New bounds on the permeability of a random array of spheres

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The recently derived variational principle of Rubinstein and Torquato (J. Fluid Mech., in press) is applied to obtain new rigorous two- and three-point upper bounds on the fluid permeability k for slow viscous flow around a random array of identical spheres which may penetrate one another in varying degrees. The n-point bounds involve up to n-point correlation function information. Both bounds are simplified and computed for the special case of mutually impenetrable spheres for a wide range of sphere volume fractions. The three-point bound is sharp and provides significant improvement over the two-point bound, especially at high sphere volume fractions (low porosities). It is the sharpest upper bound on k for a random array of impenetrable spheres developed to date and begins to approach the Kozeny–Carman empirical relation at low porosities.

I. INTRODUCTION

The slow flow of viscous fluids through microscopically disordered porous media is a subject of importance in a variety of technological areas including hydrology, oil recovery, and filtration, to mention but a few examples. In order to model such problems, it is often necessary to determine the macroscopic or effective properties of the porous medium. The effective parameters depend upon the details of the microstructure in a nontrivial manner; in general, they depend upon an infinite set of correlation functions which statistically characterize the medium. However, except for specially prepared artificial media, this set of functions is never known and hence an exact theoretical determination of the effective property is generally unobtainable.

A primary effective property of interest for describing flow through porous media is the fluid permeability k defined through Darcy's law [cf. Eq. (1)]. Various theoretical approaches have been taken to predict k. One approach seeks to idealize the geometry by considering spheres to be centered on the points of a periodic lattice.[1–3] Effective-medium approximations[4] have been used to study dilute systems of randomly arranged spheres.[5–7] More recently, effective-medium theories have been extended to treat nondilute random arrays of spheres.[8–11] The effective-medium approximations of Chang and Acrivos[11] yield permeabilities in good agreement with the well-known empirical Kozeny–Carman relation.

Another approach focuses on obtaining rigorous bounds on k. Bounds on effective parameters of random media are useful since (i) they may be used to test the merits of a theory or computer simulation experiment; (ii) as successively more microstructural information is included, the bounds (generally) become progressively narrower; and (iii) one of the bounds can typically provide a good estimate of the property, for a wide range of volume fractions, even when the reciprocal bound diverges from it.[12]

Prager[13] and Weissberg and Prager[14] were the first to derive upper bounds on k. These bounds are referred to as "three-point" bounds since they involve up to three-point correlation function information. The Prager and Weissberg–Prager variational principles were different, however. Doi,[15] claiming to have used a "new" variational principle, derived a two-point upper bound on k. Subsequently, Berryman and Milton,[16] using a volume-average approach, corrected a normalization constraint in the Prager variational principle. Torquato and Beasley[17] recently reformulated the Weissberg–Prager volume-averaged upper bound in terms of ensemble averages. The ensemble-average approach avoids the difficulties encountered by Berryman and Milton[16] in handling boundary conditions for admissible fields in the volume-average formulations. All the upper bounds described thus far involve a stochastic normalization factor which is an integral over the random stress field.

Very recently, Rubinstein and Torquato[18] derived a new, rigorous variational principle for upper bounds on k using an ensemble-average formulation. This variational principle is free of the aforementioned difficulties encountered in the past and provides a unified framework from which one may derive any of the bounds obtained previously. For example, the normalization factor that arises in the Rubinstein–Torquato bound is a given deterministic quantity, in contrast to previous formulations in which it is a stochastic integral that must be explicitly computed. Among other results, it is shown that the Doi bound corresponds to a special choice of the set of admissible fields given in Ref. 18 and not to a new variational principle, as Doi stated. It should also be noted that Rubinstein and Torquato[18] derived a new variational principle for lower bounds on the permeability.

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In this paper we shall apply the variational principle of Rubinstein and Torquato[18] to obtain new two- and three-point upper bounds on k for flow around a random array of identical spheres. The spheres are allowed, in general, to penetrate one another in varying degrees. Both the two- and three-point bounds are then simplified and evaluated for the special case of a distribution of totally impenetrable spheres for a wide range of sphere volume fractions. The three-point bound on k is calculated exactly through fourth order in the sphere volume fraction. For arbitrary density, we must resort to the use of the superposition approximation to compute the three-point bound. It is rigorously shown that through fourth order in the sphere volume fraction, the superposition approximation leads to *negligibly* small errors in the three-point bound on the permeability. The three-point bound is shown to provide significant improvement over the two-point bound, especially at high sphere volume fractions (low porosities). The three-point bound is the sharpest currently available upper bound on k for a random distribution of impenetrable spheres and is relatively close to the well-known Kozeny–Carman empirical formula at low porosities (high sphere volume fractions), the range over which the empirical relation is applicable.

II. VARIATIONAL PRINCIPLE OF RUBINSTEIN AND TORQUATO

By homogenizing the microscopic Stokes equations, Rubinstein and Torquato[18] obtained the desired macroscopic equations in an ensemble-average formulation for statistically isotropic media:

$$\mathbf{U} = -(k/\mu)\nabla p_0, \tag{1}$$

$$\nabla\cdot\mathbf{U} = 0. \tag{2}$$

Equation (1) is Darcy's law, which defines the permeability k. Here $\mathbf{U}$ is the ensemble-average velocity, ∇p_0 is the applied pressure gradient, and μ is the fluid viscosity, which henceforth is taken to be unity. The permeability k can be expressed in terms of an energy functional[18]:

$$k = \langle \boldsymbol{\sigma}(\mathbf{x}):\boldsymbol{\sigma}(\mathbf{x}) I(\mathbf{x})\rangle / 2\gamma^2, \tag{3}$$

where

$$\boldsymbol{\sigma}(\mathbf{x}) = \nabla\mathbf{u}(\mathbf{x}) + [\nabla\mathbf{u}(\mathbf{x})]^T \tag{4}$$

is the deviatoric stress tensor and $\mathbf{u}(\mathbf{x})$ is the velocity field which satisfies the Stokes equations

$$\nabla^2\mathbf{u}(\mathbf{x}) = \nabla p(\mathbf{x}) - \gamma\hat{\mathbf{e}}, \quad \mathbf{x}\in V_f, \tag{5}$$

$$\nabla\cdot\mathbf{u}(\mathbf{x}) = 0, \quad \mathbf{x}\in V_f, \tag{6a}$$

$$\mathbf{u}(\mathbf{x}) = 0, \quad \mathbf{x}\in \partial V. \tag{6b}$$

Here the characteristic function of the fluid region V_f is

$$I(\mathbf{x}) = \begin{cases} 1, & \mathbf{x}\in V_f, \\ 0, & \text{otherwise;} \end{cases} \tag{7}$$

$p(\mathbf{x})$ is the pressure field, γ is a constant, $\hat{\mathbf{e}}$ is a unit vector, ∂V denotes the solid–fluid interface, and the angular brackets denote an ensemble average. Moreover, we extend $\mathbf{u}(\mathbf{x})$ and $p(\mathbf{x})$ into the solid region to be zero. For arbitrary, random microstructures, the calculation of the rhs of (3) is generally mathematically intractable. Note that relation (3) was proved in Ref. 18 using the definition of the permeability (in terms of the average velocity in the direction of $\hat{\mathbf{e}}$) derived by employing the method of homogenization.

Rubinstein and Torquato[18] have very recently obtained the following variational bound on k. Let $\boldsymbol{\sigma}^*(\mathbf{x})$ be the class of trial stress fields that are smooth, stationary functions and that satisfy[19,20]

$$\nabla\times[\nabla\cdot\boldsymbol{\sigma}^*(\mathbf{x}) + \gamma\hat{\mathbf{e}}] = 0, \quad \mathbf{x}\in V_f, \tag{8}$$

$$\boldsymbol{\sigma}^*(\mathbf{x}) = [\boldsymbol{\sigma}^*(\mathbf{x})]^T, \quad \mathbf{x}\in V_f, \tag{9}$$

$$\boldsymbol{\sigma}^*(\mathbf{x}):\mathbf{E} = 0, \quad \mathbf{x}\in V_f. \tag{10}$$

Then the permeability is bounded from above by[18]

$$k \leqslant \langle \boldsymbol{\sigma}^*(\mathbf{x}):\boldsymbol{\sigma}^*(\mathbf{x}) I(\mathbf{x})\rangle / 2\gamma^2. \tag{11}$$

Here $\mathbf{E}$ is the unit dyadic. Note that (8) implies the existence of a trial pressure field $p^*(\mathbf{x})$. We emphasize that (11) is completely general in that we have placed no restrictions on the microstructure.

In some cases it may be advantageous to use bounds that are weaker than (11), namely,

$$k \leqslant \langle \boldsymbol{\sigma}^*(\mathbf{x}):\boldsymbol{\sigma}^*(\mathbf{x})\rangle / 2\gamma^2. \tag{12}$$

Inequality (12) is obtained by simply noting that

$$\langle \boldsymbol{\sigma}^*(\mathbf{x}):\boldsymbol{\sigma}^*(\mathbf{x})\rangle \geqslant \langle \boldsymbol{\sigma}^*(\mathbf{x}):\boldsymbol{\sigma}^*(\mathbf{x}) I(\mathbf{x})\rangle.$$

Relation (12) will be easier to compute than (11) since the former involves less microstructural information (i.e., lower-order correlation functions) than the latter.

III. NEW BOUNDS ON k FOR A RANDOM ARRAY OF PENETRABLE SPHERES

In order to apply (11) or (12) we must choose admissible fields as specified by (8)–(10). Here we consider obtaining bounds on k for an isotropic distribution of N identical, penetrable spheres of radius R centered at the positions $\mathbf{r}^N \equiv \mathbf{r}_1,\ldots,\mathbf{r}_N$ with number density ρ. Let $P_N(\mathbf{r}^N)$ be the probability density function associated with the event of finding particles $1,\ldots,N$ with configuration $\mathbf{r}^N$, respectively. Then

$$\rho_n(\mathbf{r}^n) = \frac{N!}{(N-n)!}\int P_N(\mathbf{r}^N)\,d\mathbf{r}_{n+1}\cdots d\mathbf{r}_N \tag{13}$$

is the probability density function associated with finding any subset of $n\,(<N)$ particles with configuration $\mathbf{r}^n$. The spheres may in general penetrate one another. Examples of interpenetrable-sphere models are described in Refs. 17 and 21.

A simple choice for the trial stress deviation is to assume that it is the sum of contributions from N spheres:

$$\boldsymbol{\sigma}^*(\mathbf{x}) = \frac{1}{\rho}\sum_{i=1}^{N} e(y_i)\boldsymbol{\tau}(\mathbf{y}_i) - \int_V d\mathbf{r}_1\, e(y_1)\boldsymbol{\tau}(\mathbf{y}_1), \tag{14}$$

where $\mathbf{y}_i = \mathbf{x} - \mathbf{r}_i$, and

$$e(y) = \begin{cases} 0, & y < R, \\ 1, & y > R, \end{cases} \tag{15}$$

is the characteristic function of the exterior of a single sphere. Finally, $\boldsymbol{\tau}$ is a general symmetric and traceless tensor [and thus satisfies (9) and (10)] and

$$\nabla\times[\nabla\cdot\boldsymbol{\tau}(\mathbf{x})] = 0. \tag{16}$$

Now the general form of the tensor that satisfies (9) and (10) is

$$\tau(\mathbf{r}) = [a(r)/r][\mathbf{r}\gamma + \gamma\mathbf{r} - \tfrac{2}{3}(\mathbf{r}\cdot\gamma)\mathbf{E}] + [b(r)/r^3][(\mathbf{r}\cdot\gamma)\mathbf{r}\mathbf{r} - \tfrac{1}{3}r^2(\mathbf{r}\cdot\gamma)\mathbf{E}], \quad (17)$$

where $a(r)$ and $b(r)$ are scalar functions of the magnitude of $\mathbf{r}$ and $\gamma = \gamma\hat{\mathbf{e}}$. Equation (17) satisfies condition (16) if

$$b(r) = r^2 \frac{d}{dr}\left(\frac{a(r)}{r}\right) + \frac{c}{r^2}. \quad (18)$$

Since (14) must satisfy (8), we have that $c = 3/(4\pi)$ and hence

$$b(r) = r^2 \frac{d}{dr}\left(\frac{a(r)}{r}\right) + \frac{3}{4\pi}\frac{1}{r^2}. \quad (19)$$

Note that the integral of (14) is included in order to ensure the absolute convergence of the integrals which result from taking the ensemble averages (11) or (12).[17]

We must now choose the functions $a(r)$ and $b(r)$ which satisfy (19). One could opt for functions that give the exact dilute-limit Stokes result, i.e.,

$$a(r) = (1/4\pi)(R^2/r^4) \quad (20)$$

and

$$b(r) = \frac{3}{4\pi}\frac{1}{r^2} - \frac{5}{4\pi}\frac{R^2}{r^4}. \quad (21)$$

Previous investigators[17,18] have, in fact, used such functions. Trial fields based on the exact single-sphere boundary-value problem cannot be expected to be the best choice at nondilute concentrations of spheres. We therefore introduce the more general functions containing the dimensionless parameters α and β as follows:

$$a(r) = \frac{\alpha}{4\pi}\frac{1}{r^2} + \frac{\beta}{4\pi}\frac{R^2}{r^4} \quad (22)$$

and

$$b(r) = \frac{3}{4\pi}(1-\alpha)\frac{1}{r^2} - \frac{5\beta}{4\pi}\frac{R^2}{r^4}. \quad (23)$$

The parameters α and β are to be optimized and generally should be functions of density. In the limit $\phi_2 \to 0$, α and β should become 0 and 1, respectively [cf. (20) and (21)].

To summarize, we employ the trial field (14) in conjunction with (17), (22), and (23). We now substitute this trial field into both inequalities (12) and (11) to obtain two- and three-point upper bounds, respectively.

A. Unoptimized two-point upper bound

The ensemble averaging of (12) yields

$$k \leqslant \frac{1}{2\gamma^2}\left(\frac{1}{\rho}\int d\mathbf{r}_1\, e(y_1)\tau(\mathbf{y}_1):\tau(\mathbf{y}_1) + \int\int d\mathbf{r}_1\, d\mathbf{r}_2\, h(r_{12})e(y_1) \times e(y_2)\tau(\mathbf{y}_1):\tau(\mathbf{y}_2)\right), \quad (24)$$

where $h(r) = [\rho_2(r)/\rho^2] - 1$ is the total correlation function and $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$. We refer to (24) as a *two-point* bound since it involves one- and two-point correlation function information. Bound (24) is unoptimized since the rhs has yet to be optimized with respect to the parameters α and β defined through (22) and (23). Again, we remark that the integrals are absolutely convergent.

B. Unoptimized three-point upper bound

Substitution of our trial fields into inequality (11) gives the sharper bound

$$k \leqslant \frac{1}{2\gamma^2}\left(\frac{1}{\rho^2}\int d\mathbf{r}_1\, G_2(\mathbf{y}_1)\tau(\mathbf{y}_1):\tau(\mathbf{y}_1) + \frac{1}{\rho^2}\int\int d\mathbf{r}_1\, d\mathbf{r}_2\, Q_3(\mathbf{y}_1,\mathbf{y}_2)\tau(\mathbf{y}_1):\tau(\mathbf{y}_2)\right), \quad (25)$$

where

$$Q_3(\mathbf{y}_1,\mathbf{y}_2) = G_3(\mathbf{y}_1,\mathbf{y}_2) - \rho G_2(\mathbf{y}_1) - \rho G_2(\mathbf{y}_2) + \rho^2\phi_1,$$

$$G_n(\mathbf{x};\mathbf{r}_1,\ldots,\mathbf{r}_{n-1}) \quad (26)$$

= probability of finding void at $\mathbf{x}$, the center of one (unspecified) particle in volume $d\mathbf{r}_1$ about $\mathbf{r}_1$, the center of another (unspecified) particle in volume $d\mathbf{r}_2$ about $\mathbf{r}_2$, etc.

$$= \prod_{i=1}^{n-1} e(y_i) \sum_{k=0}^{\infty} \frac{(-1)^k}{k!}\int \rho_{n+k-1}(\mathbf{r}_1,\ldots,\mathbf{r}_{n+k-1}) \times \prod_{j=n}^{n+k-1} m(y_j)d\mathbf{r}_j, \quad (27)$$

$$m(y) = 1 - e(y) = \begin{cases} 1, & y < R, \\ 0, & y > R. \end{cases} \quad (28)$$

The series representation of the n-point distribution function G_n was originally derived elsewhere.[21,22]

C. Discussion

It is useful to comment on the relationship of our new bounds (24) and (25) to previous work. First, trial fields of the type (14) were first employed in the related problem of determining bounds on the effective conductivity.[21] They have been subsequently used in bounds on the fluid permeability[17,18] and the rate of diffusion-controlled reactions.[23] Torquato and Beasley[17] and Rubinstein and Torquato[18] both employ (in the language of the present paper) a trial field of the form (14), but with the functions $a(r)$ and $b(r)$ equal to (20) and (21), respectively, i.e., the exact single-sphere solution. We employ (22) and (23), which, when optimized with respect to α and β, will yield bounds [cf. (24) and (25)] which improve upon those given in Refs. 16 and 18. Following Rubinstein and Torquato,[18] we refer to the trial field (14) and the resulting bounds (24) and (25) as "multiple-scattering" trial fields and bounds, respectively.

Before proceeding to compute optimized bounds, it is important to make remarks regarding the behavior of the bounds for high and low porosities. For dilute conditions (high porosities) such that interparticle interactions can be neglected, bounds (24) and (25) (optimized or not) give the correct Stokes dilute-limit permeability, which we denote by k_S. For a class of random arrays of spheres (such as an equilibrium distribution or random sequential addition), the bounds give an $O(\phi_2)$ correction to the scaled inverse permeability k_S/k [cf. (54), (55), (88), and (90)]. For dilute conditions, Brinkman-like effective medium theories[4-11] predict an $O(\phi_2^{1/2})$ correction to k_S/k. This nonanalytic dependence on ϕ_2 is a direct consequence of hydrodynamic screening effects. As noted in Refs. 17 and 18, it is difficult to construct trial fields that incorporate screening and simultaneously satisfy the admissibility conditions (8)–(10). From a fundamental viewpoint, it is desirable to derive such analytic behavior from bounds under dilute conditions. On the other hand, from a practical point of view, real porous media are not characterized by such high porosities. For real materials with small to moderate porosities (i.e., when the average size of the obstacles becomes comparable to the average interparticle distance), Brinkman-type equations go to the Darcy-law limit. In such instances, bounds provide the only rigorous means of estimating the permeability. It will be shown that the optimized three-point bound yields permeabilities which approach the well-known Kozeny–Carman empirical relation at high sphere volume fractions (low porosities).

In what follows, we shall compute the optimized versions of (24) and (25) for cases in which the spheres are mutually impenetrable.

IV. SIMPLIFICATION AND EVALUATION OF THE OPTIMIZED TWO-POINT BOUND

We now simplify and evaluate the weaker two-point bound (24) for a distribution of totally impenetrable spheres, i.e., $h(r) = -1$ for $r<2R$. This is accomplished using the spherical-harmonics methodology developed elsewhere.[24,25]

A. Simplification

Employing the results of the Appendix enables us to write the two-point lower bound on the *inverse* permeability as

$$k_S/k \geqslant (\mathscr{A}_2 + \mathscr{B}\phi_2)^{-1}, \tag{29}$$

where

$$k_S = 2R^2/9\phi_2 \tag{30}$$

is the exact Stokes dilute-limit result,

$$\mathscr{A}_2 = \frac{3\phi_2}{4R^2\rho}\int d\mathbf{r}\, e(r)A(r), \tag{31}$$

and

$$\mathscr{B} = \frac{1}{2R^2}\int\int d\mathbf{r}_1\, d\mathbf{r}_2\, e(r_1)e(r_2)h(r_{12}) \times\left(\frac{2}{5}B(r_1,r_2)P_1(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2) + \frac{3}{5}b(r_1)b(r_2)P_3(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)\right). \tag{32}$$

Here the sphere volume fraction $\phi_2 = 4\pi R^3\rho/3$. We see that $B(r_1,r_2)$ is given by (A11).

Substituting Eq. (A14) for $A(r)$ into (31) gives

$$\mathscr{A}_2 = \tfrac{3}{2} - \alpha - \beta + \alpha\beta + \tfrac{7}{6}\alpha^2 + \tfrac{1}{2}\beta^2. \tag{33}$$

Integrating over all of the angles of (32) except $\cos^{-1}(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)$ yields

$$\mathscr{B} = \frac{4\pi^2}{R^2}\int_0^\infty dr_1\, r_1^2 e(r_1)\int_0^\infty dr_2\, r_2^2 e(r_2) \times\int_{-1}^{+1} d(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)h(r_{12}) \times\left(\frac{2}{5}B(r_1,r_2)P_1(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2) + \frac{3}{5}b(r_1)b(r_2)P_3(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)\right). \tag{34}$$

After changing the variable of integration from $(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)$ to r_{12} and performing the integrals over dr_1 and dr_2 first, we find

$$\mathscr{B} = \int_0^2 dx\, h(x)\mathscr{B}^*(x) + (3 + 2\alpha^2)I_0, \tag{35}$$

where

$$\mathscr{B}^* = (\tfrac{1}{5}x^2 - \tfrac{1}{20}x^3)(3 + 2\alpha)^2 + (\tfrac{27}{10}x^2 - \tfrac{27}{40}x^3 - \tfrac{3}{2}x^4 + \tfrac{27}{32}x^5 - \tfrac{3}{64}x^7)(1-\alpha)^2 + (-3x^2 + \tfrac{9}{4}x^3 + \tfrac{3}{2}x^4 - \tfrac{21}{16}x^5 + \tfrac{3}{32}x^7)(1-\alpha)\beta + (\tfrac{3}{2}x^2 - \tfrac{15}{8}x^3 + \tfrac{15}{32}x^5 - \tfrac{3}{64}x^7)\beta^2, \tag{36}$$

$$I_0 = \int_2^\infty dx\, xh(x), \tag{37}$$

and $x = r_{12}/R$. The first integral of (35) can be evaluated explicitly since $h(xR) = -1$ for $x<2$, with the result

$$\mathscr{B} = \mathscr{B}_{00} + \mathscr{B}_{10}\alpha + \mathscr{B}_{01}\beta + \mathscr{B}_{11}\alpha\beta + \mathscr{B}_{20}\alpha^2 + \mathscr{B}_{02}\beta^2, \tag{38}$$

where

$$\mathscr{B}_{00} = -\tfrac{27}{5} + 3I_0, \tag{39}$$

$$\mathscr{B}_{10} = \tfrac{4}{5}, \tag{40}$$

$$\mathscr{B}_{01} = \tfrac{2}{5}, \tag{41}$$

$$\mathscr{B}_{11} = -\tfrac{2}{5}, \tag{42}$$

$$\mathscr{B}_{20} = -\tfrac{56}{15} + 2I_0, \tag{43}$$

$$\mathscr{B}_{02} = 0. \tag{44}$$

Note that the original sixfold integral (32) has been reduced to a one-dimensional quadrature involving $h(x)$.

Maximizing $(\mathscr{A} + \mathscr{B}\phi_2)^{-1}$ with respect to α and β gives the optimum values

$$\alpha^* = -\tfrac{3}{25}\phi_2^2[1 - (5 - 3I_0)\phi_2 - \tfrac{3}{25}\phi_2^2]^{-1} \tag{45}$$

and

$$\beta^* = (1 - \tfrac{2}{5}\phi_2)(1 - \alpha^*). \tag{46}$$

It is seen that in the limit $\phi_2\to 0$, $\alpha^*\to 0$, and $\beta^*\to 1$, as expected.

It is useful to compare our two-point bound with another two-point bound first derived by Doi[15] and later rederived by Rubinstein and Torquato.[18] Following Rubinstein and Torquato, we refer to the latter as an "interfacial-surface" bound. The interfacial-surface bound involves the volume fraction ϕ_2, the specific surface s, and the three two-point correlation functions—a void–void correlation F_{vv}, a surface–void correlation F_{sv}, and a surface–surface correlation F_{ss}:

$$\frac{k_S}{k} \geqslant \frac{R^2}{3\phi_2}\left\{\int_0^\infty dx\, x\left[F_{vv}(x) - 2\frac{\phi_1}{s}F_{sv}(x) + \left(\frac{\phi_1}{s}\right)^2 F_{ss}(x)\right]\right\}^{-1}. \tag{47}$$

Using the representations of the correlation functions for totally impenetrable spheres given by Torquato and Stell[26] and Torquato,[27,28] it is straightforward to express the interfacial-surface bound as

$$k_S/k \geqslant [1-(5-3I_0)\phi_2-\tfrac{1}{5}\phi_2^2]^{-1}. \quad (48)$$

Although the interfacial-surface bound has been previously computed for totally impenetrable spheres,[27] it has not been previously simplified to the form given, which is particularly easy to evaluate and useful for comparison. We observe that for the unoptimized case of $\alpha=0$ and $\beta=1$ (i.e., the single-sphere solution) our two-point bound is given by the similar expression

$$k_S/k \geqslant [1-(5-3I_0)\phi_2]^{-1}. \quad (49)$$

It is clear that the unoptimized bound (49) will always be weaker than the interfacial-surface bound (48).

B. Evaluation

The rhs of our optimized two-point multiple-scattering bound (29) and the rhs of the interfacial-surface bound (48) can be evaluated exactly through order ϕ_2^3, i.e., terms which account for four-body effects. For an equilibrium distribution of spheres, the total correlation function has the density expansion

$$h(x)=\sum_{n=0}^{\infty} h_n(x)\rho^n, \quad (50)$$

where the lowest-order terms are[29,30]

$$h_0(x)=\begin{cases}0, & x\geqslant 2,\\ -1, & \text{otherwise}\end{cases} \quad (51)$$

and

$$h_1(x)=\begin{cases}(32\pi/3)(1-\tfrac{3}{8}x+\tfrac{1}{128}x^3), & 2\leqslant x\leqslant 4,\\ 0, & \text{otherwise.}\end{cases} \quad (52)$$

The second-order term $h_2(x)$ was evaluated by Nijboer and Van Hove.[30] Simple integration leads to the expansion

$$I_0=\tfrac{22}{5}\phi_2-8.6244\phi_2^2+O(\phi_2^3). \quad (53)$$

Thus when α^* and β^* are used in our two-point bound, we find

$$k_S/k \geqslant 1+5\phi_2+(297/25)\phi_2^2+19.673\phi_2^3+O(\phi_2^4). \quad (54)$$

Similarly, substitution of (53) into (48) yields

$$k_S/k \geqslant 1+5\phi_2+12\phi_2^2+20.873\phi_2^3+O(\phi_2^4), \quad (55)$$

which gives an identical first-order coefficient as (54), but gives a second-order coefficient that is slightly better than $\frac{297}{25}$. All but the coefficient of ϕ_2^3 were obtained analytically; the coefficient -8.6244 was obtained using a Gaussian quadrature procedure. In Table I we give the two-point bounds (54) and (55) as a function of ϕ_2 up to $\phi_2=0.5$.

V. SIMPLIFICATION AND EVALUATION OF THE OPTIMIZED THREE-POINT BOUND

We now turn to the simplification and evaluation of the three-point bound (25) for totally impenetrable spheres.

A. Simplification

For such a distribution, Torquato[21,22] has shown that the infinite series (27) for the n-point distribution function G_n truncates after the second term for any n. Therefore, G_2 is a functional of $\rho_2(r)$ or the radial distribution function $g_2(r)=\rho_2(r)/\rho^2$ and G_3 is a functional of g_2 and the triplet distribution function $g_3=\rho_3/\rho^3$. Again, using the results of the Appendix enables us to express the three-point lower bound on the inverse permeability as

TABLE I. The lower bounds on k_s/k for impenetrable spheres as a function of the sphere volume fraction ϕ_2. The columns correspond to the expansion of the two-point multiple-scattering bound, Eq. (54); the expansion of the two-point interfacial-surface bound, Eq. (55); the expansion of the three-point multiple-scattering bound under the KSA, Eq. (88); the exact expansion of the three-point multiple-scattering bound, Eq. (90); and the three-point multiple-scattering bound under the KSA to all orders in ϕ_2, Eq. (56).

	k_s/k				
ϕ_2	Two-point expansion (54)	Two-point expansion (55)	Three-point expansion (88), KSA	Three-point expansion (90), exact	Three-point KSA to all orders in ϕ_2
0.01	1.051 21	1.051 22	1.058 37	1.058 37	1.058 37
0.05	1.282 16	1.282 61	1.326 41	1.326 39	1.326 5
0.10	1.638 5	1.640 9	1.752 4	1.752 3	1.756
0.15	2.083 7	2.090 4	2.299 7	2.299 2	2.322
0.20	2.632 6	2.647 0	2.990 4	2.989 2	3.070
0.25	3.299 9	3.326 1	3.846 2	3.843 9	4.056
0.30	4.100 4	4.143 6	4.889 0	4.885 0	5.348
0.35	5.048 8	5.114 9	6.147 2	6.140 8	7.043
0.40	6.159 9	6.255 9	7.642 4	7.623 3	9.357
0.45	7.448 4	7.582 0	9.358 4	9.343 8	13.20
0.50	8.929 1	9.109 1	11.386	11.368	27.66

$$k_s/k \geqslant (\mathscr{A}_3+\mathscr{B}\phi_2+\mathscr{C}\phi_2^2)^{-1}, \quad (56)$$

where

$$\mathscr{A}_3=\mathscr{A}_2-\frac{3\phi_2}{4R^2}\int\int d\mathbf{r}_1\,d\mathbf{r}_2\,e(r_1)m(r_2)g_2(r_{12})A(r_1) \quad (57)$$

and

$$\mathscr{C}=-\frac{\rho}{2R^2\phi_2}\int\int\int d\mathbf{r}_1\,d\mathbf{r}_2\,d\mathbf{r}_3\,e(r_1)e(r_2)m(r_3)\times[g_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)-g_2(r_{13})g_2(r_{23})+h(r_{13})h(r_{23})]\times\left(\frac{2}{5}B(r_1,r_2)P_1(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)+\frac{3}{5}b(r_1)b(r_2)P_3(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)\right). \quad (58)$$

Here $\mathscr{A}_2$ and $\mathscr{B}$ are the same as for the two-point bound.

The six-dimensional integral contributing to $\mathscr{A}_3$ is evaluated in the same manner as $\mathscr{B}$; expanding $g_2(r_{12})$ in Legendre polynomials, integrating over the angles, and changing the variable of integration from $(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)$ to r_{12} gives

$$\mathscr{A}_3=\mathscr{A}_2-\frac{12\pi^2\phi_2}{R^2}\int_0^\infty dr_1\,r_1e(r_1)A(r_1)\times\int_0^\infty dr_2\,r_2m(r_2)\int_{|r_1-r_2|}^{r_1+r_2}dr_{12}\,r_{12}g_2(r_{12}) \quad (59)$$

$$=\mathscr{A}_{00}+\mathscr{A}_{10}\alpha+\mathscr{A}_{01}\beta+\mathscr{A}_{11}\alpha\beta+\mathscr{A}_{20}\alpha^2+\mathscr{A}_{02}\beta^2, \quad (60)$$

where

$$\mathscr{A}_{00}=\tfrac{3}{2}-\tfrac{9}{4}\phi_2I_1, \quad (61)$$

$$\mathscr{A}_{10} = -1 + \tfrac{3}{2}\phi_2 I_1, \tag{62}$$

$$\mathscr{A}_{01} = -1 + 3\phi_2 I_3, \tag{63}$$

$$\mathscr{A}_{11} = 1 - 3\phi_2 I_3, \tag{64}$$

$$\mathscr{A}_{20} = \tfrac{7}{6} - \tfrac{7}{4}\phi_2 I_1, \tag{65}$$

$$\mathscr{A}_{02} = \tfrac{1}{2} + \phi_2(\tfrac{5}{4}I_4 + 2I_5), \tag{66}$$

$$I_1 = \frac{5}{4}\ln 3 - 1 + \int_2^\infty dx\, x h(x) \times\left[\frac{x}{(x^2-1)} - \frac{1}{2}\ln\left(\frac{x+1}{x-1}\right)\right], \tag{67}$$

$$I_3 = \frac{5}{36} - \frac{1}{16}\ln 3 + \int_2^\infty dx\, x h(x)\left(\frac{x}{(x^2-1)^3}\right), \tag{68}$$

$$I_4 = \frac{1}{32}\ln 3 - \frac{13}{648} + \int_2^\infty dx\, x h(x)\left(\frac{x}{(x^2-1)^4}\right), \tag{69}$$

and

$$I_5 = \frac{43}{1728} - \frac{5}{256}\ln 3 + \int_2^\infty dx\, x h(x)\left(\frac{x}{(x^2-1)^5}\right). \tag{70}$$

Here for numerical purposes we have replaced $g_2(x)$ with $h(x)+1$ and integrated the second term (involving unity) exactly. Note that we have again reduced a sixfold integral (57) to a one-dimensional quadrature (60).

The simplification of $\mathscr{C}$ is much more difficult. Integrals of this type have appeared in conductivity and elastic-moduli bounds in Refs. 24 and 25 and have been considerably simplified there by exploiting the freedom, afforded by the homogeneity and isotropy of the system, to change as convenience dictates the origin and orientation of the coordinate frame. Therefore, the complicated details of this procedure shall be omitted here.

Generalizing the arguments given in Refs. 20, 24, and 25, the key simplified integrals that arise are given by

$$\begin{aligned} I_{jkn} &= \frac{R^{j+k-6}}{8\pi^2}\int\int d\mathbf{r}_{12}\, d\mathbf{r}_{13}[g_3(r_{12},r_{13},r_{23}) \\ &\quad - g_2(r_{12})g_2(r_{13})]\frac{P_n(\cos\theta_{213})}{r_{12}^j r_{13}^k} \\ &= R^{j+k-6}\int_0^\infty dr_{12}\frac{1}{r_{12}^{j-1}} \\ &\quad \times\int_0^\infty dr_{13}\frac{1}{r_{13}^{k-1}}\int_{|r_{12}-r_{13}|}^{r_{12}+r_{13}} dr_{23}\, r_{23} \\ &\quad \times[g_3(r_{12},r_{13},r_{23}) \\ &\quad - g_2(r_{12})g_2(r_{13})]P_n(\cos\theta_{213}). \end{aligned} \tag{71}$$

Summarizing, we find

$$\mathscr{C} = \mathscr{C}_{00}^{(a)} + \mathscr{C}_{00}^{(b)} + \mathscr{C}_{10}\alpha + \mathscr{C}_{01}\beta + \mathscr{C}_{11}\alpha\beta + \mathscr{C}_{20}\alpha^2 + \mathscr{C}_{02}\beta^2, \tag{72}$$

where

$$\mathscr{C}_{00}^{(a)} = -\frac{27}{10}\sum_n N_1 I_{n+1,n+1,n}, \tag{73}$$

$$\mathscr{C}_{00}^{(b)} = \frac{9}{8}\sum_n (N_2(-I_{n-1,n-1,n} + I_{n-1,n+1,n} + I_{n+1,n-1,n}) - \tfrac{1}{5}N_3 I_{n+1,n+1,n}), \tag{74}$$

$$\mathscr{C}_{10} = \tfrac{4}{3}\mathscr{C}_{00}^{(a)} - 2\mathscr{C}_{00}^{(b)}, \tag{75}$$

$$\mathscr{C}_{01} = \tfrac{3}{8}\sum_n N_4(I_{n-1,n+1,n} + I_{n+1,n-1,n} - 2I_{n+1,n+1,n}), \tag{76}$$

$$\mathscr{C}_{11} = -\mathscr{C}_{01}, \tag{77}$$

$$\mathscr{C}_{20} = \tfrac{4}{9}\mathscr{C}_{00}^{(a)} + \mathscr{C}_{00}^{(b)}, \tag{78}$$

$$\mathscr{C}_{02} = -\tfrac{1}{8}\sum_n N_5 I_{n+1,n+1,n}, \tag{79}$$

$$N_1 = n/(2n+1), \tag{80}$$

$$N_2 = n(n-1)(n-2)/(2n-1), \tag{81}$$

$$N_3 = n(n-1)(10n^2+5n-14)/[(2n+1)(2n+3)], \tag{82}$$

$$N_4 = n(n-1)(n-2), \tag{83}$$

and

$$N_5 = n(n-1)(n-2)(2n-1). \tag{84}$$

Optimizing the three-point bound with respect to α and β gives

$$\alpha^* = (2\mathscr{D}_{10}\mathscr{D}_{02} - \mathscr{D}_{11}\mathscr{D}_{01})/(\mathscr{D}_{11}^2 - 4\mathscr{D}_{20}\mathscr{D}_{02}) \tag{85}$$

and

$$\beta^* = (2\mathscr{D}_{20}\mathscr{D}_{01} - \mathscr{D}_{10}\mathscr{D}_{11})/(\mathscr{D}_{11}^2 - 4\mathscr{D}_{20}\mathscr{D}_{02}), \tag{86}$$

where $\mathscr{D}_{ij} = \mathscr{A}_{ij} + \mathscr{B}_{ij}\phi_2 + \mathscr{C}_{ij}\phi_2^2$ Note that we have reduced a ninefold integral (58) to a manageable threefold integral.

B. Evaluation

To summarize, the three-point multiple-scattering bound (56) depends on the radial distribution function $g_2(r)$ and the triplet distribution function $g_3(r_{12},r_{13},r_{23})$. The first of these [which also arises in the two-point bound (29)] is easily obtainable from the accurate fit of Verlet and Weis.[31] The calculation of the triplet distribution function, as is well known in the statistical mechanics of the liquid state, is more problematical. We shall evaluate the three-point bound on the inverse permeability k^{-1}, Eq. (56), exactly through fourth order in ϕ_2 (or, equivalently, the scaled permeability k_s/k through third order in ϕ_2) using the exact low-density expansion of g_3. For *arbitrary density*, lacking any more fundamental alternative, we have resorted to the Kirkwood superposition approximation (KSA)[29]

$$g_3(r_{12},r_{13},r_{23}) = g_2(r_{12})g_2(r_{13})g_2(r_{23}) \tag{87}$$

to evaluate this quantity. The KSA (87) is exact in the zero-density limit for all particle configurations and for cases in which one particle is distant from the other two, regardless of the density. It is also accurate for equilateral-triangle configurations, especially at low densities; the approximation is not as accurate at high densities and for less symmetric triplet configurations.

Before presenting our evaluation of the three-point bound (56) for arbitrary ϕ_2 using the KSA, we first obtain exact volume fraction expansions of (56). Such expansions are useful since we can exactly study the errors introduced by using the KSA at low to moderate volume fractions. Specifically, upon use of (50), (56), (60), and (85)–(87), we find the optimized three-point bound in the KSA to have the exact expansion

$$k_s/k \geqslant 1 + (193/81 + 3\ln 3)\phi_2 + 15.5351\phi_2^2 + 29.31\phi_2^3 + O(\phi_2^4). \quad (88)$$

The first-order coefficient of ϕ_2 was obtained analytically; the remaining coefficients were computed numerically using standard quadrature techniques for integrals of the type (71).[24,25,32] First, note the significant improvement in the coefficients of ϕ_2, ϕ_2^2, and ϕ_2^3 over the two-point bounds (54) and (55). Second, since the KSA is exact through zeroth order in the density, Eq. (88) for the scaled inverse permeability is exact through second order in ϕ_2. Therefore, the coefficient of ϕ_2^3 in (88) is the first term to contain errors because of the use of the KSA.

Now the triplet distribution function can be written *exactly* as the KSA multiplied by unity plus a functional $\Gamma[h(r)]$ over the total correlation function $h(r)$ [defined under (24)],[33] i.e.,

$$g_3(r_{12},r_{13},r_{23}) = g_2(r_{12})g_2(r_{13})g_2(r_{23})\{1+\Gamma[h(r)]\}. \quad (89)$$

The functional Γ has the property that $\Gamma = 0$ in the limit $\rho \to 0$. Hence g_3 can be exactly evaluated through first order in density. Using this exact expansion for g_3 and the same methods outlined by Beasley and Torquato[32] in the related conduction problem, we find the optimized three-point bound to be given exactly by

$$k_s/k \geqslant 1 + (193/81 + 3\ln 3)\phi_2 + 15.5351\phi_2^2 + 29.16\phi_2^3 + O(\phi_2^4). \quad (90)$$

Again, we emphasize that (90) involves no approximation; it is an exact relation. Comparing the coefficients of ϕ_2^3 in (88) and (90) reveals that the KSA very slightly overestimates the bound through this order in ϕ_2. Therefore, up to moderate volume fractions, the error in using the KSA is negligibly small. As described below, this error is amplified at higher volume fractions. In Table I we include a tabulation of the three-point expansions (88) and (90). The three-point bound is seen to be sharper than either two-point bound.

For arbitrary density, we must resort to the use of the KSA. The integral (71) in conjunction with (87) and the Verlet–Weis[31] fit of $g_2(r)$ is numerically evaluated using standard techniques.[20,24,25,32] We tabulate this evaluation in Table I up to $\phi_2 = 0.5$. Comparing the tabulation of the three-point expansion in the KSA (88) with the three-point bound to all orders in ϕ_2 reveals that the former is useful up to $\phi_2 = 0.3$, where the error is about 9%. In Fig. 1 we plot these results for the three-point bound (56), along with the analogous results for the optimized two-point bound (29), versus the sphere volume fraction ϕ_2. For the former bound, we present results up to $\phi_2 = 0.5$, the point at which we believe errors due to the KSA are still tolerable. Results for the optimized two-point bound (to all orders in ϕ_2) are accurate

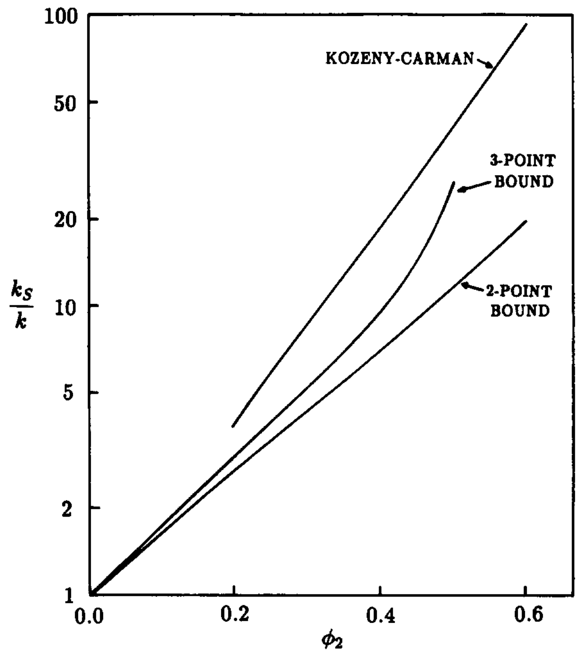

FIG. 1. The optimized two- and three-point (under KSA) multiple-scattering lower bounds, Eqs. (29) and (56), respectively, on k_s/k for a dispersion of impenetrable spheres compared with the empirical Kozeny–Carman expression, Eq. (91).

up to $\phi_2 = 0.6$. [Note that evaluation of the two-point interfacial-surface bound (48) to all orders in ϕ_2 has already been given elsewhere.[27]] The three-point bound is seen to significantly improve upon the corresponding two-point bound. The sudden rise in the three-point bound near $\phi_2 = 0.5$ indicates that the KSA overestimates the bound at high volume fractions. This is contrary to our findings with analogous three-point conductivity bounds,[34] e.g., the use of the KSA underestimates the lower bound on the effective conductivity. Included in Fig. 1 is the well-known Kozeny–Carman empirical relation

$$k_S/k = 10\phi_2/(1-\phi_2)^3. \quad (91)$$

The three-point bound shown is the closest that *any* bound has come to the Kozeny–Carman formula.

VI. CONCLUSIONS

We have derived new two- and three-point multiple-scattering upper bounds on the permeability k for (possibly overlapping) spheres using the Rubinstein–Torquato[18] variational principle. For the special case of totally impenetrable spheres, we simplified and evaluated optimized forms of these bounds [Eqs. (29) and (56)] for a wide range of sphere volume fraction ϕ_2. The three-point bound provides significant improvement over any of the two-point bounds described in this study, especially at high ϕ_2. Moreover, the three-point bound is relatively close to the empirical Kozeny–Carman relation, especially at low porosities, the range over which the empirical relation is applicable. This represents the closest that any bound has come to this empirical formula. These results are encouraging since they indicate that improved three-point bounds have the potential for providing reasonable estimates of the permeability for a wide range of porosities.

The interfacial-surface two-point bound (47) is slightly sharper than our optimized two-point multiple-scattering bound (29). The reason for this is that interfacial-surface trial fields capture the local geometry better than multiple-scattering trial fields.[18] Work is currently underway to derive and compute a three-point interfacial-surface bound on k.

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APPENDIX: SIMPLIFICATION OF THE INTEGRALS OVER TENSOR PRODUCTS

Here we will simplify the integrals over $\boldsymbol{\tau}(\mathbf{y}_1):\boldsymbol{\tau}(\mathbf{y}_1)$ and $\boldsymbol{\tau}(\mathbf{y}_1):\boldsymbol{\tau}(\mathbf{y}_2)$ [which appear in the two-point bound (24) and the three-point bound (25)] using the spherical-harmonics methodology first employed in conductivity and bulk modulus bounds[24] and subsequently in shear modulus bounds.[25] We first express the tensor $\boldsymbol{\tau}(\mathbf{r})$ in Cartesian components for $r \geqslant R$ in spherical coordinates (r,θ,ϕ):

$$\tau_{xx}(\mathbf{r}) = \gamma[-\tfrac{2}{3}a(r) + b(r)(\sin^2\theta\cos^2\phi - \tfrac{1}{3})]\cos\theta, \tag{A1}$$

$$\tau_{yy}(\mathbf{r}) = \gamma[-\tfrac{2}{3}a(r) + b(r)(\sin^2\theta\sin^2\phi - \tfrac{1}{3})]\cos\theta, \tag{A2}$$

$$\tau_{zz}(\mathbf{r}) = \gamma[\tfrac{4}{3}a(r) + b(r)(\cos^2\theta - \tfrac{1}{3})]\cos\theta, \tag{A3}$$

$$\tau_{xy}(\mathbf{r}) = \tau_{yx}(\mathbf{r}) = \gamma b(r)\cos\theta\sin^2\theta\cos\phi\sin\phi, \tag{A4}$$

$$\tau_{xz}(\mathbf{r}) = \tau_{zx}(\mathbf{r}) = \gamma[a(r) + b(r)\cos^2\theta]\sin\theta\cos\phi, \tag{A5}$$

and

$$\tau_{yz}(\mathbf{r}) = \tau_{zy}(\mathbf{r}) = \gamma[a(r) + b(r)\cos^2\theta]\sin\theta\sin\phi, \tag{A6}$$

with $a(r)$ and $b(r)$ given by Eqs. (22) and (23), respectively. Taking the scalar product, we find

$$\begin{aligned}\boldsymbol{\tau}(\mathbf{r}_1):\boldsymbol{\tau}(\mathbf{r}_2) &= \gamma^2(2[(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2) + \tfrac{1}{3}P_1(\cos\theta_1)P_1(\cos\theta_2)]a(r_1)a(r_2)\\ &+ \tfrac{2}{3}\{(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)[P_0(\cos\theta_2) + 2P_2(\cos\theta_2)]\\ &- P_1(\cos\theta_1)P_1(\cos\theta_2)\}a(r_1)b(r_2)\\ &+ \tfrac{2}{3}\{(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)[P_0(\cos\theta_1) + 2P_2(\cos\theta_1)]\\ &- P_1(\cos\theta_1)P_1(\cos\theta_2)\}a(r_2)b(r_1)\\ &+ [(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)^2P_1(\cos\theta_1)P_1(\cos\theta_2)\\ &- \tfrac{1}{3}P_1(\cos\theta_1)P_1(\cos\theta_2)]b(r_1)b(r_2)).\end{aligned} \tag{A7}$$

Now consider some arbitrary function $f(\mathbf{r}_1,\mathbf{r}_2)$ that can be expanded in Legendre polynomials:

$$f(\mathbf{r}_1,\mathbf{r}_2) = \sum_{l=0}^{\infty} F_l(r_1,r_2)P_l(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2), \tag{A8}$$

where $r_i = |\mathbf{r}_i|$ and $\hat{\mathbf{n}}_i = \mathbf{r}_i/r_i$, with expansion coefficients given by

$$F_l(r_1,r_2) = \frac{2l+1}{2}\int_{-1}^{+1} d(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)\, f(\mathbf{r}_1,\mathbf{r}_2)P_l(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2). \tag{A9}$$

Here P_l is the Legendre polynomial of order l and $d\hat{\mathbf{n}}$ denotes an element of solid angle.

Combining expansion (A8) with (A7) and observing that the statistical homogeneity of the system enables us to replace $\mathbf{y}_i$ with $\mathbf{r}_i$ gives

$$\begin{aligned}\int\!\!\int d\mathbf{r}_1\, d\mathbf{r}_2 f(\mathbf{r}_1,\mathbf{r}_2)\boldsymbol{\tau}(\mathbf{r}_1):\boldsymbol{\tau}(\mathbf{r}_2)\\ &= \gamma^2\int_0^\infty dr_1\, r_1^2\int_0^\infty dr_2\, r_2^2\sum_{l=0}^{\infty}F_l(r_1,r_2)\\ &\quad\times\int\!\!\int d\hat{\mathbf{n}}_1\, d\hat{\mathbf{n}}_2\, \boldsymbol{\tau}(\mathbf{r}_1):\boldsymbol{\tau}(\mathbf{r}_2)P_l(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)\\ &= (4\pi)^2\gamma^2\int_0^\infty dr_1\, r_1^2\int_0^\infty dr_2\, r_2^2\\ &\quad\times\Big(\frac{4}{135}F_1(r_1,r_2)B(r_1,r_2)\\ &\quad + \frac{2}{105}F_3(r_1,r_2)b(r_1)b(r_2)\Big)\\ &= \frac{2}{9}\gamma^2\int\!\!\int d\mathbf{r}_1\, d\mathbf{r}_2\, f(\mathbf{r}_1,\mathbf{r}_2)\Big(\frac{2}{5}B(r_1,r_2)P_1(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)\\ &\quad + \frac{3}{5}b(r_1)b(r_2)P_3(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2)\Big).\end{aligned} \tag{A10}$$

Here

$$B(r_1,r_2) = [1/(4\pi)^2](3+2\alpha)(1/r_1^2)(1/r_2^2). \tag{A11}$$

In obtaining (A10) we employed the addition theorem

$$\begin{aligned}P_l(\hat{\mathbf{n}}_1\cdot\hat{\mathbf{n}}_2) &= P_l(\cos\theta_1)P_l(\cos\theta_2) + 2\sum_{m=1}^{l}\frac{(l-m)!}{(l+m)!}\\ &\quad\times P_l^m(\cos\theta_1)P_l^m(\cos\theta_2)\cos[m(\phi_1-\phi_2)]\end{aligned} \tag{A12}$$

and orthogonality properties of the Legendre polynomials. Note that for the two- and three-point bounds $f(\mathbf{r}_1,\mathbf{r}_2) = e(r_1)e(r_2)h(r_{12})$ and $Q_3(\mathbf{r}_1,\mathbf{r}_2)/\rho^2$, respectively.

The simplified integrals over $\boldsymbol{\tau}(\mathbf{r}_1):\boldsymbol{\tau}(\mathbf{r}_2)$ can be obtained from the results given above by setting $\mathbf{r}_1 = \mathbf{r}_2$. We find

$$\int d\mathbf{r}_1\, f(r_1)\boldsymbol{\tau}(\mathbf{r}_1):\boldsymbol{\tau}(\mathbf{r}_1) = \frac{4\pi}{3}\gamma^2\int_0^\infty dr\, r^2 f(r)A(r), \tag{A13}$$

where

$$\begin{aligned}A(r) = \frac{1}{(4\pi)^2}\Big[&\Big(\frac{2}{3}(3-\alpha)^2 + 4\alpha^2\Big)\frac{1}{r^4}\\ &- [4(3-\alpha)\beta - 8\alpha\beta]\frac{R^2}{r^6} + 10\beta^2\frac{R^4}{r^8}\Big]\end{aligned} \tag{A14}$$

and $f(r)$ is some arbitrary function of the scalar r. Note that for the two- and three-point bounds $f(r) = e(r)/\rho$ and $G_2(r)/\rho^2$, respectively.

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