Bulk properties of two-phase disordered media. III. New bounds on the effective conductivity of dispersions of penetrable spheres

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Rigorous upper and lower bounds on the effective electrical conductivity σ^* of a two-phase material composed of equi-sized spheres distributed with an arbitrary degree of impenetrability in a matrix are obtained and studied. In general, the bounds depend upon, among other quantities, the point/n-particle distribution functions $G_n^{(i)}$, which are probability density functions associated with finding a point in phase i and a particular configuration of n spheres. The $G_n^{(i)}$ are shown to be related to the ρ_n, the probability density functions associated with finding a particular configuration of n partially penetrable spheres in a matrix. General asymptotic and bounding properties of the $G_n^{(i)}$ are given. New results for the $G_n^{(i)}$ are presented for totally impenetrable spheres, fully penetrable spheres (i.e., randomly centered spheres), and sphere distributions between these latter two extremes. The so-called first-order cluster bounds on σ^* derived here are given exactly through second order in the sphere volume fraction for arbitrary λ (where λ is the impenetrability or hardness parameter) for two different interpenetrable-sphere models. Comparison of these low-density bounds on σ^* to an approximate low-density expansion of σ^* derived here for interpenetrable-sphere models, reveals that the bounds can provide accurate estimates of the second-order coefficient for a fairly wide range of λ and phase conductivities. The results of this study suggest that general bounds derived by Beran, for dispersions of spheres distributed with arbitrary λ and through all orders in ϕ_2, are more restrictive than the first-order cluster bounds for $0 \leqslant \lambda < 1$; with the two sets of bounds being identical for the case of totally impenetrable spheres ($\lambda = 1$). For most values of λ in the range $0 \leqslant \lambda < 1$, however, the numerical differences between the Beran and cluster bounds should be small; the greatest difference occurring when $\lambda = 0$. The analysis also indicates that the cluster bounds will be easier to compute than the Beran bounds for dispersions of partially penetrable spheres.

I. INTRODUCTION

The degree of the connectivity of the constituent phases may greatly influence the transport properties of two-phase disordered materials (e.g., composite and porous media), particularly when the phase properties differ significantly.[1] For example, the pronounced decrease of the electrical resistivity of a compacted mixture of silver particles and Bakelite powder near 30% by volume of silver occurs because the more conductive phase changes from a dispersed phase to a continuously connected one.[2] Percolation theory provides a useful conceptual framework for interpreting the morphology and transport properties of two-phase composites in which one phase is infinitely conducting relative to the other.[1-3]

In this paper it is desired to estimate the effective electrical conductivity σ^* of two-phase media composed of a particulate phase of variable connectivity dispersed throughout a matrix (e.g., dispersions,[2] sandstones,[4,5] sintered materials,[4] and unglazed ceramics[4]) for any phase conductivity ratio. Equi-sized spheres distributed with an arbitrary degree of impenetrability in a matrix represent a reasonable model of such a medium. The degree of impenetrability may be characterized by some parameter λ whose value 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). The degree of connectivity of the particle phase is obviously dependent upon the degree of impenetrability λ. For example, for fully penetrable spheres ($\lambda = 0$) and totally impenetrable spheres ($\lambda = 1$), the particle phase percolates (i.e., a sample-spanning cluster appears) at a sphere volume fraction of approximately 0.3[6] and 0.64,[7] respectively. The conductivities of such models of disordered composite media shall be estimated employing rigorous bounding techniques. Bounds on σ^* are desirable since (i) comparison with bounds allows one to test the merits of a theory and (ii) bounds can provide useful estimates of σ^* even when the phase conductivities widely differ.[8] It should be remembered that all results obtained here will apply also to the thermal conductivity, dielectric constant, magnetic permeability, and diffusion coefficient associated with heterogeneous media. Examples of materials (characterized by a connected particle phase) for which it is desired to predict such properties include foams,[9] polymer blends,[10] and cermets (ceramic–metal mixtures).[11]

This is the third in a series of studies of the bulk properties of two-phase disordered media. In the first paper,[12] (hereafter referred to as I), a cluster expansion for the dielectric constant or, equivalently, electrical conductivity, of a dispersion of penetrable spheres was obtained. Rigorous bounds and an approximate expression for the effective property were derived in the subsequent paper[13] (hereafter referred to as II) through second order in the sphere volume

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fraction and for arbitrary λ for a particular interpenetrable-sphere model.

In Sec. II, formal nth-order cluster bounds on σ^* are derived using classical variational principles for media composed of spheres distributed with arbitrary λ in a matrix. First-order cluster bounds are then explicitly expressed in terms of integrals that involve, among other quantities, certain statistical distribution functions, $G_1^{(2)}$ and $G_2^{(2)}$. The point/n-particle distribution function $G_n^{(i)}$ is the probability density associated with finding a point in phase i and a particular configuration of n spheres. In Sec. III, the $G_n^{(i)}$ are rigorously defined and some of their general properties are described. Among other results, the relationship between the $G_n^{(i)}$ and the more fundamental n-particle probability densities ρ_n (defined in the text) is given here for a distribution of equi-sized spheres of variable impenetrability. General rigorous upper and lower bounds on the $G_n^{(i)}$ are presented. Some new results for the $G_n^{(i)}$ for the extreme cases of totally impenetrable spheres and fully penetrable spheres are given. The exact density expansion of $G_1^{(i)}$ and $G_2^{(i)}$, through second order in the number density ρ, is then derived for the permeable-sphere[14] and penetrable-concentric-shell[12] models. In Sec. IV the first-order cluster bounds on σ^* are given exactly through second order in the sphere volume fraction for both of the aforementioned interpenetrable-sphere models for arbitrary values of the impenetrability parameter λ. An approximate expression for the low-density expansion of σ^* for dispersions of penetrable spheres is derived. The low-density bounds described above are found to be in good agreement with the approximate expansion for a wide range of λ and phase conductivities. Lastly, in Sec. V the main results of this study are briefly summarized.

II. NEW VARIATIONAL BOUNDS

Consider a statistically isotropic two-phase medium of volume V composed of N equi-sized spheres of conductivity σ_2 dispersed throughout a matrix phase of conductivity σ_1. The volume fraction of matrix and spheres is ϕ_1 and ϕ_2 $(=1-\phi_1)$, respectively. The spheres are distributed with an arbitrary degree of impenetrability λ, $0\leqslant\lambda\leqslant 1$, where $\lambda=0$ corresponds to fully penetrable spheres and $\lambda=1$ corresponds to totally impenetrable spheres. Examples of sphere distributions involving values of λ that lie between 0 and 1 are the permeable-sphere (PS)[14] and penetrable-concentric-shell (PCS)[12] models. Employing classical variational principles,[15] a new set of rigorous upper and lower bounds on the effective conductivity of such a composite for arbitrary λ is derived here.

A. Formal nth-order cluster bounds

1. Principle of minimum potential energy

Let the average of the trial electric field $\langle\hat{\mathbf{E}}(\mathbf{r})\rangle$ (where angular brackets denote an ensemble average and $\mathbf{r}$ is a field point) be required to equal the average of the actual electric field $\langle\mathbf{E}(\mathbf{r})\rangle$. Let

$$U=\tfrac{1}{2}\langle\sigma(\mathbf{r})\mathbf{E}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})\rangle, \tag{2.1}$$

where $\sigma(\mathbf{r})$ is the local conductivity. Then among all irrotational trial electric fields, the field which makes $\sigma(\mathbf{r})\hat{\mathbf{E}}(\mathbf{r})$ solenoidal is the one that minimizes U and is unique.

This principle is general and hence applies to composite media of arbitrary microgeometry. The condition on the trial electric field implies that the tangential component of $\hat{\mathbf{E}}$ must be continuous across surfaces of discontinuity in the medium (i.e., at the particle-matrix interface for the specific geometry considered here). At its minimum value the total energy U is given by

$$U=\tfrac{1}{2}\sigma^*\langle\hat{\mathbf{E}}(r)\rangle\cdot\langle\hat{\mathbf{E}}(r)\rangle, \tag{2.2}$$

where σ^* is the effective electrical conductivity. Applying the principle of minimum potential energy and Eq. (2.2) yields the following rigorous upper bound on the effective conductivity:

$$\sigma^*\leqslant\frac{\langle\sigma\hat{\mathbf{E}}\cdot\hat{\mathbf{E}}\rangle}{\langle\hat{\mathbf{E}}\rangle\cdot\langle\hat{\mathbf{E}}\rangle}. \tag{2.3}$$

For a dispersion of N equi-sized penetrable spheres of radius R, the electric field at $\mathbf{r}$ can be expanded in a cluster expansion of the form[12]:

$$\mathbf{E}(\mathbf{r})=\langle\mathbf{E}(\mathbf{r})\rangle+\mathbf{E}^{(1)}(\mathbf{r})+\mathbf{E}^{(2)}(\mathbf{r})+\cdots. \tag{2.4}$$

The kth-order term $\mathbf{E}^{(k)}$ is the contribution to $\mathbf{E}$ that accounts for intrinsic k-body interactions and therefore involves a sum over k-tuplets of particles.[12] We require that $\langle\mathbf{E}^{(k)}\rangle=0$ for all $k\geqslant 1$. The $\mathbf{E}^{(k)}$ are derived from I by obtaining the cluster expansion of Eq. (2.10) of this reference and eliminating the applied field $\mathbf{E}_0$ in favor of the average field. If this is done then the average of $\mathbf{E}^{(k)}$ will be zero for all k. For example, from Eq. (2.22), it is obvious that $\langle\mathbf{E}^{(1)}\rangle=0$. Clearly, all the quantities in Eq. (2.4) depend upon the positions of the N spheres of the system.

An allowable trial function based on Eq. (2.4) is the following:

$$\hat{\mathbf{E}}(\mathbf{r})=\langle\mathbf{E}\rangle+\sum_{k=1}^{n}\psi_k\mathbf{E}^{(k)}(\mathbf{r}). \tag{2.5}$$

In Eq. (2.5) the quantities ψ_k are constant multipliers which are to be chosen as to minimize the upper bound (2.3). Substituting Eq. (2.5) into upper bound (2.3) and setting $\partial\sigma^*/\partial\boldsymbol{\psi}=0$, where $\boldsymbol{\psi}$ is a column vector whose elements are given by ψ_k, gives that

$$\sigma^*\leqslant\langle\sigma\rangle-\frac{\mathbf{V}^T\mathsf{W}^{-1}\mathbf{V}}{\langle\mathbf{E}\rangle\cdot\langle\mathbf{E}\rangle}. \tag{2.6}$$

Here $\mathbf{V}^T$ denotes the transpose of the column vector $\mathbf{V}$ whose elements are given by

$$V_k=\langle\mathbf{E}\rangle\cdot\langle\sigma\,\mathbf{E}^{(k)}\rangle, \tag{2.7}$$

and W^{-1} denotes the inverse of the matrix W whose elements are given by

$$W_{kl}=\langle\sigma\,\mathbf{E}^{(k)}\cdot\mathbf{E}^{(l)}\rangle. \tag{2.8}$$

Upper bound (2.6) is exact through nth order in the sphere volume fraction ϕ_2, since it is based on the exact solution of the electrostatic field equations for n interacting spheres. Accordingly, this is referred to as an nth-order cluster upper bound. Note that $\mathbf{V}$, Eq. (2.7), and W, Eq. (2.8), depend not only upon field quantities but, as a result of ensemble averaging these many-body functions, statistical quantities which characterize the spatial distribution of the inclusions. In general, it can be shown that the nth-order cluster upper bound

Eq. (2.6) depends upon the sets of distribution functions $\rho_1, \rho_2,..., \rho_{2n-1}, \rho_{2n}$, and $G_0^{(2)}, G_1^{(2)},..., G_{2n-1}^{(2)}, G_{2n}^{(2)}$ defined in the subsequent subsection. This, however, shall not be demonstrated here for arbitrary n.

2. Principle of minimum complementary potential energy

Let the average of the trial current field $\langle \hat{\mathbf{J}}(\mathbf{r}) \rangle$ be required to equal the average of the actual current field $\langle \mathbf{J}(\mathbf{r}) \rangle$. Let

$$T = \tfrac{1}{2}\langle \hat{\mathbf{J}}(\mathbf{r}) \cdot \hat{\mathbf{J}}(\mathbf{r})/\sigma(\mathbf{r}) \rangle. \tag{2.9}$$

Then among all solenoidal trial current fields, the field which makes $\hat{\mathbf{J}}(\mathbf{r})/\sigma(\mathbf{r})$ irrotational is the one that minimizes T and is unique.

The condition on the trial current field implies that the normal component of $\hat{\mathbf{J}}$ must be continuous across surfaces of discontinuity in the medium. At its minimum value the total energy T is given by

$$T = \langle \hat{\mathbf{J}} \rangle \cdot \langle \hat{\mathbf{J}} \rangle / \sigma^*. \tag{2.10}$$

The use of the principle of minimum complementary potential energy and Eq. (2.10) gives a rigorous lower bound on σ^*, namely

$$\sigma^* \geqslant \frac{\langle \hat{\mathbf{J}} \rangle \cdot \langle \hat{\mathbf{J}} \rangle}{\langle \sigma^{-1} \hat{\mathbf{J}} \cdot \hat{\mathbf{J}} \rangle}. \tag{2.11}$$

For a composite medium composed of penetrable spheres dispersed throughout a matrix, an allowable trial current field is given by

$$\hat{\mathbf{J}}(\mathbf{r}) = \langle \hat{\mathbf{J}} \rangle + \sum_{k=1}^{n} \omega_k \mathbf{J}^{(k)}(\mathbf{r}). \tag{2.12}$$

As in the case of the trial electric field, the quantity $\mathbf{J}^{(k)}$ is derived from the exact solution of the electrostatic field equations for k interacting spheres. We require that $\langle \mathbf{J}^{(k)} \rangle = 0$ for all $k \geqslant 1$. Substitution of Eq. (2.12) into lower bound (2.11) and setting $\partial\sigma^*/\partial\omega = 0$, where ω is a column vector whose elements are given by ω_k, yields that

$$\sigma^* \geqslant \left[\langle 1/\sigma \rangle - \frac{\mathsf{X}^T \mathsf{Y}^{-1} \mathsf{X}}{\langle \mathbf{J} \rangle \cdot \langle \mathbf{J} \rangle} \right]^{-1}. \tag{2.13}$$

Here X^T denotes the transpose of the column vector X whose elements are given by

$$X_k = \langle \mathbf{J} \rangle \cdot \langle \mathbf{J}^{(k)}/\sigma \rangle \tag{2.14}$$

and Y^{-1} denotes the inverse of the matrix Y whose elements are given by

$$Y_{kl} = \langle \mathbf{J}^{(k)} \cdot \mathbf{J}^{(l)}/\sigma \rangle. \tag{2.15}$$

Lower bound (2.13) is referred to as an nth-order cluster lower bound since it is exact through nth order in ϕ_2. The averaged quantities X and Y depend upon functions which statistically characterize the medium. The nth-order cluster lower bound (2.13) also can be shown to depend upon the sets of distribution functions $\rho_1, \rho_2,..., \rho_{2n}$, and $G_0^{(2)}, G_1^{(2)},..., G_{2n-1}^{(2)}, G_{2n}^{(2)}$.

B. Explicit first-order cluster bounds

Here explicit expressions for first-order cluster bounds on σ^* are derived. Setting $n = 1$ in Eqs. (2.6) and (2.13) gives, respectively,

$$\sigma^* \leqslant \left[\langle \sigma \rangle - \frac{\langle \sigma \mathbf{E}^{(1)} \rangle \cdot \langle \sigma \mathbf{E}^{(1)} \rangle}{\langle \sigma \mathbf{E}^{(1)} \cdot \mathbf{E}^{(1)} \rangle} \right] \tag{2.16}$$

and

$$\sigma^* \geqslant \left[\langle 1/\sigma \rangle - \frac{\langle \mathbf{J}^{(1)}/\sigma \rangle \cdot \langle \mathbf{J}^{(1)}/\sigma \rangle}{\langle \mathbf{J}^{(1)} \cdot \mathbf{J}^{(1)}/\sigma \rangle} \right]^{-1}. \tag{2.17}$$

The local conductivity may be expressed in terms of the characteristic functions of the phases, i.e.,

$$\begin{aligned} \sigma(\mathbf{r}) &= \sigma_1 I^{(1)}(\mathbf{r}) + \sigma_2 I^{(2)}(\mathbf{r}) \\ &= \sigma_1 + (\sigma_2 - \sigma_1) I^{(2)}(\mathbf{r}), \end{aligned} \tag{2.18}$$

where

$$I^{(i)}(\mathbf{r}) = \begin{cases} 1, & \mathbf{r} \in D_i, \\ 0, & \text{otherwise}, \quad i = 1,2 \end{cases} \tag{2.19}$$

and D_1 and D_2 are the regions of space occupied by matrix and particles, respectively. For N overlapping spheres of radius R centered at positions $\mathbf{r}^N \equiv \mathbf{r}_1, \mathbf{r}_2,..., \mathbf{r}_N$, respectively, it has been shown that[16]

$$I^{(1)}(\mathbf{r};\mathbf{r}^N) = \prod_{i=1}^{N} [1 - m(x_i)] \tag{2.20a}$$

$$\begin{aligned} &= 1 - \sum_{i=1}^{N} m(x_i) + \sum_{i<j}^{N} m(x_i) m(x_j) \\ &\quad - \sum_{i<j<k}^{N} m(x_i) m(x_j) m(x_k) + \cdots, \end{aligned} \tag{2.20b}$$

where

$$m(r) = \begin{cases} 1, & r < R, \\ 0, & r > R \end{cases} \tag{2.21}$$

and

$$x_i = |\mathbf{r} - \mathbf{r}_i|.$$

For $n = 1$ the trial fluctuation fields $\mathbf{E}^{(1)}$ and $\mathbf{J}^{(1)}$ are easily obtained from the one-sphere electrostatic boundary-value problem. Specifically, for an inhomogeneous system of N spheres, one has

$$\mathbf{E}^{(1)}(\mathbf{r};\mathbf{r}^N) = \sum_{i=1}^{N} \overline{\mathsf{K}}(\mathbf{x}_i) \cdot \langle \mathbf{E} \rangle - \int d\mathbf{r}_1 \rho_1(\mathbf{r}_1) \overline{\mathsf{K}}(\mathbf{x}_1) \cdot \langle \mathbf{E} \rangle \tag{2.22}$$

and

$$\mathbf{J}^{(1)}(\mathbf{r};\mathbf{r}^N) = \sum_{i=1}^{N} \overline{\mathsf{M}}(\mathbf{x}_i) \cdot \langle E \rangle - \int d\mathbf{r}_1 \rho_1(r_1) \overline{\mathsf{M}}(\mathbf{x}_1) \cdot \langle \mathbf{E} \rangle, \tag{2.23}$$

where $\overline{\mathsf{K}}$ and $\overline{\mathsf{M}}$ are the single-body operators[12]

$$\overline{\mathsf{K}}(\mathbf{r}) = \begin{cases} \dfrac{\beta R^3}{r^3} [3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathsf{U}], & r > R, \\ -\beta \mathsf{U}, & r < R, \end{cases} \tag{2.24}$$

$$\overline{\mathsf{M}}(\mathbf{r}) = \begin{cases} \dfrac{\sigma_1 \beta R^3}{r^3} [3\hat{\mathbf{r}}\hat{\mathbf{r}} - \mathsf{U}], & r > R, \\ 2\sigma_1 \beta \mathsf{U}, & r < R, \end{cases} \tag{2.25}$$

$$\beta = \frac{\sigma_2 - \sigma_1}{\sigma_2 + 2\sigma_1}, \tag{2.26}$$

$\mathbf{x} = \mathbf{r} - \mathbf{r}_i$, $r = |\mathbf{r}|$, $\hat{\mathbf{r}} = \mathbf{r}/r$, and U is the unit dyadic. In the volume integrals of Eqs. (2.22) and (2.23) the quantity ρ_1 is the one-particle density function defined below.

It remains now to substitute Eqs. (2.18), (2.20), (2.22), and (2.23) into the bounds (2.16) and (2.17) and obtain the necessary ensemble averages. Let $F(\mathbf{r}^N)$ denote any many-body function. Then the ensemble average of F is given by

$$\langle F(\mathbf{r}^N)\rangle = \int \cdots \int d\mathbf{r}^N F(\mathbf{r}^N) P_N(\mathbf{r}^N), \tag{2.27}$$

where $d\mathbf{r}^N \equiv d\mathbf{r}_1,\cdots,d\mathbf{r}_N$ and $P_N(\mathbf{r}^N)\, d\mathbf{r}^N$ is the probability of simultaneously finding the center of particle 1 in volume $d\mathbf{r}_1$ about $\mathbf{r}_1$, the center of particle 2 in volume $d\mathbf{r}_2$ about $\mathbf{r}_2$,..., and the center of particle N in volume $d\mathbf{r}_N$ about $\mathbf{r}_N$. It is convenient to introduce the reduced n-particle probability density $P_n(\mathbf{r}^n)$ defined by

$$P_n(\mathbf{r}^n) = \int \cdots \int d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N P_N(\mathbf{r}^N). \tag{2.28}$$

Let

$$\rho_n(\mathbf{r}^n) = [N!/(N-n)!] P_n(\mathbf{r}^n). \tag{2.29}$$

Then $\rho_n(\mathbf{r}^n)\, d\mathbf{r}^n$ is the probability that the center of exactly one (unspecified) particle is in volume $d\mathbf{r}_1$ about $\mathbf{r}_1$, the center of exactly one other (unspecified) particle is in volume $d\mathbf{r}_2$ about $\mathbf{r}_2$, etc.

The ensemble averaged quantities of Eqs. (2.16) and (2.17) for isotropic media are, after some algebraic manipulation (see Appendix A), given by

$$\langle \sigma \rangle = \sigma_1 + \phi_2(\sigma_2 - \sigma_1), \tag{2.30}$$

$$\langle 1/\sigma \rangle = 1/\sigma_1 + \phi_2(\sigma_1 - \sigma_2)/\sigma_1\sigma_2, \tag{2.31}$$

$$\langle \sigma \mathbf{E}^{(1)} \rangle = -4\pi\beta(\sigma_2 - \sigma_1)\langle \mathbf{E} \rangle \int_0^1 dz\, z^2 H_1^{(2)}(z), \tag{2.32}$$

$$\langle \mathbf{J}^{(1)}/\sigma \rangle = 8\pi\beta\left(\frac{\sigma_1 - \sigma_2}{\sigma_2}\right)\langle \mathbf{E} \rangle \int_0^1 dz\, z^2 H_1^{(2)}(z), \tag{2.33}$$

$$\frac{\langle \sigma \mathbf{E}^{(1)} \cdot \mathbf{E}^{(1)} \rangle}{\beta^2 \langle \mathbf{E} \rangle \cdot \langle \mathbf{E} \rangle} = \sigma_1 A + (\sigma_2 - \sigma_1) B, \tag{2.34}$$

$$\frac{\langle \mathbf{J}^{(1)} \cdot \mathbf{J}^{(1)}/\sigma \rangle}{\beta^2 \langle \mathbf{E} \rangle \cdot \langle \mathbf{E} \rangle} = \frac{C}{\sigma_1} + \frac{(\sigma_1 - \sigma_2)}{\sigma_1\sigma_2} D, \tag{2.35}$$

where

$$A = A_1 + A_2 + A_3, \tag{2.36}$$

$$B = B_1 + B_2 + B_3 + B_4, \tag{2.37}$$

$$C = 2A_1 + 4A_2 + A_3, \tag{2.38}$$

$$D = 4B_1 + B_2 + 4B_3 + B_4, \tag{2.39}$$

$$A_1 = 3\eta, \tag{2.40}$$

$$A_2 = \frac{9}{2}\eta^2 \int_0^1 dz\, z^2 \int_0^1 dy\, y^2 \int_{-1}^1 du\, h(x), \tag{2.41}$$

$$A_3 = 9\eta^2 \int_1^\infty \frac{dz}{z} \int_1^\infty \frac{dy}{y} \int_{-1}^1 du\, h(x) P_2(u), \tag{2.42}$$

$$B_1 = 3\eta \int_0^1 dz\, z^2 G_1^{(2)}(z)/\rho, \tag{2.43}$$

$$B_2 = 6\eta \int_1^\infty \frac{dz}{z^4} G_1^{(2)}(z)/\rho, \tag{2.44}$$

$$B_3 = \frac{9}{2}\eta^2 \int_0^1 dz\, z^2 \int_0^1 dy\, y^2 \int_{-1}^1 du\, Q(\mathbf{y},\mathbf{z})/\rho^2, \tag{2.45}$$

$$B_4 = 9\eta^2 \int_1^\infty \frac{dz}{z} \int_1^\infty \frac{dy}{y} \int_{-1}^1 du\, Q(\mathbf{y},\mathbf{z}) P_2(u)/\rho^2, \tag{2.46}$$

and

$$Q(\mathbf{y},\mathbf{z}) = G_2^{(2)}(\mathbf{y},\mathbf{z}) - \rho G_1^{(2)}(y) - \rho G_1^{(2)}(z) + \rho^2 \phi_2. \tag{2.47}$$

Here the sphere radius R is taken to be unity, $\rho = N/V$ is the number density, $\eta = \rho V_1$ is a reduced density, V_1 is the volume of one sphere, $P_2(u)$ is the Legendre polynomial of order 2 [not to be confused with the reduced two-particle probability density of Eq. (2.28)],

$$u = \frac{y^2 + z^2 - x^2}{2yz} \tag{2.48}$$

and

$$x = |\mathbf{y} - \mathbf{z}|.$$

Moreover, the quantity $G_n^{(i)}(\mathbf{r}^{n+1})\, d\mathbf{r}_2, d\mathbf{r}_3,\ldots,d\mathbf{r}_{n+1}$ gives the probability of finding phase i at $\mathbf{r}_1$, the center of one (unspecified) particle in volume $d\mathbf{r}_2$ about $\mathbf{r}_2$, the center if another (unspecified) particle in volume $d\mathbf{r}_3$ about $\mathbf{r}_3$, etc. Weissberg and Prager[17] introduced $G_1^{(1)}$ and $G_2^{(1)}$ in the related problem of determining the effective viscosity of a suspension and evaluated these quantities for a geometry of fully penetrable spheres. This appears to be the only model microstructure for which the $G_n^{(i)}$ have been evaluated. These statistical quantities, which shall be referred to here as point/n-particle distribution functions, are studied in some detail in the subsequent section. For statistically homogeneous and isotropic media, $G_1^{(i)}(\mathbf{r}_1,\mathbf{r}_2) = G_1^{(i)}(r_{12})$ and $G_2^{(i)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) = G_2^{(i)}(r_{12},r_{13},\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})$, where $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and $\hat{\mathbf{r}}_{ij} = \mathbf{r}_{ij}/r_{ij}$. The function $H_1^{(i)}$ appearing in Eqs. (2.32) and (2.33) is trivially related to $G_1^{(i)}$ through Eq. (3.15). The quantity $h(x)$ appearing in Eqs. (2.41) and (2.42) is the total correlation function and is related to the radial distribution function $g(x) \equiv \rho_2(x)/\rho^2$, i.e.,

$$h(x) = g(x) - 1. \tag{2.49}$$

In the limit $x \to \infty$, $h \to 0$, assuming the system does not possess long-range order. In Appendix A the steps leading to integrals (2.41)–(2.46) are outlined.

Weissberg[18] actually was the first to employ trial fields based upon the solution of the single-body electrostatic boundary-value problem. He did so to obtain an upper bound on σ^* for the specific model of a bed of perfectly insulating fully penetrable spheres ($\alpha = 0$, where $\alpha = \sigma_2/\sigma_1$). Weissberg did not need to compute the lower bound on σ^* since it vanishes in this case. Since Weissberg had the geometry of fully penetrable spheres specifically in mind he did not bother to express ensemble averages in terms of the general statistical quantities $h(x)$, $G_1^{(2)}(x)$, and $G_2^{(2)}(\mathbf{y},\mathbf{z})$, as is done here. For the case of fully penetrable spheres these statistical functions are trivial and so Weissberg evaluated such ensemble averages using simply probability arguments. (In Sec. III, the $G_n^{(i)}$ are, for the first time, expressed in terms of the fundamental n-particle probability densities for any sphere distribution.) The Weissberg upper bound on σ^* for $\alpha = 0$ always improves upon the Hashin–Shtrikman (HS)[19] upper bound for all σ.[2] The HS bounds give the best possible bounds on σ^* for an isotropic two-phase composite given the simplest microstructural information on the medium, the volume fraction of one of the phases. Hashin and Shtrikman also showed that in order to improve upon the HS bounds information beyond that contained in ϕ_1 or ϕ_2 must be utilized.

De Vera and Strieder[20] extended Weissberg's results for beds of fully penetrable spheres to the entire range of $\alpha(0 \leqslant \alpha \leqslant \infty)$. The De Vera and Strieder bounds improve upon the HS bounds for most ϕ and α. For the specific two-dimensional model of impenetrable circular disks in a matrix, McCoy[21] also employed trial fields based upon the one-body boundary-value problem to derive bounds on the effective conductivity.

The trial fields employed here, Eqs. (2.22) and (2.23), are actually slightly different from the ones employed by previous investigators.[18,20,21] The former trial fluctuating fields, unlike the latter, are such that their respective averages are zero, irrespective of the sample shape, and hence lead to absolutely convergent (i.e., shape-independent) integrals when they are ensemble averaged. That all of the integrals that arise in the bounds derived here are absolutely convergent is proved in Appendix A.

Employing the results of Sec. III, some of the integrals given above are easily evaluated. For example, using Eqs. (3.2), (3.7), and (3.15) one has for $n = 1$ that

$$G_1^{(2)}(x) = \rho, \quad x < 1$$

and

$$H_1^{(2)}(x) = \rho\phi_1, \quad x < 1. \tag{2.50}$$

Hence Eqs. (2.32), (2.33), and (2.43) are, respectively, given by

$$\langle \sigma \mathbf{E}^{(1)} \rangle = -\beta\eta\phi_1(\sigma_2 - \sigma_1)\langle \mathbf{E} \rangle, \tag{2.51}$$

$$\langle \mathbf{J}^{(1)}/\sigma \rangle = 2\beta\eta\phi_1 \frac{(\sigma_1 - \sigma_2)}{\sigma_2} \langle \mathbf{E} \rangle, \tag{2.52}$$

and

$$B_1 = \eta. \tag{2.53}$$

The integrals of Eqs. (2.41), (2.42), (2.44), (2.45), and (2.46) are, in general, more difficult to evaluate.

To summarize, for an isotropic composite medium consisting of equi-sized spheres of variable penetrability dispersed throughout a matrix, the effective conductivity is bounded by

$$\sigma^* \leqslant \left[\langle \sigma \rangle - \frac{\eta^2\phi_1^2(\sigma_2 - \sigma_1)^2}{\sigma_1 A + (\sigma_2 - \sigma_1)B} \right] \tag{2.54}$$

and

$$\sigma^* \geqslant \left[\langle 1/\sigma \rangle - \frac{4\eta^2\phi_1^2(\sigma_2 - \sigma_1)^2/\sigma_1\sigma_2}{C\sigma_2 + (\sigma_1 - \sigma_2)D} \right]^{-1}, \tag{2.55}$$

where A, B, C, and D are given by Eqs. (2.36)–(2.39), respectively. These general bounds are new. For partially penetrable spheres the inclusion volume fraction ϕ_2 can be related to the reduced density η.[22,23] For example, for fully penetrable and totally impenetrable spheres $\phi_2 = 1 - e^{-\eta}$ and $\phi_2 = \eta$, respectively. General expressions which relate ϕ_2 as a function of η for arbitrary values of the impenetrability parameter λ have been obtained for the PS[22] and PCS[23] models. It is important to note that although the difference between the upper and lower bounds diverge in the limits $\sigma_1/\sigma_2 \to 0$ or $\sigma_2/\sigma_1 \to \infty$, the bounds can nonetheless remain useful. Lower bounds of the type derived here should yield accurate estimates of σ^*/σ_1, provided that the volume fraction of the highly conducting phase, say phase 2, is below its percolation-threshold value ϕ_2^c.[8,13] Similarly, upper bounds of this type should give reasonable estimates of σ^*/σ_1, provided that $\phi_2 \geqslant \phi_2^c$.

III. POINT/n-PARTICLE DISTRIBUTION FUNCTIONS

Here the general point/n-particle distribution function $G_n^{(i)}$ is rigorously defined. Some properties of $G_n^{(i)}$ which immediately follow from its definition are described. The relationship between the $G_n^{(i)}$ and the n-particle probability densities ρ_n is then written down, for the first time, for a distribution of equi-sized spheres of variable impenetrability. Successive upper and lower bounds on the $G_n^{(i)}$ are given. Some general results are noted for the particular case of totally impenetrable spheres. This is followed by an evaluation of the $G_n^{(i)}$ for dispersions of fully penetrable spheres. Lastly, the low-density expansion of the point/one-particle and point/two-particle distribution functions, $G_1^{(i)}$ and $G_2^{(i)}$, respectively, are evaluated for both the PS and PCS models.

A. Definition and some properties of the $G_n^{(i)}$

The distribution function associated with finding phase i at $\mathbf{r}$ and a particular configuration of n spheres at positions $\mathbf{r}_1,\ldots,\mathbf{r}_n$ is defined as

$$G_n^{(i)}(\mathbf{r};\mathbf{r}^n) = \frac{N!}{(N-n)!} \int \cdots \int d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N I^{(i)}(\mathbf{r};\mathbf{r}^N) P_N(r^N), \tag{3.1}$$

where $I^{(i)}$ is the characteristic function of phase i given by Eq. (2.20) and P_N is the N-particle probability density defined in the previous section.

Use of Eq. (3.1) and the fact that $I^{(1)} = 1 - I^{(2)}$ gives that

$$G_n^{(1)}(\mathbf{r};\mathbf{r}^n) + G_n^{(2)}(\mathbf{r};\mathbf{r}^n) = \rho_n(\mathbf{r}^n). \tag{3.2}$$

Equation (3.2) is an obvious result; it states that, since there are only two phases, the distribution function associated with finding a point in the matrix at $\mathbf{r}$ and n spheres at positions $\mathbf{r}^n$ added to the distribution associated with finding a point in the particle phase at $\mathbf{r}$ and n spheres at positions $\mathbf{r}^n$ must be equal to ρ_n, the probability density associated with finding n spheres at positions $\mathbf{r}^n$. If n is set equal to zero in Eq. (3.1) then it is clear that $G_0^{(i)} = \langle I^{(i)} \rangle$ is equal to the volume fraction of phase i, ϕ_i, for a statistically homogeneous medium (i.e., the limit $N \to \infty$, $V \to \infty$, such that $\rho = N/V$ remains finite). It follows that $\rho_0 \equiv 1$.

The conditional distribution function $G_n^{(i)}(\mathbf{r}|\mathbf{r}^n)$ associated with finding a point in phase i given that there are n

spheres at positions $\mathbf{r}^n$ is given by

$$G_n^{(i)}(\mathbf{r}|\mathbf{r}^n) = G_n^{(i)}(\mathbf{r};\mathbf{r}^n)/\rho_n(\mathbf{r}^n). \tag{3.3}$$

Dividing Eq. (3.2) by ρ_n yields the following expected result for the conditional distribution functions:

$$G_n^{(1)}(\mathbf{r}|\mathbf{r}^n) + G_n^{(2)}(\mathbf{r}|\mathbf{r}^n) = 1. \tag{3.4}$$

Since $G_n^{(i)}$ is a joint distribution function one has the normalization conditions

$$\int \cdots \int d\mathbf{r}^n G_n^{(i)}(\mathbf{r};\mathbf{r}^n) = \langle I^{(i)}(\mathbf{r})\rangle \frac{N!}{(N-n)!} \tag{3.5}$$

and

$$\sum_{i=1}^{2} \int \cdots \int d\mathbf{r}^n G_n^{(i)}(\mathbf{r};\mathbf{r}^n) = \frac{N!}{(N-n)!}. \tag{3.6}$$

Equation (3.5) is arrived at by integrating Eq. (3.1) over positions $\mathbf{r}^n$. Equation (3.6) follows by noting that $\langle I^{(1)}\rangle + \langle I^{(2)}\rangle = 1$.

It is clear that

$$G_n^{(1)}(\mathbf{r};\mathbf{r}^n) = 0, \quad \text{if} \quad |\mathbf{r} - \mathbf{r}_i| < R, \; i = 1,\ldots,n, \tag{3.7}$$

since the point $\mathbf{r}$ cannot be in any sphere for the $G_n^{(1)}$. From Eq. (3.2) one also has that

$$G_n^{(2)}(\mathbf{r};\mathbf{r}^n) = \rho_n(\mathbf{r}^n), \quad \text{if} \quad |\mathbf{r} - \mathbf{r}_i| < R, \; i = 1,\ldots,n. \tag{3.8}$$

Expression (3.8) states that the distribution function associated with finding particle phase at $\mathbf{r}$ and a particular configuration of n spheres is simply equal to the probability density associated with finding the same configuration of n spheres whenever the point $\mathbf{r}$ is in one of the n spheres.

For the PCS model[12] the quantities ρ_n and $G_n^{(i)}$ are identically zero for certain values of their arguments. In the PCS model (depicted in Fig. 1) spheres (cylinders) of radius R are statistically distributed throughout space subject only to the condition of a mutually impenetrable core of radius λR, $0 \leqslant \lambda \leqslant 1$. Each sphere (cylinder) of radius R, therefore, is composed of an impenetrable core of radius λR encompassed by a perfectly penetrable concentric shell of thickness $(1-\lambda)R$. The PCS model should serve as a useful model of certain sintered materials. In light of this discussion one has that in the PCS model

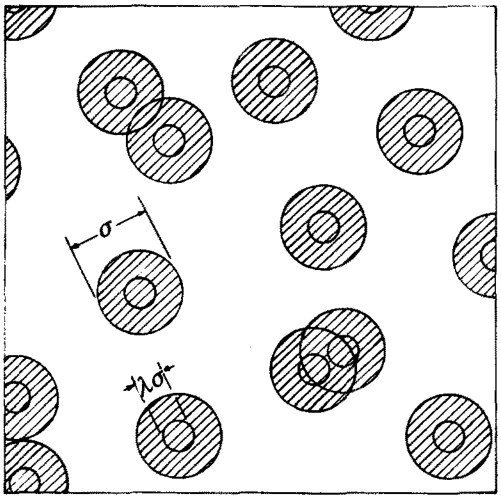

FIG. 1. A realization of a distribution of disks of radius $R = \sigma/2$ (shaded region) in a matrix (unshaded region) in the PCS model. The disks have an impenetrable core of diameter $\lambda\sigma$, indicated by a smaller circular region. Here $\lambda = 1/3$ and the particle volume fraction is about 0.28.

$$\rho_n(\mathbf{r}^n) = 0, \quad \text{if} \quad |\mathbf{r}_j - \mathbf{r}_k| < 2R\lambda \tag{3.9}$$

and

$$G_n^{(i)}(\mathbf{r};\mathbf{r}^n) = 0, \quad \text{if} \quad |\mathbf{r}_j - \mathbf{r}_k| < 2R\lambda \tag{3.10}$$

for any j and k such that $j \neq k$.

It is useful to study the asymptotic behavior of $G_n^{(i)}$ for certain limits of its arguments for any statistically inhomogeneous dispersion of spheres. First consider the $G_n^{(1)}$. The set $(\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_n)$ is partitioned into $L = L(b)$ disjoint subsets, where $(b) = (b_1|b_2|\cdots|b_L)$ is any partition of the aforementioned set, b_i is the ith subset and η_i is the number of elements in b_i. Let all of the relative distances between the η_i elements of subset b_i remain bounded, and let F_{b_i} be the polyhedron with η_i vertices located at the positions associated with the subset b_i. Denote by $\mathbf{R}_i$ the centroid of F_{b_i}. Assuming no long-range order and that the element $\mathbf{r}$ is a member of the first subset b_1, one has

$$\lim_{R_{jk}\to\infty} G_n^{(1)}(b) = G_m^{(1)}(b_1) \prod_{i=2}^{L} \rho_{\eta_i}(b_i), \tag{3.11}$$

where all $R_{jk} \to \infty$, $m = \eta_1 - 1$, R_{jk} is the relative distance between centroids of F_{b_j} and F_{b_k} and j and k are all possible values such that $1 \leqslant j < k \leqslant L$. Combination of Eqs. (3.2) and (3.11) yields

$$\lim_{R_{jk}\to\infty} G_n^{(2)}(b) = [\rho_m(b_1) - G_m(b_1)] \prod_{i=2}^{L} \rho_{\eta_i}(b_i). \tag{3.12}$$

Similar arguments were employed by Torquato and Stell[16] to study the asymptotic behavior of the so-called n-point matrix probability functions S_n.

For the particular partition $(\mathbf{r}|\mathbf{r}_1,\ldots,\mathbf{r}_n)$ Eqs. (3.11) and (3.12) yield, respectively,

$$G_n^{(1)}(\mathbf{r};\mathbf{r}^n) \to G_0^{(1)}(\mathbf{r})\rho_n(\mathbf{r}^n) = \langle I^{(1)}(\mathbf{r})\rangle \rho_n(\mathbf{r}^n) \tag{3.13}$$

and

$$G_n^{(2)}(\mathbf{r};\mathbf{r}^n) \to G_0^{(2)}(\mathbf{r})\rho_n(\mathbf{r}^n) = \langle I^{(2)}(\mathbf{r})\rangle \rho_n(\mathbf{r}^n). \tag{3.14}$$

Recall that $G_0^{(i)} = \phi_i$ for a statistically homogeneous medium. It is convenient to define a new set of point/n-particle distribution functions $H_n^{(i)}$ as follows:

$$H_n^{(i)}(\mathbf{r};\mathbf{r}^n) \equiv G_n^{(i)}(\mathbf{r};\mathbf{r}^n) - G_0^{(i)}(\mathbf{r})\rho_n(\mathbf{r}^n). \tag{3.15}$$

Clearly, when the vector $\mathbf{r}$ is infinitely far away from the set $(\mathbf{r}_1,\ldots,\mathbf{r}_n)$, $H_n^{(i)} \to 0$. The quantity $H_1^{(2)}$ is precisely the function that appears in Eqs. (2.32) and (2.33).

B. Relationship of $G_n^{(i)}$ to ρ_n

Employing definition (3.1) for $i = 1$ and Eqs. (2.20) and (2.21) yields that

$$G_n^{(1)}(\mathbf{r};\mathbf{r}^n) = \left[\prod_{i=1}^{n} e(x_i)\right] \frac{N!}{(N-n)!} \times \int \cdots \int d\mathbf{r}_{n+1},\ldots,d\mathbf{r}_N P_N(r^N) \times \prod_{i=n+1}^{N} [1 - m(x_i)], \tag{3.16}$$

where

$$e(r)=1-m(r)=\begin{cases}0, & r<R,\\ 1, & r>R.\end{cases} \tag{3.17}$$

The function $e(x_i)$ arises because the "point" particle at $\mathbf{r}$ must always lie in the matrix phase and hence the point particle at $\mathbf{r}$ and a spherical particle of radius R at $\mathbf{r}_i$ must be impenetrable to one another. Since the product appearing in the integrand of Eq. (3.16) may be expanded in the manner of Eq. (2.20b) one has

$$\begin{aligned} G_n^{(1)}(\mathbf{r};\mathbf{r}^n) &= \left[\prod_{i=1}^{n} e(x_i)\right] \frac{N!}{(N-n)!} \sum_{k=0}^{N-n} \frac{(N-n)!}{(N-n-k)!} \frac{(-1)^k}{k!} \\ &\quad \times \int \cdots \int d\mathbf{r}_{n+1},\ldots,d\mathbf{r}_{n+k} \\ &\quad \times P_{n+k}(\mathbf{r}_1,\ldots,\mathbf{r}_{n+k}) \prod_{i=n+1}^{n+k} m(x_i) \qquad (3.18) \\ &= \left[\prod_{i=1}^{n} e(x_i)\right] \sum_{k=0}^{N-n} \frac{(-1)^k}{k!} \\ &\quad \times \int \cdots \int \rho_{n+k}(\mathbf{r}_1,\ldots,\mathbf{r}_{n+k}) \prod_{i=n+1}^{n+k} m(x_i) d\mathbf{r}_i. \qquad (3.19) \end{aligned}$$

In arriving at Eqs. (3.18) and (3.19), Eqs. (2.28) and (2.29), respectively, have been employed. Note that property (3.7) follows directly from Eq. (3.19). Information regarding the penetrability of the spheres enters through the ρ_n contained in Eq. (3.19). The corresponding expression for the $G_n^{(2)}$ is obtained by substituting Eq. (3.19) into Eq. (3.2).

It is convenient to change the integration variables from $\mathbf{r}_{n+1},\mathbf{r}_{n+2},\ldots$, to $\mathbf{r}_{n+2},\mathbf{r}_{n+3},\ldots$, respectively, and to replace the variables $\mathbf{r},\mathbf{r}_1,\ldots,\mathbf{r}_n$ with $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{n+1}$, respectively. Hence, from Eq. (3.19) the matrix phase point/n-particle distribution function is given by

$$G_n^{(1)}(\mathbf{r}^{n+1})=\sum_{k=0}^{N-n} G_{n,k}^{(1)}(\mathbf{r}^{n+1}), \tag{3.20}$$

where

$$\begin{aligned} G_{n,k}^{(1)}(\mathbf{r}^{n+1}) &= \left[\prod_{i=2}^{n+1} e(r_{1i})\right] \frac{(-1)^k}{k!} \int \cdots \int \rho_{n+k}(\mathbf{r}_2,\ldots,\mathbf{r}_{n+k+1}) \\ &\quad \times \prod_{i=n+2}^{n+k+1} m(\mathbf{r}_{1i}) dr_i, \qquad (3.21) \end{aligned}$$

$$G_{n,0}^{(1)}(\mathbf{r}^{n+1}) \equiv \left[\prod_{i=2}^{n+1} e(r_{1i})\right] \rho_n(\mathbf{r}_2,\ldots,\mathbf{r}_{n+1}), \tag{3.22}$$

and

$$r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|.$$

For statistically homogeneous media the ρ_n and thus the $G_n^{(1)}$ depend only upon relative positions, i.e.,

$$G_n^{(i)}(\mathbf{r}^{n+1})=G_n^{(i)}(\mathbf{r}_{12},\mathbf{r}_{13},\ldots,\mathbf{r}_{1n+1}). \tag{3.23}$$

Equation (3.20) for the $G_n^{(1)}$ may also be derived by applying the formalism of Torquato and Stell[24] developed for a different set of statistical quantities. Using these methods it is straightforward to show that there is a one-to-one mapping between Eq. (3.20) and the Kirkwood–Salsburg[25] hierarchies for a binary mixture of spheres in equilibrium under certain limits. Specifically, one considers the Kirkwood–Salsburg equations for a binary mixture of spheres in which one of the two species consists of point particles (i.e., spheres of zero radius) in the limit of infinite dilution of the point particles. The other species consists of spheres of radius R with density ρ that are partially penetrable to each other but are impenetrable to point particles. The probability density function associated with finding a point particle at $\mathbf{r}$ and a particular configuration of n spheres of radius R for such a binary mixture in the Kirkwood–Salsburg representation is trivially related to $G_n^{(1)}$. Interestingly, although the derivation of the $G_n^{(i)}$ in this way assumes an equilibrium distribution of spheres, the Kirkwood–Salsburg representation of the $G_n^{(i)}$ is nonetheless isomorphic with Eq. (3.20) which was derived without any equilibrium assumptions.

The Kirkwood–Salsburg series for the $G_n^{(i)}$ enjoy useful bounding properties. Using geometrical arguments similar to the ones employed by Torquato and Stell[24] one has the following successive upper and lower bounds on $G_n^{(1)}$:

$$G_n^{(1)} \leqslant G_{n,0}^{(1)}, \tag{3.24a}$$

$$G_n^{(1)} \geqslant G_{n,0}^{(1)}+G_{n,1}^{(1)}, \tag{3.24b}$$

$$G_n^{(1)} \leqslant G_{n,0}^{(1)}+G_{n,1}^{(1)}+G_{n,2}^{(1)}, \tag{3.24c}$$

$$G_n^{(1)} \geqslant G_{n,0}^{(1)}+G_{n,1}^{(1)}+G_{n,2}^{(1)}+G_{n,3}^{(1)}, \tag{3.24d}$$

$$\vdots$$

where the $G_{n,k}^{(1)}$ are given in Eqs. (3.21) and (3.22).

It is interesting to note that the point/one-particle function $G_1^{(1)}(x)$ for an isotropic dispersion when $x=R$ is closely related to a function $G(R)$ introduced by Reiss, Frisch, and Lebowitz in their "scaled-particle" theory.[26] In the language of scaled-particle theory, $\rho G(R)$ gives the average density of solvent molecules (i.e., spheres of radius R) in contact with the solute point particle. Hence, $\rho G(R) = G_1^{(1)}(R)/\phi_1$.

C. The $G_n^{(i)}$ for totally impenetrable spheres

For distributions of totally impenetrable spheres the terms of the infinite series (3.20) are identically zero for $k>1$, i.e.,

$$\begin{aligned} G_n^{(1)}(\mathbf{r}^{n+1}) &= \prod_{i=2}^{n+1} e(r_{ij})\left[\rho_n(\mathbf{r}_2,\ldots,\mathbf{r}_{n+1})\right. \\ &\quad \left. - \int d\mathbf{r}_{n+2}\, \rho_{n+1}(\mathbf{r}_2,\ldots,\mathbf{r}_{n+2}) m(r_{1,n+2})\right]. \end{aligned} \tag{3.25}$$

This follows from series (3.20) since the product $m(r_{1i})\, m(r_{1j})\, \rho_n(\mathbf{r}_2,\ldots,\mathbf{r}_i\ldots,\mathbf{r}_j\ldots,\mathbf{r}_{n+1})=0$ for any $2\leqslant i<j\leqslant n+1$ for totally impenetrable spheres. This implies, for example, that $G_1^{(1)}$ depends only upon ρ_1 and ρ_2 and that $G_2^{(1)}$ depends only upon ρ_1, ρ_2, and ρ_3.

It is of interest to examine how the lower-order n-point probability functions S_1, S_2, and S_3[16] (which arise in the Beran bounds on σ^*[27]) are related to the $G_n^{(1)}$ for dispersions of totally impenetrable spheres. The $S_n(\mathbf{r}^n)$ give the probability of finding n points with positions $\mathbf{r}^n$ in one of the phases, say phase 1. For distributions of partially penetrable spheres, Torquato and Stell[16] have related the n-point "matrix" functions S_n to the ρ_n. Applying the results of Ref. 16 and employing Eq. (3.25), it can be shown that for a statistically homogeneous distribution of totally impenetrable spheres,

$$S_1 = G_0^{(1)} = \phi_1, \tag{3.26}$$

$$S_2(r_{12}) = S_1 - \int d\mathbf{r}_3 m(\mathbf{r}_{13}) G_1^{(1)}(\mathbf{r}_{23}), \tag{3.27}$$

and

$$S_3(\mathbf{r}_{12},\mathbf{r}_{13}) = S_2(r_{23}) - \int d\mathbf{r}_4 m(r_{14}) e(r_{24}) G_1^{(1)}(r_{34}) + \iint d\mathbf{r}_4 d\mathbf{r}_5 m(r_{14}) m(r_{25}) G_2^{(1)}(\mathbf{r}_{34},\mathbf{r}_{35}). \tag{3.28}$$

$G_0^{(1)}$ is obviously equal to S_1. However, given $G_1^{(1)}$ and $G_2^{(1)}$, one may obtain S_2 and S_3, respectively, by integrating over the former quantities according to Eqs. (3.27) and (3.28).

In general, it can be shown that S_n depends upon the functionals of the set $G_0^{(1)}, G_1^{(1)},\ldots,G_{n-1}^{(1)}$ for distributions of totally impenetrable spheres. Note furthermore that since $G_{n-1}^{(1)}$ depends upon a threefold integral involving ρ_{n-1} and ρ_n, then S_n depends upon a threefold integral involving ρ_1, a sixfold integral involving $\rho_2,\ldots$, and a $3n$-fold integral involving ρ_n. Consequently, the S_n generally are more difficult to compute than the $G_{n-1}^{(1)}$ for this model.

D. The $G_n^{(i)}$ for fully penetrable spheres

The point/n-particle distribution functions for distributions of fully penetrable spheres are easy to obtain using Eq. (3.20). For the case of fully penetrable spheres, the sphere centers are spatially uncorrelated, which implies that

$$\rho_n(\mathbf{r}^n) = \rho^n. \tag{3.29}$$

Substitution of Eq. (3.29) into Eq. (3.20) gives

$$\begin{aligned} G_n^{(1)}(r^{n+1}) &= \left[\prod_{i=2}^{n+1} e(r_{1i})\right] \sum_{k=0}^{\infty} \frac{(-1)^k \rho^{n+k}}{k!} \times \int\cdots\int \prod_{i=n+2}^{n+k+1} m(r_{ij}) d\mathbf{r}_i \\ &= \rho^n \phi_1 \prod_{i=2}^{n+1} e(r_{1i}) = \prod_{i=2}^{n+1} \frac{G_1^{(1)}(r_{1i})}{\phi_1^{n-1}}. \end{aligned} \tag{3.30}$$

For this model, all the $G_n^{(1)}$ are expressible simply in terms of ϕ_1 and the point/one-particle functions for $n \geqslant 1$. Weissberg and Prager[17] obtained both $G_1^{(1)}$ and $G_2^{(1)}$ for dispersions of fully penetrable spheres using simple probabilistic arguments. Combination of Eqs. (3.2), (3.29), and (3.30) yields that the complementary function for this geometry is given by

$$G_n^{(2)}(\mathbf{r}^{n+1}) = \rho^n - \frac{\prod_{i=2}^{n+1} G_1^{(1)}(r_{1i})}{\phi_1^{n-1}}. \tag{3.31}$$

Applying the general results of Ref. 16, Torquato and Stell[28] have obtained an integral representation of the n-point matrix probability function S_n for the specific geometry of fully penetrable spheres. These results combined with Eq. (3.30) give

$$S_n(\mathbf{r}^n) = 1 + \sum_{m=1}^{\infty} \frac{(-1)\rho^m}{m!} \times \int\cdots\int d\mathbf{r}_{n+1}\cdots d\mathbf{r}_{n+m} F(\mathbf{r}_1,\ldots\mathbf{r}_{n+m}) \tag{3.32}$$

$$= \exp[-\rho V_n(\mathbf{r}^n)], \tag{3.33}$$

where

$$\begin{aligned} F(\mathbf{r}_1,\ldots,\mathbf{r}_{n+m}) = 1 &- \sum_{j=n+1}^{n+m} \rho^{-n}\phi_1^{-n} \prod_{i=1}^{n} G_1^{(1)}(r_{ij}) \\ &+ \sum_{\substack{j=n+1 \\ j<k}}^{n+m} \rho^{-2n}\phi_1^{-2n+1} \prod_{i=1}^{n} G_2^{(1)}(\mathbf{r}_{ij},\mathbf{r}_{ik}) \\ &- \sum_{\substack{j=n+1 \\ j<k<l}}^{n+m} \rho^{-3n}\phi_1^{-3n+2} \times \prod_{i=1}^{n} G_3^{(1)}(\mathbf{r}_{ij},\mathbf{r}_{ik},\mathbf{r}_{il}) + \cdots, \end{aligned} \tag{3.34}$$

and $V_n(\mathbf{r}^n)$ is the union volume of n spheres of radius R with centers at $\mathbf{r}^n$. Unlike the case of totally impenetrable spheres, the S_n, for finite n, depend upon the infinite set $G_0^{(1)}, G_1^{(1)},\ldots,G_M^{(1)}$, where $M \to \infty$. However, as in the instance of totally impenetrable spheres, the S_n are more difficult to compute than the $G_{n-1}^{(1)}$.

E. Low-density expansion of $G_1^{(i)}$ and $G_2^{(i)}$

For subsequent calculations it is required to have the density expansion of $G_1^{(2)}$ and $G_2^{(2)}$ through second order in ρ in both the PS and PCS models. It is assumed that the isotropic medium possesses no long-range order and that the n-particle probability density $\rho_n(\mathbf{r}^n)$ may be expanded in powers of density. Hence the leading term is of order ρ^n and from Eq. (3.20) one has

$$\begin{aligned} G_1^{(1)}(r_{12}) &= \rho e(r_{12})\left[1 - \rho \int d\mathbf{r}_3 g_0(r_{23}) m(r_{13})\right] + O(\rho^3) \\ &= \rho e(r_{12})\left[1 - \rho V_1 - \rho \int d\mathbf{r}_3 h_0(r_{23}) m(r_{13})\right] + O(\rho^3) \end{aligned} \tag{3.35}$$

and

$$G_2^{(1)}(\mathbf{r}_{12},\mathbf{r}_{13}) = \rho^2 g_0(r_{23}) e(r_{12}) e(r_{13}) + O(\rho^3). \tag{3.36}$$

Here $V_1 = 4\pi R^3/3$, and $g_0(x) = 1 + h_0(x)$ and $h_0(x)$ are the zero-density limits of the radial distribution function $g(x)$ and total correlation function $h(x)$, respectively, as defined through Eq. (2.49).

In the PS model,[14] the zero-density limit of the total correlation function is given by

$$h_0(x;\lambda) = \begin{cases} -\lambda, & x < 2R, \\ 0, & x > 2R. \end{cases} \tag{3.37}$$

For the class of PCS models described in I, one has

$$h_0(x;\lambda) = \begin{cases} -1, & x < 2R\lambda, \\ 0, & x > 2R\lambda. \end{cases} \tag{3.38}$$

The convolution integral in the second line of Eq. (3.35) can be easily evaluated by transforming to a bipolar coordinate system.[29] In the case of the PS model this integral is simply, apart from a minus sign, the volume common to two spheres, one of radius R and the other of radius $2R$, whose centers are separated by a distance r_{12}. For the PCS model the same integral is the volume common to two spheres, one of radius R and the other of radius $2R\lambda$, whose centers are separated by a distance r_{12}. Let $V_2^{\text{int}}(x;R_1,R_2)$ be the volume common to two spheres, one of radius $R_1<R_2$ and the other of radius R_2, whose centers are separated by a distance x. Then

$$V_2^{\text{int}}(x;R_1,R_2)=\begin{cases}\dfrac{4\pi R_1^3}{3}, & 0\leqslant x\leqslant R_2-R_1\\ \dfrac{4\pi}{3}\left[\dfrac{-3(R_2^2-R_1^2)^2}{16x}+\dfrac{(R_2^3+R_1^3)}{2}-\dfrac{3x}{8}(R_2^2+R_1^2)+\dfrac{x^3}{16}\right], & R_2-R_1\leqslant x\leqslant R_2+R_1\\ 0, & x\geqslant R_2+R_1\ .\end{cases} \tag{3.39}$$

Combining the results given above with Eqs. (3.2) and (3.35) gives through order ρ^2 in the PS and PCS models, respectively, that

$$G_1^{(2)}(x)=m(x)\rho+e(x)[V_1-\lambda V_2^{\text{int}}(x;R,2R)]\rho^2 \tag{3.40}$$

and

$$G_1^{(2)}(x)=m(x)\rho+e(x)[V_1-V_2^{\text{int}}(x;a,b)]\rho^2. \tag{3.41}$$

In Eq. (3.41) $a=\min(R,2R\lambda)$ and $b=\max(R,2R\lambda)$.

The particle phase point/two-particle function through order ρ^2 is given by

$$G_2^{(2)}(\mathbf{r}_{12},\mathbf{r}_{13})=g_0(r_{23})[1-e(r_{12})e(r_{13})]\rho^2. \tag{3.42}$$

Hence, use of Eq. (2.47) yields through order ρ^2:

$$Q(\mathbf{r}_{12},\mathbf{r}_{13})=\begin{cases}0, & r_{12}>R \text{ and } r_{13}>R,\\ h_0(r_{23})\rho^2, & r_{12}<R \text{ and } r_{13}>R,\\ h_0(r_{23})\rho^2, & r_{12}>R \text{ and } r_{13}<R,\\ [h_0(r_{23})-1]\rho^2, & r_{12}<R \text{ and } r_{13}<R.\end{cases} \tag{3.43}$$

IV. LOW-DENSITY BOUNDS IN THE PS AND PCS MODELS

Here the first-order cluster bounds (2.54) and (2.55) are evaluated exactly through order ϕ_2^2 in the PS and PCS models. These calculations will not only improve our understanding of the effects of overlap or connectivity on σ^* for dilute concentrations of penetrable spheres but will provide insight into the fundamental mechanisms at work at high particle concentrations. In order to compute the bounds through second order in ϕ_2, the quantities A, B, C, and D which appear in these bounds must be evaluated through second order in η for these models.

Consider obtaining such results for the PS model first. Evaluation of the integrals (2.41), (2.42), and (2.44)–(2.46), using Eqs. (3.37), (3.39), (3.40), and (3.43), gives through order η^2 that

$$A_2=-\lambda\eta^2, \tag{4.1}$$

$$A_3=-2\lambda\eta^2, \tag{4.2}$$

$$B_2=[2-\lambda(\tfrac{7}{6}+\tfrac{3}{8}\ln 3)]\eta^2, \tag{4.3}$$

$$B_3=-(1+\lambda)\eta^2, \tag{4.4}$$

and

$$B_4=0. \tag{4.5}$$

Note that the results for A_2 and A_3 are exact through all orders in η (see Appendix B). Equation (4.2) is obtained employing the identity given in Appendix C.

Combining Eqs. (2.36)–(2.39), (2.40), and (2.53), and Eq. (4.1)–(4.5) for the PS model yields through order η^2 that

$$A=3\eta(1-\eta\lambda), \tag{4.6}$$

$$B=\eta+[1-\lambda(\tfrac{13}{6}+\tfrac{3}{8}\ln 3)]\eta^2, \tag{4.7}$$

$$C=6\eta(1-\eta\lambda), \tag{4.8}$$

and

$$D=4\eta-[2+\lambda(\tfrac{31}{6}+\tfrac{3}{8}\ln 3)]\eta^2. \tag{4.9}$$

Similarly, Eqs. (2.41), (2.42), and (2.44)–(2.46), together with Eqs. (3.38), (3.39), (3.41), and (3.43) for the PCS model, gives through order η^2 that

$$A_2=-[2\lambda^6-9\lambda^4+8\lambda^3]\eta^2, \tag{4.10}$$

$$A_3=-2[2\lambda^6-9\lambda^4+8\lambda^3]\eta^2, \tag{4.11}$$

$$B_2=\left[2+\frac{9}{2}\lambda^4-8\lambda^3+\frac{9}{4}\lambda^2+\frac{3\lambda}{4(1+2\lambda)^2}-\frac{3}{8}\ln(1+2\lambda)\right]\eta^2, \tag{4.12}$$

and

$$B_3=-[2\lambda^6-9\lambda^4+8\lambda^3+1]\eta^2. \tag{4.13}$$

Unlike the analogous results for the PS model, the results for A_2 and A_3 in the PCS model are only exact through order η^2. Equation (4.11) is derived by applying the identity of Appendix C.

Combination of Eqs. (2.36)–(2.39), (2.40), and (2.53), and Eqs. (4.10)–(4.13) for the PCS model yields through order η^2 that

$$A=3\eta-3[2\lambda^6-9\lambda^4+8\lambda^3]\eta^2, \tag{4.14}$$

$$B=\eta+\left[1-2\lambda^6+\frac{27\lambda^4}{2}-16\lambda^3+\frac{9\lambda^3}{4}+\frac{3\lambda}{4(1+2\lambda)^2}-\frac{3}{8}\ln(1+2\lambda)\right]\eta^2, \tag{4.15}$$

$$C=6\eta-6[2\lambda^6-9\lambda^4+8\lambda^3]\eta^2, \tag{4.16}$$

and

$$D=4\eta-\left[2+8\lambda^6-\frac{81\lambda^4}{2}+40\lambda^3-\frac{9\lambda^2}{4}-\frac{3\lambda}{4(1+2\lambda)^2}+\frac{3}{8}\ln(1+2\lambda)\right]\eta^2. \tag{4.17}$$

It is useful to eliminate η in favor of ϕ_2 in the results given above using the relation[13]

$$\eta = \phi_2 + G\phi_2^2. \tag{4.18}$$

For the PS and PCS models,[13] respectively,

$$G = (1-\lambda)/2 \tag{4.19}$$

and

$$G = 4(1-\lambda^3) - \tfrac{9}{2}(1-\lambda^4) + (1-\lambda^6). \tag{4.20}$$

To summarize, expanding Eqs. (2.54) and (2.55) through second order in ϕ_2 gives

$$\sigma^*/\sigma_1 \leqslant 1 + 3\beta\phi_2 + K_2^U\phi_2^2, \tag{4.21}$$

$$\sigma^*/\sigma_1 \geqslant 1 + 3\beta\phi_2 + K_2^L\phi_2^2. \tag{4.22}$$

Since Eqs. (4.21) and (4.22) coincide through order ϕ_2, then K_2^U and K_2^L are upper and lower bounds, respectively, on the exact second-order coefficient. It is useful to decompose these coefficients as follows:

$$K_2^U = K_2^{U*} + K_2^{U+}, \tag{4.23}$$

$$K_2^L = K_2^{L*} + L_2^{L+}. \tag{4.24}$$

For both the PS and PCS models

$$K_2^{U*} = 3\beta^2 + \beta^2(\alpha-1)[\tfrac{5}{6} - \tfrac{3}{8}\ln 3], \tag{4.25}$$

$$K_2^{L*} = 3\beta^2 + \beta^2\frac{(\alpha-1)}{\alpha}[\tfrac{5}{6} - \tfrac{3}{8}\ln 3], \tag{4.26}$$

and $\alpha = \sigma_2/\sigma_1$. The remaining terms K_2^{U+} and K_2^{L+} have the same form in the PS and PCS models:

$$K_2^{U+} = \beta^2(\alpha-1)a(\lambda) + (\beta/2)(\alpha-1)b(\lambda) \tag{4.27}$$

and

$$K_2^{L+} = \beta^2\frac{(\alpha-1)}{\alpha}a(\lambda) - \beta\frac{(\alpha-1)}{\alpha}b(\lambda), \tag{4.28}$$

where in the PS model,

$$a(\lambda) = (1-\lambda)(\tfrac{7}{6} + \tfrac{3}{8}\ln 3) \tag{4.29}$$

and

$$b(\lambda) = (1-\lambda), \tag{4.30}$$

and in the PCS model,

$$a(\lambda) = \frac{9}{2}\lambda^4 - 8\lambda^3 + \frac{9}{4}\lambda^2 + \frac{7}{6} + \frac{3\lambda}{4(1+2\lambda)^2} - \frac{3}{8}\ln\left(\frac{1+2\lambda}{3}\right) \tag{4.31}$$

and

$$b(\lambda) = -(2\lambda^6 - 9\lambda^4 + 8\lambda^3 - 1). \tag{4.32}$$

In arriving at these results for the PS and PCS models Eqs. (4.6)–(4.9) and Eqs. (4.14)–(4.17) have been used, respectively. As in the previous papers in this series,[12,13] the second-order coefficients are decomposed into a sum of two terms: one being the contribution from a reference dispersion of totally impenetrable spheres (i.e., K_2^{U*} and K_2^{L*}) and the other being the contribution in excess of this which arises when pairs of inclusions belong to the same cluster (i.e., K_2^{U+} and K_2^{L+}). The quantities with the superscripts * and + can be shown to depend upon the zero-density limits of the pair-blocking function $g_0^*(x)$ and pair-connectedness function $g_0^+(x)$, respectively.[13] Therefore, $K_2^{U+} = K_2^{L+} = 0$ for the case of totally impenetrable spheres ($\lambda = 1$).

The first-order cluster bounds through second order in ϕ_2 are always sharper than the HS bounds expanded through the same order in ϕ_2. For example, for $\sigma_2 > \sigma_1$, K_2^L in either the PS or PCS model is always greater than $3\beta^2$, the value of the second-order coefficient of the HS lower bound. For reasons already given in Refs. 8 and 13, $K_2^U \to \infty$ when $\alpha \to \infty$ and $K_2^L \to 0$ when $\alpha \to 0$. Hence, when $\alpha \to \infty$ and when $\alpha \to 0$, K_2^L and K_2^U, respectively, provide reasonable estimates of the actual second-order coefficient, K_2.

In Fig. 2, K_2^L is shown as a function of the impenetrability parameter λ in both the PC and PCS models for $\alpha = \infty$. Figure 3 gives the analogous plot for K_2^U at $\alpha = 0$. Note that K_2^L for the PCS model always lies above the corresponding curve for the PS model for $0 < \lambda < 1$; with the converse being true for K_2^U. This indicates that the degree of connectivity in the PCS model is greater than that in the PS model. It is expected that the actual second-order coefficients for the two models will behave in a similar manner.[30]

Evidence for such behavior is provided by considering the following approximate expression for the actual second-order coefficient K_2^+. Rearrangement of the exact result for K_2^+ given in II yields

$$K_2^+ = \frac{1}{V_1^2}\int d\mathbf{x}\left[\frac{2\pi}{3\sigma_1}\boldsymbol{\alpha}(1,2):\mathsf{U} - \frac{3\beta}{2}V_2(x)\right]g_0^+(x), \tag{4.33}$$

where

$$V_2(x) = V_1\left[1 + \frac{3}{4}\frac{x}{R} - \frac{1}{16}\frac{x^3}{R^3}\right], \quad x<2R \tag{4.34}$$

is the union volume of two overlapping spheres of radius R, $\boldsymbol{\alpha}(1,2)$ is the polarizability tensor associated with overlapping inclusions centered at $\mathbf{r}_1$ and $\mathbf{r}_2$ ($x = |\mathbf{r}_1 - \mathbf{r}_2|$), $g_0^+(x)$ is the zero-density limit of the pair-connectedness function[31] $g^+(x)$, and U is the unit dyadic. (The quantity $\rho^2 g^+(x)\, d\mathbf{r}_1\, d\mathbf{r}_2$ is the probability of simultaneously finding the center of a sphere in the volume $d\mathbf{r}_1$ about $\mathbf{r}_1$ and another particle, of the same cluster, in the volume $d\mathbf{r}_2$ about $\mathbf{r}_2$.) It is assumed that the electric field induced within the two overlapping spheres (in the presence of a uniform applied field) is equal to the field induced within a single ellipsoid having a major axis of length $R + x/2$ and two minor axes both of length R, i.e., one has

$$K_2^+(\lambda) \simeq \frac{1}{V_1^2}\int d\mathbf{x}V_2(x)\left[F(x) - \frac{3\beta}{2}\right]g_0^+(x), \tag{4.35}$$

where

$$F(x) = \frac{(\alpha-1)}{6}\left[\frac{1}{1+(\alpha-1)D_1(x)} + \frac{2}{1+(\alpha-1)D_2(x)}\right], \tag{4.36}$$

and $D_1(x)$ and $D_2(x) = D_3(x)$ are the depolarization factors associated with the major and minor axes, respectively.[32] The depolarization factors must satisfy the following relation:

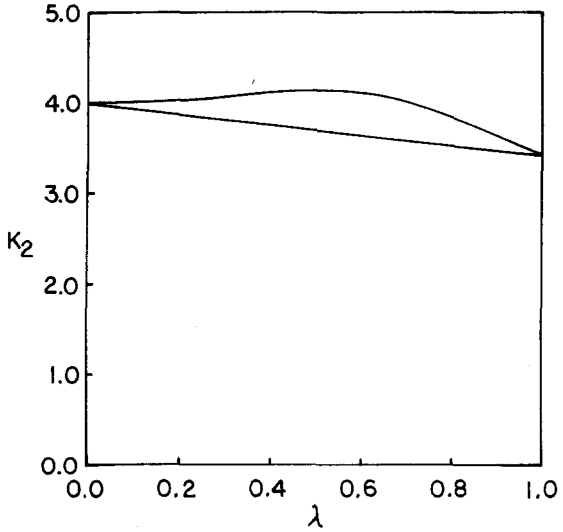

FIG. 2. The lower bounds on the second-order coefficient K_2 in the PS (lower curve) and PCS (upper curve) models as a function of the impenetrability parameter λ for the case $\alpha = \infty$.

$$D_1 + D_2 + D_3 = 1. \tag{4.37}$$

In II it was shown that $F(x)$, in the PS model, to an excellent approximation is independent of x and hence the D_i may be treated as undetermined constants. If this assumption is invoked for general models then it follows that the actual second-order coefficient $K_2 = K_2^* + K_2^+$ (where K_2^* is the contribution from a reference dispersion of totally impenetrable spheres[13]—see Table I of II), is given by the following approximate expression:

$$K_2 \simeq K_2^* + [F - (3\beta/2)]U_2, \tag{4.38}$$

where

$$U_2 = \frac{1}{V_1^2} \int d\mathbf{x}\, V_2(x) g_0^+(x). \tag{4.39}$$

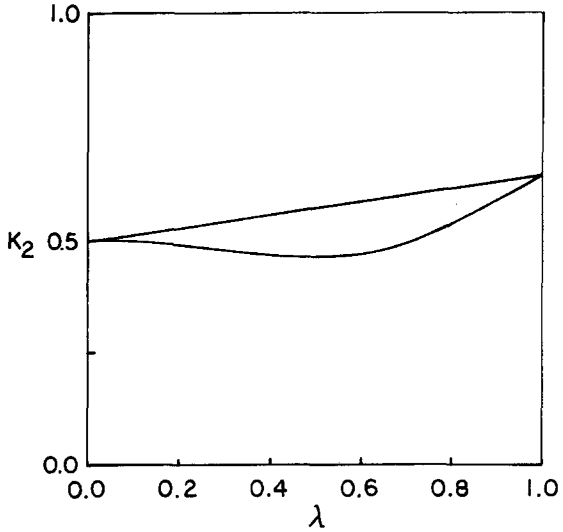

FIG. 3. The upper bounds on the second-order coefficient K_2 in the PS (upper curve) and PCS (lower curve) models as a function of the impenetrability parameter λ for the case $\alpha = 0$.

$D_1 = 0.189\,16$, and $D_2 = 0.405\,42$.[13] The D_i are determined in the same manner outlined in II. It can be shown that Eq. (4.41) is exact through second order in $(\sigma_2 - \sigma_1)$.

Using the results given in II for g_0^+, it is easy to show that in the PS and PCS models one has that

$$U_2 = 15(1-\lambda) \tag{4.40}$$

and

$$U_2 = 8(1-\lambda^3) + 9(1-\lambda^4) - 2(1-\lambda^6), \tag{4.41}$$

respectively. It is seen that U_2 (which is related to the total expected volume of dimers[34]) is always larger in the PCS model than it is in the PS model, at the same value of λ for $\lambda < 1$. In the dilute limit, therefore, this indicates that (for fixed λ) the excluded volume effects associated with spheres possessing an internal hard core of radius λR (i.e., the PCS model) results in a dispersion which has a higher degree of connectivity than one in which the probability of spheres intersecting is linear in $(1-\lambda)$ (i.e., the PS model). Referring to Eq. (4.38), this implies that for $\lambda < 1$, K_2 is larger in the former model than it is in the latter one. Combination of Eqs. (4.36), (4.38), and (4.41) yields a new approximate relation for K_2 in the PCS model. Equation (4.38) should provide a reasonable approximation to K_2 for interpenetrable-sphere models.

Relation (4.38) always lies between bounds (4.23) and (4.24). It is noteworthy that the upper bound K_2^U [Eq. (4.23)] for $0 \leqslant \alpha \leqslant 1$ is nearly equal to approximation (4.38), regardless of the value of λ, for both the PS and PCS models. Similarly, for $1 \leqslant \alpha < 10$, the lower bound K_2^L [Eq. (4.24)] is approximately equal to (4.38) for both the PS and PCS models, for any value of λ. For $\alpha > 10$ and fixed λ, the deviation of K_2^L from Eq. (4.38) increases as α increases. This discrepancy increases as λ decreases for fixed α. Note also that in the PCS model for $\alpha = \infty$, $K_2^L(\lambda)$ is approximately equal to $K_2^L(0) = 4$ for the range $0 \leqslant \lambda \leqslant 0.5$ (see Fig. 2). Approximation (4.38) in the PCS model behaves in a similar manner since U_2 for $0 < \lambda < 0.5$ is nearly equal to (but always smaller than) the corresponding quantity for fully penetrable spheres ($\lambda = 0$). Similarly, in the PCS model for $\alpha = 0$, $K_2^U(\lambda)$ is approximately equal to $K_2^U(0) = 0.5$ for the range $0 \leqslant \lambda \leqslant 0.5$. Again relation (4.38) for the PCS model predicts that $K_2(\lambda)$ is roughly equal to $K_2(0)$ for this range of λ. To summarize, the bounds on K_2 for both the PS and PCS models not only qualitatively reflect the essential physics involved when particles overlap but together can provide accurate estimates of K_2 for $0 \leqslant \alpha \leqslant 10$ at any value of λ.

In II bounds on K_2 in the PS model were derived using the Beran bounds.[27] The Beran bounds are completely general and hence, unlike the cluster bounds, are not restricted to microstructures involving various types of spherical inclusions. If $K_{2,B}^U$ and $K_{2,B}^L$ denote these upper and lower bounds, respectively, then we have[13]

$$K_{2,B}^U = 3\beta^2 + \beta^2(\alpha-1)\left[\left(\tfrac{5}{6} - \tfrac{3}{8}\ln 3\right) + (1-\lambda)0.701\,56\right] \tag{4.42}$$

and

$$K_{2,B}^{L} = 3\beta^2 + \beta^2 \frac{(\alpha-1)}{\alpha}\left[\left(\tfrac{5}{6} - \tfrac{3}{8}\ln 3\right) + (1-\lambda)0.701\,56\right]. \quad (4.43)$$

Note that for the special case totally impenetrable spheres ($\lambda = 1$) Eqs. (4.42) and (4.43) are identical to the corresponding bounds obtained from the first-order cluster bounds. This is a very interesting result since the Beran bounds, unlike the cluster bounds, depend upon the n-point probability functions[16] S_1, S_2, and S_3. Elsewhere[35] it is shown that the first-order cluster bounds (which depend upon h, $G_0^{(2)}$, $G_1^{(2)}$, and $G_2^{(2)}$ are identical to the Beran bounds through all orders in ϕ_2 for the special case of totally impenetrable spheres ($\lambda = 1$). Therefore, the functionals of h, $G_0^{(2)}$, $G_1^{(2)}$, and $G_2^{(2)}$ that arise in the first-order cluster bounds, Eqs. (2.54) and (2.55), contain precisely the same information as the functionals of S_1, S_2, and S_3, that arise in the Beran bounds. It turns out, however, that the first-order cluster bounds for $\lambda = 1$ are easier to compute than the Beran bounds for this model since the statistical quantities involved in the former are less difficult to compute than the corresponding functions that arise in the latter. (See the discussion in Sec. III C.)

For $0 \leqslant \lambda < 1$, bounds (4.42) and (4.43) are slightly more restrictive than the corresponding bounds derived here from first-order cluster bounds; the greatest difference occurring at $\lambda = 0$. For example, for $\alpha = \infty$ and $\lambda = 0$, $K_{2,B}^{L} = 4.12$, which is to be contrasted with 4.0, the value obtained from the first-order cluster lower bound. However, unlike bounds (4.42) and (4.43), the first-order cluster bounds in the PS model expanded through second order in ϕ_2 involve relatively simple integrals and hence can be expressed analytically.

Note that the computation of the Beran bounds through second order in ϕ_2 in the PCS model is even more difficult than in the PS model. Some of the integrals involved in the latter calculation had to be numerically evaluated.[13] This is to be contrasted with the corresponding analytical first-order cluster bounds easily derived here for both the PS and PCS models.

The low-density results described above suggest that the Beran bounds, for spheres distributed with arbitrary degree of impenetrability λ and through all orders in ϕ_2, are more restrictive than the first-order cluster bounds for $0 \leqslant \lambda < 1$; with the two sets of bounds being identical for $\lambda = 1$. For most values of λ in the range $0 \leqslant \lambda < 1$, however, the numerical differences between the Beran and cluster bounds should be small; the greatest difference occurring when the spheres are fully penetrable to one another (i.e., $\lambda = 0$, see Appendix D). Furthermore, the aforementioned results also strongly indicate that the cluster bounds, although nontrivial in general, will be easier to compute than the Beran bounds for dispersions of partially penetrable spheres.

V. CONCLUSIONS

It is generally desired to relate the bulk property of a two-phase composite medium to the details of its microstructure. In doing so one can then relate changes in the microstructure quantitatively to changes in the effective properties of the heterogeneous material. In order to exactly evaluate the bulk property, an infinite set of statistical functions that characterize the microstructure needs to be determined. However, apart from a few special models, this infinite set of functions is never known. Bounding techniques do provide a means of estimating the bulk property using limited microstructural information on the composite material.

In this article rigorous bounds on the effective conductivity of dispersions of spheres of variable impenetrability have been derived and shown to depend upon not only the sphere volume fraction ϕ_2 but integrals that involve the total correlation function h and the particle phase point/n-particle distribution functions, $G_1^{(2)}$ and $G_2^{(2)}$. Given the n-particle distribution functions ρ_n, one may now in principle calculate the $G_n^{(2)}$, for arbitrary values of the impenetrability parameter λ and for any n and hence nth-order cluster bounds using the results of Sec. III. Interpenetrable-sphere models should prove useful in studying the effects of connectivity of the particle phase on the effective property of the composite medium. The analytical expressions for low-density expansions of the first-order cluster bounds in the PS and PCS models obtained here suggest that cluster bounds may be the simplest nontrivial set of bounds available to estimate the effect of particle overlap or connectivity on the conductivity of composite media for arbitrary phase conductivities and volume fractions.

Note that many of the results obtained here can be easily extended to dispersions of spheres characterized by a size distribution. Moreover, analogous two-dimensional results for dispersions of multi-sized circular disks (useful models of fiber-reinforced materials) are also straightforward to derive. In subsequent articles such findings shall be reported.

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APPENDIX A

In order to illustrate how the simplified integrals of Sec. II are obtained from the original ensemble-averaged quantities the steps leading to integrals (2.41)–(2.46) are briefly outlined. It follows from Eqs. (2.18) and (2.34) that

$$A = \frac{\langle \mathbf{E}^{(1)} \cdot \mathbf{E}^{(1)} \rangle}{\beta^2 \langle \mathbf{E} \rangle \cdot \langle \mathbf{E} \rangle}, \quad (A1)$$

$$B = \frac{\langle I^{(2)} \mathbf{E}^{(1)} \cdot \mathbf{E}^{(1)} \rangle}{\beta^2 \langle \mathbf{E} \rangle \cdot \langle \mathbf{E} \rangle}. \quad (A2)$$

Consider the quantity B first. Combination of Eq. (2.22) and definition (3.1) leads to

$$B=\frac{1}{\beta^2\langle E\rangle^2}\int d\mathbf{x}_1[\overline{\mathsf{K}}(\mathbf{x}_1)\cdot\langle\mathbf{E}\rangle]\cdot[\overline{\mathsf{K}}(\mathbf{x}_1)\cdot\langle\mathbf{E}\rangle]G_1^{(2)}(x_1)+\frac{1}{\beta^2\langle E\rangle^2}\iint d\mathbf{x}_1 d\mathbf{x}_2[\overline{\mathsf{K}}(\mathbf{x}_1)\cdot\langle\mathbf{E}\rangle]\cdot[\overline{\mathsf{K}}(\mathbf{x}_2)\cdot\langle\mathbf{E}\rangle]Q(\mathbf{x}_1,\mathbf{x}_2), \quad (A3)$$

where the statistical function Q is given by Eq. (2.47) and $\langle E\rangle^2=\langle\mathbf{E}\rangle\cdot\langle\mathbf{E}\rangle$.

A spherical coordinate system shall be employed to evaluate the integrals of Eq. (A3). Let the polar axis be parallel to the constant vector $\langle\mathbf{E}\rangle$ and let the two vectors $\mathbf{z}=\mathbf{x}_1$ and $\mathbf{y}=\mathbf{x}_2$ have spherical coordinates (z,θ_z,ϕ_z) and (y,θ_y,ϕ_y), respectively. Then

$$[\overline{\mathsf{K}}(\mathbf{y})\cdot\langle\mathbf{E}\rangle]\cdot[\overline{\mathsf{K}}(\mathbf{z})\cdot\langle\mathbf{E}\rangle]=\begin{cases}\dfrac{\beta^2R^6\langle E\rangle^2}{y^3z^3}[P_2^1(u_y)P_2^1(u_z)\cos(\phi_y-\phi_z)+4P_2(u_y)P_2(u_z)], & y>R, z>R,\\ -\dfrac{2\beta^2R^3\langle E\rangle^2}{z^3}P_2(u_z), & y<R, z>R,\\ -\dfrac{2\beta^2R^3\langle E\rangle^2}{y^3}P_2(u_y), & y>R, z<R,\\ \beta^2\langle E\rangle^2, & y<R, z<R,\end{cases} \quad (A4)$$

where P_n and P_n^m are Legendre and associated Legendre polynomials of order n,[36] respectively, $u_y=\cos\theta_y$ and $u_z=\cos\theta_z$.

Consider the first integral of Eq. (A3). Substitution of Eq. (A4) into Eq. (A3) and integrating over polar and azimuthal angles gives

$$\frac{1}{\beta^2\langle E\rangle^2}\int d\mathbf{z}[\overline{\mathsf{K}}(\mathbf{z})\cdot\langle\mathbf{E}\rangle]\cdot[\overline{\mathsf{K}}(\mathbf{z})\cdot\langle\mathbf{E}\rangle]G_1^{(2)}(z)=B_1+B_2, \quad (A5)$$

where B_1 and B_2 are given Eqs. (2.43) and (2.44), respectively.

Next consider the second integral of Eq. (A3). Following Lado and Torquato,[37] the function Q is expanded in Legendre Polynomials, i.e.,

$$Q(\mathbf{y},\mathbf{z})=\sum_{n=0}^{\infty}D_n(y,z)P_n(u_{yz}), \quad (A6)$$

where

$$D_n(y,z)=\frac{2n+1}{2}\int_{-1}^{1}du_{yz}Q(\mathbf{y},\mathbf{z})P_n(u_{yz}) \quad (A7)$$

and

$$u_{yz}=\frac{\mathbf{y}\cdot\mathbf{z}}{y\cdot z}.$$

Employing the addition theorem[36]

$$P_n(u_{yz})=P_n(u_y)P_n(u_z)+2\sum_{m=1}^{n}\frac{(n-m)!}{(n+m)!}P_n^m(u_y)P_n^m(u_z)\times\cos m(\phi_y-\phi_z), \quad (A8)$$

and the orthogonality properties of the Legendre polynomials[36] it is straightforward to show that upon substitution of Eq. (A6) into the second integral of Eq. (A3) one has

$$\frac{1}{\beta^2\langle E\rangle^2}\iint d\mathbf{z}\,d\mathbf{y}\,[\overline{\mathsf{K}}(\mathbf{y})\cdot\langle\mathbf{E}\rangle]\cdot[\overline{\mathsf{K}}(\mathbf{z})\cdot\langle\mathbf{E}\rangle]Q(\mathbf{y},\mathbf{z})=B_3+B_4. \quad (A9)$$

Here B_3 and B_4 are given, respectively, by Eqs. (2.45) and (2.46).

The ensemble average A defined by Eq. (A1) may be obtained from Eq. (A3) by replacing $G_1^{(2)}$ and Q in the integrals by ρ and ρ^2h (where h is the total correlation function), respectively. Therefore

$$\frac{\rho}{\beta^2\langle E\rangle^2}=\int d\mathbf{z}[\overline{\mathsf{K}}(\mathbf{z})\cdot\langle\mathbf{E}\rangle]\cdot[\overline{\mathsf{K}}(\mathbf{z})\cdot\langle\mathbf{E}\rangle]=A_1, \quad (A10)$$

where A_1 is given by Eq. (2.40), and

$$\frac{\rho^2}{\beta^2\langle E\rangle^2}\iint d\mathbf{z}\,d\mathbf{y}[\overline{\mathsf{K}}(\mathbf{y})\cdot\langle\mathbf{E}\rangle]\cdot[\overline{\mathsf{K}}(\mathbf{z})\cdot\langle\mathbf{E}\rangle]h(x)=A_2+A_3, \quad (A11)$$

where A_2 and A_3 are given by Eqs. (2.41) and (2.42), respectively, and $x=|\mathbf{y}-\mathbf{z}|$. The ensemble averages C and D defined, respectively, by Eqs. (2.38) and (2.39) can also be simplified in the manner outlined above.

It is shown that the integrals which comprise B, Eq. (A2), are absolutely convergent. Clearly the first integral of Eq. (A2) is absolutely convergent since it decays to zero like x_1^{-6} as $x_1\to\infty$. Consider the remaining integral. Let the field point $\mathbf{r}$ be denoted by $\mathbf{r}_1$ and let the two spheres be centered at $\mathbf{r}_2$ and $\mathbf{r}_3$. Then the second integral of Eq. (A2) may be written in the equivalent form

$$\int d\mathbf{r}_{23}\int d\mathbf{r}_1[\overline{\mathsf{K}}(\mathbf{r}_{12})\cdot\langle\mathbf{E}\rangle][\overline{\mathsf{K}}(\mathbf{r}_{13})\cdot\langle\mathbf{E}\rangle]Q(\mathbf{r}_{12},\mathbf{r}_{13}),$$

where $\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$. To prove the absolute convergence of this sixfold integral one need only show that the first volume integral over $\mathbf{r}_1$ decays to zero faster than r_{23}^{-3} as $r_{23}\to\infty$, where $r_{23}=|\mathbf{r}_2-\mathbf{r}_3|$. When particle 2 is far from particle 3, there are only three possible configurations which can contribute to the integral; point 1 near particle 2 or 3 and point 1 far from both particles. When point 1 is near particle 2, then according to Eqs. (3.11) and (2.47),

$$G_2^{(2)}(\mathbf{r}_{12},\mathbf{r}_{13})\to\rho G_1^{(2)}(r_{12}),$$
$$G_1^{(2)}(r_{13})\to\rho\phi_2,$$

and

$$Q(\mathbf{r}_{12},\mathbf{r}_{13})\to 0.$$

The same result is obtained when point 1 is near particle 3. If point 1 is far from both particles, then

$$G_2^{(2)}(\mathbf{r}_{12},\mathbf{r}_{13})\to\rho^2\phi_2,$$
$$G_2^{(2)}(r_{1j})\to\rho\phi_2,\quad j=2,3,$$

and

$$Q(\mathbf{r}_{12},\mathbf{r}_{13})\to 0.$$

Hence the integral is absolutely convergent. Similar arguments may be used to prove the absolute convergence of integral (2.42) as well.

APPENDIX B

The evaluation of the integrals A_2, A_3, and B_3 given in Sec. II are straightforward to evaluate in the PS model for arbitrary λ. In the PS model, the full density-dependent total correlation function has the form[14]

$$h(x) = -\lambda H(2R-x) + H(x-2R)y(x), \tag{B1}$$

where the H is the Heaviside step function defined by

$$H(t-x) = \begin{cases} 1, & x<t \\ 0, & x>t \end{cases} \tag{B2}$$

and $y(x)$ is a continuous density-dependent function such that $y(\infty)=0$ for a system without long-range order. For spheres of unit radius the integral A_2, Eq. (2.41), depends only upon the behavior of $h(x)$ for $x<2$ and is trivially related to integral (6.3) of I. Hence, in the PS model one exactly has that

$$A_2 = -\lambda\eta^2. \tag{B3}$$

Now employing the results of Sec. III, it is easy to show, using Eq. (2.47), that for $y<1$ and $z<1$,

$$Q(\mathbf{y},\mathbf{z}) = \rho^2[h(x)-\phi_1], \tag{B4}$$

where $x=|\mathbf{y}-\mathbf{z}|$. Substitution of Eq. (B4) into Eq. (2.45) yields, for the PS model, an integral similar to A_2, namely

$$B_3 = -(\lambda+\phi_1)\eta^2. \tag{B5}$$

To evaluate integral A_3, Eq. (2.42), the identity in Appendix C is employed. Differentiating Eq. (B1) with respect to x yields

$$h'(x) = \lambda\delta(x-2) + \delta(x-2)y(x) + H(x-2)y'(x), \tag{B6}$$

where $\delta(x)$ is the Dirac delta function and a prime indicates the first derivative of a function. Using the identity given in Appendix C one has that

$$A_3 = -2\lambda\eta^2. \tag{B7}$$

Combining Eqs. (2.36), (2.40), (B3), and (B7) gives that A in the PS model is exactly given by

$$A = 3\eta(1-\lambda\eta). \tag{B8}$$

Similarly, the quantity C, which appears in the lower bound (2.55), is given by

$$C = 6\eta(1-\lambda\eta) \tag{B9}$$

for this model.

APPENDIX C

A useful integral identity is proved here. Consider the integral

$$I = \frac{9}{2}\int_1^\infty \frac{dz}{z}\int_1^\infty \frac{dy}{y}\int_{-1}^1 du\, f(x)P_2(u), \tag{C1}$$

where $P_2(u)$ is the Legendre polynomial of order two, $f(x)$ is a piecewise continuous function of x, and

$$u = \frac{y^2+z^2-x^2}{2yz}. \tag{C2}$$

Then

$$I = \frac{9}{4}\int_0^\infty dx\, f'(x)w(x), \tag{C3}$$

where $f'(x)=df/dx$ and

$$w(x) = \begin{cases} \frac{1}{72}[-x^6+18x^4-32x^3], & x<2, \\ -\frac{4}{9} & x>2. \end{cases} \tag{C4}$$

Proof: Using the fact that

$$P_2(u) = \frac{1}{2}\frac{d}{dx}(u^3-u) \tag{C5}$$

and integrating Eq. (C1) by parts gives

$$\begin{aligned} I &= \frac{9}{4}\int_0^\infty dz\, e(z)\int_0^\infty dy\, e(y)\int_{-1}^1 du\frac{f'(x)}{x}(u^3-u) \\ &= \frac{9}{4}\int_0^\infty \frac{dz}{z}e(z)\int_0^\infty \frac{dy}{y}e(y)\int_{|y-z|}^{y+z} dx\, f'(x)(u^3-u) \\ &= \frac{9}{4}\int_0^\infty dx\, f'(x)w(x), \end{aligned} \tag{C6}$$

where

$$w(x) = \int_0^\infty \frac{dz}{z}e(z)\int_{|x-z|}^{x+z}\frac{dy}{y}e(y)\left\{\left(\frac{y^2+z^2-x^2}{2yz}\right)^3 - \left(\frac{y^2+z^2-x^2}{2yz}\right)\right\} \tag{C7}$$

and

$$e(x) = \begin{cases} 0, & x<1 \\ 1, & x>1. \end{cases} \tag{C8}$$

Direct integration shows that integral (C) is given by Eq. (C4). The second line of Eq. (C6) is the result of a change of the integration variable from u to x. The third line follows when the order of integration is changed as indicated.

APPENDIX D

Here it is shown that the general first-order cluster bounds on σ^*, Eqs. (2.54) and (2.55), for the special case of a distribution of fully penetrable spheres ($\lambda=0$) in a matrix reduce to the DeVera–Strieder[20] bounds on σ^*.

For distributions of fully penetrable spheres of unit radius the total correlation function $h(x)$, defined by Eq. (2.49), and the function $Q(\mathbf{y},\mathbf{z})$, defined by Eq. (2.47), are given by

$$h(x)=0, \quad 0\leqslant x\leqslant\infty \tag{D1}$$

and

$$Q(\mathbf{y},\mathbf{z}) = \begin{cases} -\rho^2\phi_1, & y<1 \text{ and } z<1 \\ 0, & \text{otherwise}. \end{cases} \quad \text{(D2)}$$

Here the results of Sec. III D have been employed.

Substitution of Eqs. (D1) and (D2) with Eqs. (2.41), (2.42), (2.44)–(2.46) yields

$$A_2 = A_3 = B_4 = 0, \quad \text{(D3)}$$

$$B_2 = 2\eta\phi_2, \quad \text{(D4)}$$

and

$$B_3 = -\eta^2\phi_1. \quad \text{(D5)}$$

Combining these relations with (2.36)–(2.40) and (2.53)–(2.55) gives, for a bed of fully penetrable spheres, the bounds

$$\sigma^* \leqslant \left[\langle\sigma\rangle - \frac{\eta\phi_1^2(\sigma_2-\sigma_1)^2}{3\sigma_1 + (\sigma_2-\sigma_1)[1+2\phi_2-\eta\phi_1]} \right] \quad \text{(D6)}$$

and

$$\sigma^* \geqslant \left[\langle 1/\sigma\rangle - \frac{2\eta\phi_1^2(\sigma_2-\sigma_1)^2/\sigma_1\sigma_2}{3\sigma_2 + (\sigma_1-\sigma_2)[2+\phi_2-2\eta\phi_1]} \right]^{-1}. \quad \text{(D7)}$$

These bounds were originally derived by DeVera and Strieder (DS).[20]

For most ϕ_2 and $\alpha = \sigma_2/\sigma_1$, bounds (D6) and (D7) improve upon the HS bounds. For large sphere volume fractions ($\phi_2 \geqslant 0.7$), typically one of the HS bounds is better than the corresponding DS bound. This is not a surprising result for beds of fully penetrable spheres since the single-body trial functions employed here, although perfectly allowable, do not accommodate the overlap geometry of spheres at high ϕ_2.

It should also be noted that the Beran bounds[27] for the same model are found to be sharper than the DS bounds. The DS bounds enjoy the advantage, however, that they may be expressed analytically. The reason for this is that for fully penetrable spheres the point/n-particle functions $G_1^{(2)}$ and $G_2^{(2)}$ involved in the DS bounds have a simpler functional form than the n-point functions S_2 and S_3 that arise in the Beran bounds (see the discussion in Sec. III D).

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$$\frac{N(N-1)}{2V}\int_{x<2R} d\mathbf{x}\, V_2(x) g^+(x).$$

Hence, U_2 is equal to this quantity divided by $N(N-1)V_1^2/2V$ in the limit $\rho \to 0$.

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