Effective properties of two-phase disordered composite Media. I. Simplification of bounds on the conductivity and bulk modulus of dispersions of impenetrable spheres

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We consider the problem of evaluating upper and lower bounds on the effective conductivity and bulk modulus derived, respectively, by Beran and by Beran and Molyneux, for the model of impenetrable spherical inclusions randomly distributed throughout a matrix. The key multidimensional cluster integral is simplified by expanding the appropriate terms of its integrand in spherical harmonics and employing the orthogonality properties of this basis set. The resulting simplified integrals are in a form that makes them easier to compute. The approach described here can be readily and systematically extended to cases in which the inclusions are permeable to one another and to the determination of other bulk properties of composite media, such as the effective shear modulus.

I. INTRODUCTION

The problem of theoretically predicting the bulk properties of a disordered composite medium is of considerable scientific and engineering interest.[1–4] In order to predict exactly the effective electrical conductivity σ_e and the effective bulk modulus K_e of a disordered two-phase composite medium, it is necessary to know not only the phase conductivities σ_1 and σ_2, the phase bulk moduli K_1 and K_2, the phase shear moduli G_1 and G_2, and the phase volume fractions ϕ_1 and $\phi_2=1-\phi_1$, but also an infinite set of correlation functions which statistically characterize the sample.[5–7] Such a complete statistical characterization of the medium is almost never possible in practice. By means of variational principles, however, it is possible to bound σ_e and K_e rigorously given the phase property values and limited statistical information concerning the microstructure of the two-phase material. Using only the phase property values and the volume fraction of one of the phases, say ϕ_2, Hashin and Shtrikman have obtained the best possible bounds on σ_e (Ref. 8) and on K_e (Ref. 9). These are second-order bounds in the sense that they are exact through second order in the difference in the phase property values. More restrictive third-order bounds on σ_e and K_e, which include additional microstructural information in the form of a key integral that depends upon the three-point probability function of the composite, have been derived by Beran[10] and by Beran and Molyneux,[11] respectively. (The three-point probability function S_3 gives the probability of finding three points all in one of the phases.[12]) Furthermore, nth-order bounds on σ_e (Ref. 13) and on K_e (Refs. 6 and 7) have been derived. Practical application of even third-order bounds has been very limited because S_3, for general composite media, has been a very difficult quantity to determine.

In this article we consider the evaluation of the Beran bounds on σ_e and the Beran-Molyneux bounds on K_e for a statistically homogeneous and isotropic distribution of impenetrable spheres in a matrix. In Sec. II we present the Beran and Beran-Molyneux bounds and briefly discuss previous applications. In Sec. III we explicitly express the key integral involved in these bounds, for the special case of impenetrable spheres randomly dispersed throughout a matrix, in terms of one-body, two-body, and three-body distribution functions, using the results of Torquato and Stell.[14] We then simplify the complex multidimensional cluster integral that arises here by expanding appropriate terms of its integrand in spherical harmonics and exploiting the orthogonality of this basis set. The resulting simplified integrals, although still nontrivial, are in a form that makes them easier to compute. The simplified integrals obtained for distributions of impenetrable spheres are shown to be equivalent to the integrals derived by Felderhof[15] using a completely different approach. We believe the present technique has the advantage of greater generality in that it can be readily and systematically extended to cases in which the spheres are permeable to one another and to the determination of other bulk properties, such as the effective shear modulus. In Sec. IV we state our conclusions. In a later article, we shall present a numerical evaluation of the simplified integrals obtained in Sec. III and thus the Beran and Beran-Molyneux bounds, up to densities near the random close-packing value.

II. BOUNDS

Beran[10] has derived bounds on σ_e for a statistically isotropic two-phase composite material, given σ_1, σ_2, ϕ_2, and two integrals involving derivatives of certain three-point correlation functions. Beran and Molyneux[11] have obtained an analogous set of bounds on K_e for such a medium. Torquato and Stell[16] and Milton[17] independently showed that the Beran bounds on σ_e may be expressed in terms of σ_1, σ_2, ϕ_2, and a single integral ζ_1 (defined below) which depends upon the three-point probability function described in the Introduction. Milton[17] also showed that the Beran-Molyneux bounds on K_e may be expressed simply in terms of K_1, K_2, ϕ_2, and ζ_1. Using Milton's notation,[17] the Beran bounds on σ_e and the Beran-Molyneux bounds on K_e are given, respectively, by

$$\left[\langle 1/\sigma\rangle - \frac{2\phi_1\phi_2(1/\sigma_1-1/\sigma_2)^2}{2\langle 1/\tilde{\sigma}\rangle + \langle 1/\sigma\rangle_\zeta}\right]^{-1} \le \sigma_e \le \left[\langle \sigma\rangle - \frac{\phi_1\phi_2(\sigma_2-\sigma_1)^2}{\langle \tilde{\sigma}\rangle + 2\langle \sigma\rangle_\zeta}\right] \tag{2.1}$$

and

$$\left[\langle 1/K\rangle - \frac{4\phi_1\phi_2(1/K_1-1/K_2)^2}{4\langle 1/\tilde{K}\rangle + 3\langle 1/G\rangle_\zeta}\right]^{-1} \le K_e \le \left[\langle K\rangle - \frac{3\phi_1\phi_2(K_2-K_1)^2}{3\langle \tilde{K}\rangle + 4\langle G\rangle_\zeta}\right]. \tag{2.2}$$

Here we define $\langle b\rangle = b_1\phi_1 + b_2\phi_2$, $\langle b\rangle_\zeta = b_1\zeta_1 + b_2\zeta_2$, and $\langle \tilde{b}\rangle = b_1\phi_2 + b_2\phi_1$, where b represents any property. In addition, we have

$$\zeta_1 = 1-\zeta_2 = \frac{9}{2\phi_1\phi_2} I_1[\hat{S}_3] , \tag{2.3}$$

$$\hat{S}_3(r,s,t) = S_3(r,s,t) - \frac{S_2(r)S_2(s)}{S_1} , \tag{2.4}$$

where the integral operator I_1 is defined below in Eq. (3.5). The quantities $S_2(r)$ and $S_3(r,s,t)$ are, respectively, the probability of finding in phase 1 the end points of a line segment of length r and the vertices of a triangle with sides of length r, s, and t; S_1 is correspondingly just the volume fraction ϕ_1. The form of Eq. (2.4) ensures that $I_1[\hat{S}_3]$ and thus ζ_1 are absolutely convergent. The fact that ζ_1 lies in the interval [0,1] implies that the bounds (2.1) and (2.2) are always improvements on the corresponding Hashin-Shtrikman bounds on σ_e (Ref. 8) and K_e (Ref. 9).

Application of bounds (2.1) and (2.2) has been extremely limited since it has been difficult to determine the three-point function S_3 either experimentally or for nontrivial models of composite media. Until recently, the only evaluations of these bounds were those reported by Miller[18] for "symmetric-cell" materials and by Corson[19] for a two-phase metal mixture. A symmetric-cell material is constructed by partitioning space into cells of possibly varying shapes and sizes, with cells randomly and independently designated as phase 1 or phase 2 with probabilities ϕ_1 and ϕ_2, respectively. Such a mathematical construct could not be employed to model the practically important case of a dispersion of equal-sized impenetrable inclusions distributed throughout a matrix since the space could not be completely filled by such cells.

Recent theoretical and experimental developments may soon break the impasse regarding application of the third-order bounds. For example, Torquato and Stell[12] have derived expressions for the n-point probability function S_n, for statistically inhomogeneous distributions of identical inclusions (of arbitrary dimension) in a matrix such that the location of each inclusion is fully specified by a position vector, in terms of n-particle probability densities. Employing these results, the lower-order S_n have been evaluated and approximated for dispersions of fully penetrable spheres (i.e., randomly centered spheres),[20] totally impenetrable spheres,[14] and totally impenetrable rods and disks.[21] This has led to evaluation of the third-order bounds on σ_e, K_e, and the effective shear modulus due, respectively, to Beran,[10] Beran and Molyneux,[11] and McCoy,[22] for dispersions of fully penetrable spheres at all realizable inclusion volume fractions ϕ_2.[16,23] A procedure for using the well-established techniques of image processing to measure n-point probability functions has been reported recently by Berryman.[24] This promising method is automated and thus more efficient than the rather tedious experimental procedure employed by Corson.[25]

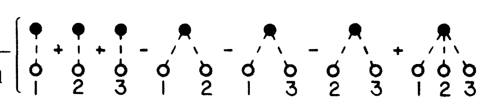
Using a method which does not directly employ the representation of the S_n in terms of n-particle probability densities,[12] Felderhof[15,26] computed the microstructural parameter ζ_1, Eq. (2.3), for dispersions of impenetrable spheres through third order in ϕ_2 and thus evaluated the Beran bounds on σ_e for such a system through fourth order in ϕ_2. Felderhof accomplishes this by using the exact cluster expansion for σ_e through terms involving triplets of inclusions and expanding it through third-order terms in $\sigma_2-\sigma_1$. By comparing this resulting expression to an expansion of the Beran bounds through third order in $\sigma_2-\sigma_1$, he obtains an expression for ζ_1 in terms of the two-particle and three-particle probability densities. In order to apply this technique for general sphere distributions, one must know the solution of the electrostatic boundary-value problem for two and three spheres in a matrix through third order in $\sigma_2-\sigma_1$ and all orders in ϕ_2.

III. SIMPLIFICATION OF $I_1[\hat{S}_3]$ FOR DISPERSIONS OF IMPENETRABLE SPHERES

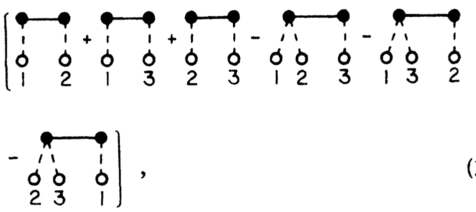
The general n-point matrix probability function S_n is defined by an infinite series; for impenetrable spheres, however, the series terminates with the nth term.[12] Thus, for the three-point matrix probability function of a homogeneous dispersion of impenetrable spheres, we have

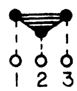
$$S_3 = 1 + S_3^{(1)}\eta + S_3^{(2)}\eta^2 + S_3^{(3)}\eta^3 , \tag{3.1}$$

where in the diagram notation of Torquato and Stell,[14,27]

$S_3^{(1)} = -\dfrac{1}{V_1}$  ,

(3.2a)

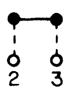
$$S_3^{(2)}=\frac{1}{V_1^2}\Bigg[$$  $$\Bigg] , \quad (3.2b)$$

$$S_3^{(3)}=-\frac{1}{V_1^3}$$  $$. \quad (3.2c)$$

In this shorthand, a solid circle represents a vector position that is integrated over the entire infinite volume and the labeled open circles stand for $\mathbf{r}_1$, $\mathbf{r}_2$, or $\mathbf{r}_3$, while the broken line represents the bond

$$m(r)=1, \quad r<a$$
$$=0, \quad r>a \quad (3.3)$$

between the two positions, the solid line stands for the pair distribution function $g_2 \equiv g$ of the spheres, and the crosshatched triangle for their triplet distribution function g_3; thus, e.g.,

 $$= \int d\mathbf{r}_4 d\mathbf{r}_5 m(r_{24}) g(r_{45}) m(r_{53}) . \quad (3.4)$$

Finally, a is the radius of the spheres, $V_1=\frac{4}{3}\pi a^3$ their volume, and $\eta=\rho V_1 \equiv \phi_2$ their volume fraction.

We need to evaluate the functional

$$I_1[f]=\frac{1}{8\pi^2}\int d\mathbf{r}_2 d\mathbf{r}_3 f(r_{12},r_{13},r_{23})\frac{P_2(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{r}}_{13})}{r_{12}^3 r_{13}^3}$$
$$=\int_0^\infty \frac{dr_{12}}{r_{12}}\int_0^\infty \frac{dr_{13}}{r_{13}}\int_{-1}^{1} d(\cos\theta_{213})P_2(\cos\theta_{213}) \times f(r_{12},r_{13},r_{23}) \quad (3.5)$$

for each of the diagrams of (3.2) in turn. This is done below. Here we note two simple rules of general utility: (a) If the function f does not depend on r_{23}, where

$$r_{23}^2=r_{12}^2+r_{13}^2-2r_{12}r_{13}\cos\theta_{213} , \quad (3.6)$$

then

$$I_1[f(r_{12},r_{13})]\equiv 0 \quad (3.7)$$

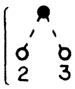
by virtue of the orthogonality of the Legendre polynomials $P_l(x)$; (b) less obviously, if f depends *only* on r_{23} then

$$I_1[f(r_{23})]=\tfrac{2}{9}[f(0)-f(\infty)] . \quad (3.8)$$

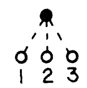
This is shown in Appendix A.

A. Evaluation of $I_1[S_3^{(1)}]$

It follows from (3.7) that the first five members of (3.2a) do not contribute to I_1; while using (3.8) we get immediately

$$I_1\Bigg[$$  $$\Bigg]=\tfrac{2}{9}$$  $$=\tfrac{2}{9}V_1 . \quad (3.9)$$

The final term of (3.2a) requires a bit more work. Keeping the origin of coordinates fixed at $\mathbf{r}_1$ and aligning the z axis along $\hat{\mathbf{r}}_{12}$ for convenience, we have

 $$= \int d\mathbf{r}_4 m(r_{14})m(r_{24})m(r_{34})$$
$$=\int_0^\infty dr_{14} r_{14}^2 m(r_{14})\int d\omega_{214} m(r_{24})m(r_{34}) . \quad (3.10)$$

The angular integrations in (3.10) can be carried out by expanding angle-dependent functions in Legendre polynomials (more generally, in spherical harmonics), following a method used originally by Barker and Monaghan[28] to evaluate virial coefficients. We write, for example,

$$m(r_{24})=m[(r_{12}^2+r_{14}^2-2r_{12}r_{14}\cos\theta_{214})^{1/2}]$$
$$=\sum_{l=0}^{\infty} M_l(r_{12},r_{14})P_l(\cos\theta_{214}) , \quad (3.11)$$

where as above we are using the convention $\theta_{jik}\equiv\cos^{-1}(\hat{\mathbf{r}}_{ij}\cdot\hat{\mathbf{r}}_{ik})$. The expansion coefficients are then given by

$$M_l(r_{12},r_{14})=\frac{2l+1}{2}\int_{-1}^{1} d(\cos\theta)P_l(\cos\theta) \times m[(r_{12}^2+r_{14}^2-2r_{12}r_{14}\cos\theta)^{1/2}] , \quad (3.12)$$

or equivalently, as shown in Appendix A, by

$$M_l(r_{12},r_{14})=\frac{2l+1}{2\pi^2}\int_0^\infty dk\, k^2 \tilde{m}(k) j_l(kr_{12}) j_l(kr_{14}) , \quad (3.13)$$

where $\tilde{m}(k)$ is the Fourier transform of $m(r)$ and $j_l(x)$ the spherical Bessel function of order l. Similarly, we write $m(r_{34})$ as

$$m(r_{34})=\sum_l M_l(r_{13},r_{14})P_l(\cos\theta_{314})$$
$$=\sum_{l,m}\frac{4\pi}{2l+1}M_l(r_{13},r_{14})Y_{lm}^*(\omega_{213})Y_{lm}(\omega_{214}) , \quad (3.14)$$

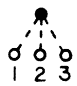
after invoking the spherical harmonic addition theorem[29] in the second equality to bring out the specific angular variables needed.

With these expansions, we now have in (3.10)

$$\int d\omega_{214} m(r_{24})m(r_{34}) = \sum_{l',l,m} \frac{4\pi}{2l+1} M_{l'}(r_{12},r_{14}) M_l(r_{13},r_{14}) Y^*_{lm}(\omega_{213}) \int d\omega_{214} P_{l'}(\cos\theta_{214}) Y_{lm}(\omega_{214})$$

$$= \sum_l \frac{4\pi}{2l+1} M_l(r_{12},r_{14}) M_l(r_{13},r_{14}) P_l(\cos\theta_{213}) \qquad (3.15)$$

and thus finally

I_1 []

$$= \frac{8\pi}{25} \int_0^\infty dr\, r^2 m(r) \left[\int_0^\infty \frac{ds}{s} M_2(s,r) \right]^2 , \qquad (3.16)$$

the original triple sum having been reduced to a single term by the orthogonality of the spherical harmonics. To complete the job in Eq. (3.16), we will use Eq. (3.13), noting that

$$\tilde{m}(k) = \frac{4\pi a^2}{k} j_1(ka) , \qquad (3.17)$$

to calculate

$$\int_0^\infty \frac{ds}{s} M_2(s,r) = \frac{10a^2}{\pi} \int_0^\infty dk\, k j_1(ka) j_2(kr) \times \int_0^\infty \frac{ds}{s} j_2(ks)$$

$$= \frac{10a^2}{3\pi} \int_0^\infty dk\, k j_1(ka) j_2(kr)$$

$$= \frac{5}{3} \left[\frac{a}{r} \right]^3 H(r-a) , \qquad (3.18)$$

where $H(x)$ is the Heaviside unit function

$$H(x) = 0, \quad x < 0$$
$$= 1, \quad x > 0 . \qquad (3.19)$$

[The Bessel function integrals used in getting (3.18) can be found in Ref. 30.] Because of the conflicting step functions, the final result for (3.16) is zero.

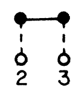
In summary, we have simply

$$I_1[S_3^{(1)}] = \tfrac{2}{9} \qquad (3.20)$$

for the coefficient of the term linear in density.

B. Evaluation of $I_1[S_3^{(2)}]$

The first two terms of (3.2b) again make no contribution, while the I_1 functional of the third is easily determined using (3.8). We note that [cf. Eq. (3.4)]

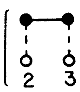


$\rightarrow 0$ as $r_{23} \rightarrow 0$

and

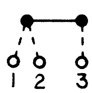
$$\rightarrow \left[\int d\mathbf{r}\, m(r) \right]^2 = V_1^2 \quad \text{as } r_{23} \rightarrow \infty ,$$

since $g(r) \rightarrow 1$ as $r \rightarrow \infty$. Thus, one finds

I_1 []

$$= -\tfrac{2}{9} V_1^2 . \qquad (3.21)$$

To evaluate the remaining terms we will again use expansions like (3.11) and (3.14). Consider first



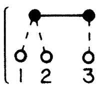
$$= \int d\mathbf{r}_4 d\mathbf{r}_5 m(r_{14}) m(r_{24}) g(r_{45}) m(r_{53})$$

$$= \int d\mathbf{r}_4 m(r_{14}) m(r_{24}) \int_0^\infty dr_{15} r_{15}^2 \int d\omega_{215} \sum_{l,m} \frac{4\pi}{2l+1} G_l(r_{14},r_{15}) Y^*_{lm}(\omega_{214}) \times Y_{lm}(\omega_{215}) \sum_{l',m'} \frac{4\pi}{2l'+1} M_{l'}(r_{13},r_{15}) Y^*_{l'm'}(\omega_{215}) Y_{l'm'}(\omega_{213})$$

$$= \int_0^\infty dr_{14} r_{14}^2 m(r_{14}) \int d\omega_{214} \sum_l M_l(r_{12},r_{14}) P_l(\cos\theta_{214}) \int_0^\infty dr_{15} r_{15}^2 \sum_{l',m'} \left[\frac{4\pi}{2l'+1} \right]^2 G_{l'}(r_{14},r_{15}) \times M_{l'}(r_{13},r_{15}) Y^*_{l'm'}(\omega_{214}) Y_{l'm'}(\omega_{213})$$

$$= \int_0^\infty dr_{14} r_{14}^2 m(r_{14}) \int_0^\infty dr_{15} r_{15}^2 \sum_l \left[\frac{4\pi}{2l+1} \right]^2 M_l(r_{12},r_{14}) G_l(r_{14},r_{15}) M_l(r_{13},r_{15}) P_l(\cos\theta_{213}) . \qquad (3.22)$$

Here the G_l are the harmonic coefficients in the expansion of $g(r_{45})$. Operating on this result with I_1 gives, after integrating over $\cos\theta_{213}$,

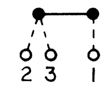
$$I_1\left[\,\right.$$  $$\left.\,\right]=\frac{2}{5}\left[\frac{4\pi}{5}\right]^2\int_0^\infty dr_{14}r_{14}^2 m(r_{14})\int_0^\infty \frac{dr_{12}}{r_{12}}M_2(r_{12},r_{14})\times\int_0^\infty dr_{15}r_{15}^2 G_2(r_{14},r_{15})\int_0^\infty\frac{dr_{13}}{r_{13}}M_2(r_{13},r_{15})$$

$$=\tfrac{2}{5}V_1^2\int_0^\infty\frac{dr_{14}}{r_{14}}m(r_{14})H(r_{14}-a)\int_0^\infty\frac{dr_{15}}{r_{15}}G_2(r_{14},r_{15})H(r_{15}-a)=0\,, \tag{3.23}$$

again because of the conflicting demands of the step functions on r_{14}; Eq. (3.18) was used in getting the second equality of (3.23).

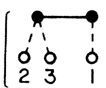
Interchanging the labels 2 and 3 clearly leads to the same integrals, hence the penultimate diagram in (3.2b) also contributes nothing to I_1.

The last term, however, does contribute. Proceeding as above, we first find that



$$=\int_0^\infty dr_{14}r_{14}^2\int_0^\infty dr_{15}r_{15}^2 m(r_{14})G_0(r_{14},r_{15})\sum_l\frac{(4\pi)^2}{2l+1}M_l(r_{13},r_{14})M_l(r_{12},r_{14})P_l(\cos\theta_{213})\,, \tag{3.24}$$

and then after the final angular integration over $\cos\theta_{213}$,

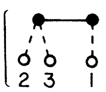
$$I_1\left[\,\right.$$  $$\left.\,\right]=2\left[\frac{4\pi}{5}\right]^2\int_0^\infty dr_{14}r_{14}^2\int_0^\infty dr_{15}r_{15}^2 m(r_{15})G_0(r_{14},r_{15})\left[\int_0^\infty\frac{ds}{s}M_2(s,r_{14})\right]^2$$

$$=2V_1^2\int_0^\infty\frac{dr_{14}}{r_{14}^4}H(r_{14}-a)\int_0^\infty dr_{15}r_{15}^2 m(r_{15})G_0(r_{14},r_{15})\,. \tag{3.25}$$

Here it is convenient to express G_0 using the analogue of Eq. (3.12) with a change of variable back to r_{45},

$$G_0(r_{14},r_{15})=\tfrac{1}{2}\int_{|r_{14}-r_{15}|}^{r_{14}+r_{15}}dr_{45}\frac{r_{45}}{r_{14}r_{15}}g(r_{45})\,, \tag{3.26}$$

so that, by interchanging the order of the r_{15} and r_{45} integrations and explicitly evaluating the innermost integrals, we get for (3.25)

$$I_1\left[\,\right.$$  $$\left.\,\right]=V_1^2\int_0^\infty\frac{dr_{14}}{r_{14}^5}H(r_{14}-a)\int_0^\infty dr_{15}r_{15}m(r_{15})\int_{|r_{14}-r_{15}|}^{r_{14}+r_{15}}dr_{45}r_{45}g(r_{45})$$

$$=V_1^2\int_\sigma^\infty dr_{45}r_{45}g(r_{45})\int_a^\infty\frac{dr_{14}}{r_{14}^5}\int_{|r_{14}-r_{45}|}^{r_{14}+r_{45}}dr_{15}r_{15}m(r_{15})=\tfrac{2}{3}a^3V_1^2\int_\sigma^\infty dr\frac{r^2g(r)}{(r^2-a^2)^3}\,. \tag{3.27}$$

Here, $\sigma=2a$ is the sphere diameter and we have used the fact that $g(r)=0$ for $r<\sigma$ to simplify the result in (3.27).

Summarizing, we find two finite contributions from (3.2b) to the quadratic coefficient of I_1:

$$I_1[S_3^{(2)}]=-\tfrac{2}{9}-\tfrac{2}{3}a^3\int_\sigma^\infty dr\frac{r^2g(r)}{(r^2-a^2)^3}\,. \tag{3.28}$$

C. Evaluation of $I_1[S_3^{(3)}]$

Simplification of the final integral is considerably aided 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. We begin by writing the desired integral in the form

$$I_1[S_3^{(3)}]=-\frac{1}{16\pi^2}\int d\mathbf{r}_5 d\mathbf{r}_6 g(r_{45},r_{46},r_{56})\times Q(r_{45},r_{46},r_{56})\,, \tag{3.29}$$

where

$$Q(r_{45},r_{46},r_{56})=\frac{2}{V_1^3}\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 m(r_{14})m(r_{25})\times m(r_{36})\frac{P_2(\cos\theta_{213})}{r_{12}^3r_{13}^3}\,. \tag{3.30}$$

The implied fixed origin for (3.29) is now at $\mathbf{r}_4$ and so we are integrating over $\mathbf{r}_1$ in Eq. (3.30), which is the expression we seek to simplify. Consider first the integral over $\mathbf{r}_3$, which requires the expansion of $m(r_{36})$. With an origin of coordinates at $\mathbf{r}_1$ and the z axis along $\hat{\mathbf{r}}_{12}$, we have

$$\int d\mathbf{r}_3 m(r_{36})\frac{P_2(\cos\theta_{213})}{r_{13}^3}=\int_0^\infty \frac{dr_{13}}{r_{13}}\int d\omega_{213}\sum_{l,m} M_l(r_{13},r_{16})Y_{lm}^*(\omega_{216})Y_{lm}(\omega_{213})P_2(\cos\theta_{213})$$
$$=\frac{4\pi}{5}P_2(\cos\theta_{216})\int_0^\infty \frac{dr_{13}}{r_{13}}M_2(r_{13},r_{16})=V_1\frac{H(r_{16}-a)}{r_{16}^3}P_2(\cos\theta_{216}) , \tag{3.31}$$

having again used Eq. (3.18). [Looking ahead to the final expression (3.29), with (3.30), we see that $r_{14}<a$ and $r_{46}>2a$ (because of g_3) so that $r_{16}>a$ necessarily and we can drop the step-function condition in (3.31).] Continuing now with the integral over $\mathbf{r}_2$, we keep the origin at $\mathbf{r}_1$ but align the z axis along $\hat{\mathbf{r}}_{16}$ and find that

$$\int d\mathbf{r}_2 m(r_{25})\frac{P_2(\cos\theta_{216})}{r_{12}^3}=V_1\frac{H(r_{15}-a)}{r_{15}^3}P_2(\cos\theta_{516}) , \tag{3.32}$$

in the same way as (3.31). [And similarly too, the step function in (3.32) will be automatically satisfied in the context of Eq. (3.29).] With these results, Eq. (3.30) now reads

$$Q(r_{45},r_{46},r_{56})=\frac{2}{V_1}\int d\mathbf{r}_1 m(r_{14})\frac{P_2(\cos\theta_{516})}{r_{15}^3 r_{16}^3} , \tag{3.33}$$

an expression that turns out to be rather more intricate to evaluate than any of the earlier ones. The difficulty arises in explicitly bringing out the orientation dependence of the integrand for the final integration over $\mathbf{r}_1$, for which we shall use the coordinate frame arrangement shown in Fig. 1. From this figure we note first the identity

$$\cos\theta_{516}=\cos\theta_{415}\cos\theta_{416}+\sin\theta_{415}\sin\theta_{416}\cos\psi , \tag{3.34}$$

where ψ is the angle between the planes 541 and 641, which leads to the addition theorem expansion

$$P_2(\cos\theta_{516})=\sum_{m=0}^{2}\alpha_m\frac{(2-m)!}{(2+m)!}P_2^m(\cos\theta_{415})\times P_2^m(\cos\theta_{416})\cos(m\psi) , \tag{3.35}$$

$$\alpha_m=1,\quad m=0$$
$$=2,\quad m>0 , \tag{3.36}$$

and so to

$$Q(r_{45},r_{46},r_{56})=\frac{2}{V_1}\sum_{m=0}^{2}\alpha_m\frac{(2-m)!}{(2+m)!}\int_0^a dr_{14}r_{14}^2\int d\omega_{641}\left[\frac{P_2^m(\cos\theta_{415})}{r_{15}^3}\right]\left[\frac{P_2^m(\cos\theta_{416})}{r_{16}^3}\right]\cos(m\psi) . \tag{3.37}$$

We then show in Appendix B that each of the expressions within large parentheses in (3.37) can be expanded in terms of the corresponding opposite angles at the base of the coordinate frame, giving now

$$Q(r_{45},r_{46},r_{56})=\frac{2}{V_1}\sum_{m=0}^{2}\alpha_m\frac{(2-m)!}{(2+m)!}\sum_{l,l'}\gamma_{lm}\gamma_{l'm}\frac{a^{l+l'-1}}{l+l'-1}\frac{1}{r_{45}^{l'+1}r_{46}^{l+1}}\int d\omega_{641}P_{l'}^m(\cos\theta_{541})P_l^m(\cos\theta_{641})\cos(m\psi) , \tag{3.38}$$

with

$$\gamma_{l0}=\tfrac{1}{2}l(l-1),\quad \gamma_{l1}=l-1,\quad \gamma_{l2}=1 , \tag{3.39}$$

after integrating over r_{14}. The next step is perhaps best seen with the aid of a second coordinate frame, rotated an angle θ_{641} from the original frame about an axis perpendicular to the $(\hat{\mathbf{r}}_{46},\hat{\mathbf{r}}_{41})$ plane; a temporary reassignment of the coordinate frame so that $\hat{\mathbf{r}}_{41}$ is in the (x,z) plane, as shown in Fig. 2, is helpful. The orientation of $\hat{\mathbf{r}}_{45}$ with

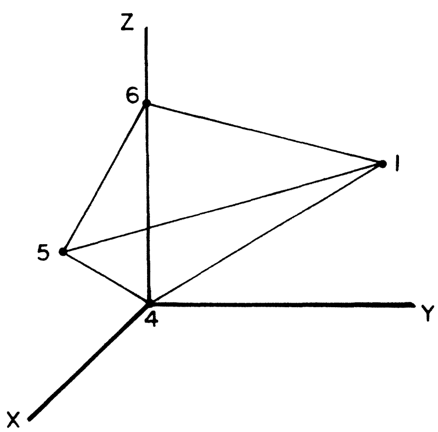


FIG. 1. Coordinate system for Eq. (3.33).

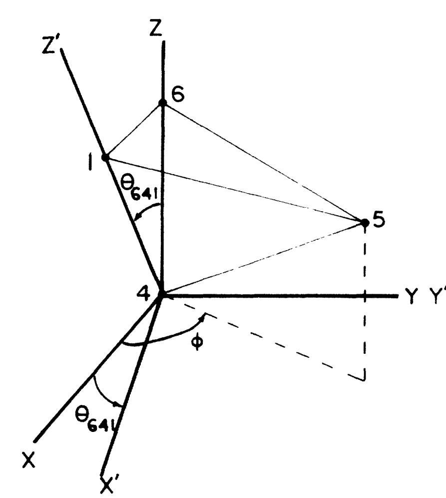


FIG. 2. Coordinate system for Eq. (3.41).

respect to the (x,y,z) frame in this figure is given by (θ_{645},ϕ), while with respect to the (x',y',z') frame, rotated θ_{641} about the y axis, it is given by (θ_{541},ψ), since ψ is the angle between the (x,z) plane and the $(\hat{\mathbf{r}}_{41},\hat{\mathbf{r}}_{45})$ plane. Thus the general transformation theorem[29]

$$Y_m(\theta',\phi')=\sum_{m'} D^l_{m'm}(\alpha\beta\gamma)Y_{lm}(\theta,\phi) \tag{3.40}$$

for rotations through the Euler angles α,β,γ becomes in this case

$$Y_{lm}(\theta_{541},\psi)=\sum_{m'} D^l_{m'm}(0,\theta_{641},0)Y_{lm'}(\theta_{645},\phi)$$

$$=\sum_{m'} d^l_{m'm}(\theta_{641})Y_{lm'}(\theta_{645},\phi) . \tag{3.41}$$

Writing this out more explicitly in terms of the associated Legendre functions, we get

$$P_l^m(\cos\theta_{541})\cos(m\psi)=\left[\frac{(l+m)!}{(l-m)!}\right]^{1/2}\sum_{m'=0}^{l}\alpha_{m'}(-1)^{m'-m}\left[\frac{(l-m')!}{(l+m')!}\right]^{1/2} d^l_{m'm}(\theta_{641})P_l^{m'}(\cos\theta_{645})\cos(m'\phi) , \tag{3.42}$$

where the left-hand side is just the factor we needed to break out for the evaluation of (3.38). We now find easily that

$$\int d(\cos\theta_{641})d\phi[P_{l'}^m(\cos\theta_{541})\cos(m\psi)]P_l^m(\cos\theta_{641})=\frac{4\pi}{2l+1}\frac{(l+m)!}{(l-m)!}P_l(\cos\theta_{645})\delta_{l'l} , \tag{3.43}$$

and finally from (3.38) that

$$Q(r_{45},r_{46},r_{56})=\frac{2}{V_1}\sum_{m=0}^{2}\alpha_m\frac{(2-m)!}{(2+m)!}\sum_l\gamma_{lm}^2\frac{4\pi}{4l^2-1}\frac{(l+m)!}{(l-m)!}\frac{a^{2l-1}}{r_{45}^{l+1}r_{46}^{l+1}}P_l(\cos\theta_{546})$$

$$=\sum_{l=2}^{\infty}l(l-1)\frac{a^{2l-4}}{r_{45}^{l+1}r_{46}^{l+1}}P_l(\cos\theta_{546}) , \tag{3.44}$$

after performing the sum over m using Eqs. (3.36) and (3.39). This completes the simplification of Eq. (3.29), which now reads

$$I_1[S_3^{(3)}]=-\frac{1}{16\pi^2}\sum_{l=2}^{\infty}l(l-1)a^{2l-4}\int d\mathbf{r}_5 d\mathbf{r}_6 g_3(r_{45},r_{46},r_{56})\frac{P_l(\cos\theta_{546})}{r_{45}^{l+1}r_{46}^{l+1}} . \tag{3.45}$$

We note that if g_3 in this expression were replaced by $g(r_{45})g(r_{46})$ the integral would vanish identically. As remarked earlier, it is convenient to retain this vanishing contribution from the second term of Eq. (2.4) to ensure the convergence of the final integrals, a point of particular interest for numerical calculations.

We can now summarize the results of this section for the simplification of Eq. (2.3) with the finding that, using Eqs. (3.1), (3.20), (3.28), and (3.45), we have

$$I_1[\hat{S}_3]=\tfrac{2}{9}\eta(1-\eta)-K , \tag{3.46}$$

where

$$K=\tfrac{2}{3}\eta^2a^3\int_\sigma^\infty dr\frac{r^2g(r)}{(r^2-a^2)^3}+\frac{\eta^3}{16\pi^2}\sum_{l=2}^{\infty}l(l-1)a^{2l-4}\int d\mathbf{r}_2 d\mathbf{r}_3[g_3(r_{12},r_{13},r_{23})-g(r_{12})g(r_{13})]\frac{P_l(\cos\theta_{213})}{r_{12}^{l+1}r_{13}^{l+1}} . \tag{3.47}$$

The integrals of K are just those obtained by Felderhof[15,26] through a completely different approach.

IV. CONCLUSIONS

For the model of impenetrable spherical inclusions randomly distributed throughout a matrix, we have simplified the key integral $I_1[\hat{S}_3]$ that arises in the Beran bounds on σ_e and the Beran-Molyneux bounds on K_e. This was accomplished by expanding appropriate terms in its integrand in spherical harmonics and utilizing the orthogonality properties of this basis set. The resulting simplified integrals are shown to depend upon the one-body, two-body, and three-body distribution functions and are equivalent to integral expressions derived by Felderhof[15,26] by means of a different procedure.

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APPENDIX A

The orthogonality of the Legendre polynomials yields the inverse of the expansion

$$h(r_{23})=\sum_{l=0}^{\infty}H_l(r_{12},r_{13})P_l(\cos\theta_{213}) \tag{A1}$$

as

$$H_l(r_{12},r_{13})=\frac{2l+1}{2}\int_{-1}^{1}d(\cos\theta_{213})h(r_{23})P_l(\cos\theta_{213}) , \tag{A2}$$

where

$$r_{23}^2=r_{12}^2+r_{13}^2-2r_{12}r_{13}\cos\theta_{213} . \quad \text{(A3)}$$

Suppose now that $h(r)$ possesses a Fourier transform $\tilde{h}(k)$, so that

$$h(r)=\frac{1}{(2\pi)^3}\int d\mathbf{k}\,\tilde{h}(k)\exp(i\mathbf{k}\cdot\mathbf{r}) . \quad \text{(A4)}$$

Then Eq. (A2) can alternatively be written in terms of the transform $\tilde{h}(k)$. For convenience, arrange the coordinate frame so that $\mathbf{r}_1$ is the origin, $\hat{\mathbf{r}}_{12}$ lies along the z axis, and the $(\hat{\mathbf{r}}_{12},\hat{\mathbf{r}}_{13})$ plane is the (x,z) plane; in this frame, let (θ,ϕ) be the angular coordinates of $\mathbf{k}$. Then we have

$$\begin{aligned}\exp(i\mathbf{k}\cdot\mathbf{r}_{23})&=\exp[i\mathbf{k}\cdot(\mathbf{r}_{13}-\mathbf{r}_{12})]=\exp(i\mathbf{k}\cdot\mathbf{r}_{13})\exp(-ikr_{12}\cos\theta)\\&=\left[4\pi\sum_{l,m}i^l j_l(kr_{13})Y_{lm}^*(\theta_{213},0)Y_{lm}(\theta,\phi)\right]\left[\sum_{l'}(2l'+1)(-i)^{l'}j_{l'}(kr_{12})P_{l'}(\cos\theta)\right] ,\end{aligned} \quad \text{(A5)}$$

having invoked the well-known expansion of plane waves in spherical waves.[31] Introduction of (A5) into (A4) then leads to

$$\begin{aligned}h(r_{23})&=\frac{1}{2\pi^2}\sum_{l',l,m}(2l'+1)i^{l-l'}Y_{lm}(\theta_{213},0)\int_0^\infty dk\,k^2\tilde{h}(k)j_{l'}(kr_{12})j_l(kr_{13})\int d\omega P_{l'}(\cos\theta)Y_{lm}(\theta,\phi)\\&=\frac{1}{2\pi^2}\sum_l(2l+1)P_l(\cos\theta_{213})\int_0^\infty dk\,k^2\tilde{h}(k)j_l(kr_{12})j_l(kr_{13}) .\end{aligned} \quad \text{(A6)}$$

Comparing this with (A1) we see immediately that

$$H_l(r_{12},r_{13})=\frac{2l+1}{2\pi^2}\int_0^\infty dk\,k^2\tilde{h}(k)j_l(kr_{12})j_l(kr_{13}) , \quad \text{(A7)}$$

an alternative to (A2) that is sometimes more convenient.

One such instance occurs for the application of the functional I_1, Eq. (3.5), to $h(r_{23})$. This produces

$$\begin{aligned}I_1[h(r_{23})]&=\int_0^\infty\frac{dr_{12}}{r_{12}}\int_0^\infty\frac{dr_{13}}{r_{13}}\int_{-1}^1 d(\cos\theta_{213})\\&\qquad\times P_2(\cos\theta_{213})h(r_{23})\\&=\int_0^\infty\frac{dr_{12}}{r_{12}}\int_0^\infty\frac{dr_{13}}{r_{13}}\frac{2}{5}H_2(r_{12},r_{13}) ,\end{aligned} \quad \text{(A8)}$$

or, using (A7),

$$\begin{aligned}I_1[h(r_{23})]&=\frac{1}{\pi^2}\int_0^\infty dk\,k^2\tilde{h}(k)\left[\int_0^\infty\frac{dr}{r}j_2(kr)\right]^2\\&=\frac{1}{9\pi^2}\int_0^\infty dk\,k^2\tilde{h}(k)=\tfrac{2}{9}h(0) .\end{aligned} \quad \text{(A9)}$$

For an otherwise well-behaved function $f(r)$ that goes to a finite value at large r, we must first subtract the finite limit to produce a function

$$h(r)=f(r)-f(\infty) \quad \text{(A10)}$$

whose transform is everywhere convergent. Then we get the more general rule

$$I_1[f(r_{23})]=I_1[h(r_{23})]=\frac{2}{9}h(0)=\frac{2}{9}[f(0)-f(\infty)] \quad \text{(A11)}$$

that is used in Sec. III. Dirichlet's conditions allow f to have a finite number of finite discontinuities.[32]

APPENDIX B

This appendix deals with the specific task of rewriting $P_2^m(\cos\phi)/t^3$ (see Fig. 3) in terms of r, s, and $\cos\theta$ for $m=0$, 1, and 2 and the condition $s<r$. The basic ingredient for the transformation is the relation

$$\frac{r}{t}=\left[1-2\frac{s}{r}\cos\theta+\frac{s^2}{r^2}\right]^{-1/2}=\sum_{l=0}^\infty\left[\frac{s}{r}\right]^l P_l(\cos\theta) \quad \text{(B1a)}$$

obtained from the law of cosines and the generating function of the Legendre polynomials.[33] Furthermore, successive differentiation of (B1a) with respect to $\cos\theta$ produces

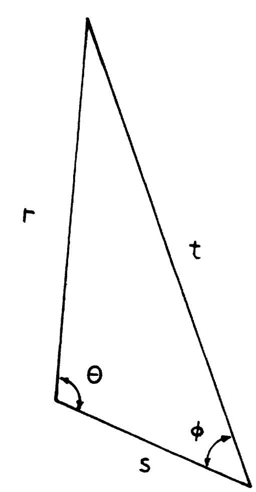

FIG. 3. Coordinate system for Appendix B.

$$\left[\frac{r}{t}\right]^3 = \sum_l \left[\frac{s}{r}\right]^{l-1} P_l'(\cos\theta) , \qquad \text{(B1b)}$$

$$\left[\frac{r}{t}\right]^5 = \tfrac{1}{3} \sum_l \left[\frac{s}{r}\right]^{l-2} P_l''(\cos\theta) , \qquad \text{(B1c)}$$

where the prime denotes differentiation.

Consider first the $m=0$ case. The law of sines yields here

$$P_2(\cos\phi) = 1 - \frac{3}{2}\left[\frac{r}{t}\right]^2 \sin^2\theta , \qquad \text{(B2)}$$

so

$$\begin{aligned}\left[\frac{r}{t}\right]^3 P_2(\cos\phi) &= \left[\frac{r}{t}\right]^3 - \frac{3}{2}\left[\frac{r}{t}\right]^5 \sin^2\theta \\ &= \sum_l \left[\frac{s}{r}\right]^{l-2} [P_{l-1}'(\cos\theta) \\ &\qquad - \tfrac{1}{2}\sin^2\theta P_l''(\cos\theta)] \\ &= \tfrac{1}{2}\sum_l l(l-1)\left[\frac{s}{r}\right]^{l-2} P_l(\cos\theta) ,\end{aligned} \qquad \text{(B3)}$$

where we have used Legendre's equation and recurrence relations[33] to simplify the right-hand side. Finally, the desired expression is

$$\frac{P_2(\cos\phi)}{t^3} = \tfrac{1}{2}\sum_l l(l-1)\frac{s^{l-2}}{r^{l+1}} P_l(\cos\theta) . \qquad \text{(B4)}$$

The procedures for $m=2$ and $m=3$ are similar. The definition of P_2^1 and the law of sines produce

$$P_2^1(\cos\phi) = 3\left[\frac{r}{t}\right]^2 \left[\cos\theta - \frac{s}{r}\right]\sin\theta , \qquad \text{(B5)}$$

so

$$\begin{aligned}\left[\frac{r}{t}\right]^3 P_2^1(\cos\phi) &= 3\left[\frac{r}{t}\right]^5 \left[\cos\theta - \frac{s}{r}\right]\sin\theta \\ &= \sum_l \left[\frac{s}{r}\right]^{l-2} [\cos\theta P_l''(\cos\theta) \\ &\qquad - P_{l-1}''(\cos\theta)]\sin\theta \\ &= \sum_l (l-1)\left[\frac{s}{r}\right]^{l-2} P_l^1(\cos\theta) ,\end{aligned} \qquad \text{(B6)}$$

and finally

$$\frac{P_2^1(\cos\phi)}{t^3} = \sum_l (l-1)\frac{s^{l-2}}{r^{l+1}} P_l^1(\cos\theta) . \qquad \text{(B7)}$$

In the last case, we start from

$$P_2^2(\cos\phi) = 3\left[\frac{r}{t}\right]^2 \sin^2\theta \qquad \text{(B8)}$$

and quickly find

$$\frac{P_2^2(\cos\phi)}{t^3} = \sum_l \frac{s^{l-2}}{r^{l+1}} P_l^2(\cos\theta) . \qquad \text{(B9)}$$

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