Effective electrical conductivity of two-phase disordered composite media

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Perturbation expansions of the effective electrical conductivity σ_e of any two-phase isotropic composite medium of arbitrary dimensionality d (where $d = 2,3$) are derived. It is shown that certain Padé approximants of a particular series representation of σ_e yield known rigorous bounds on the conductivity of the composite. The relationships between the conductivities of certain models that are exactly realized by some of these bounds and the perturbation expansions are discussed. A new expression for the conductivity of a broad class of three-dimensional dispersions of inclusions is derived. The formula for σ_e, which depends upon, among other quantities, a certain three-point probability function of the composite medium, is shown to accurately predict σ_e of both periodic and random arrays of impenetrable spheres, for a wide range of phase conductivities and inclusion volume fractions.

I. INTRODUCTION

The determination of the effective electrical conductivity σ_e of a two-phase disordered composite medium has received considerable attention in recent years.[1–4] The Maxwell formula[5] (or the Clausius–Mossotti approximation in the dielectric context) and the effective-medium approximation (EMA)[6,7] are the two most widely employed expressions used for the calculation of σ_e. For arbitrary dimensionality d, the Maxwell formula and the EMA, in terms of the conductivities σ_1, σ_2 and volume fractions ϕ_1, ϕ_2 of the pure phases, are given, respectively, by

$$\frac{\sigma_e - \sigma_1}{\sigma_e + (d-1)\sigma_1} = \phi_2 \left(\frac{\sigma_2 - \sigma_1}{\sigma_2 + (d-1)\sigma_1} \right) \quad (1)$$

and

$$\phi_1 \left(\frac{\sigma_1 - \sigma_e}{\sigma_1 + (d-1)\sigma_e} \right) + \phi_2 \left(\frac{\sigma_2 - \sigma_e}{\sigma_2 + (d-1)\sigma_e} \right) = 0. \quad (2)$$

For the trivial case $d = 1$, both equations yield the exact solution. The Maxwell formula, unlike the EMA, fails to have a nontrivial percolation threshold (i.e., for all values of ϕ_2, except 0 and 1, $\sigma_e \neq 0$ even when $\sigma_1 = 0$ or $\sigma_2 = 0$). Recently, Milton[8] has shown that the EMA is exact for a family of hierarchical models, once appropriate limits have been taken.

Since both approximations are based upon the lowest order (dipole-dipole) interactions between inclusions, the only morphological information reflected in Eqs. (1) and (2) is the dimensionality and the phase volume fractions. In general, microstructural information beyond that contained in d and ϕ_i is required to accurately calculate σ_e for all σ_2/σ_1 and realizable volume fractions, and hence the Maxwell formula and the EMA are generally inadequate. For example, for dispersions of inclusions of arbitrary shape, both approximations cannot account for multipolar effects which are especially important when the inclusion volume fraction is large.

The complex interactions that are present in dispersions of impenetrable inclusions can be estimated by assuming that the inclusions are centered on the points of a periodic lattice.[9–12] Since the effective conductivity can be obtained exactly for such a dispersion at any volume fraction, the model serves as a useful theoretical benchmark. For random suspensions, however, exact results for the entire range of inclusion volume fractions do not exist even for the simple models of a random distribution of impenetrable spheres (for $d = 3$) or of impenetrable disks (for $d = 2$) in a matrix. One of the main aims of this article is to obtain an expression for σ_e of a broad class of dispersions, for a wide range of σ_2/σ_1 and inclusion volume fractions.

In Sec. II, a perturbation expansion for σ_e of any two-phase medium of arbitrary d (where $d = 2,3$) is derived using a technique first developed by Brown[13] for $d = 3$. The interest in two-dimensional composite media is twofold. From a theoretical point of view, it is desired to know the effect of dimensionality on σ_e. Secondly, two-dimensional media are often useful models for the practically important case of fiber-reinforced materials. In Sec. III it is noted that certain Padé approximants of particular series expansions of σ_e are equal to know rigorous bounds on σ_e. The relationship between the perturbation expansion derived in the previous section and the conductivities of certain microstructures which are exactly realized by the bounds is discussed. In Sec. IV an expression for the effective conductivity of three-dimensional dispersions is derived. This relation is shown to provide accurate estimates for σ_e of both periodic and random arrays of impenetrable spheres, for a wide range of σ_2/σ_1 ($0 < \sigma_2/\sigma_1 < \infty$) and inclusion volume fractions. More generally, the new expression is expected to yield useful estimates of the effective conductivity of any dispersion, provided that the mean cluster size of the dispersed phase is much smaller than the macroscopic dimensions of the sample. For reasons of mathematical analogy, results derived here for σ_e translate immediately into equivalent results for the effective thermal conductivity, dielectric constant, magnetic permeability, and diffusion coefficient of composite media.

II. PERTURBATION EXPANSION OF σ_e FOR ARBITRARY d

Brown[13] was the first to obtain a perturbation expansion of σ_e for three-dimensional two-phase composite media. Using a different approach, Hori,[14] and Hori and Yonezawa[15]

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obtained an analogous expansion of σ_e for $d=3$ and $d=2$, respectively. Employing the essential ideas of Brown,[13] Ramshaw[16] recently has obtained a wide variety of series representations of σ_e using general perturbation expansions of response kernels. Ramshaw has pointed out that the expansions derived in Refs. 14 and 15 are flawed because of an incorrect identification of the external field. Consequently, a perturbation expansion of σ_e for $d=2$ free of this error has heretofore not been derived.

Consider obtaining a perturbation expansion of σ_e for any statistically homogeneous and isotropic two-phase disordered medium of arbitrary dimensionality d (where $d=2$ or 3). The random medium is a domain of space D of volume V (or area A) which is subdivided into two phases; one phase D_1 characterized by volume (area) fraction ϕ_1 and conductivity σ_1, and another phase D_2 characterized by a volume (area) fraction ϕ_2 and conductivity σ_2. The local conductivity at position $\mathbf{r}$ for $\mathbf{r}\epsilon D$ is given by

$$\sigma(\mathbf{r}) = \sigma_j + (\sigma_i - \sigma_j) I^{(i)}(\mathbf{r}), \quad i \neq j, \tag{3}$$

where the characteristic function of phase i is

$$I^{(i)}(\mathbf{r}) = \begin{cases} 1, & \mathbf{r}\epsilon D_i \\ 0, & \text{otherwise.} \end{cases} \tag{4}$$

For generality the composite sample is assumed to be an ellipsoid (ellipse) of finite size and arbitrary shape. Now consider subjecting the specimen to the time-independent applied electric field $\mathbb{E}_0(\mathbf{r})$. 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 $\mathbb{E}(\mathbf{r})$[17]:

$$\mathbb{E}_L(\mathbf{r}) = \mathbb{E}_0(\mathbf{r}) + \int_\delta d\mathbf{r}' \mathbb{T}(\mathbf{r}-\mathbf{r}') \cdot \mathbb{P}(\mathbf{r}'), \tag{5}$$

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

$$\mathbb{E}_L(\mathbf{r}) = \left(1 + \frac{[\sigma(\mathbf{r}) - \sigma_j]}{\sigma_j d}\right) \mathbb{E}(\mathbf{r}) \tag{6}$$

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

$$\mathbb{P}(\mathbf{r}) = \frac{[\sigma(\mathbf{r}) - \sigma_j]}{2(d-1)\pi} \mathbb{E}(\mathbf{r}). \tag{7}$$

Moreover,

$$\mathbb{T}(\mathbf{r}) = \frac{d\mathbf{r}\mathbf{r} - r^2\mathsf{U}}{\sigma_j r^{d+2}}, \tag{8}$$

appearing in Eq. (5) is the dipole-dipole interaction tensor, where $r \equiv |\mathbf{r}|$ and U is the unit dyadic. The subscript δ on the integral of Eq. (5) (which is to be integrated over the sample volume V or area A) is carried out with the exclusion of an infinitesimally small sphere (circular disk) centered at $\mathbf{r}$. Combining Eqs. (6) and (7) gives

$$\mathbb{P}(\mathbf{r}) = \frac{\sigma_j d}{2(d-1)\pi} \left(\frac{\sigma(\mathbf{r}) - \sigma_j}{\sigma(\mathbf{r}) + (d-1)\sigma_j}\right) \mathbb{E}_L(\mathbf{r})$$
$$= \frac{\sigma_j d}{2(d-1)\pi} \beta_{ij} I^{(i)}(\mathbf{r}) \mathbf{E}_L(\mathbf{r}), \quad i \neq j, \tag{9}$$

where

$$\beta_{ij} = \frac{\sigma_i - \sigma_j}{\sigma_i + (d-1)\sigma_j} \tag{10}$$

is a parameter bounded by $-(d-1)^{-1} \leqslant \beta_{ij} \leqslant 1$ and, apart from a trivial constant, is equal to the dipole polarizability of a sphere of conductivity σ_i for $d=3$ and of a circular disk of conductivity σ_i for $d=2$, imbedded in a matrix of conductivity σ_j. The second line of Eq. (9) results when Eq. (3) is substituted into the first line.

The effective conductivity of the composite medium σ_e is defined through the averaged relation

$$\langle \mathbf{P}(\mathbf{r}) \rangle = \frac{\sigma_j d}{2(d-1)\pi} \left(\frac{\sigma_e - \sigma_j}{\sigma_e + (d-1)\sigma_j}\right) \langle \mathbb{E}_L(\mathbf{r}) \rangle, \tag{11}$$

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

The method to be used to derive the perturbation expansion of σ_e for arbitrary d is that given by Brown[13] for $d=3$. Given the formal solution (5) for arbitrary d, it is straightforward to obtain the desired expression for σ_e. The essence of Brown's technique may be briefly summarized as follows. An integral equation for the polarization $\mathbf{P}(\mathbf{r})$ is obtained by combining Eq. (5) and Eq. (9). The integral equation is solved for $\mathbf{P}(\mathbf{r})$ by successive substitutions, resulting in an expansion in powers of β_{ij}, which may be formally reexpressed 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 macroscopic electrostatics, however, relations between average fields 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. (5). This resulting relation between $\langle \mathbf{E}_L(\mathbf{r}) \rangle$ and $\langle \mathbf{P}(\mathbf{r}) \rangle$ is localized, i.e., independent of the shape of the sample and hence involves absolutely convergent integrals. One may now pass to the limit of an infinite volume V without any ambiguity and obtain from this localized relation, which defines σ_e [Eq. (11)], a perturbation expansion for σ_e of a statistically homogeneous and isotropic two-phase random medium. (For algebraic details of this procedure see Ref. 13.)

The expansion which results after employing this methodology is given by

$$(\beta_{ij}\phi_i)^2 \left(\frac{\sigma_e + (d-1)\sigma_j}{\sigma_e - \sigma_j}\right) = \phi_i \beta_{ij} - \sum_{n=3}^{\infty} A_n^{(i)} \beta_{ij}^n, \tag{12}$$

where $i \neq j$. Here the coefficients $A_n^{(i)}$ are integrals over a set of n-point probability functions:

$$A_n^{(i)} = \frac{(-1)^n \phi_i^{2-n}}{d} \left(\frac{d\sigma_j}{2\pi(d-1)}\right)^{n-1}$$
$$\times \int\int \cdots \int d\mathbf{r}_2 d\mathbf{r}_3 \cdots d\mathbf{r}_n$$
$$\times \mathbb{T}(1,2) \cdot \mathbb{T}(2,3) \cdots \mathbb{T}(n-1,n) : \mathsf{U} C_n^{(i)}(1,2,\ldots,n), \tag{13}$$

where $\mathbb{T}(i,j)$ stands for $\mathbb{T}(\mathbf{r}_i - \mathbf{r}_j)$ and $C_n^{(i)}$ is the determinant

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$$C_n^{(i)} = \begin{vmatrix} S_2^{(i)}(1,2) & S_1^{(i)}(2) & 0 & \cdots & 0 & 0 \\ S_3^{(i)}(1,2,3) & S_2^{(i)}(2,3) & S_1^{(i)}(3) & \cdots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ S_{n-1}^{(i)}(1,2,...,n-1) & S_{n-2}^{(i)}(2,3,...,n-1) & S_{n-3}^{(i)}(3,4,...,n-1) & \cdots & S_2^{(i)}(n-2,n-1) & S_1^{(i)}(n-1) \\ S_n^{(i)}(1,2,...,n) & S_{n-1}^{(i)}(2,3,...,n) & S_{n-2}^{(i)}(3,4,...,n) & \cdots & S_3^{(i)}(n-2,n-1,n) & S_2^{(i)}(n-1,n) \end{vmatrix}. \quad (14)$$

Here

$$S_n^{(i)}(1,2,...,n) = S_n^{(i)}(\mathbf{r}_{12},...,\mathbf{r}_{1n}) = \langle I^{(i)}(\mathbf{r}_1)I^{(i)}(\mathbf{r}_2)...I^{(i)}(\mathbf{r}_n)\rangle, \quad (15)$$

gives the probability of finding n points with positions $\mathbf{r}_1$, $\mathbf{r}_2$,..., $\mathbf{r}_n$ all in phase i and for isotropic media only depends upon $|\mathbf{r}_{ij}|$, $1 \leqslant i < j \leqslant n$. The quantities within the angular brackets of Eq. (15) are the characteristic functions of phase i given by Eq. (3). The one-point function $S_1^{(i)}$ is simply the volume fraction of phase i, i.e., ϕ_i. The limit $V \to \infty$ ($A \to \infty$) is implicit in the integrals (13) and since the determinant $C_n^{(i)}$ identically vanishes at the boundaries of the sample (because of the asymptotic properties of the $S_n^{(i)}$[18]), the integrals are shape-independent and hence any convenient shape (such as a sphere for $d = 3$ or circular disk for $d = 2$) may be employed. Moreover, the limiting process of excluding an infinitesimally small cavity about $r_{ij} = 0$ in the integrals (13) is no longer necessary since $C_n^{(i)}$ again is identically zero for such values.

Note that result (12) actually represents two series expansions; one for $i = 1$ and $j = 2$ and the other for $i = 2$ and $j = 1$. For two-dimensional two-phase composite media, series (12) appears to be new. From Eqs. (12)–(15) it is seen that coefficients $A_n^{(i)}$ depend upon the set $S_1^{(i)}, S_2^{(i)},...,S_n^{(i)}$. Accordingly, $A_n^{(i)}$ is referred to as the n-point microstructural parameter. An exact determination of σ_e for arbitrary composite media is usually not possible since the associated set of n-point probability functions are, in general, too complex to determine. In the subsequent section the relationship between series (12) and certain exactly soluble random-media models shall be discussed.

That σ_e remains invariant under interchange of the phases in Eq. (12) implies that n-point parameters for phases 1 and 2, $A_n^{(1)}$ and $A_n^{(2)}$, respectively, are dependent upon one another. For instance, for $n = 3$ and $n = 4$, one has

$$\zeta_1 + \zeta_2 = 1 \quad (16)$$

and

$$\gamma_1 - \gamma_2 = (d-2)(\zeta_2 - \zeta_1), \quad (17)$$

where for $i \neq j$

$$\zeta_i = \frac{A_3^{(i)}}{\phi_i \phi_j (d-1)} \quad (18)$$

and

$$\gamma_i = \frac{A_4^{(i)}}{\phi_i \phi_j (d-1)}. \quad (19)$$

Brown[13] and Milton[19] for $d = 3$ and $d = 2$, respectively, showed that the three-point parameter ζ_i must lie in the closed interval [0,1]. Referring to Eqs. (12)–(14) and Eq. (18), it is straightforward to show that ζ_i in two and three dimensions is, respectively, given by

$$\zeta_i = \frac{4}{\pi \phi_1 \phi_2} \int_0^\infty \frac{dr}{r} \int_0^\infty \frac{ds}{s} \int_0^\pi d\theta \cos(2\theta) \times \left(S_3^{(i)}(r,s,\theta) - \frac{S_2^{(i)}(r) S_2^{(i)}(s)}{S_1^{(i)}} \right) \quad (20)$$

and

$$\zeta_i = \frac{9}{2\phi_1 \phi_2} \int_0^\infty \frac{dr}{r} \int_0^\infty \frac{ds}{s} \int_{-1}^1 d(\cos\theta) P_2(\cos\theta) \times \left(S_3^{(i)}(r,s,\theta) - \frac{S_2^{(i)}(r) S_2^{(i)}(s)}{S_1^{(i)}} \right), \quad (21)$$

where P_2 is the Legendre polynomial of order 2 and θ is the angle opposite the side of the triangle of length $|\mathbf{r} - \mathbf{s}|$.

Note that in two dimensions the right-hand side of Eq. (17) is zero. Some general results for the four-point parameters $A_4^{(i)}$ and γ_i are presented in the subsequent section.

III. PADÉ APPROXIMANTS AND BOUNDS

Until recently, knowledge of lower-order n-point probability functions (i.e., $S_1^{(i)}, S_2^{(i)}, S_3^{(i)}$, and $S_4^{(i)}$ has been virtually nonexistent, either experimentally or theoretically.[20] In the last several years considerable progress has been made in the determination of lower-order n-point functions for realistic models of composite media.[18,21–24] It appears that the determination of the $S_n^{(i)}$ for $n \geqslant 5$ of arbitrary media is beyond presently available technology. Thus series representations of σ_e, such as Eq. (12), cannot be exactly summed. The Padé approximant technique, however, provides a means of approximately summing a series while employing only a limited number of its terms.[25]

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Consider obtaining the expansion of the dimensionless effective conductivity σ_e/σ_j in powers of β_{ij} from series (12). The [1/1] and [2/2] Padé approximants of this series are thus, respectively

$$\frac{\sigma_e}{\sigma_j}=\frac{1+(d-1)\phi_i\beta_{ij}}{1-\phi_i\beta_{ij}} \tag{22}$$

and

$$\frac{\sigma_e}{\sigma_j}=\frac{1+[(d-1)\phi_i-\gamma_i/\zeta_i]\beta_{ij}+(1-d)[\phi_j\zeta_i+\phi_i\gamma_i/\zeta_i]\beta_{ij}^2}{1-[\phi_i+\gamma_i/\zeta_i]\beta_{ij}+[\phi_j(1-d)\zeta_i+\phi_i\gamma_i/\zeta_i]\beta_{ij}^2}, \tag{23}$$

where $i\neq j$ and the macrostructural parameters ζ_i and γ_i are given by Eqs. (18) and (19), respectively. It is important to note that Eqs. (22) and (23) are actually known rigorous second-order[26,27] and fourth-order[28,29] bounds on σ_e/σ_j, respectively. In fact, the $[m/m]$ Padé approximant of the expansion of σ_e/σ_j in powers of β_{ij} can be shown to yield the nth-order bounds, for any $n=2m$ $(m\geqslant 1)$, derived by Milton.[28] (Bounds are referred to as nth-order bounds in the sense that they are exact through nth order in the difference σ_i-σ_j.) Bounds have been typically derived using either variational principles[26,27,29,30] or by making use of the analytic properties of σ_e.[28,31] The reason why the Padé approximants provide rigorous bounds is that the effective conductivity can be written as a Stieltjes series.[25] Certain Padé approximants of Stieltjes functions are known to form converging upper and lower bounds.[25] Milton[32] has noted that particular Padé approximants of the expansion of σ_e/σ_j in powers of $(1-\sigma_j/\sigma_i)$ yield his nth-order bounds. The use of the Padé approximant method to yield bounds has yet to be fully exploited. For example, is there any particular advantage in studying one series representation of σ_e over another? The results of Sec. IV suggests there is such an advantage.

For subsequent discussion, it will be useful to understand the relationship between series (12) and the microgeometries which are realized by lower-order bounds. If $j=1$ and $\alpha=\sigma_2/\sigma_1\geqslant 1$, then Eq. (22) is the second-order lower bound derived by Hashin and Shtrikman[26] for $d=3$ and by Hashin[27] for $d=2$, and is equal to the Maxwell formula, Eq. (1), for arbitrary d. If $j=2$ and $\alpha\geqslant 1$, then Eq. (22) is the corresponding second-order upper bound.[26,27] Since second-order bounds are exactly realized for certain composite sphere (circular disk) assemblages described below, they are the best possible bounds when ϕ_i is the only known microstructural information. Note that for both of these exactly realizable models, it is seen that the n-point coefficients $A_n^{(i)}$ of series (12) are identically zero for all $n\geqslant 3$.

Equation (23) can be shown to be equivalent to fourth-order bounds on σ_e due to Milton[28] and Phan-Thien and Milton.[29] Consider first the case $d=2$. Milton[28] employed a phase-interchange theorem for $d=2$[33,34] to show that all even-order coefficients of an expansion of σ_e in powers of $\sigma_i-\sigma_j$ could be expressed in terms of all lower-order coefficients. Applying this phase–interchange theorem here reveals that the four-point parameters $A_4^{(i)}$ and γ_i, for $i=1,2$, are exactly zero for $d=2$. Equation (23) for $d=2$ is therefore given by

$$\frac{\sigma_e}{\sigma_j}=\frac{1+\phi_i\beta_{ij}-\phi_j\zeta_i\beta_{ij}^2}{1-\phi_i\beta_{ij}-\phi_j\zeta_i\beta_{ij}^2}, \tag{24}$$

where again $i\neq j$.

If $j=1$ and $\alpha\geqslant 1$, then Eq. (24) is precisely the fourth-order lower bound obtained by Milton.[28] This bound is exactly realized for a material composed of composite circular disks consisting of a core of conductivity σ_1 and radius R_c, surrounded by a concentric shell of conductivity σ_2 and outer radius R_0, which is in turn surrounded by a concentric shell of conductivity σ_1 and outer radius R. The ratio R_c^2/R_0^2 is such that it equals the constant $\phi_1\zeta_2$ and the composite disks fill all space, implying that there is a distribution in their sizes ranging to the infinitesimally small. Note that the more conducting phase (phase 2) is the dispersed or discontinuous phase and hence can only percolate at the trivial value $\phi_2=1$. This means that the fourth-order lower bound on σ_e/σ_1, always remains finite even in the limit $\alpha\to\infty$.

If $j=2$ and $\alpha\geqslant 1$, then Eq. (24) is equal to the fourth-order upper bound derived by Milton[28] and corresponds to a material with a microstructure similar to that associated with the lower bound, but where the roles of the phases are interchanged. For this microgeometry the more conducting phase is now the continuous phase and hence the fourth-order upper bound on σ_e/σ_1 diverges to infinity in the limit $\alpha\to\infty$, for $\phi_2>0$.

One need only reverse the role of the phases and the inequality signs of fourth-order bounds for $\alpha\geqslant 1$, in order to obtain fourth-order bounds for $\alpha\leqslant 1$. It is clear that in the limit $\alpha\to 0$, the fourth-order lower bound on σ_e/σ_1 vanishes identically, whereas the corresponding upper bound remains finite.

For even values of n, the nth-order bounds for $d=2$ are exactly realized for space-filling multicoated disks, where each multicoated disk has $n/2$ coatings and is similar, to within a scale factor, to any other multicoated disk in the composite. The fourth-order bounds on σ_e for $d=2$ have been evaluated for the first time by Torquato and Beasley[35] for a distribution of fully penetrable disks (i.e., randomly centered disks).

Comparing Eq. (24) for the doubly coated disk model to series (12) reveals that the n-point parameters $A_n^{(i)}$ are exactly given by

$$A_3^{(i)}=\phi_i\phi_j\zeta_i \text{ and } A_n^{(i)}=0, \quad \text{for } n\geqslant 4. \tag{25}$$

Therefore, for $\zeta_i=0$ (i.e., when the core radius $R_c=0$), the geometries corresponding to the second-order bounds are recovered. The fourth-order bounds always improve upon second-order bounds for $0<\zeta_i<1$.

Phan-Thien and Milton[29] have obtained fourth-order bounds on σ_e for $d=3$ in terms of the three-point parameter ζ_i and a four-point parameter they denote by $B^{\ddagger}$. It can be

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directly verified that the ratio γ_i/ζ_i, which appears in Eq. (23), is equal to $1-2\zeta_i-3\zeta_j B^{\ddagger}$ for $d=3$. Consequently, for $j=1$ and $\alpha\gg1$ and for $j=2$ and $\alpha\gg1$, Eq. (23) gives, respectively, the fourth-order upper and lower bounds on σ_e due to Phan-Thien and Milton. The ratio γ_i/ζ_i for $d=3$ bounded by

$$-1\leqslant\frac{\gamma_i}{\zeta_i}\leqslant 1-2\zeta_i. \qquad (26)$$

The upper bound of Eq. (26) is derived by expanding the third-order Beran upper bound on σ_e[30] through fourth-order in $\sigma_i-\sigma_j$ and comparing to the exact expansion through fourth order obtained from Eq. (12). The lower bound of Eq. (26) is obtained by employing a bound on a quantity related to the four-point parameter of Ref. 29 derived by Milton.[8]

Combination of the lower bound of Eq. (26) and Eq. (24), with $j=1$ and $\alpha\gg1$, gives a third-order lower bound on σ_e for $d=3$ due to Milton.[8,28] This lower bound improves upon the third-order lower bound of Beran[30] and is exactly realized for a material which is the three-dimensional analog of the aforementioned doubly-coated disk model. For this geometry it follows that

$$(\beta_{21}\phi_2)^2\left(\frac{\sigma_e+2\sigma_1}{\sigma_e-\sigma_1}\right)=\frac{\phi_2\beta_{21}+\phi_2\beta_{21}^2-2\phi_1\phi_2\zeta_2\beta_{21}^3}{1+\beta_{21}}. \qquad (27)$$

Expanding the right-hand side of Eq. (27) in powers of β_{21} and comparing to series (12) yields that the nth-order coefficients for this doubly coated sphere model are exactly given by

$$A_n^{(2)}=(-1)^{n+1}2\phi_1\phi_2\zeta_2, \quad \text{for } n\geqslant3. \qquad (28)$$

Since this expansion of Eq. (27) converges for $|\beta_{21}|<1$ and since β_{21} is bounded by $-0.5\leqslant\beta_{21}\leqslant1$ for $d=3$, then $\beta_{21}=1$ is the only value of β_{21} at which the series does not converge, i.e., when phase 2 is a perfect conductor relative to phase 1. It is interesting to note that unlike the present case, the n-point parameters $A_n^{(i)}$ for the two-dimensional analog of this model are all zero for $n\geqslant4$ [see Eq. (25)].

Before closing this section, it is useful to comment on the utility of bounds to estimate σ_e for cases in which one phase is highly conducting relative to the other. In light of the correspondence between nth-order bounds and certain realizable geometries described above, it is expected that nth-order lower bounds, for large n, will yield accurate estimates of σ_e/σ_1, provided that the volume fraction of the highly conducting phase, say phase 2, is below its percolation-threshold value ϕ_2^c. Similarly, nth-order upper bounds, for large n, should give accurate estimates of σ_e/σ_1, provided that $\phi_2\geqslant\phi_2^c$.

Lower-order lower bounds, such as second-, third-, and fourth-order bounds, are expected to yield good estimates of σ_e/σ_1, provided that $\phi_2<\phi_2^c$ and that the mean cluster size of phase 2, Λ_2, is much smaller than the macroscopic dimension of the sample L. A cluster of phase i is defined as the part of phase i which can be reached from a point in phase i without touching any part of phase j, $i\neq j$. For composite media composed of highly conducting inclusions in a matrix, Λ_2 is obviously comparable to L at the percolation threshold of the included phase and can be written in terms of the pair-connectedness function; a quantity which yields the probability that two inclusions belong to same cluster.[36] For spatially periodic arrays of impenetrable spheres or disks, or for equilibrium distribution of impenetrable spheres or disks, the condition $\Lambda_2\ll L$ is satisfied for all ϕ_2, except at the close-packing value, i.e., the percolation-threshold value for such systems. Lower-order upper bounds, moreover, should provide useful estimates of σ_e/σ_1, provided that $\phi_2\gg\phi_2^c$ and $\Lambda_1\ll L$, where Λ_1 is the mean cluster size of phase 1. Of course the accuracy of the lower-order bounds improve as n increases.

IV. CONDUCTIVITY OF THREE-DIMENSIONAL DISPERSIONS

Referring to Eq. (26) it is seen that as the ratio γ_2/ζ_2 for $d=3$ is varied between -1 and $1-2\zeta_2$, Eq. (23) for σ_e/σ_1 spans the possible solutions (including nth-order bounds, where $n\geqslant4$) between Milton's third-order lower bound[8,28] and Beran's third-order upper bound,[30] for $\alpha\gg1$. Ideally it would be desirable to select a ratio γ_2/ζ_2 that heavily weights the third-order lower bound for $\phi_2<\phi_2^c$ and the third-order upper bound for $\phi_2\geqslant\phi_2^c$. This is a formidable task for general microstructures. Attention here shall be focused on obtaining an expression for σ_e/σ_1 of three-dimensional isotropic dispersions, by choosing a reasonable value of γ_2/ζ_2 for such a composite, that will yield useful estimates of σ_e/σ_1 for all α and $\phi_2<\phi_2^c$. In what follows phase 2 shall be taken to be the dispersed phase and phase 1, the continuously connected matrix.

Employing expressions for σ_e of various periodic arrays of spheres[12] and corresponding values of ζ_2 for such geometries,[37] it is observed that the first two terms of series (12) for $j=1$ (i.e., terms through order β_{21}^3) provides a remarkably good approximation of the left-hand side of Eq. (12) of simple, body-centered and face-centered-cubic arrays, for the broad range of α and ϕ_2 over which the analytical expressions[12] are applicable. This implies that the remainder $\Sigma_{n=4}^{\infty}A_n^{(2)}\beta_{21}^n\simeq0$ for such microstructures and values of α and ϕ_2. If this remainder is assumed to be zero, then the expression which results by solving Eq. (12) for σ_e/σ_1 is given by

$$\frac{\sigma_e}{\sigma_1}=\frac{1+2\phi_2\beta_{21}-2\phi_1\zeta_2\beta_{21}^2}{1-\phi_2\beta_{21}-2\phi_1\zeta_2\beta_{21}^2}. \qquad (29)$$

Equation (29) is precisely Eq. (23) for $j=1$, but with γ_2/ζ_2 or γ_2 equal to 0. This is not to say that γ_2 is actually zero for such dispersions (since in fact γ_2 will depend on ϕ_2 in some complex fashion), rather setting $\gamma_2=0$ in Eq. (23) should provide a useful estimate of σ_e/σ_1 for this and similar dispersions. Specifically, for dispersions in which $\Lambda_2\ll L$, Eq. (29) will behave as an *approximate* higher-order lower bound when $\alpha\geqslant1$ and as an *approximate* higher-order upper bound when $\alpha\leqslant1$. The condition $\Lambda_2\ll L$ implies that ϕ_2 must always be below the percolation-threshold value ϕ_2^c. Setting $\gamma_2=0$ always satisfies the lower bound of Eq. (26), but satisfies the upper bound only if $\zeta_2\leqslant0.5$. [Recall that for $d=2$, γ_2 is exactly equal to zero—see Eq. (25).]

Table I lists the three-point parameter ζ_2, Eq. (21), for three cubic lattices of spheres,[37] randomly distributed impenetrable spheres,[38] and a distribution of fully penetrable

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TABLE I. The three-point parameter ζ_2, Eq. (21), for periodic arrays of spheres,[37] randomly distributed impenetrable spheres[38] and fully penetrable spheres,[22,39] for various values of the sphere volume fraction ϕ_2. The asterisk indicates a value not reported in the original source.

ϕ_2	Simple cubic	Body-centered cubic	Face-centered cubic	Random impenetrable spheres	Fully penetrable spheres
0.10	0.0003	0.0000	0.0000	0.0205	0.0564
0.20	0.0050	0.0007	0.0004	0.0398	0.1135
0.30	0.0220	0.0031	0.0021	0.0587	0.1712
0.40	0.0678	0.0107	0.0078	0.0836	0.2298
0.50	0.1738	0.0307	0.0232	0.1407	0.2897
0.60		0.0796	0.0619	0.3277	0.3511
0.65		0.1261	*		*
0.70			0.1596		0.4149
0.71			0.1756		*
0.80					0.4826
0.90					0.5584

spheres,[21,39] as a function of the volume fraction ϕ_2. For these geometries, $\zeta_2 < 0.5$ for all realizable ϕ_2 [and therefore satisfies the upper bound of Eq. (26) when γ_2 is assumed to be zero], except when $\phi_2 > 0.83$ in the case of a dispersion of fully penetrable spheres (i.e., randomly centered spheres). For the model of fully penetrable spheres, however, approximation (29) should not be applied at such high inclusion volume fractions since $\phi_2^c = 0.3$.[40] In fact large clusters of particles (smaller than L) will begin to form in this system for ϕ_2 near but smaller than ϕ_2^c. The maximum value of ϕ_2 listed in Table I for simple, body-centered and face-centered-cubic lattices are approximately 96% of their respective close-packing values. It should be noted that Felderhof[41] was the first to calculate ζ_2 for a random distribution of impenetrable spheres. He calculated ζ_2 through order ϕ_2^3 for an equilibrium distribution of impenetrable spheres by employing, among other approximations, the superposition approximation for the three-body distribution function.[42] [The three point function $S_3^{(i)}$, which arises in Eq. (21), has been shown for dispersions of impenetrable spheres to depend upon, among other quantities, the three-body distribution function.][23] The results given in Table I were calculated exactly, within the superposition approximation, through all orders in ϕ_2 for an equilibrium distribution of impenetrable spheres.[38] The value of ϕ_2^c for random impenetrable spheres is conjectured to be the random close-packing limit, i.e., $\phi_2^c \simeq 0.64$.[43] Errors in the calculated values of ζ_2 that may possibly arise because of the use of the superposition approximation will occur at moderate to high sphere volume fractions.

Figure 1 compares exact numerical results for σ_e/σ_1 of cubic lattices at the extreme condition $\alpha = \infty$ as a function of ϕ_2,[10] to corresponding results of σ_e/σ_1 predicted by Eq. (29), employing ζ_2 for the values of ϕ_2 listed in Table I. Included in Fig. 1 is the Maxwell formula, Eq. (1), or equivalently, the second-order lower bound, Eq. (22) with $j = 1$, for $d = 3$. For finite ϕ_2 the EMA [Eq. (2)] at $\alpha = \infty$ predicts an infinite value of σ_e/σ_1. Equation (29) is seen to provide an excellent estimate of σ_e/σ_1 for these microstructures, even up to volume fractions approaching ϕ_2^c, implying that it incorporates the salient multipolar effects that are especially important when ϕ_2 is large. In Fig. 1 the largest error for simple, body-centered and face-centered-cubic arrays occurs at the respective ratios ϕ_2/ϕ_2^c equal to 0.96, 0.96, and 0.92. At these volume fractions, Eq. (29) for $\alpha = \infty$ predicts σ_e/σ_1 to be 5.60(5.89), 8.45(9.03), and 9.67(9.26); where exact values[10] are given in parenthesis. For values of α in the range $0 < \alpha < \infty$, the deviation of Eq. (29) from exact results is even less than it is for the case $\alpha = \infty$.

Sangani and Acrivos[12] have derived exact expressions for σ_e/σ_1 through $O(\phi_2^9)$, for the periodic arrays of spheres considered here, which take into account poles of order 2^7. It is noteworthy that Eq. (29) provides a better estimate for σ_e/σ_1 of such dispersions for large ϕ_2 and α than do the

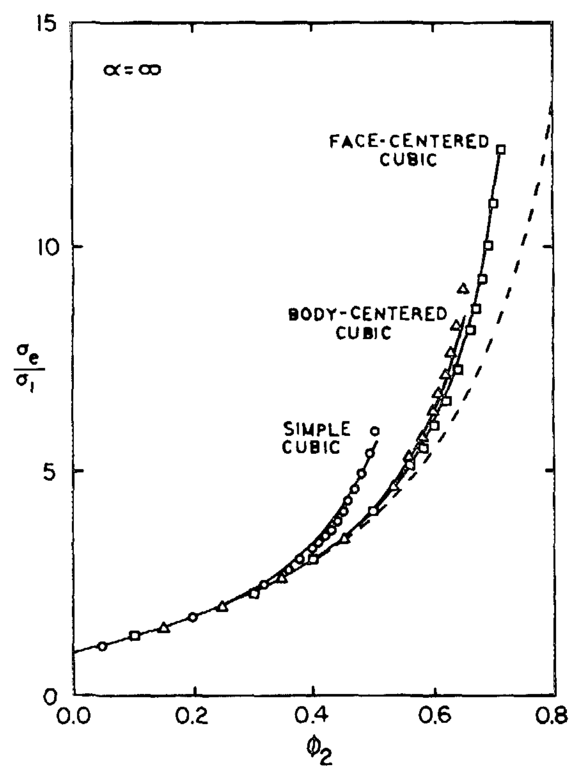

FIG. 1. The reduced effective conductivity σ_e/σ_1, for $\alpha = \sigma_2/\sigma_1 = \infty$, as a function of the sphere volume fraction ϕ_2, for three cubic lattices of spheres. Exact values for simple, body-centered, and face-centered cubic[10] are denoted by ○, Δ, and □, respectively. Solid lines represent predicted values from Eq. (29). Included is the second-order lower bound for $d = 3$, Eq. (22), which is represented by a dashed line.

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Sangani–Acrivos expressions. For low to moderate values of ϕ_2, Eq. (29) and the formulas given in Ref. 12 are in very good agreement for a wide range of α.

Turner[44] has measured the electrical conductivity of a fluidized bed of equisized impenetrable spheres for various values of ϕ_2 and α. It is not fully clear whether the static and random distribution of impenetrable spheres implied by an equilibrium distribution of such spheres is a good model of a fluidized bed of impenetrable spheres for all values of ϕ_2. Most data reported for static distributions, however, are carried out on beds of particles, i.e., at a single, close-packing volume fraction. Moreover, the particles often are characterized by a size distribution and sometimes are not spherical. Hence, Turner's data are the best measurements available for comparison to the equilibrium model employed here.

Equation (30) for an equilibrium distribution of impenetrable spheres yields reduced conductivities σ_e/σ_1 which are in very close agreement with Turner's data for a wide range of conditions, provided that both α and ϕ_2 are not very large. (The parameter ζ_2 for the model is taken from Table I.) In Fig. 2, Eq. (29) for the model at $\alpha = \infty$ is compared to Turner's measurements at $\alpha = 14\,400$. Predicted values of σ_e/σ_1 from the second-order lower bound, Eq. (22), and from an expression obtained by Chiew and Glandt[45] which is applicable specifically to equilibrium dispersions of impenetrable spheres. For very large ϕ_2 (i.e., $0.58<\phi_2<0.6$), Eq. (29) lies closer to the data than does the Chiew-Glandt expression. On the other hand, for $0.2 < \phi_2 < 0.58$, the latter expression more closely represents the data.

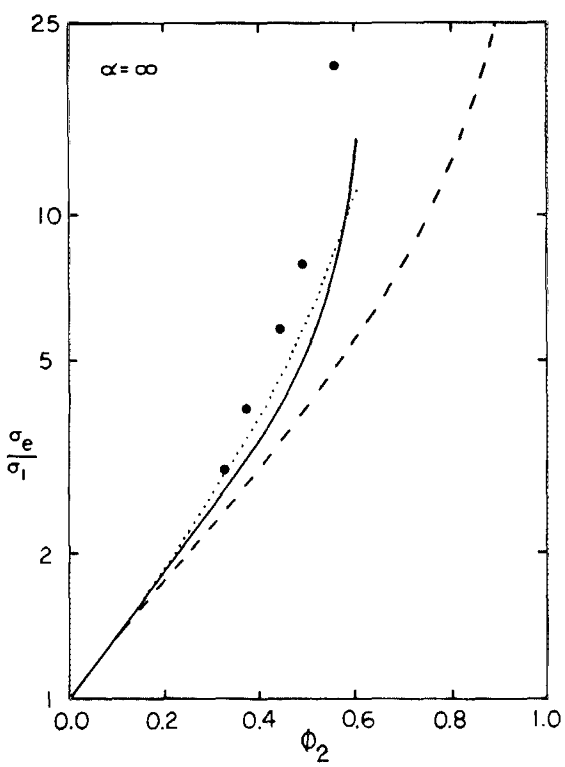

FIG. 2. The reduced effective conductivity σ_e/σ_1, for $\alpha = \sigma_2/\sigma_1 = \infty$, as a function of the sphere volume fraction ϕ_2, for random dispersions of impenetrable spheres. Filled circles are Turner's data[44] for a fluidized bed of impenetrable spheres at $\alpha = 14\,400$. Solid line represents Eq. (29) for an equilibrium distribution of impenetrable spheres. Dotted line represents predicted values from the expression obtained by Chiew and Glandt.[45] Dashed line represents the second-order lower bound for $d = 3$, Eq. (22).

There is very strong evidence to suggest, however, that the values of ζ_2 listed in Table I and, thus, the predicted values of σ_e from Eq. (29) for the model are too low at moderate to high densities because of the use of the superposition approximation.[42] First of all, Beasley and Torquato[46] have recently shown that the third-order coefficient of an expansion of ζ_2 in powers ϕ_2 is larger than the corresponding coefficient obtained by using the superposition approximation. The approximation gives the zeroth-, first-, and second-order coefficients exactly. Therefore, through third-order in ϕ_2, the exact value of ζ_2 will always be higher than the value of ζ_2 calculated using the superposition approximation. Secondly, in light of the excellent agreement found between exact results for σ_e of periodic arrays of spheres and Eq. (29) (in conjunction with exact values of ζ_2 for this geometry), it is expected that Eq. (29) should accurately represent data for dispersions of random impenetrable spheres provided that ζ_2 is precisely determined. Hence, to the extent that Turner's data is well represented by an equilibrium model, it is likely that the deviation of the predicted values of Eq. (29) from the data in Fig. 2 is largely due to errors in ζ_2 and, thus, to the use of the superposition approximation.

Unlike Eq. (29), the Chiew–Glandt formula is exact through $0(\phi_2^2)$ for an equilibrium distribution of equisized impenetrable spheres. The Chiew-Glandt expression is applicable to the specific geometry of a dispersion of impenetrable spheres. Equation (29) has the advantage of greater generality in that it can be applied to accurately predict the conductivity of a dispersion of arbitrary geometry, given the three-point parameter ζ_2 of the medium provided that the conditions described above are satisfied. The parameter ζ_2, Eq. (21), is calculated by employing the three-point probability function of the composite[47] determined either from photographs of cross sections of the material[20,24] or from theoretical considerations.[21–23,35]

It is of interest to study the low-density behavior of Eq. (29) for a dispersion of equisized spheres distributed with arbitrary degree of impenetrability. In the permeable-sphere (PS) model,[48] spherical inclusions of radius R are assumed to be structurally noninteracting when nonintersecting (i.e., where $r>2R$, where r is the distance between sphere centers), with the probability of intersecting given by $1-\lambda$, when $r<2R$. The quantity λ is an impenetrability parameter which varies between zero (in the case where the sphere centers are randomly centered, i.e., fully penetrable spheres) and unity (in the instance of totally impenetrable spheres). Expanding Eq. (29) through $O(\phi_2^2)$ and employing the low-density expansion of ζ_2 in the PS model[49] gives that

$$\sigma_e/\sigma_1 = 1 + K_1\phi_2 + K_2\phi_2^2, \qquad (30)$$

where

$$K_1 = 3\beta_{21} \qquad (31)$$

and

$$K_2 = 3\beta_{21}^2 + 6\beta_{21}^3\,[0.21068 + 0.35078\,(1-\lambda)]. \qquad (32)$$

The first-order coefficient K_1 is exact for any sphere distribution. For totally impenetrable spheres (i.e., $\lambda = 1$), the sec-

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ond-order coefficient given by Eq. (32) is in good agreement with the exact result obtained by Jeffrey,[50] for all values of α, and is exact through order β^3. For $0\leqslant\lambda<1$, Eq. (32) lies between rigorous upper and lower bounds on K_2, for all α[49] and predicts, as expected, a value of K_2 larger than that for the case of totally impenetrable spheres. Not surprisingly, Eq. (32) lies closer to the lower bound[49] for $\alpha>1$ and lies closer to the upper bound[49] for $\alpha<1$.

In summary, Eq. (29) should provide an accurate estimate for σ_e/σ_1 of dispersions for all values of α, provided that $\Lambda_2 \ll L$ and $0<\zeta_2<0.5$. The three-point parameter depends upon the three-point probability function which can be obtained either for theoretical models of composite media[21-23,35] or from photographs of cross sections of the material.[20,24] Although this expression has been tested only against known results for dispersions of equisized impenetrable spheres, it is expected that Eq. (29) will provide good estimates for σ_e/σ_1 of dispersions composed of inclusions of arbitrary shape and size, for all values of α, as long as the conditions described above are satisfied. For example, for dispersions of fully penetrable spheres,[21,39] the approximation should accurately estimate σ_e/σ_1, provided that ϕ_2 is below approximately 0.2.

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