

## CHAPTER 1

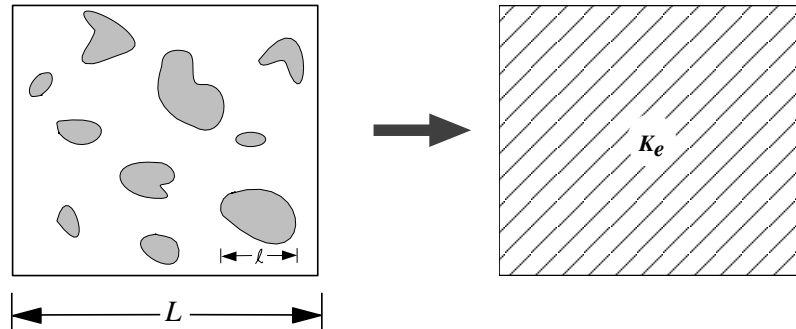
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# Motivation and Overview

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  $\phi_1$  and  $\phi_2$ . Here  $L$  and  $\ell$  represent the macroscopic and microscopic length scales, respectively. Right panel: When  $L$  is much bigger than  $\ell$ , 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

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 ( $\text{Al}_2\text{O}_3$ ) 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.

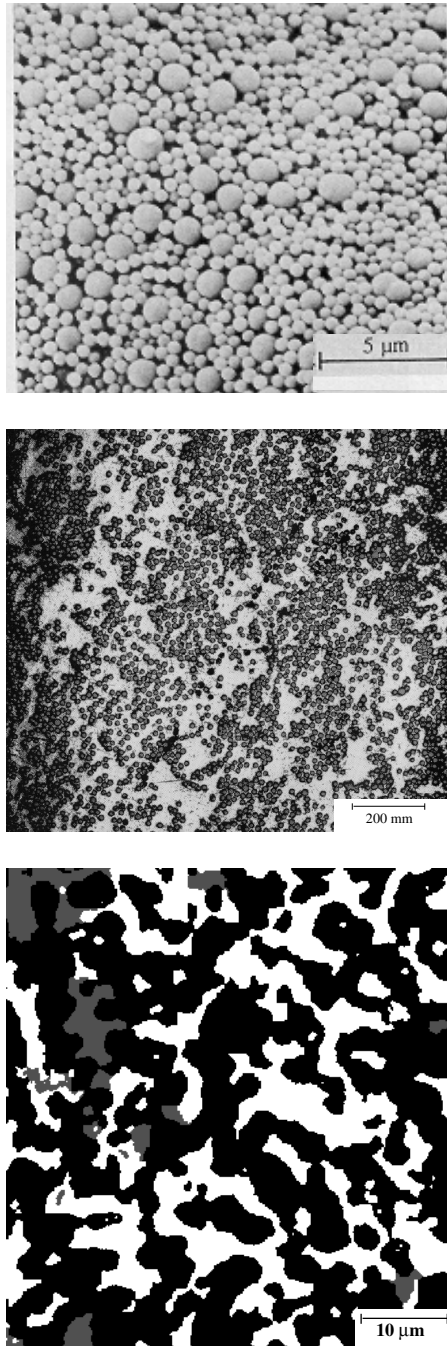
Beginning from the top, the first example of Figure 1.3 shows a planar section through a Fontainebleau sandstone obtained via X-ray microtomography. As we will see, this imaging technique enables one to obtain full three-dimensional renderings of the microstructure (see Figure 12.14), revealing that 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

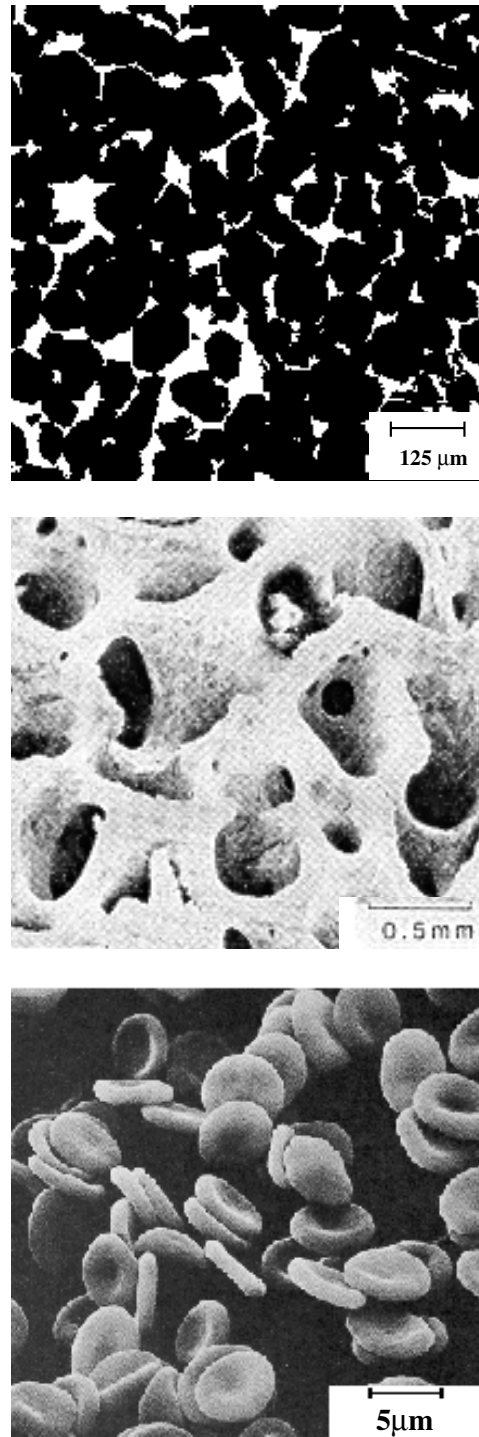
We will consider four different classes of problems as summarized in Table 1.1 on page 7. We will focus mainly on the following four steady-state (time-independent) effective properties associated with these classes:

1. Effective conductivity tensor,  $\sigma_e$
2. Effective stiffness (elastic) tensor,  $C_e$
3. Mean survival time,  $\tau$
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  $\sigma_e$  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 (nonequilibrium) 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  $\sigma_e$  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.

**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 $K_e$	Average (or Applied) Generalized Intensity $G$	Average Generalized Flux $F$
A	Thermal Conductivity	Temperature Gradient	Heat Flux
	Electrical Conductivity	Electric Field	Electric Current
	Dielectric Constant	Electric Field	Electric Displacement
	Magnetic Permeability	Magnetic Field	Magnetic Induction
	Diffusion Coefficient	Concentration Gradient	Mass Flux
B	Elastic Moduli	Strain Field	Stress Field
	Viscosity	Strain Rate Field	Stress Field
C	Survival Time	Species Production Rate	Concentration Field
	NMR Survival Time	NMR Production Rate	Magnetization Density
D	Fluid Permeability	Applied Pressure Gradient	Velocity Field
	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*  $\tau$ , 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  $\mathbf{k}$  (Beran 1968, Scheidegger 1974, Batchelor 1974, Dullien 1979, Torquato 1991b, Adler 1992). The quantity  $\mathbf{k}$  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-



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  $T_1, T_2, \dots$  and  $\Theta_1, \Theta_2, \dots$  as the diffusion and viscous relaxation times, respectively. It will be shown that these relaxation times are related to their steady-state counterparts ( $\tau$  and  $k$ ) as well as to each other.

### 1.2.6 Definitions of Effective Properties

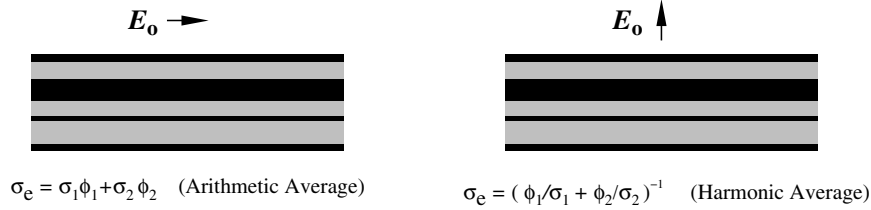
Given the phase properties  $K_1, K_2, \dots, K_M$  and phase volume fractions  $\phi_1, \phi_2, \dots, \phi_M$  of a heterogeneous material with  $M$  phases, how are its effective properties mathematically defined? It will be shown in Chapter 13 that the effective properties of the heterogeneous material 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.,

$$F \propto K_e \cdot G. \quad (1.1)$$

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



**Figure 1.4** A two-phase material consisting of alternating layers of the phases. Formulas (1.2) and (1.3) are exact when the applied field is oriented parallel (left panel) and perpendicular (right panel) to the slabs, respectively.

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.

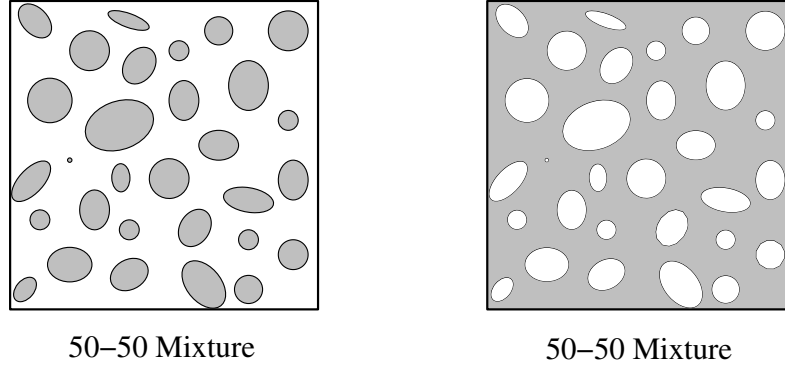
### 1.3 Importance of Microstructure

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  $\phi_1$  and the other with volume fraction  $\phi_2$ , and so  $\phi_1 + \phi_2 = 1$ . In the first case, it is desired to predict the effective conductivity  $\sigma_e$  of a composite of arbitrary microstructure with phase conductivities  $\sigma_1$  and  $\sigma_2$ . One might surmise that a reasonable estimate is a simple weighted average of the phase conductivities involving the volume fractions, such as

$$\sigma_e = \sigma_1 \phi_1 + \sigma_2 \phi_2. \quad (1.2)$$

This arithmetic-average prediction usually grossly overestimates the effective conductivity of isotropic media, especially for widely different phase conductivities. The reason 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 idealized situation and its close approximants represent a very small subset of possible composite microstructures, and therefore (1.2) can appreciably overestimate the effective 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

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

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  $\mathbf{K}_e$  is the following function:

$$\mathbf{K}_e = f(\mathbf{K}_1, \mathbf{K}_2, \dots, \mathbf{K}_M; \phi_1, \phi_2, \dots, \phi_M; \Omega), \quad (1.4)$$

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

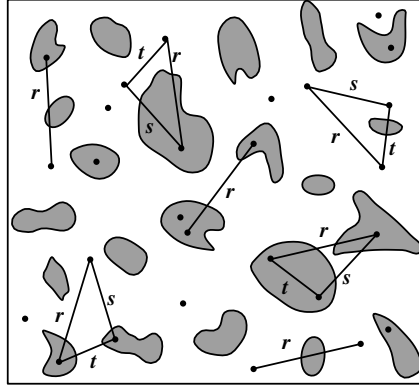
## 1.4 Development of a Systematic Theory

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 com-

plex interacting systems, such as materials science, solid and liquid state theory, and statistical physics.

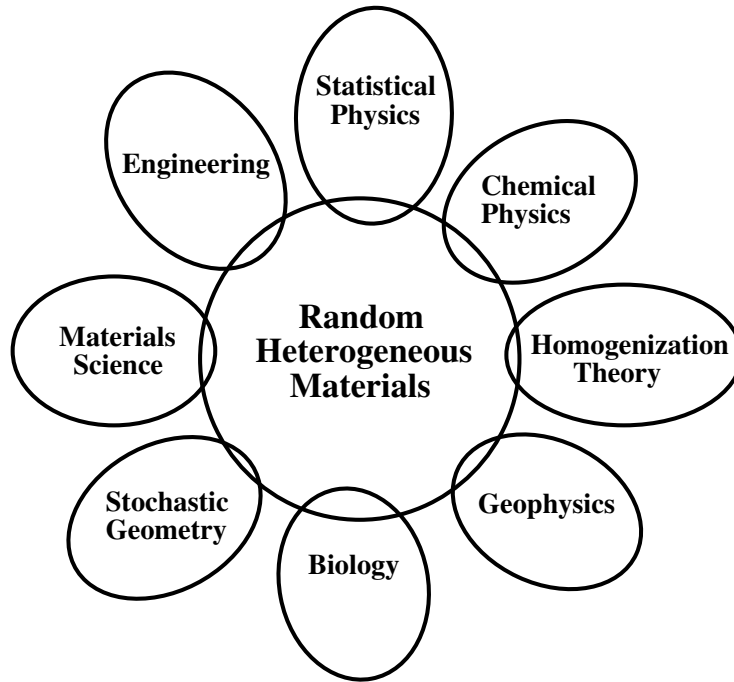
First of all, there are a few special cases in which we do have complete information and hence can compute the effective properties exactly (see Chapters 15, 16, 19, and 20). These examples lend important insight into the salient features that generally determine effective properties. Second, one can 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 three- and 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



**Figure 1.7** The various disciplines that intersect the study of random heterogeneous materials.

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 connectedness 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



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

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 computer-simulation 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.

### 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.

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