Chord-length and free-path distribution functions for many-body systems

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We study fundamental morphological descriptors of disordered media (e.g., heterogeneous materials, liquids, and amorphous solids): *the chord-length distribution function p(z)* and the *free-path distribution function p(z,a).* For concreteness, we will speak in the language of heterogeneous materials composed of two different materials or "phases." The probability density function $p(z)$ describes the distribution of chord lengths in the sample and is of great interest in stereology. For example, the first moment of $p(z)$ is the "mean intercept length" or "mean chord length." The chord-length distribution function is of importance in transport phenomena and problems involving "discrete free paths" of point particles (e.g., Knudsen diffusion and radiative transport). The free-path distribution function $p(z,a)$ takes into account the finite size of a simple particle of radius a undergoing discrete free-path motion in the heterogeneous material and we show that it is actually the chord-length distribution function for the system in which the "pore space" is the space available to a finite-sized particle of radius a. Thus it is shown that $p(z)=p(z,0)$. We demonstrate that the functions $p(z)$ and $p(z,a)$ are related to another fundamentally important morphological descriptor of disordered media, namely, the so-called lineal-path function $L(z)$ studied by us in previous work [Phys. Rev. A **45**, 922 (1992)]. The lineal path function gives the probability of finding a line segment of length z wholly in one of the "phases" when randomly thrown into the sample. We derive exact series representations of the chord-length and free-path distribution functions for systems of spheres with a polydispersivity in size in arbitrary dimension D. For the special case of spatially uncorrelated spheres (i.e., fully penetrable spheres) we evaluate exactly the aforementioned functions, the mean chord length, and the mean free path. We also obtain corresponding analytical formulas for the case of mutually impenetrable (i.e., spatially correlated) polydispersed spheres.

I. INTRODUCTION

The characterization of the microstructure of many-particle systems such as random heterogeneous materials (e.g., suspensions, composites, and porous media), liquids, and amorphous solids is of great fundamental as well as practical importance.[1–11] The goal ultimately is to ascertain what is the essential morphological information, quantify it either theoretically or experimentally, and then employ the information to estimate the desired macroscopic properties of the many-particle system. To fix ideas, we shall speak in the language of heterogeneous materials composed of two different materials or "phases." Since many of the definitions and concepts we shall employ apply to two-phase media of arbitary microgeometry (e.g., not necessarily particulate media), we shall, whenever possible, consider this more general situation.

In earlier work[12,13] we introduced the so-called "lineal-path function" $L(z)$ which gives the probability of finding a line segment of length z wholly in phase 1 when randomly thrown into the sample. It is equivalent to the *probability that a point can move along a lineal path of length z in phase 1 without passing through phase 2.* Interestingly, $L(z)$ is equivalent to the area fraction of phase 1 measured from the projected image of a slice of sample of thickness z onto a plane. Such projected images are of great importance in stereology.[11] The authors obtained exact series representations of $L(z)$ for suspensions of monodispersed[12] as well as polydispersed spheres.[13] The lineal-path function $L(z)$, in particular, was computed for both fully penetrable spheres (i.e., spatially uncorrelated spheres) and totally impenetrable spheres (i.e., spatially correlated spheres).

In this paper we shall show that $L(z)$ is related to another fundamentally important morphological descriptor of many-particle systems, namely, the so-called "chord-length distribution" $p(z)$.[14] This probability density function (defined more precisely below) describes the distribution of chord lengths in the sample. Such a quantity is of basic importance in transport problems involving "discrete free paths" and thus has application in Knudsen diffusion and radiative transport in porous media. The function $p(z)$ has also been measured for sedimentary rocks[14] for the purpose of studying fluid flow through such

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porous media. The chord-length distribution function $p(z)$ is also a quantity of great interest in stereology.[11] For example, the "mean intercept length" is the first moment of $p(z)$.

Another quantity of interest is what we call the "free-path distribution function" (defined below) $p(z,a)$ which takes into account the finite size of a spherical particle of radius a undergoing discrete free-path motion in the heterogeneous material. The function $p(z,a)$ is actually the chord-length distribution function for a system in which the "pore space" is the *space available to a finite-sized particle of radius a.* Thus it is shown that $p(z)=p(z,0)$. It is demonstrated that the free-path distribution function $p(z,a)$ is related to a generalized lineal-path function $L(z,a)$ which depends upon the size a of the particle.

In Sec. II we define the basic morphological quantities of interest for heterogeneous of arbitrary microgeometry, i.e., nearest-neighbor functions, chord-length distribution function, free-path distribution function, and lineal-path function. In Sec. III we derive the relationship between the generalized lineal-path function $L(z,a)$ and the free-path distribution function $p(z,a)$ for arbitrary statistically isotropic two-phase media. By setting $a=0$, the relationship between the lineal-path function and the chord-length distribution function follows immediately. In Sec. IV we derive exact series representations of $L(z,a)$ for systems of spheres with a polydispersivity in size in arbitrary dimension D. In Sec. V we specialize to the case of spatially uncorrelated spheres (i.e., fully penetrable spheres). For this model microstructure, we are able to evaluate exactly the lineal path function $L(z,a)$ and hence the free path and chord length distribution functions, mean free path, and mean chord length. In Sec. VI we obtain corresponding analytical formulas for the case of mutually impenetrable (i.e., spatially correlated) polydispersed spheres.

II. BASIC DEFINITIONS AND CONCEPTS

The disordered porous medium is a domain of space $\mathscr{V}(\omega)\in\mathscr{R}^3$ (here the realization ω is taken from some probability space Ω) of volume V which is composed of two regions: the void or pore region $\mathscr{V}_1(\omega)$ of volume fraction ϕ_1 and solid-phase region $\mathscr{V}_2(\omega)$ of volume fraction ϕ_2. Denote by V_i the volume of region V_i so that the total system volume $V=V_1+V_2$. Let $\partial\mathscr{V}(\omega)$ be the surface between $\mathscr{V}_1$ and $\mathscr{V}_2$, and S be the total surface area of the interface $\partial\mathscr{V}$. The characteristic function of the pore phase $I(\mathbf{x},\omega)$ is defined by

$$I(\mathbf{x},\omega)=\begin{cases}1, & \mathbf{x}\in\mathscr{V}_1,\\ 0, & \mathbf{x}\in\mathscr{V}_2\end{cases}. \tag{2.1}$$

The characteristic function of the pore-solid interface is given by

$$M(\mathbf{x})=|\nabla I(\mathbf{x})| \tag{2.2}$$

If the medium is statistically homogeneous (the focus of this article), then ensemble averages of (2.1) and (2.2) yield the porosity ϕ_1 and specific surface s (interface area per unit volume), respectively, i.e.,

$$\phi_1=\langle I\rangle=\lim_{V_1,V\to\infty} V_1/V, \tag{2.3}$$

$$\sigma=\langle M\rangle=\lim_{S,V\to\infty} S/V. \tag{2.4}$$

Here angular brackets denote an ensemble average.

Torquato[9] has developed a formalism to represent and compute the so-called *general n-point distribution function* H_n for random media composed of statistical distributions of D-dimensional (possibly) penetrating spheres. He showed that the H_n contained, as special cases, all of the different types of correlation functions which have arisen in rigorous relations for effective transport and mechanical properties of heterogeneous media. The key idea in obtaining the H_n is the *space* and *surface* available to p different "test" particles of radii b_i $(i=1,2,\ldots,p)$ inserted into the system of spheres. Because of the exclusion-volume effects, the *available* space and surface to the ith test particle of radius b_i will be different than the pore space and interface, respectively, i.e., the space and surface available to a "point" test particle.

A. Nearest neighbor distribution functions

A particularly important class of functions in the H_n is the nearest-neighbor distribution functions which was comprehensively studied by Torquato, Lu, and Rubinstein[15] for monodispersed-sphere systems. Lu and Torquato[16] subsequently generalized the analysis of Ref. 15 to the case of sphere systems with a polydispersivity in size.

Now we generalize this concept to heterogeneous media with *arbitrary microgeometries.* The nearest-surface distribution function $h^{(i)}(r)$ for general heterogeneous media can be defined such that $h^{(i)}(r)dr$ is the probability that an arbitrary point in the system the nearest surface of phase i lies at a distance between r and $r+dr$. The related surface exclusion probability $e^{(i)}(r)$ can then be defined as the probability of finding a region Ω_E, which is a D-dimensional spherical cavity of radius a centered at some arbitrary point, empty of phase i material. As in the case of many-particle systems,[16] we have the following relationship between the nearest-surface distribution function and the surface exclusion probability function:

$$e^{(i)}(r)=1-\int_{-\infty}^{r} h^{(i)}(y)dy, \tag{2.5}$$

or

$$h^{(i)}(r)=\frac{-\partial e^{(i)}(r)}{\partial r}. \tag{2.6}$$

The integral of (2.5) represents the probability of finding at least some material of phase i in region Ω_E.

The nearest surface distribution function may be written as a product of two different correlation functions:

$$h^{(i)}(r)=e^{(i)}(r)g^{(i)}(r), \tag{2.7}$$

where $g^{(i)}(r)dr$ is the probability, given that a region Ω_E is empty of phase i material, of finding phase i material in the spherical shell of volume $s_D(r)dr$ encompassing the cavity. Therefore, $g^{(i)}(r)$ is the probability that a test particle of

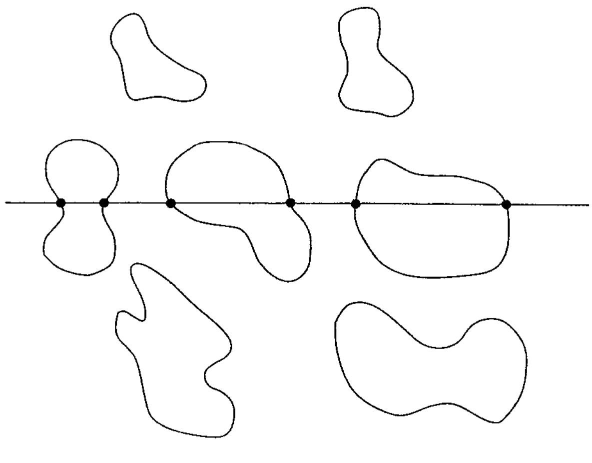

FIG. 1. Schematic of chord-length measurements for a cross section of a many-particle system. The chords are defined by the intersection of lines with the two-phase interface.

radius r is in contact with surface of phase i material. The quantity $s_D(r)$ is the surface area of a D-dimensional sphere of radius r:

$$s_1(r)=2, \tag{2.8}$$

$$s_2(r)=2\pi r, \tag{2.9}$$

$$s_3(r)=4\pi r^2. \tag{2.10}$$

From expressions (2.6) and (2.7) we have

$$e^{(i)}(r)=\exp\left(-\int_{-\infty}^{r} g^{(i)}(y)dy\right). \tag{2.11}$$

In our earlier work,[15] the quantities $e_V(r)$, $h_V(r)$, and $g_V(r)$ were used to represent the "void" exclusion probability function, the nearest-surface distribution function, and the "surface contact" correlation function, respectively, for D-dimensional sphere systems, with the subscript V indicating that the reference point is in the void phase. In terms of the present *general* notation we have that $e_V(r)=e^{(2)}(r)$ and $h_V(r)=h^{(2)}(r)$. Note that for $a=0$, $e_V(r)$ is simply equal to the porosity, i.e.,

$$e_V(0)=\phi_1. \tag{2.12}$$

The exclusion probability $e_V(r)$ and the nearest-surface function $h_V(r)$ will be useful in establishing the relationship between the chord-length distribution function $p(z)$ (defined below) and the lineal-path function $L(z)$. Similarly, such quantities will also be useful in establishing the connection between the free-path distribution function $p(z,a)$ and the generalized lineal-path function $L(z,a)$ (defined below).

B. Chord-length distribution function and free-path distribution function

Chords are the distributions of lengths between intersections of lines with the interface (see Fig. 1). A chord is then a special line segment with its end points on the interface and all other points in one of the two phases. The chord-length distribution function $p^{(i)}(z)$ is defined such that $p^{(i)}(z)dz$ is the probability of finding a chord of length between z and $z+dz$ in phase i. The chord-length distribution function $p(z)=p^{(1)}(z)$ is a fundamental morphological descriptor of heterogeneous media. It has been measured for sedimentary rocks by Krohn and Thompson.[14] To our knowledge, there is, however essentially no theoretical work on the calculation of the chord-length distribution function $p(z)$ for nontrivial models of heterogeneous materials. The mean chord length l_C is the first moment of the chord-length probability distribution function, i.e.,

$$l_C=\int_0^\infty zp(z)dz. \tag{2.13}$$

This is also referred to as the "mean intercept length" in stereology.[11]

The chord-length distribution function $p(z)$ and close relatives (described below) are intimately related to transport properties of the porous medium. For example, such quantities arise in free-path models of gas diffusion in porous media.[17–20]. This model assumes the gas molecules leave a molecule collision isotropically, and the fraction of molecules that are emitted from a small volume and travel a distance r or greater before collision with another molecule is $\exp(-r/l_0)$, where l_0 is the mean free path for molecule–molecule collisions. Molecular collisions with the solid surface are treated according to the laws of diffusive scattering. In principle, free path theories can treat the entire spectrum of possible transport, i.e., Knudsen diffusion $l_0 \gg l_S$ to continuum diffusion $l_0 \ll l_S$, where l_S is a characteristic length of the pore phase defined below. Free path models lead to the well-known Bosanquet formula for the effective diffusion coefficient D_e. The self-diffusion coefficient D in a porous medium is decreased in two ways: (1) D is reduced by a factor which accounts for porosity and tortuosity, and (2) D is reduced because of the associated decrease of the mean free path l_0 due to molecule–wall collisions. Tokunaga[20] has shown that the effective mean free path l_E is given by the following "harmonic-average" relation:

$$l_E^{-1}=l_0^{-1}+l_S^{-1}. \tag{2.14}$$

Here, l_S is the mean free path due to molecule–solid collisions and is the first moment of what we refer to as the free-path distribution function described shortly below. One of the aims of this article is to calculate l_S for nontrivial models of porous media by obtaining corresponding expressions for the free-path distribution function.

The free path for diffusing particles due to molecule–solid surface collisions is the distance the particle moves between two successive collisions with the solid surface. The free-path distribution function simply characterizes the distribution of such lengths. For "point" diffusion particles (particles of zero radius), the free-path distribution function is precisely the chord-length distribution $p(z)$ and hence

$$l_S = l_C = \int_0^\infty z p(z) dz. \tag{2.15}$$

More generally, if the diffusing particle has finite size, then the *space available* to it is less than the pore space because of exclusion-volume effects. The problem of diffusion of finite-sized Brownian particles has been recently studied by Torquato[21] and by Kim and Torquato.[22] Let us consider spherical diffusing particles of radius a and define the characteristic function of the available space $\mathscr{V}_1(a)$ as

$$I(\mathbf{x};a) = \begin{cases} 1, & \mathbf{x} \in \mathscr{V}_1(a), \\ 0, & \text{otherwise}. \end{cases} \tag{2.16}$$

The free-path distribution $p(z,a)$ is defined such that $p(z,a)dz$ is the probability of finding a free path (due to molecule–solid surface collisions) with length between z and $z+dz$. Then we have the more general definition for the mean free path $l_S(a)$, i.e.,

$$l_S(a) = \int_0^\infty z p(z,a) dz. \tag{2.17}$$

Note that the chord-length distribution function $p(z)$ is equal to the free-path distribution function when $a=0$, i.e.,

$$p(z) \equiv p(z,0). \tag{2.18}$$

C. General lineal-path function $L(z,a)$

An interesting and useful statistical measure for heterogeneous materials is the "lineal-path function" $L(z)$ introduced by Lu and Torquato.[12,13] The lineal-path function $L(z)$ gives the probability of finding a line segment of length z wholly in one of the phases, say phase 1, $\mathscr{V}_1 \equiv \mathscr{V}_1(a=0)$, or equivalently, the probability that a point can move along a lineal path of length z in the pore phase $\mathscr{V}_1$ without passing through the solid phase.

Consider now a more general lineal-path function $L(z,a)$ associated with the space available $\mathscr{V}_1(a)$ to a spherical "test" particle of radius a in the porous medium. $L(z,a)$ gives the probability of finding a line segment of length z in $\mathscr{V}_1(a)$, the space available to the test particle of radius a. Similarly the lineal-path function $L(z,a)$ is the probability that a test particle of radius a can move along a lineal path of length z without passing through the solid phase.

For arbitrary isotropic media, the general lineal-path function $L(z,a)$ has the general form[12,13]

$$L(z,a) = L(0,a) \exp[-A f(z)], \tag{2.19}$$

where $f(z)$ is a function of z such that

$$f(0) = 0 \tag{2.20}$$

and A is a structure-dependent constant. Here $L(0,a)$ is the probability of finding a test particle of radius a in phase 1, i.e., $L(0,a) = e_V(a)$, where $e_V(a)$ is the surface exclusion probability defined earlier in Sec. II (see also Ref. 16). Therefore, we generally have

$$L(z,a) = e_V(a) \exp[-A f(z)]. \tag{2.21}$$

In the analytical formulas derived in subsequent sections for $L(z,a)$ in the case of systems of spheres, we find the function $f(z) = -z$. Thus for such $f(z)$, we have

$$L(z,a) = e_V(a) \exp[-Az]. \tag{2.22}$$

III. RELATIONSHIP BETWEEN THE GENERAL LINEAL-PATH FUNCTION $L(z,a)$ AND THE FREE-PATH DISTRIBUTION FUNCTION $p(z,a)$

For general homogeneous and isotropic systems, the lineal-path function $L(z,a)$ and free-path distribution $p(z,a)$ satisfy a differential equation which we will derive below. For simplicity, we first derive the relationship between the lineal-path function $L(z) \equiv L(z,0)$ and the chord-length distribution function $p(z) \equiv p(z,0)$. The relationship between $L(z,a)$ and $p(z,a)$ for nonzero a follows immediately. For convenience of derivation, we introduce the cumulative free-path probability function

$$P(z,a) = \int_z^\infty p(r,a) dr, \tag{3.1}$$

which is the probability of finding a free path for a diffusing particle of radius a larger than the length z. Clearly, one has that $P(0,a) = 1$.

To begin with let us take $a=0$. For statistically homogeneous and isotropic materials, the chord-length distribution function $p(z)$ can be obtained by determining the distribution of chord lengths from an infinitely long line placed randomly into the system. Similarly, the lineal-path function $L(z)$ can be obtained by counting the relative number of times that a line segment of length z is wholly in phase 1 when thrown randomly onto the infinite line. Clearly the line segment (of length z) being wholly in phase 1 implies that all the points on the line segment (of length z) are in phase 1. The strategy now will be to express $L(z)$ in terms of $p(z)$ using the following probability argument. First, if we consider a special point on the line segment, say, the midpoint of the line segment referred as point A, then A has to be in phase 1. The probability that point A is in phase 1 is simply the porosity of the system, i.e., ϕ_1. Second, given the condition that the point A is in phase 1 (it is then on a chord), we ask what is the probability that point A is on a chord with length between y and $y+dy$? Since the *length fraction* of a chord with length between y and $y+dy$ is given by

$$yp(y)dy \Big/ \int_0^\infty yp(y)dy,$$

then the probability that the point A is on a chord with length between y and $y+dy$ is this length fraction multiplied by the porosity ϕ_1, i.e.,

$$\phi_1 yp(y)dy \Big/ \int_0^\infty yp(y)dy.$$

Third, that point A of a line segment of length z (*distinct from the length* y) is in phase 1, however, does not mean that the whole line segment is in phase 1. The probability that a line segment of length z is on a chord of length y under the condition that the point A is on that chord is

$(y-z)H(y-z)/y$,

where $H(x)$ is the Heaviside step function defined by

$$H(x)=\begin{cases}1, & \text{if } x>0,\\ 0, & \text{otherwise.}\end{cases} \tag{3.2}$$

Now $L(z)$, the probability that the line segment of length z is entirely in phase 1, can then be obtained by combining the results given immediately above, i.e., integrating the probability for the line segment being on chords with length between y and $y+dy$ over all possible y, we find

$$L(z)=\frac{\phi_1\int_0^\infty (y-z)p(y)dyH(y-z)}{\int_0^\infty yp(y)dy}. \tag{3.3}$$

Differentiation of (3.3) and use of (3.1) yields

$$\frac{dL(z)}{dz}=-\frac{\phi_1}{l_C}P(z). \tag{3.4}$$

Differentiation of (3.4) and rearrangement of terms gives

$$p(z)=\frac{l_C}{\phi_1}\frac{d^2L(z)}{dz^2}. \tag{3.5}$$

Formula (3.5) establishes a new connection between chord-length distribution function $p(z)$ and the lineal-path function $L(z)$. It is important to note that the above relations are valid for statistically isotropic systems of arbitrary microgeometry.

Establishment of the relationship between general lineal-path function $L(z,a)$ and the free-path distribution function $p(z,a)$ for finite-sized diffusion particles is straightforward. Since the center of a finite-sized diffusing particle is constrained to be in its available space $\mathscr{V}_1(a)$, then the chord-length distribution function of the system with "pore space" $\mathscr{V}_1(a)$ is actually the free-path distribution function $p(z,a)$. Because the average available space is $e_V(a)$, we then have

$$\frac{dL(z,a)}{dz}=-\frac{e_V(a)}{l_S}P(z,a) \tag{3.6}$$

and

$$p(z,a)=\frac{l_S}{e_V(a)}\frac{d^2L(z,a)}{dz^2}. \tag{3.7}$$

For the general lineal-path function $L(z,a)$ of the form (2.22), we see that (3.4) yields the expression

$$p(z,a)=Al_S\exp(-Az). \tag{3.8}$$

The normalization condition $P(0,a)=1$, therefore, determines the mean free path l_S as

$$l_S=1/A. \tag{3.9}$$

For such $L(z,a)$, we thus find that the free-path distribution function is of the form

$$p(z,a)=A\exp[-Az]=\frac{\exp(-z/l_S)}{l_S}. \tag{3.10}$$

IV. SERIES EXPANSIONS OF THE DISTRIBUTION FUNCTIONS FOR POLYDISPERSED SPHERES

A. System description

Let us consider the relevant distribution functions for systems of polydispersed spheres.[23] Assume that the system is composed of included particles with a continuous distribution in radius $\mathscr{R}$ characterized by the normalized probability density $f(\mathscr{R})$. Note that the continuous particle size distribution includes the discrete particle size distribution as a special case. For example, in the discrete homogeneous case with M different components, the size distributions

$$f(\mathscr{R}_j)=\sum_{\sigma=1}^{M}\frac{\rho_\sigma}{\rho}\delta(\mathscr{R}_j-R_{\sigma_j}),$$

where ρ_σ is the number density of *type* σ particles and $\delta(\mathscr{R})$ is the Dirac delta function. The system is characterized by the probability density function $\rho_n(\mathbf{r}^n;\mathscr{R}_1,...,\mathscr{R}_n)f(\mathscr{R}_1)\cdots f(\mathscr{R}_n)$ associated with finding an inclusion with radius $\mathscr{R}_1$, at $\mathbf{r}_1$, another inclusion with radius $\mathscr{R}_2$ at $\mathbf{r}_2$, etc. Clearly the case $n=1$ is degenerate in the sense that $\rho_1(\mathbf{r}_1;\mathscr{R}_1)$ is independent of $\mathbf{r}_1$ and in the instance of statistically homogeneous media is simply equal to the *total* number of density ρ.

An important dimensionless parameter that will be used throughout the ensuing sections, is the reduced density η in D dimensions. In the discrete case it is defined by

$$\eta=\sum_{\sigma=1}^{M}\frac{\pi^{D/2}}{\Gamma(1+D/2)}\rho_\sigma R_\sigma^D. \tag{4.1}$$

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

$$\eta=\frac{\pi^{D/2}}{\Gamma(1+D/2)}\rho\langle\mathscr{R}^D\rangle, \tag{4.2}$$

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

$$\langle A(\mathscr{R})\rangle=\int_0^\infty A(\mathscr{R})f(\mathscr{R})d\mathscr{R}. \tag{4.3}$$

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, $\eta>\phi_2$.

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

$$f(\mathscr{R})=\frac{1}{\Gamma(m+1)}\left(\frac{m+1}{\langle R\rangle}\right)^{m+1}\mathscr{R}^m \times\exp\left[\frac{-(m+1)\mathscr{R}}{\langle\mathscr{R}\rangle}\right],\quad m>-1, \tag{4.4}$$

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

$$\langle\mathscr{R}^n\rangle=\langle\mathscr{R}\rangle^n\frac{(m+1)^{-n}}{m}\prod_{i=0}^{n}(m+i). \tag{4.5}$$

By increasing m, the variance decreases, i.e., the distribution becomes sharper. In the monodisperse limit, $z \to \infty$, $f(\mathscr{R}) = \delta(\mathscr{R} - \langle \mathscr{R} \rangle)$. Note that for homogeneous and isotropic media, the density of the particles with radius between $\mathscr{R}$ and $\mathscr{R} + d\mathscr{R}$ is $\rho f(\mathscr{R}) d\mathscr{R}$ with ρ the total density.

B. Exact series expansions

In an earlier work,[16], we derived exact series expansion for the surface exclusion probability $e_V(r)$:

$$e_V(r) = \sum_{s=0}^{N} (-1)^s e_V^{(s)}(r), \tag{4.6}$$

where

$$e_V^{(s)}(r) = \frac{1}{s!} \int \cdots \int d\mathscr{R}_1 \cdots d\mathscr{R}_s f(\mathscr{R}_1) \cdots f(\mathscr{R}_s) \times \rho_s(\mathbf{r}^s; \mathscr{R}_1, \ldots, \mathscr{R}_s) \prod_{j=1}^{s} [m(|\mathbf{x} - \mathbf{r}_j|); r] d\mathbf{r}_j \tag{4.7}$$

and

$$e_V^{(0)}(r) \equiv 1. \tag{4.8}$$

The quantity $m(|\mathbf{x} - \mathbf{r}_j|; r)$ is an indicator function defined as

$$m(|\mathbf{x} - \mathbf{r}_j|; r) = \begin{cases} 1, & |\mathbf{x} - \mathbf{r}_j| < r + \mathscr{R}_j, \\ 0, & |\mathbf{x} - \mathbf{r}_j| \geqslant r + \mathscr{R}_j, \end{cases} \tag{4.9}$$

where $\mathbf{x}$ is an arbitrary position vector in the system. Note that the function m defined here is slightly different from the one defined in Ref. 3 in that it is the *surface* indicator function.

The derivation of the exact series representation of the general lineal-path function $L(z,a)$ for a spherical test particle of radius a follows closely the derivation of the corresponding expression for the lineal path function $L(z)$ for a point test particle as derived by Lu and Torquato.[12,13] The lineal-path function $L(z,a)$ is a special type of exclusion probability function, i.e., the probability of finding a "test" particle which is a spherocylinder of length z, and radius R empty of particle material. Therefore, center of j particle of radius $\mathscr{R}_j$ should be outside a region Ω_E, the exclusion region between a spherocylinder of length z and radius R and a sphere of radius $\mathscr{R}_j$. The region $\Omega_E(z, \mathscr{R}_j + a)$ in this case is therefore a D-dimensional spherocylinder of cylindrical length z and radius $\mathscr{R}_j + a$ with hemispherical caps of radius $\mathscr{R}_j + a$ on either end. Following Torquato[1] we introduce the exclusion region indicator function

$$m_j(\mathbf{y}; z) = \begin{cases} 1, & \mathbf{y} \in \Omega_E(z, \mathscr{R}_j + a), \\ 0, & \text{otherwise}, \end{cases} \tag{4.10}$$

where $\mathbf{y}$ is measured with respect to the centroid of the exclusion region. Using the same analysis of Lu and Torquato,[12,13] the series expansion of the general lineal-path function $L(z,a)$ is found to be given by

$$L(z,a) = 1 + \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \int d\mathscr{R}_1 \cdots d\mathscr{R}_k \rho_k(\mathbf{r}^k; \mathscr{R}_1, \ldots, \mathscr{R}_k) \times f(\mathscr{R}_1) \cdots f(\mathscr{R}_k) \prod_{j=1}^{k} m_j(\mathbf{x} - \mathbf{r}_j; z) d\mathbf{r}_j. \tag{4.11}$$

For the special case $a = 0$, series (4.11) reduces to the one derived by the authors in Ref. 13. Series (4.11) in conjunction with the expression linking the free-path distribution function $p(z,a)$ to $L(z,a)$ yields the corresponding series expression for $p(z,a)$ and thus for the chord-length distribution function $p(z) \equiv p(z,0)$.

V. EXACT RESULTS FOR FULLY-PENETRABLE-SPHERE SYSTEMS

For the special case of "overlapping" or "randomly centered" (i.e., spatially uncorrelated) homogeneous sphere systems, the ρ_n are especially simple:

$$\rho_n(\mathbf{r}^n; \mathscr{R}_1, \ldots, \mathscr{R}_n) = \prod_{j=1}^{n} \rho_1(\mathbf{r}_j, \mathscr{R}_j). \tag{5.1}$$

The simplicity of ρ_n for such polydispersed-sphere systems enables one to exactly sum the infinite series given in the previous section. Lu and Torquato[16] found that the "void" exclusion probability is given by

$$e_V(r) = \exp[-\rho \langle v_D(r + \mathscr{R}) \rangle]. \tag{5.2}$$

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

$$v_1(\mathscr{R}) = 2\mathscr{R}, \tag{5.3}$$

$$v_2(\mathscr{R}) = \pi \mathscr{R}^2, \tag{5.4}$$

$$v_3(\mathscr{R}) = \tfrac{4}{3} \pi \mathscr{R}^3. \tag{5.5}$$

Similarly, series (4.11) and Eq. (5.1) yields the exact result for the general lineal-path function as

$$L(x,a) = \exp[-\rho \langle v_E(z, \mathscr{R} + a) \rangle], \tag{5.6}$$

where $v_E(z, \mathscr{R} + a)$ is the D-dimensional volume of the exclusion region $\Omega_E(z, \mathscr{R} + a)$:

$$v_E = (4\pi/3)(\mathscr{R} + a)^3 + \pi(\mathscr{R} + a)^2 z, \quad D = 3, \tag{5.7}$$

$$v_E = \pi(\mathscr{R} + a)^2 + 2(\mathscr{R} + a) z, \quad D = 2, \tag{5.8}$$

$$v_E = 2(\mathscr{R} + a) + z, \quad D = 1. \tag{5.9}$$

By using the expressions of the surface exclusion probability $e_V(r)$ for fully penetrable spheres, the linear-path function may be written as

$$L(z,a) = e_V(a) \phi_1^{3\langle(\mathscr{R}+a)^2\rangle z/(4>\langle\mathscr{R}^3\rangle)}, \quad D = 3, \tag{5.10}$$

$$L(z,a) = e_V(a) \phi_1^{2(\langle\mathscr{R}\rangle + a) z/(\pi\langle\mathscr{R}^2\rangle)}, \quad D = 2, \tag{5.11}$$

$$L(z,a) = e_V(a) \phi_1^{z/\langle\mathscr{R}\rangle}, \quad D = 1. \tag{5.12}$$

For the special case of $a = 0$, the results reduce to those we obtained for the lineal-path function $L(z)$ in our earlier paper.[13] Results (5.10)–(5.12) for arbitrary values of a are new.

The free-path distribution function for fully penetrable spheres is obtained using the relationship (3.7) and (5.10)–(5.12):

$$p(z,a) = -\tfrac{3}{4}\ln \phi_1 \langle (\mathscr{R}+a)^2\rangle / \langle \mathscr{R}^3\rangle \times \phi_1^{3\langle(\mathscr{R}+a)^2\rangle z/\langle 4\mathscr{R}^2\rangle}, \quad D=3, \tag{5.13}$$

$$p(z,a) = -\ln \phi_1 2(\langle \mathscr{R}\rangle + a)/ (\pi\langle \mathscr{R}^2\rangle)\phi_1^{2(\langle\mathscr{R}\rangle+a)z/(\pi\langle\mathscr{R}^2\rangle)}, \quad D=2 \tag{5.14}$$

$$p(z,a) = -\ln \phi_1/\langle \mathscr{R}\rangle \phi_1^{z/\langle\mathscr{R}\rangle}, \quad D=1. \tag{5.15}$$

In obtaining relations (5.13)–(5.15) we have used the fact that $\phi_1 = e_V(0) = \exp[-\rho\langle(v_D(\mathscr{R})\rangle)]$ [cf. (5.2)]. For the special case of $a=0$, we have that the chord-length distribution function is given by

$$p(z) = -\tfrac{3}{4}\ln \phi_1 \langle \mathscr{R}^2\rangle/\langle \mathscr{R}^3\rangle \phi_1^{3\langle\mathscr{R}^2\rangle z/\langle 4\mathscr{R}^3\rangle}, \quad D=3, \tag{5.16}$$

$$p(z) = -2\ln \phi_1 \langle \mathscr{R}\rangle/(\pi\langle \mathscr{R}^2\rangle)\phi_1^{2\langle\mathscr{R}\rangle z/(\pi\langle\mathscr{R}^2\rangle)}, \quad D=2, \tag{5.17}$$

$$p(z) = -\ln \phi_1/\langle \mathscr{R}\rangle \phi_1^{z/\langle\mathscr{R}\rangle}, \quad D=1. \tag{5.18}$$

The mean free path l_S can easily be evaluated through use of Eqs. (2.17) and (5.13)–(5.15). Thus the mean free-path for fully penetrable spherical systems can be written as

$$l_S = -4\langle \mathscr{R}^3\rangle/[3\ln \phi_1\langle(\mathscr{R}+a)^2\rangle], \quad D=3, \tag{5.19}$$

$$l_S = -\pi\langle \mathscr{R}^2\rangle/(2\langle \mathscr{R}+2a\rangle \ln \phi_1), \quad D=2, \tag{5.20}$$

$$l_S = -\langle \mathscr{R}\rangle/\ln \phi_1, \quad D=1. \tag{5.21}$$

The mean chord length l_C for fully penetrable spherical systems is obtained by setting $a=0$ in the expressions immediately given above:

$$l_C = -4\langle \mathscr{R}^3\rangle/(3\ln \phi_1\langle \mathscr{R}^2\rangle), \quad D=3, \tag{5.22}$$

$$l_C = -\pi\langle \mathscr{R}^2\rangle/(2\langle \mathscr{R}\rangle \ln \phi_1), \quad D=2, \tag{5.23}$$

$$l_C = -\langle \mathscr{R}\rangle/\phi_1, \quad D=1. \tag{5.24}$$

To illustrate the results given above, we consider polydispersed systems characterized by a Schulz distribution (4.4). Recall that as the parameter m increases, the distribution becomes sharper. Clearly, the lineal-path function $L(z,a)$ is a monotonic increasing function of ϕ_1. In Figs. 2 and 3, we plot our analytical results for fully penetrable spheres for $D=3$ and $D=2$, respectively, at a sphere volume fraction $\phi_2=0.4$ and $a=0.1\,\langle\mathscr{R}\rangle$ and $a=0$ with $m=0$ and $m=\infty$ in each case. For any D, $L(z,a)$ is a monotonic decreasing function of z and a. This behavior is expected since the larger and longer is the spherocylinder, the smaller is the probability of finding it wholly in phase 1. For fixed length z, radius a, and volume fraction ϕ_2, $L(z,a)$ changes dramatically with the size distribution of particles for $D=3$ and $D=2$, and the effect of the polydispersivity is to *increase* the lineal-path function $L(z,a)$. For three-dimensional systems, this effect is much stronger than for two-dimensional systems. Note that for $D=1$, polydispersivity has no effect on $L(z,a)$ for fixed $\langle\mathscr{R}\rangle$. In Fig. 4, we plot our analytical results of $p(z,a)$ for fully penetrable spheres for $D=3$ at a sphere volume fraction $\phi_2=0.4$ for $a=0.1\,\langle\mathscr{R}\rangle$ and $a=0$ with $m=\infty$ in each case. Note that case $a=0$ yields the chord-length distribution function. The figure shows that the effect of polydispersivity is to broaden the distribution function $p(z,a)$, i.e., increasing polydispersivity decreases $p(z,a)$ for small z but increases $p(z,a)$ for large z. The same general trends are found for $D=2$ and hence this case is not shown graphically.

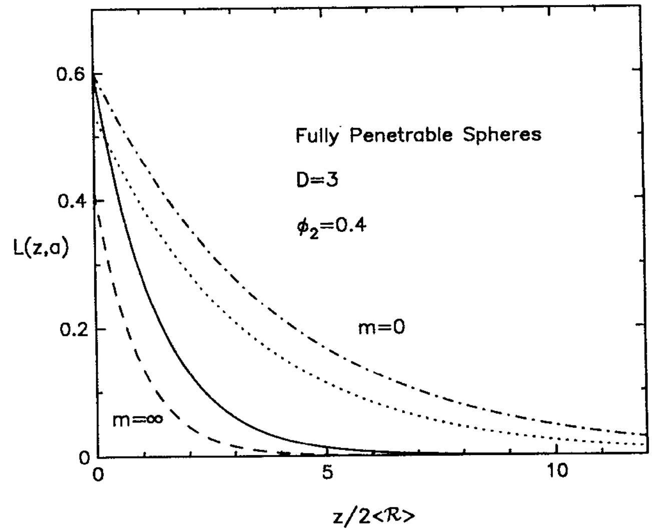

FIG. 2. Lineal-path function $L(z,a)$ versus the dimensionless distance $z/2R$ for a three-dimensional fully penetrable polydispersed system characterized by a Schulz distribution (4.4) with $m=\infty$, $a=0$ (solid line), $m=\infty$, $a=0.1\,\langle\mathscr{R}\rangle$ (dashed line), $m=0$, $a=0$ (dashed and dotted line), $m=0$, $a=0.1\,\langle\mathscr{R}\rangle$ (dotted line), at a sphere volume fraction $\phi_2=0.4$, as obtained from (5.10).

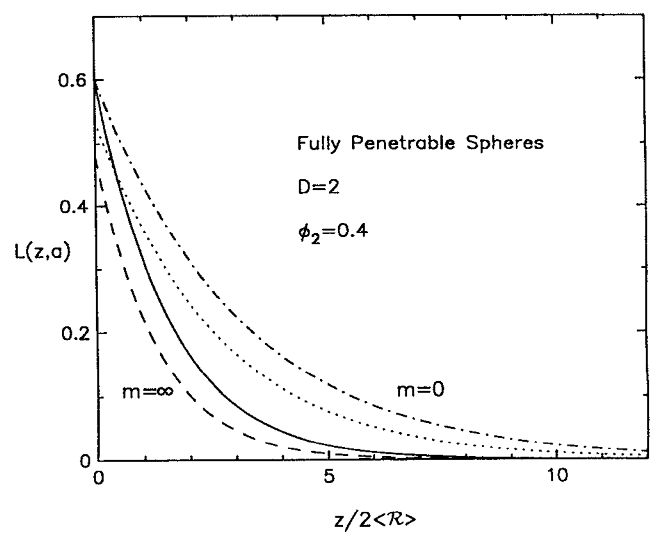

FIG. 3. As in Fig. 2, except for $D=2$ obtained from (5.11).

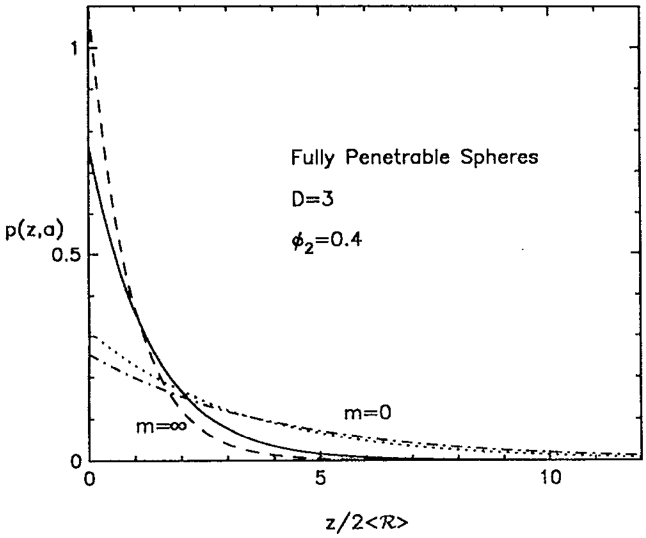

FIG. 4. Free-path distribution function $p(z,a)$ versus the dimensionless distance $z/2R$ for a three-dimensional fully penetrable polydispersed system characterized by a Schulz distribution (4.4) with $m=\infty$, $a=0$ (solid line), $m=\infty$, $a=0.1\ \langle\mathscr{R}\rangle$ (dashed line), $a=0$ (dashed and dotted line), and $m=0$, $a=0.1\ \langle\mathscr{R}\rangle$ (dotted line), at a sphere volume fraction $\phi_2=0.4$, as obtained from (5.13).

In Fig. 5, we show the analytical results of the mean-free path for fully penetrable spheres for $D=3$ [Eq. (5.19)] at a sphere volume fraction $\phi_2=0.4$ for $a=0.1\ \langle\mathscr{R}\rangle$ and $a=0$ with $m=0$ and $m=\infty$ in each case. As in the case of $p(z,a)$ [cf. Fig. 4], the effect of polydispersivity is to increase the mean-free path. We can also clearly see the effect of size variation of the diffusing particles from Figs. 4 and 5; the smaller is the diffusing particle, the broader is the probability density function $p(z,a)$. This indicates that for smaller diffusing particles, one has a larger mean free path, as expected.

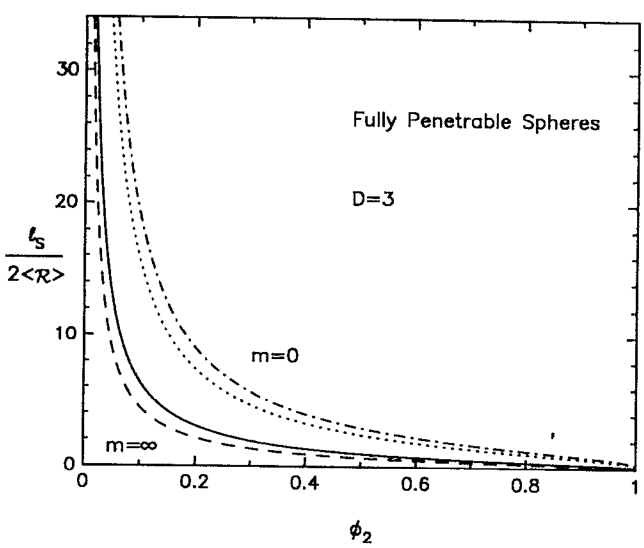

FIG. 5. Mean free path l_S versus the sphere volume fraction of ϕ_2 for a three-dimensional fully penetrable polydispersed system characterized by a Schulz distribution (4.4) with $m=\infty$, $a=0$ (sold line), $m=\infty$, $a=0.1\ \langle\mathscr{R}\rangle$ (dashed line), $a=0$ (dashed and dotted line), and $m=0,R=0.1\ \langle\mathscr{R}\rangle$ (dotted line), as obtained from (5.19).

VI. ANALYTICAL EXPRESSIONS FOR THE DISTRIBUTION FUNCTIONS FOR POLYDISPERSED HARD-SPHERE SYSTEMS

A. Results for the surface exclusion probability $e_V(r)$

In the instance of totally impenetrable or hard spheres, the exact series representation of $e_V(r)$ can only be evaluated exactly for the case $D=1$ (i.e., hard rods). It is impossible to evaluate $e_V(r)$ for $D\geqslant 2$ because the n-particle probability density $\rho_n(\mathbf{r}^n)$ are not known exactly. One must therefore devise approximate schemes to evaluate and sum the series. Lu and Torquato[16] evaluated $e_V(r)$ for polydispersed hard-sphere systems in various approximations. For example, their scaled-particle result for the exclusion probability for $D=3$ is given by

$$e_V(r)=(1-\eta)\exp[-\pi\rho(cr+dr^2+gr^3)],\quad r>0, \tag{6.1}$$

where

$$c=\frac{4\langle\mathscr{R}^2\rangle}{1-\eta}, \tag{6.2}$$

$$d=\frac{4\langle\mathscr{R}\rangle}{1-\eta}+\frac{12\xi_2}{(1-\eta)^2}\langle\mathscr{R}^2\rangle, \tag{6.3}$$

$$g=\frac{4}{3(1-\eta)}+\frac{8\xi_2\langle\mathscr{R}\rangle}{(1-\eta)^2}+\frac{16\xi_2^2}{(1-\eta)^3}\langle\mathscr{R}^2\rangle, \tag{6.4}$$

with

$$\xi_k=\rho(\pi/3)2^{k-1}\langle\mathscr{R}^k\rangle. \tag{6.5}$$

For $D=2$, the scaled-particle approximation gives the surface exclusion probability as

$$e_V(r)=(1-\eta)\exp\left[-\pi\rho\left(\frac{r^2+2\langle\mathscr{R}\rangle r}{1-\eta}+\frac{r^2\pi\rho\langle\mathscr{R}\rangle^2}{(1-\eta)^2}\right)\right],\quad r>0. \tag{6.6}$$

It is only in the case of one-dimensional hard rods that the exclusion probability function is known exactly for D-dimensional hard spheres. Specifically, one has

$$e_V(r)=(1-\eta)\exp[-2\rho r/(1-\eta)],\quad a>0. \tag{6.7}$$

B. Evaluation of the general lineal-path function $L(z,a)$

We have already developed an approach[13] to calculate the lineal-path function $L(z)$ for hard-sphere systems with polydispersivity in size in the case of point test particles ($a=0$). The method can be extended to evaluate the general lineal path function $L(z,a)$ for $a>0$. The main ideas are summarized as follows:

(1) The probability of finding a *surface* exclusion cavity which is a spherocylinder of length z and radius a is, according to statistical mechanics

$$L(z,a)=\exp[-W(z,a)/kT], \tag{6.8}$$

where $W(z,a)$ is the reversible work needed to create the surface exclusion spherocylindrical cavity and k to the Boltzmann constant and T the temperature of the system. (Note that here we are speaking about "surface-based" rather than "center-based" quantities as explained in Refs. 13 and 16.)

(2) The process of creating the spherocylinder cavity may be looked upon as a two-step process: first one creates a surface exclusion sphere cavity of radius a and then expands this sphere along one direction to form a spherocylinder. The work $W(z,a)$ then is the sum of the work for these two processes:

$$W(z,a)=W_1+W_2. \tag{6.9}$$

(3) The work $W_1(a)$ is known from the explicit expression for the surface exclusion probability $e_V(a)$, i.e.,

$$W_1=-kT\ln e_V(a), \tag{6.10}$$

and we have

$$L(z,a)=e_V(a)\exp[-W_2/kT]. \tag{6.11}$$

(4) The work W_2 can be further considered to be composed of the following two parts: the work $W_{2,p}$ related to the volume change and the work $W_{2,S}$ related to the surface area change:

$$W_2=W_{2,p}+W_{2,S}. \tag{6.12}$$

(5) The simplest way of evaluating W_2 is to calculate the elemental work from the initial infinitesimal expansion process, i.e., from a sphere of radius a to a spherocylinder of length dz and radius a. Following our previous work,[6] the calculation is quite straightforward. Within the scaled-particle approximation, we have

$$W_2(z)=\pi kT\rho z\left[\frac{(\langle \mathcal{R}+a)^2\rangle}{(1-\eta)}+\frac{6\xi_2(a^2\langle \mathcal{R}\rangle+a\langle \mathcal{R}^2\rangle)}{(1-\eta)^2}+\frac{12\xi_2^2a^2\langle \mathcal{R}^2\rangle}{(1-\eta)^3}\right],\quad D=3, \tag{6.13}$$

$$W_2(z)=2\rho kTz\left[\frac{\langle \mathcal{R}\rangle+a}{1-\eta}+\frac{\pi\rho R\langle \mathcal{R}\rangle^2}{(1-\eta)^2}\right],\quad D=2, \tag{6.14}$$

$$W_2(z)=\rho kTz/(1-\eta),\quad D=1. \tag{6.15}$$

Combination of relation (6.11) and (6.13)–(6.15) yields the lineal-path distribution function $L(z,a)$ for D-dimensional polydispersed hard-sphere systems as

$$L(z,a)=e_V(a)\exp[-Az], \tag{6.16}$$

where A is given by

$$A=\pi\rho]\frac{(\langle \mathcal{R}+a)^2\rangle}{1-\eta}+\frac{6\xi_2(a^2\langle \mathcal{R}\rangle+a\langle \mathcal{R}^2\rangle)}{(1-\eta)^2}+\frac{12\xi_2^2a^2\langle \mathcal{R}^2\rangle}{(1-\eta)^3}],\quad D=3, \tag{6.17}$$

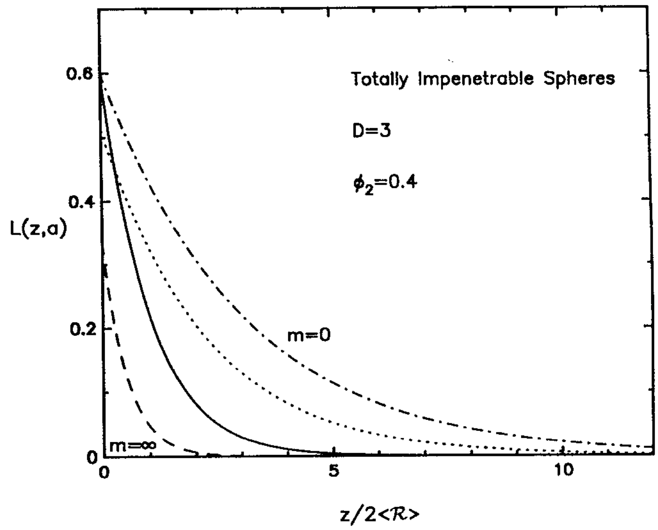

FIG. 6. Lineal-path function $L(z,a)$ versus the dimensionless distance $z/2R$ for a three-dimensional totally impenetrable polydispersed system characterized by a Schulz distribution with $m=\infty$, $a=0$ (solid line), $m=\infty$, $a=0.1\,\langle \mathcal{R}\rangle$ (dashed line), $m=0$, $a=0$ (dashed and dotted line), and $m=0$, $a=0.1\,\langle \mathcal{R}\rangle$ (dotted line), at a sphere volume fraction $\phi_2=0.4$, as obtained from (6.16) and (6.17).

$$A=2\rho\left[\frac{\langle \mathcal{R}\rangle+a}{1-\eta}+\frac{\pi\rho R\langle \mathcal{R}\rangle^2}{(1-\eta)^2}\right],\quad D=2, \tag{6.18}$$

$$A=\rho z/(1-\eta),\quad D=1. \tag{6.19}$$

Figure 6 depicts our analytical results of $L(z,a)$ [Eq. (6.16)] for totally impenetrable polydispersed sphere systems characterized by a Schulz distribution (4.4) with $m=0$ and $m=\infty$ and $a=0.1\,\langle \mathcal{R}\rangle$ and $a=0$ at the sphere volume fraction $\phi_2=0.4$ for $D=3$. The larger is the diffusing particle, the smaller is the lineal-path function $L(z,a)$. The effect of polydispersivity is qualitatively the same as in the case of fully penetrable spheres. For a broader size distribution of particles (a smaller value of m), the lineal-path function $L(z,a)$ increases. This effect is much stronger for three-dimensional systems than for two-dimensional systems. Again, for one-dimensional systems, polydispersivity has no effect on the lineal-path function (under the condition that $\langle \mathcal{R}\rangle$ remains unchanged). At fixed z and a, the effect of increasing the *impenetrability* of the inclusions is to decrease $L(z,a)$ (cf. Figs. 2 and 6).

C. Results of free-path distribution function $p(z,a)$ and mean free path l_S, chord-length distribution function $p(z)$ and mean chord-length l_C

We recall from Sec. III and Eq. (3.10), in particular, that a lineal path function of the form (6.6) yields a free-path distribution function given by

$$p(z,a)=A\exp(-Az), \tag{6.20}$$

where A is given by (6.17)–(6.19) for $D=3,2,1$, respectively. The mean free-path is simply

$$l_S=1/A. \tag{6.21}$$

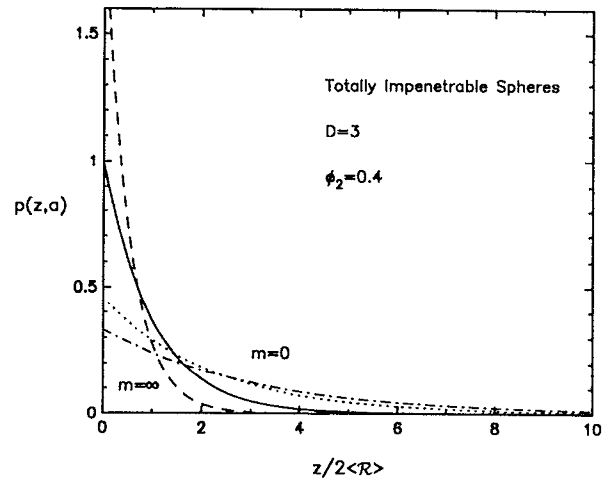

FIG. 7. Free-path distribution function $p(z,a)$ versus the dimensionless distance $z/2R$ for a three-dimensional totally impenetrable polydispersed system characterized by a Schulz distribution with $m=\infty$, $a=0$ (solid line), $m=\infty$, $a=0.1\langle\mathcal{R}\rangle$ (dashed line), $m=0$, $a=0$ (dashed and dotted line), and $m=0$, $a=0.1\langle\mathcal{R}\rangle$ (dotted line) at a sphere volume fraction $\phi_2=0.4$, as obtained from (6.20) and (6.17).

For the special case of $a=0$, we have that the chord-length distribution functions $p(z)$ are given by

$$p(z)=\frac{\pi\rho\langle\mathcal{R}^2\rangle}{1-\eta}\exp\left\{-\pi\rho z\frac{\langle(\mathcal{R}+a)^2\rangle}{1-\eta}\right\}, \quad D=3, \tag{6.22}$$

$$p(z)=\frac{2\rho\langle\mathcal{R}\rangle}{1-\eta}\exp\left[-\frac{2\rho z(\langle\mathcal{R}\rangle+a)}{1-\eta}\right], \quad D=2, \tag{6.23}$$

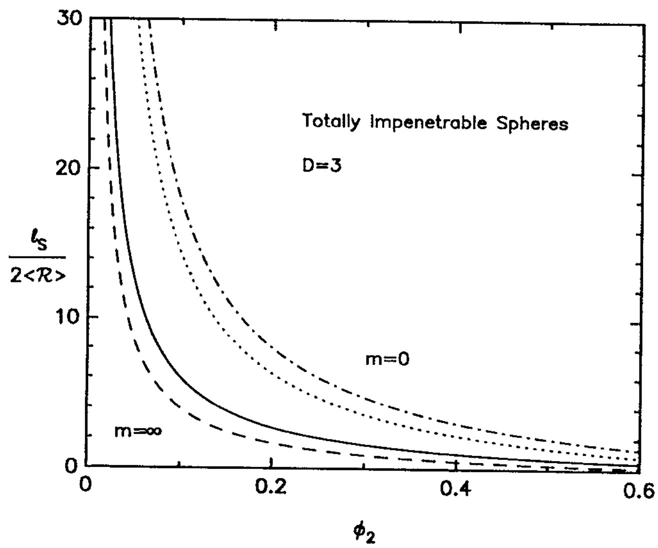

FIG. 8. Mean free path l_S versus the sphere volume fraction ϕ_2 for a three-dimensional totally impenetrable polydispersed system characterized by a Schulz distribution (4.4) with $m=\infty$, $a=0$ (solid line), $m=\infty$, $a=0.1\langle\mathcal{R}\rangle$ (dashed line), $m=0$, $a=0$ (dashed and dotted line), $a=0.1\langle\mathcal{R}\rangle$ (dotted line) as obtained from (6.21) and (6.17).

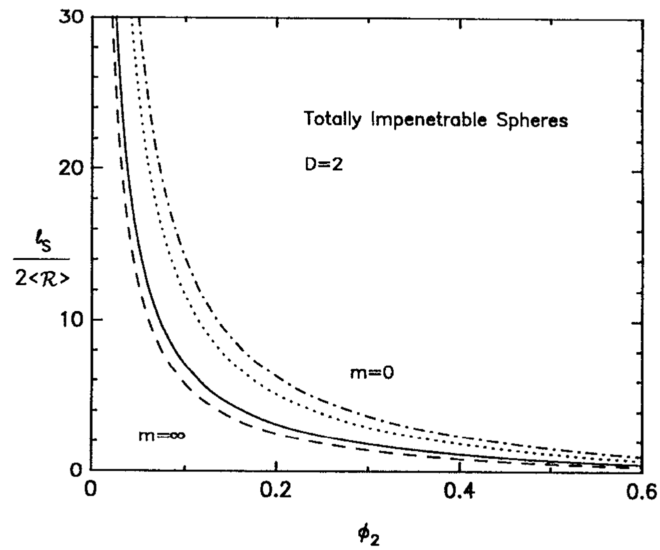

FIG. 9. As in Fig. 8, except for $D=2$ as obtained from (6.21) and (6.18).

$$p(z)=\frac{\rho z}{1-\eta}\exp\left[-\frac{\rho z}{1-\eta}\right], \quad D=1. \tag{6.24}$$

The explicit expressions for the mean chord-lengths (or "mean-intercept" lengths) are given by

$$l_C=\frac{1}{\pi\rho}\frac{1-\eta}{\langle\mathcal{R}^2\rangle}, \quad D=3, \tag{6.25}$$

$$l_C=\frac{1}{2\rho}\frac{1-\eta}{\langle\mathcal{R}\rangle}, \quad D=2, \tag{6.26}$$

$$l_C=(1-\eta)/\rho, \quad D=1. \tag{6.27}$$

In Fig. 7, we plot our analytical results of $p(z,a)$ for totally impenetrable polydispersed systems characterized by a Schulz distribution with $m=0$ and $m=\infty$ and $a=0.1\langle\mathcal{R}\rangle$ and $a=0$ at the sphere volume fraction $\phi_2=0.4$ for $D=3$ [Eq. (6.22)]. Increasing polydispersivity is again seen to broaden the function $p(z,a)$. In Figs. 8 and 9, we depict the analytical results for the mean free path for totally impenetrable spheres for $D=3$ and $D=2$, respectively, at a sphere volume fraction $\phi_2=0.4$ for $a=0.1\langle\mathcal{R}\rangle$ and $a=0$ with $m=0$ and $m=\infty$ in each case. The effect of polydispersivity is to increase the mean-free path for diffusing particles as in the case of systems for fully penetrable spheres.

ACKNOWLEDGMENTS

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