Interfacial surface statistics arising in diffusion and flow problems in porous media

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A study is made of the surface–void, surface–surface, and surface–particle correlation functions that arise in expressions for transport properties associated with diffusion-controlled reactions and flow in porous media consisting of impenetrable spherical particles distributed randomly throughout void. The relationship between these three different correlation functions is noted for this model. We present an exact low-density expansion of the surface–particle correlation for such a distribution. All of the two-point correlation functions are computed, for the first time, from integral relations that we derived elsewhere, as a function of the distance between the two points for various sphere volume fractions up to 94% of the random close-packing value.

I. INTRODUCTION

In various transport processes that occur in disordered two-phase porous media the two-phase interface area plays a critical role in determining the bulk transport properties of the heterogeneous systems. Examples of such phenomena include diffusion-controlled chemical reactions in porous media and flow of fluids in such media. The key property in the former instance is the effective rate constant and in the latter case is the fluid permeability or Darcy's constant. Rigorous bounds have been derived on the effective rate constant and on the permeability[1,2] that depend upon, among other quantities, certain one- and two-point correlation functions that involve information about the interface. The one-point correlation function is simply the specific surface (the expected interface area per unit volume) s and has been recently evaluated as a function of porosity ϕ for various porous-media models.[3–5] The three different two-point functions (defined below) have only been computed, for all ϕ, for the model of fully penetrable (i.e., randomly centered) spheres in a "matrix" or "void" phase.[1,2]

Our ability to accurately estimate interfacial-dependent transport properties of porous media rests upon a quantitative understanding of two-point and higher order correlation functions that entail interfacial information. The purpose of this article is to study and evaluate the aforementioned two-point correlation functions for the model of totally impenetrable spheres embedded in a void phase; a model which can be readily tested in the laboratory. Results are reported for various values of the sphere volume fractions $\eta = 1 - \phi$ up to $\eta = 0.6$ We shall also show the relationship between these three different sets of two-point functions for this model.

II. DEFINITIONS AND REPRESENTATIONS OF TWO-POINT CORRELATION FUNCTIONS INVOLVING THE INTERFACE

Doi[1] has obtained bounds on the effective rate constant and permeability of porous media in terms of integrals that depend upon, among other statistical functions, the specific surface s and the two-point correlation functions, $F_{sv}(\mathbf{r}_1,\mathbf{r}_2)$ and $F_{ss}(\mathbf{r}_1,\mathbf{r}_2)$. These give, respectively, the correlation associated with finding a point at position $\mathbf{r}_1$ on the interface and another point at $\mathbf{r}_2$ in the void phase, and the correlation associated with finding a point at $\mathbf{r}_1$ and another point at $\mathbf{r}_2$ both on the interface. We refer to these quantities as the surface–void and surface–surface correlation functions, respectively. The phase outside the void phase is referred to as the included or particle phase. Weissberg and Prager[2] have derived bounds on the permeability of porous media composed of spheres embedded in void in terms of integrals that depend upon the interfacial-dependent quantities, s and a function closely related to $F_{sp}(\mathbf{r}_1, \mathbf{r}_2)$. The surface–particle function $F_{sp}(\mathbf{r}_1, \mathbf{r}_2)$ gives the correlation associated with finding a point at $\mathbf{r}_1$ on the interface and a sphere *center* in the volume element $d\mathbf{r}_2$ about $\mathbf{r}_2$. Note that $\mathbf{r}_2$ describes the center of a sphere and not a position anywhere in the particle phase. For statistically isotropic media, the two-point correlation functions depend only upon the relative distances between the two points, i.e., $r = |\mathbf{r}_1 - \mathbf{r}_2|$. For $r \to \infty$, the two-point correlation functions have the asymptotic forms

$$F_{sv}(r) \to s\phi, \quad F_{ss}(r) \to s^2, \quad F_{sp}(r) \to s\rho, \tag{1}$$

where $\rho = N/V$ is the number density and V is the volume of the macroscopic sample.

Here we shall be interested in calculating and understanding the relationship between the functions F_{sv}, F_{ss}, and F_{sp}, at fixed η, for an isotropic bed of equisized totally impenetrable spheres, rather than computing the integrals over them that arise in the property bounds described above. By an isotropic system of totally impenetrable spheres, we mean one in which spheres of radius R are randomly and isotropically distributed in space subject to the additional constraint that they each possess a mutually impenetrable core of radius R. Note that information about isotropy and impenetrability does not uniquely specify the ensemble.

Torquato[6] has recently derived series representations of a general n-point distribution function H_n which statistically characterizes a mixture of p spherical "solute" or "test" particles of radius $b_1,\ldots,b_p$, respectively, and N equisized "solvent" particles of radius R, where N is sufficiently large

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to justify a statistical treatment. In general, the solvent particles are distributed with arbitrary degree of penetrability. The n-point distribution function $H_n(\mathbf{r}^m;\mathbf{r}^{p-m};\mathbf{r}^{n-p})$ gives the correlation associated with finding m points with positions $\mathbf{r}^m \equiv \{\mathbf{r}_1,\ldots,\mathbf{r}_m\}$ on certain surfaces within the system, $p-m$ of the solute particles centered at positions $\mathbf{r}^{p-m} \equiv \{\mathbf{r}_{m+1},\ldots,\mathbf{r}_p\}$ and that any $n-p$ of the solvent particles have configuration $\mathbf{r}^{n-p} \equiv \{\mathbf{r}_{p+1},\ldots,\mathbf{r}_n\}$. In the special case that all the solute particles have zero radius ($b_i = 0, i = 1,\ldots,p$) and are constrained to be in the void phase only, the H_n reduce to the aforementioned two-point correlation functions.[6,7] Specifically, in this limit

$$F_{\rm sv}(\mathbf{r}_1,\mathbf{r}_2) = H_2(\mathbf{r}_1;\mathbf{r}_2;\varnothing), \tag{2}$$

$$F_{\rm ss}(\mathbf{r}_1,\mathbf{r}_2) = H_2(\mathbf{r}_1,\mathbf{r}_2;\varnothing;\varnothing), \tag{3}$$

and

$$F_{\rm sp}(\mathbf{r}_1,\mathbf{r}_2) = H_2(\mathbf{r}_1;\varnothing;\mathbf{r}_2), \tag{4}$$

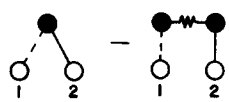
where $\varnothing$ denotes the null set.

Employing the results of Ref. 6 (in the special limit described above) for a homogeneous and isotropic distribution of totally impenetrable spheres, one may express the two-point correlations in terms of the one- and two-particle distribution functions, ρ_1 and $\rho_2(r)$, respectively. The quantity $\rho_n(\mathbf{r}^n)d\mathbf{r}^n$ (where $d\mathbf{r}^n \equiv d\mathbf{r}_1,\ldots,d\mathbf{r}_n$) gives the probability of finding the center of a particle in volume element $d\mathbf{r}_1$ about $\mathbf{r}_1$, the center of another particle in $d\mathbf{r}_2$ about $\mathbf{r}_2$, etc. For homogeneous and isotropic systems, $\rho_1 = \rho$ and $\rho_2(r)$, $r \equiv |\mathbf{r}_1 - \mathbf{r}_2|$, is related to the radial distribution function $g(r)$ according to the relation:

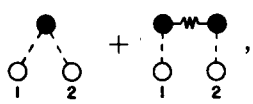
$$\rho_2(r) = \rho^2 g(r). \tag{5}$$

Specifically, it has been found[6] that

$$F_{\rm sv}(r) = s - \rho\delta \otimes m - \rho^2 g \otimes \delta \otimes m, \tag{6a}$$

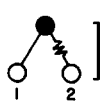
$= s -$  , (6b)

$$F_{\rm ss}(r) = \rho\delta \otimes \delta + \rho^2 g \otimes \delta \otimes \delta, \tag{7a}$$

$=$  , (7b)

and

$$F_{\rm sp}(r) = \rho\delta(\mathrm{r}-\mathrm{R})[1-\rho g \otimes \mathrm{m}] + \rho^2[1-\mathrm{m}(\mathrm{r})]\mathrm{g} \otimes \delta \tag{8a}$$

$= \rho\delta(r-R)\Big[1 -$  $\Big] + \rho[1-m(r)]$, (8b)

where

$$m(r) = \begin{cases} 1 & , \quad r < R \\ 0 & , \quad r > R \end{cases}, \tag{9}$$

$\delta(r-R)$ is the Dirac delta function, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and $r = r_{12}$. In the first lines of Eqs. (6)–(8), the symbol $\otimes$ denotes a three-dimensional convolution integral, i.e., for any pair of functions $G(r)$ and $H(r)$, $G \otimes H$ signifies

$$\int G(r)H(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'.$$

In the second lines of Eqs. (6)–(8), we have used standard graphical representation of the integrals[8];— is an m bond, --- is a δ bond, and ∼∧∼ is a g bond.

The graphical representation of the integrals helps to elucidate their physical significance. If we let $F_{si}(r)$ be the two-point correlation function associated with finding a point on the two-phase interface and another point anywhere in the included or particle phase, then clearly $F_{si}(r) + F_{\rm sv}(r)$ must be equal to the one-point correlation function s (which for totally impenetrable spheres is $4\pi R^2\rho$). The sum of the two graphs in Eq. (6b) is simply equal to $F_{si}(r)$; the first graph gives the contribution to F_{si} when point 1 is on the surface of a sphere and point 2 is anywhere inside the same sphere and the second graph gives the contribution to F_{si} when point 1 describes a position on the surface of a sphere and point 2 is anywhere inside another sphere. Hence, Eq. (6b) simply states that $F_{\rm sv} = s - F_{si}$.

Similarly, the first graph of Eq. (7b) is the contribution to $F_{\rm ss}$ when both points 1 and 2 describe positions on the surface of the same sphere. The second graph in this equation gives the contribution to $F_{\rm ss}$ when point 1 and point 2 describe the positions on the surfaces of different spheres.

The graph representing $\rho\delta(r-R)(1-\rho g \otimes m)$ in Eq. (8) accounts for the contribution to $F_{\rm sp}$ when point 1 is on the surface of the sphere centered at $\mathbf{r}_2$. Note $\rho(1-\rho g \otimes m)$ is equal to the void–particle correlation function $F_{\rm vp}(r)$ for totally impenetrable spheres described in Refs. 6 and 9. Therefore, the entire first term of Eq. (8b) is $\delta(r-R)F_{\rm vp}(r)$ which is nonzero only when $r = R$. When $r = R$, $F_{\rm vp}(r)$ is simply equal to ρ. The entire second term of Eq. (8) is the contribution to $F_{\rm sp}$ that accounts for the instance in which point 1 describes a position on the surface of a sphere and point 2 describes the center of some other sphere. The factor $[1-m(r)]$, equal to unity for $r > R$ and zero otherwise, arises here since point 1 must always lie outside of the sphere centered at $\mathbf{r}_2$.

Representation (8) for $F_{\rm sp}$ is new. Berryman[10] actually was the first to write down integral representations of $F_{\rm sv}$ and $F_{\rm ss}$ for the case of totally impenetrable spheres. Although these expressions[10] for $F_{\rm sv}$ and $F_{\rm ss}$ are equivalent to Eqs. (6) and (7), they differ from Eqs. (6) and (7) in that they do not explicitly involve the step function m and the Dirac delta function δ. The explicit appearance of m and δ in the integrands enables one to easily recognize that the integrals are in fact convolution integrals. This observation has two advantages: (1) First, one can apply Fourier-transform techniques which enable one to readily calculate the integrals for any void or sphere volume fraction and (2) the relationships between the $F_{\rm sv}$, $F_{\rm ss}$, and $F_{\rm sp}$ become immediately apparent. The last graphs in Eqs. (6) and (7), respectively, are the most difficult to evaluate. Berryman[10] used geometrical arguments to evaluate these graphs through zeroth order in ρ. He noted that this approach is not easily extended to higher order terms. However, since Berryman was interested in evaluating integrals over $F_{\rm sv}$ and $F_{\rm ss}$, he

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did not actually need to compute the correlation functions themselves.

Before evaluating the integrals in Eqs. (6)–(8), we first establish the relationship between the most complex graphs of the two-point correlation functions, which we denote by $\overline{F}_{sv}$, $\overline{F}_{ss}$, and $\overline{F}_{sp}$ and are defined by

$$\overline{F}_{sv}(r) = \rho^2 g \otimes \delta \otimes m, \tag{10}$$

$$\overline{F}_{ss}(r) = \rho^2 g \otimes \delta \otimes \delta, \tag{11}$$

$$\overline{F}_{sp}(r) = \rho^2 [1 - m(r)] g \otimes \delta. \tag{12}$$

Clearly, $\overline{F}_{sv}$ and $\overline{F}_{ss}$ can each be expressed in terms of $\overline{F}_{sp}$, i.e.,

$$\overline{F}_{sv}(r) = \left[\frac{\overline{F}_{sp}}{1-m}\right] \otimes m \tag{13}$$

and

$$\overline{F}_{ss}(r) = \left[\frac{\overline{F}_{sp}}{1-m}\right] \otimes \delta. \tag{14}$$

Torquato[6] has related the quantity $\overline{F}_{sp}/(1-m)$, for the general case of particles distributed with arbitrary degree of penetrability, to a conditional probability density function $R^{(1)}$ introduced by Weissberg and Prager.[2] $R^{(1)}(\mathbf{r},\hat{\mathbf{n}})\,d\mathbf{r}$ is the probability that, if $\mathbf{r}_1$ is on the interface and $\hat{\mathbf{n}}$ is the unit normal to the surface at $\mathbf{r}_1$, there will be a sphere center in $d\mathbf{r}$ about $\mathbf{r}_2 = \mathbf{r} + \mathbf{r}_1$. For the specific case of totally impenetrable spheres, $R^{(1)}(\mathbf{r},\hat{\mathbf{n}})d\hat{\mathbf{n}} = [1 - m(r)]\rho g(|\mathbf{r} - \mathbf{R}\hat{\mathbf{n}}|)$, and hence one has[6]

$$\rho R^2 \int R^{(1)}(\mathbf{r},\hat{\mathbf{n}})d\hat{\mathbf{n}} = \overline{F}_{sp}(r). \tag{15}$$

III. EVALUATION OF THE TWO-POINT CORRELATION FUNCTIONS F_{sv}, F_{ss}, and F_{sp}

Here we compute the two-point correlation functions F_{sv}, F_{ss}, and F_{sp} as a function of the sphere volume fraction η up to $\eta = 0.6$; a value which corresponds to approximately 94% of the random close-packing limit.[11] Having established that all of these morphological quantities can be expressed in terms of convolution integrals, we can exploit the useful property that the Fourier transform of a convolution integral is simply the product of the Fourier transforms of the individual functions. By taking the inverse Fourier transform of the transformed convolution integrals, one can then obtain the correlation functions as a function of the real space variable r. For a function $f(r)$ which depends upon the magnitude of $\mathbf{r}$, the Fourier transform and inverse Fourier transform, in three dimensions, are defined, respectively, by

$$\tilde{f}(k) = \frac{4\pi}{k}\int_0^\infty dr\, r f(r) \sin kr \tag{16}$$

and

$$f(r) = \frac{1}{2\pi^2 r}\int_0^\infty dk\, k \tilde{f}(k) \sin kr. \tag{17}$$

Here k is the magnitude of the wave number vector.

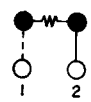
The first graphs of Eqs. (6) and (7) can readily be evaluated analytically using either Fourier transform techniques or by transforming to a bipolar coordinate system:[12]

$$= \begin{cases} \dfrac{s}{2}\left(1 - \dfrac{r}{2R}\right), & r \leqslant 2R \\ 0, & r > 2R \end{cases}, \tag{18}$$

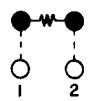
$$= \begin{cases} \dfrac{s}{2r}, & 0 < r \leqslant 2R \\ 0, & r > 2R \end{cases}, \tag{19}$$

where $s = 4\pi R^2 \rho$ is the specific surface. These graphs were first calculated by Berryman.[10]

It remains now to evaluate the nontrivial contributions to the correlation functions, i.e., $\overline{F}_{sv}$, $\overline{F}_{ss}$, and $\overline{F}_{sp}$. In light of the discussion given above, we have

$\overline{F}_{sv}(r) =$ 

$$= s\eta + \frac{\rho^2}{2\pi^2 r} \times \int_0^\infty dk\, k\tilde{h}(k)\tilde{\delta}(k)\tilde{m}(k)\sin kr, \tag{20}$$

$\overline{F}_{ss}(r) =$ 

$$= s^2 + \frac{\rho^2}{2\pi^2 r} \times \int_0^\infty dk\, k\tilde{h}(k)\tilde{\delta}(k)\tilde{\delta}(k)\sin kr, \tag{21}$$

and

$\overline{F}_{sp}(r) = \rho[1 - m(r)]$

$$= [1 - m(r)]\left\{s\rho + \frac{\rho^2}{2\pi^2 r}\int_0^\infty dk\, k\tilde{h}(k) \cdot \tilde{\delta}(k)\sin kr\right\}, \tag{22}$$

where

$$h(r) = g(r) - 1 \tag{23}$$

is the total correlation function and $\eta = 4\pi R^3\rho/3$. Here

$$\tilde{\delta}(k) = \frac{4\pi}{k} R \sin kR \tag{24}$$

and

$$\tilde{m}(k) = \frac{4\pi R^2}{k}\left[\frac{\sin kR}{(kR)^2} - \frac{\cos kR}{kR}\right]. \tag{25}$$

Note that the first terms in Eqs. (20)–(22) are the long-range values of $\overline{F}_{sv}$, $\overline{F}_{ss}$, and $\overline{F}_{sp}$, respectively. Given $\tilde{h}(k)$ for the ensemble, together with Eqs. (20)–(25), we can compute $\overline{F}_{sv}$, $\overline{F}_{ss}$, and $\overline{F}_{sp}$. We shall calculate these quantities for an equilibrium ensemble of totally impenetrable spheres. The total correlation function for such a model can be obtained by solving the Ornstein–Zernicke equation:

$$\tilde{h}(k) = \frac{\tilde{c}(k)}{1 - \rho\tilde{c}(k)}, \tag{26}$$

where $\tilde{c}(k)$ is the Fourier transform of the direct correlation function $c(r)$. Wertheim[13] solved the Ornstein–Zernicke equation for a system of totally impenetrable spheres exactly in the Percus–Yevick approximation and thus obtained $c(r)$ in this approximation. Verlet and Weis[14] have proposed a

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semiempirical modification of the Percus–Yevick total correlation function which provides a good fit to machine calculations. In Fig. 1 the Verlet–Weis radial distribution function is given as a function of radial distance for $\eta = 0.1, 0.3$, and 0.5. We shall employ the Verlet–Weis $h(r)$ to compute the integrals of Eqs. (20)–(22). The inverse Fourier transforms in these expressions are numerically computed, for arbitrary density, using standard techniques.[15]

Before presenting such numerical results, we note that the graph of Eq. (22) is relatively simple to evaluate exactly, through second order in ρ or η, by transforming to bipolar coordinates.[9,12] Specifically, we find $\overline{F}_{sp}$ is, through third order in η, given by

$$\overline{F}_{sp}(r) = [1 - m(r)]H(r;\rho), \tag{27}$$

where

$$H(r;\rho) = \rho s\{A(r) + \rho B(r) + 0(\rho^2)\}, \tag{28}$$

$$A(r) = \begin{cases} 0, & 0 \leqslant x < 1 \\ \left[\dfrac{1}{2} - \dfrac{3}{4x} + \dfrac{x}{4}\right], & 1 \leqslant x < 3 \\ 1, & x > 3, \end{cases} \tag{29}$$

$$B(r) = \begin{cases} \dfrac{\pi R^3}{120}\left[-\dfrac{431}{x} + 405 + 90x - 70x^2 + 5x^3 + x^4\right], & 1 \leqslant x < 3 \\ \dfrac{\pi R^3}{120}\left[\dfrac{625}{x} + 875 - 550x + 70x^2 + 5x^3 - x^4\right], & 3 \leqslant x < 5 \\ 0, & x \geqslant 5, \end{cases} \tag{30}$$

and

$$x = \frac{r}{R}.$$

Here we have utilized the density expansion of the total correlation function, for totally impenetrable spheres, through first order in η:[12]

$$h(r) = \begin{cases} -1, & 0 \leqslant x \leqslant 2 \\ \left[8 - 3x + \dfrac{1}{16}x^3\right]\eta, & 2 < x \leqslant 4 \\ 0, & x > 4. \end{cases} \tag{31}$$

In Figs. 2–4 we plot the quantities $\overline{F}_{sv}(r)/s\eta$, $\overline{F}_{ss}(r)/s^2$, and $\overline{F}_{sp}(r)/s\rho$, as a function of the distance r for $\eta = 0.1$, 0.3, and 0.5, respectively, as calculated from Eqs. (20)–(22) and the Verlet–Weiss $h(r)$. Tables I–III display these three quantities, respectively, at various values of r, for sphere volume fractions of 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6. Note that in the figures and tables, the two-point correlation functions defined by Eqs. (10)–(12) are scaled by their respective long-range values. These scaled two-point correlation functions oscillate about their long-range values of unity (an indication of some short-range ordering) with amplitude that becomes negligible on the scale of our figures after several radii. The variation of each function is most pronounced for r less than about $3R$. From the physical interpretations of the graphs given in the previous section, it is clear that $\overline{F}_{sv}(r)$ and $\overline{F}_{ss}(r)$ are equal to zero at $r = 0$ and $\overline{F}_{sp}(r) = 0$ for all $r \leqslant R$. $\overline{F}_{sv}(r)/s\eta$ and $\overline{F}_{ss}(r)/s^2$ rapidly go to one for $r > 3R$. The scaled surface–particle function, on the other hand, goes to one less rapidly than either $\overline{F}_{sv}(r)/s\eta$ and $\overline{F}_{ss}(r)/s^2$, and, in addition, possesses the distinctive feature of a density-independent maximum at $r = 3R$ which is discontinuous in the first derivative.

This interesting characteristic can be explained by studying the graph

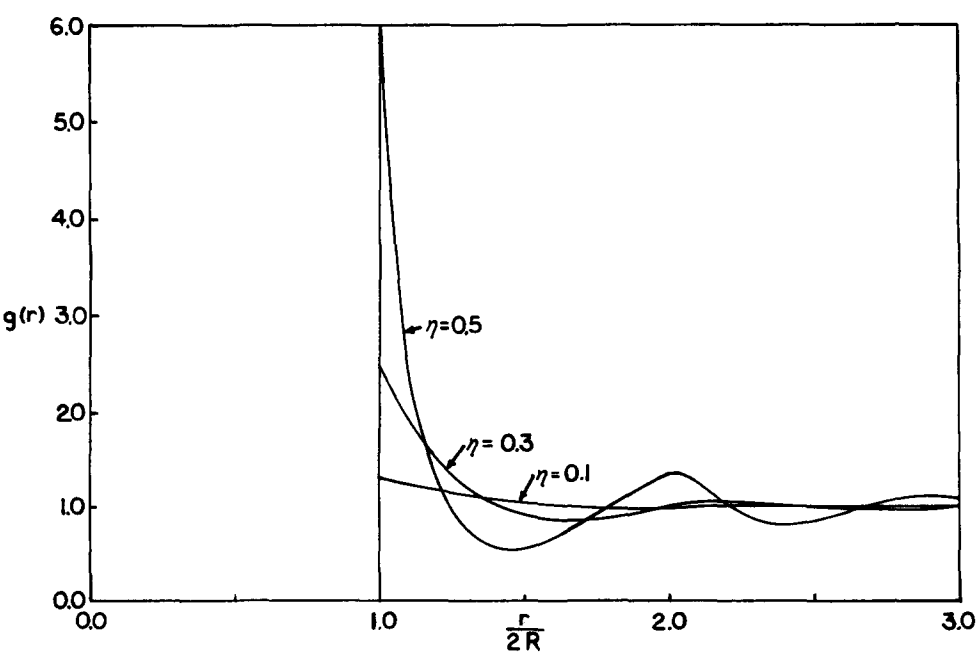

FIG. 1. The Verlet–Weis (Ref. 14) radial distribution function $g(r)$ as a function of r, for an impenetrable-sphere system at a sphere volume fraction $\eta = 0.1$, 0.3, and 0.5.

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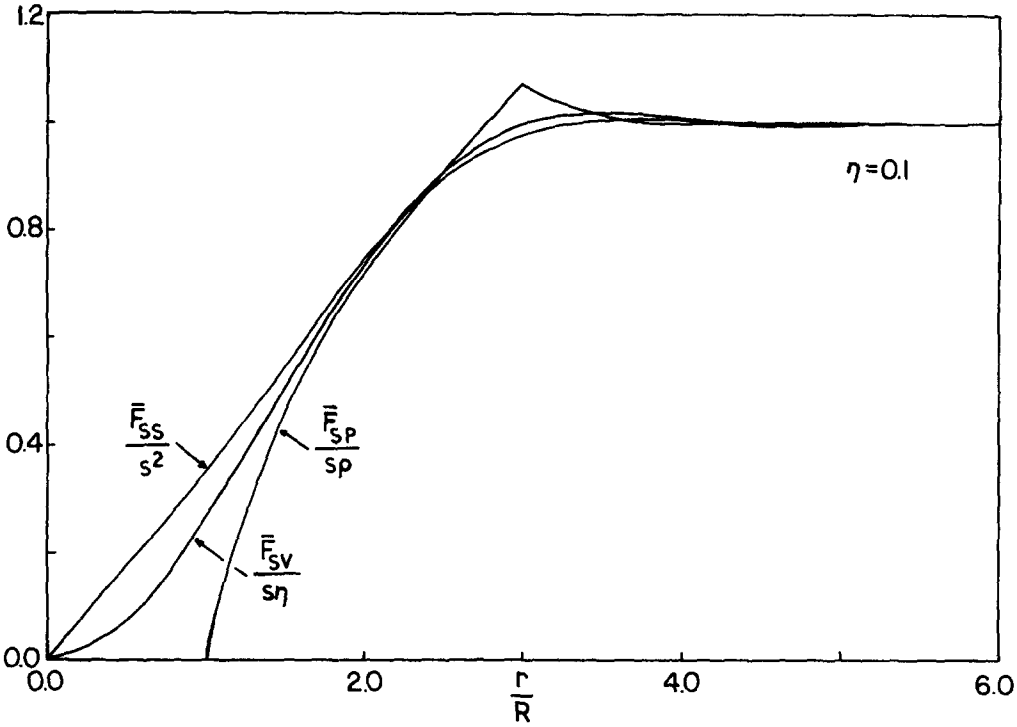

FIG. 2. The scaled two-point correlation functions $\bar{F}_{sv}(r)/s\eta$, $\bar{F}_{ss}(r)/s^2$, and $\bar{F}_{sp}(r)/s\rho$ vs r, for a distribution of impenetrable spheres of radius R at $\eta = 4\pi R^3\rho/3 = 0.1$. Here $s = 4\pi R^2\rho$ is the specific surface and ρ is the number density.

$$= \rho \int \delta(r_{13} - R) g(r_{23}) d\mathbf{r}_3$$

$$= \rho R^2 \int g(|\mathbf{r}_{12} - R\hat{\mathbf{n}}_{13}|) d\hat{\mathbf{n}}_{13} \qquad (32)$$

more closely. Here $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, $\hat{\mathbf{n}}_{13} = (\mathbf{r}_1 - \mathbf{r}_3)/|\mathbf{r}_1 - \mathbf{r}_3|$, and $d\hat{\mathbf{n}}_{13}$is the element of solid angle on the surface of the sphere centered at $\mathbf{r}_3$. Equation (32) states the convolution integral, for fixed r_{12}, is proportional to the angular average of the radial distribution function $g(r_{23})$ over the allowable surface of a sphere of radius R centered at $\mathbf{r}_1$. The integration region is depicted in Fig. 5. Clearly, for $r_{12} < 3R$, the sphere centered at $\mathbf{r}_3$ is prohibited from occupying all positions on the surface of the sphere centered at $\mathbf{r}_1$ because of the volume excluded to it due to the presence of a sphere at $\mathbf{r}_2$. We have that for $0 \leqslant \theta < \cos^{-1}[(r_{12}^2 - 3R^2)/2Rr_{12}]$, where θ is the included angle opposite the side of the triangle (described in Fig. 5) of length r_{23}, $g(r_{23}) = 0$.

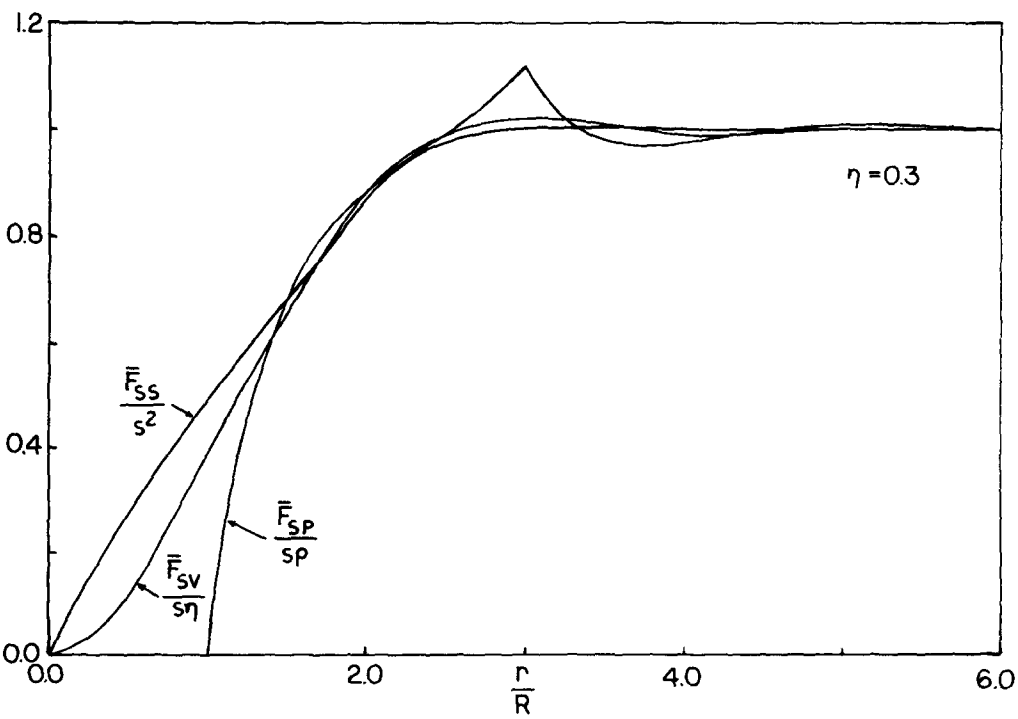

FIG. 3. As for Fig. 2 with $\eta = 0.3$.

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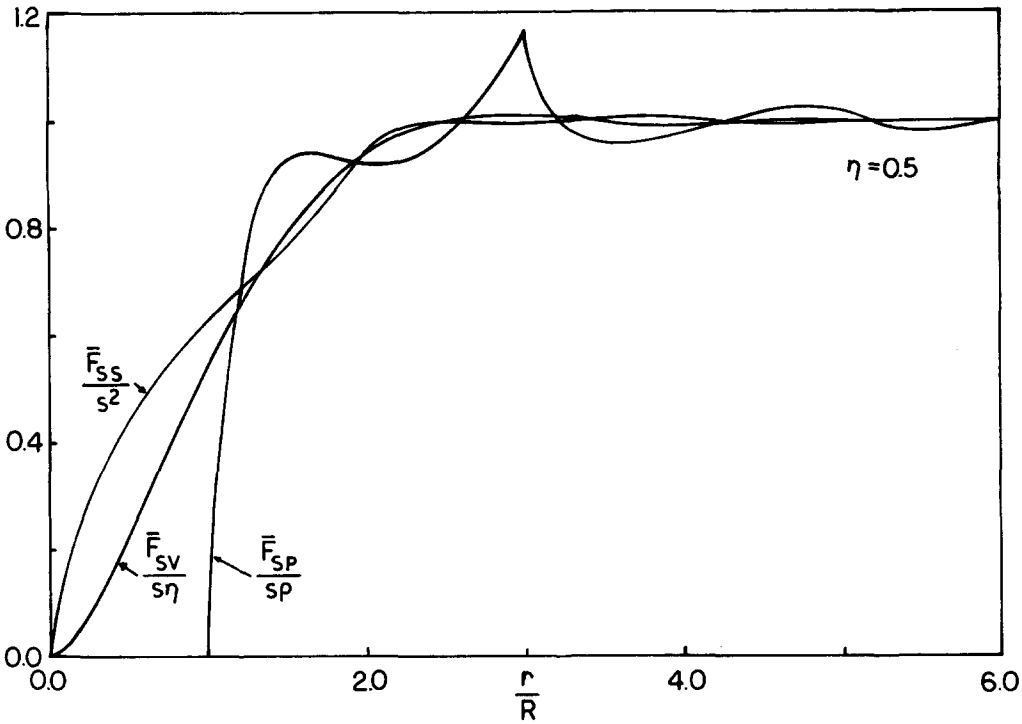

FIG. 4. As for Fig. 2 with $\eta = 0.5$.

Let us consider the functional behavior of $\overline{F}_{sp}(r_{12})$ for $r_{12} > R$ for the specific case $\eta = 0.5$. For r_{12} slightly greater than R, the radial distribution function is zero for most values of θ (cf. Fig. 1). As r_{12} is made larger, the average of $g(r_{23})$ over the surface increases (because the exclusion region decreases in size) and, thus, $\overline{F}_{sp}$ increases until r_{12} reaches a value of approximately $1.5R$. For $1.5R < r_{12} < 2R$, $\overline{F}_{sp}$ decreases slightly in value (cf. Fig. 4) since $g(r_{23})$ drops off rapidly for $2R < r_{23} < 3R$; the range of r_{23} that is heavily weighted in the integration for such r_{12}. Because $g(r_{23})$ increases for $3R < r_{23} < 4R$, the average of $g(r_{23})$ over the surface increases once again, thus explaining the reason why $\overline{F}_{sp}$ also increases for $2R < r_{12} < 3R$. For $r_{12} = 3R$, $r_{23} > 2R$, and hence $g(r_{23})$ is, for the first time, always greater than zero for all θ. For r_{12} slightly greater than $3R$, the average of $g(r_{23})$ over the surface must be less than the average of $g(r_{23})$ over the surface for $r_{12} = 3R$. Hence, although $\overline{F}_{sp}$ is continuous at $r_{12} = 3R$, its first derivative must be discontinuous. Moreover, this must also correspond to the maximum of the surface–particle correlation function $\overline{F}_{sp}$. The general arguments put forth above for r_{12} near $3R$ apply as well at other sphere volume fractions and, consequently, $\overline{F}_{sp}$ possesses a density-independent maximum at $r = 3R$ which is discontinuous in the first derivative. Indeed, the low-density expansion of $\overline{F}_{sp}$, Eq. (28), clearly exhibits this property.

Very recently, we learned that Seaton and Glandt[16] carried out a Monte Carlo simulation to compute F_{sv} and F_{ss} for impenetrable spheres at reduced densities of $\eta = 0.1, 0.2,$

TABLE I. The quantity $\overline{F}_{sv}(r)/s\eta$ at various values of r at $\eta = 0.1, 0.2, 0.3, 0.4, 0.5$, and 0.6.

	$\frac{\overline{F}_{sv}(r)}{s\cdot\eta}$					
r/R	$\eta = 0.1$	0.2	0.3	0.4	0.5	0.6
0.0	0.000	0.000	0.000	0.000	0.000	0.000
0.3	0.028	0.036	0.048	0.067	0.095	0.137
0.6	0.103	0.131	0.167	0.216	0.278	0.356
0.9	0.215	0.264	0.324	0.395	0.474	0.555
1.2	0.351	0.418	0.494	0.572	0.648	0.710
1.5	0.498	0.577	0.657	0.730	0.788	0.824
1.8	0.644	0.726	0.799	0.856	0.891	0.906
2.1	0.775	0.850	0.908	0.944	0.959	0.962
2.4	0.879	0.939	0.977	0.993	0.994	0.996
2.7	0.951	0.993	1.011	1.013	1.010	1.014
3.0	0.994	1.017	1.021	1.016	1.013	1.015
3.3	1.012	1.021	1.015	1.009	1.007	1.004
3.6	1.013	1.012	1.003	0.998	0.996	0.991
3.9	1.006	1.000	0.993	0.991	0.990	0.987
4.2	1.000	0.995	0.992	0.994	0.996	1.000
4.5	0.999	0.996	0.997	1.000	1.004	1.008

TABLE II. The quantity $\overline{F}_{ss}(r)/s^2$ at various values of r at $\eta = 0.1, 0.2, 0.3, 0.4, 0.5$, and 0.6.

	$\frac{\overline{F}_{ss}(r)}{s^2}$					
r/R	$\eta = 0.1$	0.2	0.3	0.4	0.5	0.6
0.0	0.000	0.000	0.000	0.000	0.000	0.000
0.3	0.100	0.129	0.171	0.231	0.314	0.432
0.6	0.204	0.254	0.317	0.394	0.485	0.582
0.9	0.312	0.375	0.446	0.522	0.596	0.654
1.2	0.423	0.493	0.564	0.630	0.682	0.713
1.5	0.539	0.611	0.677	0.731	0.767	0.788
1.8	0.660	0.731	0.791	0.835	0.865	0.888
2.1	0.784	0.852	0.905	0.943	0.971	0.998
2.4	0.875	0.930	0.966	0.985	0.995	0.998
2.7	0.936	0.974	0.992	0.996	0.994	0.986
3.0	0.975	0.997	1.003	1.000	0.995	0.988
3.3	0.998	1.009	1.008	1.004	1.001	1.001
3.6	1.009	1.012	1.008	1.006	1.007	1.013
3.9	1.009	1.007	1.004	1.003	1.005	1.010
4.2	1.003	1.000	0.997	0.996	0.996	0.994
4.5	1.000	0.997	0.997	0.997	0.997	0.992

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TABLE III. The quantity $\overline{F}_{sp}(r)/s\rho$ at various values of r at $\eta = 0.1$, 0.2, 0.3, 0.4, 0.5, and 0.6.

	$\frac{\overline{F}_{sp}(r)}{s\cdot\rho}$					
r/R	$\eta = 0.1$	0.2	0.3	0.4	0.5	0.6
1.0	0.000	0.000	0.000	0.000	0.000	0.000
1.2	0.222	0.288	0.381	0.511	0.699	0.920
1.5	0.457	0.559	0.678	0.805	0.926	1.008
1.8	0.627	0.728	0.824	0.899	0.933	0.895
2.1	0.760	0.845	0.908	0.936	0.918	0.868
2.4	0.871	0.936	0.971	0.972	0.949	0.938
2.7	0.970	1.018	1.036	1.034	1.035	1.071
3.0	1.058	1.094	1.108	1.129	1.167	1.249
3.3	1.031	1.032	1.014	0.993	0.984	0.960
3.6	1.011	0.999	0.980	0.969	0.960	0.925
3.9	1.001	0.988	0.977	0.975	0.969	0.956
4.2	0.997	0.988	0.987	0.991	0.993	1.010
4.5	0.996	0.994	0.999	1.007	1.017	1.048

0.3, and 0.4. Their results are in good agreement with the corresponding results given here. They did not calculate F_{sp}, however.

In this study, we have focused our attention on precise methods to characterize the microstructure of porous media rather than on bounds on transport properties which utilize this information. Elsewhere[6] we have computed the Doi[1] upper bound on the permeability (which utilizes F_{sv} and F_{ss}) for beds of impenetrable spheres using the highly accurate results of the present work. The Doi bound so calculated was compared to Berryman's results who computed the Doi bound (which involves integrals over two-point correlation functions) using a Monte Carlo integration routine. The Monte Carlo technique was found to significantly overestimate Doi's upper bound, thus implying that the Doi bound is much more accurate than Berryman originally concluded. This result has important implications since it offers hope that bounds on the permeability that incorporate the next level of microstructural information (i.e., three-point correlation functions) will lead to accurate estimates of it. An example of such a higher-order bound is the one due to Weissberg and Prager.[2]

IV. CONCLUSIONS

The two-point correlation functions $F_{sv}(r)$, $F_{ss}(r)$, and $F_{sp}(r)$ have been shown to be related to one another. The density expansion of the nontrivial contribution to the latter, denoted by $\overline{F}_{sp}$, has been presented exactly through third order in the sphere volume fraction η for a system of totally impenetrable spheres distributed throughout void. Finally, we have computed all of the two-point correlation functions for this model, as a function of r, for $\eta = 0.1$, 0.2, 0.3, 0.4, 0.5, and 0.6. Presently, we are in the process of calculating the Weissberg–Prager[2] bounds on the permeability using the results of this study and of Ref. 9.

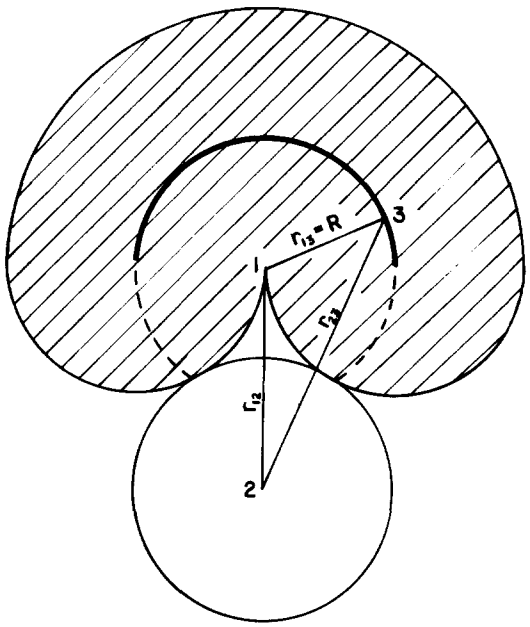

FIG. 5. Geometry for the integral of Eq. (32). The center of paricle 3 is constrained to be on the surface of a sphere of radius R centered at 1 such that the center of particle 3 is always a minimum distance of $2R$ away from a sphere centered at 2. The heavy solid and broken lines indicate the allowable and unallowable surfaces, respectively. The shaded area represents the region available to particle 3.

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