Motivation and Overview

The determination of the transport, electromagnetic, and mechanical properties of heterogeneous materials has a long and venerable history, attracting the attention of some of the luminaries of science, including Maxwell (1873), Rayleigh (1892), and Einstein (1906). In his *Treatise on Electricity and Magnetism*, Maxwell derived an expression for the effective conductivity of a dispersion of spheres that is exact for dilute sphere concentrations. Lord Rayleigh developed a formalism to compute the effective conductivity of regular arrays of spheres that is used to this day. Work on the mechanical properties of heterogeneous materials began with the famous paper by Einstein in which he determined the effective viscosity of a dilute suspension of spheres. Since the early work on the physical properties of heterogeneous materials, there has been an explosion in the literature on this subject because of the rich and challenging fundamental problems it offers and its manifest technological importance.

1.1 What Is a Heterogeneous Material?

In the most general sense, a *heterogeneous material* is one that is composed of domains of different materials (phases), such as a composite, or the same material in different states, such as a polycrystal. This book focuses attention on the many instances in which the "microscopic" length scale (e.g., the average domain size) is much larger than the molecular dimensions (so that the domains possess macroscopic properties) but much smaller than the characteristic length of the macroscopic sample. In such circumstances, the heterogeneous material can be viewed as a continuum on the microscopic scale, subject to classical analysis, and macroscopic or *effective* properties



Figure 1.1 Left panel: A schematic of a random two-phase material shown as white and gray regions with general phase properties K_1 and K_2 and phase volume fractions ϕ_1 and ϕ_2 . Here L and ℓ represent the macroscopic and microscopic length scales, respectively. Right panel: When L is much bigger than ℓ , the heterogeneous material can be treated as a homogeneous material with effective property K_e .

can be ascribed to it (see Figure 1.1). Such heterogeneous media abound in synthetic products and nature. Synthetic examples include:

- aligned and chopped fiber composites
- particulate composites
- interpenetrating multiphase composites
- cellular solids
- colloids
- gels
- foams
- microemulsions
- block copolymers
- fluidized beds
- concrete

Some examples of natural heterogeneous materials are:

- polycrystals
- soils
- sandstone
- granular media
- Earth's crust
- sea ice
- wood
- bone
- lungs
- blood
- animal and plant tissue
- cell aggregates and tumors

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The physical phenomena of interest occur on "microscopic" length scales that span from tens of nanometers in the case of gels to meters in the case of geological media. Structure on this "microscopic" scale is generically referred to as *microstructure* in this book.

In many instances, the microstructures can be characterized only statistically, and therefore are referred to as *random heterogeneous materials*, the chief concern of this book. There is a vast family of random microstructures that are possible, ranging from dispersions with varying degrees of clustering to complex interpenetrating *connected* multiphase media, including *porous media*. A glimpse of the richness of the possible microstructures can be garnered from Figures 1.2 and 1.3, which depict examples of synthetic and natural random heterogeneous materials, respectively.

Beginning from the top, the first example of Figure 1.2 shows a scanning electron micrograph of a colloidal system of hard spheres of two different sizes. The second example is an optical image of the transverse plane of a fiber-reinforced material: ceramic-metal composite (cermet) made of alumina (Al_2O_3) fibers (oriented perpendicular to the plane) in an aluminum matrix. Note the clustering of the fibers. The last example shows a processed optical image of a cermet that is primarily composed of boron carbide (black regions) and aluminum (white regions). Both of these phases are connected across the sample (interpenetrating) even though, from a planar section, it appears that only the black phase is connected. In all of these examples, the microstructure can be characterized only statistically.

Beginning from the top, the first example of Figure 1.3 shows a planar section through a Fontainebleau sandstone obtained via X-ray microtomography. As we will see, this imaging technique enables one to obtain full three-dimensional renderings of the microstructure (see Figure 12.14), revealing that the void or pore phase (white region) is actually connected across the sample. The second example shows a scanning electron micrograph of the porous cellular structure of cancellous bone. The third example shows an image of red blood cells, one of a number of different particles contained in the liquid suspension of blood.

1.2 Effective Properties and Applications

We will consider four different classes of problems as summarized in Table 1.1 on page 7. We will focus mainly on the following four steady-state (time-independent) effective properties associated with these classes:

- 1. Effective conductivity tensor, σ_e
- 2. Effective stiffness (elastic) tensor, C_e
- 3. Mean survival time, τ
- 4. Fluid permeability tensor, k

In each case, the phase properties and phase volume fractions (fractions of the total volume occupied by the phases) are taken to be given information. Depending on



Figure 1.2 Synthetic random heterogeneous materials. From top to bottom: Colloidal system of hard spheres of two different sizes (Thies-Weesie 1995), fiber-reinforced cermet (courtesy of G. Dvorak), and an interpenetrating three-phase cermet composed of boron carbide (black regions), aluminum (white regions), and another ceramic phase (gray regions) (Torquato et al. 1999a).



Figure 1.3 Natural random heterogeneous materials. From top to bottom: Fontainebleau sandstone [data taken from Coker et al. (1996)], cellular structure of cancellous bone (Gibson and Ashby 1997), and red blood cells (Alberts et al. 1997).

the physical context, each phase can be either solid, fluid or void. We will also examine certain relaxation times associated with time-dependent transport processes in heterogeneous media.

1.2.1 Conductivity and Analogous Properties

The quantity σ_e represents either the *electrical* or *thermal conductivity tensor*, which are mathematically equivalent properties. It is the proportionality constant between the average of the local electric current (heat flux) and average of the local electric field (temperature gradient) in the composite. This averaged relation is Ohm's law or Fourier's law (for the composite) in the electrical or thermal problems, respectively. More generally, for reasons of mathematical analogy, the determination of the effective conductivity translates immediately into equivalent results for the effective dielectric constant, magnetic permeability, or diffusion coefficient (see Chapter 13). Therefore, we refer to all of these problems as class A problems as described in Table 1.1, adapted after a similar table of Batchelor (1974). Of course, each local field within this class will depend on the local phase properties (as depicted in Figure 1.1) and hence generally will be different from one another. Moreover, whereas the electrical conductivity, thermal conductivity, and diffusion coefficient are transport (nonequilbrium) properties, the dielectric constant and magnetic permeability are equilibrium properties. Observe that the determination of the effective diffusion coefficient of a medium in which one phase is impermeable to mass transport is actually just a special limit of the conductivity problem, namely, the limit in which one of the phases has zero conductivity (see Chapter 13).

A key macroscopic parameter characterizing the electrical/thermal characteristics of a heterogeneous material is the effective electrical/thermal conductivity (Beran 1968, Batchelor 1974, Bergman 1978, Hashin 1983, Milton 1984, Torquato 1987). Knowledge of σ_e is of importance in a host of applications. Electrical applications include composites used as insulators for coatings or electrical components and oil drilling operations, where electrical conductivity measurements of the brine-saturated rock are used to infer information about the permeability of the pore space. Thermal applications range from composites used for insulation, heat exchangers, and heat sinks for electronic cooling to geophysical problems (e.g., determination of the geothermal temperature gradient). In the case of composites used as microwave resonator materials, capacitors, and insulators, the effective dielectric constant is a critical macroscopic characteristic. Applications involving composites with desirable values of the effective magnetic permeability include motors, generators, transformers, and computer disks. Diffusion of tracer particles in fluid-saturated porous media occurs in many industrial processes, such as chromatography, catalysis and oil recovery, and biological processes such as blood transport and transport in cells or through cell membranes. In these instances, the effective diffusion coefficient is a key parameter.

1.2: EFFECTIVE PROPERTIES AND APPLICATIONS

Table 1.1 The four different classes of steady-state effective media problems considered here. $F \propto K_e \cdot G$, where K_e is the general effective property, G is the average (or applied) generalized gradient or intensity field, and F is the average generalized flux field. Class A and B problems share many common features and hence may be attacked using similar techniques. Class C and D problems are similarly related to one another.

	Class	General Effective Property <i>K</i> _e	Average (or Applied) Generalized Intensity <i>G</i>	Average Generalized Flux F
	А	Thermal Conductivity	Temperature Gradient	Heat Flux
		Dielectric Constant	Electric Field	Electric Displacement
(注:		Magnetic Permeability Diffusion Coefficient	Magnetic Field Concentration Gradient	Magnetic Induction Mass Flux
	В	Elastic Moduli	Strain Field	Stress Field
		Viscosity	Strain Rate Field	Stress Field
	С	Survival Time	Species Production Rate	Concentration Field
		NMR Survival Time	NMR Production Rate	Magnetization Density
	D	Fluid Permeability	Applied Pressure Gradient	Velocity Field
	ľ	Sedimentation Rate	Force	Mobility

1.2.2 Elastic Moduli

The effective stiffness (elastic) tensor C_e is one of the most basic mechanical properties of a heterogeneous material (Watt, Davies and O'Connell 1976, Christensen 1979, Willis 1981, Hashin 1983, Milton 1984, Kohn 1988, Nemat-Nasser and Hori 1993, Torquato 2000a). The quantity C_e is the proportionality constant between the average stress and average strain. This relation is the averaged Hooke's law for the composite. An obvious class of composites in which it is desired to know C_e is one where the material must bear some mechanical load. This can include synthetic materials, such as structural composites used in a myriad of applications, or biological materials, such as bone or tendon. The speed and attenuation of elastic waves in fluid-saturated porous media (a detection procedure used in oil and gas exploration) depend upon, among other parameters, the elastic moduli of the media. We note that the problem of finding the effective shear viscosity of a suspension of particles in a liquid is related to the problem of determining the effective shear modulus of the suspension under special limits (Chapter 13), and hence we term these class B problems as described in Table 1.1. Moreover, under certain situations, the effective stiffness tensor completely specifies the effective thermal expansion characteristics of a heterogeneous material (Chapter 15). Finally, we note that there is a correspondence between the elastic and *viscoelastic* properties of a heterogeneous material (Chapter 15).

1.2.3 Survival Time or Trapping Constant

Physical problems involving simultaneous diffusion and reaction in heterogeneous media abound in the physical and biological sciences (Prager 1963a, Berg 1983, Zwanzig 1990, Torquato 1991a, den Hollander and Weiss 1994, Zhou and Szabo 1996, Portman and Wolynes 1999). Considerable attention in the chemical physics community has been devoted to instances in which the heterogeneous medium consists of a pore region in which diffusion (and bulk reaction) occurs and a "trap" region whose interface can absorb the diffusing species via a surface reaction. Examples are found in widely different processes, such as heterogeneous catalysis, fluorescence quenching, cell metabolism, ligand binding in proteins, migration of atoms and defects in solids, and crystal growth, to mention but a few. A key parameter in such processes is the mean survival time τ , which gives the average lifetime of the diffusing species before it gets trapped. Often it is useful to introduce its inverse, called the *trapping constant* $\gamma \propto \tau^{-1}$, which is proportional to the trapping rate. Interestingly, nuclear magnetic resonance (NMR) relaxation in porous media yields an NMR survival time that is mathematically equivalent to the aforementioned one typically studied in chemical physics, and therefore we term these class C problems, as described in Table 1.1.

1.2.4 Fluid Permeability

A key macroscopic property for describing slow viscous flow through porous media is the fluid permeability tensor k (Beran 1968, Scheidegger 1974, Batchelor 1974, Dullien 1979, Torquato 1991b, Adler 1992). The quantity k is the proportionality constant between the average fluid velocity and applied pressure gradient in the porous medium. This relation is Darcy's law for the porous medium. The flow of a fluid through a porous medium arises in a variety of technological problems. Examples include the extraction of oil or gas from porous rocks, spread of contaminants in fluid-saturated soils, and separation processes such as in chromatography, filtration, biological mem-

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branes, and bioreactors. We observe that the problem of particles sedimenting through a liquid shares some similarities to the problem of determining the fluid permeability of the suspension, and hence we term these class D problems, as indicated in Table 1.1.

1.2.5 Diffusion and Viscous Relaxation Times

Relaxation processes associated with the previous two problems of trapping and flow in porous media are also of interest. Specifically, it is desired to know how the concentration and velocity fields decay in time from initially uniform values. Such time-dependent processes are exactly described by a spectrum of relaxation times (inverse eigenvalues) that are intimately related to the pore-space topology. In the trapping and flow problems, we refer to T_1, T_2, \ldots and $\Theta_1, \Theta_2, \ldots$ as the diffusion and viscous relaxation times, respectively. It will be shown that these relaxation times are related to their steady-state counterparts (τ and k) as well as to each other.

1.2.6 Definitions of Effective Properties

Given the phase properties K_1, K_2, \ldots, K_M and phase volume fractions $\phi_1, \phi_2, \ldots, \phi_M$ of a heterogeneous material with M phases, how are its effective properties mathematically defined? It will be shown in Chapter 13 that the effective properties of the heterogeneous material are determined by averages of local fields derived from the appropriate governing continuum-field theories (partial differential equations) for the problem of concern. Specifically, any of the aforementioned effective properties, which we denote generally by K_e , is defined by a *linear* relationship between an average of a generalized local flux F and an average of a generalized local (or applied) *intensity* G, i.e.,

$$\boldsymbol{F} \propto \boldsymbol{K}_{\boldsymbol{e}} \cdot \boldsymbol{G}. \tag{1.1}$$

For the conduction, elasticity, trapping, and flow problems, the average generalized flux F represents the average local electric current (heat flux), stress, concentration, and velocity fields, respectively, and the average generalized intensity G represents the average local electric field (or temperature gradient), strain, production rate, and applied pressure gradient, respectively. The precise nature of (1.1) is discussed in Chapter 13.

Table 1.1 summarizes the average local (or applied) field quantities that determine the steady-state effective properties for all four problem classes. As already noted, the individual problems within class A are mathematically equivalent to each other; the same is true of the problems within class C. The elasticity and viscosity problems of class B share some similarities but are generally different (Chapter 13). The fluid permeability and sedimentation problems of class D are related but generally different (Chapter 13). Whereas the properties of classes A and B are *scale invariant*, the properties of classes C and D are *scale dependent* (Chapter 13). This classification scheme is made more mathematically precise in Chapter 13.

At first glance, the effective properties of one class appear to share no relationship to the effective properties of the other classes. Indeed, the governing equations are





 $\sigma_e = \sigma_1 \phi_1 + \sigma_2 \phi_2$ (Arithmetic Average)

 $\sigma_e = (\phi_1/\sigma_1 + \phi_2/\sigma_2)^{-1}$ (Harmonic Average)



different from class to class (see Chapter 13 for a complete discussion of this point). Nonetheless, it is shown in Chapter 23 that these apparently different properties can be related to each other via *cross-property* relations.

1.3 Importance of Microstructure

The effective properties of a heterogeneous material depend on the phase properties and microstructural information, including the phase volume fractions, which represent the simplest level of information. It is important to emphasize that the effective properties are generally not simple relations (mixtures rules) involving the phase volume fractions. This suggests that the complex interactions between the phases result in a dependence of the effective properties on nontrivial details of the microstructure.

To illustrate the fact that the effective properties of a random heterogeneous material depend on nontrivial features of the microstructure, we consider two examples. In both instances, we assume that the medium consists of two phases, one with volume fraction ϕ_1 and the other with volume fraction ϕ_2 , and so $\phi_1 + \phi_2 = 1$. In the first case, it is desired to predict the effective conductivity σ_e of a composite of arbitrary microstructure with phase conductivities σ_1 and σ_2 . One might surmise that a reasonable estimate is a simple weighted average of the phase conductivities involving the volume fractions, such as

$$\sigma_e = \sigma_1 \phi_1 + \sigma_2 \phi_2. \tag{1.2}$$

This arithmetic-average prediction usually grossly overestimates the effective conductivity of isotropic media, especially for widely different phase conductivities. The reasor for this discrepancy is that formula (1.2) is exact for the layered composite depicted in the left panel of Figure 1.4 in the direction along the slabs. Thus, because the more conducting phase is always connected across the system along the slab direction, the effective conductivity can be of the order of the more conducting phase. This ideal ized situation and its close approximants represent a very small subset of possible composite microstructures, and therefore (1.2) can appreciably overestimate the effect tive conductivities of general composites. On the other hand, one might try to use the





Figure 1.5 Left panel: 50-50 mixture consisting of a disconnected inclusion phase and a connected matrix phase. The gray phase is highly conducting (or stiff) relative to the white phase. Right panel: The same microstructure except the phases are interchanged.

harmonic-average formula

$$\sigma_e = \left(\frac{\phi_1}{\sigma_1} + \frac{\phi_2}{\sigma_2}\right)^{-1} \tag{1.3}$$

to estimate the effective conductivity. This expression, however, typically grossly underestimates the effective conductivity of isotropic media, since it corresponds exactly to the effective conductivity of the layered composite in the direction perpendicular to the slabs (see right panel). It is seen that if one phase is insulating relative to the other, there will be little current perpendicular to the slabs, since the phases are disconnected from one another. In conclusion, estimates based only on incorporating volume-fraction information (i.e., simple mixture rules) cannot capture crucial microstructural features required to estimate accurately the effective conductivity of most composites. Since the conductivity is one of the simplest properties, this last statement applies to all of the other effective properties as well.

In the second example, we consider a 50-50 two-phase system shown in the left panel of Figure 1.5. It consists of a *disconnected* inclusion phase and a *connected* matrix phase. Let the gray "phase" be highly conducting (or stiff) compared to the white "phase." The right panel shows a composite with exactly the same microstructure but with the phases interchanged. Which of the two composites has the higher effective conductivity (or stiffness)? Clearly, the one depicted in the right panel has the higher effective property, since the connected phase here is the more conducting (or stiffer) phase. Thus, even though both composites have the same volume fraction, their effective properties will be dramatically different, implying that the effective properties depend on microstructural information beyond that contained in the volume fractions. Such higher-order microstructural information is the main subject of Part I of this book. We have seen through both examples that connectedness is crucial higher-order information. For this reason, Chapters 9 and 10 are devoted entirely to percolation and clustering in random heterogeneous materials.

To summarize, for a random heterogeneous material consisting of M phases, the general effective property K_e is the following function:

$$\boldsymbol{K}_{\boldsymbol{e}} = f(\boldsymbol{K}_1, \boldsymbol{K}_2, \dots, \boldsymbol{K}_M; \phi_1, \phi_2, \dots, \phi_M; \boldsymbol{\Omega}), \qquad (1.4)$$

where Ω indicates functionals of higher-order microstructural information. The mathematical form that this microstructural information takes is described in the next section.

1.4 Development of a Systematic Theory

In light of the importance of determining the effective properties of heterogeneous media, a vast body of literature has evolved based upon direct measurements (either experimentally or computationally), semiempirical relations, and theoretical techniques. The time and cost to attack this problem by performing measurements on each material sample for all possible phase properties and microstructures are clearly prohibitive. Successful empirical relations tend to be more useful for correlating data rather than predicting them. Inasmuch as the effective property depends not only on the phase properties but is sensitive to the details of the microstructure, it is natural to take the broader approach of predicting the effective property from a knowledge of the microstructure. One can then relate changes in the microstructure quantitatively to changes in the macroscopic property. One of the chief aims of this book is to provide such a *systematic theory* of general random heterogeneous materials.

1.4.1 Microstructural Details

A systematic theory of random heterogeneous materials rests on our ability to describe the "details of the microstructure," by which we mean the phase volume fractions; surface areas of interfaces, orientations, sizes, shapes, and spatial distribution of the phase domains; connectivity of the phases; etc. Quantitatively speaking, we investigate certain *n*-point correlation functions that statistically describe the microstructure. As will be shown throughout this book, there are a variety of different correlation functions that naturally arise when the averaging process involved in relation (1.1) is rigorously carried out. Roughly speaking, the averaging process results in integrals in which the relevant local fields are weighted with the *n*-point correlation functions. More precisely, the averages are functionals of the *n*-point correlation functions.

Many types of correlation functions arise depending on the property and class of microstructures of interest. To give the reader a preview of the concept of a correlation function, we will discuss a specific family of such descriptors that arise in all four problem classes. For simplicity, we consider a two-phase medium that is statistically isotropic (as defined in Chapter 2) and begin with the one-point correlation function



Figure 1.6 A schematic showing attempts at sampling for the correlation functions S_1 , S_2 , and S_3 from a planar section.

denoted by S_1 . Instead of giving here a precise mathematical definition of this quantity, as is done in Chapter 2, we will describe how one would ascertain it from a planar section through the heterogeneous material. The one-point function S_1 is obtained by randomly throwing a single point onto the planar section many times and recording the fraction of times that it lands in one of the phases, say the "white" phase of Figure 1.6. It is clear that if the planar section is big enough and the number of attempts are sufficiently large, S_1 will approach the volume fraction of the white phase. Thus, S_1 is the probability that a single point falls in the white phase. The two-point correlation function $S_2(r)$ is obtained by randomly throwing a line segment of length r into the sample many times and recording the fraction of times that its end points land in the white phase (see Figure 1.6). By performing this experiment for all possible lengths r, one can generate a graph of S_2 as a function of r. Therefore, $S_2(r)$ is the probability that the two end points of a line segment of length r fall in the white phase. Clearly, variations in $S_2(r)$ reflect the extent to which the two points are correlated in the system, and thus $S_2(r)$ contains more information than S_1 , which is just a constant. Similarly, $S_3(r,s,t)$ is the probability that the three vertices of a triangle with sides of lengths r, s, and t fall in the white phase. The three-point quantity S_3 embodies more information than S_2 . In general, S_n gives the probability that *n* points with specified positions lie in the white phase.

In Chapters 19 and 20 we demonstrate, using first principles, that the effective properties are indeed generally dependent on an infinite amount of statistical information about the microstructure; this is a direct consequence of the complex field interactions that occur in the heterogeneous material. Of course, for general microstructures, the infinite amount of information can never be ascertained in practice. In light of this limitation, the faint of heart may ask whether one should give up on obtaining structure/property relations? The answer is a definitive *no* for the same reasons that structure/property relations are pursued in any discipline that concerns itself with complex interacting systems, such as materials science, solid and liquid state theory, and statistical physics.

First of all, there are a few special cases in which we do have complete information and hence can compute the effective properties exactly (see Chapters 15, 16, 19, and 20). These examples lend important insight into the salient features that generally determine effective properties. Second, one can develop estimates for the effective properties that incorporate limited microstructural information. Chapter 18 discusses well-known effective-medium approximations that include simple information (volume fractions and shapes). More sophisticated approximations that incorporate threeand four-point information are described in Chapter 21. Third, given partial statistical information on the sample (finite set of correlation functions), one can establish the range of possible values that the effective properties can take, i.e., rigorous upper and lower bounds on the properties. One of the bounds can often yield useful estimates of the effective property even when the other bound diverges from it. Moreover, the study of bounds has important implications for the optimal design of composites. The subject of bounds is treated in Chapters 14, 21, and 22.

It is noteworthy that significant advances have been made recently in the quantitative characterization of the microstructure of random heterogeneous materials both theoretically and experimentally. These breakthroughs, described in Part I, have enabled investigators to compute property estimates (including bounds) that depend upon three- and four-point information for nontrivial models and real materials.

1.4.2 Multidisciplinary Research Area

The study of random heterogeneous materials is a multidisciplinary endeavor that overlaps with various branches of materials science, engineering, physics, applied mathematics, geophysics, and biology, as schematically represented in Figure 1.7. In some cases, the intersections with these disciplines arise because existing models, methods, and results can be applied to study heterogeneous materials and vice versa. In other instances, overlap arises because they share common goals with the study of heterogeneous materials. Moreover, some of the disciplines offer a panoply of intriguing heterogeneous materials that need to be investigated.

One of the central aims of *materials science* is to formulate structure/property relations for single-phase materials (metals, ceramics, and polymers). This formulation is less well developed in the case of composite materials that are composed of combinations of single-phase materials. Because composites can be designed to exhibit the best characteristics of the individual constituents, they are ideally suited in modern technologies that require materials with an unusual combination of properties that cannot be met by conventional single-phase materials. For example, fiber-polymeric composites can be fabricated that have relatively high stiffness, strength, and toughness, and low weight. (The fiber by itself is too brittle, while the polymer alone is too compliant and of low strength.) The ability to tailor composites with a unique spectrum of properties rests fundamentally on a systematic means to relate the effective properties









to the microstructure, a basic goal of this book. Moreover, the availability of accurate structure/property relations has important implications for improved *materials processing*, since processing controls the microstructure and hence the bulk properties of the heterogeneous material.

Transport, electromagnetic, and mechanical processes that occur in heterogeneous materials are of great importance in *engineering*. In *chemical engineering*, the applications are driven by the petroleum, chemical, electronics, and pharmaceutical industries, and include filtration and separation (flow in porous media), chemical reactor design (thermal properties of packed beds), coatings (polymer dispersions), microelectronic components, inhalation therapy (two-phase aerosols), and drug-delivery systems. In *aerospace and mechanical engineering*, the applications are driven by the defense, space, electronics, transportation, and consumer products industries, and include composites as structural components in aircraft, space vehicles, and automobiles; insulation; heat exchangers; microelectromechanical systems (MEMS); and recreational products (skis and rackets). In *civil engineering*, the applications are driven by the building construction industries, infrastructure, and environmental issues, and include bridges, building materials (concrete and wood), aging of materials (pipes, pressure vessels, exterior of buildings), spread of contaminants in fluid-saturated soils, and soil mechanics. The systematic study of heterogeneous materials in engineering

often goes by the names *micromechanics* and *microhydrodynamics*, reflecting concern with primarily solid mechanical properties in the former and fluid mechanical properties in the latter. In this book, we emphasize that such distinctions are unnecessary and indeed are a hindrance, since it will be shown that it is very fruitful to view seemingly disparate phenomena under a unifying light.

The main goal of *statistical mechanics* is to relate the macroscopic properties of a system of many particles (atoms, molecules, spins, etc.) to its microscopic properties, which include the interparticle interactions as well as the spatial statistics of the particles. *Statistical physics* is the broader study of any interacting system of particles, whether it exists at the atomic scale or not. For example, an important research area within statistical physics is *percolation theory*, which seeks to understand connected-ness and clustering properties of random media at any length scale (Chapters 9 and 10). In this book we exploit the powerful methods and machinery of statistical mechanics to quantify structure at the larger "microscopic" length scales associated with random heterogeneous materials (see Figure 1.1).

Homogenization theory is an area of applied mathematics that is concerned with the behavior of the partial differential equations that are valid locally within a heterogeneous material in the limit that the ratio of the microscopic to macroscopic length scales tends to zero (Bensoussan, Lions and Papanicolaou 1978, Sanchez-Palencia 1980, Jikov, Kozlov and Olenik 1994). Mathematical questions are the following: What are the homogenized differential equations and how do the solutions converge to this asymptotic limit? A byproduct of the homogenization process is the averaged equation (1.1) that defines the effective property of interest. Chapter 13 is devoted to homogenization theory.

The area of mathematical research that seeks to provide models and methods to characterize random patterns is called *stochastic geometry* (Stoyan, Kendall and Mecke 1995). This subject grew out of the classical area of *geometrical probability* that concerned itself with less general considerations such as the famous Buffon needle question (Chapter 2). *Stereology* is a related area that seeks to recover statistical information on three-dimensional structures from one- and two-dimensional information obtained from linear or planar sections. The contributions of this book concerning the microstructure of heterogeneous materials belong to the domain of stochastic geometry. In particular, we generalize a preponderance of the results of stochastic geometry that have been derived for certain spatially *uncorrelated* models (called *Boolean* models) to a wide class of spatially *correlated* models.

Understanding the effective properties of heterogeneous materials has many applications in *geophysics*. Most earth materials are heterogeneous, frequently on a variety of different length scales. Rocks are aggregates of several different anisotropic minerals that often are characterized by widely varying properties. Determination of the properties of fluid-saturated porous rock is particularly germane to oil and gas exploration. The interpretation of changes in seismic velocities preceding earthquakes and their relation to other precursor phenomena may depend on the effects of cracks on

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the effective elastic moduli of the medium. Many of the methods and results of this book are of direct relevance in geophysical applications.

Biology is a field that will be playing a larger role in the study of heterogeneous materials in the future. Virtually all biological material systems are composites that are found to have at least one distinct structural level at a variety of length scales. This structural hierarchy is not fractal, i.e., it is neither self-similar nor is the number of levels infinite. Some of these biological materials have superior physical properties [e.g., spider silk is at least five times stronger than steel (Tirrell 1996)]. Thus, biological materials offer fundamental challenges both in terms of microstructure characterization and property predictions. From a practical standpoint, it is desired to employ lessons from biology to produce synthetic composite analogues with a unique spectrum of properties. Finally, we observe that three-dimensional imaging techniques originally developed for biological applications (e.g., confocal microscopy) are now being applied to image inorganic heterogeneous materials.

1.5 Overview of the Book

This book is divided into two parts. Part I deals with the quantitative characterization of the microstructure of heterogeneous materials via theoretical, computer-simulation, and imaging techniques. Emphasis is placed on foundational theoretical methods. Part II treats a wide variety of effective properties of heterogeneous materials and describes how they are linked to the microstructure. This is accomplished using rigorous methods. (Readers primarily interested in property prediction can skip to Part II while referring back to key portions of Part I as indicated.) Whenever possible, theoretical predictions for the effective properties are compared to available experimental and computer-simulation data. The overall goal of the book is to provide a rigorous means of characterizing the microstructure and properties of heterogeneous materials that can simultaneously yield results of practical utility. A unified treatment of both microstructure and properties is emphasized.

1.5.1 Part I

In Chapter 2 the various microstructural functions that are essential in determining the effective properties of random heterogeneous materials are defined. Chapter 3 provides a review of the statistical mechanics of particle systems that is particularly germane to the study of random heterogeneous materials, including sphere packings. In Chapter 4 a unified approach to characterize the microstructure of a large class of media is developed. This is accomplished via a canonical *n*-point function H_n from which one can derive exact analytical expressions for any microstructural function of interest. Chapters 5, 6, and 7 apply the formalism of Chapter 4 to the case of systems of identical spheres, spheres with a polydispersivity in size, and anisotropic particle systems (including laminates), respectively. In Chapter 8 the methods of Chapter 4 are extended

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to quantify the microstructure of cell models. Here the random-field approach is also discussed. Chapter 9 reviews the study of *percolation* and *clustering* on a *lattice* and introduces *continuum* percolation. Chapter 10 discusses specific developments in *continuum* percolation theory. Chapter 11 describes a means to study microstructural fluctuations that occur on local length scales. Finally, Chapter 12 discusses computersimulation techniques (primarily Monte Carlo methods) to quantify microstructure. Moreover, it is shown how to apply the same methods to compute relevant microstructural functions from two- and three-dimensional images of the material. Finally, we describe methods that enable one to reconstruct or construct microstructures from a knowledge of limited microstructural information.

It is noteworthy that the statistical descriptors discussed in Part I are quite general and may also find application in diverse fields where characterization of spatial structure is a vital objective, such as cosmology and ecology. For instance, an important branch of cosmology is concerned with the description and understanding of the spatial distribution of mass and "voids" in galaxies and clusters of galaxies in the universe (Peebles 1993, Saslaw 2000). The study of how spatial patterns arise and are maintained is a major area of research in ecological theory (Pielou 1977, Diggle 1983, Durrett and Levin 1994). It is the opinion of this author that a cross-fertilization of ideas between all of these different fields will be mutually beneficial.

1.5.2 Part II

In Chapter 13 the local governing equations for the relevant field quantities and the method of homogenization leading to the averaged equations for the effective properties are described. The aforementioned classes of steady-state and time-dependent problems are studied. In Chapter 14 minimum energy principles are derived that lead to variational bounds on all of the effective properties in terms of trial fields. Chapter 15 proves and discusses certain phase-interchange relations for the effective conductivity and elastic moduli. Chapter 16 derives and describes some exact results for each of the effective properties. In Chapter 17 we derive the local fields associated with a single spherical or ellipsoidal inclusion in an infinite medium for all problem classes. Chapter 18 presents derivations of popular effective-medium approximations for all four effective properties. In Chapter 19 cluster expansions of the effective properties of dispersions are described. Chapter 20 presents derivations of so-called strong-contrast expansions for the effective conductivity and elastic moduli of generally anisotropic media of arbitrary microstructure. In Chapter 21, rigorous bounds on all of the effective properties are derived using the variational principles of Chapter 14 and specific trial fields. Chapter 22 describes the evaluation of the bounds found in Chapter 21 for certain theoretical model microstructures as well as experimental systems using the results of Part I. Finally, cross-property relations between the seemingly different effective properties considered here are discussed and derived in Chapter 23.

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1.5.3 Scope

Many of the models, methods, and results reported in this book are obtained for two-phase random heterogeneous materials. The extension to heterogeneous materials with more than two phases is formally straightforward but will be covered less extensively. Such materials include polycrystals, which can be considered to be composites with an infinite number of anisotropic phases in which each phase is defined by the crystallographic orientation of the individual grains.

There are now a variety of computer-simulation techniques that have been developed to evaluate directly the effective properties of realizations of model microstructures (typically with periodic boundary conditions) and of real material microstructures. Such "computer experiments" are invaluable tools in providing benchmarks to test theories and in gaining insight into the nature of the structure/property relation. Some of the theoretical property predictions given in this book will be compared to available simulation data, but a treatment of such numerical methods is beyond the scope of the book. Specific citations to the numerical literature are given in Chapter 22.

Space limitations will not permit us to treat, in any detail, cases in the conduction and elasticity problems in which the multiphase interfaces of the heterogeneous material are characterized by their own properties, i.e., nonideal or imperfect interfaces (Chapter 13). However, the various techniques to obtain effective properties with ideal interfaces (described throughout Part II) may be applied to determine the effective properties with nonideal interfaces. Approaches for nonideal interfaces include approximate methods (Chiew and Glandt 1987, Benveniste 1987, Miloh and Benveniste 1999), exact results for periodic arrays of spheres (Cheng and Torquato 1997a, Cheng and Torquato 1997b), and rigorous bounding techniques (Hashin 1992, Torquato and Rintoul 1995, Lipton and Vernescu 1996, Zoia and Strieder 1997, Lipton 1997).

Heterogeneous materials with nonlinear constitutive relations are not treated. However, it is important to recognize that many of the results and methods in both parts of this book are directly relevant to nonlinear material behavior (Talbot and Willis 1987, Ponte Castaneda and Suquet 1998). In the cases of nonlinear stress-strain or current-electric field laws, it has been shown (Ponte Castaneda and Suquet 1998) that one can obtain estimates of the effective nonlinear behavior based on the behavior of a linear "comparison" material: the subject of this book. Thus, nonlinear behavior involves, at the very least, the same microstructural information as required for the linear material.

The important topic of wave propagation in random media will not be covered. The interested reader is referred to the work of Willis (1981), who discusses variational principles, and of Sheng (1995), who covers a broad range of topics on the theory and physics of wave propagation.

MICROSTRUCTURE CHARACTERIZATION

Microstructural Descriptors

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/q-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 Ω is a sample space (set of "outcomes"), \mathcal{F} is a σ -algebra of subsets of Ω (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 \mathcal{V} of *d*-dimensional Euclidean space, i.e., $\mathcal{V} \in \mathbb{R}^d$. The medium is in general statistically characterized by a random variable $\xi(\mathbf{x}, t; \omega)$, called the *structure* function, that depends on all values of the position vector $\mathbf{x} \in \mathcal{V}$ 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 $\xi(\mathbf{x}; \omega)$ will be taken to be independent of time. For a fixed ω , 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 $\xi(\mathbf{x}; \omega)$ 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 ω of the two-phase random medium occupies the region of space $\mathcal{V} \in \Re^d$ of volume V that is partitioned into two disjoint *random* sets or *phases*: phase 1, a region $\mathcal{V}_1(\omega)$ of volume fraction ϕ_1 , and phase 2, a region $\mathcal{V}_2(\omega)$ of volume fraction ϕ_2 . Since the *random* sets $\mathcal{V}_1(\omega)$ and $\mathcal{V}_2(\omega)$ are the complements of one another, then $\mathcal{V}_1(\omega) \cup \mathcal{V}_2(\omega) = \mathcal{V}$ and $\mathcal{V}_1(\omega) \cap \mathcal{V}_2(\omega) = \emptyset$. Let $\partial \mathcal{V}(\omega)$ denote the surface or interface between $\mathcal{V}_1(\omega)$ and $\mathcal{V}_2(\omega)$. Figure 2.1 shows a portion of a realization of a two-phase random medium. For a given realization ω , the structure function $\xi(\mathbf{x}; \omega)$ is just the *indicator function* $\mathcal{I}^{(i)}(\mathbf{x}; \omega)$ for phase *i*, given for $\mathbf{x} \in \mathcal{V}$ by

$$\mathcal{I}^{(i)}(\boldsymbol{x};\omega) = \begin{cases} 1, & \text{if } \boldsymbol{x} \in \mathcal{V}_i(\omega), \\ 0, & \text{otherwise,} \end{cases}$$
(2.1)



Figure 2.1 A portion of a realization ω of a two-phase random medium, where phase 1 is the white region V_1 , phase 2 is the gray region V_2 , and ∂V is the interface between the two regions.

for i = 1, 2 with

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

The random variable $\mathcal{I}^{(i)}(\mathbf{x}; \omega)$ 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 $\mathcal{M}(\mathbf{x}; \omega)$ for the interface is defined as

$$\mathcal{M}(\mathbf{x};\omega) = |\nabla \mathcal{I}^{(1)}(\mathbf{x};\omega)| = |\nabla \mathcal{I}^{(2)}(\mathbf{x};\omega)|$$
(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 ω from the notation and write $\mathcal{I}^{(i)}(x)$ for $\mathcal{I}^{(i)}(x; \omega)$ and $\mathcal{M}(x)$ for $\mathcal{M}(x; \omega)$.

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

1, which we write as

$$\mathcal{P}\left\{\mathcal{I}^{(i)}(x)=1\right\}.$$

Given this probability, it follows that

$$\mathcal{P}\left\{\mathcal{I}^{(i)}(\boldsymbol{x})=0\right\}=1-\mathcal{P}\left\{\mathcal{I}^{(i)}(\boldsymbol{x})=1\right\}.$$

A discrete random variable X can equivalently be specified by its *cumulative distribution* function F(x), defined by

$$F(x) \equiv \mathcal{P}\left\{X \le x\right\},$$

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 $\mathcal{I}^{(i)}(\mathbf{x})$ is somewhat awkward notationally and will be avoided.

We should note that the expectation (or average) of any function $f[\mathcal{I}^{(i)}(\mathbf{x})]$ can be expressed as

$$\left\langle f[\mathcal{I}^{(i)}(\mathbf{x})]\right\rangle = \mathcal{P}\left\{\mathcal{I}^{(i)}(\mathbf{x}) = 1\right\}f(1) + \mathcal{P}\left\{\mathcal{I}^{(i)}(\mathbf{x}) = 0\right\}f(0),$$

where angular brackets denote an *ensemble* average, i.e., an average over all realizations ω of the ensemble. In particular, when $f[\mathcal{I}^{(i)}(\mathbf{x})] = \mathcal{I}^{(i)}(\mathbf{x})$, this expectation relation yields

$$S_1^{(i)}(\mathbf{x}) \equiv \left\langle \mathcal{I}^{(i)}(\mathbf{x}) \right\rangle = \mathcal{P} \left\{ \mathcal{I}^{(i)}(\mathbf{x}) = 1 \right\}.$$
(2.4)

Thus, in light of the 0, 1 nature of the indicator function $\mathcal{I}^{(i)}(\mathbf{x})$, its expectation is exactly the same as the probability $\mathcal{P} \{\mathcal{I}^{(i)}(\mathbf{x}) = 1\}$. Accordingly, following Torquato and Stell (1982), we refer to $S_1^{(i)}(\mathbf{x})$ as the *one-point probability function* for phase *i*, since it gives the probability of finding phase *i* at the position \mathbf{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 $\mathcal{I}^{(i)}(\mathbf{x}; \omega)$ for all \mathbf{x} in \mathcal{V} . Therefore, we may regard the random set $\mathcal{V}_i(\omega)$ as the collection of all random variables $\mathcal{I}^{(i)}(\mathbf{x})$ for $\mathbf{x} \in \mathcal{V}$. Hence, the probability law of $\mathcal{V}_i(\omega)$ is described by the finite-dimensional distributions of the random process $\{\mathcal{I}^{(i)}(\mathbf{x}) : \mathbf{x} \in \mathcal{V}\}$. In other words, the probabilistic description of $\mathcal{V}_i(\omega)$ is given by the joint distribution of $\mathcal{I}^{(i)}(\mathbf{x}_1)\mathcal{I}^{(i)}(\mathbf{x}_2)\cdots\mathcal{I}^{(i)}(\mathbf{x}_n)$ as $n \ge 1$ varies over the integers and $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$ vary over \mathcal{V} . Of course, since the $\mathcal{I}^{(i)}(\mathbf{x})$ are either 0 or 1, this amounts to specifying the probabilities

$$\mathcal{P}\left\{\mathcal{I}^{(i)}(\boldsymbol{x}_1) = j_1, \mathcal{I}^{(i)}(\boldsymbol{x}_2) = j_2, \dots, \mathcal{I}^{(i)}(\boldsymbol{x}_n) = j_n\right\},$$
(2.5)

where each j_k is either 0 or 1.

2.2: n-POINT PROBABILITY FUNCTIONS

The expectation of the product $\mathcal{I}^{(i)}(\mathbf{x}_1)\mathcal{I}^{(i)}(\mathbf{x}_2)\cdots\mathcal{I}^{(i)}(\mathbf{x}_n)$ is a particularly important average. Following the same line of reasoning leading to (2.4), we get

$$S_n^{(i)}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) \equiv \left\langle \mathcal{I}^{(i)}(\mathbf{x}_1) \mathcal{I}^{(i)}(\mathbf{x}_2) \cdots \mathcal{I}^{(i)}(\mathbf{x}_n) \right\rangle$$

= $\mathcal{P} \left\{ \mathcal{I}^{(i)}(\mathbf{x}_1) = 1, \mathcal{I}^{(i)}(\mathbf{x}_2) = 1, \dots, \mathcal{I}^{(i)}(\mathbf{x}_n) = 1 \right\}$
= Probability that *n* points at positions $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n$ (2.6)
are found in phase *i*.

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 $S_2^{(i)}$ 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

$$\mathcal{P}\left\{\mathcal{I}^{(i)}(\mathbf{x}_{1}) = j_{1}, \mathcal{I}^{(i)}(\mathbf{x}_{2}) = j_{2}, \dots, \mathcal{I}^{(i)}(\mathbf{x}_{n}) = j_{n}\right\}$$
$$= \left\langle \prod_{k \in K} \mathcal{I}^{(i)}(\mathbf{x}_{k}) \prod_{l \in L} [1 - \mathcal{I}^{(i)}(\mathbf{x}_{l})] \right\rangle,$$
(2.7)

where $K = \{k \le n; j_k = 1\}$ and $L = \{l \le n; j_l = 0\}$, 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 $S_1^{(1)}$, $S_2^{(1)}$,..., $S_n^{(1)}$. This is easily shown, since

$$S_n^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \left\langle \prod_{j=1}^n [1 - \mathcal{I}^{(1)}(\mathbf{x}_j)] \right\rangle$$

= $1 - \sum_{j=1}^n S_1^{(1)}(\mathbf{x}_j) + \sum_{j < k}^n S_2^{(1)}(\mathbf{x}_j, \mathbf{x}_k)$
 $- \sum_{j < k < l}^n S_3^{(1)}(\mathbf{x}_j, \mathbf{x}_k, \mathbf{x}_l) + \dots + (-1)^n S_n^{(1)}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n).$ (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

$$S_{2}^{(12)}(\boldsymbol{x}_{1},\boldsymbol{x}_{2}) = \left\langle \mathcal{I}^{(1)}(\boldsymbol{x}_{1})[1 - \mathcal{I}^{(1)}(\boldsymbol{x}_{2})] \right\rangle = S_{1}^{(1)}(\boldsymbol{x}_{1}) - S_{2}^{(1)}(\boldsymbol{x}_{1},\boldsymbol{x}_{2}).$$
(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:

- effective conductivity, dielectric constant, magnetic permeability, and diffusion coefficient (Brown 1955, Prager 1963b, Beran 1968, Torquato 1980, Milton 1981a, Phan-Thien and Milton 1982, Torquato 1985a)
- effective elastic moduli (Beran 1968, McCoy 1970, Dederichs and Zeller 1973, Kroner 1977, Willis 1981, Milton 1982, Milton and Phan-Thien 1982, Torquato 1997)
- trapping constant or, equivalently, mean survival time (Prager 1963a, Torquato and Rubinstein 1989)
- fluid permeability (Prager 1961, Weissberg and Prager 1970, Berryman and Milton 1985, Rubinstein and Torquato 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 $\mathcal{V}_i(\omega)$ generated from the stochastic process { $\mathcal{I}^{(i)}(\mathbf{x}) : \mathbf{x} \in \mathcal{V}$ } is strictly statistically homogeneous, provided that for some constant vector \mathbf{y} in \mathfrak{N}^d

$$P\left\{ \mathcal{I}^{(i)}(\mathbf{x}_1) = j_1, \mathcal{I}^{(i)}(\mathbf{x}_2) = j_2, \dots, \mathcal{I}^{(i)}(\mathbf{x}_n) = j_n \right\}$$

= $P\left\{ \mathcal{I}^{(i)}(\mathbf{x}_1 + \mathbf{y}) = j_1, \mathcal{I}^{(i)}(\mathbf{x}_2 + \mathbf{y}) = j_2, \dots, \mathcal{I}^{(i)}(\mathbf{x}_n + \mathbf{y}) = j_n \right\}$



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 $n \ge 1$, and x_1, x_2, \ldots, x_n in \Re^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 \Re^d , \mathcal{V} must equal \Re^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), $\mathcal{V}_i(\omega)$ is strictly statistically homogeneous if and only if

$$S_n^{(i)}(x_1, x_2, \dots, x_n) = S_n^{(i)}(x_1 + y, x_2 + y, \dots, x_n + y)$$

= $S_n^{(i)}(x_{12}, \dots, x_{1n}),$ (2.10)

for all $n \ge 1$, 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 ϕ_i of phase *i*, i.e.,

$$S_1^{(i)} = \phi_i. \tag{2.11}$$

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



Figure 2.3 Two examples of portions of statistically homogeneous media with black and white phases. Left panel: The layered medium is statistically anisotropic. Right panel: The medium is statistically isotropic.

to infinity, i.e.,

$$S_n^{(i)}(\mathbf{x}_{12},\ldots,\mathbf{x}_{1n}) = \lim_{V \to \infty} \frac{1}{V} \int_{V} \mathcal{I}^{(i)}(\mathbf{y}) \mathcal{I}^{(i)}(\mathbf{y} + \mathbf{x}_{12}) \cdots \mathcal{I}^{(i)}(\mathbf{y} + \mathbf{x}_{1n}) d\mathbf{y}.$$
 (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 $x_{jk} = |x_{jk}|$, $1 \le j < k \le n$ (see Figure 2.3). For example, the two-point function (also known as the *autocorrelation* function) and three-point function have the form

$$S_{2}^{(t)}(x_{1}, x_{2}) = S_{2}^{(t)}(x_{12}), \tag{2.13}$$

$$S_3^{(t)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = S_3^{(t)}(\mathbf{x}_{12}, \mathbf{x}_{13}, \mathbf{x}_{23}).$$
(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 threedimensional 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 twodimensional 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 $n \ge 2$ 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 ϕ_1 is statistically identical to that of phase 2 in the system where the volume







Phase-inversion symmetric



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 ϕ_1 and $1 - \phi_1$, respectively.

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

$$S_n^{(1)}(x^n;\phi_1,\phi_2) = S_n^{(2)}(x^n;\phi_2,\phi_1), \qquad (2.15)$$

where $x^n \equiv \{x_1, x_2, ..., x_n\}$. 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

2: MICROSTRUCTURAL DESCRIPTORS

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),

$$2S_{2m+1}^{(2)} = 1 - \sum S_1^{(1)} + \sum S_2^{(1)} - \sum S_3^{(1)} + \dots + (-1)^{2m} \sum S_{2m}^{(1)} .$$
 (2.16)

Therefore, for a medium with phase-inversion symmetry at $\phi_1 = \phi_2 = 1/2$, the oddorder 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

$$S_{3}^{(i)}(\boldsymbol{x}_{1},\boldsymbol{x}_{2},\boldsymbol{x}_{3}) = \frac{1}{2} \left[S_{2}^{(i)}(\boldsymbol{x}_{1},\boldsymbol{x}_{2}) + S_{2}^{(i)}(\boldsymbol{x}_{1},\boldsymbol{x}_{3}) + S_{2}^{(i)}(\boldsymbol{x}_{2},\boldsymbol{x}_{3}) - \frac{1}{2} \right].$$
(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 \mathcal{V}_i . For statistically homogeneous but anisotropic media, $S_n^{(i)}$ is the probability that all *n* vertices of $F_n^{(i)}$ lie in \mathcal{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 \mathcal{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 $L \ge x$. The probability p that the needle crosses the lines is inversely proportional to π ; 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 $\Omega^{(n)}$, 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

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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

$$S_{n}^{(i)}(\mathbf{x}^{n}) = S_{n-q}^{(i)}(\mathbf{x}_{1}, \dots, \mathbf{x}_{i_{1}}, \overline{\mathbf{x}_{i_{2}}, \dots, \mathbf{x}_{i_{q+1}}}, \dots, \mathbf{x}_{n})$$

= $\left\langle \mathcal{I}^{(i)}(\mathbf{x}_{1}) \cdots \mathcal{I}^{(i)}(\mathbf{x}_{i_{1}}) \overline{\mathcal{I}^{(i)}(\mathbf{x}_{i_{2}}) \cdots \mathcal{I}^{(i)}(\mathbf{x}_{i_{q+1}})} \cdots \mathcal{I}^{(i)}(\mathbf{x}_{n}) \right\rangle,$ (2.18)

where a bar above a quantity indicates its absence.

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Let us now consider partitioning the set $\{x_1, x_2, ..., x_n\}$ into L subsets $\{x_1\}, \{x_2, x_3\}, \{x_4, x_5, x_6\}, ...$ Let all of the relative distances between the m elements of these subsets remain bounded, and let F_m^j be the polyhedron with m vertices located at the positions associated with the *j*th subset. We denote the centroid of F_m^j by R_j . Let R_{jk} be the relative distance between the centroids of F_m^j and F_m^k , where *j* and *k* are all possible values such that $1 \le j < k \le L$. 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:

$$\lim_{\text{all } R_{jk} \to \infty} S_n^{(i)}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_n) = \left\langle \mathcal{I}^{(i)}(\mathbf{x}_1) \right\rangle \left\langle \mathcal{I}^{(i)}(\mathbf{x}_2) \mathcal{I}^{(i)}(\mathbf{x}_3) \right\rangle \left\langle \mathcal{I}^{(i)}(\mathbf{x}_4) \mathcal{I}^{(i)}(\mathbf{x}_5) \mathcal{I}^{(i)}(\mathbf{x}_6) \right\rangle \cdots = S_1^{(i)}(\mathbf{x}_1) S_2^{(i)}(\mathbf{x}_2, \mathbf{x}_3) S_3^{(i)}(\mathbf{x}_4, \mathbf{x}_5, \mathbf{x}_6) \cdots$$
(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

$$\lim_{\|R_{\alpha\beta}\to\infty} S_n^{(i)}(x_1, x_2, \dots, x_n) = \prod_{\{\gamma\}} S_{m(\gamma)}^{(i)}(x_1, x_2, \dots, x_{m(\gamma)}), \qquad (2.20)$$

where $R_{\alpha\beta}$ is the distance between the centroids of sets α and β . 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

$$\lim_{x_{12}\to 0} S_2^{(i)}(\mathbf{x}_{12}) = \phi_i, \qquad \lim_{x_{12}\to \infty} S_2^{(i)}(\mathbf{x}_{12}) = \phi_i^2, \tag{2.21}$$

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

$$\lim_{x_{23}\to 0, x_{13}\to 0} S_3^{(i)}(\boldsymbol{x}_{12}, \boldsymbol{x}_{13}) = \phi_i, \qquad \lim_{x_{23}\to 0} S_3^{(i)}(\boldsymbol{x}_{12}, \boldsymbol{x}_{13}) = S_2^{(i)}(\boldsymbol{x}_{12}), \tag{2.22}$$

$$\lim_{\substack{x_{13}\to\infty\\x_{12} \text{ fixed}}} S_3^{(i)}(x_{12}, x_{13}) = \phi_i S_2^{(i)}(x_{12}), \qquad \lim_{\text{all } x_{ij}\to\infty} S_3^{(i)}(x_{12}, x_{13}) = \phi_i^3.$$
(2.23)

Since $0 \leq \mathcal{I}^{(i)}(x) \leq 1$ for all *x* in \mathcal{V} , we have the elementary bounds

$$0 \le S_n^{(i)}(x^n) \le S_{n-1}^{(i)}(x^{n-1}), \quad \text{for all } x^n \text{ and } n \ge 2, \quad (2.24)$$

$$0 \le S_1^{(i)}(x_1) \le 1, \quad \text{for all } x_1.$$
 (2.25)

The one-point function $S_1^{(i)}(x_1)$ (equal to the volume fraction ϕ_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

 $S_n(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n).$

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 $S_2(\mathbf{r}) \equiv S_2^{(1)}(\mathbf{r})$ for statistically homogeneous media can be obtained by randomly tossing line segments of length $r \equiv |\mathbf{r}|$ with a specified orientation and counting the fraction of times the end points fall in phase 1 (see Figure 2.6). The function $S_2(\mathbf{r})$ provides a measure of how the end points of a vector \mathbf{r} in phase 1 are correlated. For isotropic media, $S_2(\mathbf{r})$ attains its maximum value of ϕ_1 at r = 0 and eventually decays (usually exponentially fast) to its asymptotic value of ϕ_1^2 .

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

$$\chi(\mathbf{r}) \equiv \left\langle [\mathcal{I}^{(1)}(\mathbf{x}) - \phi_1] [\mathcal{I}^{(1)}(\mathbf{x} + \mathbf{r}) - \phi_1] \right\rangle = S_2(\mathbf{r}) - \phi_1^2, \tag{2.26}$$

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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 $S_2 \equiv S_2^{(1)}$ 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.

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where $\mathcal{I}^{(1)}(\mathbf{x}) - \phi_1$ is a random variable with zero mean, and $\mathcal{I}^{(1)}$ is the indicator function (2.1) for phase 1. The autocovariance $\chi(\mathbf{r})$ 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 $\chi(\mathbf{r})$ must be positive semidefinite (nonnegative) in the sense that for any finite number of spatial locations $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_m$ in \Re^d and arbitrary real numbers a_1, a_2, \ldots, a_m ,

$$\sum_{i=1}^{m} \sum_{j=1}^{m} a_i a_j \chi(\mathbf{r}_i - \mathbf{r}_j) \ge 0.$$
(2.27)

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

$$\ell_{S} = \left\{ \int_{0}^{\infty} r\chi(r)dr \right\}^{1/2} = \left\{ \int_{0}^{\infty} r\left[S_{2}(r) - \phi_{2}^{2}\right]dr \right\}^{1/2}.$$
 (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.,

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

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.,

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

where n_o 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:

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

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

$$S_2(r) = \phi_1 - \frac{s}{4}r + \mathcal{O}(r^2),$$
 (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.,

$$i(k) \sim \frac{2\pi n_o^2 s V}{k^4}, \qquad k \to \infty.$$
 (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

$$\left. \frac{dS_2^{(i)}}{dr} \right|_{r=0} = -\frac{\omega_{d-1}}{\omega_d d} s, \qquad (2.34)$$

where $S_{2}^{(i)}$, more generally, is the two-point probability function for phase *i* and

$$\omega_d = \frac{\pi^{d/2}}{\Gamma(1 + d/2)}$$
(2.35)

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

$$\frac{dS_2^{(i)}}{dr}\Big|_{r=0} = \begin{cases} -s/2 , \quad d=1, \\ -s/\pi , \quad d=2, \\ -s/4 , \quad d=3. \end{cases}$$
(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

$$S_2(r) = \phi_1 - \frac{s}{4}r \left\{ 1 - r^2 \left[\frac{1}{12S} \int K_1 K_2 \, dA + \frac{1}{32S} \int (K_1 - K_2)^2 \, dA \right] \right\} + \cdots, \qquad (2.37)$$

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

$$4\int K_1K_2dA=4\pi(1-p).$$

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

$$S_2(r) = \phi_1 - \frac{s}{4}r + \frac{Z\phi_1}{4}\left(\frac{r}{D}\right)^2 + \mathcal{O}(r^3), \qquad (2.38)$$

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

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

It follows that

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

and from Schwarz's inequality that

$$\chi(\mathbf{r})| \le \langle Y^2 \rangle - \mu^2. \tag{2.41}$$

We now state the generalization of the Wiener-Khinchtine 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 $\chi(\mathbf{r})$ of a general stochastically continuous homogeneous process $\{Y(\mathbf{x}) : \mathbf{x} \in \mathbb{R}^d\}$ is that it has the spectral (Fourier–Stieltjes) representation

$$\chi(\mathbf{r}) = \frac{1}{(2\pi)^d} \int e^{i\mathbf{k} \cdot \mathbf{r}} dZ(\mathbf{k}), \qquad (2.42)$$

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

$$\int_{\mathbb{R}^d} |\chi(\mathbf{r})| \, d\mathbf{r} < \infty, \tag{2.43}$$

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

$$\chi(\mathbf{r}) = \frac{1}{(2\pi)^d} \int \tilde{\chi}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k}, \qquad (2.44)$$

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

$$\tilde{\chi}(k) = \int \chi(r) e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \, d\boldsymbol{r} \ge 0, \quad \text{for all } \boldsymbol{k}.$$
(2.45)

Remarks:

- 1. This theorem may be proved by exploiting a general theorem due to Bochner (1936) that any continuous function $f(\mathbf{r})$ 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 $\chi(\mathbf{r})$ follows directly from the requirement that the process $Y(\mathbf{x})$ 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 $\tilde{\chi}(k) \ge 0$, 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 $\tilde{g}(k) \ge 0$.

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 $\{\mathcal{I}^{(i)}(\mathbf{x}) : \mathbf{x} \in \mathbb{R}^d\}$ 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 $\{\mathcal{I}^{(i)}(\mathbf{x}) : \mathbf{x} \in \mathbb{R}^d\}$ is a subclass of the total class that comes from the general process $\{\mathcal{I}^{(i)}(\mathbf{x}) : \mathbf{x} \in \mathbb{R}^d\}$ 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 $\chi(\mathbf{r})$ 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

1955, Shepp 1967). 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 $S_2^{(i)}(0) = \langle [\mathcal{I}^{(i)}]^2 \rangle = \langle \mathcal{I}^{(i)} \rangle = \phi_i$, the autocovariance at the origin is given by

$$\chi(0) = \phi_1 \phi_2, \quad \text{for all } \chi(\mathbf{r}) \in B, \tag{2.46}$$

which should be compared to formula (2.40) for general stochastic processes. Application of the inequalities (2.24) to the two-point function $S_2^{(i)}(\mathbf{r})$ for homogeneous media yield the bounds $0 \le S_2^{(i)}(\mathbf{r}) \le \phi_i$, 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:

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

Unlike general stochastic processes for which (2.41) applies, here we have both upper and lower bounds on $\chi(\mathbf{r})$, the lower bound deriving from the *pointwise nonnegativity* of $S_2^{(i)}(\mathbf{r})$. 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

$$\left. \frac{dS_2^{(i)}}{dr} \right|_{r=0} = \frac{d\chi}{dr} \bigg|_{r=0} < 0, \quad \text{for all } 0 < \phi_i < 1 \quad \text{and } \chi(r) \in B.$$
(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 twophase 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 $\chi(\mathbf{r})$ belongs to *B*, either condition still provides a stringent test that all physically realizable $\chi(\mathbf{r})$ 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.

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Practically speaking, it is difficult to apply the nonnegativity condition (2.27) in order to test the validity of a proposed $\chi(\mathbf{r})$. For a wide class of statistically homogeneous two-phase media, $\chi(\mathbf{r})$ tends to zero fast enough for the Fourier transform $\hat{\chi}(\mathbf{k})$ to exist [cf. (2.43)]. In such instances, it is much easier to apply the nonnegativity condition (2.45) to test the validity of a proposed $\chi(\mathbf{r})$. In what follows, we will assume that the spectral function $\hat{\chi}(\mathbf{k})$ exists and proceed to show that there are *d* different nonnegativity conditions that one can exploit if the random medium is also statistically isotropic (Torquato 1999).

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

$$\tilde{f}(k) = \int f(r)e^{-ik \cdot r} dr, \qquad (2.49)$$

and the associated inverse operation is defined by

$$f(\mathbf{r}) = \frac{1}{(2\pi)^d} \int \tilde{f}(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k},$$
(2.50)

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, and 3:

$$\tilde{f}(k) = 2 \int_0^\infty f(r) \cos kr dr, \qquad f(r) = \frac{1}{\pi} \int_0^\infty \tilde{f}(k) \cos kr dk, \qquad d = 1,$$
 (2.51)

$$\tilde{f}(k) = 2\pi \int_0^\infty f(r)r J_0(kr) dr, \quad f(r) = \frac{1}{2\pi} \int_0^\infty \tilde{f}(k)k J_0(kr) dk, \qquad d = 2, \quad (2.52)$$

$$\tilde{f}(k) = \frac{4\pi}{k} \int_0^\infty f(r) r \sin kr dr, \quad f(r) = \frac{1}{2\pi^2 r} \int_0^\infty \tilde{f}(k) k \sin kr dk, \quad d = 3, \quad (2.53)$$

where $k = |\mathbf{k}|$ 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

$$\int [S_2(\mathbf{r}) - \phi_1^2] d\mathbf{r} \ge 0.$$
(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 (see Chapter 11).

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

$$\int_0^\infty [S_2(r) - \phi_1^2] r^{d-1} dr \ge 0.$$
(2.55)

Here we have used the fact that $d\mathbf{r} = \Omega(d)r^{d-1}dr$ 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., $k \ge 0$), we have that

$$\tilde{\chi}(k;m) \ge 0, \qquad m = 1, 2, \dots, d.$$
 (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, ..., 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

$$M_n \ge 0, \qquad n = 0, 1, \dots, d-1.$$
 (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).

2.3 Surface Correlation Functions

Surface correlation functions contain information about the random interface $\partial \mathcal{V}$ 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.,

$$s(\mathbf{x}) = \langle \mathcal{M}(\mathbf{x}) \rangle,$$
 (2.60)

where $\mathcal{M}(x)$ 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

$$F_{sv}(\mathbf{x}_1, \mathbf{x}_2) = \langle \mathcal{M}(\mathbf{x}_1) \mathcal{I}(\mathbf{x}_2) \rangle, \qquad (2.61)$$

$$F_{ss}(\boldsymbol{x}_1, \boldsymbol{x}_2) = \langle \mathcal{M}(\boldsymbol{x}_1) \mathcal{M}(\boldsymbol{x}_2) \rangle, \qquad (2.62)$$

where $\mathcal{I}(\mathbf{x}) \equiv \mathcal{I}^{(1)}(\mathbf{x})$ 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 1988). For homogeneous media they depend only on the displacement $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$, and for isotropic media they depend only on the displacement $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$, and for isotropic media they depend only on the distance $\mathbf{r} = |\mathbf{r}|$. 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, $F_{sv}(\mathbf{x}_1, \mathbf{x}_2) \rightarrow s(\mathbf{x}_1)S_1(\mathbf{x}_2)$ and $F_{ss}(\mathbf{x}_1, \mathbf{x}_2) \rightarrow s(\mathbf{x}_1)s(\mathbf{x}_2)$. In the case of homogeneous media (of special interest to us in subsequent chapters), these asymptotic results for $|\mathbf{r}| \rightarrow \infty$ reduce to

$$F_{sv}(\mathbf{r}) \to \langle \mathcal{M} \rangle \langle \mathcal{I} \rangle = s\phi_1, \qquad F_{ss}(\mathbf{r}) \to \langle \mathcal{M} \rangle^2 = s^2,$$
 (2.63)

where $\phi_1 = \langle \mathcal{I} \rangle$ 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:

$$F_{ss\cdots s\upsilon \upsilon\cdots \upsilon}(\boldsymbol{x}^{m}; \boldsymbol{x}^{n-m}) = \left\langle \left[\prod_{i=1}^{m} \mathcal{M}(\boldsymbol{x}_{i})\right] \left[\prod_{j=m+1}^{n} \mathcal{I}(\boldsymbol{x}_{j})\right] \right\rangle,$$
(2.64)

where $x^{n-m} \equiv x_{m+1}, x_{m+2}, \dots, x_n$. 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.,

$$F_{ss...svv...v}(\mathbf{x}^m; \mathbf{x}^{n-m}) \ge 0, \quad \text{for all } \mathbf{x}^n \text{ in } \mathcal{V}.$$

$$(2.65)$$

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 *lineal-path func*tion $L^{(i)}$ (Lu and Torquato 1992a). For statistically isotropic media, it is defined as follows:

 $L^{(i)}(z) =$ Probability that a line segment of length z lies wholly in phase *i* 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 *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 *connectedness* information about phase *i*, albeit only along a *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

$$L^{(i)}(0) = \phi_i, \qquad L^{(i)}(\infty) = 0,$$

where ϕ_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:

 $p^{(i)}(z) =$ Probability of finding a chord of length between z and z + dz (2.67) in phase *i*.

2: MICROSTRUCTURAL DESCRIPTORS

Since it is a probability density function (having dimensions of inverse length), $p^{(i)}(z) \ge 0$ for all z, and it normalizes to unity, i.e.,

$$\int_0^\infty p^{(i)}(z)dz = 1.$$
 (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 ϕ_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 ϕ_i , i.e.,

$$\frac{\phi_i y p^{(i)}(y) dy}{\int_0^\infty y p^{(i)}(y) dy}.$$

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

$$\Theta(x) = \begin{cases} 0, & \text{if } x < 0, \\ 1, & \text{if } x \ge 0. \end{cases}$$
(2.69)

2.5: CHORD-LENGTH DENSITY FUNCTION

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

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

Differentiating (2.70) yields

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

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

$$\ell_C^{(i)} = \int_0^\infty z p^{(i)}(z) dz.$$
 (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., $G(z) = \mathcal{P}\{z \le Z\} = -(\ell_C/\phi_i)dL^{(i)}/dz$ (where Z is the associated continuous random variable). Differentiation of (2.71) and rearrangement of terms gives

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

$$\ell_{C}^{(i)} = \frac{\phi_{i}}{-\frac{dS_{2}^{(i)}}{dr}} = \frac{\omega_{d} \phi_{i} d}{\omega_{d-1}} \frac{1}{s},$$
(2.74)

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

$$\ell_{C}^{(i)} = \begin{cases} \frac{2\phi_{i}}{s} , & d = 1, \\ \frac{\pi\phi_{i}}{s} , & d = 2, \\ \frac{4\phi_{i}}{s} , & d = 3. \end{cases}$$
(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 $\ell_C^{(i)}$ and ϕ_i remain invariant when determined from (d - 1)-dimensional cuts through a *d*-dimensional isotropic medium, then from (2.75) we immediately obtain

$$s(d=3) = \frac{4}{\pi}s(d=2) = 2 \ s(d=1).$$
 (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:

 $P(\delta)d\delta = \text{Probability that a randomly chosen point in } \mathcal{V}_1(\omega) \text{ lies at a} \\ \text{distance between } \delta \text{ and } \delta + d\delta \text{ from the$ *nearest* $point on the} \\ \text{pore-solid interface.}$ (2.77)

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

$$\int_{0}^{\infty} P(\delta) d\delta = 1.$$
 (2.78)

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

$$P(0) = \frac{s}{\phi_1}, \qquad P(\infty) = 0,$$
 (2.79)

where s/ϕ_1 is the interfacial area per unit pore volume. The associated *complementary* cumulative distribution function $F(\delta) = \mathcal{P}\{\Delta \ge \delta\}$ (where Δ is the associated continuous random variable)

$$F(\delta) = \int_{\delta}^{\infty} P(r) dr$$
 (2.80)

is a nonincreasing function of δ such that

$$F(0) = 1, \qquad F(\infty) = 0.$$
 (2.81)

Thus, $F(\delta)$ is the fraction of pore space that has a pore radius larger than δ .

2.6: PORE-SIZE FUNCTIONS

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

$$\langle \delta^n \rangle = \int_0^\infty \delta^n P(\delta) d\delta, \qquad (2.82)$$

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:

$$\langle \delta^n \rangle = n \int_0^\infty \delta^{n-1} F(\delta) d\delta.$$
 (2.83)

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 δ 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 *intrinsi-cally 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" nearestneighbor 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

$$P(\delta) = \frac{H_V(\delta + R)}{\phi_1}, \qquad \delta \ge 0, \tag{2.84}$$

$$F(\delta) = \frac{E_V(\delta + R)}{\phi_1}, \qquad \delta \ge 0.$$
(2.85)

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

$$P(\delta) = \frac{h_V(\delta)}{\phi_1}, \qquad \delta \ge 0, \tag{2.86}$$

$$F(\delta) = \frac{e_V(\delta)}{\phi_1}, \qquad \delta \ge 0. \tag{2.87}$$

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 $j \neq i$. 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 $C_2^{(i)}(x_1, x_2)$, defined to be the probability of finding two points at x_1 and x_2 in the same cluster of phase *i*. Thus, $C_2^{(i)}$ is the analogue of $S_2^{(i)}$, but unlike its predecessor, it contains nontrivial topological "connectedness" information. The measurement of $C_2^{(i)}$ for a three-dimensional material sample cannot be made from a two-dimensional crosssection of the material, since it is an intrinsically three-dimensional microstructural function.

Further mathematical details about $C_2^{(i)}$ and other existing percolation-sensitive quantities have been deferred until Chapters 9 and 10. Chapter 12 describes, among other considerations, the evaluation of $C_2^{(i)}$ 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 ρ 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



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, Hefland, Reiss, Frisch and Lebowitz 1960). This quantity (defined more precisely below) essentially characterizes the probability of finding a nearestneighbor 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:

- $H_V(r)dr$ = Probability that at an arbitrary point in the system the center of the nearest particle lies at a distance between r and r+dr. (2.88)
- $H_P(r)dr$ = Probability that at an arbitrary particle center in the system the center of the nearest particle lies at a distance between (2.89) r and r + dr.

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:

- $E_V(r)$ = Probability of finding a region $\Omega_V(r)$ (which is a *d*dimensional spherical cavity of radius *r* centered at some arbitrary point) empty of particle centers.
 - = Expected fraction of space available to a "test" sphere of radius r D/2 inserted into the system. (2.90)
- $E_P(r) =$ Probability of finding a region $\Omega_P(r)$ (which is a *d*dimensional spherical cavity of radius *r* centered at some (2.91) arbitrary particle center) empty of other particle centers.

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

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

and

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

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cle center in regions $\Omega_V(r)$ and $\Omega_P(r)$. Differentiating the exclusion-probability relations with respect to r gives

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

and

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

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

and

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

where

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

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:

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

- = Average number of particles at a radial distance between r and r+dr from the center of $\Omega_V(r)$, given that this region (2.99) is empty of particle centers.
- $\rho s_1(r)G_P(r)dr$ = Given that region $\Omega_P(r)$ (sphere of radius *r* 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 $s_1(r)dr$ surrounding the central particle.
 - = Average number of particles at a radial distance between r and r+dr from the center of $\Omega_P(r)$, given that this region (2.100) is empty of particle centers.

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

$$E_{V}(r) = \exp\left[-\int_{0}^{r} \rho s_{1}(y)G_{V}(y)dy\right],$$
(2.101)

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

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

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

and

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

We see that once any one of the triplet H_V , E_V , G_V (H_P , E_P , G_P) 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

$$H_V(R) = s, \qquad E_V(R) = \phi_1,$$
 (2.105)

where s and ϕ_1 are the specific surface and volume fraction of phase 1, respectively. This expression combined with (2.96) yields

$$G_V(R) = \frac{s}{\rho s_1(R)\phi_1}.$$
 (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:

$$E_V(0) = H_V(0) = G_V(0) = 0, \qquad E_V(\infty) = H_V(\infty) = 0.$$

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

$$E_P(0)=1, \qquad E_P(\infty)=H_P(\infty)=0.$$

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

2.8: NEAREST-NEIGHBOR FUNCTIONS

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

$$\ell_P = \int_D^\infty r H_P(r) dr, \qquad (2.108)$$

which is equivalent to

$$\ell_P = D + \int_D^\infty E_P(r) dr$$

= $D + \int_D^\infty \exp\left[-\int_0^r \rho s_1(y) G_P(y) dy\right] dr.$ (2.109)

Since, as we will see in Chapter 5, $E_P \ge 0$ for impenetrable spheres, it follows that $\ell_P \ge D$.

Finally, we would like to describe related nearest-neighbor functions. The nearestneighbor 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

$$h_V(r) = H_V(r+R), \quad e_V(r) = E_V(r+R).$$
 (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:

 $h_V(r)dr$ = Probability that the nearest particle surface lies at a distance between r and r + dr from an arbitrary point in the system. (2.111) $h_P(r)dr$ = Probability that the nearest particle surface lies at a distance between r and r+dr from the center of an arbitrary (2.112) particle of radius R.

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.,

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

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

$$h_V(r) = -\frac{\partial e_V}{\partial r}, \qquad h_P(r) = -\frac{\partial e_P}{\partial r}.$$
 (2.115)

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

$$h_V(r) = g_V(r)e_V(r), \qquad h_P(r) = g_P(r)e_P(r).$$
 (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

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

The quantity s/ϕ_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:

$$\lambda_P = \int_0^\infty r h_P(r) dr - R. \qquad (2.118)$$

For the special case of impenetrable spheres, this definition, after integration by parts, is equivalent to

$$\lambda_P = \int_R^\infty e_P(r) dr. \tag{2.119}$$

We refer to λ_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 $r^q \equiv \{r_1, \ldots, r_q\}$ denote the positions of q sphere centers and let $dr^q \equiv dr_1 dr_2 \cdots dr_q$. The point/q-particle correlation (or "distribution") function $G_n^{(i)}(\mathbf{x}; \mathbf{r}^q)$ is defined as follows (Torquato 1986b):

 $G_n^{(i)}(x; r^q)dr^q =$ Probability of finding a point in phase *i* at *x* and the center of a sphere in volume element dr_1 about r_1 , the center of another sphere in volume element dr_2 about r_2, \ldots , and the center of another sphere in volume element dr_q about r_q , 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

$$\int G_n^{(i)}(\mathbf{x}; \mathbf{r}^q) d\mathbf{r}^q = \frac{N!}{(N-q)!} S_1^{(i)}(\mathbf{x}), \tag{2.121}$$

where $S_1^{(i)}(\mathbf{x})$ is the one-point probability function for phase *i* defined in Section 2.2.1. Note that $G_n^{(i)}(\mathbf{x}; \mathbf{r}^q)$ 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 $\mathcal{I}^{(i)}(\mathbf{x})$ for phase *i* given

by (2.1) [see also (4.46) and (4.74)]. Using this expression, it is easy to demonstrate that

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

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

$$G_n^{(1)}(\mathbf{x}; \mathbf{r}^q) = 0$$
 if $|\mathbf{x} - \mathbf{r}_k| < R$, $k = 1, ..., n$,

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

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

The asymptotic properties of the $G_n^{(i)}(\mathbf{x}; \mathbf{r}^q)$ 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:

 $F_{sp}(x; r_1) =$ Correlation function associated with a point being on the interface at x and the probability of finding the center of (2.122)

a sphere in volume element dr_1 about r_1 .

This function obeys the normalization condition

$$\int F_{sp}(\boldsymbol{x};\boldsymbol{r}_1)d\boldsymbol{r}_1 = Ns(\boldsymbol{x}), \qquad (2.123)$$

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).

CHAPTER 3

Statistical Mechanics of Many-Particle Systems

Statistical mechanics is the branch of theoretical physics that attempts to predict, by starting at the level of atoms, molecules, spins, or other small "particles," the bulk properties of systems in which a large number of these particles interact with one another. In other words, it links the microscopic properties of matter (molecular interactions and structure), as determined from the laws of quantum or classical mechanics, to its macroscopic properties (e.g., pressure of a liquid). The province of statistical physics is more general, extending to any situation in which one is interested in the collective behavior of interacting *entities*, from population dynamics through solids, liquids, and gases to cosmology as well as *random heterogeneous materials*. Systems composed of many interacting particles (albeit much larger than molecular dimensions) are often useful models of random heterogeneous materials, and thus one can exploit the powerful machinery of statistical mechanics to study such materials. Moreover, as we will see in subsequent chapters, the formalism of statistical mechanics can be extended to nonparticulate systems.

The purpose of this chapter is to introduce foundational statistical-mechanical notions and results that we will heavily employ in the remaining chapters of Part I. Readers interested in a more general and comprehensive treatment of statistical mechanics are referred to the books by Tolman (1979), Hansen and McDonald (1986), Hill (1987), and Huang (1987).

The chapter begins with a review of well-established concepts and techniques, such as *n*-particle probability density functions to characterize structure, interparticle potentials, and the Ornstein–Zernike integral equation formalism. Many of these ideas are applied in subsequent chapters. Since the structure of particle systems at high densities is primarily determined by repulsive interactions between the particles, we devote an appreciable portion of this chapter to the discussion of *hard-particle* systems