Characterization of the microstructure of disordered media: A unified approach

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(Received 28 October 1986)

Transport and mechanical properties of porous and other two-phase composite media have been expressed in terms of different sets of statistical correlation functions. A general methodology is put forth which provides a means of deriving and computing all of these different types of correlation functions (for a certain class of model microstructures), and of establishing the relationships between these functions. This is done by obtaining series representations of a new and general n-point distribution function $H_n$. The distribution function $H_n$ also characterizes the structure of liquids. Applications of this treatment to compute bulk properties are described.

It is well known that the bulk properties (e.g., electrical conductivity, elastic moduli, and fluid permeability) of two-phase composite media depend upon an infinite set of correlation functions which statistically characterize the microstructure. The particular set of functions is not unique and, as a result, a variety of different types of correlation functions have arisen in the literature because of basic differences in either the physical processes one chooses to study or in the approaches taken to characterize a particular physical process.\textsuperscript{1-10}

The $n$-point correlation functions $S_n(x^n)$ (which give the probability of finding $n$ points with positions $x^n = \{x_1, \ldots, x_n\}$ in one of the phases, say phase 1) are fundamental to the study of the conductivity of composite materials,\textsuperscript{1,2} fluid permeability,\textsuperscript{3,4} of porous media, effective rate constant in porous media,\textsuperscript{5} and the elastic moduli of composite materials.\textsuperscript{6,7} For the case of spheres distributed throughout a matrix or void, bounds on the conductivity,\textsuperscript{8} and fluid permeability\textsuperscript{9} have been derived which depend upon the point/n-particle distribution functions $G_n^{(1)}(x^n; r^n)$ (which give the correlation associated with finding a point $x_1$ in the matrix and a configuration of $n$ spheres with coordinates $r^n$).

Other important descriptors of the microstructure of disordered media involve information about the two-phase interface. For example, bounds on the rate constant and fluid permeability of porous media have been obtained which are given in terms of the specific surface $s$ (expected interface area per unit volume—a one-point correlation function) and the surface-matrix $F_{sm}(x_1, x_2)$ and surface-surface $F_{ss}(x_1, x_2)$ correlation functions.\textsuperscript{10} $F_{sm}$ and $F_{ss}$ give the correlations associated with finding a point on the two-phase interface and another point in the matrix phase or on the interface, respectively. For beds of spheres, the fluid permeability has also been shown\textsuperscript{9} to be closely related to a surface-particle (center) correlation function $F_{sp}(x_i; r_1)$. A systematic means of representing and calculating surface correlation functions for nontrivial models has been lacking, and hence application of property relations which depend upon such information has been very limited.

This work is concerned with the development of a general framework from which one may derive and calculate the various kinds of correlation functions described above ($S_n$, $G_n^{(1)}$, $F_{sm}$, $F_{ss}$, and $F_{sp}$), which have been treated separately in the past, and their generalizations (e.g., $F_{mp}$, $F_{app}$, $F_{isp}$, etc.). Such a formalism will enable one, moreover, to establish the relationships between these correlation functions. This is accomplished by obtaining series representations of the general $n$-point distribution function $H_n$, which characterizes the special mixture of particles described below. Interestingly, the $H_n$ (as described below) also characterize the structure of liquids. For simplicity, we shall consider media composed of equisized spheres distributed, throughout the matrix (or void), with an arbitrary degree of penetrability.\textsuperscript{11} The concept of a distribution of spheres becomes very general if one allows the spheres to penetrate one another in varying degrees.\textsuperscript{8,12-14}

Consider adding $p$ spherical “test” particles of radius $b_1, \ldots, b_p$, respectively, to a system of $n$ equisized, spherical included particles of radius $R$ centered at $r^n$. The $p$ test particles are capable of excluding the centers of the included particles from spheres of radius $a_1, \ldots, a_p$, respectively, surrounding the test particles. For $b_i > 0$, $a_i = R + b_i$, and for $b_1 = 0$, we allow the test particles to penetrate the included particles so that $a_i = R - c_i$ ($0 \leq c_i \leq R$), where $a_i$ is the minimum distance between test and included particles (see Fig. 1). It is natural to associate with each test particle $i$ a subdivision of space in two regions: the space available to the $i$th test particle $D_i$ and the complement space $D_i^c$. Let $\delta_i$ denote the surface between $D_i$ and $D_i^c$. The $n$-point distribution function $H_n(x^n, x^{p-n}; r^q)$ characterizes the correlation associated with finding test particle 1 centered at $x_1$ on the surface $\delta_1$, . . . , and test particle $m$ centered at $x_m$ on $\delta_m$, and test particle $m+1$ centered at $x_{m+1}$ in $D_{m+1}$, . . ., , and test particle $p$ centered at $x_p$ in $D_p$, and of finding any $q$ of the included particles with configuration $r^q$, where $n = p + q$. Here $x^{p-n} = x_{m+1}, \ldots, x_p$.

From this single function $H_n$, one can obtain all of the various sets of correlation functions described above by letting the radii of all the solute particles shrink to zero ($b_i = 0$) and setting $a_i = R$, $i = 1, \ldots, p$. For example, in this limit, the $n$-point matrix probability function $S_n(x^n) = H_n(\emptyset; x^n; \emptyset)$ and $G_n^{(1)}(x_1; r^n) = H_n(\emptyset; x_1; r^n)$, where $\emptyset$ denotes the null set. Similarly, the two-point surface-correlation functions in this limit are given by
and

$$m^{(p)}(x_p; \tau_j) = 1 - \prod_{i=1}^{p} [1 - m(y_{ij}; \alpha_i)].$$

(4)

Here $m(r; a) = 1 - e(r; a)$ is the step function which is unity for $r < a$ and zero otherwise, $y_{ij} = |x_i - x_j|$, and $\rho_n(r^n)$ is the commonly employed $n$-particle probability density (which characterizes the configuration of $n$-included particles). Accordingly, given the $\rho_n$ for the model, one can calculate the $H_n$ using Eqs. (1)–(4). The K.S representation is equivalent to the Mayer representation but involves probability density functions that are different from the $\rho_n$ of (3). The Mayer and K.S representations of the $H_n$ enable one to compute all of the correlations described above and their generalizations. These series expressions also provide a means of establishing the relationship between the various types of correlation function that have arisen in the literature.

We should note that these equations generalize series representations of the $S_n$ derived by Torquato and Stell and the $G_{\phi}^{(1)}$ obtained by Torquato for composite media. In the context of liquids, the representations of the $H_n$ provide generalizations of certain expected values that arise in potential distribution theory and in scaled-particle theory.

Elsewhere, this formalism was applied to exactly evaluate the $H_n$ (for any $n$) for fully penetrable (i.e., randomly centered) spheres. The methodology described above, moreover, has enabled us to show that conductivi-

FIG. 1. Schematic of a mixture of test and included particles. The included particles of radius $R$ and test particles with radii $b_i > 0$ ($i = 1, \ldots, p$) are indicated by the shaded and unshaded particles, respectively.

$$F_{nm}(x_1; x_2) = H_2(x_1; x_2; \psi), \quad F_{n^2}(x_1; x_2) = H_2(x_1; x_2; \psi; \psi), \quad F_{n^p}(x_1; x_2) = H_2(x_1; \psi; \psi; \psi).$$

In some cases, the sizes of the test particles one wishes to introduce in a porous medium are not always negligible compared to the pore size, and hence the distribution functions will depend upon the relative size of the particle and pore. Such generalized quantities have a particularly simple application in the theory of gel chromatography.

We have derived two equivalent but topologically different series representations of the $H_n$ for general ensembles of particles. Interestingly, in the special case of an equilibrium ensemble, these two expressions for the $H_n$ can be shown to be (for $m = 0$) isomorphic to the well-known Mayer and Kirkwood-Salsburg (KS) hierarchies of liquid-state statistical mechanics, for a certain mixture of spheres. For this reason, we refer to them as the Mayer and KS representations. In general, both series have the general form

$$H_n = \sum_{s=0}^n (-1)^s H_n^{(s)},$$

(1)

where $H_n^{(s)}$ is an integral that depends upon certain probability density functions which describe the microstructure; quantities which, in principle, are known for the ensemble under consideration. For example, the 5th term of Eq. (1) in the Mayer representation is given by

$$H_n^{(5)}(x^m, x^p, \psi; \tau^q) = (-1)^m \frac{\partial}{\partial a_1} \cdots \frac{\partial}{\partial a_m} G_n^{(s)}(x^p, \tau^q),$$

(2)

where

$$G_n^{(s)}(x^p, \tau^q) = \prod_{l=1}^{q} \prod_{k=1}^{p} e^{(y_{lk}; \alpha_k)} \int \rho_{q+s}(\tau^{q+s}) \prod_{j=q}^{q+s} m^{(p)}(x_p; \tau_j) d\tau_j.$$

(3)
ty bounds due to Beran (which involve the \( S_n \)) and to Torquato (which involve the \( G_n^{(1)} \)) are, in fact, identical to the same for dispersions of impenetrable spheres.

Using Eqs. (1)–(4), the two-point surface correlation functions \( F_{im} \) and \( F_{is} \) have been recently computed and related to one another for an equilibrium distribution of rigid spheres as a function of the sphere volume fraction \( \phi_2 \), for virtually all \( \phi_2 \). These results for \( F_{im} \) and \( F_{is} \) were utilized in Ref. 17 to compute the Doi lower bound on the inverse permeability \( k^{-1} \) for such a porous medium with heretofore unattained accuracy. Figure 2 shows, for the first time, that rigorous bounds on \( k^{-1} \) that depend upon one- and two-point correlation functions can yield results which are relatively close to the well-known Kozeny-Carman empirical formula. This indicates that rigorous bounds which depend upon additional three-point information on the medium, such as the Weissberg-Prager bound, may lead to accurate estimates of \( k \) for a wide range of \( \phi_2 \). We are currently in the process of calculating the Weissberg-Prager bound for rigid spheres using Eqs. (1)–(4).

Lastly, we would like to point out that the nature of the infinite series (1) enables us to obtain successive upper and lower bounds on the \( n \)-point function \( H_n \). We find that for even \( m \)

\[
H_n \geq W_n^{(l)} \text{ for } l \text{ odd}, \tag{5a}
\]

\[
H_n \leq W_n^{(l)} \text{ for } l \text{ even}, \tag{5b}
\]

where

\[
W_n^{(l)} = \sum_{k=0}^{l} (-1)^k H_n^{(k)} \tag{6}
\]

is the partial sum. For odd \( m \), the inequalities in (5) are reversed. The importance of bounds lies in the fact that, in general, the \( H_n^{(e)} \) of (1) become progressively more difficult to compute as \( k \) increases. Bounds on the \( H_n \), therefore, offer a means of approximating the \( H_n \) when an exact determination is out of the question. The KS representation of the \( H_n \) turns out to provide a means of bounding the distribution function that is more powerful than the corresponding Mayer representation. The Mayer series, however, proves to be superior to the KS series for the purposes of exactly evaluating the \( H_n \).

We gratefully acknowledge the support of the Office of Basic Energy Sciences, U. S. Department of Energy, under Grant No. DE-FG05-86ER13482.

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