Bounds on the Effective Transport and Elastic Properties of a Random Array of Cylindrical Fibers in a Matrix

S. Torquato
Associate Professor.
Department of Mechanical and Aerospace Engineering and Department of Chemical Engineering,
Box 7910.
Mem. ASME

F. Lado
Professor.
Department of Physics,
Box 8202.

North Carolina State University,
Raleigh, NC 27695

This paper studies the determination of rigorous upper and lower bounds on the effective transport and elastic moduli of a transversely isotropic fiber-reinforced composite derived by Silnutzer and by Milton. The third-order Silnutzer bounds on the transverse conductivity σ_e, the transverse bulk modulus k_e, and the axial shear modulus μ_e, depend upon the microstructure through a three-point correlation function of the medium. The fourth-order Milton bounds on σ_e and μ_e depend not only upon three-point information but upon the next level of information, i.e., a four-point correlation function. The aforementioned microstructure-sensitive bounds are computed, using methods and results of statistical mechanics, for the model of aligned, infinitely long, equisized, circular cylinders which are randomly distributed throughout a matrix, for fiber volume fractions up to 65 percent. For a wide range of volume fractions and phase property values, the Silnutzer bounds significantly improve upon corresponding second-order bounds due to Hill and to Hashin; the Milton bounds, moreover, are narrower than the third-order Silnutzer bounds. When the cylinders are perfectly conducting or perfectly rigid, it is shown that Milton's lower bound on σ_e or μ_e provides an excellent estimate of these effective parameters for the wide range of volume fractions studied here. This conclusion is supported by computer-simulation results for σ_e and by experimental data for a graphite-plastic composite.

1 Introduction

The problem of predicting the effective transport and elastic properties of composite materials is an outstanding one in science and engineering, and has received considerable attention in recent years (see Christensen, 1979; Chou and Kelly, 1980; Hashin, 1983; Torquato, 1987; and references therein). From a fundamental as well as design standpoint, it is desirable to calculate the effective properties from a knowledge of the microstructure of the composite medium; one can then relate changes in the microstructure quantitatively to changes in the macroscopic variables. Unfortunately, in order to exactly predict the effective property, an infinite set of correlation functions, which statistically characterize the microstructure, must be known (Milton, 1981; Torquato, 1985). Except in a few special cases (e.g., idealized periodic arrays—see Perrins, McKenzie, and McPhedran, 1979), the infinite set of correlation functions is never known and, hence, an exact determination of the effective property, for all phase property values and volume fractions, is generally out of the question, even for simple random materials (e.g., random array of impenetrable cylinders).

Rigorous bounding methods, however, provide a means of estimating the effective property given a *limited* amount of microstructural information on the composite material. Rigorous upper and lower bounds on the effective properties are useful because: (*i*) They enable one to test the merits of a theory; (*ii*) As successively more microstructural information is included, the bounds become progressively tighter; (*iii*) One of the bounds can typically provide a relatively accurate estimate of the property even when the reciprocal bound diverges from it (Torquato, 1987).

We shall be concerned with the evaluation of bounds on the effective transverse thermal (electrical) conductivity σ_e, effective transverse bulk modulus k_e, and effective axial shear modulus μ_e of transversely isotropic fiber-reinforced materials composed of two different materials (phases). By "fiber-reinforced" material we mean any material whose phase boundaries are cylindrical surfaces, with generators parallel to one axis (Hill, 1964; Hashin, 1965). Continuous glass, carbon, or graphite fibers in an epoxy matrix are examples of composites that fall within this category (Hashin, 1983).

Given only the phase volume fractions, conductivities, bulk

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moduli, and shear moduli, denoted respectively by ϕ_1 and ϕ_2, σ_1 and σ_2, K_1 and K_2, and G_1 and G_2, the best possible rigorous bounds on σ_e, k_e, and μ_e have been derived by Hill (1964) and by Hashin (1965, 1970). More restrictive bounds on these effective properties which include additional microstructural information on the transversely isotropic fiber-reinforced material have been obtained by Silnutzer (1972) and by Milton (1981, 1982). The Silnutzer bounds on σ_e, k_e, and μ_e incorporate the three-point probability function S_3. The quantity $S_n(\mathbf{r}_1, \ldots, \mathbf{r}_n)$ gives the probability of finding n points at positions $\mathbf{r}_1, \ldots, \mathbf{r}_n$ all in one of the phases, say phase 2. Milton's bounds on σ_e depend not only upon S_3 but upon S_4. Application of the Silnutzer and Milton bounds for disordered composites has been virtually nonexistent because of the difficulty involved in determining S_3 and S_4, either experimentally or theoretically. Substantial progress in the quantitative characterization of the microstructure of disordered heterogeneous media has been made in the past several years, including experimental (Berryman and Blair, 1986), computer-simulation (Haile, Massobrio, and Torquato, 1985; Seaton and Glandt, 1986; Smith and Torquato, 1988) and theoretical (Torquato and Stell, 1982; Torquato and Stell, 1985; Torquato, 1986) advances.

In this article, we shall compute the Silnutzer and Milton bounds on the aforementioned effective properties for the practically useful model of impenetrable, parallel, infinitely long, equisized, circular cylinders (or circular disks in two dimensions) distributed randomly throughout a matrix. To our knowledge, such calculations have heretofore not been carried out. This is accomplished here, for a wide range of cylinder or fiber volume fractions, employing the recent theoretical formalism developed by Torquato and Stell (1982) to represent the n-point probability functions in terms of the n-particle distribution functions, and using methods and results of statistical mechanics.

The remaining part of the paper is organized as follows. In Section 2, we present and discuss the Silnutzer and Milton bounds on the effective properties. These bounds depend upon a multidimensional integral ζ_2 involving lower-order n-point probability functions. In Section 3, we greatly simplify ζ_2 for the aforementioned model of randomly distributed impenetrable, parallel cylinders and evaluate it for this microstructure as a function of fiber volume fraction up to a value of 65 percent. The analysis described here is general in that it may be applied to composites consisting of inclusions of arbitrary shape, size, and penetrability (e.g., circular cylinders with particle-size distributions, elliptical cylinders, partially penetrable cylinders, etc.) In Section 4, we compute the Silnutzer and Milton bounds on the effective properties for our model, for a wide range of phase property values and volume fractions. Comparison of Milton's lower bound with computer-simulation results for σ_e and experimental data of a graphite-plastic composite are presented.

2 Third and Fourth-Order Bounds on σ_e, k_e, and μ_e

For any transversely isotropic fiber-reinforced material, Silnutzer (1972) derived bounds on σ_e and k_e which depend upon the phase volume fractions and properties, and two integrals involving certain three-point correlation functions. Milton (1982) demonstrated that both integrals may be expressed in terms of a single integral ζ_2 (defined below) which depends upon the three-point probability function described in the Introduction. The simplified form of the Silnutzer bounds (Milton, 1982) for the transverse conductivity and bulk modulus are, respectively, given by

$$\sigma_L^{(3)} \le \sigma_e \le \sigma_U^{(3)}, \tag{1}$$

where

$$\sigma_U^{(3)} = \left[<\sigma> - \frac{\phi_1\phi_2(\sigma_2-\sigma_1)^2}{<\tilde{\sigma}> + <\sigma>_\zeta} \right], \tag{2}$$

$$\sigma_L^{(3)} = \left[<1/\tilde{\sigma}> - \frac{\phi_1\phi_2(1/\sigma_2-1/\sigma_1)^2}{<1/\tilde{\sigma}> + <1/\sigma>_\zeta} \right]^{-1}; \tag{3}$$

and

$$k_L^{(3)} \le k_e \le k_U^{(3)}, \tag{4}$$

where

$$k_U^{(3)} = \left[<k> - \frac{\phi_1\phi_2(k_2-k_1)^2}{<\tilde{k}> + <G>_\zeta} \right], \tag{5}$$

$$k_L^{(3)} = \left[<1/k> - \frac{\phi_1\phi_2(1/k_2-1/k_1)^2}{<1/\tilde{k}> + <1/G>_\zeta} \right]^{-1}. \tag{6}$$

Here we define $<b> = b_1\phi_1 + b_2\phi_2$, $<\tilde{b}> = b_1\phi_2 + b_2\phi_1$, and $<b>_\zeta = b_1\zeta_1 + b_2\zeta_2$, where b represents any property. The quantities k_1 and k_2 are the transverse bulk moduli of the phases for transverse compression without axial extension and may be expressed in terms of the isotropic phase moduli as $k_i = K_i + G_i/3$ $(i = 1, 2)$. The microstructural parameter $\zeta_2 = 1 - \zeta_1$, which must lie in the closed internal [0, 1], is defined by

$$\zeta_2 = \frac{2}{\pi\phi_1\phi_2}\int_0^\infty \frac{dr}{r}\int_0^\infty \frac{ds}{s}\int_0^{2\pi} d\theta \left[S_3(r,s,t) - \frac{S_2(r)S_2(s)}{\phi_2} \right]\cos 2\theta. \tag{7}$$

The quantities $S_2(r)$ and $S_3(r, s, t)$ are, respectively, the probabilities of finding in phase 2 the end points of a line segment of length r and the vertices of a triangle with sides of length r, s, and t; θ is the angle opposite the side of length t. One can drop the factor S_2S_2/ϕ_2 appearing in equation (7), since it makes no contribution to the integral. Its presence, however, ensures the absolute convergence of the integral (Torquato, 1985).

It should be noted that the simplified version of the Silnutzer bounds on σ_e is not entirely new. Schulgasser (1976) simplified Silnutzer's upper bound on σ_e, by rewriting it in terms of a single microstructural parameter, and using a certain two-dimensional symmetry property, derived a lower bound on σ_e (in terms of the same parameter) which, as noted by Milton (1981), is equavalent to Silnutzer's lower bound.

As noted by Hashin (1970), the problem of determining the effective transverse conductivity σ_e (given σ_1 and σ_2) has the same underlying mathematics as the problem of determining the effective *axial* shear modulus μ_e (given G_1 and G_2) and, hence, results for the former translate immediately into results for the latter and vice versa. Replacement of σ_i with G_i $(i = 1, 2)$ in relation (1), therefore, gives the corresponding bounds on μ_e.

The expressions (1) and (4) are referred to as third-order bounds since they are exact through third order in the difference $(\sigma_2 - \sigma_1)$ and $(k_2 - k_1)$, respectively. At the extreme values of the three-point parameter ζ_2, $\zeta_2 = 0$ and $\zeta_2 = 1$, the Silnutzer bounds on σ_e and k_e coincide and equal one of the corresponding second-order bounds obtained by Hill (1964) and by Hashin (1965). For all possible values of $\zeta_2 (0 \le \zeta_2 \le 1)$, the third-order bounds are alwaysmore restrictive than the corresponding second-order bounds. It should be noted that Silnutzer (1972) also derived analogous third-order bounds for the effective *transverse* shear modulus that were shown (Milton 1982) to depend on not only ζ_2 but another three-point parameter η_2. In practice, η_2 is more difficult to obtain than ζ_2. The evaluation of η_2 and, hence, third-order bounds on the effective transverse shear modulus for the model composite considered here, shall be the subject of a future investigation.

Milton (1981) obtained fourth-order bounds on σ_e for transversely isotropic fiber-reinforced materials which depend not only upon σ_1, σ_2, ϕ_2, and ζ_2, but upon a multidimensional integral that involves the four-point probability function S_4. Utilizing a phase-interchange theorem for fiber-reinforced materials, Milton showed that the integral involving S_4 can be expressed in terms of ϕ_2 and ζ_2 only. The fourth-order bounds derived by Milton are, for the case $\sigma_2 \geq \sigma_1$, given by

$$\sigma_L^{(4)} \leq \sigma_e \leq \sigma_U^{(4)}, \tag{8}$$

$$\sigma_U^{(4)} = \sigma_2 \left[\frac{(\sigma_1+\sigma_2)(\sigma_1+<\sigma>) - \phi_2\zeta_1(\sigma_2-\sigma_1)^2}{(\sigma_1+\sigma_2)(\sigma_2+<\tilde{\sigma}> - \phi_2\zeta_1(\sigma_2-\sigma_1)^2} \right], \tag{9}$$

$$\sigma_L^{(4)} = \sigma_1 \left[\frac{(\sigma_1+\sigma_2)(\sigma_2+<\sigma>) - \phi_1\zeta_2(\sigma_2-\sigma_1)^2}{(\sigma_1+\sigma_2)(\sigma_1+<\tilde{\sigma}> - \phi_1\zeta_2(\sigma_2-\sigma_1)^2} \right]. \tag{10}$$

Thus the three-point parameter ζ_2 determines third-order bounds on σ_e (or μ_e) and k_e, and fourth-order bounds on σ_e or μ_e. To date, ζ_2 has been computed only for two models of disordered fiber-reinforced materials, namely, symmetric-cell materials (Beran and Silnutzer, 1971) and fully penetrable cylinders (Torquato and Beasley, 1986; Joslin and Stell, 1986). Symmetric-cell materials (Miller, 1969) are constructed by partitioning space into cells of possibly varying shapes and sizes, with cells randomly designated as phase 1 or phase 2 with probabilities ϕ_1 and ϕ_2, respectively. Although a useful mathematical construct, a symmetric-cell material could not be employed as a model of the more realistic microstructure of a distribution of equisized impenetrable cylinders in a matrix, since the space could not be completely filled by such cells. By "fully penetrable" cylinders, we mean a distribution of randomly centered, and thus spatially uncorrelated, cylinders. As the fiber volume fraction is increased for such a model, the fibers tend to form clusters (because the fibers may overlap each other), and eventually, at the percolation threshold $\phi_2^c \cong 0.68$ (Gawlinski and Stanley, 1981), the fiber phase changes from a discontinuous phase to a continuous one. The space ultimately can be entirely filled with cylinders. Fully penetrable-cylinder distributions, therefore, are not good models (at high fiber volume fractions) of a large class of fiber-reinforced materials which are characterized by impenetrable fibers.

3 Simplification and Calculation of the Parameter ζ_2 for Rigid Cylinders

The general n-point probability function for the ith phase of a two-phase system of arbitrary dimensionality consisting of inclusions distributed throughout a matrix phase has been shown by Torquato and Stell (1982) to be an infinite series. For the specific instance of an isotropic distribution of identical, impenetrable disks (infinitely long, parallel cylinders) of radius R at an area (volume) fraction ϕ_2, the infinite series for the probability function associated with the included phase (phase 2) terminates with the nth term (Torquato and Stell 1985); in the case $n = 3$, it is given by

$$S_3(r_{12},r_{13},r_{23}) = S_3^{(1)}(r_{12},r_{13},r_{23}) + S_3^{(2)}(r_{12},r_{13},r_{23}) + S_3^{(3)}(r_{12},r_{13},r_{23}), \tag{11}$$

where

$$S_3^{(1)} = \rho \int m(r_{14})m(r_{24})m(r_{34})d\mathbf{r}_4, \tag{12}$$

$$S_3^{(2)} = \rho^2 \int\int m(r_{14})m(r_{24})m(r_{35})g_2(r_{45})d\mathbf{r}_4 d\mathbf{r}_5 + \rho^2 \int\int m(r_{14})m(r_{25})m(r_{34})g_2(r_{45})d\mathbf{r}_4 d\mathbf{r}_5 + \rho^2 \int\int m(r_{15})m(r_{24})m(r_{34})g_2(r_{45})d\mathbf{r}_4 d\mathbf{r}_5, \tag{13}$$

and

$$S_3^{(3)} = \rho^3 \int\int\int m(r_{14})m(r_{25})m(r_{36})g_3(r_{45},r_{46},r_{56})d\mathbf{r}_4 d\mathbf{r}_5 d\mathbf{r}_6. \tag{14}$$

Here ρ is the number density of disks (cylinders), $m(r)$ is the particle indicator function which, for the simple case of a disk or a sphere, is equal to one for $r < R$ and zero otherwise, g_2 is the pair (radial) distribution function, g_3 is the triplet distribution function, and $r_{ij} \equiv |\mathbf{r}_j - \mathbf{r}_i|$. In general, the quantity $\rho^n g_n$ is the probability density associated with finding a particular configuration of n inclusions. Note that the disk area fraction (or cylinder volume fraction) is simply related to the number density, i.e., $\phi_2 = \rho\pi R^2$. The domain of integration in each of the integrals in (12)–(14) is the infinite area of the macroscopic sample. When points 2 and 3 coincide (i.e., when $r_{13} = r_{23} = 0$), $S_3(r_{12}, r_{13}, r_{23}) \rightarrow S_2(r_{12})$ and, hence, $S_2(r_{ij})$ can be obtained from equation (11) whenever points j and k coincide, under all permutations of i, j, and k.

Each term of equation (11) has a simple interpretation. Recall that $S_3(r_{12}, r_{13}, r_{23})$ gives the probability of finding all three points $\mathbf{r}_1$, $\mathbf{r}_2$ and $\mathbf{r}_3$ in the included phase. $S_3^{(1)}$ (a two-fold integral) gives the contribution of S_3 when all three points lie in the same disk (cylinder)—a quantity trivially related to the intersection area (volume) of three disks (cylinders) with centers separated by the distances r_{12}, r_{13}, and r_{23} (Torquato and Stell, 1982; Torquato and Stell 1985; Torquato and Beasley, 1986). $S_3^{(2)}$ (a four-fold integral) gives the contribution to S_3 when one point is in one disk (cylinder) and the two other points are in another disk (cylinder); this quantity must obviously involve the pair distribution function g_2 [cf. equation (13)]. Finally, $S_3^{(3)}$ (a six-fold integral) gives the contribution to S_3 when all three points lie in different disks (cylinders) and, hence, depends upon the triplet distribution function g_3 [cf. equation (14)]. Note that S_n in the paper by Torquato and Stell, unlike the present work, denotes the probability function associated with the matrix phase; the latter quantity is simply related to the included-phase analog (Torquato and Stell, 1982).

It is important to note that the three-point probability function for dispersions containing particles of arbitrary shape and size has the same functional form as equations (11)–(14). For the case of identical inclusions of arbitrary shape, one simply lets $\mathbf{r}_i$ (i = 4, 5, 6) denote not only the center-of-mass coordinate but the orientation of the particle and, hence, in general, g_2 and g_3 depend upon absolute coordinates, i.e., $g_2(\mathbf{r}_4, \mathbf{r}_5)$ and $g_3(\mathbf{r}_4, \mathbf{r}_5, \mathbf{r}_6)$. The particle indicator function m is retained in the equations but now, of course, its argument is a position vector $\mathbf{r}$ measured with respect to the centroid of the inclusion; it still is unity when $\mathbf{r}$ is inside the particle and zero otherwise. This simple generalization of equations (11)–(14) enables one to determine S_3 for anisotropic as well as inhomogeneous suspensions of identical inclusions of arbitrary shape (e.g., oriented, finite cylinders or ellipsoids); the probabilistic interpretations of the integrals $S_3^{(i)}$ given previously for disks or spheres hold for these more general suspensions as well. The generalization of equation (11) to particles with size distributions is formally straightforward; such a formalism is provided by Torquato and Stell (1983).

Substitution of equations (11)–(14) into the key integral ζ_2, equation (7), reveals that one must perform five-fold, seven-fold, and nine-fold integrations. These complicated "cluster" integrals are reminiscent of those that arise in the study of the statistical mechanics of the liquid state. The cluster integrals can be greatly simplified by employing a technique analogous to the one used by Lado and Torquato (1986) in the three-dimensional problem. For isotropic three-dimensional two-phase media, the three-point parameter (which determines third-order bounds) is similar to (7) but involves the Legendre polynomial of degree 2 instead of $\cos 2\theta$. For isotropic distributions of impenetrable spheres, Lado and Torquato (1986) greatly simplified the cluster integrals (associated with the three-point parameter) by expanding angle-dependent terms in the integrands in spherical harmonics and employing the orthogonality properties of this basis set. For the problem at hand, the analogous procedure involves expanding angle-dependent terms in circular harmonics (i.e., Chebyshev polynomials) and using the orthogonality properties of this basis set. Application of this technique leads to the following substantially simplified expression for the three-point parameter for impenetrable disks of unit diameter

$$\zeta_2 = \frac{2}{\pi\phi_1}\left[c_2\phi_2 + c_3\phi_2^2\right], \tag{15}$$

where

$$c_2 = \frac{\pi}{4}\int_1^\infty dr\,\frac{r\,g_2(r)}{(r^2-1/4)^2} \tag{16}$$

and

$$c_3 = \sum_{n=2}^{\infty}\frac{n-1}{4^{n-3}}\int_1^\infty \frac{dr}{r^{n-1}}\int_1^r \frac{ds}{s^{n-1}}\int_0^\pi d\theta\left[g_3(r,s,t) - g_2(r)g_2(t)\right]T_n(\cos\theta). \tag{17}$$

The details leading to equations (15)–(17) are somewhat complicated and lengthy and, hence, will not be given here; they are described, however, in another article (Torquato and Lado, 1988). Note that the original five, seven, and nine-fold cluster integrals have been reduced to a one and three-fold integral; cf., equations (16) and (17). In equation (17), $T_n(\cos\theta) = \cos n\theta$ is the Chebyshev polynomials of the first kind. As noted in the Introduction, the analysis which leads to equations (15)–(17) can be applied to composites consisting of particles of arbitrary shape, size, and penetrability.

In order to compute the two and three-body integrals of equation (15), we need to know the density-dependent pair g_2 and triplet g_3 distribution functions for the model. Determination of g_2 and g_3 for general random distributions is at best a highly formidable task. We shall assume an equilibrium distribution of impenetrable, parallel cylinders since: (*i*) The structure of this model has been extensively studied in the study of the liquid state (Lado, 1968); (*ii*) Such a model may be viewed as the most random distribution of cylinders subject to the constraint of impenetrability and thus a reasonable model of a real fiber-reinforced material. Specifically, we employ the accurate Percus-Yevick approximation to g_2 for impenetrable disks obtained numerically by Lado (1968).

The calculation of the triplet distribution function, as is well known in liquid-state theory, is more problematical. Lacking any more fundamental alternative, we have resorted to the familiar Kirkwood Superposition Approximation (KSA) (Hansen and McDonald, 1976),

$$g_3(r_{12},r_{13},r_{23}) \approx g_2(r_{12})g_2(r_{13})g_2(r_{23}) \tag{18}$$

to evaluate this quantity. The KSA (18) is exact in the zero-density limit for all particle configurations and for cases in which one particle is distant from the other two, regardless of the density. For equilateral-triangle configurations, the KSA is accurate, especially at high densities; the approximation is not as accurate at low densities and for less symmetric triplet configurations. Beasley and Torquato (1986) showed that the use of the KSA in computing the three-dimensional analog of ζ_2 for dispersions of spheres slightly underestimates ζ_2; the error increases with increasing density. It must be emphasized that incorporation of a value of ζ_2 smaller than the exact value (at some fixed volume fraction) in two or three-dimensional conductivity bounds still results in rigorous bounds on σ_e, albeit weaker bounds than ones employing the exact ζ_2. Since the integral (7) bears a strong similarity to its three-dimensional counterpart, it is expected that the use of the KSA in equation (17) should not lead to significantly large errors in ζ_2 (see also, discussion of Section 4).

Table 1 Three-point parameter ζ_2 for three models of disordered fiber-reinforced materials: (*i*) symmetric-cell material with cylindrical cells (Beran and Silnutzer, 1971; Milton, 1982); (*ii*) fully penetrable cylinders (Torquato and Beasley, 1986) (*iii*) equilibrium distribution of impenetrable cylinders calculated in the present study

ϕ_2	ζ_2		
	Symmetric-Cell Material	Fully Penetrable Cylinders	Random Impenetrable Cylinders
0.0	0.0	0.0	0.0
0.1	0.1	0.061	0.032
0.2	0.2	0.123	0.063
0.3	0.3	0.186	0.092
0.4	0.4	0.249	0.121
0.5	0.5	0.312	0.165
0.55	0.55	----	0.194
0.60	0.60	0.377	0.251
0.65	0.65	----	0.372
0.70	0.70	0.444	
0.80	0.80	0.514	
0.90	0.90	0.590	

Given the Percus-Yevick $g_2(r)$ (Lado, 1968), the two-body integral c_2 of equation (16) can be evaluated employing any standard numerical quadrature technique. To compute the three-fold integral c_3, equation (17), we use a Gaussian-Chebyshev quadrature technique (*Handbook of Mathematical Functions*, 1964). Such numerical integration methods have been utilized to accurately evaluate related multifold integrals (Torquato and Beasley, 1986). The integration domain for (17) was subdivided so that 24 Gaussian points in each dimension gave convergence to four significant figures. In principle, the expansion (17) in Chebyshev polynomials is infinite but, in practice, only the first seven to nine terms are needed to give convergence to four significant figures. To compute c_3 at large cylinder volume fractions (the most time intensive cases), the Gaussian quadrature scheme required about 48 min of CPU time on a VAX 785. The one-fold integral c_2, equation (16), was also evaluated using the same Gaussian method; here we used 64 Gaussian points.

In Table 1, the three-point parameter ζ_2 for our model of a random array of impenetrable cylinders is given at selected values of the cylinder volume fraction ϕ_2. Since the Percus-Yevick approximation, for the pair distribution function, appears to break down as the random close-packing volume fraction $\phi_2 \cong 0.81$ (Stillinger, DiMarzio and Kornegay, 1964) is approached, the highest volume fraction reported here is $\phi_2 = 0.65$, at which the Percus-Yevick results are still in relatively good agreement with Monte Carlo simulations. The percolation threshold ϕ_2^c for an equilibrium distribution of impenetrable disks has been conjectured to be the random-packing limit.

The microstructural parameter ζ_2 can be evaluated exactly through second order in ϕ_2. We find

$$\zeta_2 = \frac{1}{3}\,\phi_2 - 0.05707\,\phi_2^2 + 0\left(\phi_2^3\right). \tag{19}$$

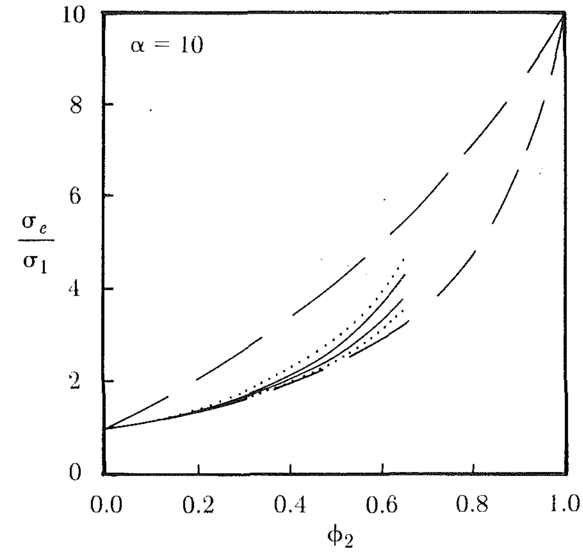

Fig. 1 Bounds on the scaled effective transverse conductivity σ_e/σ_1 versus the fiber volume fraction ϕ_2 at $\alpha = \sigma_2/\sigma_1 = 10$; ———— second-order Hashin (1965, 1970) bounds; .... third-order Silnutzer (1970) bounds; and ——— fourth-order Milton (1981) bounds, for a random distribution of impenetrable cylinders

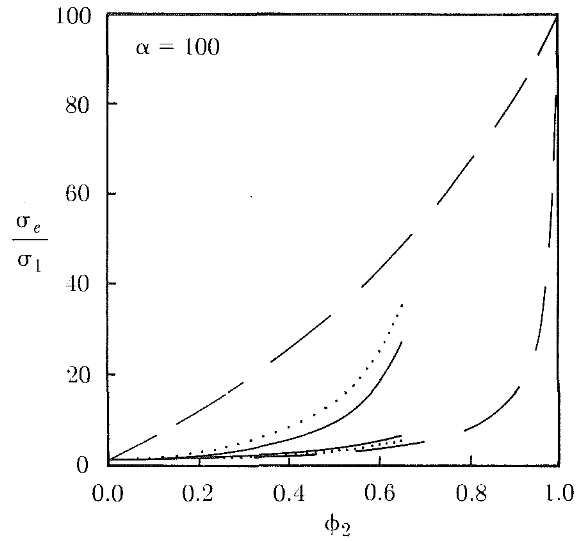

Fig. 2 As in Fig. 1, with $\alpha = 100$

The details of this calculation are given by Torquato and Lado (1988). The first-order coefficient depends upon the zero-density limit of g_2. The second-order coefficient depends upon g_2 through order ρ and the zero-density limit of the triplet distribution functions g_3 in which case the superposition approximation (18) is exact. Therefore, equation (19) is an exact result. Note that the low-density expansion (19) provides a relatively good approximation of our calculations of ζ_2 through all orders in ϕ_2 (Table 1) for the range $0 \leq \phi_2 \leq 0.4$.

For purposes of comparison, we include in Table 1 the parameter ζ_2 for the symmetric-cell material with cylindrical cells (Beran and Stilnutzer, 1971; Milton, 1982) for which $\zeta_2 = \phi_2$ and for fully penetrable cylinders (Torquato and Beasley, 1986). As noted earlier, these latter two geometries represent the only other random-media models for which ζ_2 has been computed. The physical significance of ζ_2 for general microstructures is described by Torquato and Lado (1988). It suffices here to make the following observations. The parameter ζ_2 for the random-impenetrable case is always below the corresponding values of ζ_2 for the other two models for the values of ϕ_2 calculated here (i.e., $\phi_2 \leq 0.65$). For the model examined in the present study, ζ_2 is approximately linear for the range $0 \leq \phi_2 \leq 0.4$ and significantly increases with ϕ_2 as the maximum random-close-packing volume fraction ($\phi_2^c \cong 0.81$) is approached. This is to be contrasted with the symmetric-cell material, for which ζ_2 is exactly linear in ϕ_2, and the fully penetrable-cylinder model, for which ζ_2 is approximately linear for all ϕ_2; in both cases ϕ_2 can take on all possible values, i.e., $0 \leq \phi_2 \leq 1$.

4 Evaluation of Bounds on σ_e, k_e, and μ_e for Rigid Cylinders

Before presenting third and fourth-order bounds for the effective properties for our model, it is useful to first comment on the general utility of bounds when the phase property values widely differ. For the case of conduction, all nth-order lower bounds (for finite n) tend to zero as $\alpha \rightarrow 0$ and all nth-order upper bounds tend to infinity as $\alpha \rightarrow 0$, where $\alpha = \sigma_2/\sigma_1$. Similarly, for the elasticity problem, all nth-order lower bounds tend to zero as $\beta = G_2/G_1 \rightarrow 0$ (i.e., when phase 2 is a void phase) and all nth-order upper bounds tend to infinity as $\beta \rightarrow \infty$ (i.e., when phase 2 is infinitely more rigid than phase 1). This does not mean that bounds cannot be employed to estimate effective properties, however, since the reciprocal bounds in the aforementioned instances remain finite and can provide a useful estimate of them. Specifically, Torquato (1985) has observed that lower-order lower bounds (such as second, third, and fourth-order bounds) should yield good estimates of σ_e/σ_1 for $\alpha \gg 1$, provided that ϕ_2 is not only below its percolation-threshold value ϕ_2^c but that the mean cluster size of phase 2, Λ_2, is much smaller than the macroscopic length of the sample L. (A cluster of phase i is defined as that part of phase i which can be reached from a point in phase i without touching any part of phase j, $i \neq j$). Of course, the accuracy of the lower-order lower bounds increases as the order increases. Note that since the mean cluster size Λ_2 at the percolation point ϕ_2^c becomes infinitely large, the foregoing condition $\Lambda_2 \ll L$ implies that the system is below the percolation threshold (i.e., $\phi_2 < \phi_2^c$). For periodic arrays of disks and for an equilibrium distribution of rigid disks, the condition $\Lambda_2 \ll L$ is satisfied for all ϕ_2, except at the close-packing or percolation-threshold value. Similarly, lower-order upper bounds should provide a useful estimate of σ_e/σ_1 for $\alpha \gg 1$, provided that $\phi_2 > \phi_2^c$ and $\Lambda_1 \ll L$, where Λ_1 is the mean cluster size of phase 1. The accuracy of the lower-order upper bounds of course will improve as n increases. Analogous statements apply as well to bounds on k_e and μ_e.

Using the tabulation of ζ_2 for a random array of impenetrable cylinders obtained in the previous section, we evaluate third and fourth-order bounds on σ_e (or μ_e) and k_e described in Section 2. In Fig. 1, we plot third and fourth-order bounds on the scaled effective conductivity σ_e/σ_1 [equations (1) and (8)] as a function of cylinder volume fraction ϕ_2 for the case $\alpha = 10$. Included in this figure is the corresponding second-order bounds derived by Hashin. The third-order Silnutzer bounds substantially improve upon the second-order bounds; the fourth-order Milton bounds, in turn, are more restrictive than the third-order bounds. At $\phi_2 = 0.5$, the third-order bounds are about 3.7 times narrower than the second-order bounds, whereas the fourth-order bounds are about 2.1 times more restrictive than the third-order bounds and, hence, almost 8 times narrower than the Hashin bounds. Note that most of the improvement provided by the third and fourth-order bounds is provided by the upper bounds rather than the lower bounds. For the case $\alpha = 0.1$ (not shown here), the Silnutzer and Milton bounds provide similar improvement over the Hashin bounds, except that

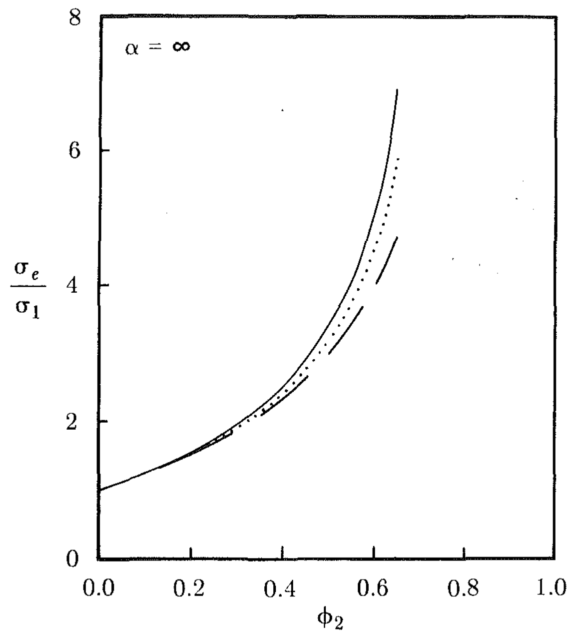

Fig. 3 As in Fig. 1, with $\alpha = \infty$; upper bounds are not shown since they diverge to infinity in this limit

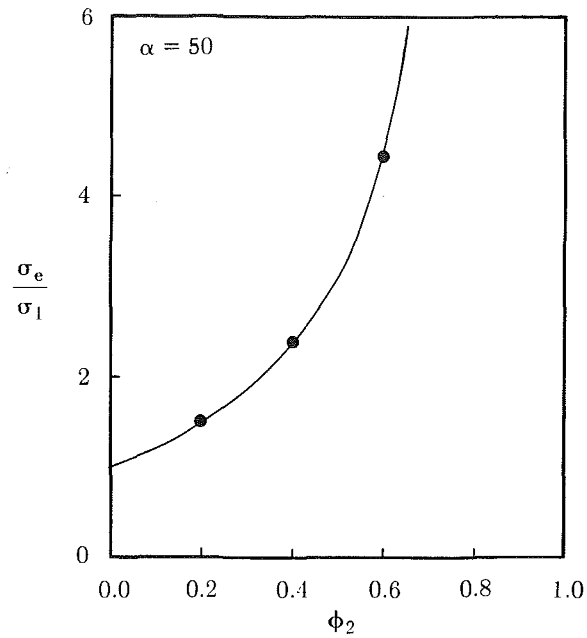

Fig. 4 Comparison of the fourth-order lower bound on the scaled effective transverse conductivity to simulation results (solid circles) for the same equilibrium model of cylinders examined here (Durand and Ungar, 1988) for $\alpha = 50$

most of the improvement is in the lower bound. To summarize, for the range $0.1 \leq \alpha \leq 10$, the fourth-order Milton bounds are sharp enough to give a good estimate of σ_e/σ_1 for the entire range of volume fractions.

In Fig. 2, we plot all three bounds on the reduced conductivity σ_e/σ_1 versus ϕ_2 for inclusions which are *100* times more conducting than the matrix phase, i.e., $\alpha = 100$. As expected, all the bounds widen. At $\phi_2 = 0.5$, the third-order bounds are about 2.8 times narrower than the second-order bounds; the fourth-order bounds are about 1.7 times narrower than the third-order bounds and, therefore, are almost 5 times more restrictive than the second-order bounds. For the range $0.01 \leq \alpha \leq 100$, the fourth-order Milton bounds are restrictive enough to give good estimates of the effective conductivity for the volume fraction range $0 \leq \phi_2 \leq 0.4$.

As noted above, the fact that the bounds diverge as α is made large does not imply that they cannot be utilized to estimate the effective conductivity. Since ϕ_2 is below the percolation threshold ($\phi_2^c \cong 0.81$) for randomly distributed cylinders and because there are no particle contacts ($\Lambda_2 \ll L$), the lower bound is expected to yield a relatively good estimate of σ_e for $\alpha \gg 1$. In Fig. 3, we plot all three lower bounds on σ_e/σ_1 for the most difficult and extreme instance of $\alpha = \infty$, i.e., perfectly conducting cylinders—the case in which all upper bounds diverge to infinity. Milton's fourth-order lower bound should yield a good estimate of σ_e, with the maximum error occurring at the maximum volume fraction reported here, i.e., at $\phi_2 = 0.65$ or equivalently, at 80 percent of the closing-packing volume fraction ($\phi_2/\phi_2^c \cong 0.80$). We can estimate the maximum error by comparing the Milton lower bound (10) for square and hexagonal arrays (McPhedran and Milton, 1981) at $\phi_2/\phi_2^c = 0.8$ and $\alpha = \infty$ to the exact results of Perrins, McKenzie, and McPhedran (1979) for these idealized periodic arrays. (For periodic arrays, the symmetry associated with the periodicity enables one to obtain σ_e exactly numerically. Such geometries share an important property with equilibrium distributions of cylinders, namely, there are no particle contacts ($\Lambda_2 \ll L$) until the respective close-packing volume fraction is attained.) For square arrays at $\phi_2/\phi_2^c = 0.80$ and $\alpha = \infty$, $\sigma_L^{(4)}/\sigma_1 = 4.89$, whereas the exact result for $\sigma_e/\sigma_1 = 4.93$. For hexagonal arrays under the same conditions, $\sigma_L^{(4)}/\sigma_1 = 6.51$, whereas the exact result for $\sigma_e/\sigma_1 = 6.53$. Therefore, the maximum error in using Milton's lower bound to estimate σ_e for a random array of perfectly conducting cylinders is about 1 percent for the range $0 \leq \phi_2 \leq 0.65$. For values of α in the range $1 \leq \alpha < \infty$, the deviation of Milton's lower bound from exact results is even less than it is for $\alpha = \infty$. In short, Milton's lower bound provides an excellent estimate of the actual effective conductivity of our model system for all α and for $0 \leq \phi_2 \leq 0.65$.

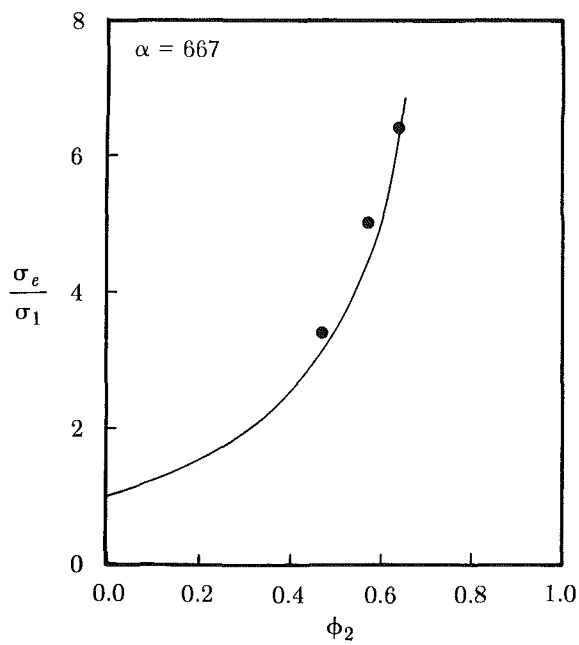

Fig. 5 Comparison of the fourth-order lower bound on the scaled effective transverse conductivity to experimental data (solid circles) for a graphite-plastic composite (Thornburgh and Pears, 1965) with $\alpha = 667$

In Fig. 4, we compare the fourth-order lower bound on σ_e/σ_1 for $\alpha = 50$ to exact simulation results (for the equilibrium model studied here) very recently obtained by Durand and Ungar (1988) using the Boundary Element Method (BEM). The fourth-order lower bound, not surpris-

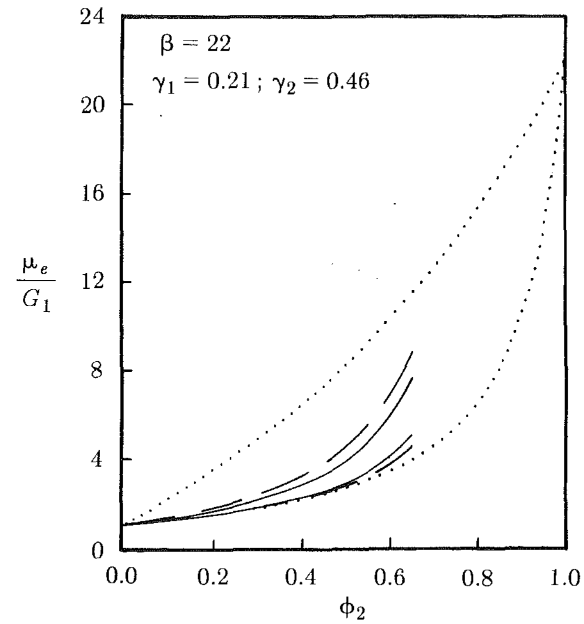

Fig. 6 Bounds on the scaled effective axial shear modulus μ_e/G_1 versus ϕ_2 for a glass-epoxy composite for which $\beta = G_2/G_1 = 22$; legend is the same as in the previous figures

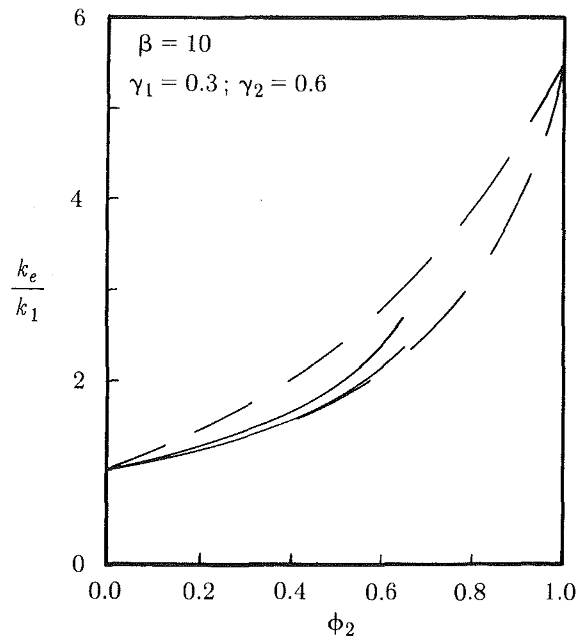

Fig. 7 Bounds on the scaled effective transverse bulk modulus k_e/k_1 versus ϕ_2 for $\beta = 10$, $\gamma_1 = 0.3$, $\gamma_2 = G_2/K_2 = 0.6$; ———— second-order bounds (Hill, 1964; Hashin, 1965); ——— third-order Silnutzer (1972) bounds for a random distribution of impenetrable cylinders

ingly, is seen to predict the effective conductivity extremely accurately. This supports our assertion that bounds, which incorporate nontrivial microstructural information on the medium, can be used to accurately estimate effective properties, even when the phase properties are widely different.

In Fig. 5, we compare the fourth-order lower bound on σ_e/σ_1 to the experimental data of Thornburgh and Pears (1965) for a composite composed of highly conducting graphite fibers in a plastic matrix for which $\alpha = 667$. As expected, the fourth-order lower bound provides an excellent estimate of the experimental data. This further supports our claims about the utility of bounds.

Before discussing evaluation of the bounds for the elastic moduli, it is useful to remark on the suitability of the KSA, equation (18), to compute the integral ζ_2 [cf., equations (15) and (17)]. The fact that the fourth-order lower bound on σ_e for our model provides an excellent estimate of the conductivity indicates that the use of the KSA in equation (17) does not lead to significantly large errors in ζ_2.

As noted in Section 2, results obtained for σ_e/σ_1 given α translate immediately into equivalent results for the scaled axial shear modulus μ_e/G_1 given $\beta = G_2/G_1$. Therefore, the general conclusions made about third and fourth-order bounds on the effective conductivity previously described apply as well to μ_e. For example, when the cylindrical fibers are perfectly rigid ($\beta = \infty$), the fourth-order lower bound should provide an excellent estimate of μ_e/G_1. It is useful, nonetheless, to show the bounds on μ_e/G_1 using elastic moduli property values for a real composite material. This is done in Fig. 6 for a typical glass-epoxy composite of which $\beta = 22$, $\gamma_1 = G_1/K_1 = 0.21$ and $\gamma_2 = G_2/K_2 = 0.46$ (Chou and Kelly, 1980). The ratio $\gamma = (3 - 6\nu)/(2\nu + 2)$, where ν is Poisson's ratio and $0 \leq \nu \leq 0.5$, then $0 \leq \gamma \leq 1.5$. The bounds given in Fig. 6 are of course independent of the γ_i; the γ_i are required in general, however.

Figure 7 shows the third-order Silnutzer bounds on the scaled effective transverse bulk modulus k_e/k_1 [cf., equation (4)], for our model, as a function of ϕ_2 for $\beta = 10$, $\gamma_1 = 0.3$ and $\gamma_2 = 0.6$. Included in the figure are the corresponding second-order bounds (Hill, 1964; Hashin, 1965). The third-

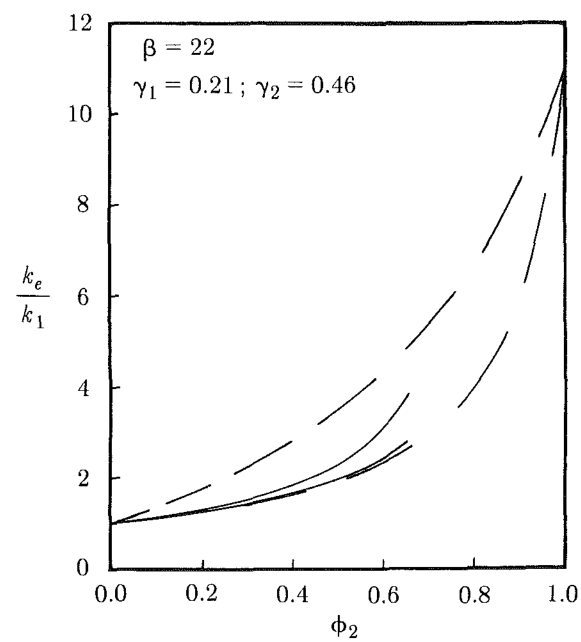

Fig. 8 As in Fig. 7, for a glass-epoxy composite, for which $\beta = 22$, $\gamma_1 = 0.21$, and $\gamma_2 = 0.46$

order bounds provide significant improvement over the second-order bounds. In Fig. 8, we plot the same bounds for a glass-epoxy composite for which $\beta = 22$, $\gamma_1 = 0.21$, and $\gamma_2 = 0.46$.

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