

General formalism to characterize the microstructure of polydispersed random media

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The general n -point distribution function H_n characterizes the microstructure of disordered composite and porous media, liquids, and amorphous solids. In this Rapid Communication we obtain an exact analytical representation of H_n for inhomogeneous ensembles of d -dimensional spheres with a polydispersivity in size. Polydispersivity constitutes a fundamental aspect of the structure of random systems of particles.

Torquato¹ has developed a methodology to represent and compute the general n -point distribution function H_n for random media composed of statistical distributions of d -dimensional identical spheres. $H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q)$ characterizes the correlation associated with finding m points with positions $\mathbf{x}^m \equiv \{\mathbf{x}_1, \dots, \mathbf{x}_m\}$ on certain surfaces in the system, $p-m$ points with positions $\mathbf{x}^{p-m} \equiv \{\mathbf{x}_{m+1}, \dots, \mathbf{x}_p\}$ in certain regions exterior to the spheres, and any q of the spheres with configuration \mathbf{r}^q , where $n = p + q$. The general n -point distribution function H_n contains as special cases the variety of different types of correlation functions that arise in the study of the transport and mechanical properties of disordered composite media,²⁻⁹ liquid-state theory,^{10,11} and amorphous solids.¹² Specific examples of such functions shall be described below.

The purpose of this Rapid Communication is to derive the appropriate series representation of the H_n for media composed of distributions of d -dimensional spheres with a polydispersivity in size. Polydispersivity constitutes a fundamental aspect of the microstructure of a host of random media.

Following Torquato,¹ we consider adding p spherical "test" particles of radii b_1, \dots, b_p , respectively, to a system of N spherical included particles having M components with composition N_1, \dots, N_M , such that $\sum_{\sigma=1}^M N_{\sigma} = N$. Let R_{σ_j} be the radius of the type σ included particle which is centered at \mathbf{r}_j ($\sigma_j = 1, \dots, M$). The i th test particle is capable of excluding the center of the type σ_j included particle from spheres of radius $a_i^{(j)}$. For $b_i > 0$, $a_i^{(j)} = b_i + R_{\sigma_j}$, and for $b_i = 0$, we allow the test particle to penetrate the included particles so that $0 \leq a_i^{(j)} \leq R_{\sigma_j}$. It is natural to associate with each test particle i a subdivision of space into 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^* . The general n -point distribution function $H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q)$ specifically characterizes the correlation associated with finding test

particle 1 centered at \mathbf{x}_1 on surface \mathcal{S}_1, \dots , test particle m centered at \mathbf{x}_m on \mathcal{S}_m , test particle $m+1$ centered at \mathbf{x}_{m+1} in D_{m+1}, \dots , test particle p centered at \mathbf{x}_p in D_p , and finding any q included particles with configuration \mathbf{r}^q , with $n = p + q$. The appearance of the argument \mathbf{r}^q makes it implicit that H_n depends upon $R_{\sigma_1}, \dots, R_{\sigma_q}$.

We have derived two equivalent but topologically different series representation of the H_n for ensemble systems with polydispersed spherical inclusions.¹³ In the special case of an equilibrium ensemble, these two expressions can be shown to be (for $m=0$) isomorphic to the well-known Mayer and Kirkwood-Salsburg hierarchies of liquid-state statistical mechanics¹⁴ for a certain mixture of spheres, and therefore we refer to them as the Mayer and Kirkwood representations. Both series have the general form

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

where $H_n^{(s)}$ is an integral over the n -particle probability density function ρ_n that characterizes a configuration of n -included spheres. In the case of discrete number of components, the integrals also involve summations over the components.¹³ For included particles with a continuous distribution in radius \mathcal{R} characterized by the normalized probability density $f(\mathcal{R})$, the sums are replaced with integrals over the radii and $a_i^{(j)}$ is replaced by $a_i^{(j)} = b_i + \mathcal{R}_j$. Since the continuous representation is more general and concise, we report our results here in the continuous form.

The s th term of Eq. (1) is given by

$$H_n^{(s)}(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q) = (-1)^m \frac{\partial}{\partial b_1} \dots \frac{\partial}{\partial b_m} G_n^{(s)}(\mathbf{x}^p; \mathbf{r}^q), \tag{2}$$

where, in the Mayer representation,

$$G_n^{(s)}(\mathbf{x}^p; \mathbf{r}^q) = \prod_{l=1}^q \prod_{k=1}^p [1 - m(|\mathbf{x}_k - \mathbf{r}_l|; a_k^{(l)})] \frac{1}{s!} \int \dots \int d\mathcal{R}_{q+1} \dots d\mathcal{R}_{q+s} f(\mathcal{R}_1) \dots f(\mathcal{R}_{q+s}) \times \rho_{q+s}(\mathbf{r}^{q+s}; \mathcal{R}_1, \dots, \mathcal{R}_{q+s}) \prod_{j=q+1}^{q+s} m^{(p)}(\mathbf{x}^p; \mathbf{r}_j) d\mathbf{r}_j, \tag{3}$$

and

$$m^{(p)}(\mathbf{x}^p; \mathbf{r}_j) = 1 - \prod_{i=1}^p [1 - m(|\mathbf{x}_i - \mathbf{r}_j|; a_i^{(j)})], \quad (4)$$

$$m(|\mathbf{x}_i - \mathbf{r}_j|; a_i^{(j)}) = \begin{cases} 1 & \text{if } |\mathbf{x}_i - \mathbf{r}_j| < a_i^{(j)}, \\ 0 & \text{otherwise.} \end{cases} \quad (5)$$

Here, $\rho_n(\mathbf{r}^n; \mathcal{R}_1, \dots, \mathcal{R}_n) f(\mathcal{R}_1) \dots f(\mathcal{R}_n)$ is the probability density function associated with finding an inclusion with radius \mathcal{R}_1 at \mathbf{r}_1 , another inclusion with radius \mathcal{R}_2 at

$$\int \rho_{q+s}(\mathbf{r}^{q+s}) \{ \dots \} d\mathbf{r}_{q+1} \dots d\mathbf{r}_{q+s} \rightarrow \int d\mathcal{R}_{q+1} \dots d\mathcal{R}_{q+s} \prod_{k=1}^{q+s} f(\mathcal{R}_k) \rho_{q+s}(\mathbf{r}_{q+s}; \mathcal{R}_1, \dots, \mathcal{R}_{q+s}) \{ \dots \} \times d\mathbf{r}_{q+1} \dots d\mathbf{r}_{q+s}, \quad (6)$$

where the left-hand side (LHS) and right-hand side (RHS) are the monodisperse and polydisperse results, respectively. Moreover, $m(r; a_i)$ in Ref. 1 must be replaced by $m(r; a_i^{(j)})$ for an included particle with radius \mathcal{R}_j .

From the single function H_n , one can obtain all of the various sets of correlation functions that arise in the study of transport and mechanical properties of composite media by letting the radii of the test particles shrink to zero ($b_1=0$) and setting $a_i^{(j)} = \mathcal{R}_j$, $i=1, \dots, p$. For example, in this limit, the n -point matrix probability function $S_n(\mathbf{x}^n) = H_n(\emptyset; \mathbf{x}^n; \emptyset)$ and the point- q -particle distribution function $G_n(\mathbf{x}_1; \mathbf{r}^q) = H_n(\emptyset; \mathbf{x}_1; \mathbf{r}^q)$, where \emptyset is the empty set. The former is fundamental to the study of the conductivity² and elastic moduli⁶ of composite materials, and the fluid permeability^{3,4} and trapping constant⁵ of porous media. The latter arises in bounds on the conductivity,⁷ fluid permeability^{4,8} and trapping constant.⁵ Similarly, the surface-void, surface-surface, and surface-particle center correlation functions in this limit are given by $F_{SV}(\mathbf{x}_1, \mathbf{x}_2) = H_2(\mathbf{x}_1; \mathbf{x}_2; \emptyset)$, $F_{SS}(\mathbf{x}_1, \mathbf{x}_2) = H_2(\mathbf{x}_1, \mathbf{x}_2; \emptyset)$, and $F_{SP}(\mathbf{x}_1, \mathbf{r}_2) = H_2(\mathbf{x}_1; \emptyset; \mathbf{r}_2)$, respectively. These surface correlation functions arise in bounds on the fluid permeability^{4,9} and trapping constant.^{5,9} In this limit, H_n provides generalizations of all of the aforementioned func-

\mathbf{r}_2 , etc. The case $n=1$ is degenerate in the sense that $\rho_1(\mathbf{r}_1; \mathcal{R}_1)$ is independent of \mathcal{R}_1 and in the instance of statistically homogeneous media is simply equal to the total number of density ρ . Note that the results for discrete size distributions are easily obtained from the above results¹⁵ and as in Ref. 1 we have successive upper and lower bounds on H_n .¹⁶

A comparison of Eqs. (1)–(5) with the corresponding monodisperse expressions of Torquato¹ reveals that there is a simple prescription to map monodisperse results into polydisperse results:

tions, e.g., F_{SVP} , F_{SSP} , F_{SSV} , etc. 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 ($b_i > 0$), and hence the distribution function 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.¹⁷

In the context of liquids, the representation of the H_n provide generalizations of certain expected values that arise in potential distribution theory¹⁰ and scaled-particle theory.¹¹ H_n also contains the nearest-neighbor distribution function which is fundamental to the study of theory of liquids and amorphous solids. The subject of nearest-neighbor distribution functions for polydispersed hard spheres is studied elsewhere.¹³

The evaluation of the integrals of (1) for H_n is generally nontrivial because of the appearance of the ρ_n . For the special case of “overlapping” or “randomly centered” (i.e., spatially uncorrelated) spheres, the ρ_n are especially simple:

$$\rho_n(\mathbf{r}^n; \mathcal{R}_1, \dots, \mathcal{R}_n) = \prod_{j=1}^n \rho_1(\mathbf{r}_j; \mathcal{R}_j). \quad (7)$$

Substitution of (7) into (1) yields

$$H_n(\mathbf{x}^m; \mathbf{x}^{p-m}; \mathbf{r}^q) = (-1)^m \frac{\partial}{\partial b_1} \dots \frac{\partial}{\partial b_m} \prod_{i=1}^q \prod_{k=1}^p [1 - m(|\mathbf{x}_k - \mathbf{r}_i|; a_k^{(i)})] \prod_{j=1}^q \rho_1(\mathbf{r}_j; \mathcal{R}_j) f(\mathcal{R}_j) \times \exp \left[- \int \rho_1(\mathbf{r}_1) \left[1 - \prod_{i=1}^p [1 - m(|\mathbf{x}_i - \mathbf{r}_1|; a_i^{(1)})] \right] f(\mathcal{R}_1) d\mathcal{R}_1 d\mathbf{r}_1 \right]. \quad (8)$$

For a statistically homogeneous system, we have

$$\int \rho_1(\mathbf{r}_1) \left[1 - \prod_{i=1}^p [1 - m(|\mathbf{x}_i - \mathbf{r}_1|; a_i^{(1)})] f(\mathcal{R}_1) \right] d\mathcal{R}_1 d\mathbf{r}_1 = \rho \langle V_p(\mathbf{x}^p; a_1^{(1)}, \dots, a_p^{(p)}) \rangle, \quad (9)$$

where $V_p(\mathbf{x}^p; a_1^{(1)}, \dots, a_p^{(p)})$ is the d -dimensional union volume of p spheres of radii $a_1^{(1)}, \dots, a_p^{(1)}$ centered at \mathbf{x}_p , respectively. Here the average of any function $A(\mathcal{R})$ is given by

$$\langle A(\mathcal{R}) \rangle = \int_0^\infty A(\mathcal{R}) f(\mathcal{R}) d\mathcal{R}. \quad (10)$$

Relation (8) is the polydispersed generalization of the monodispersed result obtained by Torquato.¹

In the special limit $a_i^{(j)} \rightarrow \mathcal{R}_j, \forall i$, and in the instance of homogeneous overlapping spheres, relation (8) recovers the one-point correlation functions $H_1(\mathbf{x}_1; \emptyset; \emptyset)$ and $H_1(\emptyset; \mathbf{x}_1; \emptyset)$ obtained by Chiew and Glandt,¹⁸ the $S_n(\mathbf{x}^n)$ obtained by Stell and Rikvold,¹⁹ and the two-point surface correlation functions F_{SV} and F_{SS} derived by Torquato and Lu.²⁰ For other H_n in this limit and for the general case where $b_i > 0$, relation (8) is entirely new.

For the case of spheres with some finite-sized hard core, the H_n are generally difficult to compute because of the

complexity of the ρ_n . For hard cores having the same radii as the included particles, the infinite series (1) for the H_n truncates after n -body terms in the limit $a_i^{(j)} \rightarrow \mathcal{R}_j, \forall i$.¹ For example, for such inhomogeneous models in the limit, the various two-point correlation functions are given by the expressions

$$F_{VP}(\mathbf{x}_1, \mathbf{r}_1) = \lim_{a_i^{(j)} \rightarrow \mathcal{R}_j, \forall i} H_2(\mathbf{x}_1; \emptyset; \mathbf{r}_1) = [1 - m(|\mathbf{x}_1 - \mathbf{r}_1|; \mathcal{R}_1)] \times \left[\rho_1(\mathbf{r}_1) f(\mathcal{R}_1) - \int \int d\mathcal{R}_2 f(\mathcal{R}_2) d\mathbf{r}_2 \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathcal{R}_1, \mathcal{R}_2) m(|\mathbf{x}_1 - \mathbf{r}_2|; \mathcal{R}_2) \right], \quad (11)$$

$$F_{SP}(\mathbf{x}_1, \mathbf{r}_1) = \lim_{a_i^{(j)} \rightarrow \mathcal{R}_j, \forall i} H_2(\mathbf{x}_1; \emptyset; \mathbf{r}_1) = [1 - m(|\mathbf{x}_1 - \mathbf{r}_1|; \mathcal{R}_1)] \times \left[\rho_1(\mathbf{r}_1) f(\mathcal{R}_1) - \int \int d\mathcal{R}_2 f(\mathcal{R}_2) d\mathbf{r}_2 \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathcal{R}_1, \mathcal{R}_2) \delta(|\mathbf{x}_1 - \mathbf{r}_2| - \mathcal{R}_2) \right], \quad (12)$$

$$F_{VV}(\mathbf{x}_1, \mathbf{x}_2) = \lim_{a_i^{(j)} \rightarrow \mathcal{R}_j, \forall i} H_2(\mathbf{x}_1; \emptyset; \mathbf{r}_1) = 1 - \int \int d\mathcal{R}_1 f(\mathcal{R}_1) \rho_1(\mathbf{r}_1) d\mathbf{r}_1 \left[1 - \prod_{i=1}^2 [1 - m(|\mathbf{x}_i - \mathbf{r}_1|; \mathcal{R}_1)] \right] + \int \int \int \int d\mathcal{R}_1 d\mathcal{R}_2 f(\mathcal{R}_1) f(\mathcal{R}_2) d\mathbf{r}_1 d\mathbf{r}_2 \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathcal{R}_1, \mathcal{R}_2) m(|\mathbf{x}_1 - \mathbf{r}_1|; \mathcal{R}_1) m(|\mathbf{x}_2 - \mathbf{r}_2|; \mathcal{R}_2), \quad (13)$$

$$F_{VS}(\mathbf{x}_1, \mathbf{x}_2) = \lim_{a_i^{(j)} \rightarrow \mathcal{R}_j, \forall i} H_2(\mathbf{x}_1; \emptyset; \mathbf{r}_1) = \int \int d\mathcal{R}_1 f(\mathcal{R}_1) d\mathbf{r}_1 \rho_1(\mathbf{r}_1) \delta(|\mathbf{x}_1 - \mathbf{r}_1| - \mathcal{R}_1) - \int \int \int \int d\mathcal{R}_1 d\mathcal{R}_2 f(\mathcal{R}_1) f(\mathcal{R}_2) d\mathbf{r}_1 d\mathbf{r}_2 \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathcal{R}_1, \mathcal{R}_2) \delta(|\mathbf{x}_2 - \mathbf{r}_2| - \mathcal{R}_2) m(|\mathbf{x}_1 - \mathbf{r}_1|; \mathcal{R}_1), \quad (14)$$

$$F_{SS}(\mathbf{x}_1, \mathbf{x}_2) = \lim_{a_i^{(j)} \rightarrow \mathcal{R}_j, \forall i} H_2(\mathbf{x}_1; \emptyset; \mathbf{r}_1) = \int \int d\mathcal{R}_1 f(\mathcal{R}_1) d\mathbf{r}_1 \rho_1(\mathbf{r}_1) \delta(|\mathbf{x}_1 - \mathbf{r}_1| - \mathcal{R}_1) \delta(|\mathbf{x}_2 - \mathbf{r}_2| - \mathcal{R}_2) + \int \int \int \int d\mathcal{R}_1 d\mathcal{R}_2 f(\mathcal{R}_1) f(\mathcal{R}_2) d\mathbf{r}_1 d\mathbf{r}_2 \rho_2(\mathbf{r}_1, \mathbf{r}_2; \mathcal{R}_1, \mathcal{R}_2) \delta(|\mathbf{x}_1 - \mathbf{r}_1| - \mathcal{R}_1) \delta(|\mathbf{x}_2 - \mathbf{r}_2| - \mathcal{R}_2). \quad (15)$$

In the special case of *isotropic* polydispersed hard spheres in equilibrium, Blum and Stell²¹ have given ρ_2 in the Percus-Yevick approximation. We learned very recently that Given and Stell²² have used this approximate solution to ρ_2 to compute F_{VV} , F_{SP} , and F_{SS} . The two-point functions F_{VP} and F_{SP} and high-order functions have not been heretofore computed for this useful model, however.

Although the formalism given here was for simplicity

restricted to d -dimensional spheres, it is possible to generalize it to ensembles of particles with nonspherical shapes.²³ Finally, we emphasize that the formalism is valid for equilibrium as well as nonequilibrium ensembles of particles.

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¹⁵For example, in the discrete homogeneous case with M different components, the size distributions $f(\mathcal{R}_j)$ in relation (3) become unity for $j=1, \dots, q$ and $\sum_{\sigma=1}^M (\rho_\sigma/\rho) \delta(\mathcal{R}_j - \mathcal{R}_\sigma)$ for $j=q+1, \dots, q+s$, where ρ_σ is the number density of type σ particles and $\delta(\mathcal{R})$ is the Dirac δ function.

¹⁶The nature of the infinite series (1) enables one to obtain successive upper and lower bounds on H_n (see Ref. 1). We find for even m , $H_n \geq W_n^{(l)}$ for l odd, and $H_n \leq W_n^{(l)}$ for l even, where $W_n^{(l)} = \sum_{k=0}^l (-1)^k H_n^{(k)}$ is the partial sum. For odd m , the above inequalities are reversed.

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