

Nearest-surface distribution functions for polydispersed particle systems

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Nearest-neighbor distribution functions characterize the probability of finding a nearest neighbor at some given distance from a *reference* point in systems of interacting particles and are of fundamental importance in a variety of problems in the physical and biological sciences. We extend the formalism of Torquato, Lu, and Rubinstein [Phys. Rev. A **41**, 2059 (1990)] for identical spheres to obtain exact series representation of nearest-neighbor functions (*void* and *particle* probability densities) and closely related quantities for systems of interacting D -dimensional spheres with a polydispersivity in size. Polydispersivity constitutes a basic feature of the structure of random systems of particles and leads to a wider choice of possible definitions for nearest-neighbor functions. The most relevant definition for a polydispersed system of particles involves the “nearest particle surface” rather than the “nearest particle center” and thus we refer to them as “nearest-surface distribution functions.” For the special cases of D -dimensional hard and overlapping spheres, we obtain analytical expressions for the nearest-surface functions that are accurate for a wide range of sphere concentrations. Employing these results, we are able to compute the corresponding *mean nearest-surface distances* for polydispersed hard spheres. Finally, we determine the nearest-surface functions for bidispersed systems from Monte Carlo computer simulations and find that our theoretical results are in very good agreement with the data.

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I. INTRODUCTION

In many-body systems, nearest-neighbor distribution functions characterize the probability of finding a nearest neighbor at some given distance from a reference point in the system. Knowledge of nearest-neighbor distribution functions (and their close relatives) is of fundamental importance in a host of problems in the physical and biological sciences, including liquids and amorphous solids [1–9], transport properties of suspensions and composite materials [10–13], stellar dynamics [14], and the structure of some cell membranes [15], to mention but a few examples. From such nearest-neighbor functions, one can obtain other important statistical measures of the system such as the *mean nearest-neighbor distance* and, in the case of hard-sphere systems, the *random close-packing density*.

Virtually all previous theoretical results have treated systems of identical spheres with hard-sphere interactions. Recently, Torquato, Lu, and Rubinstein [8] have obtained exact series representations of various types of nearest-neighbor functions for systems of identical spheres that interact with an *arbitrary potential*. Unfortunately, since these series cannot be summed for general potentials, exact solutions are generally out of the question. One must therefore resort to various approximation schemes, even in the simple case of hard-sphere interactions [1,4,8,9]. As it turns out, the approximation schemes can yield very good agreement with Monte Carlo simulations [8,9].

The purpose of this paper is to extend the formalism of Torquato, Lu, and Rubinstein [8] for monodisperse spheres to study the case of spheres with a polydispersivity in size. Polydispersed-sphere systems are useful models of the many random heterogeneous media characterized by many length scales [16]. *Polydispersivity leads to a wider choice of possible definitions for nearest-neighbor functions*. For example, one can speak of the “nearest center” or the “nearest surface,” which are not generally the same in a polydispersed system. It will be shown that the definition based upon the nearest surface is the most useful. We shall consider the two types of “reference points”: one involving the centers of the particles themselves (*particle quantities*) and another involving points that may lie anywhere exterior to the particles (*void quantities*).

In Sec. II, we define for polydispersed systems the nearest-neighbor functions (and closely related quantities) for both the void and particle quantities, mean nearest-neighbor distance, and (in the case of hard-sphere systems) the random close-packing density. In Sec. III, we give exact series representations of the void and particle nearest-surface functions for D -dimensional systems of polydispersed spheres. In Secs. IV and V, we obtain accurate approximations of the aforementioned quantities for hard-sphere systems, respectively. In Sec. VI, we derive explicit expressions for mean nearest-neighbor distances for D -dimensional systems of hard spheres. Finally, in Sec. VII, we obtain the nearest-neighbor functions for bidispersed systems from computer simulations and compare the data to our theoretical results.

II. DEFINITIONS AND FUNDAMENTAL RELATIONS

A. Different types of nearest-neighbor functions

For a polydispersed particle system, a variety of definitions for the nearest-neighbor functions can be given. There are, however, essentially two different kinds of nearest-neighbor functions for D -dimensional spherical particle systems: (i) one specifying the nearest sphere *surface* to a reference point, and (ii) the other specifying the nearest sphere *center* to a reference point. For a monodispersed particle system, the nearest sphere surface and the nearest sphere center involve the same sphere and therefore these two nearest-neighbor functions contain the same information. This monodispersed case was treated by us in an earlier study [8] using the center-based quantities. The nearest-surface distribution function for the monodispersed case has recently been applied in connection with the problem of diffusion among traps [17]. For polydispersed D -dimensional spherical systems, however, the nearest-surface distribution functions and nearest-center distribution functions are generally distinctly different. An example is shown in Fig. 1. The nearest surface to point A is on the particle to the left of point A , but the center of this particle is not the closest sphere center to point A because of its large radius relative to the other particles. The nearest sphere center to point A is the one to the right of point A . Clearly, the nearest-surface distribution functions are the most relevant for polydispersed systems and will be the focus of this paper. Possible definitions of the nearest-neighbor functions can also be given for polydispersed spherical systems (see the Appendix).

B. Polydispersed spherical particle systems

We shall study nearest-surface distribution functions and closely related quantities for a system of N interacting D -dimensional polydispersed spheres. In general, po-

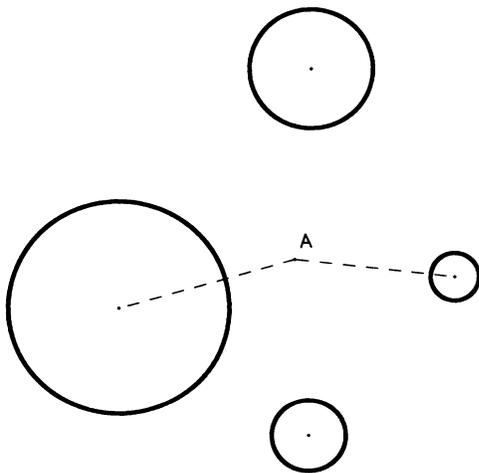


FIG. 1. Local environment around a reference point A . The nearest surface to point A is on the particle to the left of point A . The nearest sphere center to point A is the one to the right of point A .

lydispersivity may manifest itself because of variation in charge, chemical properties, and mass, as well as size. In this paper, we are interested in systems of spherical particles with polydispersivity in radii or diameters. The method applied here can also be used to study other kinds of polydispersivity.

Let the N -particle system be composed of M different types of spherical particles (M components). N_σ and R_σ denote the number and radius of σ types of particles, respectively. The N particles are spatially distributed in the D -dimensional space of volume V according to the N -particle density $P_N(\mathbf{r}^N)$, which is in turn determined by the system Hamiltonian and, in general, dynamical processes. $P_N(\mathbf{r}^N)$ characterizes the probability of finding the particles labeled $1, 2, \dots, N$ with configuration $\mathbf{r}^N \equiv \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$, respectively. The ensemble average of any many-body function $F(\mathbf{r}^N)$ is given by

$$\overline{F(\mathbf{r}^N)} = \int F(\mathbf{r}^N) P_N(\mathbf{r}^N) d\mathbf{r}^N. \quad (2.1)$$

As we have shown in previous work [8], according to whether or not there is a particle center at the reference point, there are two different types of nearest-neighbor distribution functions: the *void* nearest-neighbor distribution function and the *particle* nearest-neighbor distribution function. For polydispersed spherical systems, the void nearest-surface distribution function $h_V(r)$ is defined such that $h_V(r)dr$ is the probability that at an arbitrary point in the system the nearest particle surface lies at a distance between r and $r+dr$. The particle nearest-surface distribution function $h_{P_i}(r)$ is defined such that $h_{P_i}(r)dr$ is the probability that, given any D -dimensional sphere of radius R_i at some arbitrary position in the system, there is a nearest particle surface at a distance between r and $r+dr$. The closely related void “exclusion” probability $e_V(r)$ can then be defined as the 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 material. The particle exclusion probability $e_{P_i}(r)$ is defined as the probability of finding a region Ω_P , which is a sphere of radius r encompassing a central particle of radius R_i , empty of particle material. Since it is clear that the particle quantities are associated with the center of a specified-type particle as the reference point, henceforth we will simply write $e_{P_i}(r)$ as $e_P(r)$ and $h_{P_i}(r)$ as $h_P(r)$, unless otherwise stated. Note that for continuous polydispersed systems with an infinite range of sizes, r generally will lie in the closed interval $[-\infty, \infty]$. The significance of negative values of r follows from our definition that the reference point can sometimes lie in the *particle phase* itself and thus may involve an infinitely large particle (see Sec. IV for further details of this point).

The exclusion probabilities are related to the nearest-neighbor distribution functions by the expressions

$$e_V(r) = 1 - \int_{-\infty}^r h_V(y) dy, \quad (2.2)$$

$$e_P(r) = 1 - \int_{-\infty}^r h_P(y) dy. \quad (2.3)$$

The integrals of (2.2) and (2.3), respectively, represent the

probabilities of finding at least some portion of a particle in regions Ω_V and Ω_P . Differentiating the exclusion-probability relations with respect to r gives

$$h_V(r) = \frac{-\partial e_V(r)}{\partial r} \quad (2.4)$$

and

$$h_P(r) = \frac{-\partial e_P(r)}{\partial r} . \quad (2.5)$$

The nearest-neighbor distribution functions may be written as a product of two different correlation functions. For D -dimensional spherical particles let

$$h_V(r) = g_V(r)e_V(r) \quad (2.6)$$

and

$$h_P(r) = g_P(r)e_P(r) . \quad (2.7)$$

Equations (2.6) and (2.7) are expressions involving conditional probabilities. The quantity $g_V(r)$ in (2.6) is the probability, given that region Ω_V (spherical cavity of radius r) is empty of particle material, of finding particle surface in the spherical shell of volume $s_D(r)dr$ encompassing the cavity. The quantity s_D is the surface area of a D -dimensional sphere of radius r :

$$s_1(r) = 2 , \quad (2.8)$$

$$s_2(r) = 2\pi r , \quad (2.9)$$

$$s_3(r) = 4\pi r^2 . \quad (2.10)$$

The quantity $g_P(r)$ in (2.7) is the probability, given that region Ω_P (sphere of radius r encompassing the particle centered at some arbitrary position) is empty of particle material, of finding particle surface in the D -dimensional spherical shell of volume $s_D(r)dr$ surrounding the central particle.

The exclusion probabilities $e_V(r)$ and $e_P(r)$ are related to $g_V(r)$ and $g_P(r)$, respectively, via the expressions

$$e_V(r) = \exp \left[- \int_{-\infty}^r g_V(y) dy \right] , \quad (2.11)$$

$$e_P(r) = \exp \left[- \int_{-\infty}^r g_P(y) dy \right] , \quad (2.12)$$

which are obtained by use of (2.4)–(2.7). The combination of (2.4), (2.5), (2.11), and (2.12) yields

$$h_V(r) = g_V(r) \exp \left[- \int_{-\infty}^r g_V(y) dy \right] \quad (2.13)$$

and

$$h_P(r) = g_P(r) \exp \left[- \int_{-\infty}^r g_P(y) dy \right] . \quad (2.14)$$

In our earlier work on monodispersed spherical particle systems, we examined the corresponding center-based “void” functions $E_V(r)$, $H_V(r)$, and $G_V(r)$, and center-based “particle” functions $E_P(r)$, $H_P(r)$, and $G_P(r)$. The function $E_V(r)$ gives the probability of finding a region Ω_V , a spherical cavity of radius r centered at some arbitrary point, empty of particle centers. Similarly, $E_P(r)$

gives the probability that given a particle at the origin, the region Ω_P , a sphere of radius r encompassing this central particle, is empty of particle centers. The quantity $H_V(r)dr$ is the probability that at an arbitrary point in the system the center of the nearest particle lies at a distance between r and $r+dr$. Similarly, $H_P(r)dr$ is the probability that, given a particle at the origin, the center of the nearest particle lies at a distance between r and $r+dr$. The quantity $\rho s_D(r)G_V(r)dr$ is the probability that, given a region Ω_V empty of particle centers, particle centers are contained in the shell of volume $s_D(r)dr$ encompassing the cavity. Similarly, $\rho s_D(r)G_P(r)dr$ is the probability that, given a region Ω_P empty of particle centers, particle centers are contained in the shell of volume $s_D(r)dr$ surrounding the central particle. For identical particles of diameter σ , it is simple to relate surface-based quantities to center-based quantities, e.g., $e_V(r) = E_V(r + \sigma/2)$, $h_V(r) = H_V(r + \sigma/2)$, and $g_V(r) = G_V(r + \sigma/2)$. As noted earlier, the surface-based quantities are the most natural to employ when the particles have polydispersity in size .

C. Specific nearest-surface distribution function

In this section we describe the “specific” nearest-surface distribution functions. The specific void nearest-surface distribution function $h_{V,j}(r)$ can be defined as the probability that at an arbitrary point in the system, the nearest surface of particle of type j lies at a distance between r and $r+dr$. In the same way, the specific particle nearest-neighbor distribution function $h_{P,j}(r)$ is defined as the probability that, given any D -dimensional sphere (of radius R_j) at some arbitrary position in the system, one finds the nearest surface of particle of type j at a distance between r and $r+dr$. The specific void and particle nearest-surface distribution function can be expressed in the following way:

$$h_{V,j}(r) = g_{V,j}(r)e_{V,j}(r) \quad (2.15)$$

and

$$h_{P,j}(r) = g_{P,j}(r)e_{P,j}(r) . \quad (2.16)$$

The quantity $g_{V,j}$ in (2.15) is the probability, given that region Ω_V (spherical cavity of radius r) is empty of particle material, of finding the surface of j -type particles in the spherical shell of volume $s_D dr$ encompassing the cavity. The quantity $g_{P,j}$ in (2.16) is the probability, given a region Ω_P (sphere of radius r encompassing the particle centered at some arbitrary position) empty of particle material, of finding the surface of j -type particles in the spherical shell of volume $s_D(r)dr$ surrounding the central particle. Because of independence, the generic distribution functions h_V , h_P , g_V , and g_P are related to the specific distribution functions $h_{V,j}(r)$, $h_{P,j}(r)$, $g_{V,j}(r)$, and $g_{P,j}(r)$ by the relations

$$h_V(r) = \sum_j h_{V,j}(r) , \quad (2.17)$$

$$h_P(r) = \sum_j h_{P,j}(r) , \quad (2.18)$$

$$g_V(r) = \sum_j g_{V,j}(r), \quad (2.19)$$

$$g_P(r) = \sum_j g_{P,j}(r). \quad (2.20)$$

The relations immediately above and expressions (2.2), (2.3), (2.11), and (2.12) yield

$$e_V(r) = 1 - \int_{-\infty}^r \sum_j h_{V,j}(y) dy, \quad (2.21)$$

$$e_P(r) = 1 - \int_{-\infty}^r \sum_j h_{P,j}(y) dy, \quad (2.22)$$

$$e_V(r) = \exp \left[- \int_{-\infty}^r \sum_j g_{V,j}(y) dy \right], \quad (2.23)$$

$$e_P(r) = \exp \left[- \int_{-\infty}^r \sum_j g_{P,j}(y) dy \right]. \quad (2.24)$$

We define further $\rho_j s_D(r) G_{V,j}(r)$ as the probability that, given a region Ω_V (spherical cavity of radius r) empty of particle centers, j -type particle centers are contained in the spherical shell of volume $s_D(r) dr$ encompassing the cavity. In the same way, we define $\rho_j s_D(r) G_{P,j}(r)$ as the probability that, given a region Ω_P (sphere of radius r encompassing reference particle centered at some arbitrary position) empty of particle centers, j -type particle centers are contained in the spherical shell of volume $s_D(r) dr$ surrounding the central particle. We then have the following relations:

$$g_{V,j}(r) = \rho_j s_D(r + R_j) G_{V,j}(r + R_j) \quad (2.25)$$

$$g_{P,j}(r) = \rho_j s_D(r + R_j) G_{P,j}(r + R_j), \quad (2.26)$$

where R_j is the radius of a j -type particle. The relations (2.17)–(2.26) are of basic importance in understanding and calculating the nearest-surface distribution functions and related quantities.

An important dimensionless parameter that will be used throughout the following sections is the reduced density η in D dimensions defined by

$$\eta = \sum_{i=1}^M \frac{\pi^{D/2}}{\Gamma(1+D/2)} \rho_i R_i^D. \quad (2.27)$$

In the case of included particles with a continuous distribution radius \mathcal{R} characterized by the normalized probability density $f(\mathcal{R})$, we have

$$\eta = \frac{\pi^{D/2}}{\Gamma(1+D/2)} \rho \langle \mathcal{R}^D \rangle, \quad (2.28)$$

where the average of any function $A(\mathcal{R})$ is given by

$$\langle A(\mathcal{R}) \rangle = \int_0^\infty A(\mathcal{R}) f(\mathcal{R}) d\mathcal{R}. \quad (2.29)$$

Note that one can obtain the discrete result (2.27) from (2.28) by letting $f(\mathcal{R}) = \sum_{i=1}^M (\rho_i / \rho) \delta(\mathcal{R} - R_i)$. Finally, we note that only in the case of hard spheres is η equal to the sphere volume fraction ϕ_2 . For penetrable-sphere systems, $\eta > \phi_2$.

D. Mean nearest surface-surface distance and the random-close-packing density

Another quantity of fundamental interest in a many-particle system is the *mean nearest surface-surface distance* defined as the mean distance between the surface of a reference particle i and the nearest particle surface. It is given in terms of the nearest-surface distribution function by

$$l_{P_i} = \int_0^\infty r h_{P_i}(r) dr - \mathcal{R}_i. \quad (2.30)$$

The integral in (2.30) represents the distance from the center of the reference particle of radius \mathcal{R}_i to the nearest surface of another particle. Henceforth, we will simply write l_{P_i} as l_P . A basic quantity of hard-particle systems is the *random close-packing density*, which to our knowledge has not been properly defined and quantitatively investigated for polydispersed particle systems. For polydispersed systems, when the density of particles increases, the mean nearest surface-surface distance associated with any reference particle i will decrease, and eventually a critical point will be approached at which the mean nearest surface-surface distance associated with any of the reference particles tends to zero. We then define the random close-packing density as the density at which l_P tends to zero for any of the reference particles. The definition and the evaluation of the random close-packing density is of great interest.

Another quantity of interest is the *mean void nearest-surface distance*. The mean void nearest-surface distance l_V can be defined as

$$l_V = \int_0^\infty r h_V(r) dr. \quad (2.31)$$

Integrating (2.26) by parts, we have

$$l_V = \int_0^\infty e_V(r) dr. \quad (2.32)$$

We will calculate l_P and l_V for systems of fully penetrable spheres and totally impenetrable spheres in Sec. VI.

III. SERIES EXPANSIONS FOR THE VOID AND PARTICLE QUANTITIES

For a monodispersed particle system, Torquato, Lu, and Rubinstein [8] have obtained exact series expansions for the void quantities $H_V(r)$, $E_V(r)$, and $G_V(r)$ for systems of monodispersed spheres that interact with an arbitrary potential. For the general n -point distribution function H_n defined below, Lu and Torquato [18] found that there is a simple prescription for mapping monodisperse results into polydisperse results. The H_n contain, as special cases, the nearest-surface functions. In what follows, we shall give exact series expressions for nearest-surface distribution functions and related quantities for polydispersed systems of spheres.

A. Void quantities

Torquato [19] has developed a methodology to represent and compute a general n -point distribution function H_n for random media composed of statistical

distributions of D -dimensional identical spheres. $H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q)$ characterizes the correlation associated with finding m points with positions $\mathbf{x}^m \equiv \{\mathbf{x}_1, \dots, \mathbf{x}_m\}$ on certain surfaces in the system, $p-m$ points with positions $\mathbf{x}^{p-m} \equiv \{\mathbf{x}_{m+1}, \dots, \mathbf{x}_p\}$ in certain regions exterior to the spheres, and any q of the spheres with configuration \mathbf{r}^q , where $n=p+q$. The general n -point distribution function H_n contains as special cases a variety of different types of correlation functions that arise in the study of the transport and mechanical properties of disordered composite media [20], liquid-state theory [21], and amorphous solids [5]. A representation of the general n -point distribution function for a polydispersed system was subsequently given [18]. The void nearest-surface distribution functions are special cases of the general n -point distribution functions [18]

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

$$e_V(r) = H_1(\emptyset; \mathbf{x}_1; \emptyset). \quad (3.2)$$

Here the radius of the test particle is equal to r , as opposed to b , the notation used in Ref. [18]. From the general expressions [18] of H_n , we have the following expansion for $e_V(r)$:

$$e_V(r) = \sum_{s=0}^N (-1)^s e_V^{(s)}(r), \quad (3.3)$$

where

$$e_V^{(s)}(r) = \frac{1}{s!} \int \cdots \int d\mathcal{R}_1 \cdots d\mathcal{R}_s f(\mathcal{R}_1) \cdots f(\mathcal{R}_s) \\ \times \rho_s(\mathbf{r}^s; \mathcal{R}_1, \dots, \mathcal{R}_s) \\ \times \prod_{j=1}^s m(|\mathbf{x} - \mathbf{r}_j|; r) d\mathbf{r}_j \quad (3.4)$$

and

$$e_V^{(0)}(r) \equiv 1. \quad (3.5)$$

The series expansion for $h_V(r)$ is given by

$$h_V(r) = \sum_{s=1}^N (-1)^s h_V^{(s)}(r), \quad (3.6)$$

with

$$h_V^{(s)}(r) = -\frac{1}{s!} \frac{\partial}{\partial r} \int \cdots \int d\mathcal{R}_1 \cdots d\mathcal{R}_s f(\mathcal{R}_1) \cdots f(\mathcal{R}_s) \\ \times \rho_s(\mathbf{r}^s; \mathcal{R}_1, \dots, \mathcal{R}_s) \\ \times \prod_{j=1}^s m(|\mathbf{x} - \mathbf{r}_j|; r) d\mathbf{r}_j. \quad (3.7)$$

The results above have been expressed for a system of included particles with a continuous distribution in radius \mathcal{R} characterized by the normalized probability density $f(\mathcal{R})$. It will sometimes be convenient to employ the diameter of the particle denoted by $\sigma = 2\mathcal{R}$. The continuous representation is more general and concise than the one for the discrete case. From the expressions for the

continuous case, one can easily obtain the results of the discrete case. For example, in the discrete homogeneous case with M different components, the size distributions $f(\mathcal{R}_j)$ in relation (3.6) become $\sum_{\sigma=1}^M (\rho_\sigma/\rho) \delta(\mathcal{R}_j - \mathcal{R}_{\sigma j})$ where ρ_σ is the number density of type σ particles and $\delta(\mathcal{R})$ is the Dirac delta function. In (3.7), $\rho_n(\mathbf{r}^n; \mathcal{R}_1, \dots, \mathcal{R}_n) f(\mathcal{R}_1) \cdots f(\mathcal{R}_n)$ is the probability density function associated with finding an inclusion with radius \mathcal{R}_1 at \mathbf{r}_1 , another inclusion with radius \mathcal{R}_2 at \mathbf{r}_2 , etc. The case $n=1$ is degenerate in the sense that $\rho_1(\mathbf{r}_1; \mathcal{R}_1)$ is independent of \mathbf{r}_1 and in the instance of statistically homogeneous media is simply equal to the total number of density ρ . The quantity $m(|\mathbf{x} - \mathbf{r}_i|; r)$ is an indicator function defined as

$$m(|\mathbf{x} - \mathbf{r}_i|; r) = \begin{cases} 1, & |\mathbf{x} - \mathbf{r}_i| < r + \mathcal{R}_i \\ 0, & |\mathbf{x} - \mathbf{r}_i| \geq r + \mathcal{R}_i. \end{cases} \quad (3.8)$$

Note that the function m defined here is slightly different from the one defined in Ref. [16] in that it is the surface indicator function.

In the special case of a monodispersed spherical system with particle diameter σ , we have

$$e_V(r) = E_V(r + \sigma/2), \quad (3.9)$$

$$h_V(r) = H_V(r + \sigma/2), \quad (3.10)$$

$$g_V(r) = \rho s_D(r + \sigma/2) G_V(r + \sigma/2), \quad (3.11)$$

where $E_V(r)$, $H_V(r)$, and $G_V(r)$ have been defined in Ref. [8] and in Sec. II.

The evaluation of the void quantities is generally non-trivial because of the appearance of the ρ_n . For the special case of "overlapping" or "randomly centered" (i.e., spatially uncorrelated) homogeneous sphere systems, the ρ_n are especially simple:

$$\rho_n(\mathbf{r}^n; \mathcal{R}_1, \dots, \mathcal{R}_n) = \prod_{j=1}^n \rho_1(\mathbf{r}_j, \mathcal{R}_j). \quad (3.12)$$

We then have the following results:

$$e_V(r) = \exp[-\rho \langle v_D(r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle], \quad (3.13)$$

$$h_V(r) = \rho \langle s_D(r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle \\ \times \exp[-\rho \langle v_D(r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle]. \quad (3.14)$$

Here $v_D(\mathcal{R})$ is the volume of a D -dimensional sphere with radius \mathcal{R} , i.e.,

$$v_1(\mathcal{R}) = 2\mathcal{R}, \quad (3.15)$$

$$v_2(\mathcal{R}) = \pi\mathcal{R}^2, \quad (3.16)$$

$$v_3(\mathcal{R}) = \frac{4}{3}\pi\mathcal{R}^3. \quad (3.17)$$

and $\Theta(x)$ is the Heaviside step function. Note that relations (3.13) and (3.14) are valid for both $r > 0$ and $r < 0$. In the case of $r > 0$, the distance between the nearest sur-

face and the reference point can be obtained by subtracting the radius of the nearest particle from the distance between the reference point and the center of the nearest-surface particle. When the distance between the reference point and the center of the nearest particle is smaller than the radius of the particle, the reference point is in the particle phase, and we have that $r < 0$. The exclusion probability $e_V(r)$ for $r < 0$ is then the probability that there is no particle material that penetrates the reference point with a depth larger than $-r$. The nearest-surface distribution $h_V(r)$ is the probability density associated with finding the nearest surface a distance $-r$ away while the reference point is in the particle phase.

Another useful model is a system of totally impenetr-

$$e_p^{(s)}(r) = \frac{1}{\rho_1(\mathcal{R}_1)s!} \int \cdots \int d\mathcal{R}_1 \cdots d\mathcal{R}_{s+1} f(\mathcal{R}_2) \cdots f(\mathcal{R}_{s+1}) \times \rho_{s+1}(\mathbf{r}^{s+1}; \mathcal{R}_1, \dots, \mathcal{R}_{s+1}) \prod_{j=2}^{s+1} m(|\mathbf{r}_1 - \mathbf{r}_j|; r) d\mathbf{r}_j \quad (3.19)$$

and

$$e_p^{(0)}(r) = 1. \quad (3.20)$$

The *particle* nearest-surface distribution function is given by

$$h_p(r) = \sum_{s=1}^{N-1} (-1)^{s+1} h_p^{(s)}(r), \quad (3.21)$$

where

$$h_s^{(s)}(r) = \frac{1}{s!} \frac{\partial}{\partial r} \int \cdots \int d\mathcal{R}_1 \cdots d\mathcal{R}_{s+1} f(\mathcal{R}_2) \cdots f(\mathcal{R}_{s+1}) \times \rho_{s+1}(\mathbf{r}^{s+1}; \mathcal{R}_1, \dots, \mathcal{R}_{s+1}) \times \prod_{j=2}^{s+1} m(|\mathbf{r}_1 - \mathbf{r}_j|; r) d\mathbf{r}_j. \quad (3.22)$$

For statistically homogeneous media, the conditional pair distribution function $g_p(r)$ can be obtained through the relations (2.6) and (2.7).

For the simple case of fully penetrable spheres, it is straightforward to obtain the following expressions from (3.18)–(3.22):

$$e_p(r) = \exp[-\rho \langle v_D(r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle], \quad (3.23)$$

$$h_p(r) = \rho \langle s_D(r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle \times \exp[-\rho \langle v_D(r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle]. \quad (3.24)$$

As expected [8], these relations are identical to (3.13) and (3.14).

IV. CALCULATIONS OF THE VOID QUANTITIES

We now consider the evaluation of the void nearest-surface functions for D -dimensional hard-sphere models

able (hard) spheres whose corresponding results are reported in Sec. V.

B. Particle quantities

The exact integral representations for the particle quantities $e_p(r)$, $h_p(r)$, and $g_p(r)$ for systems of spheres that interact with an arbitrary potential can be obtained in the same way as the void quantities. We have

$$e_p(r) = \sum_{s=0}^{N-1} (-1)^s e_p^{(s)}(r), \quad (3.18)$$

where

for arbitrary density that are accurate over a wide range of densities. The probability density $h_V(r)$ shall be made dimensionless by multiplying it by the average diameter, but instead of writing $\langle \sigma \rangle h_V(r)$ we will simply write $h_V(r)$, taking $\langle \sigma \rangle = 1$.

A. Formula for calculating the void quantities

Since for impenetrable spheres the reference point can only be inside one of the particles with radius $0 < -r < \mathcal{R}$, we then have

$$e_V(r) = 1 - \rho \langle v_D(r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle, \quad r < 0 \quad (4.1)$$

where $v_D(\mathcal{R})$ is the volume of the D -dimensional sphere and $\Theta(x)$ is the Heaviside step function. The corresponding nearest-surface distribution function can then be expressed as

$$h_V(r) = \rho \langle s_D(r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle, \quad r < 0. \quad (4.2)$$

The general formula for calculating the void exclusion probability function for the case of $r > 0$ can be obtained easily from (2.23) as

$$e_V(r) = (1 - \eta) \exp \left[-\rho \left\langle \int_0^r s_D(y + \mathcal{R}) G(y + \mathcal{R}) dy \right\rangle \right], \quad r > 0. \quad (4.3)$$

Similarly,

$$h_V(r) = (1 - \eta) \rho \langle s_D(r + \mathcal{R}) G(r + \mathcal{R}) \rangle \times \exp \left[-\rho \left\langle \int_0^r s_D(y + \mathcal{R}) G(y + \mathcal{R}) dy \right\rangle \right], \quad r > 0 \quad (4.4)$$

where $G(r + \mathcal{R})$ is the value of the radial distribution function at contact for pairs of particles with radii r and \mathcal{R} .

B. Hard rods

For an equilibrium distribution of one-dimensional impenetrable spheres, i.e., hard rods, one can evaluate the series (3.4) and (3.6) 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 [22]. Higher-order probability densities are given in terms of products of two-particle probability densities. For polydispersed systems, Lebowitz, Helfand, and Praesegaard [23] have given the scaled-particle theory of fluid mixture. The expression for the contact value for pairs of particles with radius r and \mathcal{R} is

$$G(r + \mathcal{R}) = \frac{1}{1 - \eta}, \quad r > 0, \tag{4.5}$$

which is in fact independent of the size of the test particle. We then have

$$e_V(r) = (1 - \eta) \exp \left[\frac{-2\rho r}{1 - \eta} \right], \quad r > 0, \tag{4.6}$$

$$h_V(r) = 2\eta \exp \left[\frac{-2\rho r}{1 - \eta} \right], \quad r > 0 \tag{4.7}$$

where η is the reduced density defined by (2.24) and (2.25). For $r < 0$, we have the result

$$e_V(r) = 1 - 2\rho \langle (\mathcal{R} + r) \Theta(\mathcal{R} + r) \rangle, \quad r < 0. \tag{4.8}$$

A commonly employed size distribution function $f(\mathcal{R})$ is the Schulz distribution function, which is defined as

$$f(\mathcal{R}) = \frac{1}{\Gamma(z + 1)} \left[\frac{z + 1}{\langle \mathcal{R} \rangle} \right]^{z + 1} \mathcal{R}^z \exp \left[\frac{-(z + 1)\mathcal{R}}{\langle \mathcal{R} \rangle} \right], \tag{4.9}$$

$z > -1$

where $\Gamma(x)$ is the gamma function. The n th moment of the Schulz distribution function is

$$\langle \mathcal{R}^n \rangle = \langle \mathcal{R} \rangle^n \frac{(z + 1)^{-n}}{z} \prod_{i=0}^{n-1} (z + i). \tag{4.10}$$

By increasing z , the variance decreases, i.e., the distribution becomes sharper. In the monodisperse limit $z \rightarrow \infty$, $f(\mathcal{R}) = \delta(\mathcal{R} - \langle \mathcal{R} \rangle)$. It is easy to see that (4.6) and (4.7) agree with (4.12) and (4.13) of Ref. [8] in the monodisperse case.

C. Hard disks

For two- and higher-dimensional systems of hard spheres, exact evaluation of the series (3.4)–(3.6) are impossible for arbitrary density because the n -particle probability densities are not exactly known. One must therefore settle for an approximate means of computing these series. The scaled-particle (SP) theory [23] provides one approximation scheme. For $D = 2$ the scaled-particle approximation gives the radial distribution function at the contact value as

$$G(r + \mathcal{R}) = \frac{1}{1 - \eta} + \frac{\pi \rho \langle \mathcal{R} \rangle \mathcal{R} r}{(1 - \eta)^2 (r + \mathcal{R})}. \tag{4.11}$$

The exclusion probability function is then from (4.1) and (4.3) given by

$$e_V(r) = \begin{cases} 1 - \pi \rho \langle (r + \mathcal{R})^2 \Theta(r + \mathcal{R}) \rangle, & r < 0 \\ (1 - \eta) \exp \left[-\pi \rho \left[\frac{r^2 + 2\langle \mathcal{R} \rangle r}{1 - \eta} + \frac{\pi \rho \langle \mathcal{R} \rangle^2 r^2}{(1 - \eta)^2} \right] \right], & r > 0. \end{cases} \tag{4.12}$$

$$h_V(r) = \begin{cases} 2\pi \rho \langle (r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle, & r < 0 \\ \pi \rho \left[2r + 2\langle \mathcal{R} \rangle + \frac{2r\pi \rho \langle \mathcal{R} \rangle^2}{(1 - \eta)} \right] \exp \left[-\pi \rho \left[\frac{r^2 + 2r\langle \mathcal{R} \rangle}{1 - \eta} + \pi \rho \langle \mathcal{R} \rangle^2 \frac{r^2}{(1 - \eta)^2} \right] \right], & r > 0. \end{cases} \tag{4.13}$$

The void nearest-surface distribution function in this case can then be written as

$$h_V(r) = \begin{cases} 2\pi \rho \langle (r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle, & r < 0 \\ \pi \rho \left[2r + 2\langle \mathcal{R} \rangle + \frac{2r\pi \rho \langle \mathcal{R} \rangle^2}{(1 - \eta)} \right] \exp \left[-\pi \rho \left[\frac{r^2 + 2r\langle \mathcal{R} \rangle}{1 - \eta} + \pi \rho \langle \mathcal{R} \rangle^2 \frac{r^2}{(1 - \eta)^2} \right] \right], & r > 0. \end{cases} \tag{4.14}$$

$$h_V(r) = \begin{cases} 2\pi \rho \langle (r + \mathcal{R}) \Theta(r + \mathcal{R}) \rangle, & r < 0 \\ \pi \rho \left[2r + 2\langle \mathcal{R} \rangle + \frac{2r\pi \rho \langle \mathcal{R} \rangle^2}{(1 - \eta)} \right] \exp \left[-\pi \rho \left[\frac{r^2 + 2r\langle \mathcal{R} \rangle}{1 - \eta} + \pi \rho \langle \mathcal{R} \rangle^2 \frac{r^2}{(1 - \eta)^2} \right] \right], & r > 0. \end{cases} \tag{4.15}$$

In the special case of a system with monodispersed particles, we have

$$\pi \rho = 4\eta. \tag{4.16}$$

Introducing the scaled distance $x = r / (2\langle \mathcal{R} \rangle)$ and taking $2\langle \mathcal{R} \rangle = 1$, we have the following expressions for a monodispersed system:

$$e_V(x) = \begin{cases} 1 - 4\eta (x + \frac{1}{2})^2 \Theta(x + \frac{1}{2}), & x < 0 \\ (1 - \eta) \exp \left[\frac{-4\eta}{(1 - \eta)^2} (x^2 + x - x\eta) \right], & x > 0 \end{cases} \tag{4.17}$$

$$e_V(x) = \begin{cases} 1 - 4\eta (x + \frac{1}{2})^2 \Theta(x + \frac{1}{2}), & x < 0 \\ (1 - \eta) \exp \left[\frac{-4\eta}{(1 - \eta)^2} (x^2 + x - x\eta) \right], & x > 0 \end{cases} \tag{4.18}$$

$$h_V(x) = \begin{cases} 8\eta(x + \frac{1}{2})\Theta(x + \frac{1}{2}), & x < 0 \\ \frac{4\eta}{1-\eta}(2x + 1 - \eta)\exp\left[\frac{-4\eta}{(1-\eta)^2}(x^2 + x - x\eta)\right], & x > 0. \end{cases} \tag{4.19}$$

$$\tag{4.20}$$

Equations (4.18) and (4.20) can be obtained from (4.21) and (4.24) of Ref. [8], by using the relationship $e_V(x) = E_V(x + \frac{1}{2})$. Note, in expressions (4.19) and (4.20) h_V was made dimensionless by multiplying by the diameter of inclusions, but instead of writing σh_V we simply wrote h_V , taking $\sigma = 1$. In Fig. 2, the results of $e_V(r)$ for two-dimensional systems are shown for the Schulz distribution with $z = 0$ (solid lines) and $z = \infty$ (dashed lines) for $\phi_2 = 0.2$ and 0.6 , respectively. Note that $e_V(r)$ is a monotonic decreasing function of r for the same reasons as in the monodisperse case ($z = \infty$), as explained in Ref. [8]. For large r , the effect of polydispersivity is to increase both $e_V(r)$ and $h_V(r)$ relative to the monodisperse result. The reason for this behavior can be seen by referring to (2.28) and noting that, at fixed η , the dimensional number density ρ will be smaller in the polydispersed system than for the monodispersed system, whereas the average volume of a particle will be larger in the polydispersed case than in the monodisperse case. Therefore, the probability of finding a large void region in the polydispersed system is larger than in the monodispersed system.

D. Hard spheres

For the case of three-dimensional spherical systems, we have, according to Refs. [23–25], that the radial distribution function at contact is given by

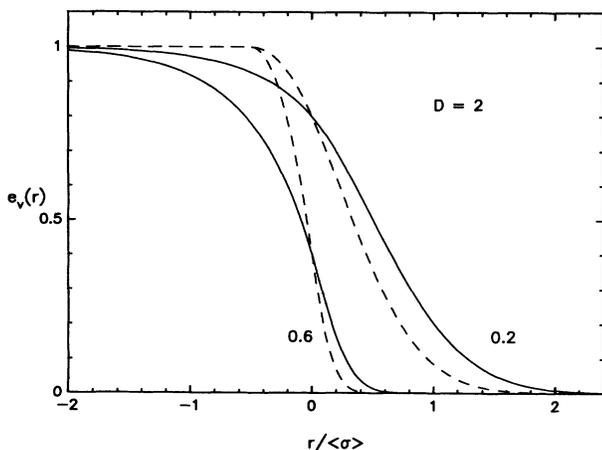


FIG. 2. Void exclusion probability $e_V(r)$ for the two-dimensional hard-sphere polydispersed system characterized by a Schulz distribution with $z = 0$ (solid lines) and $z = \infty$ (dashed line) for particle volume fractions $\phi_2 = 0.2$ and 0.6 , respectively.

$$G(r + \mathcal{R}) = \frac{1}{1 - \xi_3} + \frac{6r\mathcal{R}}{r + \mathcal{R}} \frac{\xi_2}{(1 - \xi_3)^2} + A \left[\frac{2r\mathcal{R}}{r + \mathcal{R}} \right]^2 \frac{\xi_2^2}{(1 - \xi_3)^2}, \tag{4.21}$$

where

$$\xi_k = \frac{\pi}{3} \rho 2^{k-1} \langle \mathcal{R}^k \rangle, \tag{4.22}$$

with $A = 2$ being the Carnahan-Starling (CS) approximation, $A = 3$ being the SP approximation, and $A = 0$ being the Percus-Yevick (PY) approximation. The void exclusion probability is then according to (4.1) and (4.3) given by

$$e_V(r) = \begin{cases} 1 - \frac{4\pi}{3} \rho \langle (r + \mathcal{R})^3 \Theta(r + \mathcal{R}) \rangle, & r < 0 \\ (1 - \eta) \exp[-\pi\rho(cr + dr^2 + gr^3)], & r > 0 \end{cases} \tag{4.23}$$

$$\tag{4.24}$$

with

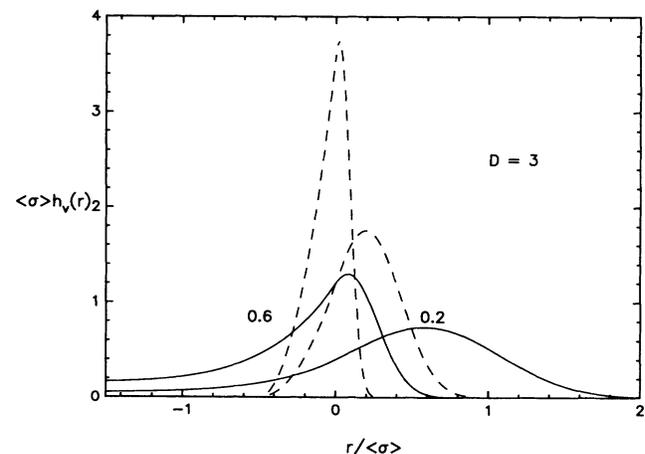


FIG. 3. Void nearest-surface distribution function $h_V(r)$ for the three-dimensional hard-sphere polydispersed system characterized by a Schulz distribution with $z = 0$ (solid lines) and $z = 3$ (dashed lines) for particle volume fractions $\phi_2 = 0.3$ and 0.5 , respectively.

$$c = \frac{4\langle \mathcal{R}^2 \rangle}{1-\eta}, \quad (4.25)$$

$$d = \frac{4\langle \mathcal{R} \rangle}{1-\eta} + \frac{12\xi_2}{(1-\xi_3)^2} \langle \mathcal{R}^2 \rangle, \quad (4.26)$$

$$g = \frac{4}{3(1-\eta)} + \frac{4\xi_2}{(1-\eta)^2} + \frac{16}{3} \frac{A\xi_2^2}{(1-\eta)^3} \langle \mathcal{R}^2 \rangle. \quad (4.27)$$

The void nearest-neighbor distribution function is given by

$$h_V(r) = \begin{cases} 4\pi\rho\langle (r+\mathcal{R})^2\Theta(r+\mathcal{R}) \rangle, & r < 0 \\ \pi\rho(c+2dr+3gr^2)(1-\eta)\exp[-\pi\rho(cr+dr^2+gr^3)], & r > 0. \end{cases} \quad (4.28)$$

In the special case of a monodispersed particle system, we have

$$\langle \sigma^2 \rangle = 1, \quad (4.30)$$

$$\xi_2 = \xi_3 = \eta. \quad (4.31)$$

The expressions for the exclusion probability and the nearest-surface distribution function in terms of scaled $x = r/(2\mathcal{R})$ are

$$e_V(x) = 1 - 8\eta(x + \frac{1}{2})^3\Theta(x + \frac{1}{2}), \quad x < 0, \quad (4.32)$$

$$h_V(x) = 24\eta(x + \frac{1}{2})^2\Theta(x + \frac{1}{2}), \quad x < 0, \quad (4.33)$$

$$e_V(x) = (1-\eta)\exp\left[-\eta\left[\frac{6x}{1-\eta} + \frac{12+6\eta}{(1-\eta)^2}x^2 + \frac{8[(A-2)\eta^2+\eta+1]}{(1-\eta)^3}x^3\right]\right], \quad x > 0, \quad (4.34)$$

$$h_V(x) = \eta\left[6 + \frac{(24+12\eta)}{1-\eta}x + \frac{24[(A-2)\eta^2+\eta+1]}{(1-\eta)^2}\right] \times \exp\left[-\eta\left[\frac{6x}{1-\eta} + \frac{12+6\eta}{(1-\eta)^2}x^2 + \frac{(A-2)\eta^3+\eta+1}{(1-\eta)^3}x^3\right]\right], \quad x > 0. \quad (4.35)$$

Equations (4.34) and (4.35) can be obtained from the expressions (4.33) and (4.34) of Ref. [8] using the relationships (3.9) and (3.10).

Figure 3 shows the void nearest-surface distribution function for a three-dimensional hard-sphere system with a Schulz distribution $z=0$ (solid lines) and $z=\infty$ (dashed lines) for $\phi_2=0.2$ and 0.6 , respectively. A broader distribution for h_V has been found for polydispersed systems for the same general reasons described above for Fig. 2.

V. CALCULATIONS OF THE PARTICLE QUANTITIES

Here we consider computing the particle quantities $e_P(r)$, $h_P(r)$, and $g_P(r)$ for statistically homogeneous and

isotropic distributions of D -dimensional impenetrable inclusions.

A. Fundamental relationships between void quantities and particle quantities

As we have revealed in a previous paper [8] for monodispersed systems, the void and particle quantities are related for statistically homogeneous hard-sphere distributions. For polydispersed systems, a similar relationship exists. The essence of the relationship is that $e_P(r)$ can be expressed as a conditional probability that, in the thermodynamic limit, yields an exact relationship, namely,

$$e_P(r) = \frac{e_V(r)}{e_V(\mathcal{R})}, \quad r > \mathcal{R} \quad (5.1)$$

where \mathcal{R} is the radius of the reference particle. From the relationship above, we have the following relationship for the nearest-surface distribution function:

$$h_P(r) = \frac{h_V(r)}{e_V(\mathcal{R})}, \quad r > \mathcal{R}. \quad (5.2)$$

We also have the relationship for $g_P(r)$ and $g_V(r)$,

$$g_P(r) = g_V(r), \quad r > \mathcal{R}. \quad (5.3)$$

These relationships state that the environment around a hard sphere of radius \mathcal{R} is the same as the environment around a sphere void region of radius \mathcal{R} for statistically homogeneous media.

B. Hard rods

The particle quantities for one-dimensional systems can be obtained from relationships (5.1) and (5.2) using the expressions (4.6) and (4.7) for the void quantities. We have that

$$e_P(r) = \exp\left[\frac{-2\rho(r-\mathcal{R})}{1-\eta}\right], \quad (5.4)$$

$$h_P(r) = \frac{2\rho}{1-\eta} \exp\left[\frac{-2\rho(r-\mathcal{R})}{1-\eta}\right]. \quad (5.5)$$

Note that the given expressions immediately indicate the dependence of $h_P(r)$ on the radius of the reference particle \mathcal{R} .

C. Hard disks

In the case of hard disks ($D=2$), we make use of the void SP approximation (4.13) and (4.15). These expressions combined with Eqs. (5.1) and (5.2) yield

$$e_p(r) = \exp \left[\frac{\pi\rho}{(1-\eta)}(r^2 - \mathcal{R}^2 + 2(r - \mathcal{R})\langle \mathcal{R} \rangle) + \frac{\pi\rho\langle \mathcal{R} \rangle^2(r^2 - \langle \mathcal{R} \rangle^2)}{1-\eta} \right], \quad (5.6)$$

$$h_p(r) = \frac{\pi\rho}{1-\eta} \left[2r + 2\langle \mathcal{R} \rangle + \frac{2\pi\rho\langle \mathcal{R} \rangle^2 r}{1-\eta} \right] \times \exp \left[\frac{\pi\rho}{(1-\eta)}(r^2 - \mathcal{R}^2 + 2(r - \mathcal{R}) + \frac{\pi\rho\langle \mathcal{R} \rangle^2(r^2 - \langle \mathcal{R} \rangle^2)}{1-\eta}) \right]. \quad (5.7)$$

For the special case of monodispersed particles of unit diameter, the expressions (5.6) and (5.7) become

$$e_p(x) = \exp \left[\frac{-4\eta}{(1-\eta)^2} \left[x^2 + x - \frac{3}{4} - (x - \frac{1}{2})\eta \right] \right], \quad (5.8)$$

and

$$h_p(x) = \frac{4\eta}{(1-\eta)^2} (2x + 1 - \eta) \times \exp \left[\frac{-\pi\rho}{(1-\eta)^2} \left[x^2 + x - \frac{3}{4} - (x - \frac{1}{2})\eta \right] \right]. \quad (5.9)$$

These results correspond to the monodisperse results (5.13) and (5.14) of Ref. [8], i.e.,

$$E_p(x) = \exp \left[\frac{-4\eta}{(1-\eta)^2} [(x^2 - 1) - \eta(x - 1)] \right], \quad (5.10)$$

$$H_p(x) = \frac{4\eta(2x - \eta)}{(1-\eta)^3} \times \exp \left[\frac{-4\eta}{(1-\eta)^2} [(x^2 - 1) - \eta(x - 1)] \right]. \quad (5.11)$$

Recall in (5.10) and (5.11) that x is the sum of the radius of the test particle and the inclusion radius scaled to the diameter of inclusion particles.

D. Hard spheres

For the case of hard spheres ($D=3$), we obtain the particle quantities in three different approximations: PY, CS, and SP approximations corresponding to $A=0, 2, 3$, respectively, in the following expressions:

$$e_p(r) = \exp \{ -\pi\rho c [(r - \mathcal{R}) + d(r^2 - \mathcal{R}^2) + g(r^3 - \mathcal{R}^3)] \}, \quad (5.12)$$

$$h_p(r) = \pi\rho(c + 2dr + 3gr^2) \times \exp \{ -\pi\rho c [(r - \mathcal{R}) + d(r^2 - \mathcal{R}^2) + g(r^3 - \mathcal{R}^3)] \}, \quad (5.13)$$

where c, d, g are given in (4.25)–(4.27).

In the case of monodispersed particles, we have

$$e_p(x) = (1-\eta) \exp \left[-\eta \left[\frac{6(x - \frac{1}{2})}{1-\eta} + \frac{12+6\eta}{(1-\eta)^2} (x^2 - \frac{1}{4}) + \frac{(A-2)\eta^2 + \eta + 1}{(1-\eta)^3} (x^3 - \frac{1}{8}) \right] \right], \quad (5.14)$$

$$h_p(x) = \eta \left[6 + \frac{(24+12\eta)x}{(1-\eta)} + \frac{24[(A-2)\eta^2 + \eta + 1]}{(1-\eta)^2} x^2 \right] \exp \left[-\eta \left[\frac{6(x - \frac{1}{2})}{1-\eta} + \frac{12+6\eta}{(1-\eta)^2} (x^2 - \frac{1}{4}) + \frac{8[(A-2)\eta^2 + \eta + 1]}{(1-\eta)^3} (x^3 - \frac{1}{8}) \right] \right]. \quad (5.15)$$

Figure 4 shows the particle exclusion probability e_p for a Schulz distribution with $z=3$ and 0 at two different particle volume fractions. As expected, polydispersity increases e_p at fixed r . In Fig. 5, the particle nearest-surface distribution function $h_p(r)$ is shown for the

Schulz distribution with $z=0$ for $\phi_2=0.3$ and 0.5 with reference particle diameters $\sigma=0.5$ and 2, respectively. For large reference particles, h_p has a large value near the surface of the reference particle, but it decreases more rapidly than h_p for smaller reference particles.

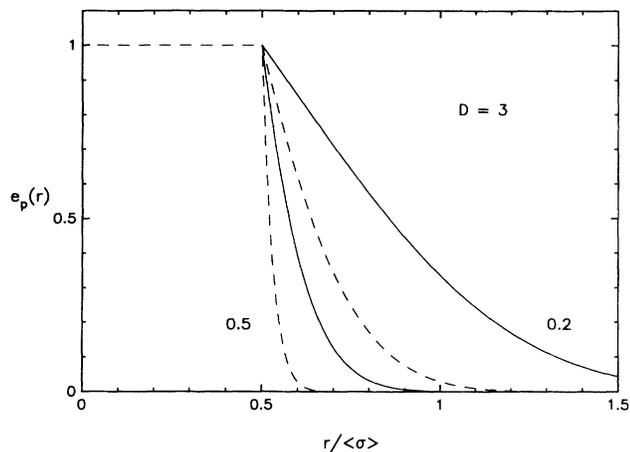


FIG. 4. The particle exclusion probability $e_p(r)$ for the three-dimensional hard-sphere polydispersed system characterized by a Schulz distribution with $z=3$ (solid lines) and $z=\infty$ (dashed lines) for particle volume fractions $\phi_2=0.2$ and 0.6 , respectively. The diameter of the reference particle is $\langle\sigma\rangle$.

VI. MEAN NEAREST SURFACE-SURFACE DISTANCE AND MEAN VOID NEAREST-SURFACE DISTANCE

Here we shall compute the mean nearest surface-surface distance l_p defined by (2.30), for distributions of D -dimensional impenetrable inclusions using the results of the preceding section. Integration of (2.30) by parts and using (2.5) gives the following general expression:

$$l_p = \int_{\mathcal{R}}^{\infty} e_p(r) dr. \quad (6.1)$$

In the case $D=1$, substitution of (5.4) into (6.1) yields,

upon integration, the following simple result:

$$l_p = \frac{1-\eta}{2\rho}. \quad (6.2)$$

Equation (6.2) indicates that for one-dimensional hard-rod systems, the mean nearest surface-surface distance is independent of the type of reference particle.

For two-dimensional systems of hard spheres, by employing expressions (5.7) and (6.1), we obtain the following results:

$$l_p = \frac{\pi^{1/2}}{2a^{1/2}} \exp[a(\mathcal{R}+b/2)^2] \operatorname{erfc}[a^{1/2}(\mathcal{R}+b/2)], \quad (6.3)$$

where $\operatorname{erfc}(x)$ is the complementary error function and

$$a = \frac{\pi\rho(1-\eta+\pi\rho\langle\mathcal{R}\rangle^2)}{(1-\eta)^2}, \quad (6.4)$$

$$b = \frac{2\langle\mathcal{R}\rangle(1-\eta)}{1-\eta+\pi\rho\langle\mathcal{R}\rangle^2}. \quad (6.5)$$

In relation (6.3), \mathcal{R} is the radius of the reference particle. For two-dimensional systems, the mean nearest surface-surface distance is a function of the radius of the reference particle. When \mathcal{R} is very large, l_p is proportional to \mathcal{R}^{-1} . On average, bigger particles have more neighbors than smaller particles, and therefore such bigger particles have a better chance of having a nearest particle a shorter distance away. For infinitely large particles, the probability that one of the other particles will touch it will tend to unity. The expression (6.3) is shown for the Schulz distribution in Fig. 6. We plot $l_p/\langle\sigma\rangle$ as a function of ϕ_2^{-1} for the Schulz distribution with $z=0$ (solid lines), and $z=\infty$ (dashed line). For $z=0$, we plot the results for the diameters of reference particles $\langle\sigma\rangle$ (lower solid line) and $0.01\langle\sigma\rangle$ (upper solid line). The effect of the polydispersity is to increase the surface-surface distance between

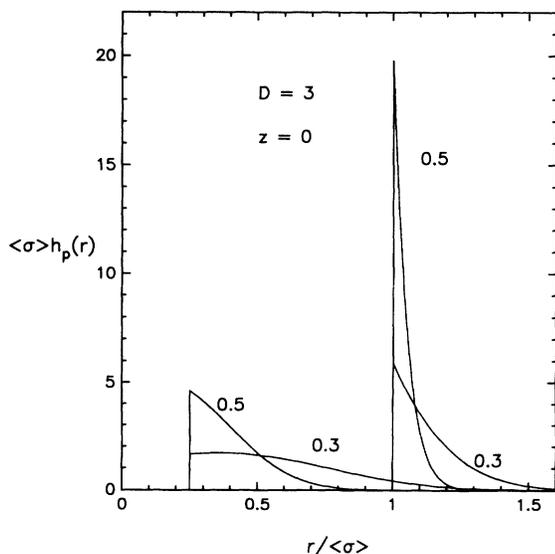


FIG. 5. Particle nearest-surface distribution function $h_p(r)$ for the three-dimensional hard-sphere polydispersed system characterized by a Schulz distribution with $z=0$ for particle volume fractions $\phi_2=0.3$ and 0.5 . The diameters of the reference particle are $0.5\langle\sigma\rangle$ and $2\langle\sigma\rangle$.

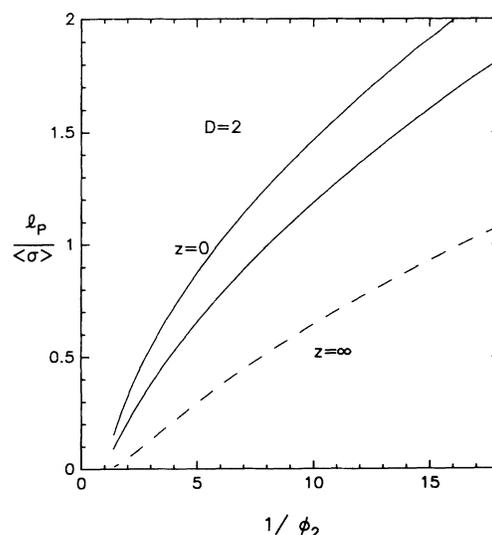


FIG. 6. Mean nearest surface-surface distance l_p vs ϕ_2^{-1} for the two-dimensional hard-sphere polydispersed system characterized by a Schulz distribution with $z=0$ (solid lines) and $z=\infty$ (dashed line). Here the diameters of the reference particles for $z=0$ are $\langle\sigma\rangle$ and $0.01\langle\sigma\rangle$.

particles. The figure also clearly shows that smaller reference particles yield larger surface-surface distances.

For three-dimensional systems, from (5.12) and (6.1) we have

$$l_P = \int_{\mathcal{R}}^{\infty} \exp\{-\pi\rho c[(r-\mathcal{R}) + d(r^2-\mathcal{R}^2) + g(r^3-\mathcal{R}^3)]\} dr. \quad (6.6)$$

This integration is carried out numerically. The numerical results are summarized in Fig. 7, demonstrating how the composition of particles affects the average surface-surface distance for three-dimensional hard-sphere systems. Again, because of the polydispersity, the particle surface-surface distance is increased. From the mean nearest surface-surface distance, one may calculate the random close-packing density through extrapolation. This is a difficult task for particles with a continuous size distribution, since it is difficult to approximate well infinitesimally small particles at high densities.

The mean "void" nearest-surface distance can be calculated using (2.32) through known results of $e_V(r)$ in Sec. IV. For systems of hard rods, we have the following simple result:

$$l_V = \frac{(1-\eta)^2}{2\rho}. \quad (6.7)$$

For systems of hard disks, we find

$$l_V = \frac{(1-\eta)^2}{2} [\rho(1-\eta + \pi\rho\langle\mathcal{R}\rangle^2)]^{-1/2} \times \exp\left[\frac{\pi\rho\langle\mathcal{R}\rangle^2}{(1-\eta + \pi\rho\langle\mathcal{R}\rangle^2)}\right] \times \operatorname{erfc}[(\pi\rho)^{1/2}\langle\mathcal{R}\rangle(1-\eta + \pi\rho\langle\mathcal{R}\rangle^2)^{-1/2}]. \quad (6.8)$$

For three-dimensional hard-sphere systems, according to

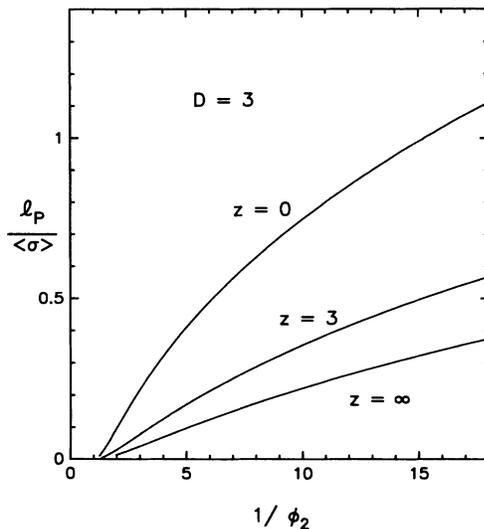


FIG. 7. Mean nearest surface-surface distance l_P as a function of ϕ_2^{-1} for a three-dimensional hard-sphere polydispersed system characterized by a Schulz distribution with $z=0, 3$, and ∞ . The diameter of the reference particle is $\langle\sigma\rangle$.

the definition of (2.31) and expression (2.32), the mean void nearest-surface distance is an integration of (4.24). For the function (4.24) numerical integration is required. The numerical results of l_V as a function of the fraction of particle phase ϕ_2 for hard-sphere systems with a Schulz distribution $z=0$ and 3 are shown in Fig. 8. The same effect of polydispersity as for the surface-surface distance is found.

The results of l_V for fully penetrable spheres can be calculated similarly. For one-dimensional fully penetrable rods, we have

$$l_V = \frac{1-\eta}{\rho}. \quad (6.9)$$

For two-dimensional fully penetrable disks, the result is

$$l_V = \frac{1-\eta}{2} \rho^{-1/2} \exp(\rho\pi/4) \operatorname{erfc}(\pi^{1/2}\rho^{1/2}/2). \quad (6.10)$$

For fully penetrable sphere systems with $D=3$ and the Schulz distribution in particle size, we have

$$l_V = (1-\eta) \int_0^{\infty} \exp\left[-\frac{4\pi\rho}{3} \left[r^3 + \frac{3r^2}{\langle\mathcal{R}\rangle} + \frac{3r}{\langle\mathcal{R}^2\rangle} \frac{z+2}{z+1}\right]\right] dr. \quad (6.11)$$

The numerical results of l_V for three-dimensional fully penetrable spheres are shown in Fig. 9 as a function of particle volume fraction ϕ_2 for the Schulz distribution with $z=0$ and 3 , respectively. Note, for fully penetrable three-dimensional sphere systems with the Schulz distribution function, the particle number density can be expressed as

$$\rho = -\ln(1-\eta) \frac{3}{4\pi\langle\mathcal{R}\rangle^3} \frac{(z+1)^2}{(z+2)(z+3)}. \quad (6.12)$$

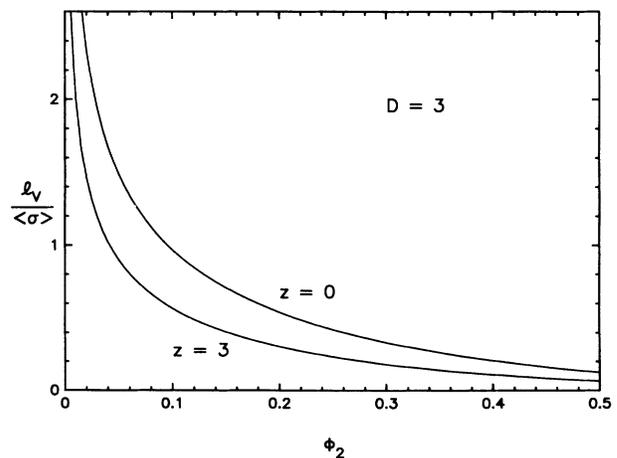


FIG. 8. Mean "void" nearest-surface distance l_V as a function of particle fraction ϕ_2 for three-dimensional hard-sphere systems by a Schulz distribution with $z=0$ and 3 .

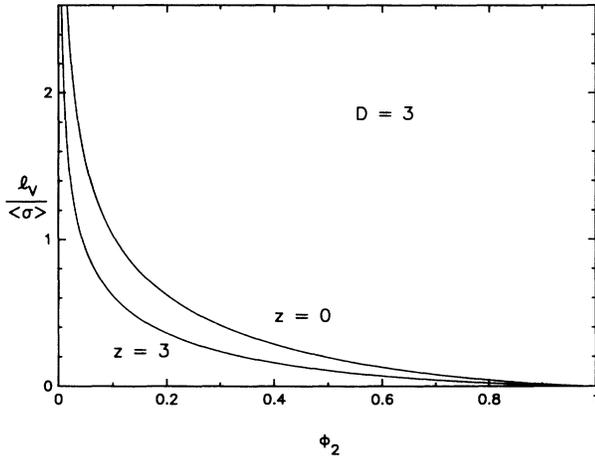


FIG. 9. Mean “void” nearest-surface distance l_V as a function of particle fraction ϕ_2 for a fully penetrable polydispersed sphere system characterized by a Schulz distribution with $z=0$ and 3.

VII. RESULTS FOR DISCRETE-SIZE DISTRIBUTIONS AND COMPUTER SIMULATIONS

In this section, we give general expressions for nearest-surface distribution functions for spherical systems with a finite number of components. We then compute these functions for the case of bidispersed systems and compare them to computer simulations.

A. General expressions for the discrete case

Particle systems with M components can be viewed as a special case of continuously distributed particle systems with a size distribution function $f(\mathcal{R}) = \sum_{\sigma=1}^M (\rho_\sigma / \rho) \delta(\mathcal{R} - \mathcal{R}_\sigma)$. Substituting this expression into relations (4.1), (4.2), (4.3), and (4.4) yields the following expressions for $e_V(r)$ and $h_V(r)$:

$$e_V(r) = \begin{cases} 1 - \sum_i \rho_i V_D(r + \mathcal{R}_i) \Theta(r + R_i), & r < 0 \\ (1 - \eta) \exp \left[- \int_0^r \sum_i \rho_i s_D(r + R_i) G(r + R_i) dr \right], & r > 0 \end{cases} \tag{7.1}$$

$$e_V(r) = \begin{cases} 1 - \sum_i \rho_i V_D(r + \mathcal{R}_i) \Theta(r + R_i), & r < 0 \\ (1 - \eta) \exp \left[- \int_0^r \sum_i \rho_i s_D(r + R_i) G(r + R_i) dr \right], & r > 0 \end{cases} \tag{7.2}$$

and

$$h_V(r) = \begin{cases} \sum_i \rho_i s_D(r + R_i) \Theta(r + R_i), & r < 0 \\ (1 - \eta) \sum_i \rho_i s_D(r + R_i) G(r + R_i) \exp \left[- \int_0^r \rho_i s_D(r + R_i) G(r + R_i) dr \right], & r > 0. \end{cases} \tag{7.3}$$

$$h_V(r) = \begin{cases} \sum_i \rho_i s_D(r + R_i) \Theta(r + R_i), & r < 0 \\ (1 - \eta) \sum_i \rho_i s_D(r + R_i) G(r + R_i) \exp \left[- \int_0^r \rho_i s_D(r + R_i) G(r + R_i) dr \right], & r > 0. \end{cases} \tag{7.4}$$

Expressions for particle quantities can be easily obtained by using the relationships (5.1) and (5.2).

B. Bidispersed systems

Here we consider a specific three-dimensional bidispersed system of particles with the reduced density of the two types of particles $\eta_1 = \eta_2$ and radii $R_1 = 2R_2$. This is a system in which $\rho_2 = 8\rho_1$ and the particle size distribution function can be written as

$$f(\mathcal{R}) = \frac{1}{3} \delta(\mathcal{R} - R_1) + \frac{8}{3} \delta(\mathcal{R} - R_2). \tag{7.5}$$

The average value of the radius of the particles can be easily obtained:

$$\langle \mathcal{R} \rangle = \frac{5}{9} R_1. \tag{7.6}$$

The second moment is given by

$$\langle \mathcal{R}^2 \rangle = \frac{1}{3} R_1^2. \tag{7.7}$$

The results for the void and particle quantities can then be easily obtained. We obtain results for different η by changing the size of particles in the system with

$$R_1 = \frac{1}{2} \left[\frac{50}{\pi} \eta \right]^{1/3}. \tag{7.8}$$

C. Computer-simulation procedure

To test our theoretical results, computer simulation is performed. Here we describe the simulation procedure employed to compute the exclusion probabilities $e_V(r)$ and $e_P(r)$. The simulation procedure consists of two basic steps: (i) generating equilibrium realizations of configurations of the particle system, and (ii) sampling for the desired quantities.

We employed a conventional Metropolis algorithm to generate equilibrium distributions of the impenetrable spheres of two different types of particles of radii R_1 and

$R_1/2$. Particles were initially placed in a cubical system of volume L^3 on the sites of a regular lattice with big particles and small particles arranged uniformly. Periodic boundary conditions were employed. Each particle was moved by a randomly determined small distance to a new position, provided that no particle overlap occurred. This process was repeated until equilibrium was achieved. The simulations were carried out for systems consisting of 540 particles for various values of the reduced density $\eta = 4\pi(\rho_1 R_1^3 + \rho_2 R_2^3)/3$. Among the 540 particles, 60 particles were the large particles with a radius R_1 as determined by (7.8). The radius of the other 480 smaller particles is $R_2 = R_1/2$. To ensure that equilibrium was achieved, every particle was moved 1000 times before we sampled. For every new realization, every particle was then moved 20 times.

The sampling procedure is very much like the case of the simulation of the monodispersed system [17]. However, here we determine the nearest surface as opposed to the nearest center as in Ref. [9]. To evaluate the void exclusion probability, 1000 void points have been randomly chosen for every configuration. We surrounded each reference point in the central system with concentric spherical shells of radii $r_i = i\Delta r$, $i = 1, 2, 3, \dots$, and thickness Δr (where $\Delta r \ll R_1$). For every reference point, the particle that has the nearest surface to the reference point is found and the distance between the reference point and the nearest surface is measured. The number of shells containing nearest-surface points is then ascertained. Subsequently, all the shells with distances smaller than the shell of radius r_i are counted as a success. For the i th shell the total number of successes divided by the total number of the experiments, multiplied by $1 - \eta$, is the void exclusion probability. For particle exclusion probabilities, the same procedure is employed, except that instead of using void points as reference points we use the centers of the real particles as reference

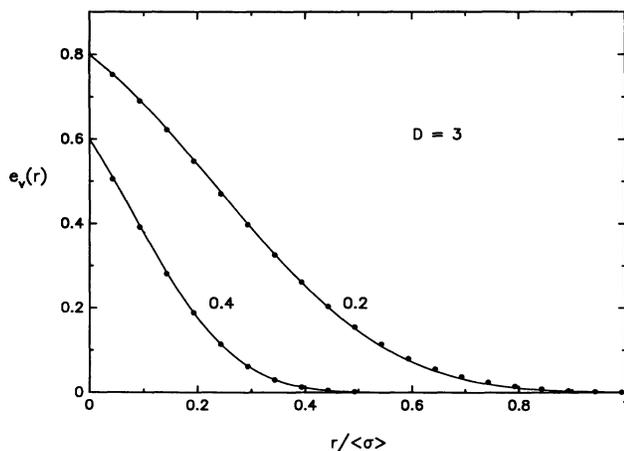


FIG. 10. Void exclusion probability $e_v(r)$ for a three-dimensional hard-sphere system with two components as described in Sec. VII. The particle volume fractions are $\phi_2 = 0.2$ and 0.4. The circles are computer-simulation results and the solid lines are our analytical results.

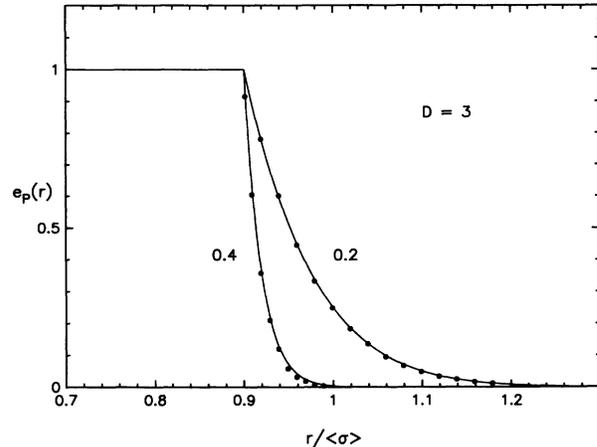


FIG. 11. Particle exclusion probability $e_p(r)$ for a three-dimensional hard-sphere system with two components as described in Sec. VII. The particle volume fractions are $\phi_2 = 0.2$ and 0.4. The diameter of the reference particle is $1.8\langle\sigma\rangle$. The circles are computer-simulation results and the solid lines are our analytical results.

points. Note here again, since we have two different types of particles, we must count the particle nearest-surface distribution functions separately for the two different types of particles. Since the number of bigger particles is only $\frac{1}{8}$ of the smaller particles, more realizations are necessary to get a statistically reliable result of $e_p(r)$ for bigger particles.

D. Computer-simulation results

The results of the computer simulation are shown in Figs. 10 and 11, in conjunction with the corresponding analytical results. Figure 10 plots the results of the void nearest-surface exclusion probability $e_v(r)$ for $r > 0$ for $\eta = 0.2$ and 0.4, respectively. Figure 11 compares the computer-simulation data with analytical results for the particle exclusion probability for the bigger particles with $\eta = 0.2$ and 0.4, respectively. It is seen that all the results of computer simulation agree well with the analytical results.

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APPENDIX: OTHER DEFINITIONS OF NEAREST-SURFACE DISTRIBUTION FUNCTIONS

As we mentioned in Sec. II, for polydispersed spherical particle systems, a number of different definitions of nearest-surface distribution functions can be given. Let us consider a different type of nearest neighbor, referred to as a "nearest j -type neighbor," i.e., the nearest neighbor among the j -type particles only. Based on such a definition, the void nearest j -type surface distribution

function $\hat{h}_{V,j}(r)$ may be defined as the probability that at an arbitrary point in the system the nearest j type of particle surface lies at a distance between r and $r+dr$. Whereas $\hat{h}_{V,j}(r)$ is concerned with the nearest j -type particles, $h_{V,j}(r)$ (used in the main text) is concerned with nearest particles of *any* type. The “ j -type particle exclusion probability” $\hat{e}_{V,j}(r)$ can then be defined as the probability of finding a region Ω_V , which is a D -dimensional spherical cavity of radius r (centered at some

arbitrary point), empty of j -type particle material. We clearly have the following relationship:

$$\hat{e}_{V,j}(r) = 1 - \int_{-\infty}^r \hat{h}_{V,j}(x) dx . \quad (\text{A1})$$

In the same way, we can define $\hat{h}_{P,j}(r)$, $\hat{e}_{P,j}(r)$ and $\hat{g}_{V,j}(r)$, $\hat{g}_{P,j}(r)$ with similar relationships as those for the monodisperse case.

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