We have seen that random heterogeneous materials exhibit a remarkably broad spectrum of rich and complex microstructures. Our focus in Part I of this book is to develop a machinery to characterize statistically this broad class of microstructures, i.e., to develop a statistical, or stochastic, geometry of heterogeneous materials. How or where does one begin to address this challenging task? The answer, of course, depends on what is the goal of the statistical characterization. Our goal is ultimately the prediction of the macroscopic or effective physical properties of the random heterogeneous material, and thus this determines our starting point. The diverse effective properties that we are concerned with in this book naturally and necessarily lead to a wide variety of microstructural descriptors, generically referred to as microstructural correlation functions. As we noted in Chapter 1, such descriptors have applicability in other seemingly disparate fields, such as cosmology (Peebles 1993, Saslaw 2000) and ecology (Pielou 1977, Diggle 1983, Durrett and Levin 1994).

In this chapter we will define and discuss the following microstructural correlation functions, which are fundamental to determining the effective properties of random heterogeneous materials:

- $n$-point probability functions
- surface correlation functions
- lineal-path function
- chord-length density function
- pore-size functions
- percolation and cluster functions
- nearest-neighbor functions
• point/particle correlation functions
• surface-particle function

Whereas the first six types of quantities describe random media of arbitrary microstructure, the last three apply specifically to random particle dispersions. Chapter 4 describes a general formalism to represent and obtain all of these quantities from a canonical correlation function. Chapters 5–8, 10, and 12 deal with the evaluation of these functions for specific models and materials.

2.1 Preliminaries

The use of the term random heterogeneous material or simply random medium rests on the assumption that any sample of the medium is a realization of a specific random or stochastic process (or random field). An ensemble is a collection of all the possible realizations of a random medium generated by a specific stochastic process. We let \((\Omega, \mathcal{F}, \mathcal{P})\) be some fixed probability space, where \(\Omega\) is a sample space (set of “outcomes”), \(\mathcal{F}\) is a \(\sigma\)-algebra of subsets of \(\Omega\) (set of “events”), and \(\mathcal{P}\) is a probability measure (a function that assigns probabilities to “events”) (Durrett 1996). Let each point \(\omega \in \Omega\) correspond to a realization of the random medium that occupies some subset \(V\) of \(d\)-dimensional Euclidean space, i.e., \(V \subset \mathbb{R}^d\). The medium is in general statistically characterized by a random variable \(\xi(x, t; \omega)\), called the structure function, that depends on all values of the position vector \(x \in V\) and on the time \(t\). The time dependence allows for evolving microstructures (e.g., shear flow in a suspension or growth processes in random media).

In this book we will assume that the microstructures are static or can be approximated as static, and therefore the structure function \(\xi(x; \omega)\) will be taken to be independent of time. For a fixed \(\omega\), the structure function may be a continuously varying function of position (e.g., porosity of geologic media or orientation of crystals in a polycrystal), or it may take on discrete values (e.g., fiber composites or colloids). Our primary focus will be on two-phase random media, i.e., cases in which \(\xi(x; \omega)\) takes on two different values. However, generalizations to multiphase media with an arbitrary number of discrete phases follow in the obvious way. Some of the results given in this book will apply to multiphase media as well.

Each realization \(\omega\) of the two-phase random medium occupies the region of space \(V \subset \mathbb{R}^d\) of volume \(V\) that is partitioned into two disjoint random sets or phases: phase 1, a region \(V_1(\omega)\) of volume fraction \(\phi_1\), and phase 2, a region \(V_2(\omega)\) of volume fraction \(\phi_2\). Since the random sets \(V_1(\omega)\) and \(V_2(\omega)\) are the complements of one another, then \(V_1(\omega) \cup V_2(\omega) = V\) and \(V_1(\omega) \cap V_2(\omega) = \emptyset\). Let \(\partial V(\omega)\) denote the surface or interface between \(V_1(\omega)\) and \(V_2(\omega)\). Figure 2.1 shows a portion of a realization of a two-phase random medium. For a given realization \(\omega\), the structure function \(\xi(x; \omega)\) is just the indicator function \(I^{(i)}(x; \omega)\) for phase \(i\), given for \(x \in V\) by

\[
I^{(i)}(x; \omega) = \begin{cases} 
1, & \text{if } x \in V_i(\omega), \\
0, & \text{otherwise},
\end{cases}
\]  

(2.1)
for $i = 1, 2$ with

$$I^{(1)}(x; \omega) + I^{(2)}(x; \omega) = 1. \quad (2.2)$$

The random variable $I^{(i)}(x; \omega)$ is also called the characteristic function in the heterogeneous media community, but we will not use this term, since it is usually reserved to mean the Fourier transform of the probability density function in probability theory and stochastic processes. The indicator function $M(x; \omega)$ for the interface is defined as

$$M(x; \omega) = |\nabla I^{(1)}(x; \omega)| = |\nabla I^{(2)}(x; \omega)| \quad (2.3)$$

and therefore is a generalized function (e.g., a function involving Dirac delta functions) that is nonzero when $x$ is on the interface. Depending on the physical context, phase $i$ can be a solid, fluid, or void characterized by some general tensor property. Unless otherwise stated, we will drop $\omega$ from the notation and write $I^{(i)}(x)$ for $I^{(i)}(x; \omega)$ and $M(x)$ for $M(x; \omega)$.

In what follows we will consider the probabilistic descriptions of these and other random variables. It is assumed that the reader is familiar with the basic notion of a probability distribution of a random variable. The books by Cinlar (1975), Priestley (1981), Vanmarcke (1983), Cressie (1993), and Durrett (1996) cover, in varying depths, fundamental concepts in probability theory and stochastic processes.

### 2.2 $n$-Point Probability Functions

#### 2.2.1 Definitions

For fixed $x$, the indicator function $I^{(i)}(x)$ has only two possible values; i.e., for some realizations $\omega$ it will be 0 and some other $\omega$ it will be 1. Thus, the random variable $I^{(i)}(x)$ does not possess a probability density function (if Dirac delta functions are excluded). The probabilistic description of $I^{(i)}(x)$ is given simply by the probability that $I^{(i)}(x)$ is
1, which we write as
\[ P \{ \mathcal{I}^{(i)}(x) = 1 \}. \]

Given this probability, it follows that
\[ P \{ \mathcal{I}^{(i)}(x) = 0 \} = 1 - P \{ \mathcal{I}^{(i)}(x) = 1 \}. \]

A discrete random variable \( X \) can equivalently be specified by its cumulative distribution function \( F(x) \), defined by
\[ F(x) \equiv P \{ X \leq x \}, \]
which has the properties that it is a nondecreasing, right-continuous function of \( x \) with \( F(-\infty) = 0 \) and \( F(+\infty) = 1 \). However, this latter description for the simple binary random variable \( I^{(i)}(x) \) is somewhat awkward notationally and will be avoided.

We should note that the expectation (or average) of any function \( f[I^{(i)}(x)] \) can be expressed as
\[ \langle f[I^{(i)}(x)] \rangle = P \{ I^{(i)}(x) = 1 \} f(1) + P \{ I^{(i)}(x) = 0 \} f(0), \]
where angular brackets denote an ensemble average, i.e., an average over all realizations \( \omega \) of the ensemble. In particular, when \( f[I^{(i)}(x)] = I^{(i)}(x) \), this expectation relation yields
\[ S_1^{(i)}(x) \equiv \langle I^{(i)}(x) \rangle = P \{ \mathcal{I}^{(i)}(x) = 1 \}. \]  
(2.4)

Thus, in light of the 0, 1 nature of the indicator function \( I^{(i)}(x) \), its expectation is exactly the same as the probability \( P \{ \mathcal{I}^{(i)}(x) = 1 \} \). Accordingly, following Torquato and Stell (1982), we refer to \( S_1^{(i)}(x) \) as the one-point probability function for phase \( i \), since it gives the probability of finding phase \( i \) at the position \( x \). It is sometimes also referred to as the one-point correlation function for the phase indicator function.

Knowing a realization \( \mathcal{V}_i(\omega) \) is the same as knowing \( \mathcal{I}^{(i)}(x; \omega) \) for all \( x \) in \( \mathcal{V} \). Therefore, we may regard the random set \( \mathcal{V}_i(\omega) \) as the collection of all random variables \( \mathcal{I}^{(i)}(x) \) for \( x \in \mathcal{V} \). Hence, the probability law of \( \mathcal{V}_i(\omega) \) is described by the finite-dimensional distributions of the random process \( \{ \mathcal{I}^{(i)}(x) : x \in \mathcal{V} \} \). In other words, the probabilistic description of \( \mathcal{V}_i(\omega) \) is given by the joint distribution of \( \mathcal{I}^{(i)}(x_1)\mathcal{I}^{(i)}(x_2)\cdots\mathcal{I}^{(i)}(x_n) \) as \( n \geq 1 \) varies over the integers and \( x_1, x_2, \ldots, x_n \) vary over \( \mathcal{V} \). Of course, since the \( \mathcal{I}^{(i)}(x) \) are either 0 or 1, this amounts to specifying the probabilities
\[ P \{ \mathcal{I}^{(i)}(x_1) = j_1, \mathcal{I}^{(i)}(x_2) = j_2, \ldots, \mathcal{I}^{(i)}(x_n) = j_n \}, \]  
(2.5)
where each \( j_k \) is either 0 or 1.
2.2: n-Point Probability Functions

The expectation of the product \( T^{(i)}(x_1)T^{(i)}(x_2)\cdots T^{(i)}(x_n) \) is a particularly important average. Following the same line of reasoning leading to (2.4), we get

\[
S_n^{(i)}(x_1,x_2,\ldots,x_n) \equiv \left\{ T^{(i)}(x_1)T^{(i)}(x_2)\cdots T^{(i)}(x_n) \right\}
\]

\[
= \mathcal{P} \left\{ T^{(i)}(x_1) = 1, T^{(i)}(x_2) = 1, \ldots, T^{(i)}(x_n) = 1 \right\}
\]

\[
= \text{Probability that } n \text{ points at positions } x_1,x_2,\ldots,x_n \text{ are found in phase } i. \tag{2.6}
\]

Following Torquato and Stell (1982), we will refer to \( S_n^{(i)} \) as the n-point probability function for phase i. Although it is correct to refer to it as an n-point correlation function, we prefer the former term, since it emphasizes its special nature as a probability function. Geometrical probability interpretations of the \( S_n^{(i)} \) are given in Section 2.2.3; see also Figure 1.6 for such interpretations of lower-order \( S_n^{(i)} \). As we will see, the problem of finding the two-point function \( S_2^{(2)} \) bears a close relationship to the classical Buffon needle game of geometrical probability (Kendall and Moran 1962).

The special nature of the indicator function makes it possible to specify the general joint distributions of (2.5) by giving the set of n-point probability functions \( S_1^{(i)}, S_2^{(i)}, \ldots, S_n^{(i)} \) for phase i defined by (2.6). This can be seen by noting that

\[
\mathcal{P} \left\{ T^{(i)}(x_1) = j_1, T^{(i)}(x_2) = j_2, \ldots, T^{(i)}(x_n) = j_n \right\}
\]

\[
= \left( \prod_{k \in K} T^{(i)}(x_k) \prod_{l \in L} [1 - T^{(i)}(x_l)] \right), \tag{2.7}
\]

where \( K = \{k \leq n; j_k = 1\} \) and \( L = \{l \leq n; j_l = 0\} \), and thus the expectation of the product in (2.7) is computable in terms of the set of n-point probability functions \( S_1^{(i)}, S_2^{(i)}, \ldots, S_n^{(i)} \) for phase i.

In particular, one can express the probability \( S_n^{(2)} \) of finding \( n \) points in phase 2 in terms of the set of phase 1 probabilities \( S_1^{(1)}, S_2^{(1)}, \ldots, S_n^{(1)} \). This is easily shown, since

\[
S_n^{(2)}(x_1,x_2,\ldots,x_n) = \left( \prod_{j=1}^{n} [1 - T^{(1)}(x_j)] \right)
\]

\[
= 1 - \sum_{j=1}^{n} S_1^{(1)}(x_j) + \sum_{j<k}^{n} S_2^{(1)}(x_j,x_k)
\]

\[
- \sum_{j<k<l}^{n} S_3^{(1)}(x_j,x_k,x_l) \cdots + (-1)^s S_n^{(1)}(x_1,x_2,\ldots,x_n). \tag{2.8}
\]

Note that the sth sum in (2.8) contains \( n!/[(n-s)!s!] \) terms and carries the factor \((-1)^s\).

Indeed, the probability of finding any subset \( n_1 \) of the \( n \) points in phase 2 and the remaining \( n_2 = n - n_1 \) in phase 1 can be expressed purely in terms of the set of phase 1 probabilities \( S_1^{(1)}, S_2^{(1)}, \ldots, S_n^{(1)} \) (or the set of phase 2 probabilities) (Torquato and Stell 1982). For example, the probability \( S_2^{(12)} \) of two "dissimilar ends" (i.e., the probability
that a point at \( x_1 \) is in phase 1 and a point at \( x_2 \) is in phase 2) is given by

\[
S_{2(12)}(x_1, x_2) = \left( I^{(1)}(x_1)[1 - I^{(1)}(x_2)] \right) = S_1^{(1)}(x_1) - S_2^{(1)}(x_1, x_2). \tag{2.9}
\]

The \( n \)-point probability functions were introduced in the context of determining the effective transport properties of random media by Brown (1955). These statistical descriptors arise in rigorous expressions for the effective transport and mechanical properties of random heterogeneous media, including the following:

- trapping constant or, equivalently, mean survival time (Prager 1963a, Torquato and Rubinstein 1989)

Some general properties of the \( n \)-point probability functions have been studied by Frisch and Stillinger (1963) and Torquato and Stell (1982, 1983a). Moreover, lower-order \( S_n^{(i)} \) were calculated for various sphere models (Torquato and Stell 1983b, Torquato and Stell 1984, Torquato and Stell 1985a). In Chapters 4–8, we discuss the determination of lower-order \( S_n^{(i)} \) for various particle, cell, and random-field models. Chapter 12 describes how to extract such correlation functions from computer simulations and images of real materials.

In what follows we describe some basic properties of the \( n \)-point probability functions.

### 2.2.2 Symmetries and Ergodicity

If the \( n \)-point probability function \( S_n^{(i)} \) depends generally on the absolute positions \( x_1, x_2, \ldots, x_n \), then we say that the medium is statistically inhomogeneous. Indeed, even the one-point function \( S_1^{(i)} \) can depend on the local position \( x_1 \) and then can be interpreted as a position-dependent volume fraction of phase \( i \). Figure 2.2 depicts two examples of statistically inhomogeneous media.

The medium is strictly spatially stationary or strictly statistically homogeneous if the joint probability distributions describing the stochastic process are translationally invariant, i.e., invariant under a translation (shift) of the space origin. Thus, the random set \( \mathcal{V}(\omega) \) generated from the stochastic process \( \{ I^{(0)}(x) : x \in \mathcal{V} \} \) is strictly statistically homogeneous, provided that for some constant vector \( y \) in \( \mathbb{R}^d \)

\[
\mathcal{P} \left\{ I^{(0)}(x_1) = j_1, I^{(0)}(x_2) = j_2, \ldots, I^{(0)}(x_n) = j_n \right\}
= \mathcal{P} \left\{ I^{(0)}(x_1 + y) = j_1, I^{(0)}(x_2 + y) = j_2, \ldots, I^{(0)}(x_n + y) = j_n \right\}.
\]
2.2: n-POINT PROBABILITY FUNCTIONS

Figure 2.2 Two examples of statistically inhomogeneous media. Left panel: Density of the gray phase decreases in the upward direction. Right panel: Density of the gray phase decreases radially from the center.

for all $n \geq 1$, and $x_1, x_2, \ldots, x_n$ in $\mathbb{R}^d$, and $j_1, j_2, \ldots, j_n$ in $\{0, 1\}$. (We emphasize that for this statement to have any meaning for $y$ in $\mathbb{R}^d$, $\mathcal{V}$ must equal $\mathbb{R}^d$, i.e., the volume $V$ must be infinite.) Equivalently, since such probabilities can be expressed in terms of the $n$-point probability functions for phase $i$ (see Section 2.1), $\mathcal{V}(\omega)$ is strictly statistically homogeneous if and only if

$$
S_n^{(i)}(x_1, x_2, \ldots, x_n) = S_n^{(i)}(x_1 + y, x_2 + y, \ldots, x_n + y) = S_n^{(i)}(x_{12}, \ldots, x_{1n}),
$$

for all $n \geq 1$, and $x_1, x_2, \ldots, x_n$ in $\mathbb{R}^d$, and $y$ in $\mathbb{R}^d$, where $x_{jk} = x_k - x_j$. We see that for statistically homogeneous media, the $n$-point probability function depends not on the absolute positions but on their relative displacements. Thus, there is no preferred origin in the system, which in relation (2.10) we have chosen to be the point $x_1$. In particular, the one-point probability function is a constant everywhere, namely, the volume fraction $\phi_i$ of phase $i$, i.e.,

$$
S_1^{(i)} = \phi_i.
$$

The medium is said to be statistically homogeneous but anisotropic if $S_n^{(i)}$ depends on both the orientations and magnitudes of the vectors $x_{12}, x_{13}, \ldots, x_{1n}$ (see Figure 2.3).

When the system is statistically homogeneous, it is meaningful to define volume averages. Roughly speaking, the property of statistical homogeneity states that all regions of space are similar as far as statistical properties of the stochastic process are concerned. This suggests an ergodic hypothesis: i.e., the result of averaging over all realizations of the ensemble is equivalent to averaging over the volume for one realization in the infinite-volume limit. Thus, complete probabilistic information can be obtained from a single realization of the infinite medium. The ergodic hypothesis enables us to replace ensemble averaging with volume averaging in the limit that the volume tends
to infinity, i.e.,

\[
S_n^{(i)}(x_{12}, \ldots, x_{1n}) = \lim_{V \to \infty} \frac{1}{V} \int_{V} I^{(i)}(y) I^{(i)}(y + x_{12}) \cdots I^{(i)}(y + x_{1n}) dy. \quad (2.12)
\]

We will refer to such systems as ergodic media.

The medium is said to be strictly statistically isotropic if the joint probability distributions describing the stochastic process are rotationally invariant, i.e., invariant under rigid-body rotation of the spatial coordinates. For such media, this implies that \( S_n^{(i)} \) depends only on the distances \( x_{jk} = |x_{jk}|, 1 \leq j < k \leq n \) (see Figure 2.3). For example, the two-point function (also known as the autocorrelation function) and three-point function have the form

\[
S_2^{(i)}(x_1, x_2) = S_2^{(i)}(x_{12}), \quad (2.13)
\]

\[
S_3^{(i)}(x_1, x_2, x_3) = S_3^{(i)}(x_{12}, x_{13}, x_{23}). \quad (2.14)
\]

Relation (2.14) for \( S_3^{(i)} \) remains invariant under all permutations of its arguments \( x_{12}, x_{13}, \) and \( x_{23} \). Both \( S_2^{(i)} \) and \( S_3^{(i)} \) can be obtained from any planar cut through a three-dimensional medium when it is isotropic (see Figure 2.4). In practice, this means that the two- and three-point functions can be extracted from cross-sections or two-dimensional images of the isotropic sample (see Figure 1.6), provided that the planar representation is sufficiently large. Moreover, the autocorrelation function \( S_2^{(i)} \) can also be found from a linear cut through an isotropic medium (see Figure 2.4).

In general, the \( n \)-point probability functions for \( n \geq 2 \) cannot be expressed in terms of lower-order \( q \)-point functions, \( q < n \). However, in the special case of a medium possessing “phase-inversion” symmetry at \( \phi_1 = \phi_2 = 1/2 \), it is possible to determine the odd-order probability functions \( S_{2m+1}^{(i)} \) from \( S_{2m}^{(i)}, S_{2m-1}^{(i)}, \ldots, S_1^{(i)} \). We say that a random medium possesses phase-inversion symmetry if the morphology of phase 1 at volume fraction \( \phi_1 \) is statistically identical to that of phase 2 in the system where the volume fraction \( \phi_2 \) is
2.2: \( n \)-Point Probability Functions

\[ S(n) \equiv \{x_1, x_2, \ldots, x_n\} \]

\( S(n) \) can be obtained from a planar cut and \( S(n) \) can be extracted from a linear cut.

**Figure 2.4** Planar and linear cuts through three-dimensional isotropic media. In the infinite-system limit, \( S(n) \) and \( S(n) \) can be obtained from a planar cut and \( S(n) \) can be extracted from a linear cut.

**Figure 2.5** Examples of systems possessing phase-inversion symmetry (top) and phase-inversion asymmetry (bottom). In the leftmost and rightmost systems, the volume fractions of phase 1 are \( \phi_1 \) and \( 1 - \phi_1 \), respectively.

Fraction of phase 1 is \( 1 - \phi_1 \) (see Figure 2.5) and hence

\[ S(n) = S(n) \quad (2.15) \]

where \( x_n = \{x_1, x_2, \ldots, x_n\} \). The notion of phase-inversion symmetry introduced here quantitatively generalizes the notion of a "symmetric" two-phase material at \( \phi_1 = \phi_2 = 1/2 \) [discussed by Beran (1968)] to arbitrary volume fractions. Examples of systems with phase-inversion symmetry are symmetric-cell materials described in Chapter 8 (see Figures 8.5 and 8.6). To a good approximation, interpenetrating cermets, such as
the one depicted in Figure 1.2, can be made to have phase-inversion symmetry. At the point \( \phi_1 = \phi_2 = 1/2 \), a medium possessing phase-inversion symmetry has the special property that the \( n \)-point probability functions for each phase are identical, or in other words, the geometry of one phase is statistically indistinguishable from the other. Thus, from (2.8),

\[
2S_{2m+1}^{(2)} = 1 - \sum S_1^{(1)} + \sum S_2^{(1)} - \sum S_3^{(1)} + \cdots + (-1)^{2m} \sum S_{2m}^{(1)}. \tag{2.16}
\]

Therefore, for a medium with phase-inversion symmetry at \( \phi_1 = \phi_2 = 1/2 \), the odd-order probability functions \( S_{2m+1}^{(i)} \) can be expressed in terms of all the lower-order probability functions. For example, for such a symmetric medium with \( m = 1 \), we deduce from (2.16) that

\[
S_3^{(i)}(x_1, x_2, x_3) = \frac{1}{2} \left[ S_2^{(i)}(x_1, x_2) + S_2^{(i)}(x_1, x_3) + S_2^{(i)}(x_2, x_3) - \frac{1}{2} \right]. \tag{2.17}
\]

However, the even-order functions \( S_{2m}^{(i)} \) cannot be expressed in terms of the lower-order functions, since the last term in (2.8) is always positive.

It is noteworthy that most random media do not possess phase-inversion symmetry. A common example of a system with such phase-inversion asymmetry is a dispersion of particles (see Figure 2.5 and Chapters 3–7).

### 2.2.3 Geometrical Probability Interpretation

The geometrical-probabilistic significance of the \( n \)-point probability function is easily seen for any microstructure. Let \( F_n^{(i)} \) be a polyhedron with \( n \) vertices located at positions \( x_1, x_2, \ldots, x_n \). Then for statistically inhomogeneous media, \( S_n^{(i)} \) is the probability that all \( n \) vertices of \( F_n^{(i)} \) with fixed positions \( x_1, x_2, \ldots, x_n \) lie in \( V_i \). For statistically homogeneous but anisotropic media, \( S_n^{(i)} \) is the probability that all \( n \) vertices of \( F_n^{(i)} \) lie in \( V_i \) when the polyhedron is randomly placed in the volume at fixed orientation i.e., over all translations of the polyhedron. For statistically isotropic media, \( S_n^{(i)} \) can be interpreted as the probability that all \( n \) vertices of \( F_n^{(i)} \) lie in \( V_i \) when the polyhedron is randomly placed in the volume, i.e., over all translations and solid-body rotations of the polyhedron.

In light of the above, one can view the determination of \( S_n^{(i)} \) as a generalization of the Buffon needle game (Kendall and Moran 1962), in which one tosses a needle of length \( x \) onto a grid of equidistant parallel lines separated by a distance \( L \geq x \). The probability \( p \) that the needle crosses the lines is inversely proportional to \( \pi \); specifically, \( p = 2x/(\pi L) \). One can see that \( p \) is closely related to the probability of two dissimilar ends given by (2.9) and thus to the two-point function \( S_2^{(i)} \).

For statistically homogeneous media composed of identical spheres of radius \( R \) (phase 2) distributed throughout another material (phase 1), we may infer yet another geometrical-probabilistic interpretation of these functions (Torquato and Stell 1982). The function \( S_n^{(1)}(x_1, x_2, \ldots, x_n) \) may be interpreted to be the probability that a region \( \Omega^{(i)} \), the union volume of \( n \) spheres of radius \( R \) centered at \( x_1, x_2, \ldots, x_n \), contains no sphere centers. (Chapters 5 and 6 discuss the evaluation of the \( n \)-point probability
functions for such models.) A similar interpretation may be inferred for particles of arbitrary shape with a size distribution.

2.2.4 Asymptotic Properties and Bounds

We determine asymptotic properties of and bounds on $S_n^{(i)}$ that apply to any statistically inhomogeneous two-phase random medium.

When any subset of $q + 1$ points coincide, so that $x_{i_1} = x_{i_2} = \cdots = x_{i_{q+1}}$, we have

$$S_n^{(i)}(x^n) = S_n^{(i)}(x_1, \ldots, x_{i_1}, x_{i_2}, \ldots, x_{i_{q+1}}, \ldots, x_n)$$

$$= \left\{ \tau^{(i)}(x_1) \cdots \tau^{(i)}(x_{i_1}) \tau^{(i)}(x_{i_2}) \cdots \tau^{(i)}(x_{i_{q+1}}) \cdots \tau^{(i)}(x_n) \right\},$$

where a bar above a quantity indicates its absence.

Let us now consider partitioning the set $\{x_1, x_2, \ldots, x_n\}$ into $L$ subsets $\{x_1\}$, $\{x_2, x_3\}$, $\{x_4, x_5, x_6\}$, $\ldots$. Let all of the relative distances between the $m$ elements of these subsets remain bounded, and let $F_m$ be the polyhedron with $m$ vertices located at the positions associated with the $j$th subset. We denote the centroid of $F_m$ by $R_j$. Let $R_{jk}$ be the relative distance between the centroids of $F_m$ and $F_m$, where $j$ and $k$ are all possible values such that $1 \leq j < k \leq L$. A system is said to possess no long-range order if the events $R_{jk} \to \infty$ for all $i$ and $j$ are statistically independent, i.e., the $n$-point function factorizes into $L$ products as follows:

$$\lim_{\text{all } R_{\alpha\beta} \to \infty} S_n^{(i)}(x_1, x_2, \ldots, x_n)$$

$$= \left\{ \tau^{(i)}(x_1) \right\} \left\{ \tau^{(i)}(x_2) \tau^{(i)}(x_3) \right\} \left\{ \tau^{(i)}(x_4) \tau^{(i)}(x_5) \tau^{(i)}(x_6) \right\} \cdots$$

$$= S_1^{(i)}(x_1) S_2^{(i)}(x_2, x_3) S_3^{(i)}(x_4, x_5, x_6) \cdots \quad (2.19)$$

The above partition, however, is just one of the possible ways to partition the set $\{x_1, x_2, \ldots, x_n\}$. In general, for any partition into sets $\{\gamma\}$, each with $m(\gamma)$ elements, we have in the absence of long-range order that

$$\lim_{\text{all } R_{\alpha\beta} \to \infty} S_n^{(i)}(x_1, x_2, \ldots, x_n) = \prod_{\gamma} S_m^{(i)}(x_1, x_2, \ldots, x_{m(\gamma)}),$$

where $R_{\alpha\beta}$ is the distance between the centroids of sets $\alpha$ and $\beta$. An example of a system with long-range order, and thus one that does not obey the asymptotic result (2.20), is an infinitely large crystalline (periodic) array of identical spheres.

For concreteness, we apply the aforementioned general asymptotic results for the cases $n = 2$ and $n = 3$ for statistically homogeneous media without long-range order. We have for $n = 2$

$$\lim_{x_{12} \to -\infty} S_2^{(i)}(x_{12}) = \phi_i, \quad \lim_{x_{12} \to \infty} S_2^{(i)}(x_{12}) = \phi_i^2,$$ \quad (2.21)

and for $n = 3$, under permutations of the distances $x_{12}$, $x_{13}$, and $x_{23}$,

$$\lim_{x_{12} \to 0, x_{13} \to 0} S_3^{(i)}(x_{12}, x_{13}) = \phi_i, \quad \lim_{x_{23} \to 0} S_3^{(i)}(x_{12}, x_{13}) = S_2^{(i)}(x_{12}),$$ \quad (2.22)
\[
\lim_{x_{12} \to \infty} s_3^{(i)}(x_{12}, x_{13}) = \phi_i s_2^{(i)}(x_{12}), \quad \lim_{x_i \to \infty} S_3^{(i)}(x_{12}, x_{13}) = \phi_i^3.
\] (2.23)

Since \(0 \leq \mathcal{I}^{(i)}(x) \leq 1\) for all \(x\) in \(\mathcal{V}\), we have the elementary bounds
\[
0 \leq S_n^{(i)}(x^n) \leq S_{n-1}^{(i)}(x^{n-1}), \quad \text{for all } x^n \text{ and } n \geq 2, \tag{2.24}
\]
\[
0 \leq S_1^{(i)}(x_1) \leq 1, \quad \text{for all } x_1. \tag{2.25}
\]

The one-point function \(S_1^{(i)}(x_1)\) (equal to the volume fraction \(\phi_i\) for homogeneous media) is an upper bound on \(S_n^{(i)}(x^n)\) for all \(x^n\) and \(n\).

A word on notation is in order here. When possible, we will suppress the superscript in \(S_n^{(i)}\) indicating phase \(i\) and simply denote the function by
\[
S_n(x_1, x_2, \ldots, x_n).
\]

In such instances, the phase to which it refers will be specified.

### 2.2.5 Two-Point Probability Function

As noted earlier, the two-point or autocorrelation function \(S_2(r) \equiv S_2^{(1)}(r)\) for statistically homogeneous media can be obtained by randomly tossing line segments of length \(r \equiv |r|\) with a specified orientation and counting the fraction of times the end points fall in phase 1 (see Figure 2.6). The function \(S_2(r)\) provides a measure of how the end points of a vector \(r\) in phase 1 are correlated. For isotropic media, \(S_2(r)\) attains its maximum value of \(\phi_1\) at \(r = 0\) and eventually decays (usually exponentially fast) to its asymptotic value of \(\phi_2^1\).

The form of \(S_2(r)\) provides information about certain gross features of the microstructure, as discussed in detail in Chapter 5–7 and 12. For example, two different autocorrelation functions for isotropic particle systems and their associated microstructures are shown in Figure 2.7. In the first case of nonoverlapping disks (Section 5.2.1), \(S_2(r)\) exhibits oscillations for small \(r\) (short-range order) with periodicity roughly equal to the particle diameter \(D\). This is reflective of spatial correlations between the particles due to exclusion-volume (hard-core) effects. In the second case of overlapping disks (Section 5.1.1), \(S_2(r)\) exhibits no short-range order but rather monotonically decays to its asymptotic value at exactly \(r = D\). This indicates that particles of characteristic size \(D\) are spatially uncorrelated. However, the form of \(S_2\) here belies the fact that there are a statistically significant number of clusters in the system that are appreciably larger than \(D\) (see Figure 2.7). Quantities that are better able to capture cluster and percolation information are discussed in Section 2.7 and Chapters 9 and 10.

We see that one must be careful in interpreting length scales associated with \(S_2\). To further remark on this point, it is convenient to define, for statistically homogeneous media, the autocovariance of phase 1
\[
\chi(r) \equiv \left[\mathcal{I}^{(1)}(x) - \phi_1\right]\left[\mathcal{I}^{(1)}(x + r) - \phi_1\right] = S_2(r) - \phi_1^2, \tag{2.26}
\]
Figure 2.6  A schematic depicting events that contribute to lower-order functions for random media of arbitrary microstructure. Shown are the two-point probability function $S_2 \equiv S_2^{(2)}$ for phase 1 (white region) defined by (2.6) with $n = 2$, surface–void and surface–surface functions $F_{sv}$ and $F_{ss}$ defined by (2.61) and (2.62), lineal-path function $L \equiv L^{(1)}$ defined by (2.66), and the pore-size density function $P$ defined by (2.77).

Figure 2.7  The two-point probability function $S_2(r)$ for phase 1 for two different systems at $\phi_1 = \phi_2 = 1/2$: a correlated system of nonoverlapping disks (top) and an uncorrelated system of overlapping disks (bottom). Here $D$ is a disk diameter.
where $I^{(1)}(x) - \phi_1$ is a random variable with zero mean, and $I^{(1)}$ is the indicator function (2.1) for phase 1. The autocovariance $\chi(r)$ has the limiting values $\chi(0) = \phi_1 \phi_2$ and $\chi(\infty) = 0$, the latter applying in the absence of long-range order. Moreover, the function $\chi(r)$ must be positive semidefinite (nonnegative) in the sense that for any finite number of spatial locations $r_1, r_2, \ldots, r_m$ in $\mathbb{R}^d$ and arbitrary real numbers $a_1, a_2, \ldots, a_m$,

$$\sum_{i=1}^{m} \sum_{j=1}^{m} a_i a_j \chi(r_i - r_j) \geq 0. \tag{2.27}$$

A variety of length scales associated with $S_2$ can be defined. One length scale, which we refer to as $\ell_S$, is rooted in rigorous considerations:

$$\ell_S = \left\{ \int_0^{\infty} r \chi(r) dr \right\}^{1/2} = \left\{ \int_0^{\infty} r [S_2(r) - \phi_2^2] dr \right\}^{1/2}. \tag{2.28}$$

This length scale arises in rigorous bounds on the fluid permeability (Prager 1961) and trapping constant (Rubinstein and Torquato 1988) of three-dimensional isotropic random porous media. Since application of (2.8) for any statistically homogeneous medium leads to the result that the autocovariance of phase 1 is equal that of phase 2, i.e.,

$$\chi(r) = S_2^{(1)}(r) - \phi_1^2 = S_2^{(2)}(r) - \phi_2^2, \tag{2.29}$$

it is clear that measures based on the two-point function for the phases are not capable of distinguishing length scales of phase 1 from length scales of phase 2. For example, for isotropic media, the length scale defined by (2.28) for phase 1 is identical to the corresponding one for phase 2.

Debye and Bueche (1949) showed that the two-point probability function $S_2(r)$ of an isotropic porous solid can also be obtained via scattering of radiation. Here phases 1 and 2 are the void and solid phases, respectively. The normalized scattered intensity $i(k)$ at a wave number $k$ for a three-dimensional isotropic porous medium of volume $V$ is proportional to the Fourier transform of the autocovariance $\chi(r)$, i.e.,

$$i(k) = 4\pi V n_e^2 \int_0^{\infty} \chi(r) r^2 \frac{\sin(kr)}{kr} \, dr, \tag{2.30}$$

where $n_e$ is the mean density of electrons. To get the real-space two-point function $S_2(r)$ from the scattered intensity $i(k)$, one need only perform the inverse Fourier transform:

$$\chi(r) = S_2(r) - \phi_1^2 = \frac{1}{2\pi^2 V n_e^2} \int_0^{\infty} i(k) k^2 \frac{\sin(kr)}{kr} \, dk. \tag{2.31}$$

The accuracy of (2.31) depends on whether the “experimentally bandlimited” scattering curve $i(k)$ approximates sufficiently closely the entire function $i(k)$. The spectral properties of $\chi$ will be explored further below.

It has been shown (Guinier and Fournet 1955, Debye, Anderson and Brumberger 1957) that the expansion of the two-point probability function $S_2(r)$ through terms
2.2: \( n \)-Point Probability Functions

linear in \( r \) for any three-dimensional isotropic medium is given by

\[
S_2(r) = \phi_1 - \frac{s}{4} r + O(r^2),
\]

(2.32)

where \( s \) is the specific surface, defined to be the interface area per unit volume. This formula is valid for any three-dimensional, isotropic two-phase heterogeneous medium, porous or not. The coefficient of the linear term \( r \) in (2.32) can be shown (Guinier and Fournet 1955, Debye et al. 1957) to be proportional to the leading term in the asymptotic expansion of the scattering curve \( i(k) \) for \( k \to \infty \), i.e.,

\[
i(k) \sim \frac{2\pi n_0^2 s V}{k^4}, \quad k \to \infty.
\]

(2.33)

Thus, given that this asymptotic region can be reached with the value of the wavelength employed, this formula provides a measurement technique to determine the specific surface \( s \) of isotropic porous media. Berryman (1987) has shown that formula (2.32) applies to anisotropic media as well after angular averaging.

We see that the derivative of \( S_2(r) \) at the origin is proportional to the specific surface \( s \) for three-dimensional isotropic media. Indeed, for \( d \)-dimensional isotropic media, we can extend the arguments of Debye et al. (1957) to obtain for finite \( s \) that

\[
\left. \frac{dS_2^{(i)}}{dr} \right|_{r=0} = \frac{\omega_{d-1}}{\omega_d d} s,
\]

(2.34)

where \( S_2^{(i)} \), more generally, is the two-point probability function for phase \( i \) and

\[
\omega_d = \frac{\pi^{d/2}}{\Gamma(1+d/2)}
\]

is the \( d \)-dimensional volume of a sphere of unit radius, with \( \omega_0 \equiv 1 \). For the first three space dimensions, we have that

\[
\left. \frac{dS_2^{(i)}}{dr} \right|_{r=0} = \begin{cases} 
-s/2, & d = 1, \\
-s\pi, & d = 2, \\
-s/4, & d = 3.
\end{cases}
\]

(2.36)

Kirste and Porod (1962) examined the next term in the asymptotic expansion of the scattering curve \( i(k) \) (proportional to \( k^{-6} \)). This was done for a special isotropic medium whose surface separating the void phase from the solid phase could be developed locally in a canonical power series in the local derivatives of the principal radii of curvature \( R_1, R_2 \) of the surface (Frisch and Stillinger 1963). The two-point probability function is then given by

\[
S_2(r) = \phi_1 - \frac{s}{4} r \left[ 1 - r^2 \left\{ \frac{1}{12 S} \int K_1 K_2 \, dA + \frac{1}{32 S} \int (K_1 - K_2)^2 \, dA \right\} \right] + \cdots,
\]

(2.37)

where the integrals are taken over the interface, \( S \) is the mean interface area, \( K_1 = 1/(2R_1), K_2 = 1/(2R_2) \), and \( r < 1/\max(K_1, K_2) \). The first integral in relation (2.37) is
related to the topological genus $p$ of the surface by the Gauss–Bonnet integral formula

$$4 \int K_1 K_2 \, dA = 4\pi(1 - p).$$

Notice that there is no quadratic term $r^2$ in (2.37). Relation (2.37) is valid only for surfaces containing no edges, corners, multiple points, or generally any singular points at which the radii of convergence of the aforementioned canonical expansion of the surface shrink to zero.

Therefore, (2.37) necessarily breaks down for isotropic dispersions of convex impenetrable particles that form interparticle contacts. Indeed, Frisch and Stillinger (1963) showed that for random systems of identical three-dimensional impenetrable spheres of diameter $D$, $S_2(r)$ is given by

$$S_2(r) = \phi_1 - \frac{s}{4} r + \frac{Z\phi_1}{4} \left( \frac{r}{D} \right)^2 + O(r^3),$$

where $Z$ is the mean coordination number defined to be the average number of contacts a given sphere has with its neighbors.

**Realizability and Spectral Representation**

What are the existence conditions for a valid (i.e., physically realizable) autocorrelation or autocovariance function? In the study of time series (one-dimensional random processes) (Priestley 1981) and the theory of turbulence (Batchelor 1959), it is well known that there are certain nonnegativity conditions involving the spectral representation of the autocovariance $\chi(r)$ that must be obeyed. Here we investigate such results for statistically homogeneous two-phase random media in any space dimension $d$ (Torquato 1999). Importantly, we show that these nonnegativity conditions are necessary but not sufficient conditions that a valid autocovariance $\chi(r)$ of a statistically homogeneous two-phase random medium must meet. We also show that if the random medium is also statistically isotropic, there are $d$ different nonnegativity conditions that one can exploit (Torquato 1999).

Consider an arbitrary stochastically continuous homogeneous process $\{Y(x) : x \in \mathbb{R}^d\}$ with mean $\mu = \langle Y \rangle$ and autocovariance function

$$\chi(r) = \langle [Y(x) - \mu][Y(x + r) - \mu] \rangle.$$  \hspace{1cm} (2.39)

It follows that

$$\chi(0) = \langle Y^2 \rangle - \mu^2$$  \hspace{1cm} (2.40)

and from Schwarz's inequality that

$$|\chi(r)| \leq \langle Y^2 \rangle - \mu^2.$$  \hspace{1cm} (2.41)

We now state the generalization of the Wiener–Khintchine theorem (Priestley 1981) developed for processes in time to this multidimensional spatial stochastic process (Cressie 1993).
Theorem 2.1 A necessary and sufficient condition for the existence of an autocovariance function $\chi(r)$ of a general stochastically continuous homogeneous process $\{Y(x) : x \in \mathbb{R}^d\}$ is that it has the spectral (Fourier–Stieltjes) representation

$$\chi(r) = \frac{1}{(2\pi)^d} \int e^{ik \cdot r} dZ(k),$$

(2.42)

where $Z(k)$ is a nonnegative bounded measure. If $\chi(r)$ is absolutely integrable, i.e.,

$$\int_{\mathbb{R}^d} |\chi(r)| \, dr < \infty,$$

(2.43)

then $dZ(k)$ can be written as $\tilde{\chi}(k) dk$ and thus (2.42) becomes the standard Fourier representation

$$\chi(r) = \frac{1}{(2\pi)^d} \int \tilde{\chi}(k) e^{ik \cdot r} dk,$$

(2.44)

where the spectral function $\tilde{\chi}(k)$ is positive semidefinite, i.e.,

$$\tilde{\chi}(k) = \int \chi(r) e^{-ik \cdot r} \, dr \geq 0, \quad \text{for all } k.$$

(2.45)

Remarks:
1. This theorem may be proved by exploiting a general theorem due to Bochner (1936) that any continuous function $f(r)$ is positive semidefinite in the sense of (2.27) if and only if it has a Fourier–Stieltjes representation with a nonnegative bounded measure. The continuity of $\chi(r)$ follows directly from the requirement that the process $Y(x)$ is stochastically continuous. Thus, Theorem 2.1 may be regarded to be a special case of Bochner’s theorem.
2. The quantity $Z/\chi(0)$ is often called the spectral distribution function. If $dZ(k) = \tilde{\chi}(k) dk$ where $\tilde{\chi}(k) \geq 0$, then $\tilde{g}(k) \equiv \tilde{\chi}(k)/\chi(0)$ is referred to as the spectral density, since it has the properties of a probability density function, i.e., $\int \tilde{g}(k) dk = 1$ and $\tilde{g}(k) \geq 0$.

Although the existence condition of Theorem 2.1 is known in the context of random media (Torquato 1999), it is not commonly known that not all autocovariances can be generated by stochastic processes $\{I^{(i)}(x) : x \in \mathbb{R}^d\}$ that take only two values, zero or one (Section 2.1). In other words, the class $B$ of autocovariances that comes from the binary stochastic process $\{I^{(i)}(x) : x \in \mathbb{R}^d\}$ is a subclass of the total class that comes from the general process $\{Y(x) : x \in \mathbb{R}^d\}$ and meets the existence condition of Theorem 2.1. Therefore, the condition of Theorem 2.1 is only necessary but not sufficient for $B$. An example of a function $\chi(r)$ that meets the requirement of Theorem 2.1 but may not belong to $B$ has been analyzed by Torquato (1999) and is discussed in Section 12.6 [cf. (12.19)].

The task of determining the necessary and sufficient conditions that $B$ must possess is very complex. In the context of stochastic processes in time (one-dimensional processes), it has been shown that autocovariances in $B$ must not only meet the condition of Theorem 2.1 but another condition on “corner-positive” matrices (McMillan...
Since little is known about corner-positive matrices, this theorem is very difficult to apply in practice. Thus, a meaningful characterization of $B$ remains an open and interesting problem, especially in the context of $d$-dimensional two-phase random media.

We will not attempt to address the complete characterization of $B$ here but instead will summarize some simple necessary conditions, in addition to Theorem 2.1, that characterize $B$ (Torquato 1999). We have seen that since $S_2^{(i)}(0) = \langle [I^{(i)}]_2^2 \rangle = \phi_i$, the autocovariance at the origin is given by

$$\chi(0) = \phi_1 \phi_2, \quad \text{for all } \chi(r) \in B,$$

which should be compared to formula (2.40) for general stochastic processes. Application of the inequalities (2.24) to the two-point function $S_2^{(i)}(r)$ for homogeneous media yield the bounds $0 \leq S_2^{(i)}(r) \leq \phi_i$, which are a direct consequence of the binary (i.e., zero-one) nature of the process. Combination of these bounds with relations (2.26) and (2.29) give the corresponding bounds that all autocovariances in $B$ must obey:

$$-\min(\phi_1^2, \phi_2^2) \leq \chi(r) \leq \phi_1 \phi_2, \quad \text{for all } \chi(r) \in B. \quad (2.47)$$

Unlike general stochastic processes for which (2.41) applies, here we have both upper and lower bounds on $\chi(r)$, the lower bound deriving from the pointwise nonnegativity of $S_2^{(i)}(r)$. Of course, in the absence of long-range order, $\chi(\infty) = 0$, but this condition is not special to binary processes. Another consequence of the binary nature of the process in the case of isotropic media is that the specific surface $s$ is strictly positive when both phases are present and so (2.34) yields that

$$\left. \frac{dS_2^{(i)}}{dr} \right|_{r=0} = \left. \frac{d\chi}{dr} \right|_{r=0} < 0, \quad \text{for all } 0 < \phi_i < 1 \text{ and } \chi(r) \in B. \quad (2.48)$$

In other words, the slope of $\chi(r)$ at $r = 0$ is strictly negative for nontrivial volume fractions in the range $0 < \phi_i < 1$. Thus, an autocovariance $\chi(r)$ of an isotropic two-phase random medium can neither have a zero nor a positive slope at $r = 0$ when $0 < \phi_i < 1$ (Yeong and Torquato 1998a). Note that when the Fourier transform $\tilde{\chi}(k)$ exists, condition (2.45) implies only that the slope of $\chi(r)$ at $r = 0$ is nonpositive (i.e., negative semidefinite). We recall from an earlier part of this section that $S_2$ and thus $\chi(r)$ will generally possess not only a linear term $r$ but a quadratic term $r^2$ for sufficiently small $r$ [cf. (2.38)], although the quadratic term will be zero for a certain subclass of $B$ [cf. (2.37)].

Although the nonnegativity condition of Theorem 2.1 or, equivalently, condition (2.27) is not sufficient to ensure that $\chi(r)$ belongs to $B$, either condition still provides a stringent test that all physically realizable $\chi(r)$ must meet. Experience shows that the nonnegativity condition coupled with the “binary” conditions (2.46)–(2.48) provide a practical (if not exact) means to test the validity of proposed autocovariances for a wide class of two-phase random media; see Yeong and Torquato (1998a), Cule and Torquato (1999), Torquato (1999), and Section 12.6.
Practically speaking, it is difficult to apply the nonnegativity condition \(2.27\) in order to test the validity of a proposed \(\chi(r)\). For a wide class of statistically homogeneous two-phase media, \(\chi(r)\) tends to zero fast enough for the Fourier transform \(\hat{\chi}(k)\) to exist \([\text{cf. (2.43)}]\). In such instances, it is much easier to apply the nonnegativity condition \(2.45\) to test the validity of a proposed \(\chi(r)\). In what follows, we will assume that the spectral function \(\hat{\chi}(k)\) exists and proceed to show that there are \(d\) different nonnegativity conditions that one can exploit if the random medium is also statistically isotropic \((\text{Torquato 1999})\).

The Fourier transform of some absolutely integrable function \(f(r)\) in \(d\) dimensions is given by

\[
\tilde{f}(k) = \int f(r)e^{-ik \cdot r}dr,
\]

and the associated inverse operation is defined by

\[
\hat{f}(r) = \frac{1}{(2\pi)^d} \int \tilde{f}(k)e^{ik \cdot r}dk,
\]

where \(k\) is the wave vector. When the function depends only on the magnitude \(r = |r|\), then we have the following simpler expressions for \(d = 1, 2, \text{and } 3:\)

\[
\tilde{f}(k) = 2 \int_0^\infty f(r) \cos krdr, \quad f(r) = \frac{1}{\pi} \int_0^\infty \tilde{f}(k) \cos krdk, \quad d = 1, \quad (2.51)
\]

\[
\tilde{f}(k) = 2\pi \int_0^\infty f(r)rJ_0(kr)dr, \quad f(r) = \frac{1}{2\pi} \int_0^\infty \tilde{f}(k)kJ_0(kr)dk, \quad d = 2, \quad (2.52)
\]

\[
\tilde{f}(k) = \frac{4\pi}{k} \int_0^\infty f(r)r \sin krdr, \quad f(r) = \frac{1}{2\pi^2} \int_0^\infty \tilde{f}(k)k \sin krdk, \quad d = 3, \quad (2.53)
\]

where \(k = |k|\) and \(J_0(x)\) is the zeroth-order Bessel function of the first kind.

The nonnegativity condition \(2.45\) holds for any wave vector \(k\). In particular, it holds for \(k = 0\), i.e., the real-space volume integral of \(\chi(r)\) must be positive semidefinite or

\[
\int [S_2(r) - \phi_1^2]dr \geq 0. \quad (2.54)
\]

The integral condition \(2.54\) holds for statistically homogeneous but anisotropic media. This nonnegativity condition could also have been obtained immediately from the work of Lu and Torquato (1990a) on the coarseness, or standard deviation of the local volume fraction. In particular, it can be obtained from the asymptotic expression \((11.20)\) for large window sizes and the fact that the coarseness is positive semidefinite \((\text{see Chapter 11})\).

If the medium is also statistically isotropic, then the two-point correlation function depends only on the magnitude \(r = |r|\), and \(2.54\) simplifies as

\[
\int_0^\infty [S_2(r) - \phi_1^2]r^{d-1}dr \geq 0. \quad (2.55)
\]
Here we have used the fact that $dr = \Omega(d) r^{d-1} dr$ in a $d$-dimensional spherical coordinate system, where

$$\Omega(d) = \frac{2\pi^{d/2}}{\Gamma(d/2)}$$

(2.56)

is the positive $d$-dimensional solid angle and $\Gamma(x)$ is the gamma function. If we let

$$M_n = \int_0^\infty [S_2(r) - \phi_1^2] r^n dr$$

(2.57)

denote the $n$th moment of the function $S_2(r) - \phi_1^2$, then (2.55) states that the moment $M_{d-1}$ is positive semidefinite for isotropic two-phase random media in $d$ dimensions.

Thus far, we have shown that there is one nonnegativity condition for a $d$-dimensional homogeneous medium, namely, condition (2.45). However, the symmetry possessed by isotropic media enables one to obtain $d$ different nonnegativity conditions. In particular, Torquato (1999) demonstrated that for an isotropic autocorrelation function $S_2(r)$ in $d$ dimensions, the one-, two-, ... , and $d$-dimensional Fourier transforms of $\chi(r)$ are all positive semidefinite. Let $\tilde{\chi}(k; m)$ denote the $m$-dimensional Fourier transform of $\chi(r)$. Then, for all values of the wave number $k$ (i.e., $k \geq 0$), we have that

$$\tilde{\chi}(k; m) \geq 0, \quad m = 1, 2, \ldots, d.$$  

(2.58)

This is easily proved by recalling that for $d$-dimensional isotropic media, $S_2(r)$ can be extracted from a cut of the $d$-dimensional medium with an $m$-dimensional subspace ($m = 1, 2, \ldots, d - 1$). The $m$-dimensional subspace represents a lower-dimensional random medium but with the same $S_2$ as in $d$ dimensions. Thus, the nonnegativity condition (2.45) applies to this lower-dimensional random medium, yielding (2.58).

It follows immediately from (2.55) and (2.58) that

$$M_n \geq 0, \quad n = 0, 1, \ldots, d - 1.$$  

(2.59)

Thus, for three-dimensional isotropic media, the zeroth, first, and second moments of $S_2(r) - \phi_1^2$ must be positive semidefinite. For two-dimensional isotropic media, the zeroth and first moments must be positive semidefinite, whereas for one-dimensional media, only the zeroth moment need be positive semidefinite. The real-space conditions (2.54) and (2.59) are special cases of the more general and restrictive integral conditions (2.45) and (2.58), respectively.

Algorithms have been developed recently to construct realizations of two-phase random media with specified microstructural correlation functions (see Chapter 12). One can use the integral nonnegativity conditions (2.45) and (2.58) as well as the “binary” conditions (2.46)-(2.48) to test whether hypothetical autocorrelation or autocovariance function meet necessary realizability conditions. The zero-wave number integral conditions (2.54) and (2.59) may first be checked, since they are easier to compute than the full Fourier transform; if they are negative, then there is no need to compute the Fourier transform. We note that nonnegativity conditions on certain integrals involving the three- and two-point probability functions have also been obtained (Torquato 1980, Milton 1981b, Milton and McPhedran 1982, Torquato 1999, Markov 1999).
Surface Correlation Functions

Surface correlation functions contain information about the random interface \( \partial V \) and are of basic importance in the trapping and flow problems. In this context, we will let phase 1 denote the fluid or “void” phase, and phase 2 the “solid” phase. The simplest surface correlation function is the specific surface \( s(x) \) (interface area per unit volume) at point \( x \), which is a one-point correlation function for statistically inhomogeneous media, i.e.,

\[
s(x) = \langle M(x) \rangle, \tag{2.60}
\]

where \( M(x) \) is the interface indicator function given by (2.3). Note that the nonnegative specific surface cannot be interpreted as a probability, since the chance that a point at \( x \) lands on the interface is zero. For homogeneous media, it is a constant everywhere, which we will denote simply by \( s \).

Two-point surface correlation functions for statistically inhomogeneous media are defined by

\[
F_{sv}(x_1, x_2) = \langle M(x_1) I(x_2) \rangle, \tag{2.61}
\]

\[
F_{ss}(x_1, x_2) = \langle M(x_1) M(x_2) \rangle, \tag{2.62}
\]

where \( I(x) \equiv I^{(1)}(x) \) is the indicator function for the void phase. These functions are called the surface–void and surface–surface correlation functions, respectively, and they arise in rigorous bounds on the trapping constant (Doi 1976, Rubinstein and Torquato 1988) and fluid permeability (Doi 1976, Rubinstein and Torquato 1989). For homogeneous media they depend only on the displacement \( r = x_2 - x_1 \), and for isotropic media they depend only on the distance \( r = |r| \). The functions \( F_{sv} \) and \( F_{ss} \) can be obtained from any plane cut through a medium that is isotropic. Figure 2.6 shows events that contribute to these functions. When the two points are far from one another in systems without long-range order, \( F_{sv}(x_1, x_2) \to s(x_1) s(x_2) \) and \( F_{ss}(x_1, x_2) \to s(x_1) s(x_2) \).

In the case of homogeneous media (of special interest to us in subsequent chapters), these asymptotic results for \( |r| \to \infty \) reduce to

\[
F_{sv}(r) \to \langle |M| I \rangle = s \phi_1, \quad F_{ss}(r) \to \langle |M|^2 \rangle = s^2, \tag{2.63}
\]

where \( \phi_1 = \langle I \rangle \) is the porosity, or the volume fraction of the void phase.

The generalization to an \( n \)-point surface correlation function in which a subset of \( m \) of the \( n \) points is associated with the interface and the remaining \( n - m \) points are associated with the void space is obvious:

\[
F_{ss...ss...sv...v}(x^m; x^{n-m}) = \left[ \prod_{i=1}^{m} M(x_i) \right] \left[ \prod_{j=m+1}^{n} I(x_j) \right], \tag{2.64}
\]

where \( x^{n-m} \equiv x_{m+1}, x_{m+2}, \ldots, x_n \). As we have emphasized, surface correlation functions are not probability functions. However, by associating with the two-phase interface a
finite thickness, a probabilistic interpretation can be given in the limit that the thickness tends to zero; see Sections 4.1, 4.2.1, and 12.4.3. Observe that since the indicator functions in expression (2.64) are nonnegative, the surface correlation function is also nonnegative, i.e.,

\[ F_{ss,...,ss}(x^m; x^{m-n}) \geq 0, \quad \text{for all } x^n \text{ in } V. \] (2.65)

Such correlation functions and their generalizations have been studied for particle systems (Torquato 1986a), as discussed in Chapter 4. In Chapters 4–6 and 12 we discuss the determination of \( F_{sv} \) and \( F_{ss} \) for particle models.

### 2.4 Lineal-Path Function

Another interesting and useful statistical measure is what we call the \textit{lineal-path function} \( L^{(i)} \) (Lu and Torquato 1992a). For statistically isotropic media, it is defined as follows:

\[ L^{(i)}(z) = \text{Probability that a line segment of length } z \text{ lies wholly in phase } i \text{ when randomly thrown into the sample.} \] (2.66)

In stochastic geometry, the quantity \( \phi_i [1 - L^{(i)}(z)] \) is sometimes referred to as the \textit{linear contact distribution function} (Stoyan et al. 1995). Figure 2.6 shows an event that contributes to the lineal-path function. We see that \( L^{(i)}(z) \) contains a coarse level of \textit{connectedness} information about phase \( i \), albeit only along a \textit{lineal path} of length \( z \) in phase \( i \). The lineal-path function is a lower-order microstructural function, since it is a lower-order case of the canonical \( n \)-point correlation function discussed in Section 4.4.

The lineal-path function is a monotonically decreasing function of \( z \), since the space available in phase \( i \) to a line segment of length \( z \) decreases with increasing \( z \). At the extreme values of \( L^{(i)}(z) \), we have that

\[ L^{(i)}(0) = \phi_i, \quad L^{(i)}(\infty) = 0, \]

where \( \phi_i \) is the volume fraction of phase \( i \). The “tail” of \( L^{(i)}(z) \) (i.e., large \( z \) behavior) provides information about the largest lineal paths in phase \( i \). If we define \( L^{(12)}(z) \) to be the probability that a line segment of length \( z \) intersects any parts of the two-phase interface when randomly thrown into the sample, then it is clear that

\[ L^{(1)}(z) + L^{(2)}(z) + L^{(12)}(z) = 1. \]

For three-dimensional media, we observe that \( L^{(i)}(z) \) is equivalent to the area fraction of phase \( i \) measured from the projected image of a three-dimensional slice of thickness \( z \) onto a plane, as depicted in Figure 2.8. It is a problem of long-standing interest in stereology to find the projected area fraction or, equivalently, the lineal-path function \( L^{(i)}(z) \), for three-dimensional particle systems. Its evaluation for nontrivial microstructures remains a challenging theoretical problem because of, in the language of
Figure 2.8 In two dimensions, the lineal-path function is the fraction of phase $i$ obtained from a projection of a slab of thickness $z$ onto a line.

Figure 2.9 Chords are the line segments between the intersections of an infinitely long line with the two-phase interface.

Underwood (1970), “overlap” effects due to projection of the three-dimensional image and “truncation” effects due to slicing the system (see Figure 2.8).

For statistically homogeneous but anisotropic media, $L^{(i)}(z)$ will depend not only on the magnitude of vector $z$ but on its orientation. For statistically inhomogeneous media, $L^{(i)}(x_1, x_2)$ will depend on the absolute positions $x_1$ and $x_2$ of the end points of the vector $z = x_2 - x_1$.

### 2.5 Chord-Length Density Function

A quantity related to the lineal-path function $L^{(i)}(z)$ is the chord-length probability density function $p^{(i)}(z)$ (Matheron 1975, Torquato and Lu 1993). (The latter has been also called the chord-length “distribution” function.) Chords are all of the line segments between intersections of an infinitely long line with the two-phase interface (see Figure 2.9). The density function $p^{(i)}(z)$ is defined for statistically isotropic media as follows:

$$p^{(i)}(z) = \text{Probability of finding a chord of length between } z \text{ and } z + dz \text{ in phase } i.$$  \hspace{1cm} (2.67)
Since it is a probability density function (having dimensions of inverse length), \( p^{(i)}(z) \geq 0 \) for all \( z \), and it normalizes to unity, i.e.,

\[
\int_0^\infty p^{(i)}(z)dz = 1. \tag{2.68}
\]

Knowledge of the chord-length density function is of basic importance in transport problems involving "discrete free paths" and thus has application in Knudsen diffusion and radiative transport in porous media (Ho and Strieder 1979, Tokunaga 1985, Tassopoulos and Rosner 1992). The function \( p^{(i)}(z) \) has also been measured for sedimentary rocks (Thompson, Katz and Krohn 1987) for the purpose of studying fluid flow through such porous media. The chord-length density function \( p^{(i)}(z) \) is also a quantity of great interest in stereology (Underwood 1970). For example, the mean chord (or intercept) length is the first moment of \( p^{(i)}(z) \).

We now show that \( p^{(i)}(z) \) is related to the lineal-path function \( L^{(i)}(z) \) using a simple probability argument (Torquato and Lu 1993). First, we observe that the lineal-path function \( L^{(i)}(z) \) can be obtained by counting the relative number of times that a line segment of length \( z \) is wholly in phase \( i \) when thrown randomly onto an infinite line in the system. Denote by \( A \) the midpoint of the line segment. The probability that point \( A \) is in phase \( i \) is simply \( \phi_i \), the volume fraction of phase \( i \). Second, given that the point \( A \) is in phase \( i \) (it is then on a chord), 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

\[
\frac{yp^{(i)}(y)dy}{\int_0^\infty yp^{(i)}(y)dy},
\]

then the probability that the point \( A \) is on a chord with length between \( y \) and \( y + dy \) is this length fraction multiplied by \( \phi_i \), i.e.,

\[
\frac{\phi_iyp^{(i)}(y)dy}{\int_0^\infty yp^{(i)}(y)dy}
\]

Third, just because point \( A \) of a line segment of length \( z \) (distinct from the length \( y \) ) is in phase \( i \) does not mean that the whole line segment is in phase \( i \). 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

\[
\frac{(y - z)\Theta(y - z)}{y},
\]

where \( \Theta(x) \) is the Heaviside step function defined to be

\[
\Theta(x) = \begin{cases} 
0, & \text{if } x < 0, \\
1, & \text{if } x \geq 0.
\end{cases} \tag{2.69}
\]

The function \( p^{(i)}(z) \) has also been measured for sedimentary rocks (Thompson, Katz and Krohn 1987) for the purpose of studying fluid flow through such porous media. The chord-length density function \( p^{(i)}(z) \) is also a quantity of great interest in stereology (Underwood 1970). For example, the mean chord (or intercept) length is the first moment of \( p^{(i)}(z) \).

We now show that \( p^{(i)}(z) \) is related to the lineal-path function \( L^{(i)}(z) \) using a simple probability argument (Torquato and Lu 1993). First, we observe that the lineal-path function \( L^{(i)}(z) \) can be obtained by counting the relative number of times that a line segment of length \( z \) is wholly in phase \( i \) when thrown randomly onto an infinite line in the system. Denote by \( A \) the midpoint of the line segment. The probability that point \( A \) is in phase \( i \) is simply \( \phi_i \), the volume fraction of phase \( i \). Second, given that the point \( A \) is in phase \( i \) (it is then on a chord), 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

\[
\frac{yp^{(i)}(y)dy}{\int_0^\infty yp^{(i)}(y)dy},
\]

then the probability that the point \( A \) is on a chord with length between \( y \) and \( y + dy \) is this length fraction multiplied by \( \phi_i \), i.e.,

\[
\frac{\phi_iyp^{(i)}(y)dy}{\int_0^\infty yp^{(i)}(y)dy}
\]

Third, just because point \( A \) of a line segment of length \( z \) (distinct from the length \( y \) ) is in phase \( i \) does not mean that the whole line segment is in phase \( i \). 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

\[
\frac{(y - z)\Theta(y - z)}{y},
\]

where \( \Theta(x) \) is the Heaviside step function defined to be

\[
\Theta(x) = \begin{cases} 
0, & \text{if } x < 0, \\
1, & \text{if } x \geq 0.
\end{cases} \tag{2.69}
\]
Now $L^{(i)}(z)$, the probability that the line segment of length $z$ is entirely in phase $i$, can be obtained by combining the results given immediately above. Integrating the probability that the line segment is on chords with length between $y$ and $y + dy$ over all possible $y$, we obtain

$$L^{(i)}(z) = \frac{\phi_i \int_0^\infty (y-z)p^{(i)}(y)\Theta(y-z)dy}{\int_0^\infty y p^{(i)}(y)dy}. \quad (2.70)$$

Differentiating (2.70) yields

$$\frac{dL^{(i)}(z)}{dz} = -\frac{\phi_i}{\ell_C} \int_z^\infty p^{(i)}(y)dy, \quad (2.71)$$

where $\ell_C^{(i)}$ is the mean chord length for phase $i$ given by

$$\ell_C^{(i)} = \int_0^\infty z p^{(i)}(z)dz. \quad (2.72)$$

The first derivative of the lineal-path function is related to the cumulative distribution function $G(z)$ associated with $p(z)$, i.e., $G(z) = P\{z \leq Z\} = -\left(\ell_C/\phi_i\right) dL^{(i)}(z)/dz$ (where $Z$ is the associated continuous random variable). Differentiation of (2.71) and rearrangement of terms gives

$$p^{(i)}(z) = \ell_C \frac{d^2L^{(i)}(z)}{dz^2}. \quad (2.73)$$

Formula (2.73) establishes the connection between the chord-length probability density function $p^{(i)}(z)$ and the lineal-path function $L^{(i)}(z)$. The determination of both of these quantities for particle systems as well as digitized samples of real media is dealt with in Chapters 5, 6, and 12.

It is important to note that the above relations are valid for statistically isotropic systems of arbitrary microstructure. For such media it is simple to show that the mean chord length $\ell_C^{(i)}$ is related to the slope of the two-point probability function $S_2^{(i)}$ at the origin via the expression

$$\ell_C^{(i)} = \frac{\phi_i}{\frac{dS_2^{(i)}}{dr}} \bigg|_{r=0} = \frac{\omega_d \phi_i d}{\omega_{d-1}} \frac{1}{s}, \quad (2.74)$$

where we have used (2.34). For the first three space dimensions, we have

$$\ell_C^{(i)} = \begin{cases} \frac{2\phi_i}{s}, & d = 1, \\ \frac{\pi\phi_i}{s}, & d = 2, \\ \frac{4\phi_i}{s}, & d = 3. \end{cases} \quad (2.75)$$

The results (2.75) are well known in stereology (Underwood 1970).
For a three-dimensional isotropic medium we can use (2.75) to relate the specific surface in three dimensions \( s(d = 3) \) to the interface perimeter per unit area \( s(d = 2) \) (measured from a planar cut through the medium) and the number of interface points per unit length \( s(d = 1) \) (measured from a linear cut through the medium). Since \( \ell_C \) and \( \phi \) remain invariant when determined from \((d - 1)\)-dimensional cuts through a \( d \)-dimensional isotropic medium, then from (2.75) we immediately obtain

\[
s(d = 3) = \frac{4}{\pi} s(d = 2) = 2 s(d = 1). \tag{2.76}
\]

These results are also well known in stereology, albeit using the notation \( S_V \equiv s(d = 3) \), \( L_A \equiv s(d = 2) \) and \( P_L \equiv s(d = 1) \) (Underwood 1970).

### 2.6 Pore-Size Functions

The pore-size probability density function \( P(\delta) \) (also referred to as pore-size “distribution” function) first arose to characterize the void or “pore” space in porous media (Prager 1963a). Actually, \( P(\delta) \) can be used to probe either phase 1 or phase 2 of general random media consisting of two material phases. For simplicity, we will define \( P(\delta) \) for phase 1, keeping in mind that it is equally well defined for phase 2. The function \( P(\delta) \) for isotropic media is defined as follows:

\[
P(\delta)d\delta = \text{Probability that a randomly chosen point in } V_1(\omega) \text{ lies at a distance between } \delta \text{ and } \delta + d\delta \text{ from the nearest point on the pore-solid interface.} \tag{2.77}
\]

Since it is a probability density function (having dimensions of inverse length), \( P(\delta) \geq 0 \) for all \( \delta \) and it normalizes to unity, i.e.,

\[
\int_0^\infty P(\delta)d\delta = 1. \tag{2.78}
\]

At the extreme values of \( P(\delta) \), we have that

\[
P(0) = \frac{s}{\phi_1}, \quad P(\infty) = 0, \tag{2.79}
\]

where \( s/\phi_1 \) is the interfacial area per unit pore volume. The associated complementary cumulative distribution function \( F(\delta) = \mathcal{P}\{\Delta \geq \delta\} \) (where \( \Delta \) is the associated continuous random variable)

\[
F(\delta) = \int_{\delta}^\infty P(r)dr \tag{2.80}
\]

is a nonincreasing function of \( \delta \) such that

\[
F(0) = 1, \quad F(\infty) = 0. \tag{2.81}
\]

Thus, \( F(\delta) \) is the fraction of pore space that has a pore radius larger than \( \delta \).
Figure 2.6 shows an event that contributes to the pore-size density function. In stochastic geometry, the quantity $1 - F(\delta)$ is sometimes referred to as the *spherical contact distribution function* (Stoyan et al. 1995).

The moments of $P(\delta)$, defined as

$$\langle \delta^n \rangle = \int_0^\infty \delta^n P(\delta) d\delta,$$

provide useful characteristic length scales of the random medium. Integrating by parts and using (2.80) gives the alternative representation of the moments in terms of the cumulative distribution function:

$$\langle \delta^n \rangle = n \int_0^\infty \delta^{n-1} F(\delta) d\delta.$$  

Lower-order moments of $P(\delta)$ arise in bounds on the mean survival and principal relaxation times (Prager 1963a, Torquato and Avellaneda 1991).

For a three-dimensional system, $P(\delta)$ is related to the probability of inserting a sphere of radius $\delta$ into the system. Thus, it contains a coarse level of *three-dimensional connectedness* information about phase 1. The pore-size function, therefore, cannot be extracted from a two-dimensional cross-section of the material; it is an intrinsically three-dimensional descriptor. It is noteworthy that the mathematically well-defined function $P(\delta)$ is not the usual pore-size “distribution” function obtained experimentally from mercury porosimetry (Scheidegger 1974, Dullien 1979).

The quantities $P(\delta)$ and $F(\delta)$ are actually trivially related to the “void” nearest-neighbor probability density function $H_V(r)$ and “void” exclusion probability $E_V(r)$, respectively, studied by Torquato, Lu and Rubinstein (1990) for systems of spherical inclusions and defined in Section 2.8. For example, consider any system of interacting identical spheres of radius $R$. Then using the definitions (2.88) and (2.90) for $H_V(r)$ and $E_V(r)$, it is clear that $\delta = r - R$, and so

$$P(\delta) = \frac{H_V(\delta + R)}{\phi_1}, \quad \delta \geq 0,$$

$$F(\delta) = \frac{E_V(\delta + R)}{\phi_1}, \quad \delta \geq 0.$$  

Similarly, for spheres with a polydispersivity in size, $P$ and $F$ are related to the “void” nearest-surface functions $h_V$ and $e_V$ (described in Section 2.8) via the relations

$$P(\delta) = \frac{h_V(\delta)}{\phi_1}, \quad \delta \geq 0,$$

$$F(\delta) = \frac{e_V(\delta)}{\phi_1}, \quad \delta \geq 0.$$  

We note that the pore-size functions are *lower-order* microstructural functions, since the void nearest-neighbor and nearest-surface functions are as well (see Section 2.8). In Chapters 4–6 and 12 we discuss the determination of the pore-size functions for particle models, as well as digitized media.
2.7 Percolation and Cluster Functions

The formation of very large “clusters” of a phase in a heterogeneous material (on the order of the system size) can have a dramatic influence on its macroscopic properties. A cluster of phase \( i \) is defined as the part of phase \( i \) that can be reached from a point in phase \( i \) without passing through phase \( j \not= i \). A critical point, known as the percolation threshold, is reached when a sample-spanning cluster first appears. Unfortunately, any of the lower-order microstructural functions described thus far do not adequately reflect information about nontrivial cluster formation in the system. Torquato, Beasley and Chiew (1988) have introduced and represented the so-called two-point cluster function \( C^0_2(\mathbf{x}_1, \mathbf{x}_2) \), defined to be the probability of finding two points at \( \mathbf{x}_1 \) and \( \mathbf{x}_2 \) in the same cluster of phase \( i \). Thus, \( C^0_2 \) is the analogue of \( S^0_2 \), but unlike its predecessor, it contains nontrivial topological “connectedness” information. The measurement of \( C^0_2 \) for a three-dimensional material sample cannot be made from a two-dimensional cross-section of the material, since it is an intrinsically three-dimensional microstructural function.

Further mathematical details about \( C^0_2 \) and other existing percolation-sensitive quantities have been deferred until Chapters 9 and 10. Chapter 12 describes, among other considerations, the evaluation of \( C^0_2 \) from computer simulations.

2.8 Nearest-Neighbor Functions

All of the aforementioned statistical descriptors are defined for random media of arbitrary microstructure. In the special case of random media composed of particles (phase 2) distributed randomly throughout another material (phase 1), there is a variety of natural morphological descriptors. We describe some of them below for statistically isotropic media composed of identical spherical particles of diameter \( D \) (or radius \( R = D/2 \)) at number density \( \rho \) distributed throughout another phase. (The reader is referred to Chapter 3 for a treatment of the statistical mechanics of particle systems.) We begin by defining nearest-neighbor functions.

In considering a many-body system of interacting particles, a key fundamental question to ask is the following: What is the effect of the nearest neighbor on some reference particle in the system? The answer to this query requires knowledge of the probability associated with finding the nearest neighbor at some given distance from a reference particle, i.e., the “particle” nearest-neighbor probability density function \( H_p \). (This has been also called the nearest-neighbor “distribution” function.) Knowing \( H_p \) is of importance in a host of problems in the physical and biological sciences, including transport processes in heterogeneous materials (Keller, Rubenfeld and Molyneux 1967, Rubinstein and Torquato 1988, Rubinstein and Torquato 1989), stellar dynamics (Chandrasekhar 1943), spatial patterns in biological systems (McNally and Cox 1989), and the molecular physics of liquids and amorphous solids (Reiss, Frisch and Lebowitz 1959, Bernal...
2.8: **NEAREST-NEIGHBOR FUNCTIONS**

Figure 2.10 A schematic showing events that contribute to lower-order functions for random arrays of spheres (phase 2). Shown is the “particle” nearest-neighbor probability density $H_p$ defined by (2.89), point/particle function $G_2 \equiv G_2^{(1)}$ defined by (2.120), and the surface-particle function $F_{sp}$ defined by (2.122).

1964, Finney 1970, Zallen 1983, Torquato et al. 1990). Hertz (1909) was the first to consider its evaluation for a system of spatially uncorrelated “point” particles, i.e., particles whose centers are Poisson distributed (see Section 3.1.2). The calculation of $H_p$ for nonoverlapping particles is nontrivial.

A different nearest-neighbor function, $H_V$, arises in the scaled-particle theory of liquids (Reiss et al. 1959, Helfand, Reiss, Frisch and Lebowitz 1960). This quantity (defined more precisely below) essentially characterizes the probability of finding a nearest-neighbor particle center at a given distance from an arbitrary point in the system. Since $H_V$ is nontrivial when the point is located in the space exterior to the particles, we refer to it as the “void” nearest-neighbor probability density function.

There are other quantities closely related to $H_V$ and $H_p$ that we also consider. These are the so-called exclusion probabilities $E_V$ and $E_P$ and the conditional pair distributions $G_V$ and $G_P$ as defined below.

The nearest-neighbor functions $H_V(r)$ and $H_P(r)$ are defined as follows:

\[
H_V(r)dr = \text{Probability that at an arbitrary point in the system the center of the nearest particle lies at a distance between } r \text{ and } r + dr. \tag{2.88}
\]

\[
H_P(r)dr = \text{Probability that at an arbitrary particle center in the system the center of the nearest particle lies at a distance between } r \text{ and } r + dr. \tag{2.89}
\]

Note that since both $H_V(r)$ and $H_P(r)$ are probability density functions, they are nonnegative for all $r$, normalize to unity, and have dimensions of inverse length. Observe further that for statistically inhomogeneous media, $H_V(r)$ and $H_P(r)$ will depend also upon the position of the arbitrary point and the location of the central particle, respectively.

Figure 2.10 shows an event that contributes to $H_P(r)$.
It is useful to introduce the associated dimensionless “exclusion” probabilities $E_V(r)$ and $E_P(r)$ defined as follows:

$$E_V(r) = \text{Probability of finding a region } \Omega_V(r) \text{ (which is a } d\text{-dimensional spherical cavity of radius } r \text{ centered at some arbitrary point) empty of particle centers.}$$

$$= \text{Expected fraction of space available to a “test” sphere of radius } r - D/2 \text{ inserted into the system.} \quad (2.90)$$

$$E_P(r) = \text{Probability of finding a region } \Omega_P(r) \text{ (which is a } d\text{-dimensional spherical cavity of radius } r \text{ centered at some arbitrary particle center) empty of other particle centers.} \quad (2.91)$$

Figure 2.11 gives a schematic representation of the regions $\Omega_V(r)$ and $\Omega_P(r)$. The first and second lines of (2.90) are equivalent, since the region excluded to a particle center of radius $D$ by a “test” particle of radius $r - D/2$ is a sphere of radius $r$ (see also Chapter 4). Thus, the test particle serves to probe the space available to it. For this reason, the density function $H_V(r)$ can also be interpreted to be the expected surface area per unit volume of the interface between available and unavailable spaces.

It follows that the exclusion probabilities are *complementary cumulative distribution functions* associated with the density functions and thus are related to the latter via

$$E_V(r) = 1 - \int_0^r H_V(x)dx \quad (2.92)$$

and

$$E_P(r) = 1 - \int_0^r H_P(x)dx. \quad (2.93)$$

Thus, both of these functions are monotonically decreasing functions of $r$. The integrals of (2.92) and (2.93) respectively represent the probabilities of finding at least one parti-
cle center in regions $\Omega_V(r)$ and $\Omega_P(r)$. Differentiating the exclusion-probability relations with respect to $r$ gives

$$H_V(r) = -\frac{\partial E_V}{\partial r} \quad (2.94)$$

and

$$H_P(r) = -\frac{\partial E_P}{\partial r}. \quad (2.95)$$

Note that generalizations of these quantities describing events in which exactly $n$ particle centers are contained within the regions $\Omega_V(r)$ and $\Omega_P(r)$ have been studied by Vezzetti (1975), Ziff (1977), and Truskett, Torquato and Debenedetti (1998) and by Truskett et al. (1998), respectively.

It is helpful to write the probability density functions as a product of two different functions. Specifically, for $d$-dimensional particles, let

$$H_V(r) = \rho s_1(r) G_V(r) E_V(r) \quad (2.96)$$

and

$$H_P(r) = \rho s_1(r) G_P(r) E_P(r), \quad (2.97)$$

where

$$s_1(r) = \frac{2\pi^{d/2}r^{d-1}}{\Gamma(d/2)} \quad (2.98)$$

is the surface area of a single $d$-dimensional sphere of radius $r$. For example, for $d = 1$, 2, and 3, $s_1(r)$ equals $2$, $2\pi r$, and $4\pi r^2$, respectively.

Given definitions (2.88)–(2.92), the conditional pair “distribution” functions $G_V$ and $G_P$ must have the following interpretations:

$$\rho s_1(r) G_V(r) dr = \text{Given that region } \Omega_V(r) \text{ (spherical cavity of radius } r) \text{ is empty of particle centers, the probability of finding particle centers in the spherical shell of volume } s_1(r) dr \text{ encompassing the cavity.}$$

$$= \text{Average number of particles at a radial distance between } r \text{ and } r + dr \text{ from the center of } \Omega_V(r), \text{ given that this region is empty of particle centers.} \quad (2.99)$$

$$\rho s_1(r) G_P(r) dr = \text{Given that region } \Omega_P(r) \text{ (sphere of radius } r \text{ encompassing any particle centered at some arbitrary position) is empty of particle centers, the probability of finding other particle centers in the spherical shell of volume } s_1(r) dr \text{ surrounding the central particle.}$$

$$= \text{Average number of particles at a radial distance between } r \text{ and } r + dr \text{ from the center of } \Omega_P(r), \text{ given that this region is empty of particle centers.} \quad (2.100)$$
The exclusion probabilities are related to the pair distribution functions via the expressions

\[ E_V(r) = \exp \left[ - \int_0^r \rho s_1(y)G_V(y)dy \right], \quad (2.101) \]
\[ E_P(r) = \exp \left[ - \int_0^r \rho s_1(y)G_P(y)dy \right], \quad (2.102) \]

which are obtained by use of (2.94)–(2.97). Combination of (2.94), (2.95), (2.101), and (2.102) yields

\[ H_V(r) = \rho s_1(r)G_V(r)\exp \left[ - \int_0^r \rho s_1(y)G_V(y)dy \right] \quad (2.103) \]

and

\[ H_P(r) = \rho s_1(r)G_P(r)\exp \left[ - \int_0^r \rho s_1(y)G_P(y)dy \right]. \quad (2.104) \]

We see that once any one of the triplet \( H_V, E_V, G_V \) is known, any of the other the nearest-neighbor functions can be ascertained via the interrelations (2.92)–(2.97) and (2.101)–(2.104). The nearest-neighbor functions are lower-order microstructural functions, since they are lower-order cases of the canonical \( n \)-point correlation function discussed in Section 4.4.

We note that there are exact conditions that the void quantities must obey when \( r \) equals the sphere radius \( R \) for any system of identical spheres. By definitions (2.88) and (2.90), we have that

\[ H_V(R) = s, \quad E_V(R) = \phi_1, \quad (2.105) \]

where \( s \) and \( \phi_1 \) are the specific surface and volume fraction of phase 1, respectively. This expression combined with (2.96) yields

\[ G_V(R) = \frac{s}{\rho s_1(R)\phi_1}. \quad (2.106) \]

These relations are true even if the spheres overlap to varying degrees. Most of the void quantities at their extreme values are known exactly:

\[ E_V(0) = H_V(0) = G_V(0) = 0, \quad E_V(\infty) = H_V(\infty) = 0. \]

Some of the particle quantities at their extreme values are known exactly:

\[ E_P(0) = 1, \quad E_P(\infty) = H_P(\infty) = 0. \]

The behavior of the functions \( H_P \) and \( G_P \) at \( r = 0 \) and of \( G_V \) and \( G_P \) at \( r = \infty \) are microstructure-dependent (see Chapters 5 and 6).

Consider the spatial moments of \( H_V \) and \( H_P \). The moments of \( H_V \) are trivially related to moments of the pore-size function \( P(\delta) \) for the special case of spheres (see
Section 2.6). The \( n \)th moment of \( H_P(r) \) is defined as
\[
m_n = \int_0^\infty r^n H_P(r) \, dr. \tag{2.107}
\]
The lower limit of zero in the integral allows for particles that can get arbitrarily close to one another, such as in a Poisson distribution of spheres. A particularly important moment is the first moment \( \ell_P \equiv m_1 \), which is just the mean nearest-neighbor distance between particles. In the special case of ensembles of statistically isotropic impenetrable spheres of diameter \( D \), the mean nearest-neighbor distance is given as
\[
\ell_P = \int_D^\infty r H_P(r) \, dr, \tag{2.108}
\]
which is equivalent to
\[
\ell_P = D + \int_D^\infty E_P(r) \, dr \\
= D + \int_D^\infty \exp \left[ - \int_0^r \rho_s(y) G_P(y) \, dy \right] \, dr. \tag{2.109}
\]
Since, as we will see in Chapter 5, \( E_P \geq 0 \) for impenetrable spheres, it follows that \( \ell_P \geq D \).

Finally, we would like to describe related nearest-neighbor functions. The nearest-neighbor functions discussed thus far have involved finding nearest centers of particles at given locations. One can instead define nearest-neighbor functions in the same way as before but in terms of finding nearest surfaces of particles (Lu and Torquato 1992b). Let us denote the surface counterparts by \( h_V \), \( e_V \), and \( g_V \) in the case of the void quantities and by \( h_P \), \( e_P \), and \( g_P \) in the case of the particle quantities. For spheres that are monodispersed in size (i.e., identical), the “surface” quantities contain the same information as the “center” quantities. Indeed, for identical spheres of radius \( R \), we have that
\[
h_V(r) = H_V(r + R), \quad e_V(r) = E_V(r + R). \tag{2.110}
\]
However, for spheres with a polydispersivity in size, the surface quantities are more meaningful, since the sphere with the nearest surface may not be the sphere with the nearest center.

As already remarked, the surface quantities are defined similarly to the center quantities except that the former are concerned with nearest surfaces. For example, following Lu and Torquato (1992b), the probability densities for polydisperse sphere systems are defined as follows:
\[
h_V(r) \, dr = \text{Probability that the nearest particle surface lies at a distance between } r \text{ and } r + dr \text{ from an arbitrary point in the system.} \tag{2.111}
\]
$h_p(r)dr = \text{Probability that the nearest particle surface lies at a distance between } r \text{ and } r+dr \text{ from the center of an arbitrary particle of radius } R.$ (2.112)

It is important to emphasize that the radius $R$ of the reference particle in the particle nearest-surface quantity $h_p$ must be specified.

The corresponding exclusion probabilities are, as before, complementary cumulative distribution functions associated with $h_V$ and $h_p$, i.e.,

$$e_V(r) = 1 - \int_{-\infty}^{r} h_V(x) \, dx$$ (2.113)

and

$$e_p(r) = 1 - \int_{-\infty}^{r} h_p(x) \, dx.$$ (2.114)

In each case the lower integration limit is $-\infty$ to allow for polydispersivity with sizes ranging to the infinitely large. Accordingly, $r$ will generally lie in the interval $(-\infty, \infty)$ because the reference point may sometimes lie in the particle phase itself. This rather bizarre notion can be readily understood by appealing to Section 4.2, which describes the space available to “test” particles when added to a system of spheres of radius $R$. Allowing a test particle to have a negative radius $r$ (down to $-R$) enables it to penetrate into the particle phase. It follows from (2.113) and (2.114) that

$$h_V(r) = -\frac{\partial e_V}{\partial r}, \quad h_p(r) = -\frac{\partial e_p}{\partial r}.$$ (2.115)

The conditional pair functions $g_V$ and $g_p$ are defined through the following relations:

$$h_V(r) = g_V(r)e_V(r), \quad h_p(r) = g_p(r)e_p(r).$$ (2.116)

Notice that surface quantities $g_V$ and $g_p$ are defined differently from $G_V$ and $G_P$ in that the former absorb the surface area terms not contained in the latter. Moreover, for any polydisperse system of spheres, the void quantities evaluated at the origin are, by definition, given as

$$h_V(0) = s, \quad e_V(0) = \phi_1, \quad g_V(0) = s/\phi_1.$$ (2.117)

The quantity $s/\phi_1$ is the interface area per unit volume of phase 1.

One can compute spatial moments of either $h_V$ or $h_p$. The moments of $h_V$ are trivially related to moments of the pore-size density function for systems of spheres (see Section 2.6). The natural generalization of the first moment of $H_P$ given by (2.108) for monodisperse systems is the following definition for polydisperse systems for a reference particle of radius $R$:

$$\lambda_P = \int_{0}^{\infty} rh_p(r)dr - R.$$ (2.118)
For the special case of impenetrable spheres, this definition, after integration by parts, is equivalent to
\[
\lambda_P = \int_R^\infty e_P(r) dr.
\] (2.119)
We refer to \( \lambda_P \) as the mean surface–surface distance.

The determination of the nearest-neighbor functions for monodisperse and polydisperse sphere systems is taken up in Chapters 4–6.

2.9 Point/q-Particle Correlation Functions

Consider statistically inhomogeneous media composed of \( N \) identical spherical particles of radius \( R \) (phase 2) distributed throughout another phase (phase 1). Let \( r^q = \{r_1, \ldots, r_q\} \) denote the positions of \( q \) sphere centers and let \( dr^q = dr_1 dr_2 \cdots dr_q \). The point/q-particle correlation (or “distribution”) function \( G_n^{(i)}(x; r^q) \) is defined as follows (Torquato 1986b):
\[
G_n^{(i)}(x; r^q) dr^q = \text{Probability of finding a point in phase } i \text{ at } x \text{ and the center of a sphere in volume element } dr_1 \text{ about } r_1, \text{ the center of another sphere in volume element } dr_2 \text{ about } r_2, \ldots, \text{ and the center of another sphere in volume element } dr_q \text{ about } r_q, \text{ where } n = 1 + q.
\] (2.120)

The correlation function \( G_n^{(i)}(x; r^q) \) is a hybrid quantity: It is a probability function with respect to the position \( x \) and a joint probability density function (up to a trivial factor) with respect to the positions \( r^q \) of the \( q \) particles. In light of this nature, it obeys the normalization condition
\[
\int G_n^{(i)}(x; r^q) dr^q = \frac{N!}{(N-q)!} S_1^{(i)}(x),
\] (2.121)
where \( S_1^{(i)}(x) \) is the one-point probability function for phase \( i \) defined in Section 2.2.1.

Note that \( G_n^{(i)}(x; r^q) \) divided by the right side of (2.121) is indeed a probability density function, since it is nonnegative and normalizes to unity. Originally, \( G_n^{(i)} \) was denoted as \( G_q^{(i)} \) by Torquato (1986b).

For statistically homogeneous media, \( G_n^{(i)} \) depends only on the relative displacements \( y_1, \ldots, y_q \), where \( y_k = x - r_k \). For isotropic media, it depends only on the distances between all of the \( n \) points. Figure 2.10 shows an event that contributes to the two-point quantity \( G_2(y) \), where \( y = |x - r_1| \). The point/q-particle correlation function arises in bounds on the effective conductivity (Torquato 1986b), effective elastic moduli (Quintanilla and Torquato 1995), trapping constant (Rubinstein and Torquato 1988), and fluid permeability (Rubinstein and Torquato 1989).

Torquato (1986b) showed that the point/q-particle correlation function can be expressed as a special ensemble average of the indicator function \( I^{(i)}(x) \) for phase \( i \) given
by (2.1) [see also (4.46) and (4.74)]. Using this expression, it is easy to demonstrate that

\[ G_n^{(1)}(x; r^q) + G_n^{(2)}(x; r^q) = \rho_q(r^q), \]

where \( \rho_q(r^q) \) is the \( q \)-particle probability density function associated with finding \( q \) spheres with configuration \( r^q \), described more fully in Chapter 3. We see that since \( G_1^{(i)} = S_1^{(i)} \), then we define \( \rho_0 \equiv 1 \). It is clear that

\[ G_n^{(1)}(x; r^q) = 0 \quad \text{if} \quad |x - r_k| < R, \quad k = 1, \ldots, n, \]

since the point \( x \) cannot be in any sphere for the \( G_n^{(1)} \). The last two expressions then give

\[ G_n^{(2)}(x; r^q) = \rho^q(r^q) \quad \text{if} \quad |x - r_k| < R, \quad k = 1, \ldots, n. \]

The asymptotic properties of the \( G_n^{(i)}(x; r^q) \) have been given by Torquato (1986b). Chapters 4–6 discuss the determination of the point/\( q \)-particle correlation function for monodisperse and polydisperse sphere systems.

### 2.10 Surface/Particle Correlation Function

The surface/particle correlation function \( F_{sp}(x; r_1) \) for statistically inhomogeneous systems of \( N \) identical spheres is defined as follows:

\[ F_{sp}(x; r_1) = \text{Correlation function associated with a point being on the interface at } x \text{ and the probability of finding the center of a sphere in volume element } d r_1 \text{ about } r_1. \]

(2.122)

This function obeys the normalization condition

\[ \int F_{sp}(x; r_1) d r_1 = N s(x), \]

(2.123)

where \( s(x) \) is the local specific surface defined by (2.60). The \( n \)-point generalization of this function is discussed in Chapter 4.

For homogeneous media, \( F_{sp} \) depends only on the displacement \( y = x - r_1 \). For isotropic media, it depends only on the distance \( y = |y| \). Figure 2.10 shows an event that contributes to \( F_{sp}(y) \). The surface/particle function \( F_{sp} \) arises in rigorous bounds on the fluid permeability of random beds of spheres (Torquato and Beasley 1987).
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