Microstructure of two-phase random media. III. The *n*-point matrix probability functions for fully penetrable spheres

S. Torquato

Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina 27607

G. Stell

Departments of Mechanical Engineering and Chemistry, State University of New York, Stony Brook, New York 11794
(Received 14 December 1982; accepted 27 April 1983)

We examine the n-point matrix probability functions S_n (which give the probability of finding n points in the matrix phase of a two-phase random medium), for a model in which the included material consists of fully penetrable spheres of equal diameter (i.e., a system of identical spheres such that their centers are randomly distributed in the matrix). Exploiting the special simplicity of the model we give an explicit closed-form expression for S_3 as well as sharp bounds on S_3 and S_4. Our best lower bound on S_3 and our corresponding upper bound on S_4 satisfy certain asymptotic forms (for both small and large separation of points) that are satisfied by the exact S_3 and S_4 for impenetrable as well as penetrable spheres, even though the bounding properties of our expressions can only be guaranteed for penetrable spheres. These expressions (and the resulting approximation for S_4 in terms of S_1 and S_2 obtained from them) are thus highly appropriate approximants for both systems to be used in composite-media transport-coefficient expressions that involve integrals over the S_n. The S_3 expression has in fact been suggested some time ago by Weissberg and Prager; our methods here provide further justification for this expression as well as one means of systematically generalizing it to S_n for higher n.

I. INTRODUCTION

This is the third of a series of papers on the microstructure of two-phase random media. In the first two papers of this series,[1,2] we examined the microstructure of media composed of spheres in a uniform matrix. We related n-point matrix probability functions, S_n (which give the probability of finding n points in the matrix phase), to n-body distribution functions (which describe spatial correlations between n sphere centers) for any n, we showed how the Mayer–Montroll and Kirkwood–Salsburg hierarchies of statistical mechanics, for a certain binary mixture, become equations for the S_n, and we obtained rigorous upper and lower bounds on the S_n. The aforementioned work was formal in nature to the extent that the results were not used to calculate the S_n for particular interparticle potentials. The object of this study is to further examine the S_n for a system of fully penetrable spheres (i.e., a system of spheres such that the particle centers are completely uncorrelated), exploiting the special simplicity of the model in order to obtain sharper results than those that come out of a general analysis. Such a model might be used in instances in which the actual two-phase material possesses included regions of nearly random shape and size[3–5]; it has been employed, with success, by Weissberg,[6] Weissberg and Prager,[7,8] DeVera and Strieder,[9] and Torquato and Stell[10] for the purpose of predicting various bulk properties of two-phase random media.

In what follows, we give an explicit expression for S_3 in terms of S_1, S_2 (which are elementary[6] for this model) and the intersection volume of three spheres (apparently for the first time, although the various ingredients for such an expression have long been known). We also give the expression for the four-point matrix probability function in terms of S_1, S_2, S_3, and the intersection volume of four spheres. We then obtain rigorous upper and lower bounds on both S_3 and S_4 using simple geometrical arguments. Such bounds appear good enough to be used as approximations for these lower-order n-point matrix functions when they appear in the rather complicated integrals that must be used in evaluating certain transport properties[10] of the model.

We use the phrase "*fully* penetrable spheres" frequently in this paper, in describing the model we study, rather than just penetrable spheres or "overlapping spheres." This is because it is easy to define models of included particles that are mutually penetrable only upon the expenditure of some energy, and, further, to parametrize the interaction potential associated with pairs of such particles so that the model includes impenetrable spheres at one end of the range of parametrization and fully penetrable spheres at the other. One of us has already considered such a model—the "permeable sphere" model—in another context,[11] and we utilize it in a subsequent study of two-phase media as well.[10]

For the reasons discussed in Sec. IV we expect both our lower bound on S_3 and our approximant for S_4 in terms of S_1 and S_2 to represent useful approximations for impenetrable spheres (and for the permeable-sphere model) as well as for fully penetrable spheres. The expression for S_3 has already been suggested on essentially the same grounds for impenetrable spheres by Weissberg and Prager.[13] Our bounds on S_3 and S_4 and the latter's approximant in terms of S_1 and S_2 are new.

 0021-9606/83/151505-06$02.10

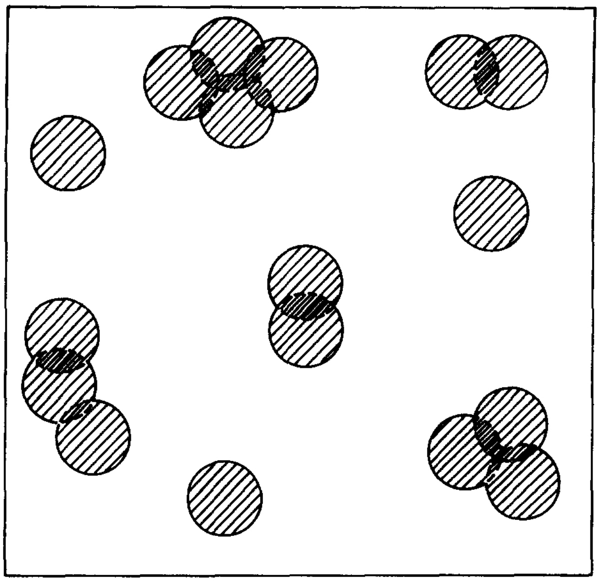

FIG. 1. Realizable configuration for two-phase random medium in which particles are fully penetrable spheres.

II. THE S_n IN THE FULLY PENETRABLE-SPHERE CASE

For any homogeneous sphere system of volume V we have shown that the Mayer–Montroll representation of the S_n is given by

$$S_n(\mathbf{r}_{12}, \mathbf{r}_{13}, \ldots, \mathbf{r}_{1n}) = 1 + \sum_{s=1}^{\infty} (-1)^s \frac{\rho^s}{s!} \int \cdots \iint g_s(\mathbf{r}_{n+1}, \mathbf{r}_{n+2}, \ldots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} \left\{ 1 - \prod_{i=1}^{n} [1 - m(r_{ij})] \right\} d\mathbf{r}_j , \quad (1)$$

where

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

g_s is the s-body distribution function, ρ is the number density of spheres equal to N/V, N is the number of particles in the system, and R is the radius of a sphere.[1,2]

In the case of fully penetrable (overlapping) spheres of equal radius, the probability of observing a particle at particular locations in space is independent of the location of the other particles in the system (Fig. 1). Under such conditions, we have for a statistically homogeneous system

$$g_N^{(s)}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_s) = g_N^{(1)}(\mathbf{r}_1) g_N^{(2)}(\mathbf{r}_2) \cdots g_N^{(s)}(\mathbf{r}_s) = 1 , \quad (2)$$

i.e., there exists no spatial correlation between particle centers. Substituting Eq. (2) into Eq. (1) gives

$$S_n(\mathbf{r}_{12}, \mathbf{r}_{13}, \ldots, \mathbf{r}_{1n}) = 1 + \sum_{s=1}^{\infty} (-1)^s \frac{\rho^s}{s!} \times \int \cdots \int \prod_{j=n+1}^{n+s} m^{(n)}(r_{1j}, r_{2j}, \ldots, r_{nj}) d\mathbf{r}_j . \quad (3)$$

Recall[1] that the volume integral of $m^{(n)}(r_{1j}, r_{2j}, \ldots, r_{nj})$ over $\mathbf{r}_j$ is equal to the union volume of n spheres of unit radius V_n with sphere centers at $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$. Therefore, Eq. (3) becomes

$$\begin{aligned} S_n(\mathbf{r}_{12}, \mathbf{r}_{13}, \ldots, \mathbf{r}_{1n}) &= 1 + \sum_{s=1}^{\infty} (-1)^s \frac{\rho^s}{s!} \prod_{j=n+1}^{n+s} V_n(r_{1j}, r_{2j}, \ldots, r_{nj}) \\ &= 1 + \sum_{s=1}^{\infty} (-1)^s \frac{\rho^s}{s!} [V_n]^s \\ &= \exp[-\rho V_n] . \end{aligned} \quad (4)$$

Equation (4) states that the probability of finding n points separated by the relative distances $r_{12}, r_{13}, \ldots, r_{1n}$ in the matrix phase of a two-phase system having a particle phase consisting of fully penetrable spheres, is simply the exponential of minus the density times the union volume of n spheres V_n. Although trivial, the ensemble method of deriving the general result for fully penetrable spheres given by Eq. (4) is new.

One may also obtain Eq. (4) using simple probability arguments, and the interpretation that S_n, for any particle geometry, is the probability that a region which is the union volume of n spheres of radius R contain no sphere centers.[1] Consider S_n, the probability of setting N sphere centers at random in large finite volume V in such a way that a smaller volume V_n is empty of sphere centers. Since each random placement is independent of the location of the other particle centers, we have that the probability is

$$\begin{aligned} S_n &= \left[\frac{V - V_n}{V} \right]^N \\ &= \left[1 - \frac{\rho V_n}{N} \right]^N . \end{aligned} \quad (5)$$

In the limit $N \to \infty$, holding ρ and V_n fixed, Eq. (5) becomes Eq. (4). This method of derivation was put forth by Weissberg.[6]

III. EXPLICIT REPRESENTATION OF SOME LOWER ORDER S_n

Given the union volume of n spheres V_n, we may calculate S_n through Eq. (4). In the case of the one-point matrix function (the volume fraction of matrix phase ϕ), we have

$$S_1 \equiv \phi = \exp[-\rho V_1] , \quad (6)$$

where V_1 is the union volume of one sphere or, simply, the volume of one sphere $4\pi R^3/3$. The volume fraction of matrix phase for fully penetrable spheres is always greater than the corresponding volume fraction for impenetrable spheres, at the same density, since $\exp[-\rho V_1] > 1 - \rho V_1$.

The union volume of two spheres of unit radius separated by distance x may be written in terms of the volume common to two such spheres. The union volume of two spheres of unit radius whose centers are separated by a distance x is given by

$$V_2(x) = \begin{cases} \dfrac{4\pi}{3} \left[1 + \dfrac{3}{4} x - \dfrac{x^3}{16} \right], & x < 2, \\ \dfrac{8\pi}{3} , & x > 2. \end{cases} \quad (7)$$

Substituting Eq. (7) into Eq. (4) gives the two-point matrix function for fully penetrable spheres first given by Weissberg[6]

$$S_2(x) = \begin{cases} \exp\left\{-\rho\,\frac{4\pi}{3}\left[1+\frac{3}{4}x-\frac{x^3}{16}\right]\right\}, & x<2, \\ \exp\left\{-\rho\,\frac{8\pi}{3}\right\}, & x>2. \end{cases} \tag{8}$$

Note that as $x \to 0$, $S_2 = \exp(-\rho V_1) = \phi$ and as $x \to \infty$, $S_2 = \exp(-\rho 2V_1) = \phi^2$, as expected.[1]

For fully penetrable spheres the three-point function is given by

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) = \exp[-\rho V_3(\mathbf{r}_{12}, \mathbf{r}_{13})], \tag{9}$$

and has already been stated by Strieder and Aris.[12] [To our knowledge, however, no one has ever explicitly substituted the expression for the union volume of three spheres into Eq. (9) for purposes of calculation.] The beauty of Eq. (9) is that it provides an exact expression for the three-point matrix function for a useful particle-phase geometry. When dealing with impenetrable[10,13] (or partially penetrable[10]) spheres, the three-point function can only be known approximately.

The union volume of three spheres of unit radius separated by the distances x, y, and z may be expressed as

$$V_3(x,y,z) = V_2(x) + V_2(y) + V_2(z) + V_3^I(x,y,z) - 3V_1, \tag{10}$$

where V_3^I is the intersection volume of three spheres. An expression for the volume common to three spheres has been obtained by van der Waals, by Weissberg and Prager, by Rowlinson, by Powell, and by Ree *et al.*[14] Powell's form is

$$\begin{aligned} V^I(x,y,z) = {} & \frac{Q}{6}xyz + \frac{4}{3}\tan^{-1}\left\{\frac{Q\cdot xyz}{x^2+y^2+z^2-8}\right\} \\ & - x\left(1-\frac{x^2}{12}\right)\tan^{-1}\left\{\frac{2Q\cdot yz}{-x^2+y^2+z^2}\right\} \\ & - y\left(1-\frac{y^2}{12}\right)\tan^{-1}\left\{\frac{2Q\cdot xz}{x^2-y^2+z^2}\right\} \\ & - z\left(1-\frac{z^2}{12}\right)\tan^{-1}\left\{\frac{2Q\cdot xy}{x^2+y^2-z^2}\right\}; \\ & 0 \le \tan^{-1} \le \pi, \end{aligned} \tag{11}$$

where

$$Q = \frac{\sqrt{1-L^2}}{L}$$

and where

$$L = \frac{xyz}{\sqrt{(x+y+z)(-x+y+z)(x-y+z)(x+y-z)}}$$

is the circumradius of the triangle formed by x, y, and z. The expression (11) is valid only if $L < 1$, that is, if a common volume exists. If $L > 1$, then either there is no volume common to three spheres or else the common volume is expressible in terms of the intersection volume of two spheres. The latter case is illustrated in Fig. 2. Substituting Eq. (10) in conjunction with Eqs. (7) and (11), into Eq. (9) gives the three-point matrix function in the fully penetrable-sphere case:

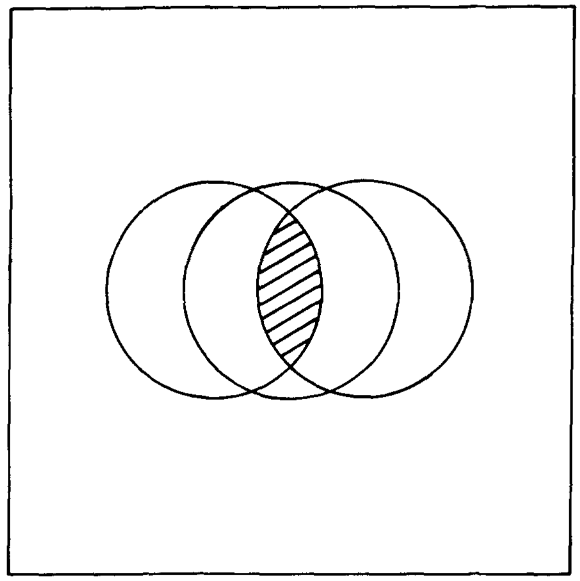

FIG. 2. Volume common to three spheres of unit radius when $L > 1$ represented by shaded region.

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) = \frac{S_2(r_{12})S_2(r_{13})S_2(r_{23})}{\phi^3}\exp[-\rho V_3^I(\mathbf{r}_{12}, \mathbf{r}_{13})]. \tag{12}$$

Note that Eq. (12) meets all the proper limiting values of S_3, i.e., it meets the following conditions under all permutations of the labels 1, 2, and 3.

$$\lim_{\substack{\text{all } r_{1j}\to 0 \\ 2\le j\le 3}} S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) = \phi, \tag{13a}$$

$$\lim_{r_{23}\to 0} S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) = S_2(r_{12}), \tag{13b}$$

$$\lim_{\substack{r_{12}\to\infty \\ r_{13}\text{ fixed}}} S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) = \phi S_2(r_{13}), \tag{13c}$$

$$\lim_{\substack{\text{all } r_{ij}\to\infty \\ 1\le i<j\le 3}} S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) = \phi^3. \tag{13d}$$

We recall[1] that these conditions are met by the exact S_3 (again under all permutations of the labels 1, 2, and 3) for both penetrable and impenetrable spheres. Elsewhere, we shall use Eq. (13) to determine the effective properties of two-phase random media whose particle phase is modeled to be fully penetrable spheres.[10]

That both the two- and three-point matrix probability functions for fully penetrable spheres should prove useful in predicting bulk properties of real two-phase systems is supported by other work. Corson has examined the microstructure of random two-phase solid mixtures having regions of matrix of random shape and size.[3] He has fitted the two- and three-point matrix functions, which are represented by sums of exponentials, to experimental data associated with random two-phase solid mixtures. These empirical functions were then used, with success, to predict various properties of heterogeneous materials. Debye *et al.* have shown the two-point matrix function to be proportional to an exponential in the case of a distribution of "holes" of random shape and size in a solid.[5] In light of the aforementioned studies, it is not surprising to obtain exponential functions for the two-point and three-point functions in the case of spheres which are spatially uncorrelated.

The four-point matrix probability function for a system of fully penetrable spheres is equal to

$$S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) = \exp[-\rho V_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14})] . \tag{14}$$

It is clear that the union volume of four spheres may be expressed as

$$\begin{aligned} V_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) = {} & 4V_1 - V_2(r_{12}) - V_2(r_{13}) - V_2(r_{14}) - V_2(r_{23}) \\ & - V_2(\mathbf{r}_{24}) - V_2(\mathbf{r}_{34}) + V_3(\mathbf{r}_{12}, \mathbf{r}_{13}) \\ & + V_3(\mathbf{r}_{12}, \mathbf{r}_{14}) + V_3(\mathbf{r}_{13}, \mathbf{r}_{14}) + V_3(\mathbf{r}_{23}, \mathbf{r}_{24}) \\ & - V_4^I(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) , \end{aligned} \tag{15}$$

where V_4^I is the intersection volume of four spheres of equal radius. Substituting Eq. (15) into Eq. (14) gives

$$\begin{aligned} & S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) \\ & = \frac{\phi^4 S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) S_3(\mathbf{r}_{12}, \mathbf{r}_{14}) S_3(\mathbf{r}_{13}, \mathbf{r}_{14}) S_3(\mathbf{r}_{23}, \mathbf{r}_{24})}{S_2(\mathbf{r}_{12}) S_2(\mathbf{r}_{13}) S_2(\mathbf{r}_{14}) S_2(\mathbf{r}_{23}) S_2(\mathbf{r}_{24}) S_2(\mathbf{r}_{34})} \\ & \quad \times \exp[\rho V_4^I(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14})] \end{aligned} \tag{16}$$

which is a new result. For any particle geometry, S_4 gives the probability of finding the vertices of a tetrahedron of variable geometry in the matrix and, as such, is more difficult to evaluate (experimentally or theoretically) than the quantities S_2 or S_3 which are defined in a plane. To our knowledge, the four-point matrix function has never been evaluated for any geometry by either experimental or theoretical means. Note that Eq. (16) properly meets the following conditions[1] under all permutations of the labels 1, 2, 3, and 4:

$$\lim_{\substack{\text{all } r_{1j}\to 0 \\ 2\le j\le 4}} S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) = \phi , \tag{17a}$$

$$\lim_{\substack{r_{12}\to 0 \\ r_{34}\to 0}} S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) = S_2(\mathbf{r}_{13}) , \tag{17b}$$

$$\lim_{r_{12}\to 0} S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) = S_3(\mathbf{r}_{13}, \mathbf{r}_{14}) , \tag{17c}$$

$$\lim_{\substack{r_{14}\to\infty \\ r_{12}, r_{13} \text{ fixed}}} S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) = \phi S_3(r_{12}, r_{13}) , \tag{17d}$$

$$\lim_{\substack{r_{13}\to\infty \\ r_{24}\to\infty \\ r_{12}, r_{34} \text{ fixed}}} S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) = S_2(r_{12}) S_2(r_{34}) , \tag{17e}$$

$$\lim_{\substack{r_{1i}\to\infty,\, i=2,3 \\ r_{14} \text{ fixed}}} S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) = \phi^2 S_2(r_{14}) , \tag{17f}$$

$$\lim_{\substack{\text{all } r_{ij}\to\infty \\ 1\le i\le j\le 4}} S_4(r_{12}, r_{13}, r_{14}) = \phi^4 . \tag{17g}$$

In addition to presenting the new result given by Eq. (16), we shall obtain rigorous upper and lower bounds on S_1, S_2, S_3, and S_4 (for fully penetrable spheres) by employing simple geometrical arguments.

IV. BOUNDS ON THE S_n IN THE FULLY PENETRABLE-SPHERE CASE

A. General bounds on lower-order S_n

In this section, we obtain some useful bounds on lower-order S_n for the fully penetrable-sphere model from purely geometrical considerations. It is clear that the union volume of three spheres $V_3(x, y, z)$ is greater than or equal to the union volume of two spheres $V_2(r)$ (the argument r being x or y or z) which in turn is greater than or equal to V_1:

$$V_3 \ge V_2 \ge V_1 \tag{18}$$

and, therefore,

$$\exp[-\rho V_3] \le \exp[-\rho V_2] \le \exp[-\rho V_1] ,$$

$$S_3 \le S_2 \le S_1 , \tag{19}$$

using Eq. (4). Since $NV_1/V \ge 0$ we have that $S_1 \le 1$ and, therefore,

$$S_3 \le S_2 \le S_1 \le 1 , \tag{20}$$

which is intuitively obvious from the definition of the S_n. The bounds expressed by Eq. (20) are, in fact, valid for any particle geometry.[1]

Since $V_2(x) \le 2V_1$, we have that

$$\exp[-\rho V_2(x)] \ge \exp[-\rho 2V_1] = \phi^2 ,$$

$$S_2(x) \ge \phi^2 . \tag{21}$$

We see that the bound given by Eq. (21) is also valid for any particle geometry.[1]

B. Upper and lower bounds on S_3

We should like to obtain bounds on S_3 in terms of S_1 and S_2 for the fully penetrable-sphere model. We may do so by first noting that

$$V_3^I \le V_1 \tag{22}$$

and

$$V_3^I \le V_2^I(z) ; \quad z \text{ being } r_{12},\ r_{13}, \text{ or } r_{23} , \tag{23}$$

where

$$V_2^I(z) = 2V_1 - V_2(z) .$$

Here V_2^I is the intersection volume of two spheres whose centers are separated by distance z. Equation (12) in conjunction with bounds (22) and (23) give

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) \ge \frac{S_2(r_{12}) S_2(r_{13}) S_2(r_{23})}{\phi^2} \tag{24}$$

and

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) \ge \frac{S_2(x) S_2(y)}{\phi} , \tag{25}$$

respectively. Here x and y are the remaining pair of r_{ij} after z is chosen. Clearly, the lower bound given by expression (25) is the most stringent of the two since the upper bound on V_3^I, given by Eq. (23), is better than the one given by Eq. (22). It is important to note that the right-hand side of Eq. (25) satisfies condition (13a) exactly. Moreover, it also satisfies condition (13b) exactly except when z is chosen to be r_{23} in Eq. (13b), in which case

$$\frac{S_2(x)S_2(y)}{\phi} \to \frac{S_2^2(x)}{\phi} . \tag{26}$$

Condition (13c) is always satisfied exactly by the right-hand side of Eq. (25) except when z remains finite, in which case

$$\frac{S_2(x)S_2(y)}{\phi} \to \phi^3 . \tag{27}$$

Inequality (25) always satisfies condition (13d).

The fact that the right-hand side of Eq. (25) does not satisfy Eqs. (13b) and (13c) for certain conditions can be remedied by specifying that x and y are the smallest and next-to-smallest of the three lengths r_{12}, r_{13}, and r_{23}. Thus,

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) \geq \frac{S_2(x)S_2(y)}{\phi} \quad , \quad x \leq y \leq z . \tag{28}$$

In light of the fact that the right-hand side of Eq. (28) becomes exact under all the limits outlined above, it seems reasonable to use it as an approximation for the exact S_3, especially for other particle geometries (e.g., impenetrable spheres) for which exact expressions for the S_3 do not exist, and, in fact, Weissberg and Prager[13] have already used this bound as an approximation to S_3 for mutually impenetrable spheres. Their justification was similar but they did not consider the questions of whether the approximation is a bound on S_3 for fully penetrable spheres or what its quantitative accuracy is in that case.

We may also obtain two upper-bound expressions for S_3 by noting that

$$V_3^I \geq V_1 - V_2(z) \; ; \quad z \text{ being } r_{12}, \; r_{13}, \text{ or } r_{23} \tag{29}$$

and

$$V_3^I \geq 0 . \tag{30}$$

The lower bounds (29) and (30) together with Eq. (12) give the upper bounds

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) \leq \frac{S_2(x)S_2(y)}{\phi^2} \tag{31}$$

and

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) \leq \frac{S_2(r_{12})S_2(r_{13})S_2(r_{23})}{\phi^3} , \tag{32}$$

respectively. Here x and y stand for any pair of the three r_{ij}. The bound given by Eq. (32) is seen to be a better upper bound on S_3 than Eq. (31) since the bound (30) is a better lower bound on V_3^I than Eq. (29). Note that the right-hand side of (32) satisfies conditions (13c) and (13d) but does not satisfy conditions (13a) and (13b) which give S_3 for cases in which its arguments vanish. Combining inequalities (25) and (32), we have, in the case of fully penetrable spheres,

$$\frac{S_2(x)S_2(y)}{\phi} \leq S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) \leq \frac{S_2(r_{12})S_2(r_{13})S_2(r_{23})}{\phi^3} . \tag{33}$$

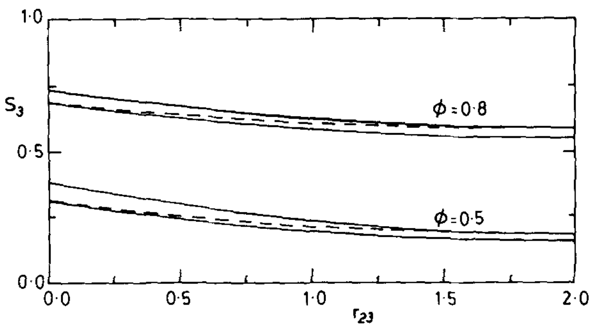

FIG. 3. Comparison of the exact S_3 for fully penetrable spheres (dotted line) to the upper and lower bounds of expression (33) for $\phi = 0.8$ and $\phi = 0.5$. Here $r_{12} = r_{13} = 1$.

In Fig. 3 we compare the exact three-point function for fully penetrable spheres with the upper and lower bounds given by Eq. (33) for $r_{12} = r_{13} = 1$ and with $\phi = 0.8$ and $\phi = 0.5$. The upper and lower bounds (33) are seen to bound the exact S_3 quite closely. Note that S_3 for the equilateral configuration is almost exactly midway between the bounds.

C. Upper and lower bounds on S_4

We may obtain upper and lower bounds on S_4 in the case of fully penetrable spheres by noting that

$$V_4^I(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) \leq V_3^I(\mathbf{r}_{ij}, \mathbf{r}_{ik}) \tag{34}$$

and

$$V_4^I(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) \geq 0 . \tag{35}$$

Here r_{ij} and r_{ik} are largest and second largest lengths, respectively, of all the possible relative distances obtainable between $\mathbf{r}_1$, $\mathbf{r}_2$, $\mathbf{r}_3$, and $\mathbf{r}_4$. Note that both r_{ij} and r_{ik} are measured from the same point. Substituting Eqs. (34) and (35) into Eq. (16) gives

$$\frac{\phi^4 S_3(\mathbf{r}_{12}, \mathbf{r}_{13})S_3(\mathbf{r}_{12}, \mathbf{r}_{14})S_3(\mathbf{r}_{13}, \mathbf{r}_{14})S_3(\mathbf{r}_{23}, \mathbf{r}_{24})}{S_2(r_{12})S_2(r_{13})S_2(r_{14})S_2(r_{23})S_2(r_{24})S_2(r_{34})}$$
$$\leq S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14})$$
$$\leq \frac{\phi S_3(\mathbf{r}_{il}, \mathbf{r}_{ik})S_3(\mathbf{r}_{il}, \mathbf{r}_{ij})S_3(\mathbf{r}_{ik}, \mathbf{r}_{ij})}{S_2(r_{il})S_2(r_{ik})S_2(r_{ij})} , \tag{36}$$

where r_{il} is the shortest of the three lengths r_{il}, r_{ij}, and r_{ik}.

It is clear that the lower bound on S_4 satisfies conditions (17d), (17e), and (17f) but it does not satisfy conditions (17a), (17b), and (17c). The upper bound on S_4, on the other hand, satisfies all the limiting conditions of Eq. (17). Accordingly, it is reasonable to use the upper bound (36) as an approximation to S_4 for arbitrary particle geometry:

$$S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) \cong \frac{\phi S_3(\mathbf{r}_{il}, \mathbf{r}_{ik})S_3(\mathbf{r}_{il}, \mathbf{r}_{ij})S_3(\mathbf{r}_{ik}, \mathbf{r}_{ij})}{S_2(r_{il})S_2(r_{ik})S_2(r_{ij})} . \tag{37}$$

To our knowledge S_3 is available exactly for spheres only in the fully penetrable case. For arbitrary penetrability we would have to approximate S_3 with, for example, the right-hand side of Eq. (28) to yield:

$$S_4(\mathbf{r}_{12}, \mathbf{r}_{13}, \mathbf{r}_{14}) \cong \frac{S_2(x_1)S_2(y_1)S_2(x_2)S_2(y_2)S_2(x_3)S_2(y_3)}{\phi^3 S_2(r_{il})S_2(r_{ik})S_2(r_{ij})} \tag{38}$$

TABLE I. The integral $I(P_2)$ of Eq. (39) for fully penetrable spheres compared with its approximant $\hat{I}(P_2)$ obtained by approximating $S_3(r_{12}, r_{13}, r_{23})$ by the right-hand-side of Eq. (41). Here ϕ is the volume fraction of matrix phase.

ϕ	$I(P_2)$	$\hat{I}(P_2)$
1.0	0.0	0.0
0.9	0.0189	0.0188
0.8	0.0315	0.0313
0.7	0.0387	0.0382
0.6	0.0411	0.0406
0.5	0.0395	0.0389
0.4	0.0346	0.0343
0.3	0.0273	0.0273
0.2	0.0184	0.0188
0.1	0.00883	0.00949
0.0	0.0	0.0

Here x_1 and y_1 are the shortest and second shortest of the lengths r_{il}, r_{ik}, and r_{lk}; x_2 and y_2 are the shortest and second shortest of the lengths r_{il}, r_{ij}, and r_{lj}; and x_3 and y_3 are the shortest and second shortest of the lengths r_{ik}, r_{ij}, and r_{kj}.

Because Eq. (38) is derived from approximations for S_4 and S_3 that satisfy Eqs. (17) and (13), respectively, it has the optimal asymptotic properties that one can hope to achieve in an expression for S_4 that is wholly in terms of S_2 and ϕ, not only for fully penetrable spheres but for impenetrable (and permeable) spheres as well, even though the bounding properties of the right-hand sides of Eqs. (28) and (37) can only be guaranteed for fully penetrable spheres, for which one can say a bit more. Since Eq. (37) can be expected to yield an approximant a little on the high side—it is an upper bound—and since the use of Eq. (28) can be expected to lower this somewhat—Eq. (28) is a lower bound—the resulting Eq. (38) may well prove just as quantitatively accurate, if not more accurate, than Eq. (37), as a result of the cancellation of errors.

In bounding or approximating effective transport coefficients for a two-phase composite, knowledge of S_n typically enters through a few key integrals. In the case of the dielectric constant[15] or the thermal conductivity,[16] of an arbitrarily large (i.e., "macroscopic") sample, for instance, S_3 appears via

$$I(P_2) = \lim_{V\to\infty} \frac{1}{8\pi^2} \int_V \int_V \hat{S}_3(r_{12}, r_{13}, r_{23}) \frac{P_2(\cos\theta)}{r_{12}^3 r_{13}^3} d\mathbf{r}_{12}\, d\mathbf{r}_{13} , \tag{39}$$

where θ is the angle opposite r_{23}, P_2 is the Legendre polynomial, and

$$\hat{S}_3(r_{12}, r_{13}, r_{23}) = S_3(r_{12}, r_{13}, r_{23}) - S_2(r_{12}) S_2(r_{13}) \phi^{-1} . \tag{40}$$

Equation (39) can in fact be simplified somewhat. The form of $\hat{S}_3$ ensures that $I(P_2)$ is independent of sample shape,[15] and if one restricts oneself to a spherical sample of volume V in Eq. (39) as one lets $V\to\infty$, one can drop the $S_2 S_2 \phi^{-1}$ since its contribution to the integral then vanishes by symmetry for all V. It is clear from this that the simplest use of Eq. (25) as a approximation in Eq. (39)—setting $x = r_{12}$ and $y = r_{13}$—will yield the trivial result $I(P_2) \approx 0$. Perhaps the simplest nontrivial form of Eq. (25) to be used in connection with Eq. (39) is not Eq. (28) with its $x \le y \le z$ but

$$S_3(r_{12}, r_{13}, r_{23}) \simeq S_2(r_{23}) [S(r_{12}) + S(r_{13})] / 2\phi . \tag{41}$$

We have tested the use of Eq. (41) in Eq. (39) in the case of fully penetrable spheres, for which S_3 is known exactly as described in this article. The resulting approximant $\hat{I}(P_2)$ is compared to $I(P_2)$ in Table I. [Plotted as functions of ϕ, $I(P_2)$ and $\hat{I}(P_2)$ are indistinguishable on the scale of a journal figure of typical size.] The result is very encouraging but in assessing its significance two points must be kept in mind. First, additional transport coefficients in general involve related but different integrals that weigh S_3 in somewhat different ways. For example, analogous estimates of elastic moduli[17] require not only $I(P_2)$, but also $I(P_4)$, for which $P_2(\cos\theta)$ is replaced by the Legendre polynomial $P_4(\cos\theta)$ in Eq. (39). Second, it is not immediately clear if the closeness of approximation of $I(P_2)$ can be expected to carry over from penetrable spheres to the case of impenetrable spheres.

ACKNOWLEDGMENTS

The authors wish to acknowledge the support of their work at Stony Brook by the Office of Basic Energy Sciences, U.S. Department of Energy. S. Torquato is also indebted to the National Science Foundation for partial support.

[1] S. Torquato and G. Stell, J. Chem. Phys. **77**, 2071 (1982).
[2] S. Torquato and G. Stell, J. Chem. Phys. 78, 3262 (1983).
[3] P. B. Corson, J. Appl. Phys. **45**, 3159, 3165 (1974).
[4] P. B. Corson, J. Appl. Phys. **45**, 3171, 3180 (1974).
[5] P. Debye, H. R. Anderson, and H. Brumberger, J. Appl. Phys. **28**, 279 (1957).
[6] H. L. Weissberg, J. Appl. Phys. **34**, 2636 (1963).
[7] H. L. Weissberg and S. Prager, Trans. Rheology Soc. **9**, 321 (1965).
[8] H. L. Weissberg and S. Prager, Phys. Fluids **13**, 2958 (1970).
[9] A. L. DeVera and W. Strieder, J. Phys. Chem. **81**, 1783 (1977).
[10] S. Torquato and G. Stell (to be published).
[11] L. Blum and G. Stell, J. Chem. Phys. **71**, 42 (1979); **72**, 2212 (1980); J. J. Salacuse and G. Stell, *ibid.* **77**, 3714 (1982).
[12] W. Strieder and R. Aris, *Variational Methods Applied to Problems of Diffusion and Reaction* (Springer, Berlin, 1973).
[13] H. L. Weissberg and S. Prager, Phys. Fluids **5**, 1390 (1962).
[14] J. D. van der Waals, Proc. R. Acad. Sci. Amsterdam **1**, 138 (1890); H. L. Weissberg and S. Prager, Phys. Fluids **5**, 1390 (1962); J. S. Rowlinson, Mol. Phys. **6**, 517 (1963); M. J. D. Powell, *ibid.* 7, 591 (1964); F. H. Ree, R. N. Keeler, and S. L. McCarthy, J. Chem. Phys. **44**, 3407 (1966).
[15] W. F. Brown, J. Chem. Phys. **23**, 1514 (1955).
[16] W. F. Brown, Trans. Rheology Soc. **9**, 357 (1965); M. Beran, Nuovo Cimento **38**, 771 (1965).
[17] G. W. Milton, Phys. Rev. Lett. **46**, 542 (1981).