Bulk properties of two-phase disordered media. II. Effective conductivity of a dilute dispersion of penetrable spheres

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The calculation of the effective electrical conductivity σ^* of a dilute dispersion of equisized spheres of radius R distributed with arbitrary degree of penetrability is considered. It is demonstrated that σ^*, through second order in the inclusion volume fraction ϕ_2, can be written in terms of the zero-density limits of the pair-connectedness and pair-blocking functions, and certain polarizability tensors which involve one and two inclusions. Rigorous upper and lower bounds on σ^*, through order ϕ_2^2, are shown to depend upon, among other quantities, the aforementioned pair distribution functions and are evaluated for two models: an interpenetrable-sphere model and a certain sphere distribution in which the minimum distance between sphere centers is greater than or equal to $2R$. An approximate expression obtained for the low-density expansion of σ^* for dispersions of penetrable spheres always lies between the derived bounds on σ^*. The study demonstrates that the effect of connectivity of the inclusion phase on σ^*, through second order in ϕ_2, can be substantial relative to the conductivity of dispersions of spheres characterized by a pair-connectedness function that is zero for all sphere separations.

I. INTRODUCTION

The determination of the sensitivity of the bulk property of a disordered multiphase medium to its morphology (or microstructure) continues to be an important fundamental as well as practical question. This paper is concerned with the prediction of the effective electrical conductivity σ^*, of a dilute dispersion of equisized spheres, with conductivity σ_2 and volume fraction ϕ_2, statistically distributed throughout a matrix, with conductivity σ_1 and volume fraction ϕ_1. Of particular interest is the extent to which the connectedness of pairs of inclusions influences σ^* through terms of order ϕ_2^2. Virtually all previous published results for dilute suspensions have dealt with distributions of impenetrable spheres in which the coordination number (i.e., average number of spheres physically touching each sphere) is implicitly taken to be zero and therefore media in which pairs of spheres (monomers) can never combine to form a cluster of size two (i.e., a dimer). In this article the connectedness shall be introduced by allowing the spheres to be penetrable to one another in varying degrees. Such a sphere distribution may serve as a useful model of certain porous media, sintered materials, composite media, and polymer solutions. For reasons of mathematical analogy, results obtained here translate immediately into equivalent results for the dielectric constant, thermal conductivity, or magnetic permeability of two-phase media, or the diffusion coefficient associated with flow past fixed inclusions.

In Sec. II it is shown that a certain decomposition of the expression for σ^* through order ϕ_2^2, derived in the previous paper in this series[1] (henceforth referred to as I), is tantamount to a decomposition of the zero-density limit of the radial distribution function into a sum of two terms: one involving the pair-connectedness function and the other the pair-blocking function. In Sec. III the Beran bounds on σ^* are briefly discussed and, among other things, are employed to derive rigorous upper and lower bounds on the second-order coefficient K_2, associated with the expansion of σ^*, for a general suspension of inclusions of arbitrary shape, in powers of ϕ_2. The derived bounds are shown to depend upon the low-density expansion of the microstructural quantity J_1; an important integral that depends upon a certain three-point probability function. An expression for K_2, exact through third order in $\delta = \sigma_2 - \sigma_1$, is obtained for a general dispersion of spheres. In Sec. IV the low-density expansion of J_1 is evaluated for sphere distributions of variable penetrability and for sphere distributions in which the minimum distance between sphere centers is greater than or equal to $2R$. Finally, an approximation for K_2 of a dispersion of spheres of variable penetrability is obtained and compared to rigorous upper and lower bounds on K_2 derived in the previous section.

II. SECOND-ORDER COEFFICIENT IN TERMS OF CONNECTEDNESS AND BLOCKING FUNCTIONS

In I the cluster expansion for the effective dielectric constant (or equivilently, electrical conductivity) of a dispersion of equisized penetrable spheres of radius R, through all orders in the number of inclusions, was derived. Employing this formalism, an expansion for σ^* of such a statistically isotropic suspension, exact through second order in ϕ_2, was obtained. The second-order coefficient of this expansion K_2 involves various volume integrals which depend upon certain polarizability tensors associated with a single inclusion and pairs of inclusions, and the zero-density limit of the radial distribution functions $g_0(x)$. It was found that it is natural to divide up the region of integration into two parts: one for $x > 2R$, which gives the contribution to K_2 for a *reference* dispersion of totally impenetrable spheres, and one for

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$x<2R$, which gives the contribution to K_2 (over and above the first) due entirely to overlap or clustering effects. It is now noted that this decomposition of the integration region is tantamount to a decomposition of $g_0(x)$ such that

$$g_0(x) = g_0^*(x) + g_0^+(x). \tag{2.1}$$

For arbitrary number density ρ, $g^*(x;\rho)$ is the pair-blocking function and is defined such that $\rho^2 g^*(x;\rho)d\mathbf{r}_1 d\mathbf{r}_2$ is the probability of simultaneously finding the center of a particle in the volume $d\mathbf{r}_1$ about position $\mathbf{r}_1$ and another particle, *not* belonging to the same cluster, in the volume $d\mathbf{r}_2$ about position $\mathbf{r}_2$, where $x = |\mathbf{r}_2 - \mathbf{r}_1|$.[2] The quantity $g^+(x;\rho)$ is the pair-connectedness function and is defined such that $\rho^2 g^+(x;\rho)d\mathbf{r}_1\, d\mathbf{r}_2$ is the probability of simultaneously finding the center of a particle 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 $\mathbf{r}_2$.[2] In Eq. (2.1), $g_0^*(x) \equiv g^*(x;\rho=0)$ and $g_0^+(x) \equiv g^+(x;\rho=0)$. The pair-connectedness function has come to be recognized as a fundamental quantity in studying percolation, clustering, and gelation.[2–4] From this discussion it is clear that

$$g_0^+(x) = 0, \qquad x > 2R \tag{2.2}$$

and

$$g_0^*(x) = 0, \qquad x \leqslant 2R. \tag{2.3}$$

It is conceptually useful to explicitly express σ^* for a dispersion of spheres, through terms of order ϕ_2^2, in terms of the pair-blocking and pair-connectedness functions. Employing the results of I, it is straightforward to show (using a somewhat different notation) that

$$\frac{\sigma^*}{\sigma_1} = 1 + K_1\phi_2 + K_2\phi_2^2, \tag{2.4}$$

where

$$K_1 = \frac{4\pi}{3\sigma_1 V_1}\boldsymbol{\alpha}(1):\mathsf{U} = 3\beta, \tag{2.5}$$

$$K_2 = K_2^* + K_2^+, \tag{2.6}$$

$$K_2^* = A + B, \tag{2.7}$$

$$K_2^+ = C + D + K_1 G, \tag{2.8}$$

$$A = \frac{2\pi}{3\sigma_1 V_1^2}\int d\mathbf{x}\, g_0^*(x)[\boldsymbol{\alpha}(1,2) - 2\boldsymbol{\alpha}(1)]:\mathsf{U} - \frac{4\pi}{3\sigma_1 V_1^2}\int_{x>2R} d\mathbf{x}[\boldsymbol{\alpha}(1|2) - \boldsymbol{\alpha}(1)]:\mathsf{U}, \tag{2.9}$$

$$B = -\frac{4\pi}{3\sigma_1 V_1^2}\int_{x<2R} d\mathbf{x}[\boldsymbol{\alpha}(1|2) - \boldsymbol{\alpha}(1)]:\mathsf{U}, \tag{2.10}$$

$$C = \frac{2\pi}{3\sigma_1 V_1^2}\int d\mathbf{x}\, g_0^+(x)\boldsymbol{\alpha}(1,2):\mathsf{U}, \tag{2.11}$$

$$D = -\frac{4\pi}{3\sigma_1 V_1^2}\int d\mathbf{x}\, g_0^+(x)\boldsymbol{\alpha}(1):\mathsf{U}, \tag{2.12}$$

$$G = \frac{1}{2V_1}\int d\mathbf{x}\, g_0^+(x)\left[1 - \tfrac{3}{4}\frac{x}{R} + \tfrac{1}{16}\frac{x^3}{R^3}\right], \tag{2.13}$$

$$\beta = \frac{\sigma_2 - \sigma_1}{\sigma_2 + 2\sigma_1}, \tag{2.14}$$

and where V_1 is the volume of one sphere, $4\pi R^3/3$. Equation (6.9) of I is essentially the same as Eq. (2.4). The latter expression, unlike the former, is expressed in terms of the connectedness and blocking functions. Both equations state that K_2 [Eq. (2.6)] may be written as the sum of the contribution from a reference dispersion of totally impenetrable spheres K_2^*, characterized by a specific $g_0^*(x)$, and a contribution in excess of K_2^* equal to K_2^+, which results when pairs of inclusions belong to the same cluster. (Note that the expressions in I that correspond to the integrals A, B, C, and D [i.e., Eqs. (5.7)–(5.10), respectively, of I] are incorrectly missing the factor of 3 present in the respective denominators here.[5]) When dimers cannot form in the medium, then $K_2^+ = 0$ and hence $K_2 = K_2^*$.

The quantity $\boldsymbol{\alpha}(1)$ ($= \sigma_1\beta R^3\mathsf{U}$, where U is the unit dyadic), which appears in Eqs. (2.9), (2.10), and (2.12), is the polarizability tensor of a single inclusion centered at $\mathbf{r}_1$.[1] Moreover, the quantities $\boldsymbol{\alpha}(1,2)$ and $\boldsymbol{\alpha}(1|2)$, which arise in Eqs. (2.9)–(2.11), are polarizability tensors associated with pairs of inclusions centered at $\mathbf{r}_1$ and $\mathbf{r}_2$.[1] The first-order coefficient K_1 [Eq. (2.5)] contains no information about the local structure of the medium and was first evaluated by Maxwell.[6] The calculation of the second-order coefficient K_2^* [Eq. (2.7)], however, requires knowledge of the zero-density limit of the pair-blocking function $g_0^*(x)$ for the model, and the solutions of the electrostatic boundary-value problems for one sphere and for two impenetrable spheres (as a function of the separation distance x), in the presence of an applied field $\mathbf{E}_0$. [Jeffrey[7] and Felderhof, Ford, and Cohen[8] have evaluated K_2^* for a certain $g_0^*(x)$—see the Appendix.] In order to compute K_2^+ [Eq. (2.8)], one needs to know the zero-density limit of the pair-connectedness function $g_0^+(x)$ for the model, and the solutions of the boundary-value problems for one sphere and for two interpenetrating spheres, $0 \leqslant x \leqslant 2R$, in the presence of $\mathbf{E}_0$. In the Appendix, certain known results germane to the present work are summarized for the permeable-sphere (PS)[9] and concentric-shell (CS)[1] models in the language of the pair-blocking and pair-connectedness functions.

The evaluation of the two-body cluster integral C, Eq. (2.11), requires knowledge of the polarizability tensor $\boldsymbol{\alpha}(1,2)$ for $0 \leqslant x \leqslant 2R$ and, thus, the solution of the nontrivial boundary-value problem for two interpenetrating spheres; a problem which does not appear to have been solved. Instead of seeking an exact evaluation of the integral C, rigorous bounds on C and, hence, on K_2, for all possible values of the ratio σ_2/σ_1 (i.e., $0 \leqslant \sigma_2/\sigma_1 \leqslant \infty$) in the PS model for arbitrary λ (where λ, $0 \leqslant \lambda \leqslant 1$, is the impenetrability parameter described in the Appendix) is obtained. In doing so, an exact evaluation of C through third order in $(\sigma_2 - \sigma_1)$ for arbitrary λ in the PS model is derived. An approximate expression of C for all σ_2/σ_1 is also obtained and is shown to always lie within the bounds of C.

III. BOUNDS ON THE CONDUCTIVITY OF DILUTE DISPERSIONS OF INCLUSIONS

A. Some general results

Variational bounds on the effective conductivity may be employed to obtain useful rigorous bounds on the second-

order coefficient K_2 for dispersions of inclusions of arbitrary shape. Beran[10] has obtained upper and lower bounds on σ^* for any statistically isotropic two-phase medium given σ_1, σ_2, ϕ_2, and two integrals involving derivatives of certain three-point correlation functions. Torquato and Stell[11] and Milton[12] independently simplified the Beran bound and showed that they may be expressed in terms of σ_1, σ_2, ϕ_2, and a single microstructural parameter J_1 which depends upon a certain three-point probability. Specifically, they found that

$$\sigma_L^* \leqslant \sigma^* \leqslant \sigma_U^*, \tag{3.1}$$

where

$$\sigma_U^* = \left[\langle\sigma\rangle - \frac{\phi_1\phi_2(\sigma_2-\sigma_1)^2}{3\sigma_2 + (\sigma_1-\sigma_2)(\phi_2+2J_1)}\right], \tag{3.2}$$

$$\sigma_L^* = \left[\langle 1/\sigma\rangle - \frac{2\phi_1\phi_2(1/\sigma_2-1/\sigma_1)^2}{3/\sigma_1 + 2(1/\sigma_2-1/\sigma_1)(\phi_1+J_2/2)}\right]^{-1}, \tag{3.3}$$

$$J_1 = \frac{9}{2\phi_1\phi_2} I_1[S_3(r,s,\mu)], \tag{3.4}$$

$$J_2 = 1 - J_1, \tag{3.5}$$

and where I_1 is the integral operator defined by

$$I_1[\,] = \lim_{L\to\infty}\lim_{\Delta\to 0}\int_\Delta^L \frac{dr}{r}\int_\Delta^L \frac{ds}{s}\int_{-1}^1 d\mu[\,]P_2(\mu). \tag{3.6}$$

Here $S_3(r,s,\mu)$ is the three-point probability function which gives the probability of finding the vertices of a triangle with sides of length r and s angle $\cos^{-1}(\mu)$ in phase 1. $P_2(\mu)$ is the Legendre polynomial of order two. Angular brackets denote an ensemble average. The Beran bounds are third-order bounds in the sense that they are exact through third order in $(\sigma_2-\sigma_1)$.

The fact that J_1 lies in the interval [0,1] implies that the third-order Beran bounds always improve upon the well-known second-order bounds due to Hashin and Shtrikman (HS).[13] Since the latter are realized for a certain composite sphere assemblage (CSA) they are the best possible bounds on σ^* for statistically isotropic two-phase composite materials given only σ_1, σ_2, and ϕ_2.[14] For $J_1 = 0$, the upper bound (3.2) coincides with the lower bound (3.3) and is equal to the HS upper bound when $\sigma_2 \geqslant \sigma_1$. Similarly, for $J_2 = 0$, the lower bound (3.3) coincides with the upper bound (3.2) and is equal to the HS lower bound for $\sigma_2 \geqslant \sigma_1$. Hence, $J_1 = 0$ and $J_2 = 0$ for the CSA model corresponding to the HS upper bound and the HS lower bound, respectively.

Progress in the evaluation of the Beran bounds has been very slow since it has been difficult to ascertain the three-point function S_3 for the composite media. Until recently, the only evaluations of the Beran bounds for all realizable ϕ_2 were reported by Corson[15] for a two-phase metal mixture and by Miller[16] for "symmetric-cell" materials. In the last several years considerable progress has been made in the determination of lower-order S_n for realistic models of composite media.[17–23] This has led to evaluations of the important microstructural parameter J_1, Eq. (3.7), and thus the Beran bounds for such models.[11,19,24] The parameter J_1 has also been determined for spatially periodic media.[25] Despite these new developments, the physical significance of the parameter J_1 has yet to be fully elucidated. In Sec. III B, J_1 is, for the first time, obtained exactly through order ϕ_2 for sphere distributions in the PS model for $0 \leqslant \lambda \leqslant 1$, and in the CS model, for $\lambda \geqslant 1$.

For arbitrary microstructures, the Beran upper and lower bounds expanded in powers of ϕ_2 are, through order ϕ_2^2, respectively, given by

$$\frac{\sigma^*}{\sigma_1} \leqslant 1 + \frac{(\sigma_2-\sigma_1)}{\sigma_1}\left[1 - \frac{\beta}{1+2\beta(1-f_0)}\right]\phi_2 + \frac{(\sigma_2-\sigma_1)}{\sigma_1}\beta\left[\frac{1}{1+2\beta(1-f_0)} - \beta(1+2f_1)\right]\phi_2^2 \tag{3.7}$$

and

$$\frac{\sigma^*}{\sigma_1} \geqslant 1 + \frac{(\sigma_2-\sigma_1)}{\sigma_2}\left[1 + \frac{2\beta}{1+\beta(f_0-1)}\right]\phi_2 + \left\{\frac{(\sigma_2-\sigma_1)^2}{\sigma_2^2}\left(1 + \frac{2\beta}{1+\beta(f_0-1)}\right)^2 + \frac{2(\sigma_1-\sigma_2)}{\sigma_2}\beta\left[\frac{1}{1+\beta(f_0-1)} + \beta(2+f_1)\right]\right\}\phi_2^2. \tag{3.8}$$

Assuming that J_1 can be expanded in powers of ϕ_2, the coefficients f_0 and f_1 are defined through the relation

$$J_1 = f_0 + f_1\phi_2 + 0(\phi_2^2). \tag{3.9}$$

Using definition (3.4) and the general results of Torquato and Stell for the S_n,[17] it is easy to show that, for dispersions of inclusions of arbitrary shape, f_0 depends upon one-body information and f_1 depends upon one-body and two-body information, assuming S_3 can be expanded in powers of ϕ_2. The corresponding volume-fraction expansions of the HS bounds (for $\sigma_2 \geqslant \sigma_1$) may be obtained from Eqs. (3.7) and (3.8) by setting $f_0 = 0$ and $f_1 = 0$, and $f_0 = 1$ and $f_1 = 0$, respectively. Note that these bounds do not coincide through first order in ϕ_2.[26]

One may immediately determine the value of f_0 for dispersions of randomly oriented ellipsoids, without directly evaluating the zeroth-order integral of Eq. (3.4), by expanding the dilute-concentration conductivity result of Polder and Van Santen[27] for such a dispersion through third order in $\delta = (\sigma_2-\sigma_1)/\sigma_1$ and comparing this expression to such an expansion of the bounds (3.1), which are exact through order δ^3. When this is done it is found that

$$f_0 = \tfrac{3}{2}[1 - (D_1^2 + D_2^2 + D_3^2)], \tag{3.10}$$

where the D_i are the depolarization factors of the ellipsoid.[28] For example, for a needle-shaped ($D_1 = D_2 = 1/2$, $D_3 = 0$), disk-shaped ($D_1 = D_2 = 0$, $D_3 = 1$), and sphere-shaped ($D_1 = D_2 = D_3 = 1/3$) inclusion, $f_0 = 3/4$, $f_0 = 0$, and $f_0 = 1$, respectively. In general, therefore, the value of the parameter J_1 at $\phi_2 = 0$ depends upon the shape of the inclusion. Clearly, the slope of J_1 (i.e., f_1) will generally involve not only information about the shape of the inclusion but also information concerning the relative position of the two inclusions, i.e., it depends on $g_0^*(x)$ and $g_0^+(x)$.

For distributions of spheres, therefore, the bounds (3.7) and (3.8), respectively reduce to

$$\frac{\sigma^*}{\sigma_1} \leqslant 1 + 3\beta\phi_2 + K_2^U\phi_2^2 \tag{3.11}$$

and

$$\frac{\sigma^*}{\sigma_1} \geqslant 1 + 3\beta\phi_2 + K_2^L\phi_2^2, \tag{3.12}$$

where

$$K_2^U = 3\beta^2 - \frac{2(\sigma_2-\sigma_1)^3}{\sigma_1(\sigma_2+2\sigma_1)^2} f_1 \tag{3.13}$$

and

$$K_2^L = 3\beta^2 - \frac{2(\sigma_2-\sigma_1)^3}{\sigma_2(\sigma_2+2\sigma_1)^2} f_1. \tag{3.14}$$

It is seen that the third-order Beran bounds for sphere distributions, unlike the second-order HS bounds, coincide through order ϕ_2 because of the incorporation of information regarding the shape of the inclusion as contained in f_0. Equations (3.7), (3.8), and (3.10) show that the Beran bounds do not, in general, coincide through order ϕ_2 for inclusions of arbitrary shape. Since Eqs. (3.11) and (3.12) coincide through order ϕ_2, then we have the following upper and lower bounds on the second-order coefficient, $K_2 = K_2^* + K_2^+$,

$$K_2^L \leqslant K_2 \leqslant K_2^U, \tag{3.15}$$

or

$$-\left[A + D + 3\beta G + \frac{2(\sigma_2-\sigma_1)^3}{\sigma_2(\sigma_2+2\sigma_1)^2} f_1\right] \leqslant C \leqslant -\left[A + D + 3\beta G + \frac{2(\sigma_2-\sigma_1)^3}{\sigma_1(\sigma_2+2\sigma_1)^2} f_1\right], \tag{3.16}$$

where Eqs. (2.5)–(2.8) and (A8) have been employed. Since A is given by Eq. (A7) for the $g_0^*(x)$ defined in the Appendix and because D and G are easily calculated for models in which the zero-density limit of the pair-connectedness function g_0^+ is nonzero, relation (3.16) provides bounds on C, i.e., the nontrivial contribution to K_2^+. Although bounds (3.11) and (3.12) include some information regarding the distribution of pairs of inclusions (by virtue of their respective dependence upon f_1), it is incomplete and therefore the bounds for $\sigma_2 \neq \sigma_1$ do not coincide through order ϕ_2^2, i.e., $K_2^L \neq K_2^U$. The coefficients K_2^U and K_2^L diverge to positive infinity as $\sigma_2/\sigma_1 \to \infty$ and to negative infinity as $\sigma_2/\sigma_1 \to 0$, respectively. This does not mean, however, that the bounds are not useful under such conditions since K_2^U and K_2^L shall be shown to remain finite and provide reasonable estimates of the exact second-order coefficient when $\sigma_2/\sigma_1 \to 0$ and when $\sigma_2/\sigma_1 \to \infty$, respectively.

B. J_1 For dilute dispersions of spheres in the PS and CS models

In order to apply the bonds (3.11) and (3.12) for sphere distributions, the first-order coefficient f_1 [defined by Eq. (3.9)] must be known for the model. Hence, consider obtaining the expansion of the integral $I_1[S_3]$, given by Eq. (3.4), in powers of ϕ_2 through order ϕ_2^2. If one applies the results of Torquato and Stell for the S_n[17] and decomposes the zero-density limit of the radial distribution function according to Eq. (2.1), then it is easy to show that the probability of finding three points with position vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ in the matrix phase has the following expansion in reduced density $\eta = \rho 4\pi R^3/3$:

$$S_3(r_{12},r_{13},\mu) = 1 + S_3^{(1)}(r_{12},r_{13},\mu)\eta + S_3^{(2)}(r_{12},r_{13},\mu)\eta^2 + O(\eta^3), \tag{3.17}$$

where

$$S_3^{(1)} = -\frac{1}{V_1}\int_V \left\{1 - \prod_{i=1}^{3}[1 - m(r_{i4})]\right\} d\mathbf{r}_4, \tag{3.18}$$

$$S_3^{(2)} = S_3^{(2)*} + S_3^{(2)+}, \tag{3.19}$$

$$S_3^{(2)*} = \frac{1}{2V_1^2}\int_V\int_V g_0^*(r_{45}) \prod_{j=4}^{5}\left\{1 - \prod_{i=1}^{3}[1 - m(r_{ij})]\right\} d\mathbf{r}_j, \tag{3.20}$$

$$S_3^{(2)+} = \frac{1}{2V_1^2}\int_V\int_V g_0^+(r_{45}) \prod_{j=4}^{5}\left\{1 - \prod_{i=1}^{3}[1 - m(r_{ij})]\right\} d\mathbf{r}_j, \tag{3.21}$$

$$m(r) = \begin{cases} 1, & r < R \\ 0, & r > R \end{cases}, \tag{3.22}$$

$r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$, and $\mu = \mathbf{r}_{12}\cdot\mathbf{r}_{13}/(r_{12}r_{13})$. Each volume integral given above is to be integrated over the sample volume V with the understanding that $V \to \infty$. Note that the first-order coefficient $S_3^{(1)}$ is, in general, a single-body integral and as such depends only upon the geometry of the inclusions through the appearance in the integral of the step function m, which is nonzero whenever the position vector (measured with respect to the center of mass of the inclusion) is inside the inclusion. Equation (3.18) is trivially related to the union volume of three spheres of radius R.[17,19] The second-order coefficient $S_3^{(2)}$ is a two-body integral and therefore may be written as a sum involving an integral depending upon g_0^* and one depending upon g_0^+. Combining Eqs. (3.6) and (3.17)–(3.21) gives through order η^2

$$I_1[S_3] = I_1[S_3^{(1)}]\eta + \{I_1[S_3^{(2)*}] + I_1[S_3^{(2)+}]\}\eta^2. \tag{3.23}$$

Employing the relationship between η and ϕ_2 derived in I, one has

$$I_1[S_3] = I_1[S_3^{(1)}]\phi_2 + \{I_1[S_3^{(2)*}] + I_1[S_3^{(2)+}] + GI_1[S_3^{(1)}]\}\phi_2^2 + O(\phi_2^3), \tag{3.24}$$

where G is given by Eq. (2.13).

Use of Eqs. (3.4), (3.9), and (3.24) yields

$$f_0 = \tfrac{9}{2} I_1[S_3^{(1)}] = 1, \tag{3.25}$$

$$f_1^* = \tfrac{9}{2}\{I_1[S_3^{(2)*}] + I_1[S_3^{(1)}]\}, \tag{3.26}$$

$$f_1^+ = \tfrac{9}{2}\{I_1[S_3^{(2)+}] + GI_1[S_3^{(1)}]\}, \tag{3.27}$$

and

$$f_1 = f_1^* + f_1^+. \tag{3.28}$$

The zeroth-order coefficient f_0, equal to 1 for any sphere distribution, was determined in Sec. III A without directly evaluating the integral $I_1[S_3^{(1)}]$. Lado and Torquato[24] have recently computed this integral analytically.

The quantities f_1^* and f_1^+ are, respectively, the contributions to the first-order coefficient f_1 from a reference system of a dispersion of totally impenetrable spheres and from effects which arise when pairs of inclusions belong to the same cluster. The ninefold integrals $I_1[S_3^{(2)*}]$ and $I_1[S_3^{(2)+}]$, appearing in Eqs. (3.26) and (3.27), respectively,

are evaluated in the PS model, for $0<\lambda<1$, and the CS model, for $\lambda\geqslant 1$, by expanding appropriate terms in the integrals in spherical harmonics. By employing the standard addition theorem for spherical harmonics and by using their orthogonality properties the original integrals are substantially simplified. This technique has been used by Barker and Monaghan[29] to calculate virial coefficients and has recently been applied by Lado and Torquato[24] to evaluate $I_1[S_3]$ for distributions of totally impenetrable spheres ($\lambda = 1$) where $I_1[S_3^{(2)+}] = G = 0$ and hence where $f_1^+ = 0$. For this reason we do not present any details of the calculations but instead simply report the final results.

In the PS model,

$$f_1^* = \tfrac{3}{16}\ln 3 - \tfrac{5}{12} = -0.210\,68, \tag{3.29}$$

$$I_1[S_3^{(2)+}] = -0.189\,06(1-\lambda), \tag{3.30}$$

and therefore using Eqs. (3.27) and (A11) yields

$$f_1^+ = -0.350\,78(1-\lambda) \tag{3.31}$$

and

$$J_1 = 1 - [0.210\,68 + 0.350\,78(1-\lambda)]\phi_2. \tag{3.32}$$

In arriving at these expressions Eqs. (A1) and (A2) have been employed. Result (3.29) was first obtained by Felderhof[30] using a method which did not directly make use of $S_3^{(2)*}$. Lado and Torquato[24] later also obtained this result employing the spherical-harmonics technique described above. All but two of the six cluster integrals which contribute to $I_1[S_3^{(2)+}]$ could be evaluated analytically. Two of these cluster integrals (i.e., the ones involving five m bonds and six m bonds, respectively) could only be reduced to rapidly converging sums of three-dimensional integrals, which had to be evaluated numerically.[31]

For dispersions of spheres in which monomers can only exist [i.e., when $g_0^+(x) = 0$ for all x], it is of interest to study the effect of the zero-density limit of the pair-blocking function $g_0^*(x)$ on $I_1[S_3^{(2)*}]$. To do so, consider evaluating $I_1[S_3^{(2)*}]$ in the CS model as a function of λ, for $\lambda\geqslant 1$. Employing the integration procedure described above and Eqs. (3.6), (3.20), (3.21), (3.26), (3.27), (A5), and (A6), it is found that in this model

$$f_1^* = \tfrac{3}{16}\ln\left[\frac{2\lambda+1}{2\lambda-1}\right] - \frac{3\lambda(4\lambda^2+1)}{4(4\lambda^2-1)^2}, \tag{3.33}$$

$$f_1^+ = 0, \tag{3.34}$$

and

$$J_1 = 1 + \left\{\tfrac{3}{16}\ln\left[\frac{2\lambda+1}{2\lambda-1}\right] - \frac{3\lambda(4\lambda^2+1)}{4(4\lambda^2-1)^2}\right\}\phi_2. \tag{3.35}$$

In general, the first derivative of J_1 with respect to ϕ_2 reflects not only information about the shape of the inclusion but also depends upon the distribution of pairs of inclusions when they are not part of the same cluster and the distribution of pairs of inclusions when they are part of the same cluster. From Eq. (3.32) it is seen that the magnitude of the first derivative of J_1 increases monotonically from its minimum value of 0.210 68 for $\lambda = 1$ (i.e., for the reference suspension of totally impenetrable spheres) to its maximum value of 0.561 46 for the case of fully penetrable spheres (i.e., $\lambda = 0$), demonstrating that the contribution to it due to overlap effects can be quite substantial. Therefore, the largest discrepancy between bound (3.12) and the HS lower bound will arise when $\lambda = 0$ since this corresponds to the maximum deviation of J_1 from 1. On the other hand, when only monomers are present in the dispersion, Eq. (3.35) indicates that the magnitude of the slope of J_1 decreases monotonically from its maximum value of 0.210 68 for $\lambda = 1$ to its minimum value of zero when the particles are well separated, i.e., for $\lambda\gg 1$. Therefore, for $\lambda\gg 1$, $J_1\sim 1$, implying that the bounds (3.11) and (3.12) coincide and therefore to this order correspond to the CSA model associated with the HS lower bound for $\sigma_2>\sigma_1$. Furthermore, this means that, through order ϕ_2, $J_1 = 1$, or $f_1 = 0$ for regular arrays of spheres (see the Appendix).

IV. APPROXIMATE EXPRESSION FOR THE SECOND-ORDER COEFFICIENT K_2 IN THE PS MODEL

The cluster integral C [Eq. (2.11)] in the PS model through third order in $\delta = (\sigma_2-\sigma_1)/\sigma_1$, is given exactly by

$$C = \tfrac{15}{2}(1-\lambda)\delta - \tfrac{5}{2}(1-\lambda)\delta^2 + 0.911\,28(1-\lambda)\delta^3. \tag{4.1}$$

This result is obtained by expanding Eq. (2.4) through third order in δ and comparing to such an expansion of either bounds (3.11) or (3.12),[32] both of which are exact through order δ^3. Moreover, Eqs. (3.32), (A9), and (A11) are employed here.

It is interesting to note that the first two terms of Eq. (4.1) are rigorously equal to the corresponding terms that would result by assuming that the field induced within the two overlapping spheres (whose centers are separated by the distance x), in a uniform applied field $\mathbf{E}_0$, is equal to the field induced within a single ellipsoid, having a major axis of length $R + x/2$ and two minor axes both equal to R, in the presence of $\mathbf{E}_0$. Although this assumption is at its worst for x near $2R$ (i.e., for slightly overlapping configurations), it is a reasonable one for most other values of x.

This suggests that such an approximation may be profitably used to estimate the effect of overlap on C and thus on K_2. Specifically, using the exact results of Polder and Van Santen[27] for randomly oriented ellipsoids, one has

$$C \cong \frac{(\sigma_2-\sigma_1)}{6\sigma_1 V_1^2}\int d\mathbf{x}\, g_0^+(x)V_2(x) \times\left[\frac{\sigma_1}{\sigma_1+(\sigma_2-\sigma_1)D_1(x)} + \frac{2\sigma_1}{\sigma_1+(\sigma_2-\sigma_1)D_2(x)}\right], \tag{4.2}$$

where $V_2(x)$ is the actual volume occupied by two intersecting equisized spheres of radius R whose centers are separated by a distance x, i.e., it is the union volume of two such spheres:

$$V_2(x) = \begin{cases} \dfrac{4\pi}{3}R^3\left[1+\dfrac{3}{4}x-\dfrac{x^3}{16}\right], & x<2R \\ \dfrac{8\pi R^3}{3}, & x>2R\,. \end{cases} \tag{4.3}$$

$D_1(x)$ and $D_2(x) = D_3(x)$ are the depolarization factors associated with the major axis and minor axes, respectively. In general, the depolarization factors must satisfy the following relation:

$$D_1 + D_2 + D_3 = 1. \tag{4.4}$$

Equation (4.2) is easily numerically evaluated for all σ_2/σ_1 in the PS model using tablulated values of D_i.[28] Noting that the D_i are weak functions of x for $0 \leqslant x \leqslant 2R$, we also computed C in the PS model by assuming the D_i are undetermined constants. The constants D_i are then determined by requiring the resulting integral, through order δ^3, to agree with Eq. (4.1) and by employing conditon (4.4). The latter approximate method gives results which are in excellent agreement with the numerical evaluation of Eq. (4.2) for all σ_2/σ_1 and λ, i.e., the maximum error, which occurs at the extreme condition $\sigma_2/\sigma_1 = \infty$, is less than 1%. In the PS model, the approximate evaluation of Eq. (4.2) yields

$$C(\lambda) = \tfrac{5}{2}(1-\lambda)\left[\frac{\delta}{1+\delta D_1} + \frac{2\delta}{1+\delta D_2}\right], \tag{4.5}$$

where

$$D_1 = 0.189\,16$$

and

$$D_2 = 0.405\,42.$$

Employing the results given immediately above and Eqs. (2.5)–(2.8), the second-order coefficient of Eq. (2.6) is, in the PS model, given approximately by

$$K_2 \cong A + B + \tfrac{5}{2}(1-\lambda)\left[\frac{\delta}{1+\delta(0.189\,16)} + \frac{2\delta}{1+\delta(0.405\,42)} - 9\beta\right]. \tag{4.6}$$

Here A and B, given, respectively, by Eqs. (A7) and (A8), are the contributions from the reference dispersion of totally impenetrable spheres characterized by a $g_0^*(x)$ defined by Eq. (A1).

TABLE I. Tablulation of second-order coefficients K_2^U, K_2^L and K_2 [Eqs. (3.13), (3.14), and (4.6), respectively] in the PS model at $\lambda = 0$ (i.e., fully penetrable spheres) for various values of σ_2/σ_1. For purposes of comparison, the coefficient K_2^*, the value of K_2 when $\lambda = 1$, for the same values of σ_2/σ_1 is included.

σ_2/σ_1	K_2^U	K_2^L	K_2	K_2^*
0	0.469	$-\infty$	0.345	0.588
0.02	0.447	−12.2	0.336	0.558
0.1	0.365	−1.31	0.296	0.450
0.5	0.096	0.075	0.094	0.110
1.0	0	0	0	0
2.0	0.258	0.223	0.243	0.208
5.0	2.45	1.28	1.69	1.23
50.0	51.5	3.64	6.37	3.90
∞	∞	4.12	7.56	4.51

V. RESULTS

Table I demonstrates that approximation (4.6) for K_2 always lies between the upper bound (3.13) and lower bound (3.14) for the case of fully penetrable spheres (i.e., $\lambda = 0$). This is also true for any other value of λ in the PS model. At the extreme instance of a perfectly conducting particle phase (i.e., $\sigma_2/\sigma_1 \to \infty$) the second-order coefficient for $\lambda = 0$ is seen to be almost twice as large as K_2^*, i.e., the second-order coefficient of the reference dispersion of totally impenetrable spheres. For a perfectly insulating particle phase, allowing the spheres to overlap depresses the value of the second-order coefficient K_2 relative to K_2^*, as expected. These last two points are also illustrated in Fig. 1 where K_2 is given as a function of $\log(\sigma_2/\sigma_1)$ for $\lambda = 0$, 0.5, and 1. The deviation of K_2 from the curve corresponding to K_2^* is clearly K_2^+, the entire overlap contribution.

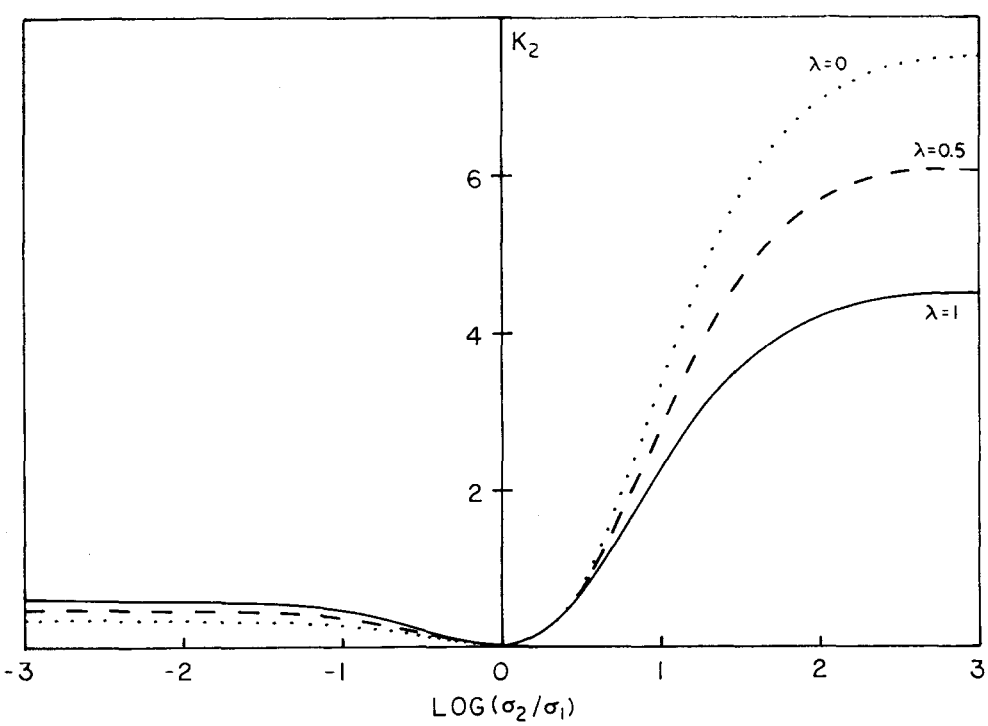

FIG. 1. The second-order coefficient K_2 [Eq. (4.6)] in the PS model as a function of $\log(\sigma_2/\sigma_1)$ for $\lambda = 1$ (which is Jeffrey's result[7]), $\lambda = 0.5$ and $\lambda = 0$ (which corresponds to a dispersion of fully penetrable spheres). The deviation of $K_2(\lambda)$ from $K_2(\lambda = 1)$ is precisely K_2^+ defined by Eq. (2.6).

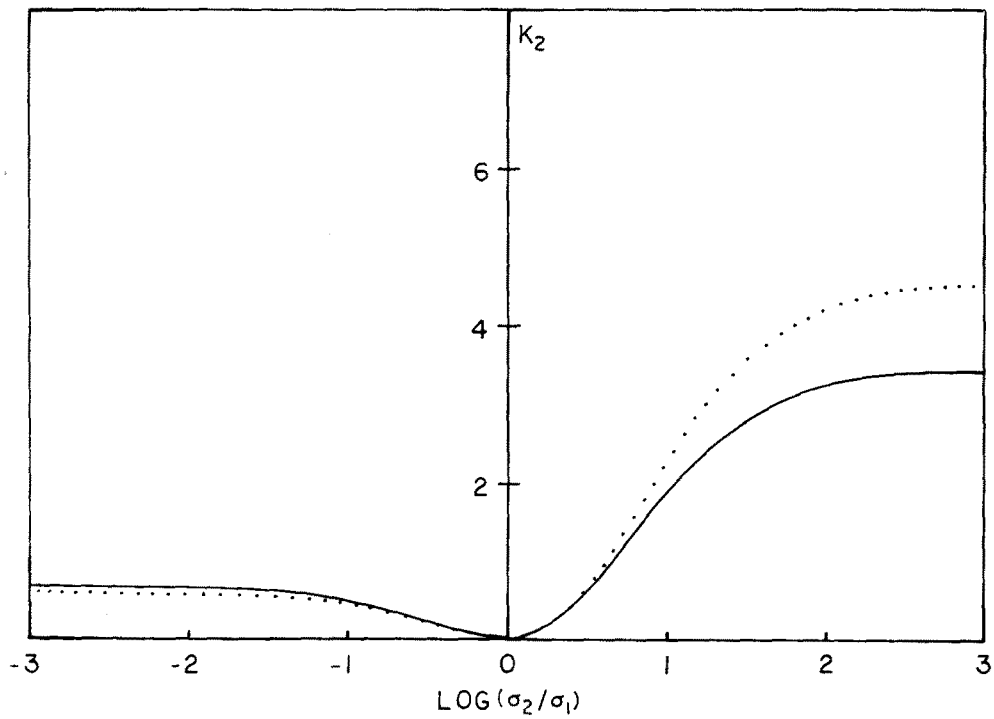

FIG. 2. The second-order coefficient K_2 [Eq. (4.6)] in the PS model as a function of $\log(\sigma_2/\sigma_1)$ at $\lambda = 1(\cdots)$, and for both $\sigma_2 > \sigma_1$ and $\sigma_1 > \sigma_2$, compared to K_2^U [Eq. (3.13)] at $\lambda = 1$ for $\sigma_1 < \sigma_2$(—) and to K_2^L [Eq. (3.14)] at $\lambda = 1$ for $\sigma_2 > \sigma_1$ (—), as functions of $\log(\sigma_2/\sigma_1)$.

In general, it is the upper bound, rather than the lower bound, that provides the better estimate of K_2 and thus of σ^* (through order ϕ_2^2) when the particle phase is less conducting than the matrix phase [i.e., $(\sigma_2/\sigma_1 < 1)$]. On the other hand, the lower bound gives the better estimate of the aforementioned quantities when the particle phase is conducting relative to the matrix phase [i.e., $(\sigma_2/\sigma_1) > 1$]. However, as λ decreases from its maximum value of 1 to its minimum value of 0, Figs. 2–4 illustrate that the magnitude of the deviations $K_2 - K_2^U$, for $\sigma_2/\sigma_1 < 1$, and $K_2 - K_2^L$, for $\sigma_2/\sigma_1 > 1$, increase, respectively, from their minimum values to their maximum values. These deviations, as λ decreases, must in fact become larger when terms of higher order than ϕ_2^2 are included. Indeed, a dispersion of fully penetrable spheres percolates at a value of ϕ_2 approximately equal to 0.3,[33] yet the Beran lower bound for this model at $\sigma_2/\sigma_1 = \infty$ and $\phi_2 = 0.3$ remains finite and only slightly above the corresponding value of the HS lower bound.[13]

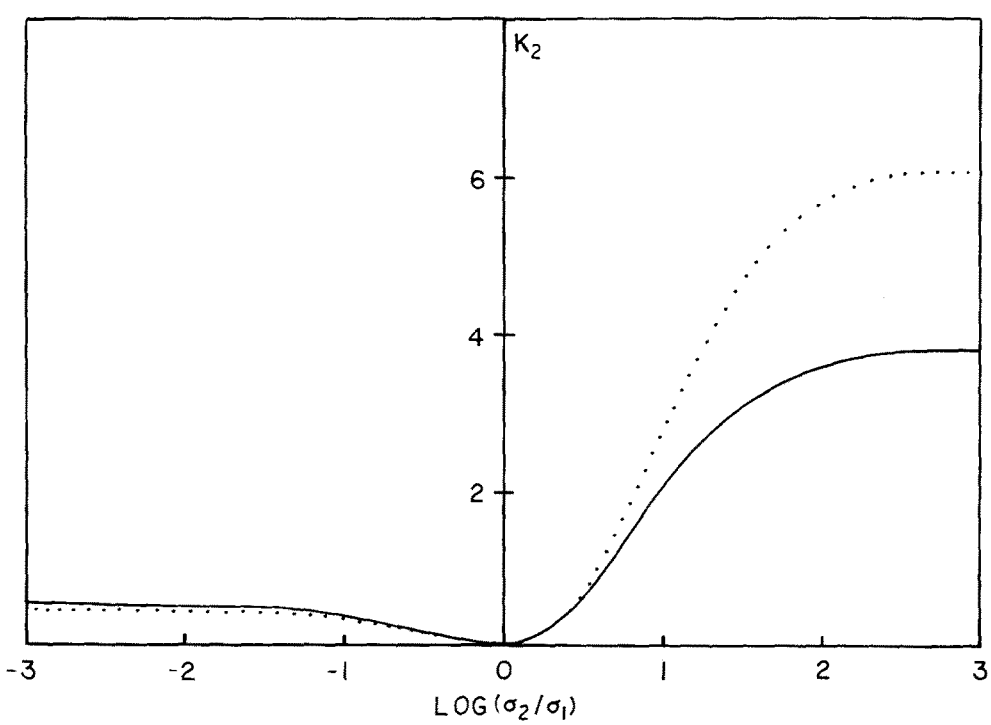

FIG. 3. As for Fig. 2 with $\lambda = 0.5$.

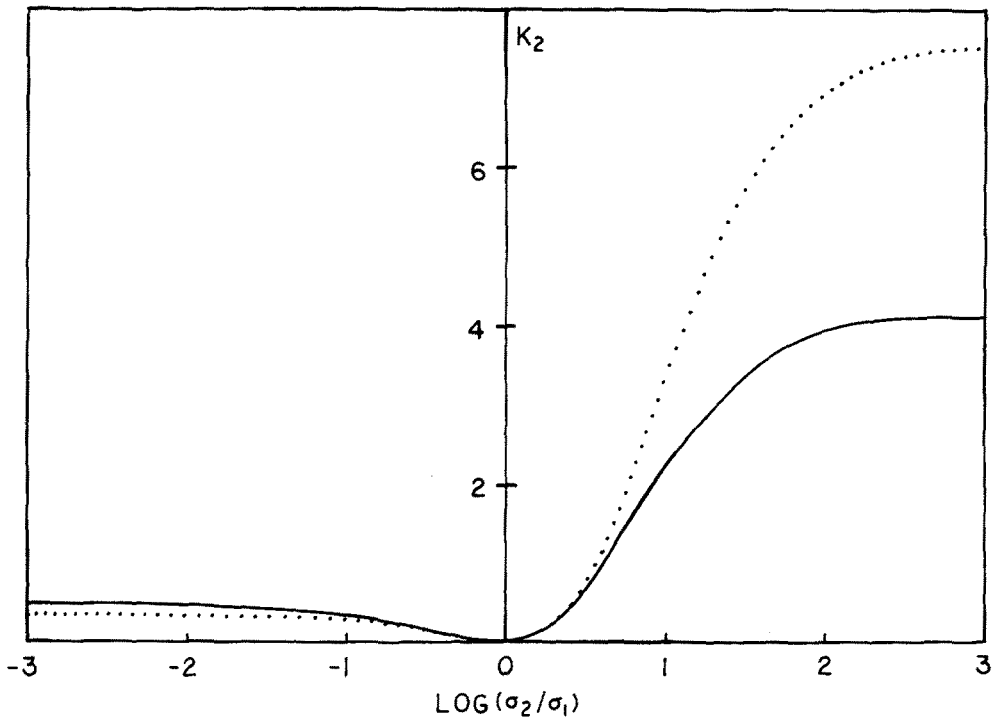

FIG. 4. As for Fig. 3 with $\lambda = 0$ (i.e., dispersion of fully penetrable spheres).

It is seen, therefore, that approximation (4.6) not only lies within the rigorous bounds (3.13) and (3.14) for arbitrary λ and σ_2/σ_1 in the PS model (and hence is exact through order δ^3), but it contains the salient features that come into play when particles overlap for all σ_2/σ_1 and λ. Expression (4.6) is expected to yield good estimates of K_2 for $0.1 \leqslant \sigma_2/\sigma_1 < 10$ and any λ and, at the very least, should provide the proper qualitative behavior of K_2, for arbitrary λ, for $\sigma_2/\sigma_1 > 10$ and $\sigma_2/\sigma_1 < 0.1$.

Upper and lower bounds on K_2 in the CS model for $\lambda \geqslant 1$ may be obtained by employing Eqs. (3.13), (3.14), and (3.35). In Fig. 5 such bounds are given as a function of $\log(\sigma_2/\sigma_1)$ for $\lambda = 2$ and $\lambda = 4$. As the minimum distance between sphere centers increases (i.e., as λ is made larger), the bound width decreases and asymptotically approaches zero, i.e., for $\lambda \gg 1$, $K_2^U \sim 3\beta^2$ and $K_2^L \sim 3\beta^2$. For $\sigma_2 > \sigma_1$ and for $\sigma_1 > \sigma_2$, the lower and upper bounds depicted in Fig. 5, respectively are indistinguishable from one another and are nearly equal to

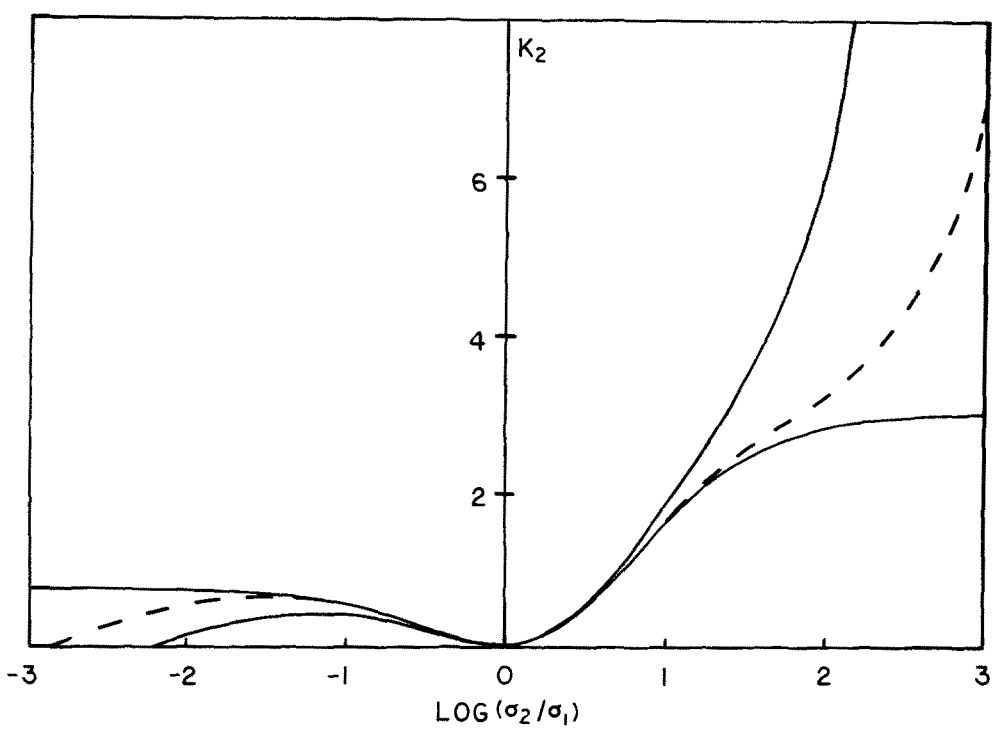

FIG. 5. Upper and lower bounds, K_2^U [Eq. (3.13)] and K_2^L [Eq. (3.14)] in the CS model as a function of $\log(\sigma_2/\sigma_1)$ for $\lambda = 2$(—) and $\lambda = 4$(---). For $\sigma_2 > \sigma_1$, the lower bound for $\lambda = 2$ is indistinguishable from the lower bound for $\lambda = 4$ on the scale of this figure. For $\sigma_1 > \sigma_2$, the upper bounds are indistinguishable from one another on the scale of this figure.

$3\beta^2$; the result for the well-separated dispersion described in the Appendix.

For dispersions of impenetrable spheres characterized by a coordination number equal to zero, it has long been known that for $\sigma_2 > \sigma_1$ the HS bound provides a good approximation to σ^* over a large range of σ_2/σ_1 and ϕ_2.[34] The analysis above, however, demonstrates that second- and third-order lower bounds are not as useful in estimating σ^*, at arbitrary ϕ_2 and large σ_2/σ_1, for dispersions of spheres in which clusters of various sizes may form at values of ϕ_2 below that of the percolation-threshold value of dispersions of totally impenetrable spheres in which the percolation transition and close-packing limit[35] occur at the same ϕ_2.

ACKNOWLEDGMENTS

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APPENDIX: SOME RESULTS IN THE PS AND CS MODELS

Using the definitions of the pair-blocking and pair-connectedness functions given in Sec. II, $g_0^*(x)$ and $g_0^+(x)$ may be immediately obtained in the PS[9] and CS[1] models discussed in I. In the PS model,

$$g_0^*(x) = \begin{cases} 0, & x \leqslant 2R \\ 1, & x > 2R \end{cases} \tag{A1}$$

and

$$g_0^+(x) = \begin{cases} 1-\lambda, & x \leqslant 2R \\ 0, & x > 2R. \end{cases} \tag{A2}$$

For the class of CS models described in I, one has, for $0 \leqslant \lambda \leqslant 1$,

$$g_0^*(x) = \begin{cases} 0, & x \leqslant 2R \\ 1, & x > 2R \end{cases} \tag{A3}$$

and

$$g_0^+(x) = \begin{cases} 0, & x \leqslant 2R\lambda \\ 1, & 2R\lambda < x \leqslant 2R \\ 0, & x > 2R, \end{cases} \tag{A4}$$

and for $\lambda \geqslant 1$,

$$g_0^*(x) = \begin{cases} 0, & x \leqslant 2R\lambda \\ 1, & x > 2R\lambda \end{cases} \tag{A5}$$

and

$$g_0^+(x) = 0, \qquad 0 \leqslant x \leqslant \infty. \tag{A6}$$

For the models described by Eqs. (A1)–(A4), $g_0^*(x)$ is the same and the impenetrability of the inclusions is characterized by the parameter λ whose value varies between zero, in the case of fully penetrable spheres (i.e., randomly centered spheres) and unity in the case of totally impenetrable spheres. In the PS model, the probability that the spheres overlap is given by the constant $1-\lambda$. Note that when $0 \leqslant \lambda \leqslant 1$ in the CS model, each sphere of radius R may be thought of as being composed of an impenetrable core of radius λR, encompassed by a perfectly penetrable concentric shell of thickness $(1-\lambda)R$. (In I this subset of the CS model was referred to as the penetrable concentric-shell model.) For $\lambda > 1$ in the CS model, there is an impenetrable shell of thickness $(\lambda - 1)R$ that encompasses each sphere, and hence only monomers can exist. In the PS model and the CS model for $\lambda \leqslant 1$, the concept of connectivity is equivalent to that of overlap. Note that for $\lambda = 1$ (i.e., totally impenetrable spheres) in the models considered above, the function $g_0^+(x)$ is zero even when the particles touch, i.e., the coordination number is zero. For totally impenetrable sphere distributions in which the coordination number is nonzero, the radial distribution function and, therefore, the pair-connectedness function must be characterized by a singular contribution when the spheres are in contact. For example, in the adhesive-sphere model of Baxter[36] the zero-density limit of the radial distribution function at contact involves a Dirac-delta function contribution and hence, according to Eqs. (2.1)–(2.3), so does the zero-density limit of the pair-connectedness function. The full pair-connectedness functions in the PS and adhesive-sphere models were determined by Chiew and Glandt[3] in the Percus-Yevick approximation.

Consider the evaluation of K_2^*, Eq. (2.7), for dispersions of spheres characterized by a $g_0^*(x)$ given by Eq. (A1). Such a calculation has been reported by Jeffrey[7] and by Felderhof, Ford, and Cohen[8] employing a radial distribution function equal to Eq. (A1). Jeffrey[7] found that

$$A = 3\beta^2 \sum_{n=6}^{\infty} \frac{C_n}{(n-3)2^{n-3}}, \tag{A7}$$

where the coefficients C_n are functions of β (and are equivalent to $B_n - 3A_n$ in Jeffrey's notation) and A is given by Eq. (2.9). It was shown by Jeffrey that

$$B = 3\beta^2, \tag{A8}$$

where β is given by Eq. (2.14). He noted that if the dispersion is one in which the average distance between nearest neighbors d is such that $d \gg 2R$ [and therefore a suspension not characterized by Eq. (A1)], then $A\phi_2^2$ [where A is defined through Eqs. (2.7) and (2.9)] is of smaller order than ϕ_2^2, implying that B is the only contribution to K_2^* for such a well-separated suspension. Furthermore, through order ϕ_2^2, the expression for σ_e of regular arrays of spheres[37,38] is equal to the conductivity of a well-separated dispersion.

Consider the trivial contribution D, Eq. (2.12), to the excess quantity K_2^+, Eq. (2.8). Using Eqs. (A2) and (A4) and the polarizability tensor of a sphere, it is easy to show that the cluster integral D, Eq. (2.14), in the PS model and in the CS model for $0 \leqslant \lambda \leqslant 1$ [defined by Eq. (A4)] is, respectively, given by[1]

$$D = -24\beta(1-\lambda) \tag{A9}$$

and

$$D = -24\beta(1-\lambda^3). \tag{A10}$$

Moreover, the integral G, Eq. (2.13), in the PS model and CS model for $0 \leqslant \lambda \leqslant 1$ is, respectively, equal to[1]

$$G = \frac{(1-\lambda)}{2} \tag{A11}$$

and

$$G = 4(1-\lambda^3) - \tfrac{9}{2}(1-\lambda^4) + (1-\lambda^6). \tag{A12}$$

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[32]This comparison also yields that $a_3 = -2f_1^*/9 = -0.046\,818$ in the PS model, where Eq. (3.29) has been used. Here a_3 is the third-order coefficient of an expansion of the integral (2.9) in powers of $\delta = (\sigma_2 - \sigma_1)/\sigma_1$.

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