}-\phi_i\mathsf{a}_3^{(i)})^{-1}\times(\phi_i\mathsf{U}\cdot\mathsf{a}_4^{(i)}-\mathsf{a}_2^{(i)}\cdot\mathsf{a}_3^{(i)}) , \tag{4.23}$$

and

$$\mathsf{q}_2^{(i)} = -\phi_i^{-1}(\mathsf{a}_3^{(i)}+\mathsf{a}_2^{(i)}\mathsf{q}_1^{(i)}) . \tag{4.24}$$

For reasons given immediately below, it is conjectured that (4.18) represents rigorous fourth-order bounds for general anisotropic two-phase media given, for the first time, explicitly in terms of the two-, three-, and four-point correlation functions: (4.18) yielding $\sigma_e^{(4U)}$ for $i=1$, $j=2$, and $\sigma_e^{(4L)}$ for $i=2$, $j=1$, when $\sigma_2>\sigma_1$.

First, in the isotropic limit, these Padé approximants reduce to the fourth-order bounds derived by Milton.[5] Furthermore, we have applied Milton's scheme[14] to generate fourth-order bounds and found them to be identical to (4.18) when the microstructural tensors possess *common principal axes,* i.e., when they commute. For such symmetric media, our [2,2] Padé approximants are much more compactly written in terms of the normalization factors N_1 and N_2 and the weights $\mathsf{W}_1^{(i)}$ [cf. Eqs. (2.16)–(2.18), (3.10), (3.24), and (3.29)]:

$$\frac{\sigma_e^{(4)}}{\sigma_j} = [\sigma_i(\langle\sigma\rangle\mathsf{N}_1+\langle\tilde{\sigma}\rangle_\zeta) + (\sigma_1\sigma_2\mathsf{U}+\langle\sigma\rangle\langle\sigma\rangle_\zeta\mathsf{N}_1)\cdot\mathsf{N}_2]\cdot[\sigma_1\sigma_2\mathsf{N}_1+\langle\tilde{\sigma}\rangle\langle\tilde{\sigma}\rangle_\zeta+\sigma_j(\langle\tilde{\sigma}\rangle\mathsf{U}+\langle\sigma\rangle_\zeta\mathsf{N}_1)\cdot\mathsf{N}_2]^{-1} . \tag{4.25}$$

In light of the fact that the general result (4.18) reduces to rigorous bounds in the isotropic limit and in the anisotropic case in which the microstructural tensors commute and because of the connection we have established between lower-order Padé approximants and lower-order anisotropic bounds, it is conjectured that (4.18) represents rigorous fourth-order bounds for general anisotropic media.

In a sequel to this paper, we shall consider application of these bounds. Specifically, we will study a certain distribution of parallel cylinders of finite aspect ratio.

V. CONCLUDING REMARKS

We have derived a new perturbation expansion for σ_e of a macroscopically anisotropic d-dimensional composite of arbitrary microstructure through all orders in the perturbation parameter. The n-point microstructural parameters $\mathsf{A}_n^{(i)}$ which arise are given explicitly in terms of multidimensional integrals over the set of n-point probability functions $S_1^{(i)},\ldots,S_n^{(i)}$ $(i=1,2)$. We studied general properties and relations involving the $\mathsf{A}_n^{(i)}$. Practically, it is very difficult to ascertain the $\mathsf{A}_n^{(i)}$ for $n\geq 5$ for general microstructures. Thus an exact solution of σ_e is generally out of the question. Using nontrivial but limited information (such as $\mathsf{A}_2^{(i)}$, $\mathsf{A}_3^{(i)}$, and $\mathsf{A}_4^{(i)}$), bounding methods provide a means of estimating σ_e even when the phase conductivities widely differ.[10,23] We derive rigorous first-, second-, third-, and fourth-order bounds on σ_e by employing a Padé approximant methodology. This is the first time that such bounds have been explicitly given in terms of the $\mathsf{A}_n^{(i)}$. Elsewhere we shall compute these bounds for a certain distribution of parallel cylinders of finite aspect ratios.

The Hilbert-space formalism of Milton[14] complements the approach we have taken to the problem. Milton does not express his weight and normalization factor tensors ($\mathsf{W}_n^{(i)}$ and N_n, respectively) explicitly in terms of integrals over the n-point correlation functions. In this sense Milton's results are formal in that one could not directly compute σ_e either theoretically or experimentally from a knowledge of the n-point correlation functions. On the other hand, the tensor properties and relations involving

the $W_n^{(i)}$ and N_n arise quite naturally in his formalism for any n. This is to be contrasted with our results. We express all the $A_n^{(i)}$ in terms of integrals over the $S_n^{(i)}$ and relate lower-order $A_n^{(i)}$ $(n=2,3,4)$ to his weights and normalization factors. However, in our approach the tensor properties are much more difficult to obtain because of their explicit dependence upon the $S_n^{(i)}$.

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