Bounds on the conductivity of a suspension of random impenetrable spheres

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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 ϕ_2 and a three-point parameter ζ_2, which is an integral over a three-point correlation function. We evaluate ζ_2 exactly through third order in ϕ_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 ζ_2. The results indicate that the exact ζ_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.[1-4] 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 σ_1 and σ_2 and volume fractions ϕ_1 and ϕ_2. The most well-known bounds are due to Hashin and Shtrikman (HS).[7] These provide the best possible bounds on the effective conductivity σ_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 ϕ_2, are restrictive only for a limited range of α and ϕ_2. In order to extend the range of utility, it becomes necessary to introduce statistical information beyond that contained in ϕ_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 ϕ_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 ϕ_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 σ_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

$$\left(\left\langle\frac{1}{\sigma}\right\rangle - \frac{4\phi_1\phi_2\left(\frac{1}{\sigma_2}-\frac{1}{\sigma_1}\right)^2}{6\frac{1}{\sigma_1} + (4\phi_1 + 2\zeta_2)\left(\frac{1}{\sigma_2}-\frac{1}{\sigma_1}\right)}\right)^{-1} < \sigma_e < \left(\langle\sigma\rangle - \frac{\phi_1\phi_2(\sigma_2-\sigma_1)^2}{3\sigma_1 + (\phi_1 + 2\zeta_2)(\sigma_2-\sigma_1)}\right), \qquad (1)$$

involves a single three-point parameter

$$\zeta_2 = 1 - \frac{1}{16\phi_1\phi_2\pi^2}\iint d\mathbf{r}_{12}\, d\mathbf{r}_{13}\, \frac{P_2(\cos\theta_{213})}{r_{12}^3 r_{13}^3} \times\left(S_3(r_{12},r_{13},r_{23}) - \frac{S_2(r_{12})S_2(r_{13})}{S_1}\right). \qquad (2)$$

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Here σ 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]

$$\left\{\left\langle\frac{1}{\sigma}\right\rangle - \left[4\phi_1^2\,\eta^2\left(\frac{1}{\sigma_2}-\frac{1}{\sigma_1}\right)^2\right]\Big/\left[C\frac{1}{\sigma_1}+D\left(\frac{1}{\sigma_2}-\frac{1}{\sigma_1}\right)\right]\right\}^{-1}$$
$$\leq \sigma_e \leq \left[\langle\sigma\rangle - \frac{\phi_1^2\eta^2(\sigma_2-\sigma_1)^2}{A\sigma_1+B(\sigma_2-\sigma_1)}\right], \quad (3)$$

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

$$A = A_1 + A_2 + A_3, \quad (4)$$

$$B = B_1 + B_2 + B_3 + B_4, \quad (5)$$

$$C = 2A_1 + 4A_2 + A_3, \quad (6)$$

$$D = 4B_1 + B_2 + 4B_3 + B_4, \quad (7)$$

$$A_1 = 3\eta, \quad (8)$$

$$A_2 = \frac{9}{2}\eta^2\int_0^1 dr_{12}\,r_{12}^2\int_0^1 dr_{13}r_{13}^2 \times\int_{-1}^{+1} d(\cos\theta_{213})h(r_{23}), \quad (9)$$

$$A_3 = 9\eta^2\int_1^\infty \frac{dr_{12}}{r_{12}}\int_1^\infty \frac{dr_{13}}{r_{13}} \times\int_{-1}^{+1} d(\cos\theta_{213})P_2(\cos\theta_{213})h(r_{23}), \quad (10)$$

$$B_1 = 3\eta\int_0^1 dr_{12}r_{12}^2\,\frac{G_1^{(2)}(r_{12})}{\rho}, \quad (11)$$

$$B_2 = 6\eta\int_1^\infty dr_{12}\frac{1}{r_{12}^4}\frac{G_1^{(2)}(r_{12})}{\rho}, \quad (12)$$

$$B_3 = \frac{9}{2}\eta^2\int_0^1 dr_{12}r_{12}^2\int_0^1 dr_{13}r_{13}^2 \times\int_{-1}^{+1} d(\cos\theta_{213})\,\frac{Q(\mathbf{r}_{12},\mathbf{r}_{13})}{\rho^2}, \quad (13)$$

$$B_4 = 9\eta^2\int_1^\infty \frac{dr_{12}}{r_{12}}\int_1^\infty \frac{dr_{13}}{r_{13}} \times\int_{-1}^{+1} d(\cos\theta_{213})P_2(\cos\theta_{213})\,\frac{Q(\mathbf{r}_{12},\mathbf{r}_{13})}{\rho^2}, \quad (14)$$

and

$$Q(\mathbf{r}_{12},\mathbf{r}_{13}) = [G_2^{(2)}(r_{12},r_{13},r_{23}) - \rho G_1^{(2)}(r_{12}) - \rho G_1^{(2)}(r_{13}) + \rho^2 G_0^{(2)}]. \quad (15)$$

In the equations given above, ρ is the number density of spheres, $\eta = \frac{4}{3}\pi\rho$ is a dimensionless number density, $h(r)$ [$\equiv g^{(2)}(r) - 1$, where $g^{(2)}$ is the pair or radial distribution function] is the total correlation 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 $\mathbf{r}_1$ in phase 2 and any sphere center in volume element $d\mathbf{r}_2$ about $\mathbf{r}_2$, another sphere center in $d\mathbf{r}_3$ about $\mathbf{r}_3,\ldots$, and another sphere center in $d\mathbf{r}_n$ about $\mathbf{r}_n$. For statistically homogeneous media, $G_0^{(2)}$ is simply equal to the sphere volume fraction ϕ_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]

$$m(r) = \begin{cases} 0, & r > 1 \\ 1, & r < 1. \end{cases} \quad (16)$$

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]

$$G_0^{(2)} = \phi_2, \quad (17)$$

$$G_1^{(2)}(r_{12}) = \rho m(r_{12}) + \rho^2 e(r_{12})\int d\mathbf{r}_{13}\, m(r_{13})g^{(2)}(r_{23}), \quad (18)$$

and

$$G_2^{(2)}(r_{12},r_{13},r_{23}) = \rho^2[m(r_{12}) + m(r_{13}) - m(r_{12})m(r_{13})]g^{(2)}(r_{23}) + \rho^3 e(r_{12})e(r_{13})\int d\mathbf{r}_{14} m(r_{14})g^{(3)}(r_{23},r_{24},r_{34}), \quad (19)$$

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

$$S_1 = 1 - G_0^{(2)} = \phi_1, \quad (20)$$

$$S_2(r_{12}) = S_1 + \int d\mathbf{r}_{13}\, m(r_{13})[G_1^{(2)}(r_{23}) - \rho], \quad (21)$$

and

$$S_3(r_{12},r_{13},r_{23}) = S_2(r_{23}) + \int d\mathbf{r}_{14}\, m(r_{14})[G_1^{(2)}(r_{34}) - \rho] - \iint d\mathbf{r}_{14}\, d\mathbf{r}_{15}\, m(r_{14})m(r_{25}) \times[G_2^{(2)}(r_{34},r_{35},r_{45}) - \rho^2 g^{(2)}(r_{45})]. \quad (22)$$

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

$$A = 3\phi_1\phi_2, \quad (23)$$

$$B = \phi_1^2\phi_2 + 2\zeta_2\phi_1\phi_2, \quad (24)$$

$$C = 6\phi_1\phi_2, \quad (25)$$

and

$$D = 4\phi_1^2\phi_2 + 2\zeta_2\phi_1\phi_2, \quad (26)$$

then the bounds are equivalent.

Lado and Torquato[17] reduce Eq. (2) for ζ_2 for dispersions of impenetrable spheres. Using the representations of the S_n from Ref. 16 for impenetrable spheres, they obtained

$$\zeta_2 = (3\Omega\phi_2 + \Lambda\phi_2^2)/\phi_1, \tag{27}$$

where

$$\Omega = \int_2^\infty dr \frac{r^2}{(r^2-1)^3} g^{(2)}(r) \tag{28}$$

and

$$\Lambda = \frac{9}{32\pi^2} \sum_{l=2}^{\infty} l(l-1) \iint d\mathbf{r}_{12} d\mathbf{r}_{13} \times [g^{(3)}(r_{12},r_{13},r_{23}) - g^{(2)}(r_{12})g^{(2)}(r_{13})] \frac{P_l(\cos\theta_{213})}{r_{12}^{l+1} r_{13}^{l+1}}. \tag{29}$$

Felderhof[18] 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 $\zeta_2 = (9/2\phi_1\phi_2)K$.]

Consider now Eqs. (9) and (10) for A_2 and A_3. Making the change of variable $\cos\theta_{213} = (r_{12}^2 + r_{13}^2 - r_{23}^2)/2r_{12}r_{13}$ and changing the order of integration results in

$$A_2 = \eta^2 \int_0^2 dr(\tfrac{3}{16} r^5 - \tfrac{9}{4} r^3 + 3r^2)h(r) \tag{30}$$

and

$$A_3 = 2A_2. \tag{31}$$

Notice that the resulting expressions depend on the total correlation function only through r values inside the diameter. For impenetrable spheres of unit radius $h(r) = -1$ for $r<2$ and, therefore, $A_2 = -\phi_2^2$.

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

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

where

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

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

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

$$Q(\mathbf{r}_{12},\mathbf{r}_{13}) = \begin{cases} \rho^2[g^{(2)}(r_{23}) - 2 + \phi_2], & r_{12}<1, r_{13}<1 \\ \rho^3 \int d\mathbf{r}_{14}\, m(r_{14})[g^{(3)}(r_{23},r_{24},r_{34}) - g^{(2)}(r_{24})g^{(2)}(r_{34}) + h(r_{24})h(r_{34})], & r_{12}>1, r_{13}>1. \end{cases} \tag{34}$$

Substituting Eq. (34) into Eqs. (13) and (14) gives $B_3 = -2\phi_2^2 + \phi_2^3$ and, after some rearrangement,

$$B_4 = 2\rho^3 \iiint d\mathbf{r}_{12}\, d\mathbf{r}_{13}\, d\mathbf{r}_{14}\, e(r_{12})e(r_{13})m(r_{14}) \times \frac{P_2(\cos\theta_{213})}{r_{12}^3 r_{13}^3} [g^{(3)}(r_{23},r_{24},r_{34}) - g^{(2)}(r_{24})g^{(2)}(r_{34})]. \tag{35}$$

The $h(r_{24})h(r_{34})$ term has been dropped due to orthogonality of the Legendre polynomials, but the $g^{(2)}(r_{24})g^{(2)}(r_{34})$ 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 $B_4 = 2\Lambda\phi_2^3$.

In summary,

$$A = 3\phi_2 - 3\phi_2^2, \tag{36}$$

$$B = \phi_2 - 2\phi_2^2 + \phi_2^3 + 6\Omega\phi_2^2 + 2\Lambda\phi_2^3, \tag{37}$$

$$C = 6\phi_2 - 6\phi_2^2, \tag{38}$$

and

$$D = 4\phi_2 - 8\phi_2^2 + 4\phi_2^3 + 6\Omega\phi_2^2 + 2\Lambda\phi_2^3. \tag{39}$$

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 from the same variational principles, namely, the minimum potential and complementary potential energy principles. For the case of impenetrable spheres, the trial fields employed by Beran and by Torquato give rise to precisely the same system energy. This energy is equal to that resulting from interaction between up to three impenetrable spheres which interact with induced dipole moments such that only single reflections between spheres are considered. This is equivalent to stating that the fields are assumed to be a constant vector added to a sum of contributions from individual isolated spheres.

In the more general case of spheres distributed with arbitrary degree of penetrability, the trial fields employed by Torquato do not correctly include the interaction effects due to overlap, and hence result in bounds which, although still useful, are not as restrictive as the Beran bounds which do correctly include the overlap interaction effects. However, for partially penetrable spheres, the $G_n^{(2)}$ and hence the Torquato bounds are easier to evaluate.[10]

III. EVALUATION OF ζ_2 FOR IMPENETRABLE SPHERES

Felderhof[19] considered an equilbrium dispersion of impenetrable spheres and computed ζ_2 through third order in ϕ_2 (the volume fraction of spheres). Unfortunately, there appears to be an error in the coefficient of ϕ_2^3. Torquato and Lado[20] later extended this result to calculate ζ_2 for ϕ_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 ζ_2. Here we obtain the correct results for ζ_2 in the superposition approximation through order ϕ_2^3. Moreover, through the same order in ϕ_2, we calculate ζ_2 exactly and thus determine the error involved in using the superposition approximation.

A. The density expansion of ζ_2 for impenetrable spheres

The integrals for Ω and Λ can be expanded in density by making use of the density expansions of the correlation functions:

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

and

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

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

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

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

$$\zeta_2 = \sum_{n=1}^{\infty} c_n \phi_2^n, \tag{44}$$

$$\Omega_n = \int_2^{\infty} dr \frac{r^2}{(r^2-1)^3} \frac{g_n^{(2)}(r)}{V_1^n}, \tag{45}$$

$$\Lambda_n = \frac{9}{32\pi^2} \sum_{l=2}^{\infty} l(l-1) \iint d\mathbf{r}_{12} d\mathbf{r}_{13} \frac{P_l(\cos\theta_{213})}{r_{12}^{l+1} r_{13}^{l+1}} \times \left(\frac{g_n^{(3)}(r_{12},r_{13},r_{23})}{V_1^n} - \sum_{m=0}^{n} \frac{g_m^{(2)}(r_{12}) g_{n-m}^{(2)}(r_{13})}{V_1^n} \right), \tag{46}$$

$$c_1 = 3\Omega_0, \tag{47}$$

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 Ω_n

Analytical expressions for $g_0^{(2)}(r)$, $g_1^{(2)}(r)$, and $g_2^{(2)}(r)$ are known.[21,22] The two lowest-order terms are

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

and

$$g_1^{(2)}(r) = \begin{cases} \frac{32}{3}\pi\left[1 - \frac{3}{8}(r) + \frac{1}{128}(r)^3\right], & 2 \leqslant r \leqslant 4 \\ 0, & \text{otherwise.} \end{cases} \tag{50}$$

Simple integration leads to $\Omega_0 = \frac{5}{36} - \frac{1}{16}\ln 3$ and $\Omega_1 = \frac{25}{72} + \frac{51}{96}\ln 5 - \ln 3$. Nijboer and Van Hove[22] give the analytical expression for $g_2^{(2)}(r)$ and we find numerically that $\Omega_2 \simeq 0.080\,980$. The values for Ω_0, Ω_1, and Ω_2 were first obtained by Felderhof.

C. Evaluation of the Λ_n

The first term in the density expansion of $g^{(3)}$ 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 Λ_0 then becomes

$$\Lambda_0 = \frac{9}{32\pi^2} \sum_{l=2}^{\infty} l(l-1) \iint d\mathbf{r}_{12} d\mathbf{r}_{13} g_0^{(2)}(r_{12}) g_0^{(2)}(r_{13}) \times [g_0^{(2)}(r_{23}) - 1] \frac{P_l(\cos\theta_{213})}{r_{12}^{l+1} r_{13}^{l+1}}. \tag{52}$$

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 θ_{213} is related to the angles θ_2, θ_3, ϕ_2, and ϕ_3 by the addition theorem:

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

TABLE I. The three-point parameter ζ_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).

	ζ_2		
ϕ_2	Eq. (68)	Ref. 20	Eq. (69)
0.0001	0.000 021 1	0.000 021 1	0.000 021 1
0.005	0.001 052	0.001 052	0.001 052
0.010	0.002 102	0.002 102	0.002 102
0.025	0.005 236	0.005 236	0.005 238
0.050	0.010 41	0.010 41	0.010 42
0.075	0.015 50	0.015 51	0.015 54
0.100	0.020 51	0.020 53	0.020 60
0.125	0.025 43	0.025 47	0.025 61
0.150	0.030 25	0.030 33	0.030 55
0.175	0.034 97	0.035 11	0.035 44
0.200	0.039 57	0.039 83	0.040 28
0.225	0.044 04	0.044 50	0.045 06
0.250	0.048 39	0.049 16	0.049 78
0.275	0.052 59	0.053 88	0.054 44
0.300	0.056 65	0.058 75	0.059 05
0.325	0.060 55	0.063 90	0.063 60
0.350	0.064 29	0.069 54	0.068 10
0.375	0.067 85	0.075 95	0.072 54
0.400	0.071 23	0.083 56	0.076 92
0.425	0.074 43	0.093 01	0.081 25
0.450	0.077 43	0.105 1	0.085 53
0.475	0.080 23	0.120 3	0.089 75
0.500	0.082 81	0.140 7	0.093 92
0.525	0.085 17	0.168 1	0.098 03
0.550	0.087 30	0.205 1	0.102 1
0.575	0.089 20	0.256 3	0.106 1
0.600	0.090 85	0.327 7	0.110 1

After applying the expansion and performing the angular integrations, Eq. (52) becomes

$$\Lambda_0 = \frac{9}{2} \sum_{l=2}^{\infty} \frac{l(l-1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} \times g_0^{(2)}(r) g_0^{(2)}(s) A_l(r,s;g_0^{(2)}-1). \quad (56)$$

An alternate method was employed by Felderhof[19] to transform Eq. (52) to an integration in wave vector space

$$\Lambda_0 = \frac{3}{\pi\phi_2} \sum_{l=2}^{\infty} l(l-1) \int_0^\infty dk\, [S_0(k)-1] [F_l^{(0)}(k)]^2 k^2, \quad (57)$$

where

$$F_l^{(n)}(k) = \int_0^\infty dr\, j_l(kr) \frac{g_n^{(2)}(r)}{r^{l-1}} \quad (58)$$

and

$$S_n(k) - 1 = \frac{\phi_2}{V_1} \int d\mathbf{r} [g_n^{(2)}(r) - \delta_{n0}] \exp(i\mathbf{k}\cdot\mathbf{r}). \quad (59)$$

Here $S(k)$ is the usual structure function, j_l is a spherical Bessel function, and δ_{ij} 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 $\Lambda_0 = \frac{169}{6} - \frac{49}{6}\sqrt{13} + \frac{3}{4}\ln(17 - 4\sqrt{13})$. This result was first obtained by Felderhof. Under the superposition approximation the next term in the expansion of $g^{(3)}$ is given by

$$g_1^{(3)}(r_{12},r_{13},r_{23}) = \sum_{i=1}^{3} g_{\delta_{i1}}^{(2)}(r_{12}) g_{\delta_{i2}}^{(2)}(r_{13}) g_{\delta_{i3}}^{(2)}(r_{23}). \quad (60)$$

Reducing the expression for Λ_1^{sa} as before gives

$$\Lambda_1^{sa} = \frac{9}{2} \sum_{l=2}^{\infty} \frac{l(l-1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} \times \left(\frac{g_0^{(2)}(r) g_1^{(2)}(s)}{V_1} + \frac{g_0^{(2)}(s) g_1^{(2)}(r)}{V_1} \right) \times A_l(r,s;g_0^{(2)}-1) + \frac{9}{2} \sum_{l=2}^{\infty} \frac{l(l-1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \times \frac{1}{(rs)^{l-1}} g_0^{(2)}(r) g_0^{(2)}(s) A_l\left(r,s;\frac{g_1^{(2)}}{V_1}\right) \quad (61)$$

or

$$\Lambda_1^{sa} = \frac{3}{\pi\phi_2} \sum_{l=2}^{\infty} l(l-1) \int_0^\infty dk\, S_1(k) [F_l^{(0)}(k)]^2 k^2 + \frac{6}{\pi\phi_2} \sum_{l=2}^{\infty} l(l-1) \times \int_0^\infty dk\, S_0(k) F_l^{(0)}(k) F_l^{(1)}(k) k^2, \quad (62)$$

where the superscript sa refers to the use of the superposition approximation.

Felderhof obtained the correct Λ_1^{sa} value for $l=2$ of $-\frac{23}{32} + \frac{2357}{3360} \approx -0.017\,26$. Felderhof, however, appears to have incorrectly determined the value for $l=3$ and truncating the series after this term found $\Lambda_1^{sa} \approx -0.0298$. From either Eq. (61) or (62) we find that for $l=3$ $\Lambda_1^{sa} = (-187\,863/788\,480) \approx -0.238\,26$. Numerically, we find through $l=7$ $\Lambda_1^{sa} \approx -0.282\,42$.

D. Corrections to the superposition approximation

The exact first-order term in the expansion of $g^{(3)}$ is[23]

$$g_1^{(3)}(r_{12},r_{13},r_{23}) = \sum_{i=1}^{3} g_{\delta_{i1}}^{(2)}(r_{12}) g_{\delta_{i2}}^{(2)}(r_{13}) g_{\delta_{i3}}^{(2)}(r_{23}) + g_0^{(2)}(r_{12}) g_0^{(2)}(r_{13}) g_0^{(2)}(r_{23}) \times \int d\mathbf{r}_{14} f(r_{14}) f(r_{24}) f(r_{34}). \quad (63)$$

The quantity $f(r)$ is the Mayer-f function which, for impenetrable spheres of unit radius, is equal to -1 for $r<2$ and zero otherwise. For impenetrable spheres of unit radius, the integral over the product of three Mayer-f functions turns out to be minus the intersection volume of three spheres of radius 2 with centers separated by r_{12}, r_{13}, and r_{23}, respectively. Analytical solutions exist for this volume,[24,25] denoted here by V_3^I. The resulting integral for Λ_1 is exactly

$$\Lambda_1 = \frac{9}{2} \sum_{l=2}^{\infty} \frac{l(l-1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} \left(\frac{g_0^{(2)}(r) g_1^{(2)}(s)}{V_1} + \frac{g_0^{(2)}(s) g_1^{(2)}(r)}{V_1} \right) A_l(r,s;g_0^{(2)}-1)$$
$$+ \frac{9}{2} \sum_{l=2}^{\infty} \frac{l(l-1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} g_0^{(2)}(r) g_0^{(2)}(s) A_l\left(r,s;\frac{g_1^{(2)}}{V_1}\right)$$
$$- \frac{9}{2} \sum_{l=2}^{\infty} \frac{l(l-1)}{2l+1} \int_0^\infty dr \int_0^\infty ds \frac{1}{(rs)^{l-1}} g_0^{(2)}(r) g_0^{(2)}(s) A_l\left(r,s;g_0^{(2)} \frac{V_3^I}{V_1} - 1\right), \quad (64)$$

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

In summary we find that

$$\Omega = 0.070\,226 + 0.103\,62\phi_2 + 0.080\,980\phi_2^2, \quad (65)$$

$$\Lambda^{sa} = -0.568\,47 - 0.282\,42\phi_2, \quad (66)$$

$$\Lambda = -0.568\,47 - 0.193\,54\phi_2, \quad (67)$$

$$\zeta_2^{sa} = 0.210\,68\phi_2 - 0.046\,93\phi_2^2 - 0.086\,41\phi_2^3, \quad (68)$$

and

$$\zeta_2 = 0.210\,68\phi_2 - 0.046\,93\phi_2^2 + 0.002\,47\phi_2^3. \quad (69)$$

Equations (68) and (69) show that the exact ζ_2 will always be greater than ζ_2^{sa} through order ϕ_2^3. A comparison of the predicted values from Eqs. (68) and (69) with the results of Torquato and Lado[20] (who calculated ζ_2 in the superposition approximation through all orders in ϕ_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 $\phi_2 \approx 0.15$. For values greater than $\phi_2 \approx 0.15$, the terms of order higher than ϕ_2^3, which are included in Torquato and Lado's work, appreciably contribute to ζ_2^{sa}.

Evidence that the correct value of ζ_2 is greater than ζ_2^{sa} through all orders in ϕ_2 is given by Torquato,[6] who has recently derived a highly accurate expression for σ_e of dispersions which depends upon ζ_2. Using this expression together with the tabulation of ζ_2^{sa} of Ref. 20, Torquato[6] found that the predicted value of σ_e was somewhat lower than the experimental data of Turner,[26] for impenetrable spheres indicating that ζ_2^{sa} is smaller than the exact value ζ_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.[10]

We have also evaluated ζ_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 ϕ_2 in the superposition approximation and exactly. The exact ζ_2 is found to be greater than ζ_2^{sa}. 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 σ_e) obtained using ζ_2^{sa} is an underestimation of the exact lower bound on σ_e.

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