Bounds on the conductivity of a suspension of random impenetrable spheres

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(Received 2 June 1986; accepted for publication 11 July 1986)

We compare the general Beran bounds on the effective electrical conductivity of a two-phase composite to the bounds derived by Torquato for the specific model of spheres distributed throughout a matrix phase. For the case of impenetrable spheres, these bounds are shown to be identical and to depend on the microstructure through the sphere volume fraction \( \phi_2 \) and a three-point parameter \( \xi_2 \), which is an integral over a three-point correlation function. We evaluate \( \xi_2 \) exactly through third order in \( \phi_2 \) for distributions of impenetrable spheres. This expansion is compared to the analogous results of Felderhof and of Torquato and Lado, all of whom employed the superposition approximation for the three-particle distribution function involved in \( \xi_2 \). The results indicate that the exact \( \xi_2 \) will be greater than the value calculated under the superposition approximation. For reasons of mathematical analogy, the results obtained here apply as well to the determination of the thermal conductivity, dielectric constant, and magnetic permeability of composite media and the diffusion coefficient of porous media.

I. INTRODUCTION

The determination of the bulk or effective properties of two-phase composite materials is of great practical and theoretical importance.\(^1\)\(^2\) A two-phase composite material is a heterogeneous mixture of two different homogeneous materials. The fundamental problem is to determine the bulk property of the composite in terms of the phase property values and the details of the microstructure. In this article we shall be interested in the electrical conductivity of statistically homogeneous dispersions and, thus, because of mathematical analogy, the thermal conductivity, dielectric constant, magnetic permeability, and diffusion coefficient of such media.

In general, the microstructure is completely characterized by an infinite set of correlation functions.\(^5\)\(^6\) Knowledge of the complete set of statistical functions is almost never known in practice. Variational bounds, however, provide a means of estimating the effective property for a wide range of phase conductivities \( \sigma_1 \) and \( \sigma_2 \) and volume fractions \( \phi_1 \) and \( \phi_2 \). The most well-known bounds are due to Hashin and Shtrikman (HS).\(^7\) These provide the best possible bounds on the effective conductivity \( \sigma_e \), given the simplest of microstructural parameters; the volume fraction of one of the phases. As is well known, the HS lower bound for \( \sigma_2 > \sigma_1 \) is identical to a formula derived by Maxwell.\(^8\)

The HS bounds, while providing rigorous limits for all \( \alpha = \sigma_2/\sigma_1 \) and \( \phi_2 \), are restrictive only for a limited range of \( \alpha \) and \( \phi_2 \). In order to extend the range of utility, it becomes necessary to introduce statistical information beyond that contained in \( \phi_2 \). The bounds due to Beran\(^9\) and Torquato\(^10\) introduce such additional morphological information; information not contained in the Maxwell formula or the effective medium approximation of Bruggeman.\(^11\)

In Sec. II we describe the Beran and Torquato bounds and the statistical quantities involved therein, and show that the bounds are identical for microstructures made up of dispersions of impenetrable spheres. For the case of impenetrable spheres, the bounds depend not only upon the sphere volume fraction \( \phi_2 \) but also upon a microstructural parameter that involves a three-point correlation function. In Sec. III we evaluate this key three-point parameter through third order in \( \phi_2 \), for an equilibrium distribution of impenetrable spheres in a matrix, in the superposition approximation and exactly.

II. THE BOUNDS OF BERAN AND OF TORQUATO

Rigorous bounds on \( \sigma_e \) may be derived using the variational principles of minimum potential and minimum complementary potential energy. Both Beran\(^9\) and Torquato\(^10\) employed these variational principles using trial fields of the same general form.

Beran\(^9\) employed the first two terms from the perturbation series expansions for the trial fields to obtain bounds which were later simplified by Torquato and Stell\(^12\) and Milton.\(^13\) The resulting expression

\[
\left( \frac{1}{\sigma} - \frac{4\phi_1\phi_2(1 - \frac{1}{\sigma_2})^2}{6\frac{1}{\sigma_1} + (4\phi_1 + 2\xi_2)(1 - \frac{1}{\sigma_2} + \frac{1}{\sigma_1})} \right)
\]

\[
\times \left( \frac{\phi_2(\phi_2(\sigma_2 - \sigma_1)^2)}{3\sigma_1 + (\phi_1 + 2\xi_2)(\sigma_2 - \sigma_1)} \right),
\]

(1)

involves a single three-point parameter

\[
\xi_2 = 1 - \frac{1}{16\phi_1\phi_2^2} \left( \int dr_{12} dr_{13} r_{12} r_{13} P_2(r_{12}, r_{13}) \right)
\]

\[
\times \left( \frac{S_2(r_{12}, r_{13})}{S_1} - \frac{S_2(r_{12}, r_{13}) S_2(r_{13})}{S_1} \right).
\]

(2)

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Here $\sigma$ is the local conductivity and angular brackets denote an ensemble average. The statistical quantities $S_n$ are called $n$-point matrix probability functions and give the probability of simultaneously finding $n$ points in the matrix phase.$^{14-16}$

Torquato, on the other hand, uses the first two terms from the cluster expansion for a dispersion of spherical particles (phase 2) in a matrix (phase 1) for the trial fields. More specifically, the trial fields are taken to be a constant vector added to the sum of contributions from individual isolated spheres. Torquato's bounds$^{10}$

$$\left\langle \sigma \right\rangle = \left\langle \sigma \right\rangle_1 + \left\langle \sigma \right\rangle_2,$$

for spheres of unit radius, involve the four parameters $A$, $B$, $C$, and $D$, where

$$A = A_1 + A_2 + A_3,$$

$$B = B_1 + B_2 + B_3 + B_4,$$

$$C = 2A_1 + 4A_2 + A_3,$$

$$D = 4B_1 + B_2 + 4B_3 + B_4,$$

$$A_1 = 3\eta,$$

$$A_2 = \frac{3}{2} \eta^2 \int_0^1 d\tau_1 \int_0^1 d\tau_2 \int_0^1 d\tau_3 \int_0^1 d\tau_4 \frac{G(\tau_1, \tau_2, \tau_3, \tau_4)}{\rho},$$

$$A_3 = \frac{9}{2} \eta^3 \int_0^1 d\tau_1 \int_0^1 d\tau_2 \int_0^1 d\tau_3 \int_0^1 d\tau_4 \frac{G^{(2)}(\tau_1, \tau_2, \tau_3, \tau_4)}{\rho},$$

$$B_1 = 3\eta \int_0^1 d\tau_1 \int_0^1 d\tau_2 \int_0^1 d\tau_3 \int_0^1 d\tau_4 \frac{G^{(2)}(\tau_1, \tau_2, \tau_3, \tau_4)}{\rho},$$

$$B_2 = 6\eta \int_0^1 d\tau_1 \int_0^1 d\tau_2 \int_0^1 d\tau_3 \int_0^1 d\tau_4 \frac{G^{(2)}(\tau_1, \tau_2, \tau_3, \tau_4)}{\rho},$$

$$B_3 = \frac{9}{2} \eta^2 \int_0^1 d\tau_1 \int_0^1 d\tau_2 \int_0^1 d\tau_3 \int_0^1 d\tau_4 \frac{G^{(2)}(\tau_1, \tau_2, \tau_3, \tau_4)}{\rho},$$

$$B_4 = 9\eta^3 \int_0^1 d\tau_1 \int_0^1 d\tau_2 \int_0^1 d\tau_3 \int_0^1 d\tau_4 \frac{G^{(2)}(\tau_1, \tau_2, \tau_3, \tau_4)}{\rho},$$

and

$$Q(\tau_1, \tau_2, \tau_3, \tau_4) = \int_0^1 d\tau_5 \frac{G^{(2)}(\tau_1, \tau_2, \tau_3, \tau_5, \tau_4)}{\rho}.$$

In the equations given above, $\rho$ is the number density of spheres, $\eta = \int_0^1 \tau d\tau$ is a dimensionless number density, $h(r)$ is the pair or radial distribution function, $P_2$ is the second Legendre polynomial, and the $G_n^{(2)}$ are point/n-particle correlation functions. The $G_n^{(2)}$ give the probability of finding a point at $\tau_1$ in phase 2 and any sphere center in volume element $d\tau_2$ about $\tau_2$, another sphere center in $d\tau_3$ about $\tau_3$, ..., and another sphere center in $d\tau_4$ about $\tau_4$. For statistically homogeneous media, $G_0^{(2)}$ is simply equal to the sphere volume fraction $\phi_2$. The Beran bounds are more general than the Torquato bounds which are restricted to spherical inclusions of arbitrary penetrability. However, for spheres of intermediate penetrability the statistical functions in the Torquato bounds, and hence the bounds themselves, are easier to calculate.

For microstructures made up of dispersions of impenetrable spheres the $G_n^{(2)}$ and the $S_n$ can be expressed in terms of the $n$-particle distribution functions $g^{(n)}$ and the sphere indicator function $10$

$$m(r) = \begin{cases} 0, & r > 1 \\ 1, & r < 1. \end{cases}$$

Note that the $g^{(n)}$ correspond to the $g_n$ of Ref. 10. For this specific case, the low-order $G_n^{(2)}$ are given by$^{10}$

$$G^{(2)}_1(r_{12}) = \rho m(r_{12}) + \rho^2 e(r_{12}) \int d\tau_3 m(r_{12}, r_{13}) g_2(r_{13}),$$

$$G^{(2)}_2(r_{12}) = \rho^2 m(r_{12}) + \rho^3 e(r_{12}) \int d\tau_3 m(r_{12}, r_{13}) g_2(r_{13}),$$

and

$$G^{(2)}_3(r_{12}, r_{13}, r_{23}) = \rho^3 [m(r_{12}) + m(r_{13}) - m(r_{12}) m(r_{13})] g_2(r_{23})$$

$$+ \rho^4 e(r_{12}) e(r_{13}) \int d\tau_4 m(r_{12}, r_{14}) g_2(r_{14}, r_{23}, r_{24}),$$

where $e(r) = 1 - m(r)$. The low order $S_n$ can be expressed in terms of the $G_n^{(2)}$

$$S_1 = 1 - G_0^{(2)} = \phi_1,$$

$$S_2(r_{12}) = S_1 \int d\tau_3 m(r_{12}, r_{13}) [G^{(2)}_2(r_{13}) - \rho],$$

and

$$S_3(r_{12}, r_{13}, r_{23}) = S_1 \int d\tau_4 m(r_{12}, r_{14}) [G^{(2)}_2(r_{14}, r_{23}) - \rho]$$

$$- \int d\tau_4 \tau d\tau_5 m(r_{14}, r_{25})$$

$$\times \left[ G^{(2)}_2(r_{25}, r_{34}, r_{45}) - \rho^2 g_2(r_{45}) \right].$$

We now show that for dispersions of impenetrable spheres the Beran and Torquato bounds are identical. Comparing Eq. (1) with Eq. (3) and noting $\eta = \phi_2$ for impenetrable spheres, we find that if

$$A = 3\phi_1 \phi_2,$$

$$B = \phi_1 \phi_2 + 2\phi_1 \phi_2,$$

$$C = 6\phi_1 \phi_2,$$

and

$$D = 4\phi_1 \phi_2 + 2\phi_1 \phi_2,$$

then the bounds are equivalent.

Lado and Torquato$^{17}$ reduce Eq. (2) for $\xi_2$ for disper-
sions of impenetrable spheres. Using the representations of the $S_n$ from Ref. 16 for impenetrable spheres, they obtained

$$\xi_2 = \frac{3 \Omega \phi_2 + \Lambda \phi_2^3}{\phi_1},$$  \hspace{1cm} (27)

where

$$\Omega = \int_0^{\infty} dr \frac{r^2}{(r^2 - 1)^2} g^{(2)}(r),$$  \hspace{1cm} (28)

and

$$A = \frac{9}{32 \pi^2} \sum_{l=2}^{\infty} (l(l - 1)) \int dr_1 dr_2 \frac{P_l(\cos \theta)}{r_1^{12} r_2^{12} r_3^{12}}.$$  \hspace{1cm} (29)

Felderhof also obtained Eqs. (27), (28), and (29). He did not, however, start with Eq. (2) and the $S_n$, but arrived at his result by an alternate method. In both Felderhof's and Lado and Torquato's notation $\xi_2 = (9/2 \phi_2 \phi_3) K.$

Consider now Eqs. (9) and (10) for $A_2$ and $A_3$. Making the change of variable $\cos \theta = \cos \theta_1 = \frac{r_1^2 + r_2^2 - r_3^2}{2r_1 r_2}$ and changing the order of integration results in

$$A_2 = \eta^2 \int_0^{2 \pi} \sin \phi dr_3 \left[ \frac{\rho^2 [g^{(2)}(r_2) - 2 + \phi_2], \ r_2 < 1, r_3 < 1}{\rho^3 \int dr_4 \ m(r_4) \left[ (g^{(3)}(r_2, r_4) - g^{(2)}(r_4) g^{(2)}(r_3) + h(r_2) h(r_3)] \right.} \right. \left. \right].$$  \hspace{1cm} (30)

Substituting Eq. (34) into Eqs. (13) and (14) gives $B_3$

$$B_3 = 2 \rho \int \int dr_1 dr_2 \ m(r_1) \left[ (g^{(3)}(r_2, r_4) - g^{(2)}(r_4) g^{(2)}(r_3) + h(r_2) h(r_3)] \right. \left. \right].$$  \hspace{1cm} (31)

Expanding the $h(r_2) h(r_3)$ term has been dropped due to orthogonality of the Legendre polynomials, but the $g^{(2)}(r_2) g^{(2)}(r_3)$ term has been retained to facilitate subsequent numerical calculations. Except for a trivial factor, Eq. (35) is identical with an intermediate expression in Ref. 17 which leads to $B_3 = 2 \Lambda \phi_2^3$.

In summary,

$$A = 3 \phi_2 - 3 \phi_2^3,$$  \hspace{1cm} (36)

$$B = \phi_2 - 2 \phi_2^3 + 6 \Omega \phi_2^5 + 2 \Lambda \phi_2^5,$$  \hspace{1cm} (37)

$$C = 6 \phi_2 - 2 \phi_2^3,$$  \hspace{1cm} (38)

and

$$D = 4 \phi_2 - 8 \phi_2^3 + 4 \phi_2^5 + 6 \Omega \phi_2^7 + 2 \Lambda \phi_2^7.$$  \hspace{1cm} (39)

Combining Eqs. (27)–(29) and (36)–(39) along with the relation $\phi_1 = 1 - \phi_2$ verifies Eqs. (23)–(26) and hence shows the equivalence of the Beran and Torquato bounds for impenetrable spheres.

We have shown that for the special case of impenetrable spheres the Beran and Torquato bounds are identical. This result is not unexpected. Both sets of bounds are derived and

$$A_3 = 2A_2.$$  \hspace{1cm} (31)

Notice that the resulting expressions depend on the total correlation function only through $r$ values inside the diameter. For impenetrable spheres of unit radius $h(r) = -\frac{1}{2}$ for $r < 2$ and, therefore, $A_3 = -\frac{1}{2} \phi_2$. From Eqs. (11) and (18) it is obvious that $B_1 = \phi_2$. It can also be shown in a manner similar to that for $A_2$ and $A_3$ that

$$B_2 = 6 \eta^2 \int_0^{\infty} dr \ r^2 g^{(2)}(r) \chi(r),$$  \hspace{1cm} (32)

where

$$\chi(r) = \begin{cases} 1/(r^2 - 1)^3, & r > 2 \\ \{ (r/[16(r + 1)]^3) (12 + 12r - r_3^2), & r < 2. \end{cases}$$  \hspace{1cm} (33)

For impenetrable spheres of unit radius, $g^{(2)}(r) = 0$ for $r < 2$ and $B_2 = 6 \Omega \phi_2^5$.

Combining Eqs. (15) with Eqs. (17)–(19) for impenetrable spheres of unit radius yields

$$A_3 = 2A_2.$$  \hspace{1cm} (31)

III. EVALUATION OF $\xi_2$ FOR IMPENETRABLE SPHERES

Felderhof considered an equilibrium dispersion of impenetrable spheres and computed $\xi_2$ through third order in $\phi_2$ (the volume fraction of spheres). Unfortunately, there appears to be an error in the coefficient of $\phi_2^3$. Torquato and Lado later extended this result to calculate $\xi_2$ for $\phi_2$ up to about 94% of the random-close-packing value. Both Felderhof and Torquato and Lado used the superposition approximation for the triplet correlation function involved in the
calculation of $\xi_2$. Here we obtain the correct results for $\xi_2$ in
the superposition approximation through order $\phi_2^4$. Moreover,
through the same order in $\phi_2$, we calculate $\xi_2$ exactly
and thus determine the error involved in using the superposition
approximation.

A. The density expansion of $\xi_2$ for impenetrable
spheres

The integrals for $\Omega$ and $\Lambda$ can be expanded in density by
making use of the density expansions of the correlation functions:

$$g^{(2)}(r) = \sum_{n=0}^{\infty} g_n^{(2)}(r) r^n \tag{40}$$

and

$$g^{(3)}(r,s,t) = \sum_{n=0}^{\infty} g_n^{(3)}(r,s,t) r^n. \tag{41}$$

Substituting Eqs. (40) and (41) into Eqs. (27), (28), and (29)
gives

$$\Omega = \sum_{n=0}^{\infty} \Omega_n \phi_2^n, \tag{42}$$

$$\Lambda = \sum_{n=0}^{\infty} \Lambda_n \phi_2^n, \tag{43}$$

$$\xi_2 = \sum_{n=1}^{\infty} c_n \phi_2^n, \tag{44}$$

$$\Omega_n = \int_2^\infty dr \frac{r^2}{(r^2-1)^3} \frac{g^{(2)}_n(r)}{V^1}, \tag{45}$$

$$\Lambda_n = \frac{9}{32\pi^2 \gamma_2} \sum_{l=2}^{\infty} \frac{l(l-1)}{2} \int dr_2 dr_3 \frac{P_l(\cos \theta_{213})}{r_2^{l+1} r_3^{l+1}} \times \left[ \frac{g^{(3)}_n(r_2,r_3,r_23)}{V^1} - \sum_{m=0}^{\infty} \frac{g_m^{(3)}(r_2) g^{(2)}_m(r_3) g^{(2)}_n(r_3)}{V^1} \right]. \tag{46}$$

c_1 = 3\Omega_0, \tag{47}

and

$$c_{n+1} = c_n + 3\Omega_n + \Lambda_{n-1}, \quad n = 1, 2, 3, \ldots. \tag{48}$$

Here $V_1 = \frac{4}{3} \pi$ is the volume of a sphere of unit radius.

B. Evaluation of the low order $\Omega_n$

Analytical expressions for $g_0^{(2)}(r)$, $g_1^{(2)}(r)$, and $g_2^{(2)}(r)$ are
known. The two lowest-order terms are

$$g_0^{(2)}(r) = \begin{cases} \frac{1}{r^2}, & r > 2 \\ 0, & \text{otherwise} \end{cases} \tag{49}$$

and

$$g_1^{(2)}(r) = \begin{cases} \frac{2}{r^2} [1 - r(1 + 12 \phi_2^3)], & 2 < r < 4 \\ 0, & \text{otherwise}. \end{cases} \tag{50}$$

Simple integration leads to $\Omega_0 = \frac{\pi}{6} - \frac{1}{12} \ln 3$ and $\Omega_1 = \frac{\pi}{6} + \frac{8}{12} \ln 5 - \ln 3$. Nijboer and Van Hove22 give the analytical
expression for $g_2^{(2)}(r)$ and we find numerically that $\Omega_2 \approx 0.080980$. The values for $\Omega_0$, $\Omega_1$, and $\Omega_2$ were first
obtained by Felderhof.

C. Evaluation of the $\Lambda_n$

The first term in the density expansion of $g^{(2)}$ is simply a
product of three $g_0^{(2)}$s, specifically

$$g_0^{(3)}(r_12,r_13;r_23) = g_0^{(2)}(r_12) g_0^{(2)}(r_13) g_0^{(2)}(r_23). \tag{51}$$

The expression for $\Lambda_n$ then becomes

$$\Lambda_0 = \frac{9}{32\pi^2 \gamma_2} \sum_{l=2}^{\infty} \frac{l(l-1)}{2} \int dr_2 dr_3 \frac{P_l(\cos \theta_{213})}{r_2^{l+1} r_3^{l+1}} \times \left[ g_0^{(2)}(r_23) - 1 \right] P_l(\cos \theta_{213}). \tag{52}$$

Angular integrations are performed by expanding angle dependent
functions in Legendre polynomials

$$f(r_{23}) = \sum_{l=0}^{\infty} A_l(r_{12},r_{13};f) P_l(\cos \theta_{213}), \tag{53}$$

where the expansion coefficients are given by

$$A_l(r_{12},r_{13};f) = -\frac{2l+1}{2} \int_{-1}^{1} d(\cos \theta_{213}) f(r_{23}) P_l(\cos \theta_{213}). \tag{54}$$

The angle $\theta_{213}$ is related to the angles $\theta_2, \theta_3, \phi_2$, and $\phi_3$ by the
addition theorem:

$$P_l(\cos \theta_{213}) = P_l(\cos \theta_2) P_l(\cos \theta_3) + 2 \sum_{s=0}^{l} \frac{(l-s)!}{(l+s)!} \times P_l(\cos \theta_2) P_s(\cos \theta_3) \cos[l(\phi_2 - \phi_3)]. \tag{55}$$

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TABLE I. The three-point parameter $\xi_2$ for impenetrable spheres as a function of sphere volume fraction. The columns correspond to the density expansion under the superposition approximation Eq. (68), the work of Torquato and Lado (Ref. 21), and the exact density expansion Eq. (69).
After applying the expansion and performing the angular integrations, Eq. (52) becomes

$$A_0 = \frac{9}{2} \sum_{i=1}^{\infty} \frac{l(l+1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} \times g_0^{(2)}(r)g_0^{(2)}(s)A_i(r,s;g_0^{(2)} - 1).$$  

(56)

An alternate method was employed by Felderhof to transform Eq. (52) to an integration in wave vector space

$$A_0 = \frac{3}{\pi \phi_2} \sum_{i=1}^{\infty} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} \times g_0^{(2)}(r)g_0^{(2)}(s)A_i(r,s;g_0^{(2)} - 1).$$

(57)

where

$$F_1^{(n)}(k) = \int_0^\infty dr j_i(kr) \frac{g_0^{(2)}(r)}{r^{l-1}}$$

and

$$S_n(k) - 1 = \frac{\phi_2}{V_1} \int_0^\infty dr \left[ g_0^{(2)}(r) - \delta_{n,0} \right] \exp(ikr).$$

(59)

Here $S(k)$ is the usual structure function, $j_i$ is a spherical Bessel function, and $\delta_{n,0}$ equals 1 for $i = j$ and 0 otherwise. The two reduction methods (i.e., the expansion in Legendre polynomials and transformation to wave-vector space) are equivalent and thus agreement between the results obtained from them should provide a self-consistent check on our calculations.

Evaluation of the integrals in Eqs. (56)–(59) lead to $A_0 = \frac{17}{18} - \frac{\ln(17)}{18} + \frac{3}{4} \ln(17 - 4\phi_1^2)$. This result was first obtained by Felderhof. Under the superposition approximation, the next term in the expansion of $g^{(3)}$ is given by

$$g_1^{(3)}(r_{12},r_{13},r_{23}) = \sum_{i=1}^{3} g_0^{(2)}(r_{12})g_0^{(2)}(r_{13})g_0^{(2)}(r_{23}).$$

(60)

Reducing the expression for $\Lambda_{1s}$ as before gives

$$\Lambda_{1s} = \frac{9}{2} \sum_{i=1}^{\infty} \frac{l(l+1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} \times \left( \frac{g_0^{(2)}(r)g_0^{(2)}(s)}{V_1} + \frac{g_0^{(2)}(s)g_0^{(2)}(r)}{V_1} \right)$$

$$\times A_i(r,s;g_0^{(2)} - 1) + \frac{9}{2} \sum_{i=1}^{\infty} \frac{l(l+1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} \times \frac{g_0^{(2)}(r)g_0^{(2)}(s)}{V_1}$$

$$\Lambda_1 = \frac{3}{\pi \phi_2} \sum_{i=1}^{\infty} \frac{l(l+1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} \times \left( \frac{g_0^{(2)}(r)g_0^{(2)}(s)}{V_1} + \frac{g_0^{(2)}(s)g_0^{(2)}(r)}{V_1} \right) A_i(r,s;g_0^{(2)} - 1)$$

$$+ \frac{9}{2} \sum_{i=1}^{\infty} \frac{l(l+1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} g_0^{(2)}(r)g_0^{(2)}(s)A_i(r,s;g_0^{(2)} - 1)$$

$$- \frac{9}{2} \sum_{i=1}^{\infty} \frac{l(l+1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} g_0^{(2)}(r)g_0^{(2)}(s)A_i(r,s;g_0^{(2)} - 1),$$

(64)

which numerically results in $\Lambda_1 \approx -0.19354$.

In summary we find that

$$\Omega = 0.070 226 + 0.103 626 \phi_2 + 0.080 980 \phi_2^2,$$

$$\Lambda^{\infty} = -0.568 47 - 0.282 42 \phi_2^2,$$

$$\Lambda = -0.568 47 - 0.193 54 \phi_2^2,$$

$$\xi_{2} = 0.210 68 \phi_2 - 0.046 93 \phi_2^2 + 0.002 47 \phi_2^3.$$

(65)

(66)

(67)

(68)

(69)

Equations (68) and (69) show that the exact $\xi_2$ will always be greater than $\xi_2^{\infty}$ through order $\phi_2^3$. A comparison of the predicted values from Eqs. (68) and (69) with the results of Torquato and Lado shows that the superposition approximation through all orders in $\phi_2$ is
made in Table I. We find excellent agreement between Eq. (68) and the results of Torquato and Lado up to a value of $\phi_2 \sim 0.15$. For values greater than $\phi_2 \sim 0.15$, the terms of order higher than $\phi_2^2$, which are included in Torquato and Lado's work, appreciably contribute to $\xi^a_2$.

Evidence that the correct value of $\xi_2$ is greater than $\xi^a_2$ through all orders in $\phi_2$ is given by Torquato, who has recently derived a highly accurate expression for $\sigma_2$ of dispersions which depends upon $\phi_2$. Using this expression together with the tabulation of $\xi^a_2$ of Ref. 20, Torquato found that the predicted value of $\sigma_2$ was somewhat lower than the experimental data of Turner, indicating that $\xi^a_2$ is smaller than the exact value $\xi_2$.

IV. CONCLUSIONS

The general bounds of Beran have been compared to the Torquato bounds for suspensions of spheres. For the special case of impenetrable spheres, these bounds are shown to be identical. For partially penetrable spheres, the Torquato bounds are not as restrictive as the Beran bounds. The Torquato bounds, however, appear to be much easier to compute when the spheres are allowed to overlap.

We have also evaluated $\xi_2$, a microstructural parameter that arises in both the Beran and Torquato bounds, for suspensions of impenetrable spheres through third-order in the sphere volume fraction $\phi_2$ in the superposition approximation and exactly. The exact $\xi_2$ is found to be greater than $\xi^a_2$. In the case of spheres which are more conducting than the matrix, this implies that the lower bound (the bound that provides the better estimate of $\sigma_2$) obtained using $\xi^a_2$ is an underestimation of the exact lower bound on $\sigma_2$.

ACKNOWLEDGMENTS

The authors are grateful to Professor F. Lado for very useful discussions. This work was supported in part by the National Science Foundation Grant No. CBT-8514841.