

Microstructure of two-phase random media. V. The n -point matrix probability functions for impenetrable spheres

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(Received 24 August 1984; accepted 27 September 1984)

We examine the two- and three-point matrix probability functions for a two-phase random and homogeneous system of impenetrable spheres. For such a system, we give an exact analytical expression for the two-point matrix function S_2 through second order in the number density of particles. Moreover, the two-point matrix function is evaluated, for the first time, for a very wide range of densities. We also discuss the evaluation of the three-point matrix function S_3 for an impenetrable-sphere system and provide new expressions that may be used to estimate it.

I. INTRODUCTION

This is the fifth in a series of studies of the structure of certain two-phase random media.¹⁻⁴ In this paper we address the problem of determining the two-point and three-point matrix probability functions, S_2 and S_3 , respectively, in the case of a statistically homogeneous two-phase material consisting of impenetrable spheres of equal radius statistically distributed throughout a matrix. The n -point matrix probability function, $S_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$, gives the probability of simultaneously finding n points at the positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n$, respectively, all in the matrix phase. The S_n arise in expressions for various bulk properties of two-phase disordered media.⁵⁻⁹ Until the recent work of Torquato and Stell,¹⁻⁴ knowledge of the S_n for nontrivial model microstructures has been virtually nonexistent and thus progress in the evaluation of expressions for effective properties which depend upon the S_n has been hampered. Torquato and Stell¹⁰ and Torquato, Stell, and Beasley,¹¹ have only recently evaluated bounds on the effective thermal conductivity and effective elastic moduli, respectively, which depend upon the S_2 and S_3 of the model, for a dispersion of fully penetrable spheres³ (i.e., randomly centered spheres). There is a need to evaluate lower-order S_n for other nontrivial microstructures.

We begin by exhibiting the general expressions for S_1 , S_2 , and S_3 associated with a statistically homogeneous dispersion of impenetrable spheres of radius R , in terms of n -body distribution functions g_n defined in Ref. 1. Among other things, we discuss the evaluation of S_3 for such a microstructure and provide new bounds on S_3 that may prove useful. Assuming that the zero-density limit of the radial distribution function is equal to unity when $r > 2R$ and zero when $r < 2R$ (where r is the distance between two sphere centers), we give a new exact analytical expression for S_2 through $O(\rho^2)$ (where ρ is the number density of spheres). Lastly, assuming the medium

is formed under conditions of thermal equilibrium, we evaluate, for the first time, the two-point matrix probability function $S_2(r)$ with high quantitative accuracy as a function of the distance r over a wide range of densities.

II. THE S_n IN THE IMPENETRABLE-SPHERE CASE

For a statistically homogeneous system of impenetrable spheres of radius R , we have given^{1,2} a representation (the Mayer-Montroll representation) of the S_n :

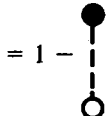
$$S_n(\mathbf{r}_{12}, \mathbf{r}_{13}, \dots, \mathbf{r}_{1n}) = 1 + \sum_{s=1}^n (-1)^s \frac{\rho^s}{s!} \int \dots \int \times g_s(\mathbf{r}_{n+1}, \mathbf{r}_{n+2}, \dots, \mathbf{r}_{n+s}) \times \prod_{j=n+1}^{n+s} \left\{ 1 - \prod_{i=1}^n [1 - m(r_{ij})] \right\} d\mathbf{r}_j,$$

where

$$m(r) = \begin{cases} 1, & r < R \\ 0, & r > R \end{cases}. \quad (2.1)$$

Here g_s is the s -body distribution function defined in Ref. 1. In general, the S_n are infinite series but the condition of impenetrability results in a truncated series, i.e., any term for which $s > n$ is identically zero.²

Setting $n = 1$ in Eq. (2.1) gives the expected result for the probability of finding a point in the matrix phase:

$$S_1 = 1 - \rho \int m(r_{12}) d\mathbf{r}_2$$


$$= 1 - \rho V_1 = \phi, \quad (2.2)$$

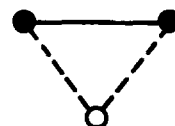
where we have used standard graphical representation¹²; the ---- is an m bond, ϕ is the volume fraction of the matrix phase, and V_n is the union volume of n spheres. Note that Eq. (2.2) involves only one-body contributions ($g_1 = 1$), consistent with the geometrical interpretation that S_1 is also the probability that no sphere centers are inside a region $\Omega^{(1)}$, the volume of one sphere¹. The region $\Omega^{(1)}$ is large enough to accommodate one center but not large enough to accommodate two or more centers of impenetrable spheres. Hence, any integral involving correlations between two or more particles must be zero. Similarly, setting $n = 2$ we have from Eq. (2.1):

$$\begin{aligned}
 S_2(r_{12}) &= 1 - \rho V_2(r_{12}) + \frac{\rho^2}{2!} \iint g_2(r_{34}) \\
 &\quad \times [m(r_{13}) + m(r_{23}) - m(r_{13})m(r_{23})] \\
 &\quad \times [m(r_{14}) + m(r_{24}) - m(r_{14})m(r_{24})] dr_3 dr_4 \\
 &= 1 - \text{[diagram 1]} - \text{[diagram 2]} + \text{[diagram 3]} + \text{[diagram 4]} + \text{[diagram 5]} \\
 &\quad + \text{[diagram 6]} - \text{[diagram 7]} - \text{[diagram 8]} + \text{[diagram 9]}.
 \end{aligned} \tag{2.3}$$

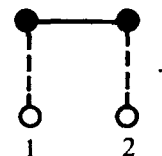
Here — is a g_2 bond and

$$V_2(r) = \begin{cases} \frac{4\pi}{3} \left[1 + \frac{3}{4} - \frac{r^3}{16} \right], & r < 2 \\ \frac{8\pi}{3}, & r > 2 \end{cases} \tag{2.4}$$

for spheres of unit radius. Equation (2.3) simplifies considerably by noting that terms containing the graph



are identically zero since, for example, $g_2(r_{34}) = 0$ for $r_{34} < 2$ and $m(r_{ij}) = 0$ for $r_{ij} > 1$, $3 \leq j \leq 4$. The only graph of order ρ^2 which is nonzero is the double-convolution volume integral given by



The two-point matrix probability function is the probability that no sphere centers are inside a region $\Omega^{(2)}$, the union volume of two spheres. The region $\Omega^{(2)}$ is large enough to accommodate one or two centers but not large enough to accommodate three or more centers of impenetrable spheres; thus the truncations for all $s > 2$. (Although not explicitly denoted, the two-point probability function for impenetrable spheres contains all powers in the density since the two-body function may be expanded in powers of density.) Summarizing, the two-point matrix function for an isotropic impenetrable-sphere system is exactly

$$\begin{aligned}
 S_2(r_{12}) &= 1 - \rho V_2(r_{12}) + \rho^2 \iint g_2(r_{34}) m(r_{13}) m(r_{24}) dr_3 dr_4 \\
 &= 1 - \text{[diagram 1]} - \text{[diagram 2]} + \text{[diagram 3]} + \text{[diagram 4]}.
 \end{aligned} \tag{2.5}$$

In the limit $r_{12} \rightarrow 0$, Eq. (2.5) simplifies to

$$S_2(0) = 1 - \text{[diagram 1]} = 1 - \rho V_1 = S_1 = \phi. \tag{2.6}$$

For $r_{12} \rightarrow \infty$, Eq. (2.5) again simplifies to become

$$\begin{aligned}
 S_2(\infty) &= 1 - \text{[diagram 1]} - \text{[diagram 2]} + \text{[diagram 3]} \times \text{[diagram 4]} \\
 &= 1 - 2\rho V_1 + \rho^2 V_1^2 = S_1^2 = \phi^2
 \end{aligned} \tag{2.7}$$

since $g_2(r) \rightarrow 1$ for $r \rightarrow \infty$.

The three-point matrix function is obtained from Eq. (2.1) by setting $n = 3$:

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) = 1 - \rho V_3(r_{12}, r_{13}) + \frac{\rho^2}{2!} \iint g_2(r_{45}) m^{(3)}(r_{14}, r_{24}, r_{34}) m^{(3)}(r_{15}, r_{25}, r_{35}) d\mathbf{r}_4 d\mathbf{r}_5 \\ - \frac{\rho^3}{3!} \iiint g_3(r_{45}, r_{46}) m^{(3)}(r_{14}, r_{24}, r_{34}) m^{(3)}(r_{15}, r_{25}, r_{35}) m^{(3)}(r_{16}, r_{26}, r_{36}) d\mathbf{r}_4 d\mathbf{r}_5 d\mathbf{r}_6, \quad (2.8)$$

where

$$m^{(3)}(r_{1j}, r_{2j}, r_{3j}) = 1 - \prod_{i=1}^3 1 - m(r_{ij}). \quad (2.9)$$

The union volume of three spheres of equal radius V_3 has been given by several investigators.³ The properties of g_2 , g_3 , and m permit us to simplify Eq. (2.8) to yield

$$S_3(r_{12}, r_{13}) = 1 - \rho V_3(r_{12}, r_{13}) - \text{[Diagram 1]} - \text{[Diagram 2]} \\ - \text{[Diagram 3]} + \text{[Diagram 4]} + \text{[Diagram 5]} + \text{[Diagram 6]} + \text{[Diagram 7]} \\ - \text{[Diagram 8]}, \quad (2.10)$$

The diagrams represent various configurations of three spheres (labeled 1, 2, 3) and their intersections. Diagram 1 shows two spheres intersecting. Diagram 2 shows two spheres intersecting with a third sphere. Diagram 3 shows three spheres intersecting. Diagrams 4-7 show various combinations of intersections. Diagram 8 shows the intersection of all three spheres, represented by a triangle with horizontal lines.

where  represents g_3 . Since

$$V_3(r_{12}, r_{13}) = V_2(r_{12}) + V_2(r_{13}) + V_2(r_{23}) + V_3^I(r_{12}, r_{13}) - 3V_1,$$

we have, upon use of Eqs. (2.2) and (2.5), the following alternative representation:

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) = 1 - 3S_1 + S_2(r_{12}) + S_2(r_{13}) + S_2(r_{23}) - \rho V_3^I(r_{12}, r_{13}) \\ - \text{[Diagram 1]} - \text{[Diagram 2]} - \text{[Diagram 3]} - \text{[Diagram 4]}, \quad (2.11)$$

The diagrams represent various configurations of three spheres (labeled 1, 2, 3) and their intersections. Diagram 1 shows two spheres intersecting. Diagram 2 shows two spheres intersecting with a third sphere. Diagram 3 shows three spheres intersecting. Diagram 4 shows the intersection of all three spheres, represented by a triangle with horizontal lines.

The quantity V_3^I is the intersection volume of three spheres of equal radius and is given by

$$V_3^I = \text{[Diagram 1]} \quad (2.12)$$

The diagram shows three spheres (labeled 1, 2, 3) intersecting at a central point, forming a triangular shape.

It is readily seen by use of Eqs. (2.10) or (2.11), that S_3 takes on its expected² short-range and long-range behavior.

These exact results for S_3 provide us with a number of rigorous bounds and suggest as well a variety of new

approximations. For example, since each of the last four graphs illustrated in Eq. (2.11) is nonnegative we can generate three different upper bounds to S_3 upon omitting the last graph, the first three graphs, or all four graphs. The first of these bounds becomes exact when any $r_{ij} \rightarrow 0$ while the second bound becomes exact when all $r_{ij} \rightarrow \infty$. With the use of a high speed computer quantitative evaluation of all but the last graph will be relatively routine. The last graph will be manageable only if g_3 is approximated in the superposition approximation¹² or related approximation, such as¹²

$$g_3(\mathbf{r}_{ij}, \mathbf{r}_{ik}) = g_2(\mathbf{r}_{ij})g_2(\mathbf{r}_{ik}) \quad (2.13)$$

whenever $r_{ij} < r_{jk}$, $r_{ik} < r_{jk}$.

Lower bounds on S_3 can be readily generated from the Kirkwood-Salsburg equations for the S_s using the techniques already discussed in Ref. 2. Using Eqs. (77), (81), and (62) of that reference, we have, for example,

$$S_3(\mathbf{r}_{12}, \mathbf{r}_{13}) \geq S_2(\mathbf{r}_{23}) + S_2(\mathbf{r}_{13}) - \phi + \phi \rho \int m(r_{14})m(r_{24})g_{UV}(r_{34})d\mathbf{r}_4. \quad (2.14)$$

As noted in Ref. 2, however, bounds such as Eq. (2.14) become weak when \mathbf{r}_1 , \mathbf{r}_2 , and \mathbf{r}_3 are widely separated.

III. EVALUATION OF THE TWO-POINT MATRIX PROBABILITY FUNCTION

The two-point matrix function has been evaluated for an isotropic system of impenetrable spheres through order ρ , to yield,⁷

$$S_2(r) = 1 - \rho V_2(r) + O(\rho^2). \quad (3.1)$$

The quantity $1 - \rho V_2(r)$, besides being an obviously poor approximation for large ρ , underestimates S_2 in the limit $r \rightarrow \infty$. This is not unexpected, since $1 - \rho V_2(r)$ is actually a lower bound on S_2 .² The two-point matrix function has never been evaluated for a dense, isotropic distribution of impenetrable spheres. In fact, the correction to Eq. (3.1) of order ρ^2 has only been recently determined for such media.¹³ In order to evaluate expression (2.5) for S_2 , at arbitrary density of spheres, knowledge of the nontrivial radial distribution function, $g(r) \equiv g_2(r)$, associated with an ensemble of spheres subject to the condition of impenetrability and isotropy, is required. Such an ensemble is not unique.² One may consider an ensemble associated with an isotropic distribution of impenetrable spheres in thermal equilibrium (e.g., canonical ensemble of equilibrium statistical mechanics) or any nonequilibrium ensemble which satisfy the conditions stated above.

A. Density expansion of S_2

Assuming we may expand the radial distribution function in powers of the density, we have

$$g(r) = H(r - 2R) \sum_{n=0}^{\infty} \rho^n y_n(r). \quad (3.2)$$

The fact that the Heaviside step function $H(r)$ multiplies the infinite sum ensures that $g(r)$ takes on its proper value of zero for $r < 2R$. The coefficients $y_n(r)$ are clearly dependent upon the particular ensemble employed for study. In the case of an equilibrium distribution of spheres of unit radius the first two coefficients are given by

$$y_0(r) = 1 \quad (3.3)$$

and

$$y_1(r) = H(4 - r) \left[\frac{32}{3} \left(1 - \frac{3}{8}r + \frac{r^3}{128} \right) \right], \quad (3.4)$$

respectively.¹² We note that Eq. (3.3), i.e., the leading-order coefficient $y_0(r)$, also holds for the nonequilibrium distribution of random sequential addition of hard spheres.¹⁴

The density expansion of S_2 is obtained by combining Eqs. (2.5) and (3.2):

$$S_2(r) = 1 - \rho V_2(r) + \rho^2 M(r), \quad (3.5)$$

where

$$M(r) = \sum_{n=0}^{\infty} \rho^n M_n(r) \quad (3.6)$$

and

$$M_n(r) = \iint m(r_{13})m(r_{24})H(r_{34} - 2R)y_n(r_{34})d\mathbf{r}_3 d\mathbf{r}_4. \quad (3.7)$$

Given that $S_2(r)$ must become ϕ for $r \rightarrow 0$ and ϕ^2 for $r \rightarrow \infty$ (assuming no long-range order), the function $M(r)$ must obey the following conditions:

$$M(0) = 0, \quad (3.8)$$

$$M(\infty) = M_0(\infty) = V_1^2, \quad (3.9)$$

and

$$M_n(\infty) = 0; \quad n \geq 1. \quad (3.10)$$

B. An exact expression for S_2 through $O(\rho^2)$

Torquato and Stell¹³ were the first to obtain the leading-order term of Eq. (3.6), i.e., the coefficient

$$M_0(r) = \iint m(r_{13})m(r_{24})H(r_{34} - 2R)y_0(r_{34})d\mathbf{r}_3 d\mathbf{r}_4. \quad (3.11)$$

They did so by inserting into the integral given by Eq. (3.11) expression (3.3) for $y_0(r)$. Noting that this integral had already been evaluated by McQuarrie¹⁶ for a different problem, they found

$$M_0(r) = \begin{cases} \left[-\frac{16}{9} + \frac{r^3}{3} - \frac{r^4}{10} + \frac{r^6}{1260} \right] \pi^2 + \frac{16\pi^2}{9}, & 0 \leq r \leq 2 \\ \left[\frac{256}{35r} - \frac{128}{9} + \frac{32r}{5} - \frac{5r^3}{9} + \frac{r^4}{10} - \frac{r^6}{1260} \right] \pi^2 + \frac{16\pi^2}{9}, & 2 \leq r \leq 4 \\ \frac{16\pi^2}{9}, & r \geq 4 \end{cases} \quad (3.12)$$

for spheres of unit radius.

Assuming $y_0(r)$ is given by Eq. (3.3), the two-point matrix probability function through order ρ^2 , therefore, is given exactly by

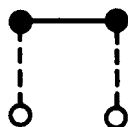
$$S_2(r) = 1 - \rho V_2(r) + \rho^2 M_0(r), \quad (3.13)$$

where $M_0(r)$ is given by Eq. (3.12). As aforementioned,

Eq. (3.13) applies not only to an equilibrium distribution of spheres but also to certain nonequilibrium distributions such as random sequential addition. Note that when $r \rightarrow 0$, Eq. (3.13) becomes $S_1 = \phi$ and when $r > 4$, Eq. (3.13) reduces to the proper long range value of ϕ^2 .

C. Calculation of S_2 for arbitrary density of spheres

We have seen that the graph



associated with the quantity $\rho^2 M(r)$ is a double-convolution integral, i.e.,

$$M(r) = g \oplus m^2, \quad (3.14)$$

where \oplus denotes the three-dimensional convolution integral. We define the three-dimensional Fourier transform of a function $G(r)$ to be

$$\hat{G}(k) = \int G(r) e^{-ik \cdot r} dr, \quad (3.15)$$

where k is the wave number vector. The inverse Fourier transform is given by

$$G(r) = \frac{1}{8\pi^3} \int \hat{G}(k) e^{ik \cdot r} dk. \quad (3.16)$$

Taking the Fourier transform of Eq. (3.14) we have, for an isotropic system of spheres of unit radius

$$\hat{M}(k) = \hat{g}(k) \hat{m}^2(k), \quad (3.17)$$

where

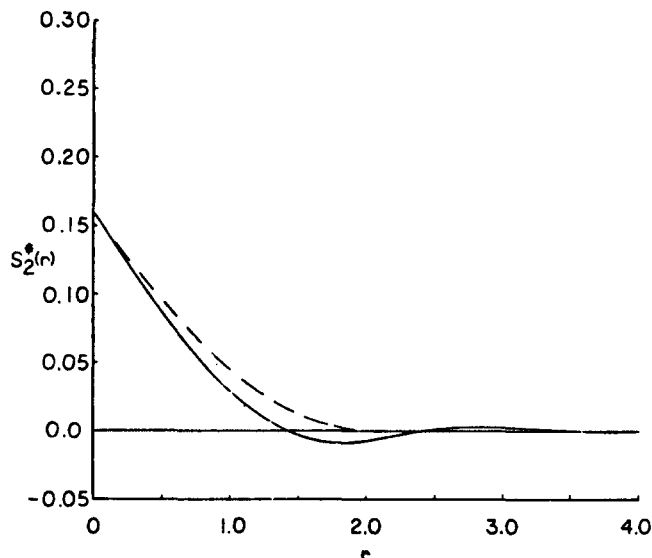


FIG. 2. The two-point void function S_2^* for impenetrable (solid) and fully penetrable (dashed) spheres at a particle concentration of 0.2.

$$\hat{m}(k) = \frac{4\pi}{k} \left[\frac{\sin k}{k^2} - \frac{\cos k}{k} \right], \quad (3.18)$$

$\hat{g}(k)$ is the Fourier transform of the radial distribution function and $k = |\mathbf{k}|$. Given $\hat{g}(k)$ and using Eq. (3.18) we may invert Eq. (3.17) to find

$$M(r) = \frac{1}{2\pi^2 r} \int_0^\infty \hat{g}(k) \hat{m}^2(k) k \sin(kr) dk. \quad (3.19)$$

We shall evaluate the integral given by Eq. (3.19), and thus $S_2(r)$, for an equilibrium distribution of spheres for arbitrary ρ . The radial distribution function for such a system can be obtained by solving the Ornstein-Zernike equation¹²:

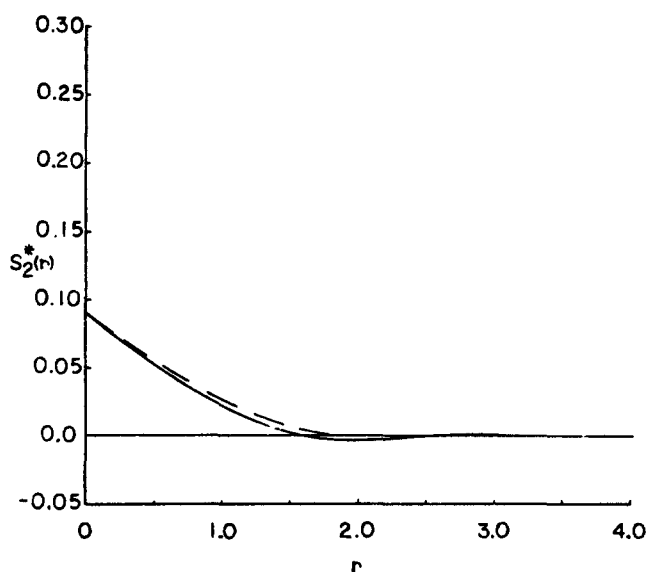


FIG. 1. The two-point matrix probability function minus its long-range value, $S_2^*(r)$, for impenetrable (solid line) and fully penetrable (dashed line) spheres at a particle concentration of 0.1.

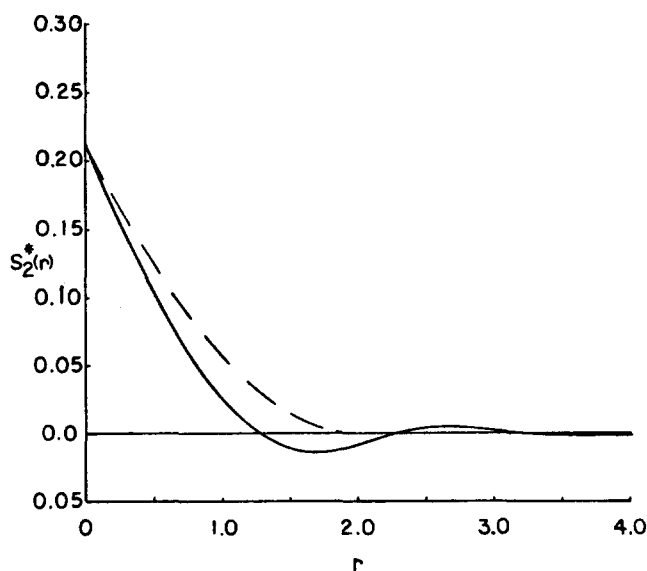


FIG. 3. The two-point void function S_2^* for impenetrable (solid) and fully penetrable (dashed) spheres at a particle concentration of 0.3.

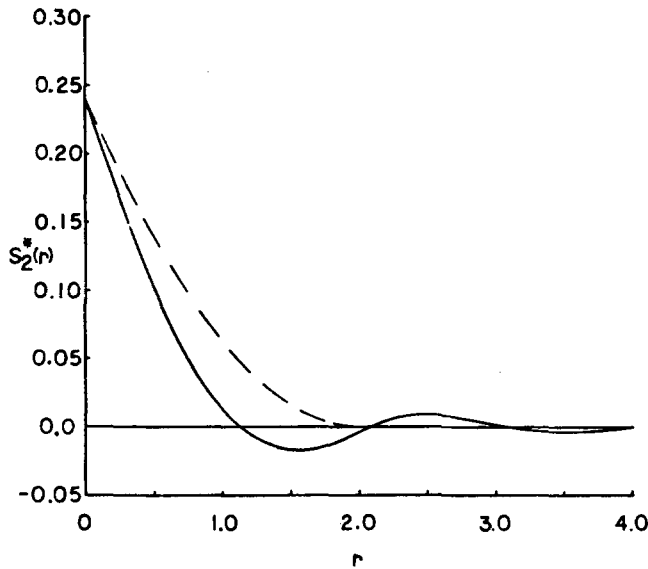


FIG. 4. The two-point void function S_2^* for impenetrable (solid) and fully penetrable (dashed) spheres at a particle concentration of 0.4.

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{23})c(r_{13})d\mathbf{r}_3, \quad (3.20)$$

where

$$h(r) = g(r) - 1 \quad (3.21)$$

is the total correlation function and $c(r)$ is the direct correlation function. By taking the Fourier transform of Eqs. (3.20) and (3.21) and employing Eq. (3.19), we have

$$M(r) = \frac{1}{2\pi^2 r} \int_0^\infty \frac{\hat{c}(k)}{1 - \rho \hat{c}(k)} \hat{m}^2(k) k \sin(kr) dk + \frac{16\pi^2}{9}. \quad (3.22)$$

Thiele¹⁷ and Wertheim¹⁸ independently solved the Ornstein-Zernike equation (3.20) for a system of hard spheres exactly in the Percus-Yevick (PY) approximation.

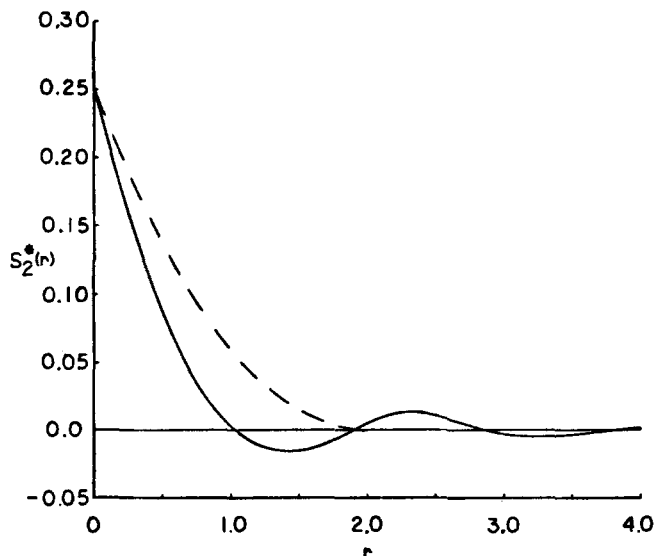


FIG. 5. The two-point void function S_2^* for impenetrable (solid) and fully penetrable (dashed) spheres at a particle concentration of 0.5.

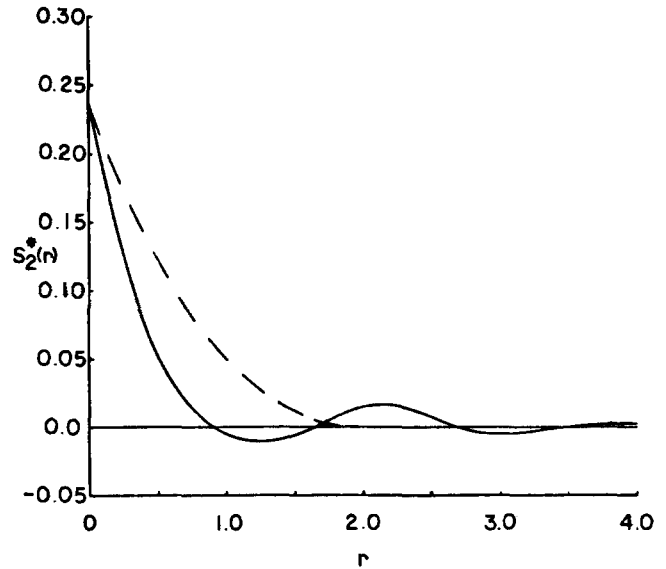


FIG. 6. The two-point void function S_2^* for impenetrable (solid) and fully penetrable (dashed) spheres at a particle concentration of 0.62.

The PY solution for hard spheres of unit radius is given by

$$c(r) = \begin{cases} -\lambda_1 - 3\eta\lambda_2 r - \frac{1}{16} \eta\lambda_1 r^3, & r < 2 \\ 0, & r > 2, \end{cases} \quad (3.23)$$

where

$$\lambda_1 = \frac{(1 + 2\eta)^2}{(1 - \eta)^4}, \quad \lambda_2 = -\frac{(1 + \eta/2)^2}{(1 - \eta)^4}, \quad (3.24)$$

and where $\eta = 4\pi\rho/3$ is the reduced density. The Fourier transform of the direct correlation function is

$$\begin{aligned} c(k) = & \frac{-4\pi}{3} \left\{ \lambda_1 [\sin(2k) - 2 \cos(2k)] \right. \\ & + \frac{3\eta\lambda_2}{k} [4k \sin(2k) + (2 - 4k^2)\cos(2k) - 2] \\ & + \frac{1}{16} \frac{\eta\lambda_1}{k^3} [(48k^2 - 24 - 16k^4)\cos(2k) \\ & \left. + (32k^3 - 48k)\sin(2k) + 24 \right\}. \end{aligned} \quad (3.25)$$

Integration of Eq. (3.22) using Eqs. (3.18) and (3.25) gives the PY radial distribution function which is shown to be in good agreement with the actual impenetrable-sphere $g(r)$ for densities up to and including the dense fluid state, i.e., up to reduced densities of 0.49. However, the PY approximation is found to present two defects when compared to machine calculations of $g(r)$, the first flaw being that the value of $g(r)$ at contact, $r = 2$, is too low. The second defect lies in the oscillations of $g(r)$ for large r ; $g(r)$ oscillates slightly out of phase with computer results and, in addition, the amplitude of these oscillations decreases too slowly with increasing r . Verlet and Weis¹⁹ have proposed a semiempirical modification of the PY

radial distribution function which corrects these faults. It is this modified Verlet-Weis version of the PY approximation that we employ in evaluating $S_2(r)$.

The evaluation of $M(r)$, and thus $S_2(r)$, Eq. (3.5), has been reduced to a one-dimensional quadrature. Using the scheme described by Verlet and Weis, the integral (3.22) was numerically evaluated using two different techniques; a one-dimensional Gaussian quadrature and the fast Fourier transform method. The difference between the results produced by application of these two numerical procedures were negligible on the scale of our figures and tables. In Figs. 1-6 we plot the quantity $S_2^* \equiv S_2 - \phi^2$ as a function of distance r for particle concentrations of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.62, respectively. For purposes of comparison, these figures also include the corresponding results for fully penetrable spheres.³ In Tables I and II we tabulate the two-point matrix probability function for the same values of $1 - \phi$ given in the figures. For impenetrable spheres there exists a maximum particle concentration value. For face-centered-cubic the exact close-packing reduced density $\eta (= 1 - \phi)$ is equal to $\sqrt{2} \cdot \pi/6 = 0.7405$. For impenetrable-sphere systems there exists a fluid-solid phase transition at $\eta \approx 1/2$ between a state which is characterized by no long-range order (a fluid phase) and a distinctly different state, which is characterized by some degree of long-range order (a solid phase). The Verlet-Weis $g(r)$ is not a good approximation of the structure of the solid phase. In order to model the impenetrable-sphere solid one must use approximations for $g(r)$ such as the one given by Kincaid and Weis.²⁰ However, it has been suggested²¹ that the PY and Verlet-Weis $g(r)$ contains all the essential features of correlations of the "glassy state" when evaluated at densities near close packing. A glass is formed when the density is increased still further

TABLE I. $S_2(r)$ as a function of r for an equilibrium distribution of impenetrable spheres at $1 - \phi = 0.1, 0.2$, and 0.3 .

| r | $S_2(r)$ | | |
|-----|------------------|--------|--------|
| | $1 - \phi = 0.1$ | 0.2 | 0.3 |
| 0.0 | 0.9000 | 0.8000 | 0.7000 |
| 0.4 | 0.8705 | 0.7411 | 0.6119 |
| 0.8 | 0.8441 | 0.6908 | 0.5418 |
| 1.2 | 0.8233 | 0.6539 | 0.4958 |
| 1.6 | 0.8104 | 0.6339 | 0.4758 |
| 2.0 | 0.8072 | 0.6327 | 0.4814 |
| 2.4 | 0.8091 | 0.6393 | 0.4932 |
| 2.8 | 0.8100 | 0.6416 | 0.4943 |
| 3.2 | 0.8102 | 0.6411 | 0.4911 |
| 3.6 | 0.8101 | 0.6401 | 0.4887 |
| 4.0 | 0.8100 | 0.6396 | 0.4889 |
| 4.4 | | 0.6398 | 0.4901 |
| 4.8 | | 0.6400 | 0.4905 |
| 5.2 | | 0.6401 | 0.4902 |
| 5.6 | | 0.6401 | 0.4899 |
| 6.0 | | 0.6400 | 0.4898 |
| 6.4 | | | 0.4900 |
| 6.8 | | | 0.4901 |
| 7.2 | | | 0.4900 |
| 7.6 | | | 0.4900 |
| 8.0 | | | 0.4900 |

TABLE II. $S_2(r)$ as a function of r for an equilibrium distribution of impenetrable spheres at $1 - \phi = 0.4, 0.5$, and 0.62 .

| r | $S_2(r)$ | | |
|------|------------------|--------|--------|
| | $1 - \phi = 0.4$ | 0.5 | 0.62 |
| 0.0 | 0.6000 | 0.5000 | 0.3800 |
| 0.4 | 0.4828 | 0.3546 | 0.2053 |
| 0.8 | 0.4003 | 0.2709 | 0.1416 |
| 1.2 | 0.3544 | 0.2360 | 0.1309 |
| 1.6 | 0.3417 | 0.2347 | 0.1405 |
| 2.0 | 0.3560 | 0.2548 | 0.1587 |
| 2.4 | 0.3693 | 0.2631 | 0.1554 |
| 2.8 | 0.3652 | 0.2518 | 0.1420 |
| 3.2 | 0.3584 | 0.2451 | 0.1417 |
| 3.6 | 0.3567 | 0.2477 | 0.1465 |
| 4.0 | 0.3596 | 0.2527 | 0.1479 |
| 4.4 | 0.3617 | 0.2523 | 0.1430 |
| 4.8 | 0.3608 | 0.2488 | 0.1418 |
| 5.2 | 0.3594 | 0.2482 | 0.1452 |
| 5.6 | 0.3593 | 0.2502 | 0.1464 |
| 6.0 | 0.3601 | 0.2513 | 0.1442 |
| 6.4 | 0.3605 | 0.2502 | 0.1427 |
| 6.8 | 0.3602 | 0.2492 | 0.1444 |
| 7.2 | 0.3598 | 0.2496 | 0.1457 |
| 7.6 | 0.3598 | 0.2504 | 0.1445 |
| 8.0 | 0.3601 | 0.2504 | 0.1434 |
| 8.4 | 0.3601 | 0.2498 | 0.1441 |
| 8.8 | 0.3600 | 0.2497 | 0.1452 |
| 9.2 | 0.3599 | 0.2500 | 0.1447 |
| 9.6 | 0.3600 | 0.2503 | 0.1438 |
| 10.0 | 0.3600 | 0.2501 | 0.1441 |

without crystallization occurring, i.e., there is no ordering, even at high densities. The aforementioned particle-particle concentration value of 0.62 corresponds to the highest observed density for the glassy state of hard spheres.

The exact result for S_2 through $O(\rho^2)$, Eq. (3.13), served as a check on the numerical results. Agreement between this exact result and our numerical results was excellent. We note that for either sphere distribution $S_2^* \rightarrow \phi(1 - \phi)$ as $r \rightarrow 0$ and $S_2^* \rightarrow 0$ as $r \rightarrow \infty$, as expected. The quantity S_2^* , for impenetrable spheres, is a damped oscillating function, oscillating about zero with amplitude that becomes negligible on the scale of our figures after several diameters (an indication of some short-range order). As the density of spheres is increased, in the case of impenetrable spheres, the correlation length is seen to increase. For example, the function S_2^* at $1 - \phi = 0.1$ attains its long-range value when r is equal to about two sphere diameters but the corresponding function at $1 - \phi = 0.62$ does not reach its long-range value on the scale of our figures until r is equal to roughly eight sphere diameters. By contrast, the corresponding S_2^* for fully penetrable spheres is seen to exponentially decay to zero when r is equal to a sphere diameter, and remains zero for $r > 2$. It is worth reporting that the PY and Verlet-Weis approximations to $S_2^*(r)$ are virtually indistinguishable on the scale of our figures except at the very highest density that we have considered, $1 - \phi = 0.62$. In contrast similarly sized figures exhibiting the PY and

Verlet $g_2(r)$ show a noticeable difference for $1 - \phi = 0.4$ and 0.5 as well as 0.62.

ACKNOWLEDGMENTS

S. Torquato gratefully acknowledges support of the National Science Foundation. G. Stell wishes to acknowledge support of the Office of Basic Sciences, U.S. Department of Energy.

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 S. Torquato and G. Stell, J. Chem. Phys. **79**, 1505 (1983).

⁴ S. Torquato and G. Stell, J. Chem. Phys. **80**, 878 (1984). The work of Refs. 1–4 and 10 is summarized, along with a few of the results herein, by G. Stell, in *The Mathematics and Physics of Disordered Media*, edited by B. D. Hughes and B. W. Ninham (Springer, Berlin, 1983).

⁵ W. F. Brown, J. Chem. Phys. **23**, 1514 (1955).

⁶ S. Prager, Phys. Fluids **4**, 1477 (1961).

⁷ H. L. Weissberg and S. Prager, Phys. Fluids **5**, 1390 (1962).

⁸ S. Prager, Physica **29**, 129 (1963).

⁹ M. J. Beran, *Statistical Continuum Theories* (Wiley, New York, 1968).

¹⁰ S. Torquato and G. Stell, Lett. Appl. Eng. Sci. (in press).

¹¹ S. Torquato, G. Stell, and J. D. Beasley, Lett. Appl. Eng. Sci. (in press).

¹² G. Stell, in *The Equilibrium Theory of Classical Fluids*, edited by H. L. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).

¹³ S. Torquato and G. Stell, Microscopic Approach to Transport in Two-Phase Random Media, CEAS Report #352, 1980.

¹⁴ B. Widom, J. Chem. Phys. **44**, 3888 (1966).

¹⁵ Subsequent to our work, Berryman independently obtained S_2 through order ρ^2 ; J. G. Berryman, J. Comput. Phys. **52**, 142 (1983).

¹⁶ D. A. McQuarrie, J. Chem. Phys. **40**, 3455 (1964).

¹⁷ E. Thiele, J. Chem. Phys. **39**, 474 (1963).

¹⁸ M. S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963); J. Math. Phys. **5**, 643 (1964).

¹⁹ L. Verlet and J. J. Weis, J. Chem. Phys. **5**, 939 (1972).

²⁰ J. M. Kincaid and J. J. Weis, Mol. Phys. **34**, 931 (1978).

²¹ See, e.g., G. Stell and J. S. Høye, Phys. Rev. Lett. **36**, 1569 (1976), J. D. Weeks, Philos. Mag. **35**, 1345 (1977).