Nearest-neighbor distribution functions in many-body systems

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The probability of finding a nearest neighbor at some given distance from a reference point in a many-body system of interacting particles is of importance in a host of problems in the physical as well as biological sciences. We develop a formalism to obtain two different types of nearest-neighbor probability density functions (*void* and *particle* probability densities) and closely related quantities, such as their associated cumulative distributions and conditional pair distributions, for many-body systems of D-dimensional spheres. For the special case of impenetrable (hard) spheres, we compute low-density expansions of each of these quantities and obtain analytical expressions for them that are accurate for a wide range of sphere concentrations. Using these results, we are able to calculate the mean nearest-neighbor distance for distributions of D-dimensional impenetrable spheres. Our theoretical results are found to be in excellent agreement with computer-simulation data.

I. INTRODUCTION

In considering a many-body system of interacting particles, a key fundamental question to ask is the following: What is the effect of the nearest neighbor on some reference particle in the system? The answer to this query requires knowledge of the probability density which characterizes the probability of finding the nearest neighbor at some given distance from the reference particle, i.e., the nearest-neighbor distribution function H_P. Knowing H_P is of importance in a host of problems in the physical and biological sciences, including stellar dynamics,[1] liquids and amorphous solids,[2] and the transport properties of heterogeneous materials,[3−5] to mention but a few examples. Hertz[6] evidently was the first to consider its evaluation for a system of "point" particles, i.e., particles whose centers are Poisson distributed. To our knowledge, however, there is presently no theoretical formalism to obtain H_P for distributions of *finite-sized* interacting particles at arbitrary density. One of the goals of this paper is to provide such a formalism for D-dimensional spheres and to compute H_P for such models.

A different nearest-neighbor distribution function H_V arises in the *scaled-particle* theory of liquids.[7,8] This quantity (defined more precisely in Sec. II) essentially characterizes the probability of finding a nearest-neighbor particle center at a given distance from an arbitrary point located in the space *exterior* to the particles. Interestingly, although H_V and H_P are different quantities, we show here that they are, in fact, related to one another for a certain range of nearest-neighbor distances.

We refer to H_V and H_P as the "void" and "particle" nearest-neighbor distribution functions, respectively.

There are other quantities closely related to the nearest-neighbor probability densities that we also obtain representations for and compute in this study. These are the so-called exclusion probabilities E_V and E_P, and the conditional pair distribution functions G_V and G_P, defined in Sec. II.

In Sec. II, we define and describe the void and particle nearest-neighbor distribution functions, exclusion probabilities, and conditional pair distribution functions for distributions of identical, interacting D-dimensional spheres. In Sec. III, we obtain exact integral representations of each of the void and particle quantities for such model microstructures. In Sec. IV, we calculate low-density expansions of the void quantities for D-dimensional impenetrable (hard) spheres and, for arbitrary density, compute them exactly for $D = 1$ and approximately for $D = 2$ and 3. In Sec. V, we carry out analogous calculations for the particle quantities which, to our knowledge, are all new results. In Sec. VI, we use the results of the previous section to compute the mean nearest-neighbor distances for hard-sphere systems. Finally, we make concluding remarks in Sec. VII.

II. DEFINITIONS AND GENERAL RELATIONS

A. Systems of interacting spheres

We shall consider studying nearest-neighbor distribution functions and closely related quantities for a general

system of N identical, interacting D-dimensional spheres of diameter σ spatially distributed in a volume V according to the N-particle probability density $P_N(\mathbf{R}^N)$. $P_N(\mathbf{R}^N)$ characterizes the probability of finding the particles labeled $1, 2, \ldots, N$ with configuration $\mathbf{R}^N \equiv \{\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N\}$, respectively, and normalizes to unity. Then the reduced n-particle probability density ρ_n $(n < N)$ is defined by

$$\rho_n(\mathbf{R}^n) = \frac{N!}{(N-n)!} \int P_N(\mathbf{R}^N) d\mathbf{R}^{N-n} , \qquad (2.1)$$

where $d\mathbf{R}^{N-n} \equiv d\mathbf{R}_{n+1} \cdots d\mathbf{R}_N$. $\rho_n(\mathbf{R}^n)$ characterizes the probability of simultaneously finding the center of a particle in volume element $d\mathbf{R}_1$ about $\mathbf{R}_1$, the center of another particle in volume element $d\mathbf{R}_2$ about $\mathbf{R}_2$, etc.

The ensemble average of any many-body function $F(\mathbf{R}^N)$ is given by

$$\langle F(\mathbf{R}^N) \rangle = \int F(\mathbf{R}^N) P_N(\mathbf{R}^N) d\mathbf{R}^N . \qquad (2.2)$$

If the medium is statistically homogeneous, the $\rho_n(\mathbf{R}^n)$ depend upon the relative displacements $\mathbf{R}_2 - \mathbf{R}_1$, $\mathbf{R}_3 - \mathbf{R}_1, \ldots, \mathbf{R}_n - \mathbf{R}_1$. In such instances, it is implied that the "thermodynamic limit" has been taken, i.e., $N \to \infty$ and $V \to \infty$, such that $\rho = N/V = \rho_1(\mathbf{R}_1)$ is some finite constant. We should note that many of the results of this paper will be valid for the general case of statistically *inhomogeneous* media.

Let us examine two different types of nearest-neighbor distribution functions $H_V(r)$ and $H_P(r)$ defined as follows:

$H_V(r)dr = $ Probability that at an arbitrary point in the system the center of the nearest

particle lies at a distance between r and $r + dr$;   (2.3)

$H_P(r)dr = $ Probability that, given any D-dimensional sphere of diameter σ at some arbitrary position

in the system, the center of the nearest particle lies at a distance between r and $r + dr$.   (2.4)

H_V and H_P are referred to as void and particle nearest-neighbor distribution functions, respectively. We refer to the $H_V(r)$ as a *void* nearest-neighbor distribution function since it provides a measure of the probability associated with finding the nearest particle at a distance r from a spherical *cavity* centered in the void region (when $r \geq \sigma/2$), i.e., the region exterior to the spheres. $H_P(r)$ is termed a *particle* nearest-neighbor distribution function since it provides a measure of the probability associated with finding the nearest particle at a distance r from an actual particle at the origin. The void nearest-neighbor distribution function defined here is identical to the one defined in the scaled-particle theory of Reiss, Frisch, and

Lebowitz.[7] To our knowledge, the distinction between H_V and H_P, however, has heretofore not been made. Indeed, in the past, these functions have been incorrectly thought to be identical to one another. Note that both these functions are actually probability density functions and have dimensions of inverse length. Observe further that for statistically *inhomogeneous* media, $H_V(r)$ and $H_P(r)$ will depend also upon the position of the arbitrary point and the location of the central particle, respectively.[9]

It is useful to introduce "exclusion" probabilities $E_V(r)$ and $E_P(r)$ defined as follows:

$E_V(r) = $ Probability of finding a region Ω_V, which is a D-dimensional spherical cavity

of radius r (centered at some arbitrary point), empty of particle centers ,

$= $ Probability of inserting a "test" particle of radius $r - \sigma/2$ (at some arbitrary

position) in the system of N particles ;   (2.5)

$E_P(r) = $ Probability that, given any D-dimensional sphere at some arbitrary position, the region Ω_P, which is a

sphere of radius r encompassing this central particle, is empty of particle centers .   (2.6)

Figure 1 gives a schematic representation of the regions Ω_V and Ω_P. Note that the first and second lines of (2.5) are equivalent since the region excluded to a particle center of radius $\sigma/2$ by a test particle of radius $r - \sigma/2$ is

a sphere of radius r. The *test* particle serves to probe the void region. It follows that the exclusion probabilities are related to the nearest-neighbor distribution functions by the expressions
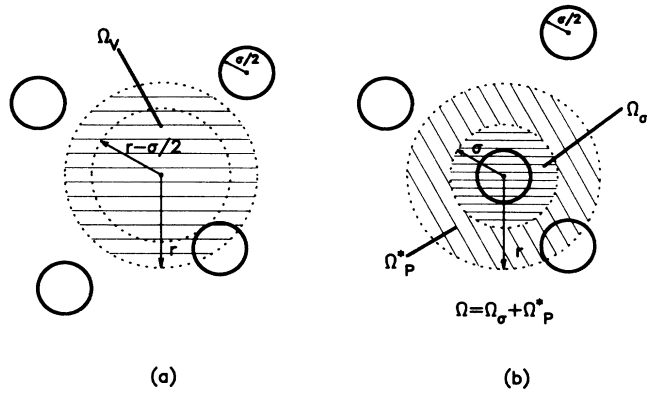
FIG. 1. Schematic representations of the regions Ω_V and Ω_P: (a) Ω_V is the cross hatched region which is a sphere of radius r. The sphere of radius $r-\sigma/2$ can be interpreted as a "test" particle of the same radius; (b) $\Omega=\Omega_P^*+\Omega_\sigma$ is a sphere of radius r surrounding the central particle. Ω_P^* is the crosshatched region which is the concentric shell of inner radius σ and outer radius r. Ω_σ is the crosshatched region which is a sphere of radius σ.

$$E_V(r)=1-\int_0^r H_V(x)dx \tag{2.7}$$

and

$$E_P(r)=1-\int_0^r H_P(x)dx \ . \tag{2.8}$$

The integrals of (2.7) and (2.8), respectively, represent the probabilities of finding at least one particle center in re-

gions Ω_V and Ω_P. Differentiating the exclusion-probability relations with respect to r gives

$$H_V(r)=\frac{-\partial E_V(r)}{\partial r} \tag{2.9}$$

and

$$H_P(r)=\frac{-\partial E_P(r)}{\partial r} \ . \tag{2.10}$$

For statistically homogeneous media, it is helpful to write the nearest-neighbor distribution functions as a product of two different correlation functions. Specifically, for D-dimensional particles let

$$H_V(r)=\rho s_D(r)G_V(r)E_V(r) \tag{2.11}$$

and

$$H_P(r)=\rho s_D(r)G_P(r)E_P(r) \ , \tag{2.12}$$

where s_D is the surface area of a D-dimensional sphere of radius r,

$$s_1(r)=2 \ , \tag{2.13}$$

$$s_2(r)=2\pi r \ , \tag{2.14}$$

$$s_3(r)=4\pi r^2 \ . \tag{2.15}$$

Given definitions (2.3)–(2.6), the *conditional* "pair" distribution functions G_V and G_P must have the following interpretations:

$\rho s_D(r)G_V(r)dr=$Probability that, given a region Ω_V (spherical cavity of radius r)

is empty of particle centers, particle centers

are contained in the spherical shell of volume $s_D dr$ encompassing the cavity ;   (2.16)

$\rho s_D(r)G_P(r)dr=$Probability that, given a region Ω_P (sphere of radius r encompassing any particle centered

at some arbitrary position) is empty of particle centers, particle centers are contained in the

spherical shell of volume $s_D dr$ surrounding the central particle .   (2.17)

Note that $G_V(r)$ is simply the "radial" distribution function for the test particle (of radius $r-\sigma/2$) and a particle (of radius $\sigma/2$) at contact, i.e., when this pair of particles are separated by the distance r [cf. Eq. (2.5)]. Equations (2.11) and (2.12) may be regarded as definitions of G_V and G_P, respectively. When $r=\sigma$, then $G_V(\sigma)=G_P(\sigma)$ is just the standard radial distribution function $g_2(\sigma)$ for identical spheres at contact, i.e., at an interparticle separation of σ. For equilibrium distributions of hard spheres, $g_2(\sigma)$ is simply related to the pressure of the system.[10] Also as $r\to\infty$, the sphere of radius r (in either the void or particle problems) may be regarded as a plane rigid wall relative to the particles and, in particular, to the particles in contact with the wall, hence $G_V(\infty)=G_P(\infty)$. To summarize, G_V and G_P are identical when $r=\sigma$ and

$r=\infty$. We know generally they are not the same for $r\le\sigma$ [cf. (2.25) and (2.31)]; but are they related to one another for $r\ge\sigma$? This interesting question, for the special case of impenetrable spheres, is examined shortly.

The exclusion probabilities are related to the pair distribution functions via the expressions

$$E_V(r)=\exp\left[-\int_0^r \rho s_D(y)G_V(y)dy\right] \ , \tag{2.18}$$

$$E_P(r)=\exp\left[-\int_0^r \rho s_D(y)G_P(y)dy\right] \ , \tag{2.19}$$

which are obtained by use of (2.9)–(2.12). The combination of (2.9), (2.10), (2.18), and (2.19) yields

$$H_V(r)=\rho s_D(r)G_V(r)\exp\left[-\int_0^r \rho s_D(y)G_V(y)dy\right] \tag{2.20}$$

and

$$H_P(r) = \rho s_D(r) G_P(r) \exp\left[-\int_0^r \rho s_D(y) G_P(y) dy\right] . \quad (2.21)$$

Therefore one can compute the nearest-neighbor distribution functions given either the exclusion probability functions [cf. (2.9) and (2.10)] or the pair distribution functions [cf. (2.20) and (2.21)].

Finally, we can write down an expression for the "mean nearest-neighbor distance" l between particles as follows:

$$l = \int_0^\infty r H_P(r) dr . \quad (2.22)$$

Thus l is defined to be the first moment of r, where r is distributed according to the particle nearest-neighbor distribution function.

For the case of hard-sphere systems described below, Eq. (2.22) can be used to obtain a operational definition for the random close-packing density. Specifically, one can define it to be the density for which $l \to \sigma$. This is reasonable since each particle at the random close-packing density must touch its nearest neighbor.

B. Systems of impenetrable spheres

Consider the special case of distributions of mutually impenetrable (hard) spheres of diameter σ, i.e., systems of spheres characterized by a pair potential which is zero when the interparticle distance x is greater than σ and infinite when $x \leq \sigma$. Calculations of the nearest-neighbor distribution functions and the auxiliary quantities, the exclusion probabilities and conditional pair distribution functions, are generally nontrivial for such models. However, for such microstructures, one can state exact relations for certain small ranges of r. For instance, it is clear from the definitions (2.4) and (2.8) that

$$E_P(r) = 1, \quad \text{for } 0 \leq r \leq \sigma \quad (2.23)$$

$$H_P(r) = 0, \quad \text{for } 0 \leq r \leq \sigma \quad (2.24)$$

because one particle excludes another from occupying the same space. From (2.12) or (2.19) it immediately follows that

$$G_P(r) = 0, \quad \text{for } 0 \leq r \leq \sigma . \quad (2.25)$$

Furthermore, in the case of the void problem, a spherical cavity of radius r and volume rs_D/D can contain at most one particle center if $r \leq \sigma/2$. Thus, for statistically

homogeneous media, the exclusion probability is then given by

$$E_V(r) = 1 - \rho\frac{rs_D(r)}{D}, \quad \text{for } 0 \leq r \leq \sigma/2 \quad (2.26)$$

and hence by (2.9) we also have

$$H_V( ) = \rho s_D(r), \quad \text{for } 0 \leq r \leq \sigma/2 . \quad (2.27)$$

For $r \leq \sigma/2$, $\rho rs_D/D$ is just the probability that the cavity of radius r is occupied and hence $E_V(r)$ is just one minus this latter quantity. Note that for $r < \sigma/2$, the test particle may be regarded as a *point particle* that is capable of *penetrating* the mutually impenetrable particles. Hence, for $r < \sigma/2$, decreasing r then increases E_V, according to Eq. (2.26), until E_V reaches its maximum value of unity at $r = 0$. Note that for $r = \sigma/2$,

$$E_V(\sigma/2) = 1 - \eta$$
$$= 1 - \phi_2 = \phi_1 , \quad (2.28)$$

where

$$\eta = \rho v_D(\sigma/2) \quad (2.29)$$

is a D-dimensional reduced density, equal to the particle volume fraction ϕ_2; therefore $\phi_1 = 1 - \phi_2$ is just the *void* volume fraction. Here

$$v_D(r) = \frac{rs_D(r)}{D} , \quad (2.30)$$

and, therefore, the quantity $v_D(\sigma/2)$ appearing in (2.29) is the volume of a D-dimensional of particle. From (2.11) or (2.13) and the equations immediately above, one also has

$$G_V(r) = \frac{1}{1 - \rho rs_D(r)/D}, \quad \text{for } 0 \leq r \leq \sigma/2 . \quad (2.31)$$

For particles that can overlap one another, relations (2.23)–(2.27) and (2.31) will not hold. This point shall be elaborated upon in the ensuing sections.

Although the void and particle quantities are not the same for $r < \sigma$, they are, in fact, related to one another for $r \geq \sigma$ in the case of a *statistically homogeneous* medium of hard spheres. This is demonstrated by reinterpreting the *particle* exclusion probability $E_P(r)$. Referring to Fig. 1 and noting that any particle center can come no closer than a diameter σ to the central particle, $E_P(r)$ for $r \geq \sigma$ is the following *conditional* probability:

$E_P(r) =$ Probability that, given that a region Ω_σ (which is a sphere of radius σ centered at some arbitrary position) is empty of sphere centers, the region Ω_P^* is empty of sphere centers .   (2.32)

A key part of (2.32) is the conditional statement *that a sphere of radius σ is empty of sphere centers*. This condition (for a statistically homogeneous medium of hard spheres) is effectively equivalent to placing a hard sphere of radius $\sigma/2$ at the same point as the spherical void re-

gion. In other words, the environment around a hard sphere of radius $\sigma/2$ is the same as the environment around a spherical void region of radius σ. Therefore, since the *void* exclusion probability $E_V(r)$ gives the probability of finding the region $\Omega_V = \Omega_\sigma + \Omega_P^*$ empty of

sphere centers, we have, in the *thermodynamic limit*, that

$$E_P(r) = \frac{E_V(r)}{E_V(\sigma)}, \quad r \geq \sigma \ . \tag{2.33}$$

The combination of (2.33) with (2.9) and (2.10) gives the following expression relating the different nearest-neighbor distribution functions:

$$H_P(r) = \frac{H_V(r)}{E_V(\sigma)}, \quad r \geq \sigma \ . \tag{2.34}$$

Now from (2.11) and (2.12) we exactly have

$$\frac{G_P(r)}{G_V(r)} = \frac{H_P(r)}{H_V(r)} \frac{E_V(r)}{E_p(r)}, \quad r \geq \sigma \ . \tag{2.35}$$

The substitution of (2.33) and (2.34) into (2.35) then yields

$$G_P(r) = G_V(r), \quad r \geq \sigma \ . \tag{2.36}$$

It is important to emphasize that relations (2.33), (2.34), and (2.36) are valid only for infinite hard-sphere systems. For inhomogeneous systems of hard spheres, these equations will not hold. We shall make use of these relations in Sec. V.

In closing, we note that for an *equilibrium* distribution of D-dimensional impenetrable spheres, one can relate the void pair distribution function at $r = \sigma$ to this function at $r = \infty$; for $D = 1$, 2, and 3, respectively, one has[7,8]

$$G_V(\infty) = G_V(\sigma) \ , \tag{2.37}$$

$$G_V(\infty) = 1 + 2\eta G_V(\sigma) \ , \tag{2.38}$$

$$G_V(\infty) = 1 + 4\eta G_V(\sigma) \ . \tag{2.39}$$

Hence, in light of our previous observations that $G_V(\sigma) = G_P(\sigma)$ and $G_V(\infty) = G_P(\infty)$, we also have analogous relations for the particle pair distribution functions which are identical to Eqs. (2.37)–(2.39). Note that relations (2.37)–(2.39) are simply the scaled equations of state (reduced pressures) for $D = 1$, 2, and 3, respectively.

III. EXACT INTEGRAL EQUATIONS FOR THE VOID AND PARTICLE QUANTITIES

Torquato[11] has given exact series representations of a very general n-point distribution function H_n from which one can obtain the void quantities H_V, E_V, and G_V for systems of spheres which interact with an arbitrary potential. The coefficients of these series are multidimensional integrals involving the n-particle probability density functions ρ_N [cf. Eq. (2.1)]. In what follows, we shall briefly review the procedure used by Torquato to derive the aforementioned series representation; this is instructive since we shall subsequently use a similar formalism to obtain integral representations, for the first time, for the particle quantities H_P, E_P, and G_P.

A. Void quantities

Torquato[11] actually considered adding $p \geq 1$ test particles to the system and, as a result, was able to consider a very general n-point distribution function

$H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{R}^q)$, which depends (in his notation) upon the radii $b_1, \ldots, b_p$ of the test particles, where $n = p + q$. The arguments $\mathbf{x}^m$, $\mathbf{x}^{p-m}$, and $\mathbf{R}^q$ refer to positions of m points on certain surfaces within the system, the centers of $p - m$ test particles, and the centers of q particles, respectively. H_V, E_V, and G_V are subsets of H_n. In particular, to obtain the void quantities, we need only consider the addition of *one* test particle of radius $r - \sigma/2$ (or b_1 in Torquato's notation), with the correspondence that

$$H_V(r) = H_1(\mathbf{x}_1; \emptyset; \emptyset) \ , \tag{3.1}$$

$$E_V(r) = H_1(\emptyset; \mathbf{x}_1; \emptyset) \ , \tag{3.2}$$

$$G_V(r) = \lim_{|\mathbf{x}_1 - \mathbf{R}_1| \to r} \frac{H_2(\emptyset; \mathbf{x}_1; \mathbf{R}_1)}{\rho E_V(r)} \ , \tag{3.3}$$

where $\emptyset$ denotes the null set. Note that since we are considering statistically homogeneous media, the right-hand sides of (3.1) and (3.3) do not depend upon the position $\mathbf{x}_1$, but, as noted earlier, implicitly depend upon the radius $b_1 = r - \sigma/2$ of the test particle.

The starting point for the development of the formalism of Ref. 11 is an explicit expression for the characteristic function of the space D_1 available to a test particle centered at $\mathbf{x}_1 \equiv \mathbf{x}$,

$$I(\mathbf{x}; r) = \begin{cases} 1, & \mathbf{x} \in D_1 \\ 0, & \text{otherwise} \end{cases} \tag{3.4}$$

in terms of the positions of the particles $\mathbf{R}^N$. It was found that

$$I(\mathbf{x}; r) = \prod_{i=1}^{N} [1 - m(|\mathbf{x} - \mathbf{R}_i|; r)] \ , \tag{3.5}$$

where

$$m(y; r) = \begin{cases} 1, & y < r \\ 0, & y > r. \end{cases} \tag{3.6}$$

Torquato and Stell[12] were the first to state and use result (3.5) for point test particles, i.e., $r = \sigma/2$.

It turns out that $E_V(r)$ is simply the ensemble average of $I(\mathbf{x}; r)$. From Ref. 11, we have

$$E_V(r) = \sum_{k=0}^{N} (-1)^k E_V^{(k)}(r) \ , \tag{3.7}$$

where

$$E_V^{(k)}(r) = \frac{1}{k!} \int \rho_k(\mathbf{R}^k) \prod_{i=1}^{k} m(|\mathbf{x} - \mathbf{R}_i|; r) d\mathbf{R}_i \ ,$$

$$E_V^{(0)}(r) = 1 \ .$$

Result (3.7) was first given by Reiss, Frisch, and Lebonitz,[7] using a different argument. Differentiating (3.7) according to relation (2.9) yields an explicit series representation for $H_V(r)$ in terms of the ρ_n,

$$H_V(r) = \sum_{k=1}^{N} (-1)^k H_V^{(k)}(r) \ ,$$

$$\tag{3.8}$$

$$H_V^{(k)}(r) = -\frac{1}{k!} \frac{\partial}{\partial r} \int \rho_k(\mathbf{R}^k) \prod_{i=1}^{k} m(|\mathbf{x} - \mathbf{R}_i|; r) d\mathbf{R}_j \ .$$

Observe that expressions (3.7) and (3.8) are valid for statistically *inhomogeneous* media as well; for such media, E_V and H_V will depend not only upon r but upon the position of the test particle $\mathbf{x}$.

Finally, we can get an expression for the void pair distribution function $G_V(r)$ by use of (2.11), (3.7), and (3.8) or by evaluating the function H_2 of Ref. 11 according to Eq. (3.3). The latter procedure, for statistically homogeneous media, yields

$$G_V(r)= \lim_{|\mathbf{x}-\mathbf{R}_1|\to r} \frac{1}{\rho E_V(r)}\left[\rho+\sum_{k=1}^{\infty}\frac{(-1)^k}{k!}\int \rho_{k+1}(\mathbf{R}^{k+1})\prod_{i=2}^{k+1} m(|\mathbf{x}-\mathbf{R}_i|;r)d\mathbf{R}_i\right].\tag{3.9}$$

This particular representation of G_V, to our knowledge, is new. This result may be rewritten as

$$G_V(r)=\sum_{k=0}^{\infty}(-1)^k G_V^{(k)}(r),\tag{3.10}$$

where the $G_V^{(k)}(r)$ are obtained by combining (3.7) with (3.9); for example, the first two terms are given by

$$G_V^{(0)}(r)=1,$$

$$G_V^{(1)}(r)= \lim_{|\mathbf{x}-\mathbf{R}_1|\to r}\frac{1}{\rho}\int[\rho_2(\mathbf{R}_1,\mathbf{R}_2)-\rho^2]m(|\mathbf{x}-\mathbf{R}_2|;r)d\mathbf{R}_2.$$

The comparison of (3.9) to (2.11) reveals that the quantity within the large parentheses of (3.9) is related to the nearest-neighbor distribution functions, i.e.,

$$H_V(r)= \lim_{|\mathbf{x}-\mathbf{R}_1|\to r} s_D(r)\left[\rho+\sum_{k=1}^{\infty}\frac{(-1)^k}{k!}\int \rho_{k+1}(\mathbf{R}^{k+1})\prod_{i=2}^{k+1} m(|\mathbf{x}-\mathbf{R}_i|;r)d\mathbf{R}_i\right].\tag{3.11}$$

Thus, although (3.11) is equivalent to (3.8), it is a different representation of $H_V(r)$.

To summarize, given the n-particle probability density functions ρ_n for the ensemble under consideration, we can now determine E_V, H_V, and G_V using the exact expressions (3.7), (3.8), and (3.9), respectively, for general distributions of spheres.

1. Impenetrable particles

Consider the case of a random distribution of mutually impenetrable particles. Let us first use the series (3.7)–(3.9) to verify the exact relations (2.26), (2.27), and (2.29), which apply when $r\leq\sigma/2$. For this model, the product

$$\rho_k(\mathbf{R}^k)\prod_{i=1}^{k} m(|\mathbf{x}-\mathbf{R}_i|;r),$$

appearing in the kth term of (3.7), is identically zero when $r\leq\sigma/2$ for all $k\geq2$, since $m(y;r)=0$ for $y>r$ while $\rho_k(\mathbf{R}^k)=0$ for all $|\mathbf{R}_i-\mathbf{R}_j|<\sigma$, for any i and j such that $1\leq i<j\leq k$, i.e., we have exactly

$$E_V(r)=1-\int \rho_1(\mathbf{R}_1)m(|\mathbf{x}-\mathbf{R}_1|;r)d\mathbf{R}_1,$$

which is identical to (2.26) in the case of homogeneous media. Equation (3.8), under such conditions, yields (2.27) for $H_V(r)$. In general, the expression within the large parentheses of (3.9) is nontrivial; however, in the limit $|\mathbf{x}-\mathbf{R}_1|\to r\leq\sigma/2$, it is simply given by ρ and hence

(3.9) for $G_V(r)$ reduces exactly to (2.29).

Exact evaluations of series (3.7)–(3.9) for impenetrable particles is generally not possible because the infinite set $\rho_2\cdots\rho_n(n\to\infty)$ is never known. However, density expansions of these series can be obtained, and, in addition, accurate approximations of E_V, H_V, and G_V can be derived and computed. Such results are reported in Sec. V. We emphasize here that these quantities depend upon r, σ, and ρ.

2. Fully penetrable particles

Consider now the case of fully penetrable particles, i.e., randomly centered or spatially uncorrelated spheres. This simple model may be regarded as a uniform distribution of independent point particles (hence the sphere diameter becomes a meaningless parameter) for which the n-particle probability densities are trivial, namely, $\rho_n=\rho^n$, and therefore we find from (3.7)–(3.9) that

$$E_V(r)=\exp[-\rho v_D(r)],\tag{3.12}$$

$$H_V(r)=\rho s_D(r)E_V(r),\tag{3.13}$$

and

$$G_V(r)=1.\tag{3.14}$$

These results are well known and date back to at least the work of Hertz,[6] who obtained these quantities for $D=3$. For this simple model, the corresponding particle quanti-

ties are exactly the same (in the thermodynamic limit), as shall be shown. Note that $E_V(\sigma/2)=\exp(-\eta)=\phi_1$, where ϕ_1 is the *void* volume fraction and η is the reduced density defined by (2.29). Hence, for fully penetrable inclusions, the inclusion volume fraction $\phi_2=1-\phi_1 = 1-\exp(-\eta)$, in contrast to the totally impenetrable case for which $\phi_2=\eta$ [cf. (2.28)].

B. Particle quantities

Here we derive, for the first time, exact integral representations for the particle quantities E_P, H_P, and G_P for systems of spheres which interact with an arbitrary potential. Following the procedure used above for the void quantities, we define the characteristic function

$$
\begin{aligned}
J(\mathbf{R}_1;r)&=\prod_{i=2}^{N}[1-m(|\mathbf{R}_1-\mathbf{R}_i|;r)]\\
&=1-\sum_{i=2}^{N}m(|\mathbf{R}_1-\mathbf{R}_i|;r)+\sum_{\substack{i=2\\i<j}}^{N}m(|\mathbf{R}_1-\mathbf{R}_i|;r)m(|\mathbf{R}_1-\mathbf{R}_j|;r)\\
&\quad-\sum_{\substack{i=2\\i<j<k}}^{N}m(|\mathbf{R}_1-\mathbf{R}_i|;r)m(|\mathbf{R}_1-\mathbf{R}_j|;r)m(|\mathbf{R}_1-\mathbf{R}_k|;r)+\cdots ,
\end{aligned}
\tag{3.15}
$$

where m is the step function defined by (3.6). Note that we are singling out particle 1 (unlike the case of the void quantities) since the particle quantities always involve a centrally located particle at some position which we take here to be $\mathbf{R}_1$. In the second line of (3.15), the nth sum is over all unordered n tuplets of particles and hence contains $(N-1)!/[(N-n-1)!n!]$ terms.

Now the particle exclusion probability E_P is related to the ensemble average of NJ over all possible configurations of the particles, except the one located at $\mathbf{R}_1$,

$$
N\int J(\mathbf{R}_1;r)P_N(\mathbf{R}^N)d\mathbf{R}^{N-1} ,
$$

where the specific N-particle probability density P_N is defined above (2.1). This quantity gives the probability of finding a region Ω_P (surrounding an particle centered at position $\mathbf{R}_1$) empty of other particle centers (see Fig. 1). Hence, since E_P is the conditional probability defined by (2.6), we find

$$
E_P(r)=\frac{N}{\rho_1(\mathbf{R}_1)}\int J(\mathbf{R}_1;r)P_N(\mathbf{R}^N)d\mathbf{R}^{N-1} .
\tag{3.16}
$$

Substitution of the second line of (3.15) into (3.16) yields

$$
\begin{aligned}
E_P(r)&=1-\frac{N(N-1)}{\rho_1(\mathbf{R}_1)}\int m(|\mathbf{R}_1-\mathbf{R}_2|;r)P_N(\mathbf{R}^N)d\mathbf{R}^{N-1}\\
&\quad+\frac{N(N-1)(N-2)}{2\rho_1(\mathbf{R}_1)}\int m(|\mathbf{R}_1-\mathbf{R}_2|;r)m(|\mathbf{R}_1-\mathbf{R}_3|;r)P_N(\mathbf{R}^N)d\mathbf{R}^{N-1}-\cdots\\
&=1-\frac{1}{\rho_1(\mathbf{R}_1)}\int m(|\mathbf{R}_1-\mathbf{R}_2|;r)\rho_2(\mathbf{R}_1,\mathbf{R}_2)d\mathbf{R}_2\\
&\quad+\frac{1}{2\rho_1(\mathbf{R}_1)}\int m(|\mathbf{R}_1-\mathbf{R}_2|;r)m(|\mathbf{R}_1-\mathbf{R}_3|;r)\rho_3(\mathbf{R}_1,\mathbf{R}_2,\mathbf{R}_3)d\mathbf{R}_2 d\mathbf{R}_3-\cdots\\
&=\sum_{k=0}^{N-1}(-1)^k E_P^{(k)}(r) ,
\end{aligned}
\tag{3.17}
$$

where

$$
E_P^{(k)}(r)=\frac{1}{\rho_1(\mathbf{R}_1)k!}\int \rho_{k+1}(\mathbf{R}^{k+1})\prod_{i=2}^{k+1}m(R_{1i};r)d\mathbf{R}_i ,
$$
$$
k\geq1
$$

and

$$
E_P^{(0)}(r)=1 .
$$

Here $R_{ij}=|\mathbf{R}_i-\mathbf{R}_j|$. The second line of (3.17) follows from definition (2.1). The partial sum of (3.17) from $k=1$ to $k=N-1$, multiplied by -1, represents the probability E_P^* of finding at least one particle center in a region Ω_P, which is a concentric shell, of inner radius $\sigma/2$ and outer radius r, encompassing any particle (centered at $\mathbf{R}_1$). [E_P^* is also given by the integral of Eq. (2.8).] Hence the first term of this partial sum of (3.17) (apart from a minus sign) is the probability of finding *any* single particle in Ω_P. Now since this term by itself overestimates the contribution to E_P^*, then one must add the probability of finding any two particles in Ω_P, which is

just the second term of the partial sum. Now we have added too much and so we must subtract the triplet contribution which is just the third term of the aforementioned partial sum, etc. Hence the absolute value of the kth term of the sum of (3.17) gives the probability of finding any $k+1$ particles in Ω_P. Result (3.17) is valid for statistically inhomogeneous media in which case E_P will depend upon r and the position $\mathbf{R}_1$.

From relation (2.10) and (3.17), the particle nearest-neighbor distribution function is given by

$$H_P(r)=\sum_{k=1}^{N-1}(-1)^{k+1}H_P^{(k)}(r) \; , \tag{3.18}$$

where

$$H_P^{(k)}(r)=\frac{1}{k!}\frac{\partial}{\partial r}\int \rho_{k+1}(\mathbf{R}^{k+1})\prod_{i=2}^{k+1} m(|\mathbf{R}_1-\mathbf{R}_i|;r)d\mathbf{R}_i \; .$$

For statistically homogeneous media, the conditional pair distribution function is expressed as

$$G_P(r)=\sum_{k=0}^{\infty}(-1)^k G_P^{(k)}(r) \; , \tag{3.19}$$

where the $G_P^{(k)}$ are obtained by combining relations (3.17) and (3.18) with the definition (2.12); for example, the first two terms are given by

$$G_P^{(0)}(r)=\frac{\rho_2(r)}{\rho^2} \; ,$$

$$G_P^{(1)}(r)=\frac{\rho_2(r)}{\rho}\int m(R_{12};r)\rho_2(\mathbf{R}_{12})d\mathbf{R}_2$$

$$-\frac{1}{\rho^2 s_D(r)}\int \delta(R_{12}-r)m(R_{13};r)$$

$$\times\rho_3(\mathbf{R}_{12},\mathbf{R}_{13})d\mathbf{R}_2 d\mathbf{R}_3 \; .$$

In general, $G_P^{(k)}$ is arrived at by collecting all $(k+2)$-body diagrams. Of course, by (2.36), (3.19) is equivalent to (3.9) for *hard spheres* when $r\geq\sigma$, but is a different representation.

It is interesting to note that both E_P and H_P are also special cases of the general n-point distribution function H_n studied by Torquato.[11] Specifically, for the exclusion probability we find

$$E_P(r)=\lim_{|\mathbf{x}_1-\mathbf{R}_1|\to 0}\frac{H_2(\emptyset;\mathbf{x}_1;\mathbf{R}_1)}{\rho_1(\mathbf{R}_1)} \; . \tag{3.20}$$

Using (3.20) and relation (2.10) yields the corresponding expression for the nearest-neighbor distribution function $H_P(r)$.

1. Impenetrable particles

For $r\leq\sigma$, series (3.17) is trivial to compute for the case of impenetrable particles since the quantity

$$m(R_{12};r)\rho_n(\mathbf{R}_1,\ldots,\mathbf{R}_n) \; ,$$

which appears in the kth term of this series, is identically zero for such r. In other words, we recover (2.23). Using similar arguments it is easy to verify (2.24) and (2.25)

from (3.18) and (3.19), respectively. In Sec. V, we shall compute the particle quantities for $r>\sigma$. We again emphasize that the particle quantities E_P, H_P, and G_P generally depend upon r, σ and ρ.

2. Fully penetrable particles

Let us again consider the simple case of fully penetrable particles. Since $\rho_n=\rho^n$, then it is a simple matter to evaluate the series (3.17)–(3.19) for the particle quantities. It is found that

$$E_P(r)=\exp[-\rho v_D(r)] \; , \tag{3.21}$$

$$H_P(r)=\rho s_D(r)E_P(r) \; , \tag{3.22}$$

$$G_P(r)=1 \; . \tag{3.23}$$

For reasons mentioned earlier, these results are identical to the corresponding void results (3.12)–(3.14). Recall that for this geometry, $\eta=-\ln(1-\phi_2)$, where $\eta=\rho v_D(\sigma/2)$.

C. Bounds on the void and particle quantities

Torquato[11] has given rigorous upper and lower bounds on the general n-point distribution function $H_n(\mathbf{x}^m;\mathbf{x}^{p-m};\mathbf{R}^q)$ for particles which interact with a positive pair potential. Since the void and particle exclusion probabilities and nearest-neighbor distribution functions are just special cases of H_n, then we also have strict bounds on them for such models. Let X represent either E_V, H_V, E_P, or H_P and $X^{(k)}$ represent the kth terms of either the sums (3.7), (3.8), (3.17), or (3.18). Furthermore, let

$$W=\sum_{k=0}^{l}(-1)^k X^{(k)} \tag{3.24}$$

be the partial sum. Then it follows from Ref. 11 that for any of the exclusion probabilities or nearest-neighbor distribution functions, we have the bounds

$$X\leq W, \quad \text{for } l \text{ even} \tag{3.25}$$

$$X\geq W, \quad \text{for } l \text{ odd} \; . \tag{3.26}$$

IV. CALCULATIONS OF THE VOID QUANTITIES

The results of Sec. III are applied to obtain exact low-density expansions of the void quantities E_V, H_V, and G_V for a statistically homogeneous and isotropic distribution of D-dimensional *impenetrable* particles. We then consider the evaluation of these functions for such models for arbitrary density and in particular obtain several approximations for $D=3$ which are accurate over a wide range of densities. H_V shall be made dimensionless by multiplying by the diameter, but instead of writing σH_V we will simply write H_V, taking $\sigma=1$.

A. Low-density expansions

In order to compute the low-density expansion of the series (3.7)–(3.9), we require the low-density expansions

of the n-particle probability densities. For example, for equilibrium as well as for some nonequilibrium distributions (such as random sequential addition[13]), one has[10]

$$\rho_2(R_{12}) = \rho^2 H(R_{12} - \sigma)[1 + \rho w_D(R_{12})] + O(\rho^4) , \quad (4.1)$$

$$\rho_3(\mathbf{R}_{12}, \mathbf{R}_{13}) = \rho^3 H(R_{12} - \sigma)$$

$$\times H(R_{13} - \sigma)H(R_{23} - \sigma) + O(\rho^4) , \quad (4.2)$$

where $w_D(x)$ is the intersection volume of two D-dimensional spheres whose centers are separated by the distance x (see, for example, Ref. 14) and $H(x)$ is the Heaviside step function.

Consider evaluating the series (3.7) through order η^2 [where η is the reduced density defined by (2.29)]. For such a calculation, we need only employ (4.1) through second order in ρ. We find the void exclusion probabilities to be given by

$$E_V(x) = 1 - 2x\eta + \frac{(2x-1)^2}{2}\eta^2, \quad x > \tfrac{1}{2} \qquad (4.3)$$

$$E_V(x) = 1 - 4x^2\eta$$

$$+ \frac{1}{\pi}\left[12x^2(4x^2-1)^{1/2} - 2(4x^2-1)^{3/2}\right.$$

$$\left. - 16x^2(1-x^2)\cos^{-1}\frac{1}{2x}\right]\eta^2, \quad x > \tfrac{1}{2} ,$$

$$(4.4)$$

$$E_V(x) = 1 - 8x^3\eta + (32x^6 - 32x^3 + 18x^2 - 1)\eta^2, \quad x > \tfrac{1}{2}$$

$$(4.5)$$

in $D = 1$, 2, and 3, respectively, where $x = r/\sigma$. Recall that for $x < \tfrac{1}{2}$, the exact result is given by (2.25).

Similarly, through order η^2, the void nearest-neighbor distribution functions [as calculated from (3.8)] are given by

$$H_V(x) = 2\eta - 2(2x-1)\eta^2, \quad x > \tfrac{1}{2} \qquad (4.6)$$

$$H_V(x) = 8x\eta - \frac{1}{\pi}\left[16x(4x^2-1)^{1/2}\right.$$

$$\left. - 32x(1-2x^2)\cos^{-1}\frac{1}{2x}\right]\eta^2, \quad x > \tfrac{1}{2}$$

$$(4.7)$$

$$H_V(x) = 24x^2\eta - (192x^5 - 96x^2 + 36x)\eta^2, \quad x > \tfrac{1}{2} \qquad (4.8)$$

in $D = 1$, 2, and 3, respectively.

Employing (2.11) and the results immediately above, we find the void pair distribution functions through order η for $D = 1$, 2, and 3, respectively,

$$G_V(x) = 1 + \eta, \quad x > \tfrac{1}{2} \qquad (4.9)$$

$$G_V(x) = 1 + \frac{1}{\pi}\left[4\pi x^2 - 2(4x^2-1)^{1/2}\right.$$

$$\left. + 4(1-2x^2)\cos^{-1}\frac{1}{2x}\right]\eta, \quad x > \tfrac{1}{2} \qquad (4.10)$$

$$G_V(x) = 1 + \left[4 - \frac{3}{2x}\right]\eta, \quad x > \tfrac{1}{2} . \qquad (4.11)$$

Recall that for impenetrable inclusions $\phi_2 = \eta$.

B. Arbitrary density calculations

1. Hard rods

For an equilibrium distribution of impenetrable spheres, i.e., hard rods, one can evaluate the series (3.7)–(3.9) through all orders in density. This is true because in one dimension the n-particle probability densities are known exactly. The two-particle probability density ρ_2 was first given by Zernike and Prins.[15] Higher-order probability densities are given in terms of products of two-particle probability densities.[16] Using these results, one can find

$$E_V(x) = (1-\eta)\exp\left[\frac{-2\eta(x-\tfrac{1}{2})}{1-\eta}\right], \quad x > \tfrac{1}{2} \qquad (4.12)$$

$$H_V(x) = 2\eta\exp\left[\frac{-2\eta(x-\tfrac{1}{2})}{1-\eta}\right], \quad x > \tfrac{1}{2} \qquad (4.13)$$

$$G_V(x) = \frac{1}{1-\eta}, \quad x > \tfrac{1}{2} . \qquad (4.14)$$

In order to get these results we actually begin with series (3.9) for $G_V(r)$. For the case of one dimension, it is shown that the quantity within the large parentheses of (3.9), in the limit $|\mathbf{x} - \mathbf{R}_1| \to r$, is exactly $\rho E_V(r)/(1-\eta)$ or $\rho E_V(r)/\phi_1$, where $\phi_1 = E_V(\sigma/2)$ is simply the void fraction and E_V is given by (3.7). This result then gives (4.14). Equations (4.12) and (4.13) are then obtained by the use of (2.18), (2.20), and (2.30).

The results [(4.12)–(4.14)] were first obtained by Hefland, Frisch, and Lebowitz[8] using physical arguments. They reasoned that for $r > \sigma/2$ (or, equivalently, $x > \tfrac{1}{2}$), since no two particles on opposite sides of the cavity of radius r can ever interact, then the particles cannot tell what size cavity they are next to for such r. Thus $G_V(r)$ must be independent of r for $r > \sigma/2$. Using this observation and the fact that $G_V(r)$ is continuous at $r = \sigma/2$, one then has that

$$G(r) = G(\sigma/2) = \frac{1}{1-\eta}, \quad r > \sigma/2 \qquad (4.15)$$

which is just Eq. (4.14).

2. Hard disks and spheres

For two- and higher-dimensional systems of hard spheres, exact evaluations of the series (3.7)–(3.9) are impossible for arbitrary density because the n-particle probability densities are not exactly known. One must therefore settle for approximate means of computing these series. The scaled-particle theory of Reiss, Frisch, and Lebowitz[7] provides one approximation scheme. In two and three dimensions, the scaled-particle approximations for the conditional pair distribution functions are given respectively by[8]

$$G_V(x) = \frac{1}{(1-\eta)^2}\left[1 - \frac{\eta}{2x}\right], \quad x > \tfrac{1}{2} \tag{4.16}$$

$$G_V(x) = a + \frac{b}{x} + \frac{c}{x^2}, \quad x > \tfrac{1}{2}. \tag{4.17}$$

In Eq. (4.17) a, b, and c are the density-dependent coefficients given by

$$a(\eta) = \frac{1+\eta+\eta^2}{(1-\eta)^3}, \tag{4.18}$$

$$b(\eta) = \frac{-3\eta(1+\eta)}{2(1-\eta)^3}, \tag{4.19}$$

$$c(\eta) = \frac{3\eta^2}{4(1-\eta)^3}. \tag{4.20}$$

The comparison of (4.16) and (4.17) to the exact low-density expansions (4.10) and (4.11) reveals that whereas (4.17) for hard spheres is exact through first order in η, (4.16) for hard disks is exact only through zeroth order in η.

The use of (2.18) in conjunction with relations (4.16) and (4.17) yields the exclusion probabilities in the scaled-particle approximation for the cases of $D=2$ and 3, respectively,

$$E_V(x) = (1-\eta)\exp\left[\frac{-\eta}{(1-\eta)^2}(4x^2 - 4\eta x + 2\eta - 1)\right],$$
$$x > \tfrac{1}{2} \tag{4.21}$$

$$E_V(x) = (1-\eta)\exp[-\eta(8ax^3 + 12bx^2 + 24cx + d)],$$
$$x > \tfrac{1}{2} \tag{4.22}$$

where

$$d(\eta) = \frac{-11\eta^2 + 7\eta - 2}{2(1-\eta)^3}. \tag{4.23}$$

Expanding these expressions for the exclusion probabilities in powers of η shows that whereas (4.21) is exact through first order η [cf. (4.4)], (4.22) is exact through second order in η [cf. (4.5)].

The combination of (2.11), (4.16), (4.17), (4.21), and (4.22) yields the void nearest-neighbor probability densities in the scaled-particle approximation for $D = 2$ and 3, respectively, as

$$H_V(x) = \frac{4\eta(2x - \eta)}{1-\eta}$$
$$\times \exp\left[\frac{-\eta}{(1-\eta)^2}(4x^2 - 4x\eta + 2\eta - 1)\right],$$
$$x > \tfrac{1}{2} \tag{4.24}$$

$$H_V(x) = 24\eta(1-\eta)(ax^2 + bx + c)$$
$$\times \exp[-\eta(8ax^3 + 12bx^2 + 24cx + d)],$$
$$x > \tfrac{1}{2}. \tag{4.25}$$

These relations could also have been obtained by use of either (2.9) or (2.20). For reasons mentioned above, (4.24)

is exact through $O(\eta)$, while (4.25) is exact through $O(\eta^2)$.

We now shall derive new expressions for the void quantities for three-dimensional systems of hard spheres. This is done by exploiting the observation that $G_V(r)$ is nothing more than the radial distribution function for a special binary mixture of spheres, namely, one for a single test particle of radius $r - \sigma/2$ (i.e., test particles at infinite dilution) and an actual inclusion of diameter σ at contact, i.e., when such particles are separated by the distance r. We consider two different approximation schemes to obtain this binary-mixture radial distribution function: the Percus-Yevick solution found by Lebowitz[17] and the Carnahan-Starling equation.[18]

If one considers Lebowitz's general Percus-Yevick solution for the exact Ornstein-Zernike integral equation of a binary mixture of hard spheres under the limits described above, one finds

$$G_V(x) = \frac{(1 + 2\eta - 3\eta/2x)}{(1-\eta)^2}, \quad x > \tfrac{1}{2}. \tag{4.26}$$

The combination of (5.26) with (2.18) and (2.20) yields in the Percus-Yevick approximation

$$E_V(x) = (1-\eta)\exp\left[-\frac{\eta}{(1-\eta)^2}[8(1+2\eta)x^3\right.$$
$$\left. - 18\eta x^2 + \tfrac{5}{2}\eta - 1]\right], \quad x > \tfrac{1}{2} \tag{4.27}$$

$$H_V(x) = \frac{24\eta}{(1-\eta)}[(1+2\eta)x^2 - \tfrac{3}{2}\eta x]$$
$$\times \exp\left[\frac{-\eta}{(1-\eta)^2}[8(1+2\eta)x^3\right.$$
$$\left. - 18\eta x^2 + \tfrac{5}{2}\eta - 1]\right], \quad x > \tfrac{1}{2}. \tag{4.28}$$
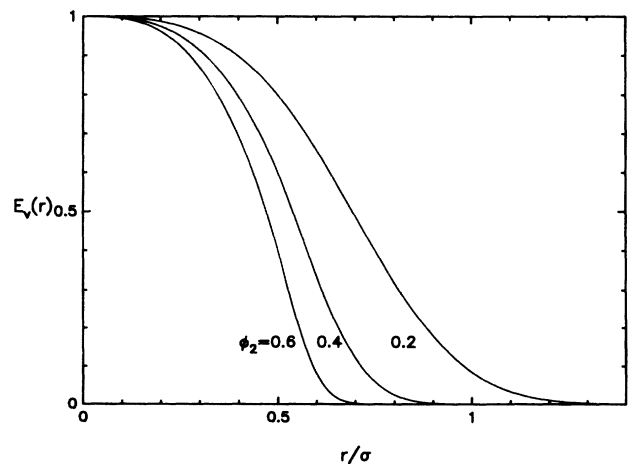

FIG. 2. Void exclusion probability $E_V(r)$ for a distribution of three-dimensional impenetrable spheres, as calculated from Eq. (4.33), for values of the sphere volume fraction $\phi_2 = \eta = 0.2$, 0.4, and 0.6.
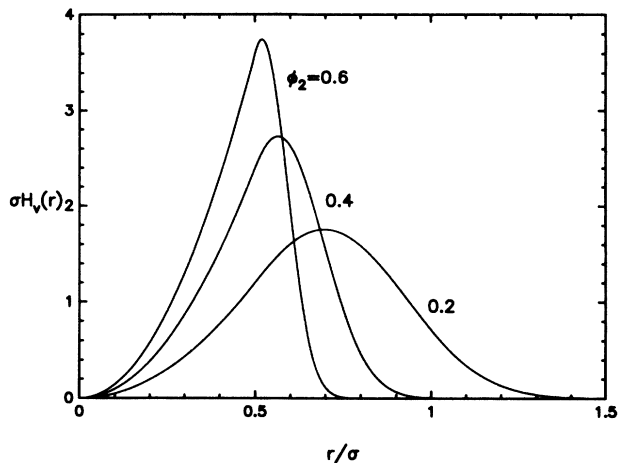
FIG. 3. Dimensionless void nearest-neighbor probability density $\sigma H_V(r)$ for a distribution of three-dimensional impenetrable spheres, as calculated from Eq. (4.34), for values of the sphere volume fraction $\phi_2 = \eta = 0.2, 0.4$, and 0.6.

To our knowledge, Eqs. (4.26)–(4.28) are new. As in the case of $D = 3$ scaled-particle expressions (4.17), (4.22), and (4.25), relations (4.26)–(4.28) are exact through the third virial level.

By studying "exact" molecular dynamics data for equisized hard-sphere virial coefficients, Carnahan and Starling[18] were able to show that these coefficients satisfied a recursive formula to a close approximation. Using this formula, they were able to find a very accurate empirical equation for the radial distribution function at contact. For binary mixtures, under the special limits described above, their equation[19] yields

$$G_V(x) = \frac{(1+2\eta - 3\eta/2x)}{(1-\eta)^2} + \frac{\eta^2(2x-1)^2}{2(1-\eta)^3 x^2}$$

$$= e + \frac{f}{x} + \frac{g}{x^2}, \quad x > \tfrac{1}{2} \qquad (4.29)$$

where

$$e(\eta) = \frac{1+\eta}{(1-\eta)^3}, \qquad (4.30)$$

$$f(\eta) = -\frac{\eta(3+\eta)}{2(1-\eta)^3}, \qquad (4.31)$$

$$g(\eta) = \frac{\eta^2}{2(1-\eta)^3}. \qquad (4.32)$$

Note that the first term on the right-hand side of (4.29) is identical to the Percus-Yevick $G_V(x)$ [cf. (4.26)]. The substitution of (4.29) into (2.18) and (2.20) yields, respectively, the new approximate relations for the exclusion and nearest-neighbor distribution functions,

$$E_V(x) = (1-\eta)\exp[-\eta(8ex^3 + 12fx^2 + 24gx + h)],$$

$$x > \tfrac{1}{2} \qquad (4.33)$$

$$H_V(x) = 24\eta(1-\eta)(ex^2 + fx + g)$$

$$\times \exp[-\eta(8ex^3 + 12fx^2 + 24gx + h)],$$

$$x > \tfrac{1}{2} \qquad (4.34)$$

where

$$h(\eta) = \frac{-9\eta^2 + 7\eta - 2}{2(1-\eta)^3}. \qquad (4.35)$$

It is of interest to determine which of the three approximations for $D = 3$ (scaled-particle, Percus-Yevick, and Carnahan-Starling approximations) is the most accurate. Torquato and Lee[20] have recently determined E_V and H_V from Monte Carlo computer simulations. Although all three approximations give values of E_V and H_V which are very close to one another and to the computer-simulation data, the Carnahan-Starling approximations yield the best agreement with the data (Percus-Yevick equations giving the next best agreement). Figures 2 and 3 depict E_V and σH_V, respectively, for values of the sphere volume fraction $\phi_2 = \eta = 0.2$, 0.4, and 0.6 as obtained from (4.33) and (4.34), respectively. (Note that $\phi_2 = 0.6$ corresponds to about 94% of the estimated random close-packing value.[21]) The largest deviations between the approximations themselves and between the approximations and the data occur at the highest densities. (For $\eta = 0.5$, the highest density studied in Ref. 20, the Carnahan-Starling relations for E_V and H_V are, on average, within 1% of the simulation data.) The Percus-Yevick approximation of the conditional pair distribution function (4.26) appreciably underestimates G_V at large ϕ_2; the Carnahan-Starling expression (4.29) being the most accurate predictor of G_V. These results for G_V are not surprising as they are consistent with similar observations made for the contact value of the radial distribution function of hard-sphere fluids.[10] A comprehensive study of the comparison of the aforementioned approximations with computer-simulation results is carried out in Ref. 20.

V. CALCULATIONS OF THE PARTICLE QUANTITIES

Here we consider computing the particle quantities E_P, H_P, and G_P for statistically homogeneous and isotropic distributions of D-dimensional impenetrable inclusions. We obtain both exact low-density expansions and formulas applicable for arbitrary density. Again, the dimensionless quantity σH_P shall be written as H_P with $\sigma = 1$. To our knowledge, all of the following results are new.

A. Low-density expansions

Consider calculating the series (3.17) for the exclusion probability through order η^2. This requires the use of expansions (4.1) for ρ_2 and (4.2) for ρ_3. Combining these equations and performing the elementary integrations yields for $D = 1, 2$, and 3, respectively,

$$E_P(x) = 1 - 2(x-1)\eta + 2(x-1)(x-2)\eta^2, \quad x > 1 \tag{5.1}$$

$$E_P(x) = 1 - 4(x^2-1)\eta + \frac{1}{\pi}\left[16\pi(1-x^2) - 6\sqrt{3} + 12x^2(4x^2-1)^{1/2} - 2(4x^2-1)^{3/2} - 16x^2(1-x^2)\cos^{-1}\frac{1}{2x}\right]\eta^2, \quad x > 1 \tag{5.2}$$

$$E_P(x) = 1 - 8(x^3-1)\eta + (32x^6 - 96x^3 + 18x^2 + 46)\eta^2, \quad x > 1 . \tag{5.3}$$

Note that at $x = 1$ (i.e., when the distance is exactly equal to a particle diameter), then $E_P(1) = 1$ as expected [cf. (2.23)].

According to (3.18), differentiation of the expressions immediately above then gives the particle nearest-neighbor distribution functions through $O(\eta^2)$ to be

$$H_P(x) = 2\eta + 2(3-2x)\eta^2, \quad x > 1 \tag{5.4}$$

$$H_P(x) = 8x\eta - \frac{1}{\pi}\left[16x(4x^2-1)^{1/2} - 32x(1-2x^2)\cos^{-1}\frac{1}{2x} - 32\pi x\right]\eta^2, \quad x > 1 \tag{5.5}$$

$$H_P(x) = 24x^2\eta - (192x^5 - 288x^2 + 36x), \quad x > 1 \tag{5.6}$$

in $D = 1, 2,$ and 3, respectively.

The corresponding conditional pair distributions are obtained by use of Eqs. (5.1)–(5.6) and the definition (2.12). One finds that

$$G_P(x) = 1 + \eta, \quad x > 1 \tag{5.7}$$

$$G_P(x) = 1 + \frac{1}{\pi}\left[4\pi x^2 - 2(4x^2-1)^{1/2} + 4(1-2x^2)\cos^{-1}\frac{1}{2x}\right]\eta, \quad x > 1 \tag{5.8}$$

$$G_P(x) = 1 + \left[4 - \frac{3}{2x}\right]\eta, \quad x > 1 \tag{5.9}$$

in $D = 1, 2,$ and 3, respectively.

It is important to note that relations (5.1)–(5.9) could have been obtained by employing the expressions derived in Sec. IV which relate particle quantities to void quantities [cf. Eqs. (2.33), (2.34), and (2.36)] and the low-density expansions of the void quantities already evaluated in Sec. V [cf. Eqs. (4.3)–(4.11)]. Thus relations (5.1)–(5.9) confirm the validity of Eqs. (2.33), (2.34), and (2.36) through the given order in density.

B. Arbitrary density calculations

Here we shall derive, for the first time, expressions for the particle quantities for arbitrary volume fractions. This is done using the expressions developed in Sec. II which relate the void quantities to the corresponding particle quantities and employing the approximations derived in Sec. IV for the void quantities. These relations are then computed for selected values of the volume fraction.

1. Hard rods

For the case of hard rods $(D = 1)$, the arbitrary-density results (4.12)–(4.14) for the void quantities are exact. Hence the combination of these equations with Eqs. (2.33), (2.34), and (2.36) yields

$$E_P(x) = \exp\left[\frac{-2\eta(x-1)}{1-\eta}\right], \quad x > 1 \tag{5.10}$$

$$H_P(x) = \frac{2\eta}{1-\eta}\exp\left[\frac{-2\eta(x-1)}{1-\eta}\right], \quad x > 1 \tag{5.11}$$

$$G_P(x) = \frac{1}{1-\eta}, \quad x > 1 . \tag{5.12}$$

2. Hard disks

In the case of hard disks $(D = 2)$, we make use of the void scaled-particle approximations (4.16), (4.21), and (4.24). These expressions combined with Eqs. (2.33), (2.34), and (2.36) yield

$$E_P(x) = \exp\left[\frac{-4\eta}{(1-\eta)^2}(x^2-1) + \eta(x-1)\right], \quad x > 1 \tag{5.13}$$

$$H_P(x) = \frac{4\eta(2x-\eta)}{(1-\eta)^2} \times \exp\left[\frac{-4\eta}{(1-\eta)^2}[(x^2-1) + \eta(x-1)]\right], \quad x > 1 \tag{5.14}$$

$$G_P(x) = \frac{1}{(1-\eta)^2}\left[1 - \frac{\eta}{2x}\right], \quad x > 1 . \tag{5.15}$$

3. Hard spheres

For the case of hard spheres $(D = 3)$, we shall obtain the particle quantities in three different approximations: scaled-particle, Percus-Yevick, and Carnahan-Starling approximations. The combination of the void scaled-particle approximations (4.17), (4.22), and (4.25) with Eqs. (2.33), (2.34), and (2.36) yields

$$E_P(x) = \exp\{-\eta[8a(x^3-1) + 12b(x^2-1) + 24c(x-1)]\}, \quad x > 1 \tag{5.16}$$

$$H_P(x) = 24\eta(ax^2 + bx + c)$$

$$\times \exp\{-\eta[8a(x^3 - 1) + 12b(x^2 - 1)$$

$$+ 24c(x - 1)]\}, \quad x > 1 \qquad (5.17)$$

$$G_P(x) = a + \frac{b}{x} + \frac{c}{x^2}, \quad x > 1 . \qquad (5.18)$$

Here the density-dependent coefficients a, b, and c are given by Eqs. (4.18)–(4.20), respectively.

The void Percus-Yevick approximations (4.26)–(4.28) in conjunction with Eqs. (2.33), (2.34), and (2.36) yields

$$E_P(x) = \exp\left|\frac{-\eta}{(1-\eta)^2}[8(1+2\eta)(x^3-1) - 18\eta(x-1)]\right|,$$

$$x > 1 \qquad (5.19)$$

$$H_P(x) = \frac{24\eta}{(1-\eta)^2}[(1+2\eta)x^2 - \tfrac{3}{2}\eta x]$$

$$\times \exp\left|\frac{-\eta}{(1-\eta)^2}[8(1+2\eta)(x^3-1)\right.$$

$$\left. - 18\eta(x-1)]\right|, \quad x > 1 \qquad (5.20)$$

$$G_P(x) = \frac{(1+2\eta - 3\eta/2x)}{(1-\eta)^2}, \quad x > 1 . \qquad (5.21)$$

The use of the void Carnahan-Starling approximations (4.29), (4.33), and (4.34) in combination with Eqs. (2.33), (2.34), and (2.36) yields the following expressions for the particle quantities:

$$E_P(x) = \exp\{-\eta[8e(x^3-1) + 12f(x^2-1)$$

$$+ 24g(x-1)]\}, \quad x > 1 \qquad (5.22)$$

$$H_P(x) = 24\eta(ex^2 + fx + g)$$

$$\times \exp\{-\eta[8e(x^3-1) + 12f(x^2-1)$$

$$+ 24g(x-1)]\}, \quad x > 1 \qquad (5.23)$$

$$G_P(x) = e + \frac{f}{x} + \frac{g}{x^2}, \quad x > 1 . \qquad (5.24)$$

Here the density-dependent coefficients e, f, and g are given by Eqs. (4.30)–(4.32), respectively.
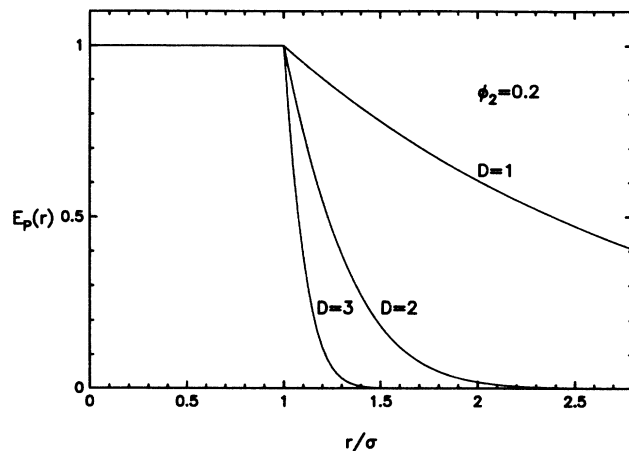
In Fig. 4, we plot the particle exclusion probability $E_P(r)$ for distributions of D-dimensional impenetrable spheres at a sphere volume fraction $\phi_2 = \eta = 0.2$. The results for $D = 1$, 2, and 3 are computed from the exact expression (5.10), the scaled-particle equation (5.13), and the Carnahan-Starling expression (5.22), respectively. For fixed r, we observe that the effect of increasing the dimensionality is to decrease the exclusion probability, as expected. For similar reasons, one expects the particle nearest-neighbor probability density $H_P(r)$ to show the same behavior (see Fig. 5) for large r. For r near σ, $H_P(r)$ should increase with increasing dimensionality. In Fig. 6, we plot the corresponding conditional pair distribution functions.

Torquato and Lee[20] also obtained E_P and H_P in their three-dimensional simulation study. For these particle

FIG. 4. Particle exclusion probability $E_P(r)$ for distributions of D-dimensional impenetrable spheres at a sphere volume fraction $\phi_2 = \eta = 0.2$. Results for $D = 1$, 2, and 3 are obtained from (5.10), (5.13), and (5.22), respectively.

quantities, the Carnahan-Starling expressions (5.22) and (5.23) are generally found to provide the best agreement with the data. The Carnahan-Starling particle expressions are very accurate up to $\phi_2 = 0.5$. In Figs. 7 and 8, we plot the predictions of (5.22) and (5.23), respectively, for three-dimensional impenetrable spheres at $\phi_2 = 0.2$ and 0.5 and compare to the corresponding simulation results of Torquato and Lee.[20] (A standard Metropolis[10] algorithm was employed to generate 200–6000 realizations
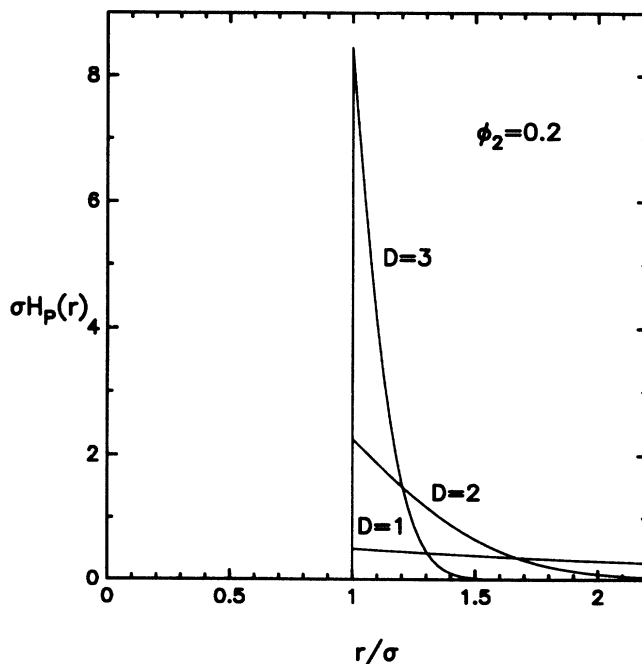

FIG. 5. Dimensionless particle nearest-neighbor probability density $\sigma H_P(r)$ for distributions of D-dimensional impenetrable spheres at a sphere volume fraction $\phi_2 = \eta = 0.2$. Results for $D = 1$, 2, and 3 are obtained from (5.11), (5.14), and (5.23), respectively.
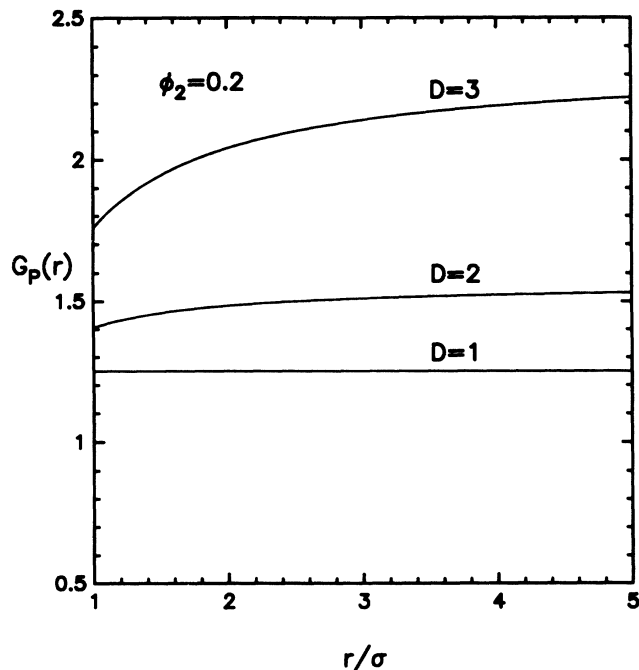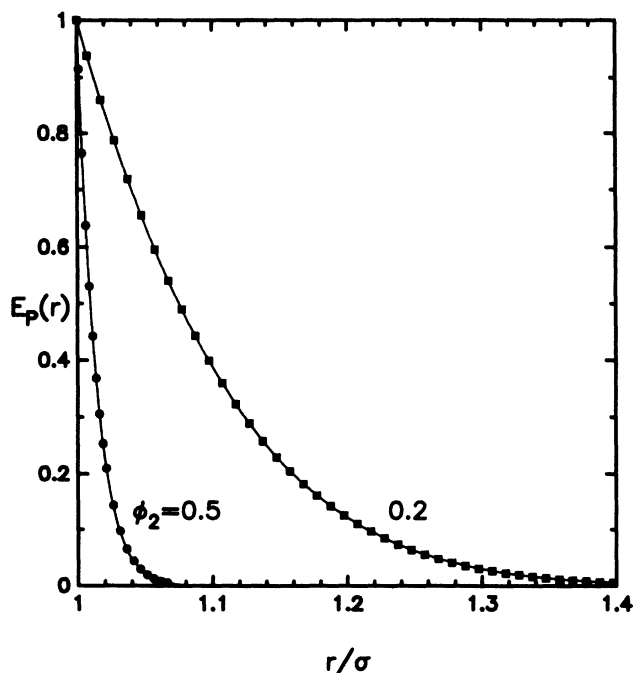
FIG. 6. Conditional pair distribution function $G_P(r)$ for a distribution of D-dimensional impenetrable spheres at a sphere volume fraction $\phi_2 = \eta = 0.2$. Results for $D = 1$, 2, and 3 are obtained from (5.12), (5.15), and (5.24), respectively.
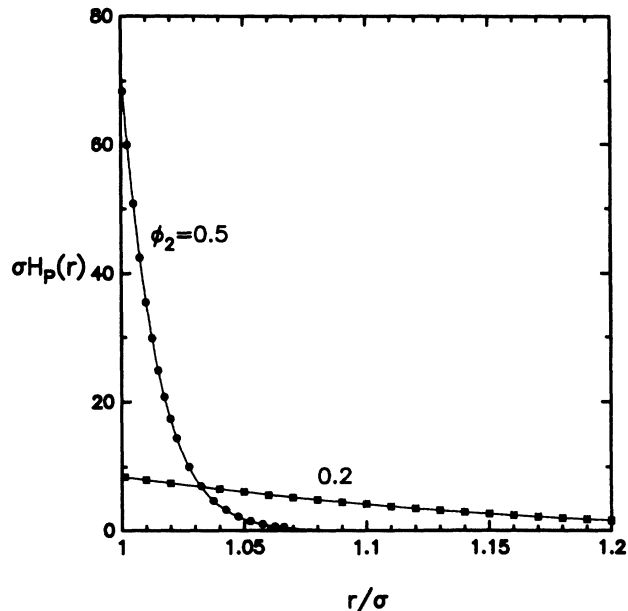

FIG. 8. Dimensionless particle nearest-neighbor distribution function $\sigma H_P(r)$ for a distribution of three-dimensional impenetrable spheres of diameter σ for values of the sphere volume fraction $\phi_2 = 0.2$ and 0.5. Solid lines are computed from (5.23), and circles and squares are Monte Carlo simulation data (Ref. 20).

FIG. 7. Particle exclusion probability $E_P(r)$ for a distribution of three-dimensional impenetrable spheres of diameter σ for values of the sphere volume fraction $\phi_2 = 0.2$ and 0.5. Solid lines are computed from (5.22), and circles and squares are Monte Carlo simulation data (Ref. 20).

of 500 hard spheres in a cubical cell with periodic boundary conditions. Simulation details shall be given in Ref. 20.) The agreement of the theory with the computer-simulation results is seen to be excellent. At fixed r, we see that $E_P(r)$ decreases as ϕ_2 is made to increase, i.e., the average nearest-neighbor distance decreases with increasing ϕ_2. For large r, $H_P(r)$ also decreases as ϕ_2 increases. However, for r near σ, $H_P(r)$ increases with increasing ϕ_2, as expected.

What is the effect of impenetrability of the spheres on the particle quantities? We noted earlier that Hertz[6] obtained the particle quantities for fully penetrable spheres. For any dimensionality, there are several general observations we can make. First, for $r < \sigma$, E_P for impenetrable particles must lie above or equal to E_P for fully penetrable particles at the same value of ϕ_2, since for the former it must be unity and for the latter it decreases monotonically from unity at $r = 0$ because the centers can overlap. For the same range of r, the converse must be true for H_P since it is identically zero for hard spheres. Second, for r very near but greater than σ, the aforementioned statement made regarding E_P for $r < \sigma$ still applies, but H_P for impenetrable spheres now must be larger than the corresponding fully penetrable quantity. The explanation for the latter conclusion is as follows. Since $G_P(r)$ for hard spheres is always larger than $G_P(r) = 1$ for fully penetrable spheres, then according to (2.12) (and previous observations) the above statement must be true. Indeed, H_P attains its maximum value at $r = \sigma$ and then monotonically decreases with increasing r since $E_P(r)$ de-
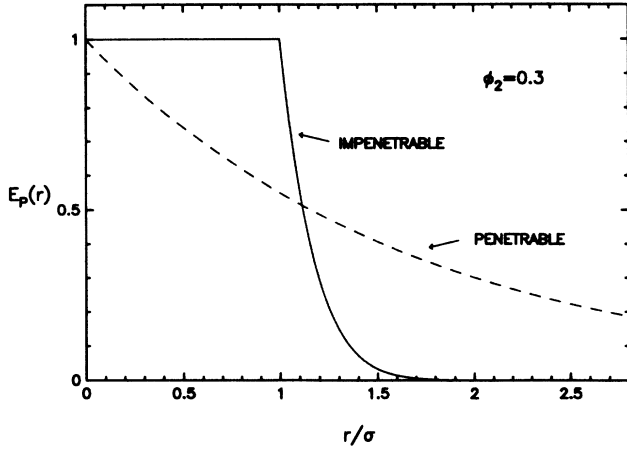
FIG. 9. Particle exclusion probability $E_P(r)$ for fully penetrable and totally impenetrable disks ($D = 2$) as calculated from (3.21) and (5.13), respectively, at $\phi_2 = 0.3$.

creases faster than $\rho s_D(r) G_P(r)$ increases. Third, for large r, E_P and H_P should be larger for fully penetrable spheres than for impenetrable spheres. The reason for this behavior is that one is more likely to find larger void regions surrounding the central particle in fully penetrable systems as the result of interparticle overlap. In Figs. 9 and 10, we plot E_P and H_P, respectively, for the two-dimensional case of distributions of fully penetrable and impenetrable disks at $\phi_2 = 0.3$. The observations made above are borne out in these figures.
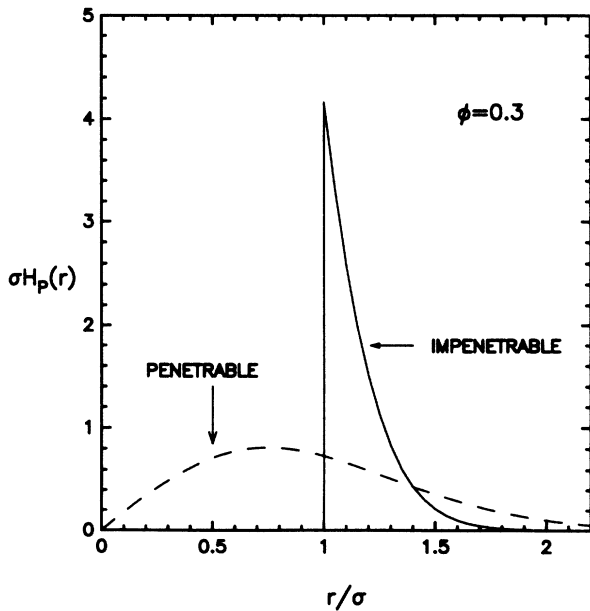
VI. MEAN NEAREST-NEIGHBOR DISTANCE

Here we shall compute the mean nearest-neighbor distance l, defined by Eq. (2.22), for distributions of D-dimensional impenetrable inclusions using the results of the previous section. Integrating (2.22) by parts and using (2.10) gives the following alternative form:

$$\frac{l}{\sigma} = \int_0^\infty E_P(x) dx \ . \tag{6.1}$$

Now since $E_P \geq 0$, then $l/\sigma \geq 0$. One may question this result on the grounds that l/σ should not only be positive but greater than unity. This result, however, applies only when the inclusions are totally impenetrable to one another. The result $l/\sigma \geq 0$ is valid for inclusions of arbitrary penetrability. For totally impenetrable inclusions of diameter σ, use of (2.23) in (6.1) yields the specific expression

$$\frac{l}{\sigma} = 1 + \int_1^\infty E_P(x) dx \ . \tag{6.2}$$

Again, since $E_P \geq 0$, then $l/\sigma \geq 1$.

A. Fully penetrable inclusions

For the case of fully penetrable inclusions, the mean nearest-neighbor distance l is obtainable analytically for all D. Substitution of (3.22) into (6.1) yields for $D = 1, 2$, and 3, respectively,

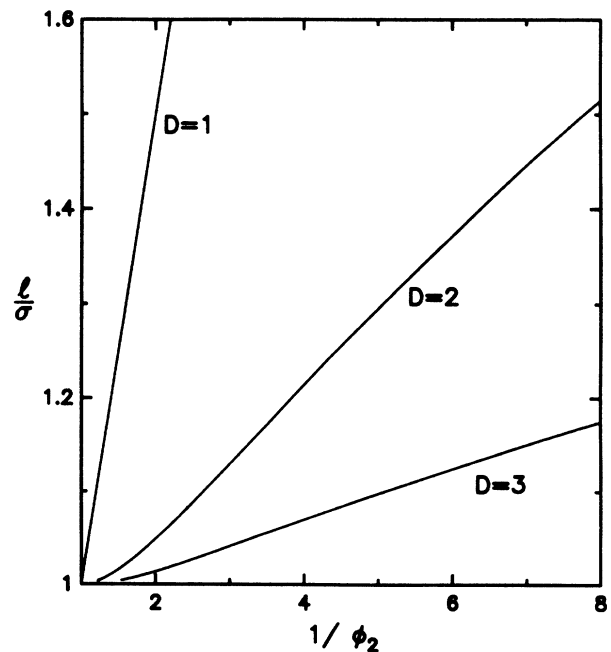$$\frac{l}{\sigma} = \frac{1}{2\ln(1 - \phi_2^{-1})} \ , \tag{6.3}$$

FIG. 10. Dimensionless particle nearest-neighbor distribution function $\sigma H_P(r)$ for fully penetrable and totally impenetrable ($D = 2$) disks as calculated from (3.22) and (5.14), respectively, at $\phi_2 = 0.3$.

FIG. 11. Dimensionless mean nearest-neighbor distance l/σ as a function of the inverse volume fraction ϕ_2^{-1} for distributions of D-dimensional impenetrable spheres. Results for $D = 1$, 2, and 3 are calculated from (6.6), (6.7), and (6.11), respectively.

$$\frac{l}{\sigma} = \frac{\sqrt{\pi}}{4[\ln(1-\phi_2)^{-1}]^{1/2}} ,$$ (6.4)

$$\frac{l}{\sigma} = \frac{\Gamma(4/3)}{2[\ln(1-\phi_2)^{-1}]^{1/3}}$$

$$= \frac{0.4465}{[\ln(1-\phi_2)^{-1}]^{1/3}} .$$ (6.5)

At fixed ϕ_2, increasing the dimensionality decreases the mean nearest-neighbor distance, as expected.

B. Totally impenetrable inclusions

Substitution of (5.10) into (6.2) yields the mean nearest-neighbor distance for totally impenetrable rods to be exactly given by

$$\frac{l}{\sigma} = \frac{1+\phi_2}{2\phi_2} .$$ (6.6)

In the case of a distribution of totally impenetrable disks, the combination of (5.13) and (6.2) yields the result

$$\frac{l}{\sigma} = 1 + \tfrac{1}{2}(\pi/a_2)^{1/2}\exp(b_2^2/4a_2)\mathrm{erfc}[b_2/2(a_2)^{1/2}] ,$$ (6.7)

where

$$a_2 = \frac{4\phi_2}{(1-\phi_2)^2} ,$$ (6.8)

$$b_2 = \frac{4\phi_2(2+\phi_2)}{(1-\phi_2)^2} ,$$ (6.9)

and erfc denotes the complementary error function. For large ϕ_2, we can get from (6.7) the asymptotic expression

$$\frac{l}{\sigma} = 1 + \frac{1}{b_2}$$

$$= 1 + \frac{(1-\phi_2)^2}{4\phi_2(2+\phi_2)} .$$ (6.10)

In practice, (6.10) is actually relatively accurate for $\phi_2 \geq 0.3$.

In the case of three-dimensional impenetrable spheres, we shall employ the Carnahan-Starling approximation (5.22) together with (6.2) to give

$$\frac{l}{\sigma} = 1 + \int_1^\infty \exp\{-\eta[8e(x^3-1)+12f(x^2-1)$$

$$+24g(x-1)]\}dx ,$$ (6.11)

This integration must be carried out numerically. For large ϕ_2, however, we find the analytical asymptotic expression

$$\frac{l}{\sigma} = 1 + \frac{(1-\phi_2)^3}{12\phi_2(2-\phi_2)} .$$ (6.12)

This expression is relatively accurate for $\phi_2 \geq 0.2$. Comparing the above relations for impenetrable particles to

(6.3)–(6.5) reveals that the mean nearest-neighbor distance for fully penetrable particles is always smaller than the corresponding quantity for hard particles as expected.

In Fig. 11 we plot the dimensionless mean nearest-neighbor distance l/σ versus the inverse sphere volume fraction ϕ_2^{-1} for one-, two-, and three-dimensional hard spheres using results (6.6), (6.7), and (6.11), respectively. The result for $D=3$ is computed using a trapezoidal rule. At fixed ϕ_2, l/σ increases with increasing D, as expected. For the case of $D=3$, (6.11) gives very accurate estimates of l/σ for $\phi_2 \leq 0.5$ or $\phi_2^{-1} \geq 2$. $\phi_2=0.5$ is about 80% of the random close-packing fraction ϕ_2^c estimated to range from 0.62 to 0.66 (see Ref. 2). Based on these observations, result (6.7) for $D=2$ should give very accurate estimates of l/σ for approximately $\phi_2 < 0.66$ or $\phi_2^{-1} \geq 1.52$. For impenetrable disks, ϕ_2^c has been estimated to range from 0.79 to 0.84 (see Ref. 2). Moreover, preliminary simulation results indicate that (6.7) and (6.11) will be relatively accurate up to about 90% of ϕ_2^c. However, unlike our exact $D=1$ result, Eq. (6.6), which correctly predicts $\phi_2^c=1$, our results (6.7) and (6.11) must break down in the near vicinity of ϕ_2^c since they both predict $\phi_2^c=1$. In future work, we shall study methods to improve our approximations for E_P and H_P in the near critical region. Note that if one linearly extrapolates our results for $D=2$ and 3 using the linear portions of the curves to the limit $l/\sigma=1$, the corresponding volume fractions fall within the respective estimated range of ϕ_2^c indicated above. Such linear extrapolations, however, are somewhat arbitrary.

VII. CONCLUSIONS

All the results for the particle quantities obtained in this study are new. These include (1) the key equations (2.33), (2.34), and (2.35), which relate the particle quantities to the void counterparts; (2) exact integral representations of E_P, H_P, and G_P [cf. (3.17)–(3.19)] for distributions of D-dimensional spheres; (3) bounds on the particle quantities; (4) low-density expansions of the particle quantities for distributions of D-dimensional spheres [cf. (5.1)–(5.9)]; (5) arbitrary density calculations for such a model [cf. (5.10)–(5.24)]; and (6) the mean nearest-neighbor distance as a function of density for D-dimensional spheres. In the case of the void quantities, we obtained, among other results, new relations for E_V, H_V, and G_V at arbitrary density for $D=3$ in both the Percus-Yevick approximations [(4.26)–(4.28)] and Carnahan-Starling approximations [(4.29)–(4.35)]. The analytical expressions we derive for the particle and void quantities turn out to be accurate over a wide range of densities. Exclusion-volume effects associated with impenetrable-particle systems lead to particle quantities which are strikingly different from the fully penetrable-particle counterparts.[21]

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[20]S. Torquato and S. B. Lee (unpublished).

[21]In passing, we would like to make one last observation about the particle and void quantities for interpenetrating spheres in the penetrable-concentric shell model [S. Torquato, J. Chem. Phys. **81**, 5079 (1984); **84**, 6345 (1986)]. In this model each D-dimensional sphere of diameter σ is composed of a hard core of diameter $\lambda\sigma$, encompassed by a perfectly penetrable concentric shell of thickness $(1-\lambda)\sigma/2$. The extreme limits of the impenetrability parameter $\lambda=0$ and 1 correspond to the cases of fully penetrable and totally impenetrable spheres, respectively. Given the totally impenetrable-sphere results of Sec. IV and V of this study, one can obtain the corresponding results for penetrable spheres ($\lambda<1$) by simply replacing σ (on the right-hand sides of the relations) with $\lambda\sigma$ since it is only the internal hard core that has meaning for particle and void quantities.