Lineal-path function for random heterogeneous materials. II. Effect of polydispersivity

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The lineal-path function \( L(z) \) for two-phase heterogeneous media gives the probability of finding a line segment of length \( z \) wholly in one of the phases, say phase \( 1 \), when randomly thrown into the sample. The function \( L(z) \) is equivalent to the area fraction of phase 1 measured from the projected image of a slab of the material of thickness \( z \) onto a plane. The lineal-path function is of interest in stereology and is an important morphological descriptor in determining the transport properties of heterogeneous media. We develop a means to represent and compute \( L(z) \) for distributions of \( D \)-dimensional spheres with a polydispersivity in size, thereby extending an earlier analysis by us for monodispersed-sphere systems. Exact analytical expressions for \( L(z) \) in the case of fully penetrable polydispersed spheres for arbitrary dimensionality are obtained. In the instance of totally impenetrable polydispersed spheres, we develop accurate approximations for the lineal-path function that apply over a wide range of volume fractions. The lineal-path function was found to be quite sensitive to polydispersivity for \( D \geq 2 \). We demonstrate how the measurement of the lineal-path function can yield the particle-size distribution of the particulate system, thus establishing a method to obtain the latter quantity.

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I. INTRODUCTION

In the most general sense, a heterogeneous material consists of domains of different materials (phases) or the same material in different states [1]. Examples of such media include suspensions, composite materials, porous media, and biological media. In considering the microstructure of such materials, an interesting and fundamental question to ask is the following: What is the probability of finding a line segment of length \( z \) wholly in phase \( \phi \)? We have referred to this quantity as the "lineal-path function" \( L^{(i)}(z) \) [2]. For three-dimensional systems, we observed that the lineal-path function \( L^{(i)}(z) \) is the area fraction of phase \( i \) measured from the parallel projected image of a three-dimensional slice of thickness \( z \) onto a plane. Evaluation of the projected area fraction for three-dimensional particle systems is a problem of long-standing interest in stereology [3]. The lineal-path function \( L^{(1)}(z) \) is also the average transmittance [4] of a photographic emulsion of thickness \( z \). Elsewhere [5] we plan to show that the lineal-path function is related to the chord-length distribution function [6], an important morphological descriptor of porous media, and the free-path distribution function [7] associated with diffusion of gases in porous media.

In the first paper of this series [2] (henceforth referred to as I), we developed a means to represent and compute the lineal-path function \( L(z) \equiv L^{(1)}(z) \) for general distributions of identical spheres (phase 2) using statistical-mechanical principles. The purpose of the present paper is to generalize the approach of I to treat spheres with a polydispersivity in size. Polydispersed-sphere systems are useful models of the many random heterogeneous media characterized by many length scales. It is shown that a knowledge of \( L(z) \) can be used to infer the size distribution of the particles.

In Sec. II we develop an exact series representation of the lineal-path function \( L(z) \) for systems of \( D \)-dimensional spheres with polydispersivity in size. In the case of fully penetrable spheres, we obtain \( L(z) \) exactly for arbitrary dimensionality \( D \). In Sec. III, we derive approximate but accurate expressions of \( L(z) \) for the instance of hard (totally impenetrable) spheres for \( D = 1, 2, \) and 3. Finally, in Sec. IV, we make some concluding remarks.

II. EXACT REPRESENTATION OF THE LINEAL-PATH FUNCTION \( L(z) \)
FOR POLYDISPERSED PARTICLE SYSTEMS

A. System description and general \( n \)-point distribution functions

Consider the determination of the lineal-path function \( L(z) \) for a system of \( N \) interacting \( D \)-dimensional spheres with a polydispersivity in size. In general, polydispersivity may manifest itself because of variation in charge, chemical properties, 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. The \( N \) particles are spatially distributed in the \( D \)-dimensional space of volume \( V \) according to the \( N \)-particle probability density \( P_N(r^N) \), which is in turn determined by the system Hamiltonian and, in general, dynamical processes. \( P_N(r^N) \) characterizes the probability of finding the particles labeled 1, 2, \ldots, \( N \) with configurations \( r^N \equiv r_{1}, r_{2}, \ldots, r_{N} \), respectively. The ensemble average of any many-body function \( F(r^N) \) is given by

\[
\langle F(r^N) \rangle = \int F(r^N) P_N(r^N) \, dr^N.
\]  

(2.1)

Torquato [8] has developed a methodology to represent and compute the general \( n \)-point distribution function \( H_n \) for random media composed of statistical distributions of \( D \)-dimensional identical spheres. A representation of the general \( n \)-point distribution function for polydispersed systems was subsequently given by Lu and Torquato [9]. \( H_n(x^m; x^p) \) characterizes the correlation associated with the \( m \) points with positions \( x\overset{m}{,} \equiv \{x_{1}, \ldots, x_{m}\} \) on certain surfaces in the system. \( p-m \) points with positions \( x\overset{p-m}{,} \equiv \{x_{m+1}, \ldots, x_{p}\} \) in certain regions exterior to the spheres, and any \( q \) of the spheres with configuration \( r^q \), where \( n=p+q \). Two different expressions for \( H_n \) have been found in terms of the \( \rho_o(x) \) which enables one to compute it. The key idea in arriving at these representations is the “available space” to “test” particles which are added to the system of \( N \) spherical included particles having \( M \) components with composition \( N_1, \ldots, N_M \), such that \( \sum_{\sigma=1}^{M} N_{\sigma} = N \). Let \( R_{\sigma_j} \) be the radius of the type \( \sigma \) included particle which is centered at \( r_j \) (\( \sigma_j = 1, \ldots, M \)) and \( b_i \) the radius of the \( i \)th test particle. The \( i \)th test particle is capable of reaching the centers of the actual inclusions of type \( \sigma_j \) from spheres of radius \( a_{ij} \). For \( b_i > 0 \), \( a_{ij} = R_{\sigma_j} + b_i \), and for \( b_i = 0 \), we allow the test particle to penetrate the included particles so that \( 0 \leq a_{ij} \leq R_{\sigma_j} \). It is natural to associate with each test particle a subdivision of space into two regions: \( D_j \), the space available to the \( j \)th test particle, and \( D_{j}^{*} \), the space unavailable to the \( j \)th test particle. Let \( S_{o} \) denote the surface between \( D_j \) and \( D_{j}^{*} \). Then, more specifically, \( H_n(x^m; x^p) \) gives the correlation associated with finding the test particle of radius \( b_j \) at \( x_j \) on \( S_{o} \), and the test particle of radius \( b_{m} \) at \( x_{m} \) on \( S_{o} \), and the test particle of radius \( b_{m+1} \) at \( x_{m+1} \) in \( D_{m+1} \), \ldots, and the test particle of radius \( b_i \) at \( x_{i} \) in \( D_{i}^{*} \), and of finding any \( q \) inclusions with configuration \( r^q \).

Another important class of correlation functions that can be obtained from the \( H_n \) are the so-called “nearest-surface distribution functions” introduced by the authors [10]. Here one need only consider the addition of a single test particle of radius \( b \). It is convenient to use the following notational change:

\[
r = b.
\]  

(2.3)

The nearest-surface quantities are then given by

\[
h_{\rho}(r) = H_1(\mathbf{x}; \mathcal{O}; \partial \mathcal{O}),
\]

(2.4)

\[
e_{\rho}(r) = H_1(\mathcal{O}; \mathbf{x}; \mathcal{O})
\]

\[
= 1 - \int_{0}^{r} h_{\rho}(y) \, dy.
\]  

(2.5)

The quantity \( h_{\rho}(r) \) is the “void” nearest-surface distribution described by Lu and Torquato [10], which is an extension of the nearest-neighbor distribution function studied earlier by Torquato, Lu, and Rubinstein [11] for monodispersed systems. The quantity \( e_{\rho}(r) \) is the “void” surface exclusion probability [2] and gives the probability of finding a region \( \Omega_{r} \), which is a spherical cavity of radius \( r \) centered at some arbitrary point, empty of particle material. We refer to \( e_{\rho}(r) \) as a “surface” exclusion probability because it is equivalent to the probability of finding any inclusion surface no closer than the radial distance \( r \) from an arbitrary point in the system. Note that \( e_{\rho}(r) \) for monodispersed particles of radius \( R \) is equivalent to the probability of finding a spherical region of radius \( r+R \) empty of sphere centers, i.e., it is equal to the “void exclusion probability” \( E_{\rho}(r+R) \) of Ref. [11].

We shall show below that the lineal-path function \( L(z) \) for polydispersed-sphere systems is actually a special type of surface exclusion probability function.

### B. Calculation of the exclusion probability function

From the general expression of \( H_n \) for the polydispersed-sphere system [9], we derived [10] the following expansion for the surface exclusion probability \( e_{\rho}(r) \):

\[
e_{\rho}(r) = \sum_{k=0}^{N} (-1)^{k} e_{\rho}^{(k)}(r),
\]  

(2.6)

where

\[
e_{\rho}^{(k)}(r) = \frac{1}{k!} \int \cdots \int d \mathcal{R}_{1} \cdots d \mathcal{R}_{k} f(\mathcal{R}_{1}) \cdots f(\mathcal{R}_{k})
\]

\[
\times \rho_{o}(r_{k}; \mathcal{R}_{1}, \ldots, \mathcal{R}_{k}) \times \prod_{j=1}^{k} m(|x-r_{j}|; r) \, dr_{j}
\]  

(2.7)

and

\[
e_{\rho}^{(0)}(r) \equiv 1.
\]  

(2.8)
The result above has been expressed for a system of included particles with a continuous distribution in radius \( R \) characterized by the normalized probability density \( f(R) \). 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 \( f(R_j) \) in relation (2.7) become unity for \( j = 1, \ldots, q \) and \( \sum_{j=q+1}^{M} \rho_j \delta(R_j - R_j) \) for \( j = q+1, \ldots, q+s \), where \( \rho_j \) is the number density of type \( \sigma \) particles and \( \delta(R) \) is the Dirac delta function. In (3.7), \( \rho_n(r^n; R_1, \ldots, R_n) = f(R_1) \cdots f(R_n) \) is the probability density function associated with finding an inclusion with radius \( R_1 \) at \( r_1 \), another inclusion with radius \( R_2 \) at \( r_2 \), etc. The case \( n = 1 \) is degenerate in the sense that \( \rho_1(r_1; R_1) \) is independent of \( r_1 \), and in the instance of statistically homogeneous media is simply equal to the total number of density \( \rho \). The quantity \( m(|x - r_j; r|) \) is an indicator function defined as

\[
m(|x - r_j; r|) = \begin{cases} 1, & |x - r_j| < r + R_j \\ 0, & |x - r_j| \geq r + R_j \end{cases}.
\]  

(2.9)

Note that the function \( m \) defined here is slightly different from the one defined in Ref. [9] in that it is the surface indicator function.

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

\[
\rho_n(r^n; R_1, \ldots, R_n) = \prod_{j=1}^{n} \rho_1(r_j; R_j). 
\]  

(10.10)

We then have the following results:

\[
ed_v(r) = \exp[-\rho(v_p(r + R))].
\]  

(11.11)

Here \( v_p(R) \) is the volume of a \( D \)-dimensional sphere with radius \( R \), i.e.,

\[
v_1(R) = 2R,
\]  

(12.12)

\[
v_2(R) = \pi R^2,
\]  

(13.13)

\[
v_3(R) = \frac{4}{3} \pi R^3.
\]  

(14.14)

An important dimensionless parameter that will be used throughout the ensuing sections is the reduced density \( \eta \) in \( D \) dimensions defined by

\[
\eta = \frac{\pi^{D/2}}{\Gamma(1 + D/2)} \rho R^D.
\]  

(15.15)

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

\[
\eta = \frac{\pi^{D/2}}{\Gamma(1 + D/2)} \rho R^D.
\]  

(16.16)

where the average of any function \( A(R) \) is given by

\[
\langle A(R) \rangle = \int_0^\infty A(R) f(R) dR.
\]  

(2.17)

Finally, we note that only in the case of hard spheres is \( \eta \) equal to the sphere volume fraction \( \phi_2 \). For penetrable-sphere systems, \( \eta > \phi_2 \).

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 \( D \geq 2 \) because the \( n \)-particle probability densities \( \rho_n(r^n) \) are not known exactly. One must devise an approximate scheme to evaluate and sum the series. Lu and Torquato [10] obtained \( e_v(r) \) from the Percus-Yevick [12], scaled-particle [13,14], and Carnahan-Starling [15] approximations of the related conditional "pair" distribution function \( G_k(r) \). For example, the scaled-particle result for the exclusion probability for \( D = 3 \) is given by

\[
e_v(r) = (1 - \eta) \exp\left(-\pi \rho \left( cr + dr^2 + gr^3 \right)\right), \quad r > 0.
\]  

(18.18)

where

\[
c = \frac{4 \langle R^2 \rangle}{1 - \eta},
\]  

(19.19)

\[
d = \frac{4 \langle R \rangle}{1 - \eta} + \frac{12 \xi_2}{(1 - \eta)^2} \langle R^2 \rangle,
\]  

(20.20)

\[
g = \frac{4}{3(1 - \eta)} + \frac{8 \xi_2 \langle R \rangle}{(1 - \eta)^2} + \frac{16 \xi_2^2 \langle R^2 \rangle}{(1 - \eta)^3},
\]  

(21.21)

with

\[
\xi_k = \rho \pi^{2k-1} \langle R^k \rangle.
\]  

(22.22)

For \( D = 2 \), the scaled-particle approximation gives the surface exclusion probability for \( r > 0 \):

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

(23.23)

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

\[
e_v(r) = (1 - \eta) \exp\left( -2\rho r \right), \quad r > 0.
\]  

(24.24)

A commonly employed size distribution function \( f(R) \) is the Schulz distribution function [16], which is defined as

\[
f(R) = \frac{1}{\Gamma(m + 1)} \left( \frac{m + 1}{R} \right)^{m + 1} R^m \exp\left( -\frac{(m + 1)R}{\langle R \rangle} \right),
\]  

(25.25)

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

\[
\langle R^n \rangle = \langle R \rangle^n \left( \frac{m + 1}{m} \right)^{n - 1} \prod_{i=0}^{n} (m + i).
\]  

(26.26)
By increasing \( z \), the variance decreases, i.e., the distribution becomes sharper. In the monodisperse limit, \( z \to \infty \), we have

\[
f(R) = \delta(R - \langle R \rangle).
\] (2.27)

Note that for statistically homogeneous and isotropic media, the density of the particles with radius between \( R \) and \( R + dR \) is \( \rho f(R)dR \) with \( \rho \) the total density.

C. Series representation of lineal-path function

The derivation of the exact series representation of the lineal-path function \( L(z) \) follows closely the derivation of the corresponding expression for the exclusion probability function \( e_p(r) \) for a spherical test particle of radius \( r \). The lineal-path function \( L(z) \) is a special type of surface exclusion probability function, i.e., the probability of finding a line segment of length \( z \) wholly in the void phase (phase 1), i.e., the space exterior to the inclusions. Therefore, the center of a particle with radius \( R_j \) should be outside a region \( \Omega_E(z, R_j) \), the exclusion region between a line of length \( z \) and a sphere of radius \( R_j \). The region \( \Omega_E(z, R_j) \) in this case is hence a \( D \)-dimensional spherocylinder of cylindrical length \( z \) and radius \( R_j \), with hemispherical caps of radius \( R_j \) on either end (see Fig. 1). Following Torquato [8], we introduce the exclusion region indicator function

\[
m_j(x; z) = \begin{cases} 
1 & x \in \Omega_E(z, R_j) \\
0 & \text{otherwise}.
\end{cases}
\] (2.28)

The derivation of the series representation of \( L(z) \) follows in exactly the same fashion as that for spherical test particles as outlined in Sec. II A and thus we find

\[
L(z) = 1 + \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \int dR_1 \cdots dR_k f(R_1) \cdots f(R_k) \times 
\times \rho_k(x; R_1, \ldots, R_k) \times \prod_{j=1}^{k} m_j(x; z) d\tau_j.
\] (2.29)

In the instance of fully penetrable spherical inclusions, results (2.10) and (2.29) yield the exact result

\[
L(z) = \exp\left[ -\rho \left( v_E(z, R) \right) \right],
\] (2.30)

where \( v_E(z, R) \) is the \( D \)-dimensional volume of the exclusion region \( \Omega_E(z, R) \):

\[
v_E = \begin{cases} 
\frac{4\pi}{3} R^3 + \pi R^2 z & (D = 3) \\
\pi R^2 + 2Rz & (D = 2) \\
2R + z & (D = 1)
\end{cases}
\] (2.31)

Since the porosity \( \phi_1 \) (i.e., the volume fraction of the space exterior to the spheres) for fully penetrable spheres is simply given by

\[
\phi_1 = \exp(-\eta),
\] (2.34)

where \( \eta \) is given by (2.13), then the lineal-path function may be written as

\[
L(z) = \begin{cases} 
\phi_1 \exp(-\rho \vec{R}^2 z), & D = 3 \\
\phi_1 \exp(-2\rho \vec{R} z), & D = 2 \\
\phi_1 \exp(-\rho z), & D = 1
\end{cases}
\] (2.35)

These results can be written as a function of \( \eta \) and the moments of particle radius distribution, i.e., we specifically have

\[
\phi_1 \exp \left[ -\frac{3\eta \vec{R}^2 z}{4 \vec{R}^2} \right] = \phi_1^{1+3(\vec{R}^2)/4 \vec{R}^2}, \quad D = 3
\] (2.38)

\[
L(z) = \phi_1 \exp \left[ -\frac{2\eta \vec{R} z}{\pi \vec{R}^2} \right] = \phi_1^{1+2(\vec{R} z)/\pi \vec{R}^2}, \quad D = 2
\] (2.39)

\[
\phi_1 \exp \left[ -\frac{\eta z}{2 \vec{R}} \right] = \phi_1^{1+z/2 \vec{R}}, \quad D = 1.
\] (2.40)

For the special case of monodispersed system, these results reduce to the expression (2.34)–(2.36) in I (Ref. [2]).

As an example, we show the results for polydispersed systems characterized by a Schulz distribution as expressed in (2.25). The lineal-path function \( L(z) \) can then be explicitly written as

\[
L(z) = \phi_1^{1+3(m+1)/4 \vec{R}^2 (m+3)}, \quad D = 3
\] (2.41)

\[
L(z) = \phi_1^{1+2(m+1)/\pi \vec{R}^2 (m+2)}, \quad D = 2
\] (2.42)

FIG. 1. Spherocylindrical exclusion region (dotted lines) for a line segment of length \( z \) and a sphere of radius \( R \). Two cases are shown: one for a sphere of radius \( R_1 \) and the other for a sphere of radius \( R_2 > R_1 \).
\[ L(z) = \phi_1^{1 + z/\langle R \rangle^2}, \quad D = 1. \] (2.43)

Note that for the one-dimensional case, if we scale the length \( z \) with \( 2\langle R \rangle \), \( L(z) \) for the polydisperse system has the same form as for identical spheres. Therefore polydispersivity has no effect on the lineal-path function \( L(z) \) for \( D = 1 \) provided the system has the same average particle size. Under the condition that the particle volume fraction is a constant, the lineal-path function changes as the ratio \( \langle R^2 \rangle / \langle R \rangle \) is varied for \( D = 3 \). For \( D = 2 \), \( L(z) \) changes with the ratio \( \langle R \rangle / \langle R^2 \rangle \). For systems of particles with a simple functional form of the size distribution, the expressions (2.38)–(2.40) provide a means to compute the size distribution of the particles by measuring the "projected" area fraction of the void phase. The expressions (2.41)–(2.43) give the explicit relationship between \( L(z) \) and the parameter \( m \) for the Schulz distribution, in particular. One can easily obtain the associated inverse expressions, i.e., relations for \( m \) in terms of \( L(z) \). For example, we have

\[ m = 2 \left( \frac{1 - \langle R \rangle}{3nZ} \left( \frac{\ln L(z)}{\ln \phi_1} - 1 \right) \right)^{-1} - 3, \] (2.44)

for three-dimensional systems.

In Figs. 2 and 3 we plot our analytical results for polydispersed fully penetrable spheres described by a Schulz distribution at values of the sphere volume fraction \( \phi_2 = 0.4 \) for \( D = 3 \) and 2, respectively, with \( m = 0 \) and \( \infty \) in each case. Recall that \( m = \infty \) corresponds to the monodisperse limit. For any \( D, L(z) \) is a monotonic decreasing function of \( z \). This behavior is expected since the larger the line segment or "slice" of material of length \( z \) is, the smaller is the probability of finding the line wholly in the matrix or the smaller is the "projected area" of the void phase. For the same \( z \) and the same volume fraction of particle phase, \( L(z) \) changes dramatically with the size distribution of particles for \( D \geq 2 \). The effect of the polydispersivity is to increase the lineal-path function \( L(z) \). For three-dimensional systems this effect is much stronger than for two-dimensional systems. Note that, for the case of identical spheres (\( m = \infty \)), \( L(z) \) for \( D = 3 \) is smaller than the \( L(z) \) for \( D = 2 \) because the spheres fill space more efficiently as \( D \) increases. However, the stronger effect of the polydispersivity leads to the fact that \( L(z) \) for \( D = 3 \) is much larger than \( L(z) \) for \( D = 2 \) at \( m = 0 \). As we have already discussed, for one-dimensional systems, the polydispersivity has no effect on the lineal-path function \( L(z) \) (under the condition that \( \langle R \rangle \) remains unchanged).

For impenetrable spherical inclusions, an exact evaluation of the series (2.29) is out of the question for reasons given earlier. The subsequent section describes the derivation of an approximate but accurate expression for \( L(z) \) for hard-sphere systems.

**III. ANALYTICAL EXPRESSIONS FOR THE LINEAL-PATH FUNCTION FOR D-DIMENSIONAL POLYDISPERSED SPHERES**

**A. Preliminary discussion**

The initial-path function \( L(z) \) for systems of \( D \)-dimensional identical hard spheres was obtained in I by calculating the reversible work to create a cavity which is empty of sphere centers [2]. For polydispersed systems, finding an arbitrary-shaped cavity empty of particle ma-
terial is equal to finding that the centers of particles of radius \( R \) (for all \( R \)) are a normal distance \( R \) away from the cavity surface. A key step in obtaining \( L(z) \) for polydisperse systems is the fact that the work needed to create a cavity empty of particle material is the sum of the work associated with excluding the center of the particle of radius \( R \) a normal distance \( R \) from the cavity surface. To elucidate this point, it is necessary to review briefly some fundamental concepts concerning the nearest-surface distribution function and related functions developed by Lu and Torquato [2,10].

For a polydisperse spherical particle system, we define the void nearest-surface distribution function \( h_V(r) \) as the probability that at an arbitrary point in the system the nearest particle surface lies at a distance between \( r \) and \( r + dr \). The closely related void "exclusion" probability \( e_V(r) \) was defined in Sec. II. The nearest-surface distribution function \( h_V(r) \) can be written as a product involving conditional probabilities:

\[
h_V(r) = g_V(r) e_V(r) \, .
\]  

The quantity \( g_V(r) \) in (3.1) is the probability, given that a region \( \Omega_V \) (spherical cavity of radius \( r \)) is empty of particle material, of finding the particle surface in the spherical shell of volume \( s_D(r)dr \) encompassing the cavity. The quantity \( s_D(r) \) is the surface area of a \( D \)-dimensional sphere of radius \( r \):

\[
s_1(r) = 2 \, ,
\]
\[
s_2(r) = 2\pi r \, ,
\]
\[
s_3(r) = 4\pi r^2 \, .
\]

It is a well-known result of statistical thermodynamics that the work done to create a spherical surface exclusion cavity of radius \( r \) is

\[
W_V(r) = -kT \ln e_V(r) = kT \int_{-\infty}^{r} g_V(y) dy \, .
\]  

The second line of (3.5) follows since the exclusion probability \( e_V(r) \) is related to conditional pair distribution function \( g_V(r) \) via the expression

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

For the discrete case, the "generic" distribution function \( g_V(r) \) is related to the "specific" distribution function \( g_{V,j}(r) \) by the relation

\[
g_V(r) = \sum_j g_{V,j}(r) \, ,
\]

where \( g_{V,j}(r)dr \) is defined to be the probability, given that region \( \Omega_V \) (spherical cavity of radius \( r \)) is empty of particle material, of finding the surface of \( j \)-type particles in the spherical shell of volume \( s_D(r)dr \) encompassing the cavity. Note that the establishment of the relationship (3.7) is based on the independence of the events associated with the specific distribution function \( g_{V,j} \). Accordingly, associated with \( g_{V,j}(r) \), we define the work \( W_{V,j}(r) \) as

\[
W_{V,j}(r) = kT \int_{-\infty}^{r} g_{V,j}(y) dy \, .
\]

Therefore, combination of (3.5) and (3.8) yields the total work to be

\[
W_V(r) = \sum_j W_{V,j}(r) \, .
\]

The specific surface distribution function \( g_{V,j}(r) \) can be further written as

\[
g_{V,j}(r) = p_j s_D(r + R_j) g_{V,j}(r + R_j) \, ,
\]

where \( p_j s_D(r) g_{V,j}(r) \) is defined as the probability that, given a region \( \Omega_V \) (spherical cavity of radius \( r \)) is empty of particle centers, \( j \)-type particle centers are contained in the spherical shell volume \( s_D(r)dr \) encompassing the cavity.

In the case of continuous particle-size distributions, we define \( g_V(r; R) dR \) as the probability, given that region \( \Omega_V \) (spherical cavity of radius \( r \)) is empty of particle material, of finding the surface of particles with radius between \( R \) and \( R + dR \) in the spherical shell of volume \( s_D(r)dr \) encompassing the cavity. Therefore we have

\[
g_V(r) = \int_0^\infty g_V(r; R) f(R) dR \, .
\]

The work associated with \( G_V(r; R) \) then can be written as \( W_V(r; R) \), and we have

\[
W_V(r) = \int_0^\infty W_V(r; R) dR \, .
\]

Further separation of the work \( W_{V,j} \) (or \( W_V(r; R) \)) produces the corresponding "pressure" \( p_j \) (or \( p(R) \)) and the "surface tension" \( \sigma_j \) (or \( \sigma(R) \)). Note that \( p(R) \) and \( \sigma(R) \) do not denote the thermodynamic pressure \( p \) (without the argument) and the surface tension \( \sigma \) (without the argument). These quantities will be defined later in this section.

**B. Analytical expression of the lineal-path function for \( D \)-dimensional hard spheres**

We assume that the system of \( D \)-dimensional hard spheres is in thermal equilibrium. This enables us to exploit the well-established concepts of equilibrium statistical mechanics to obtain approximate but accurate expressions for the lineal-path function \( L(z) \) for such models. The reversible work \( W(z) \) required for the creation of a surface exclusion cavity of line segment of length \( z \) in a \( D \)-dimensional polydisperse hard-sphere system is exactly related to the probability of finding a line segment of length \( z \) wholly in the matrix phase \( L(z) \), by

\[
L(z) = \exp \left[ -\frac{W(z)}{kT} \right] \, ,
\]

where \( k \) is the Boltzmann constant and \( T \) is the temperature of the system. Since the reversible work done to create the cavity is process independent, then we can consider the simplest process to calculate \( W(z) \). First we create a point cavity (a surface exclusion cavity of zero radius). Let the work done for this part be denoted by \( W_1 \). Then we expand this surface exclusion cavity along
one direction to create a line segment of length \( z \) and let \( W_2 \) denote the associated work. Thus we have that
\[
W(z) = W_1 + W_2(\zeta) .
\] (3.14)
The work \( W_1 \) is related to the exclusion probability \( e_\nu(r) \) evaluated at \( r = 0 \) by
\[
W_1 = -kT \ln e_\nu(0) ,
\] (3.15)
where \( e_\nu(0) = S_1 = \phi_1 \) is the volume fraction of phase 1. We then have
\[
L(z) = e_\nu(0) \exp \left\{ -\frac{W_2(z)}{kT} \right\} = \phi_1 \exp \left\{ -\frac{W_2(z)}{kT} \right\} .
\] (3.16)
As in the case of identical spheres, the simplest way of calculating this constant is to obtain \( W_2 \) from the initial infinitesimal expansion process, i.e., from a surface exclusion cavity of zero radius to a surface exclusion line segment of length \( dz \).

It is important to realize that, to a particle of radius \( \bar{R} \), creating a surface exclusion cavity of sphere of zero radius (the first step) is equal to excluding the center of the particles from a sphere of radius \( \bar{R} \). Accordingly, for the particle of radius \( \bar{R} \), the infinitesimal expansion process (the beginning of the second step) is equal to expanding a spherical cavity of radius \( \bar{R} \) to a spherocylinder of length \( dz \) and radius \( \bar{R} \). We then can use the same approach as for identical spheres. All the quantities involved in the following analysis will be purely center related quantities. The work \( W_2(\bar{R}) \) can be written as
\[
W_2(\bar{R}) = kT \int_0^\bar{R} \rho f(\bar{R}) s_D(y) G_\rho(y; \bar{R}) dy ,
\] (3.17)
and the form of the elementary work in the process can be written as
\[
dW_2(r; \bar{R}) = kT p f(\bar{R}) s_D(r) G_\rho(r; \bar{R}) dr .
\] (3.18)
The conditional pair distribution function \( G_\rho(r; \bar{R}) \) in the scaled-particle approximation is given by
\[
G_\rho(r + \bar{R}) = a_1(\bar{R}) + \frac{a_2(\bar{R})}{r + \bar{R}} + \frac{a_3(\bar{R})}{(r + \bar{R})^2} , \quad D = 3
\] (3.19)
where \( a_1(\bar{R}), a_2(\bar{R}), \) and \( a_3(\bar{R}) \) are functions of the radius of the particle:
\[
a_1(\bar{R}) = \frac{1}{1 - \eta} + \frac{6 \bar{R} \xi_2}{(1 - \eta)^2} + \frac{12 \bar{R}^2 \xi_2^2}{(1 - \eta)^3} ,
\] (3.20)
\[
a_2(\bar{R}) = -\frac{6 \bar{R} \xi_2}{(1 - \eta)^2} - \frac{24 \bar{R}^2 \xi_2^2}{(1 - \eta)^3} ,
\] (3.21)
\[
a_3(\bar{R}) = \frac{12 \bar{R}^4 \xi_2^2}{(1 - \eta)^3} .
\] (3.22)
In the case of two-dimensional hard-sphere systems (i.e., hard disks), we have from the scaled-particle approximation
\[
G_\rho(\bar{R}) = \frac{1}{1 - \eta} + \frac{\pi p(\bar{R}) \bar{R}}{(1 - \eta)^2} - \frac{\pi p(\bar{R}) \bar{R}^2}{(1 - \eta)^3} , \quad D = 2 .
\] (3.23)
The simplest instance is that for one-dimensional hard-sphere systems (i.e., hard rods), where we have the exact result
\[
G_\rho(\bar{R}) = \frac{1}{1 - \eta} , \quad D = 1 .
\] (3.24)
Following the principle idea of scaled-particle theory, the work \( W_\rho \) can be further considered to be the sum of the following two parts: the work related to the volume change and the work related to the surface change
\[
dW_\rho(r; \bar{R}) = p(\bar{R}) d\rho(r) + \sigma(\bar{R}) d\sigma_D(r) .
\] (3.25)
It is clear that the expression (3.25) is also a definition of \( p(\bar{R}) \) and \( \sigma(\bar{R}) \). The quantity \( \sigma(\bar{R}) \) can be further written as
\[
\sigma(\bar{R}) = \sigma_0(\bar{R}) \left( 1 - \frac{\delta(\bar{R})}{\bar{R}} \right) .
\] (3.26)
Substituting expressions (3.19)–(3.24) into (3.18) and comparing to (3.25), we have for \( D = 3 \)
\[
p(\bar{R}) = kT p f(\bar{R}) \left[ \frac{1}{1 - \eta} + \frac{6 \bar{R} \xi_2}{(1 - \eta)^2} + \frac{12 \bar{R}^2 \xi_2^2}{(1 - \eta)^3} \right] ,
\] (3.27)
\[
\sigma_0(\bar{R}) = -kT p f(\bar{R}) \left[ \frac{3 \xi_2 \bar{R}^2}{(1 - \eta)^2} + \frac{12 \xi_2^2 \bar{R}^3}{(1 - \eta)^3} \right] ,
\] (3.28)
\[
\delta(\bar{R}) = \frac{2 \bar{R}^3 \xi_2}{1 - \eta \xi_2} + 4 \bar{R} \xi_2 ,
\] (3.29)
for \( D = 2, \)
\[
p(\bar{R}) = kT p f(\bar{R}) \left[ \frac{1}{1 - \eta} + \frac{\pi p(\bar{R}) \bar{R}}{(1 - \eta)^2} \right] ,
\] (3.30)
\[
\sigma(\bar{R}) = -\frac{\pi p(\bar{R})}{(1 - \eta)^2} \bar{R}^2 p f(\bar{R}) kT ,
\] (3.31)
\[
\delta(\bar{R}) = 0 ,
\] (3.32)
and for \( D = 1, \)
\[
p(\bar{R}) = \frac{\sigma(\bar{R})}{1 - \eta} ,
\] (3.33)
\[
\sigma(\bar{R}) = \delta(\bar{R}) = 0 .
\] (3.34)
In the special case that the system is composed of identical spheres, our results reduce to the results obtained in Paper I.

The calculation of the work \( W_2(z; \bar{R}) \) needed to expand the spherical cavity of radius \( \bar{R} \) into a spherocylinder is then quite straightforward. We have that
\[ W_2(z; \mathcal{R}) = \rho(\mathcal{R}) \Delta V + \sigma(\mathcal{R}) \Delta S, \quad (3.35) \]

where \( \Delta V \) is the change in volume for the expansion process:

\[
\Delta V = \begin{cases} 
\pi \mathcal{R}^2 z, & D = 3 \\
2\mathcal{R} z, & D = 2 \\
z, & D = 1 
\end{cases} \quad (3.36)
\]

and

\[
\Delta S = \begin{cases} 
\pi \mathcal{R}^2 z, & D = 3 \\
2z, & D = 2 \\
0, & D = 1 
\end{cases} \quad (3.38)
\]

Substitution of the relations (3.26)–(3.34) and (3.36)–(3.40) into (3.35), and application of Eq. (3.12), yields

\[
W_2(z) = \begin{cases} 
\frac{\pi k T \rho(\mathcal{R})}{(1-\eta)} z, & D = 3 \\
2\rho k T \frac{2(\mathcal{R})}{1-\eta}, & D = 2 \\
\rho k T \frac{1}{1-\eta}, & D = 1 
\end{cases} \quad (3.42)
\]

Finally, substituting results (3.42)–(3.44) into (3.16) we obtain the lineal-path distribution function for \( D \)-dimensional polydispersed hard-sphere systems:

\[
L(z) = \begin{cases} 
(1-\eta) \exp \left\{ -\frac{\pi \rho(\mathcal{R})^2 z}{1-\eta} \right\}, & D = 3 \\
(1-\eta) \exp \left\{ -2\rho z (\mathcal{R}) / (1-\eta) \right\}, & D = 2 \\
(1-\eta) \exp \left\{ -\rho z / (1-\eta) \right\}, & D = 1 
\end{cases} \quad (3.45)
\]

These expressions can be written in terms of the reduced density \( \eta \) as

\[
L(z) = \begin{cases} 
(1-\eta) \exp \left\{ -3\eta (\mathcal{R})^2 z / [4(\mathcal{R})^2 (1-\eta)] \right\}, & D = 3 \\
(1-\eta) \exp \left\{ -\frac{2\eta z (\mathcal{R})}{(1-\eta)\pi(\mathcal{R})^2} \right\}, & D = 2 \\
(1-\eta) \exp \left\{ -\frac{\eta z}{(1-\eta)(\mathcal{R})} \right\}, & D = 1 
\end{cases} \quad (3.48)
\]

In the special instance of a polydispersed system characterized by the Schulz distribution, we have the specific results

\[
L(z) = \begin{cases} 
(1-\eta) \exp \left\{ -\frac{3\eta (m+1)z}{4(1-\eta)(m+3)(\mathcal{R})} \right\}, & D = 3 \\
(1-\eta) \exp \left\{ -\frac{2\eta (m+1)z}{(1-\eta)\pi(m+2)(\mathcal{R})} \right\}, & D = 2 \\
(1-\eta) \exp \left\{ -\frac{\eta z}{(1-\eta)(\mathcal{R})} \right\}, & D = 1 
\end{cases} \quad (3.51)
\]

For monodisperse spheres, the results given above reduce to the results we obtained previously in I and which were found to be in very good agreement with Monte Carlo simulation data. Under the condition that the particle volume fraction is a constant, the lineal-path function changes with the ratio \( \langle \mathcal{R}^2 \rangle / \langle \mathcal{R} \rangle^3 \) for \( D = 3 \), as was the case for fully penetrable spheres [cf. (2.38)]. Similarly, \( L(z) \) changes with ratio \( \langle \mathcal{R} \rangle / \langle \mathcal{R}^2 \rangle \) and \( \langle \mathcal{R} \rangle \) for \( D = 2 \) and \( 1 \), respectively. The expressions (3.51)–(3.53) can easily be inverted to yield the parameter \( m \) of the Schulz distribution in terms of \( L(z) \). For example, for \( D = 3 \), we find

\[
m = 2 \left\{ 1 - \frac{4(1-\eta)(\mathcal{R})}{3\eta z} \ln \frac{L(z)}{1-\eta} \right\}^{-1}, \quad D = 3. \quad (3.54)
\]

In Figs. 4 and 5 we plot our analytical results for totally impenetrable polydispersed systems characterized by a Schulz distribution with \( m = 0 \) and \( \infty \) at values of the sphere volume fraction \( \phi_2 = 0.4 \) for \( D = 2 \) and \( 1 \), respectively. The effect of polydispersivity is the same as in the case of fully penetrable spheres. For a broader size distribut-
bution of particles (a smaller value of \( m \)), the lineal-path function \( L(z) \) increases for fixed \( z \) and \( \phi_2 \). This effect is stronger for three-dimensional systems than for two-dimensional systems. Again, for one-dimensional systems, polydispersity has no effect on the lineal-path function (under the condition that \( \langle R \rangle \) remains fixed). Figure 6 compares the lineal-path function for fully penetrable spheres to the corresponding quantity for totally impenetrable spheres at \( \phi_2 = 0.45 \). The reason why the fully penetrable curve lies above the impenetrable curve is because the probability of finding void regions in the former system is larger than in the latter system [11].

IV. CONCLUDING REMARKS

We have generalized the formalism of I for monodispersed-particle systems to represent and compute the lineal-path function \( L(z) \) for systems of \( D \)-dimensional spheres with polydispersity in size. For fully penetrable spheres, exact results were obtained using the derived series expansion for \( L(z) \). For totally impenetrable spheres, we found approximate but accurate expressions for \( L(z) \) for arbitrary dimension. It was found that the effect of polydispersivity on \( L(z) \) depends on dimension. For one-dimensional systems with the same value of the average radius of particles, polydispersivity has no effect on the lineal-path function \( L(z) \). For \( D \geq 2 \), \( L(z) \) was strongly affected by polydispersivity. Thus the lineal-path function is a useful signature of the microstructure of the heterogeneous media as it reflects multiple length scales that may exist in the system. It was also shown that knowledge of \( L(z) \) can yield the particle-size distribution of particulate systems, thus establishing a method to measure the latter quantity.

Elsewhere [5] we plan to show that the lineal-path function \( L(z) \) is directly related to other important morphological information of heterogeneous media. For example, \( L(z) \) will be shown to be related to the chord-length distribution function \( p(z) \) by the relation

\[
p(z) = \frac{l_c}{\phi_1} \frac{d^2 L(z)}{dz^2} ,
\]

(4.1)

where \( l_c \) is the mean chord length given by

\[
l_c = \int_0^\infty z p(z) dz .
\]

(4.2)

Here \( p(z)dz \) gives the probability of finding a chord of length between \( z \) and \( z + dz \) in phase 1. Chords are the lengths between intersections of infinitely long lines with the two-phase interface. The chord-length distribution function \( p(z) \) has been measured for sedimentary rocks [6].

It will also be demonstrated [5] that the free-path distribution function associated with diffusion of gases in porous media is directly related to \( L(z) \). The former quantity determines the “effective mean free path” for the process.

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