

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 correlations (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.¹⁻¹⁰

The n -point correlation functions $S_n(\mathbf{x}^n)$ (which give the probability of finding n points with positions $\mathbf{x}^n \equiv \{\mathbf{x}_1, \dots, \mathbf{x}_n\}$ in one of the phases, say phase 1) are fundamental to the study of the conductivity of composite materials,^{1,2} fluid permeability^{3,4} of porous media, effective rate constant in porous media,⁵ and the elastic moduli of composite materials.^{6,7} For the case of spheres distributed throughout a matrix or void, bounds on the conductivity⁸ and fluid permeability⁹ have been derived which depend upon the point/ n -particle distribution functions $G_n^{(1)}(\mathbf{x}_1; \mathbf{r}^n)$ (which give the correlation associated with finding a point \mathbf{x}_1 in the matrix and a configuration of n spheres with coordinates \mathbf{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 $F_{sm}(\mathbf{x}_1, \mathbf{x}_2)$ and surface-surface $F_{ss}(\mathbf{x}_1, \mathbf{x}_2)$ correlation functions.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 shown⁹ to be closely related to a surface-particle (center) correlation function $F_{sp}(\mathbf{x}_1; \mathbf{r}_1)$. 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_{smp} , F_{ssp} , F_{ssm} , 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.¹¹ The concept of a distribution of spheres becomes very general if one allows the spheres to penetrate one another in varying degrees.^{8,12-14}

Consider adding p spherical "test" particles of radius b_1, \dots, b_p , respectively, to a system of N equisized, spherical included particles of radius R centered at \mathbf{r}^N . The p test particles are capable of excluding the centers of the included particles from spheres of radius a_1, \dots, a_p , respectively, surrounding the test particles. For $b_i > 0$, $a_i = R + b_i$, and for $b_i = 0$, 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^* . Let \mathcal{S}_i denote the surface between D_i and D_i^* .¹⁵ The n -point distribution function $H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q)$ characterizes the correlation associated with finding test particle 1 centered at \mathbf{x}_1 on the surface \mathcal{S}_1, \dots , and test particle m centered at \mathbf{x}_m on \mathcal{S}_m , and test particle $m+1$ centered at \mathbf{x}_{m+1} in D_{m+1}, \dots , and test particle p centered at \mathbf{x}_p in D_p , and of finding any q of the included particles with configuration \mathbf{r}^q , where $n = p + q$. Here $\mathbf{x}^{p-m} \equiv \mathbf{x}_{m+1}, \dots, \mathbf{x}_p$.

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 $a_i = R$, $i = 1, \dots, p$. For example, in this limit, the n -point matrix probability function $S_n(\mathbf{x}^n) = H_n(\emptyset; \mathbf{x}^n; \emptyset)$ and $G_q^{(1)}(\mathbf{x}_1; \mathbf{r}^q) = H_n(\emptyset; \mathbf{x}_1; \mathbf{r}^q)$, where \emptyset denotes the null set. Similarly, the two-point surface-correlation functions in this limit are given by

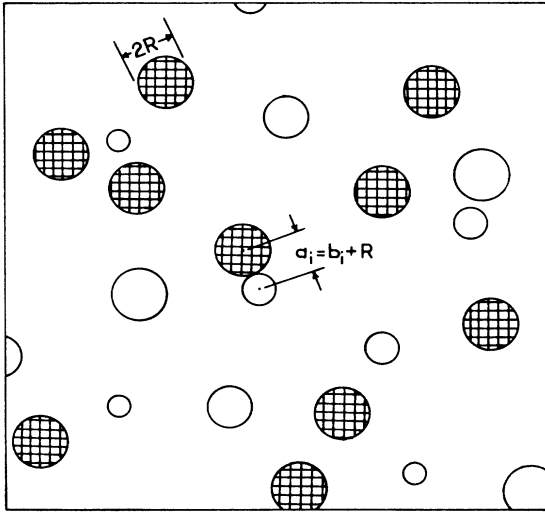


FIG. 1. Schematic of a mixture of test and included particles. The included particles of radius R and test particles with radii $b_i > 0$ ($i = 1, \dots, p$) are indicated by the shaded and unshaded particles, respectively.

$F_{sm}(\mathbf{x}_1, \mathbf{x}_2) = H_2(\mathbf{x}_1, \mathbf{x}_2; \emptyset)$, $F_{ss}(\mathbf{x}_1, \mathbf{x}_2) = H_2(\mathbf{x}_1, \mathbf{x}_2; \emptyset; \emptyset)$, and $F_{sp}(\mathbf{x}_1; \mathbf{r}_1) = H_2(\mathbf{x}_1; \emptyset; \mathbf{r}_1)$. 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.¹⁶

We have derived¹⁷ 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 $H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q)$ can be shown¹⁷ to be (for $m = 0$) isomorphic to the well-known Mayer and Kirkwood-Salsburg (KS) hierarchies of liquid-state statistical mechanics,¹⁸ 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

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

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 s th term of Eq. (1) in the Mayer representation is given by¹⁷

$$H_n^{(s)}(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q) = (-1)^m \frac{\partial}{\partial a_1} \dots \frac{\partial}{\partial a_m} G_n^{(s)}(\mathbf{x}^p; \mathbf{r}^q), \quad (2)$$

where

$$G_n^{(s)}(\mathbf{x}^p; \mathbf{r}^q) = \frac{\prod_{l=1}^q \prod_{k=1}^p e(y_{kl}; a_k)}{s!} \int \rho_{q+s}(\mathbf{r}^{q+s}) \times \prod_{j=q+1}^{q+s} m^{(p)}(\mathbf{x}^p; \mathbf{r}_j) d\mathbf{r}_j, \quad (3)$$

and

$$m^{(p)}(\mathbf{x}^p; \mathbf{r}_j) = 1 - \prod_{i=1}^p [1 - m(y_{ij}; a_i)]. \quad (4)$$

Here $m(r; a) = 1 - e(r; a)$ is the step function which is unity for $r < a$ and zero otherwise, $y_{ij} = |\mathbf{x}_i - \mathbf{r}_j|$, and $\rho_n(\mathbf{r}^n)$ is the commonly employed n -particle probability density (which characterizes the configuration of n -included particles). Accordingly, given the ρ_n for the model, one can calculate the H_n using Eqs. (1)–(4). The KS representation is equivalent to the Mayer representation but involves probability density functions that are different from the ρ_n of (3). The Mayer and KS 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 Stell¹⁹ and the $G_n^{(1)}$ obtained by Torquato⁸ 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 theory²⁰ and in scaled-particle theory.²¹

Elsewhere¹⁷ 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 us²² to show that conductivi-

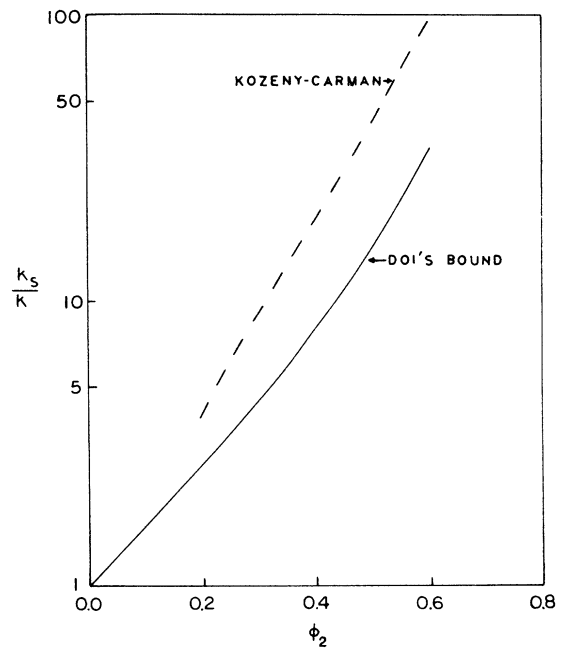


FIG. 2. Comparison of the Doi lower bound on k_s/k for a bed of impenetrable spheres (computed in Ref. 17) and the Kozeny-Carman empirical formula, as a function for the sphere volume fraction ϕ_2 . The quantity k_s is the Stokes dilute-limit permeability.

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

Using Eqs. (1)–(4), the two-point surface correlation functions F_{sm} , F_{ss} , and F_{sp} have been recently computed and related to one another for an equilibrium distribution of rigid spheres as a function of the sphere volume fraction ϕ_2 , for virtually all ϕ_2 .²³ These results for F_{sm} and F_{ss} 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,⁹ may lead to accurate estimates of k for a wide range of ϕ_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 find¹⁷ that

for even m

$$H_n \geq W_n^{(l)} \text{ for } l \text{ odd,} \quad (5a)$$

$$H_n \leq W_n^{(l)} \text{ for } l \text{ even,} \quad (5b)$$

where

$$W_n^{(l)} = \sum_{k=0}^l (-1)^k H_n^{(k)} \quad (6)$$

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 $H_n^{(k)}$ 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.

¹M. Beran, *Nuovo Cimento* **38**, 771 (1965).

²G. W. Milton, *Phys. Rev. Lett.* **46**, 542 (1981); *J. Appl. Phys.* **52**, 5294 (1981).

³S. Prager, *Phys. Fluids* **4**, 1477 (1961).

⁴J. G. Berryman and G. W. Milton, *J. Chem. Phys.* **82**, 754 (1985).

⁵R. A. Reck and S. Prager, *J. Chem. Phys.* **42**, 3027 (1965).

⁶J. J. McCoy, *Recent Advances in Engineering Sciences* (Gordon and Breach, New York, 1970), Vol. 5, pp. 235–254.

⁷G. W. Milton and N. Phan-Thien, *Proc. R. Soc. London Ser. A* **380**, 305 (1982).

⁸S. Torquato, *J. Chem. Phys.* **84**, 6345 (1986).

⁹H. L. Weissberg and S. Prager, *Phys. Fluids* **13**, 2958 (1970); S. Torquato and J. D. Beasley, *ibid.* **30**, 633 (1987).

¹⁰M. Doi, *J. Phys. Soc. Jpn.* **40**, 567 (1976).

¹¹The methodology put forth here applies as well to infinitely long, parallel cylinders in a matrix. The extension of this formalism to particles having a nonspherical shape (e.g., squares, cubes, and ellipsoids) is formally relatively straightforward.

¹²L. Blum and G. Stell, *J. Chem. Phys.* **71**, 42 (1979); J. J. Salacuse and G. Stell, *ibid.* **77**, 3714 (1982).

¹³A. L. Bug, S. A. Safran, and I. Webman, *Phys. Rev. Lett.* **54**,

1412 (1985).

¹⁴T. DeSimone, R. M. Stratt, and S. Demoulini, *Phys. Rev. Lett.* **56**, 1140 (1986).

¹⁵Note it is only when $b_i = 0$ and $a_i = R$ that D_i and \mathcal{S}_i refer to the matrix or void phase (i.e., the space outside the included particles) and the two-phase interface, respectively.

¹⁶See, e.g., W. W. Yau, J. J. Kirkland, and D. D. Bly, *Modern Size-Exclusion Liquid Chromatography* (Wiley, New York, 1979).

¹⁷S. Torquato, *J. Stat. Phys.* **45**, 843 (1986).

¹⁸J. E. Mayer, *J. Chem. Phys.* **15**, 187 (1947); J. G. Kirkwood and Z. W. Salsburg, *Discuss. Faraday. Soc.* **15**, 28 (1953); S. Baer and J. L. Lebowitz, *J. Chem. Phys.* **40**, 3474 (1964).

¹⁹S. Torquato and G. Stell, *J. Chem. Phys.* **77**, 2071 (1982); S. Torquato and G. Stell, *ibid.* **78**, 3262 (1983).

²⁰B. Widom, *J. Chem. Phys.* **39**, 2808 (1963); **41**, 74 (1964); *J. Phys. Chem.* **86**, 869 (1982), and references therein.

²¹H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).

²²J. D. Beasley and S. Torquato, *J. Appl. Phys.* **60**, 3576 (1986).

²³S. Torquato, *J. Chem. Phys.* **85**, 4622 (1986).