Microstructure of two-phase random media. I. The n-point probability functions

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The microstructure of a two-phase random medium can be characterized by a set of general n-point probability functions, which give the probability of finding a certain subset of n-points in the matrix phase and the remainder in the particle phase. A new expression for these n-point functions is derived in terms of the n-point matrix probability functions which give the probability of finding all n points in the matrix phase. Certain bounds and limiting values of the S_n follow: the geometrical interpretation of the S_n and their relationship with n-point correlation functions associated with fluctuating bulk properties is also noted. For a bed or suspension of spheres in a uniform matrix we derive a new hierarchy of equations, giving the S_n in terms of the s-body distribution functions ρ_s associated with a statistically inhomogeneous distribution P_N of spheres in the matrix, generalizing expressions of Weissberg and Prager for S_2 and S_3. It is noted that canonical ensemble of mutually impenetrable spheres and the associated set of ρ_s define, in the limit of an unbounded system, a statistically homogeneous and isotropic medium, as does (trivially) a canonical ensemble of mutually penetrable spheres.

I. INTRODUCTION

The determination of the relation between the macroscopic or bulk properties of a material to its microscopic structure is the goal of statistical mechanics. Most of the effort directed toward this goal has been for cases such as those found in liquid-state theory or kinetic theory, where the term microscopic structure refers to the geometrical arrangement and motion of individual molecules. In other important instances, however, the term microscopic structure can refer to the geometrical arrangement and local properties on an intermediate length scale which is much larger than the molecular length scale but still much smaller than the dimensions of the bulk material sample. The types of systems often referred to as "heterogeneous media," "composite materials," and "multiphase flow systems" typically fall under this latter category.

We shall examine those media composed of two phases which are separately homogeneous. One of the phases will be in the form of discrete inclusions or particles which are distributed throughout the other phase, a continuously connected matrix (which may either be fluid, solid, or void) according to some probability density function. We use the general term "two-phase random media" to refer to such systems. Our goal, ultimately, is to relate the bulk or effective properties of a two-phase random medium, such as, e.g., the dielectric constant, rigidity and bulk moduli, and viscosity, to its microscopic structure.

Since the well-known calculations of the effective electrical conductivity and viscosity of a dilute suspension of spherical particles obtained by Maxwell[1] and Einstein,[2] respectively, a great deal of effort has been expended on the extension of these, and analogous results, to particles of more general shape and to higher concentrations.[3] The former extension, though far from trivial, has proved to be a far more tractable problem than the latter, upon which progress has been impeded by a lack of full understanding of the relationships among various higher-order statistical functions as well as a means to accurately evaluate them. In particular, the set of probabilities we term n-point matrix probability functions, which gives the probability of finding n-points in the matrix phase, arise quite naturally in the study of transport in two-phase random media[4,5] but because of a lack of reliable assessment of the 2-point and 3-point matrix functions for most useful models, progress continues to be hampered.[6] The main aim of this paper is to initiate a new program of systematically representing and evaluating the n-point matrix functions for a certain class of random media.

II. THE n-POINT PROBABILITY FUNCTIONS

A. Definitions of the general n-point probability functions

The random medium is a domain of space D of volume V which is composed of two regions: a matrix phase (the continuously connected phase) D_0 with volume fraction ϕ and a particle phase D_1 with volume fraction $1-\phi$. We introduce a stochastic variable at position $\mathbf{x}$ as follows:

$$I(\mathbf{x})=\begin{cases}1, & \text{if } \mathbf{x}\in D_0,\\ 0, & \text{otherwise}.\end{cases} \tag{1}$$

The quantity $I(\mathbf{x})$ is a discrete random variable taking on the values 1 or 0 depending upon whether the position vector is in the matrix or particle phase. A complete knowledge of $I(\mathbf{x})$ gives a total specification of the matrix phase.

Consider obtaining the ensemble average of the discrete random variable $I(\mathbf{x})$ for a two-phase medium.

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Here we use notation similar to that of Frisch.[7] Consider the family of joint probabilities $S_{\epsilon_1\epsilon_2\cdots\epsilon_n}$ (henceforth referred to as the general n-point function), associated with an ensemble of two-phase media, defined to be

$$S_{\epsilon_1\epsilon_2\cdots\epsilon_n}(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_n) = P[I(\mathbf{x}_1)=\epsilon_1 \text{ and } I(\mathbf{x}_2)=\epsilon_2 \text{ and } \ldots, I(\mathbf{x}_n)=\epsilon_n] , \quad (2)$$

with $P[\cdots]$ standing for the probability of $[\cdots]$ and

$$\epsilon_i = \begin{cases} 1 , & \text{if } \mathbf{x}_i \in D_1 , \\ 0 , & \text{otherwise} . \end{cases}$$

The general n-point function $S_{\epsilon_1\epsilon_2\cdots\epsilon_n}$ is the probability that at $\mathbf{x}_1$, $I(\mathbf{x}_1)=\epsilon_1$ and at $\mathbf{x}_2$, $I(\mathbf{x}_2)=\epsilon_2$ and, ..., at $\mathbf{x}_n$, $I(\mathbf{x}_n)=\epsilon_n$. For example $S_{101}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3)$ is the probability that there is particle phase at $\mathbf{x}_1$ and $\mathbf{x}_3$ and matrix phase at $\mathbf{x}_2$. Since $S_{\epsilon_1\epsilon_2\cdots\epsilon_n}$ is a set of joint probabilities we have

$$1 = \sum_{\epsilon_1=0}^{1} \sum_{\epsilon_2=0}^{1} \cdots \sum_{\epsilon_n=0}^{1} S_{\epsilon_1\epsilon_2\cdots\epsilon_n} \quad (3)$$

and

$$S_{\epsilon_1\epsilon_2\cdots\epsilon_k} = \sum_{\epsilon_{k+1}=0}^{1} \sum_{\epsilon_{k+2}=0}^{1} \cdots \sum_{\epsilon_n=0}^{1} S_{\epsilon_1\epsilon_2\cdots\epsilon_n} \quad (4)$$

for $1 \leqq k < n$.

By a *statistically homogeneous medium* we shall mean one in which all the correlation and probability functions will depend upon the relative positions rather than on absolute positions, so that

$$S_{\epsilon_1\epsilon_2\cdots\epsilon_n}(\mathbf{x}_1, \mathbf{x}_2, \ldots \mathbf{x}_n) = S_{\epsilon_1\epsilon_2\cdots\epsilon_n}(\mathbf{x}_{12}, \mathbf{x}_{13}, \ldots \mathbf{x}_{1n}) ,$$

where

$$\mathbf{x}_{1i} = \mathbf{x}_i - \mathbf{x}_1 .$$

By an *isotropic* medium we mean one in which the correlation and probability functions further depend upon the relative positions only through the absolute differences of the x_{ij}, i.e., only through $|\mathbf{x}_i - \mathbf{x}_j|$.

Employing the definitions above, the ensemble average of the random variable $I(x)$ is given by

$$\begin{aligned} \langle I(\mathbf{x}) \rangle &= \sum_{\epsilon_1=0}^{1} \sum_{\epsilon_2=0}^{1} \cdots \sum_{\epsilon_n=0}^{1} I(\mathbf{x}_1) S_{\epsilon_1\epsilon_2\cdots\epsilon_n} \\ &= \sum_{\epsilon=0}^{1} I(\mathbf{x}) S_{\epsilon}(\mathbf{x}) \\ &= S_0(\mathbf{x}) , \end{aligned} \quad (5)$$

where angular brackets denote an ensemble average. The mean value of $I(\mathbf{x})$ is found to be equal to the probability of finding a point in the matrix region (which in turn is equal to the volume fraction of the matrix phase ϕ for a statistically homogeneous medium). Similarly, the ensemble average of the product $I(\mathbf{x}_1)[1 - I(\mathbf{x}_2)]$ may be shown to be

$$\langle I(\mathbf{x}_1)[1 - I(\mathbf{x}_2)] \rangle = S_{01}(\mathbf{x}_1, \mathbf{x}_2) , \quad (6)$$

i.e., the 2-point correlation function $\langle I(\mathbf{x}_1)[1 - I(\mathbf{x}_2)] \rangle$ is equal to the probability of finding matrix phase at $\mathbf{x}_1$ and particle phase at $\mathbf{x}_2$. More generally, it may be shown that

$$\left\langle \prod_{i=1}^{n} [\epsilon_i + (1 - 2\epsilon_i) I(\mathbf{x}_i)] \right\rangle = S_{\epsilon_1\epsilon_2\cdots\epsilon_n}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) , \quad (7)$$

which states that the general n-point correlation function is equivalent to the general n-point probability function, which may be expressed in terms of the joint probabilities associated with simultaneously finding k points ($1 \leqq k \leqq n$) in the matrix phase (henceforth referred to as the k-point matrix probability function[8]) i.e., $S_{\epsilon_1\epsilon_2\cdots\epsilon_n}$ for $1 \leqq k \leqq n$ such that $\epsilon_i = 0$ for $1 \leqq i \leqq k$. Rephrasing Eq. (7), we have

$$\begin{aligned} S_{\epsilon_1\epsilon_2\cdots\epsilon_n}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) &= \left\langle \prod_{i=1}^{n} [1 + h_i I(\mathbf{x}_i)] \right\rangle \prod_{i=1}^{n} \epsilon_i \\ &= \left[1 + \sum_{i=1}^{n} h_i S_0(\mathbf{x}_i) + \sum_{i<j}^{n} h_i h_j S_{00}(\mathbf{x}_i, \mathbf{x}_j) \right. \\ &\quad \left. + \sum_{i<j<k} h_i h_j h_k S_{000}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_n) + \cdots \right] \prod_{i=1}^{n} \epsilon_i , \end{aligned} \quad (8)$$

where

$$h_i = (1 - 2\epsilon_i)/\epsilon_i .$$

Given all k-point matrix functions ($k = 1, 2, \ldots, n$) one may obtain any general n-point probability function. For most of what follows, therefore, we consider only the n-point matrix probability function.

If $\epsilon_i = 1$ for $1 \leqq i \leqq n$ in Eq. (8), one obtains the probability of finding n-points in the particle phase in terms of the k-point matrix functions ($k = 1, 2, \ldots, n$):

$$S_{11\ldots1}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = 1 - \sum_{i=1}^{n} S_0(\mathbf{x}_i) + \sum_{i<j} S_{00}(\mathbf{x}_i, \mathbf{x}_j) - \sum_{i<j<k} S_{000}(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) + \cdots . \quad (9)$$

Note that the lth sum in Eq. (9) carries the factor $(-1)^l$. It shall be convenient to denote the probability of finding n points in the matrix phase, the n-point matrix function, by $S_n(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n)$ and the probability of finding n points in the particle phase by $\hat{S}_n(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n)$ as these particular probability functions arise frequently. The n-point matrix functions ($n \geqq 2$), in general, cannot be expressed in terms of lower order k-point ($k < n$) matrix functions. (In the special case of a "symmetric" random medium[7] it is possible to determine S_{2m+1} from S_{2m}, S_{2m-1}, ... and S_1. By a symmetric random medium we mean a random medium having the symmetry such that

$$S_{\epsilon_1\epsilon_2\cdots\epsilon_n}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = S_{\epsilon_1^*\epsilon_2^*\cdots\epsilon_n^*}(\mathbf{x}_1, \mathbf{x}_2, \ldots; \mathbf{x}_n) , \quad (10)$$

where $\epsilon_i^* = 1 - \epsilon_i$.

Such a medium is realizable if $\phi = \frac{1}{2}$ and if it is impossible to distinguish the geometry of one phase from the other. Applying the more compact notation mentioned above to Eq. (9) gives

$$\hat{S}_n = 1 - \sum S_1 + \sum S_2 - \cdots (-1)^l \sum S_l + \cdots (-1)^n S_n . \quad (11)$$

For a symmetric random medium we have, therefore,

$$2S_{2m+1} = 1 - \sum S_1 + \sum S_2 - \cdots (-1)^l \sum S_l \,. \tag{12}$$

We see that for a symmetric medium, the odd probability functions S_{2m+1} can be expressed in terms of lower order even and odd probability functions. From Eq. (11) one can see, however, that the even functions S_{2m} cannot be expressed in terms of lower order probability functions as the last term is always positive. For $m=1$ Eq. (12) gives, e.g., that

$$S_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = \tfrac{1}{2}[S_2(\mathbf{x}_1, \mathbf{x}_2) + S_2(\mathbf{x}_1, \mathbf{x}_3) + S_2(\mathbf{x}_2, \mathbf{x}_3) - \tfrac{1}{2}] \tag{13}$$

in a symmetric medium.)

Since $I(\mathbf{x})$ may be either zero or unity, then, by definition of the S_n, we have the bounds

$$S_n(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) \geqq S_{n+1}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{n+1}) \tag{14}$$

with $1 \geqq S_1$.

For a statistically homogeneous medium S_1 is simply the volume fraction of the matrix phase ϕ. Therefore, for such a medium, ϕ is an upper bound on S_n for all n. The upper bounds expressed by Eq. (14) is intuitively obvious as it states that the probability of finding n points at positions $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$ in the matrix phase is greater than the probability of finding $n+1$ points at positions $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{n+1}$ in the matrix phase.

It shall also be useful, for a homogeneous medium, to define the cumulant function S_n^* as follows:

$$S_n^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \left\langle \prod_{i=1}^{n} [I(\mathbf{x}_i) - \phi] \right\rangle . \tag{15}$$

For example, for $n=1$, 2, and 3 we have

$$S_1^*(\mathbf{x}_1) = 0 \,, \tag{16a}$$

$$S_2^*(\mathbf{x}_1, \mathbf{x}_2) = S_2(\mathbf{x}_1, \mathbf{x}_2) - S_1(\mathbf{x}_1) S_1(\mathbf{x}_2) \,, \tag{16b}$$

$$S_3^*(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) = S_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3) - S_2(\mathbf{x}_1, \mathbf{x}_2) S_1(\mathbf{x}_3) - S_2(\mathbf{x}_1, \mathbf{x}_3) S_1(\mathbf{x}_2) - S_2(\mathbf{x}_2, \mathbf{x}_3) S_1(\mathbf{x}_1) + 2 S_1(\mathbf{x}_1) S_1(\mathbf{x}_2) S_1(\mathbf{x}_2) \,, \tag{16c}$$

respectively. The S_n^* are cumulant functions that stand to the S_n as Ursell or cluster functions of statistical mechanics stand to the distribution functions,[9] apart from the trivial quantity S_1^*. (The statistical mechanical function corresponding to S_1^* is equal to unity for a homogeneous medium.)

B. Geometrical interpretation of the S_n

The geometrical significance of the n-point matrix functions is easily seen for any particle geometry. Let F_n be a polyhedron with n vertices located at $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n$. Then S_n is the probability that all n vertices of F_n when thrown randomly into D lie in D_0.

If we assume the particle phase of a statistically homogeneous two-phase random medium to be composed of N spheres of radius R, we may infer yet another geometrical interpretation of these functions. Consider the one-point matrix function $S_1 = \langle I(\mathbf{x}) \rangle$. This may be interpreted as the probability that a randomly chosen point is not contained in a particle in the system. This is equivalent to the probability that no sphere center is within a distance R of a randomly chosen point, which in turn is equal to the probability that a region of a sphere volume is empty of sphere centers. Similarly, the 2-point matrix function $S_2(\mathbf{x}_{12}) = \langle I(\mathbf{x}_1) I(\mathbf{x}_2) \rangle$ may be interpreted to be the probability that two randomly chosen points, separated by distance $x_{12} = |x_{12}|$, are both in D_0. This is equivalent to the probability that a region, the union volume of two spheres of radius R whose centers are separated by x_{12}, contains no sphere centers. In general, the n-point matrix probability function

$$S_n(\mathbf{x}_{12}, \mathbf{x}_{13}, \ldots, \mathbf{x}_{1n}) = \left\langle \prod_{i=1}^{n} I(\mathbf{x}_i) \right\rangle \,,$$

for a particle phase of spheres of radius R, may be interpreted to be the probability that a region $\Omega^{(n)}$, the union volume of n spheres of radius R, contains no sphere centers. A similar geometrical interpretation may be inferred for particles of arbitrary shape.

C. Limiting values of the S_n

We determine values of the S_n, for certain limits of its arguments, which apply to any statistically inhomogeneous two-phase random medium. By definition of the S_n, we have, when any subset of $q+1$ points coincide, so that $\mathbf{x}_{i_1} = \mathbf{x}_{i_2} = \cdots = \mathbf{x}_{i_{q+1}}$,

$$S_n(\mathbf{x}_1, \ldots, \mathbf{x}_n) \to S_{n-q}(\mathbf{x}_1, \ldots, \overline{\mathbf{x}_{i_1}, \ldots, \mathbf{x}_{i_{q+1}}}, \ldots, \mathbf{x}_n) = \langle I(\mathbf{x}_1) \cdots \overline{I(\mathbf{x}_{i_1}) \cdots I(\mathbf{x}_{i_{q+1}})} \cdots I(\mathbf{x}_n) \rangle \,, \tag{17}$$

where a bar above a quantity indicates its absence. For a statistically homogeneous medium, the left-hand side of Eq. (24) is equal to

$$S_{n-q}(\mathbf{x}_{i1}, \ldots, \overline{\mathbf{x}_{ii_1}, \ldots, \mathbf{x}_{ii_{q+1}}}, \ldots, \mathbf{x}_{in}) \,.$$

Let us now consider partitioning the set $\{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n\}$ into L subsets: $\{\mathbf{x}_1\}$, $\{\mathbf{x}_2, \mathbf{x}_3\}$, $\{\mathbf{x}_4, \mathbf{x}_5, \mathbf{x}_6\}$, ... Let all of the relative distances between the m elements of these subsets remain bounded, and let F_m^i be the polyhedron with m vertices located at the positions associated with the ith subset. We denote the centroid of the F_m^i by $\mathbf{R}_i$. Then we have, assuming no long-range order, that

$$\lim_{\text{all } R_{ij} \to \infty} S_n(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \langle I(\mathbf{x}_1) \rangle \langle I(\mathbf{x}_2) I(\mathbf{x}_3) \rangle \langle I(\mathbf{x}_4) I(\mathbf{x}_5) I(\mathbf{x}_6) \rangle \cdots, \quad L \text{ products}$$

$$= S_1(\mathbf{x}_1) S_2(\mathbf{x}_2, \mathbf{x}_3) S_3(\mathbf{x}_4, \mathbf{x}_5, \mathbf{x}_6) \cdots, \quad L \text{ products} \,.$$

Here R_{ij} is the relative distance between the centroids of F_m^i and F_m^j, where i and j are all possible values such that $1 \leqq i < j \leqq L$. The above partition, however, is just one of the possible ways to partition the set $\{\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n\}$. In general, for any partition into sets $\{\gamma\}$, each with $k(\gamma)$ elements, we have

$$\lim_{\text{all } R_{\alpha\beta} \to \infty} S_n(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n) = \prod_{\{\gamma\}} S_{k(\gamma)}(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_{k(\gamma)}), \quad L \text{ products} \tag{18}$$

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

III. THE S_n FOR A SYSTEM OF SPHERES

We shall derive expressions for the n-point matrix probability functions S_n for the case of a bed or suspension of N spheres of radius R in terms of the spatial correlations between sphere centers for arbitrary number density of spheres. We present two different procedures for obtaining the S_n. The first method makes direct use of the ensemble concept of statistical mechanics and is the more formal of the two, whereas the second employs simple probabilistic arguments (given in Appendix A) and is the more intuitive approach of the two. The procedures outlined below may be easily generalized to particles of arbitrary shape.

Ensemble method

Consider, for concreteness, the particle phase of a two-phase random medium to be composed of N spheres of unit radius distributed in space according to some ensemble. The quantity $I(\mathbf{x})$ for such a system is seen to be a function of the positions of all of the N spheres, denoted by $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$ $(\equiv r^N)$, which, clearly, are known only in a statistical sense. Varying the positions of the spheres changes the matrix space D_0 and its complement D_1 and thus causes $I(x)$ to change. Let us define an indicator function m such that

$$m(|\mathbf{x}-\mathbf{r}_i|)=\begin{cases}1, & \text{if } |\mathbf{x}-\mathbf{r}_i|<1,\\ 0, & \text{if } |\mathbf{x}-\mathbf{r}_i|>1,\end{cases} \tag{19}$$

where $\mathbf{r}_i$ is the position of the center of the ith sphere and $\mathbf{x}-\mathbf{r}_i$ is the position vector originating from the center of the ith sphere. We have

$$I(\mathbf{x};\mathbf{r}^N)=\prod_{i=1}^{N}[1-m(|\mathbf{x}-\mathbf{r}_i|)]\,. \tag{20}$$

Equation (19) gives the relationship between the quantity $I(\mathbf{x})$ and the configuration of the spheres in space. Therefore we may define the ensemble average of the product $\Pi_{i=1}^{n} I(\mathbf{x}_i;\mathbf{r}^N)$ as

$$\left\langle \prod_{i=1}^{n} I(\mathbf{x}_i;\mathbf{r}^N)\right\rangle = \int\cdots\int\left[\prod_{i=1}^{n} I(\mathbf{x}_i;\mathbf{r}^N)\right] \times P_N(\mathbf{r}^N)\,d\mathbf{r}^N = S_n(\mathbf{x}^n)\,, \tag{21}$$

where $d\mathbf{r}^N \equiv d\mathbf{r}_1, d\mathbf{r}_2, \ldots, d\mathbf{r}_N$. Here we define, for an ensemble,

$$P_N(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)\,d\mathbf{r}_1\,d\mathbf{r}_2\cdots d\mathbf{r}_N$$

as the probability of simultaneously finding the center of particle 1 in the volume $d\mathbf{r}_1$ about $\mathbf{r}_1$, the center of particle 2 in the volume $d\mathbf{r}_2$ about $\mathbf{r}_2$, ..., and the center of particle N in the volume $d\mathbf{r}_N$ about $\mathbf{r}_N$. (The canonical ensemble defines a particular P_N for a system of impenetrable spheres that we discussed in Appendix A.) The probability density P_N is normalized in such a way that

$$\int\cdots\int P_N(\mathbf{r}^N)\,d\mathbf{r}_1\cdots d\mathbf{r}_N = 1\,,$$

where each volume integral is over the volume V.

We now proceed to obtain the relationship between the n-point matrix functions and the n-body distribution functions of statistical mechanics ρ_n (see Appendix B). Expanding the right-hand side of Eq. (19) gives

$$I(\mathbf{x};\mathbf{r}^N)=1-\sum_{i=1}^{N} m(|\mathbf{x}-\mathbf{r}_i|) + \sum_{i<j}^{N} m(|\mathbf{x}-\mathbf{r}_i|)m(|\mathbf{x}-\mathbf{r}_j|) - \sum_{i<j<k}^{N} m(|\mathbf{x}-\mathbf{r}_i|) \times m(|\mathbf{x}-\mathbf{r}_j|)m(|\mathbf{x}-\mathbf{r}_k|)+\cdots\,. \tag{22}$$

The first sum is over all the N particles, the second sum is over all distinguishable pairs of particles and as such contains $N(N-1)/2$ terms, and, in general, the sth sum is over all distinguishable s-tuplets of particles and thus contains $N!/(N-s)!s!$ terms. In what follows, we consider two-phase random media which are inhomogeneous, i.e., media for which $P_N(\mathbf{r}^N)$ is not necessarily invariant under translation.

The relationship between the 1-point matrix function and the ρ_n may be obtained by substituting Eq. (22) into Eq. (20) with $n=1$:

$$S_1(\mathbf{x})=\langle I(\mathbf{x};\mathbf{r}^N)\rangle = \int\cdots\int P_N(\mathbf{r}^N) - \sum_{i=1}^{N}\int\cdots\int m(|\mathbf{x}-\mathbf{r}_i|)P_N(\mathbf{r}^N)\,d\mathbf{r}^N + \sum_{i<j}^{N}\int\cdots\int m(|\mathbf{x}-\mathbf{r}_i|)m(|\mathbf{x}-\mathbf{r}_j|)P_N(\mathbf{r}^N)\,d\mathbf{r}^N - \cdots = 1 - N\int\cdots\int m(|\mathbf{x}-\mathbf{r}_i|)P_N(\mathbf{r}^N)\,d\mathbf{r}^N + \frac{N(N-1)}{2}\int\cdots\int m(|\mathbf{x}-\mathbf{r}_1|)m(|\mathbf{x}-\mathbf{r}_2|)P_N(\mathbf{r}^N)\,d\mathbf{r}^N - \cdots\,, \tag{23}$$

where the third line follows because P_N is invariant to interchange of particles, the particles being identical. The factor $N!/(N-s)!s!$ appearing in $(s+1)$th term in Eq. (23) is the result of having $N!/(N-s)!s!$ identical integrations to perform. Using the definitions of Appendix B and integrating out $N-(s+1)$ degrees of freedom from the $(s+1)$th term gives

$$S_1(\mathbf{x})=1+\sum_{s=1}^{\infty}\frac{(-1)^s}{s!}\int\cdots\int\rho_s(\mathbf{r}^s)\prod_{j=1}^{s} m(|\mathbf{x}-\mathbf{r}_j|)\,d\mathbf{r}_j\,, \tag{24}$$

where $\rho_1(\mathbf{r})$ is the number of particles per unit volume at $\mathbf{r}$ (and is equal to N/V for a homogeneous system). Note that, in general, the 1-point matrix function is an infinite series, the sth term involving spatial correlations between s particle centers. Information concerning the penetrability between spheres is contained in the s-body distribution function ρ_s. For a homogeneous system of fully overlapping spheres, e.g.,

$$\rho_s=\prod_{i=1}^{s}\rho_1(\mathbf{r}_1)=\rho^s\ (\rho\equiv N/V)$$

since there are no correlations between the positions of particles.

One of the more important n-point matrix probability functions and one that, for most geometries, remains quantitatively unknown is S_2. Substituting Eq. (22) into Eq. (20) for $n=2$ and using the definitions of Appendix B gives, in the thermodynamic limit, through order ρ^2,

$$S_2(\mathbf{x}_1,\mathbf{x}_2)=\langle I(\mathbf{x}_1;\mathbf{r}^N)I(\mathbf{x}_2;\mathbf{r}^N)\rangle = 1-\int \rho_1(\mathbf{r}_1)[m(|\mathbf{x}_1-\mathbf{r}_1|)+m(|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_1|)-m(|\mathbf{x}_1-\mathbf{r}_1|)m(|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_1|)]\,d\mathbf{r}_1$$
$$+\frac{1}{2!}\int\int \rho_2(\mathbf{r}_1,\mathbf{r}_2)[m(|\mathbf{x}_1-\mathbf{r}_1|)+m(|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_1|)-m(|\mathbf{x}_1-\mathbf{r}_1|)m(|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_1|)]$$
$$\times[m(|\mathbf{x}_1-\mathbf{r}_2|)+m(|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_2|)-m(|\mathbf{x}_1-\mathbf{r}_2|)m(|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_2|)]\,d\mathbf{r}_1\,d\mathbf{r}_2+O(\rho^3)\,, \tag{25a}$$

where

$$\mathbf{x}_{12}=\mathbf{x}_2-\mathbf{x}_1\,.$$

It is convenient to define a function $m^{(2)}(\mathbf{x}_1,\mathbf{x}_2)$ such that

$$m^{(2)}(\mathbf{x}_1,\mathbf{x}_2)\equiv m(|\mathbf{x}_1|)+m(|\mathbf{x}_2|)-m(|\mathbf{x}_1|)m(|\mathbf{x}_2|)\,.$$

In terms of $m^{(2)}$ Eq. (25a) becomes

$$S_2(\mathbf{x}_1,\mathbf{x}_2)=1-\int \rho_1(\mathbf{r}_1)m^{(2)}(|\mathbf{x}_1-\mathbf{r}_1|,|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_1|)\,d\mathbf{r}_1$$
$$+\frac{1}{2!}\int\int \rho_2(\mathbf{r}_1,\mathbf{r}_2)m^{(2)}(|\mathbf{x}_1-\mathbf{r}_1|,|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_1|)$$
$$\times m^{(2)}(|\mathbf{x}_1-\mathbf{r}_2|,|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_2|)\,d\mathbf{r}_1\,d\mathbf{r}_2+O(\rho^3) \tag{25b}$$

or, to all orders,

$$S_2(\mathbf{x}_1,\mathbf{x}_2)=1+\sum_{s=1}^{\infty}(-1)^s s!\int\cdots\int\int \rho_s(\mathbf{r}^s)$$
$$\times\left[\prod_{j=1}^{s} m^{(2)}(|\mathbf{x}_1-\mathbf{r}_j|,|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_j|)\right]d\mathbf{r}_j\,. \tag{26}$$

It is to be noted that the volume integral of $m^{(2)}(|\mathbf{x}_1-\mathbf{r}_1|,|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_1|)$ over all $\mathbf{r}_1$ is the union volume of two spheres of unit radius whose centers are separated by the distance $x_{12}=|\mathbf{x}_{12}|$. The first two terms of $m^{(2)}$, $m(|\mathbf{x}_1-\mathbf{r}_1|)$ and $m(|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_1|)$, integrated over all $\mathbf{r}_1$ gives twice the volume of two spheres of unit radius, whereas the product term $m(|\mathbf{x}_1-\mathbf{r}_1|)m(|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_1|)$ integrated over all $\mathbf{r}_1$ yields the volume common to two spheres of unit radius (the intersection volume).

In general, for any n it may be shown that

$$S_n(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n)=1+\sum_{s=1}^{\infty}\frac{(-1)^s}{s!}\int\cdots\int\int \rho_s(\mathbf{r}^s)$$
$$\times\prod_{j=1}^{s}[m^{(n)}(|\mathbf{x}_1-\mathbf{r}_j|,|\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_j|,$$
$$\ldots|\mathbf{x}_1+\mathbf{x}_{1n}-\mathbf{r}_j|)]\,d\mathbf{r}_j\,, \tag{27}$$

where

$$m^{(n)}(\mathbf{x}_1-\mathbf{r}_j,\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_j,\ldots,\mathbf{x}_1+\mathbf{x}_{1n}-\mathbf{r}_j)$$
$$=1-\prod_{i=1}^{n}[1-m(|\mathbf{x}_1+\mathbf{x}_{1i}-\mathbf{r}_j|)]\,, \tag{28}$$

with $m(|\mathbf{x}_1+\mathbf{x}_{11}-\mathbf{r}_j|)\equiv m(|\mathbf{x}_1-\mathbf{r}_j|)$.

The volume integral of the generalized indicator function $m^{(n)}(|\mathbf{x}_1-\mathbf{r}_j|,\ |\mathbf{x}_1+\mathbf{x}_{12}-\mathbf{r}_j|,\ \ldots\ |\mathbf{x}_1+\mathbf{x}_{1n}-\mathbf{r}_j|)$ over all $\mathbf{r}_1$ will yield the union volume of n spheres of unit radius whose sphere centers are separated by the distances $|\mathbf{x}_{12}|$, $|\mathbf{x}_{13}|$, ..., $|\mathbf{x}_{1n}|$. That such a function appears in the expression for the n-point function S_n is consistent with the aforementioned geometrical interpretation of these functions. Recall that these n-point matrix functions were interpreted to be the probability that a region, the union volume of n spheres, contain no sphere centers.

It is convenient to change the dummy integration variables from $\mathbf{r}_1,\ \mathbf{r}_2,\ \ldots,\mathbf{r}_n$ to $\mathbf{r}_{n+1},\ \ldots,\mathbf{r}_{n+s}$ and to replace the variables not integrated over $\mathbf{x}_1,\ \mathbf{x}_2,\ \ldots,\mathbf{x}_n$ with $\mathbf{r}_1,\ \mathbf{r}_2,\ \ldots,\mathbf{r}_n$. We then have

$$S_n(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)$$
$$=1+\sum_{s=1}^{\infty}\frac{(-1)^s}{s!}\int\cdots\int\int \rho_s(\mathbf{r}_{n+1},\mathbf{r}_{n+2},\ldots,\mathbf{r}_{n+s})$$
$$\times\prod_{j=n+1}^{n+s} m^{(n)}(\mathbf{r}_{j1},\mathbf{r}_{j2},\ldots,\mathbf{r}_{jn})\,d\mathbf{r}_j\,, \tag{29a}$$

where

$$m^{(n)}(\mathbf{r}_{j1},\mathbf{r}_{j2},\ldots,\mathbf{r}_{jn})=1-\prod_{i=1}^{n}[1-m(\mathbf{r}_{ij})]$$
$$\mathbf{r}_{ij}=|\mathbf{r}_j-\mathbf{r}_i|\,. \tag{29b}$$

This is the desired representation of the S_n we set out to derive. It is, in general, an infinite series where the sth term of the sum involves s-tuplets of particles.[10] Given the s-body correlation functions ρ_s ($s=1,\ 2,\ 3,\ \ldots$) one can in principle evaluate the S_n for any n.

In the case of a homogeneous system $P_N(\mathbf{r}^N)$ is invariant under translation and thus implies that the arguments of the S_n will be functions of relative positions. For such a system it is convenient to express S_n in terms of another distribution function $g_n(\mathbf{r}^n)$ (see Appendix B):

$$S_n(\mathbf{r}_{12},\mathbf{r}_{13},\ldots,\mathbf{r}_{1n})$$
$$=1+\sum_{s=1}^{\infty}(-1)^2\frac{\rho^s}{s!}\int\cdots\int g_s(\mathbf{r}_{n+1},\mathbf{r}_{n+2},\ldots,\mathbf{r}_{n+s})$$
$$\times\prod_{j=n+1}^{n+s} m^{(n)}(\mathbf{r}_{j1},\mathbf{r}_{j2},\ldots,\mathbf{r}_{jn})\,d\mathbf{r}_j\,. \tag{30}$$

Elsewhere[11] we have demonstrated that there is a one-to-one mapping between the n-point function S_n and the Mayer–Montroll equations[12] for a binary mixture in which one of the two species consists of "point" particles (i.e., spheres of zero radius), in the limit of infinite

dilution of the point particles. There we also have found that for such a binary mixture the Kirkwood–Salsburg equations[13] become equations for the S_n. The Kirkwood–Salsburg representation of the S_n is new and gives us a means of approximating and bounding the S_n that is more powerful than that provided by the Mayer–Montroll representation. In Appendix A we derive expressions for the S_n using simple probabilistic arguments.

We note that, since the g_s are analytic in density, Eq. (30) immediately yields a power-series representation of S_n in density when such a representation is desired.

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APPENDIX A: PROBABILISTIC METHOD OF DERIVING THE S_n

We now proceed to present an alternative method of deriving expressions for the n-point matrix probability function in terms of the ρ_n for an inhomogeneous system of N spheres. The derivation is a simple extension of the probabilistic arguments put forth by Reiss, Frisch, and Lebowitz[14] to determine the probability of finding no sphere centers in a spherical region of radius r in a uniform system of N rigid spheres. [Their argument, which goes back to Boltzmann, leads them to obtain an equation equivalent to the first Mayer–Montroll equation or as we shall see, the equation for S_1, $(=\phi)$ when r is equal to the radius of a sphere.[7]] The procedure used by Reiss *et al.* may be exploited for the case of a system of N spheres with arbitrary interparticle potential and where the region, absent of sphere centers, is of an arbitrary configuration. This simple observation coupled with the aforementioned geometrical interpretation of the S_n for a system of N spheres leads to the following probabilistic argument.

Let $p_0(\Omega)$, $p_1(\Omega)$, etc. denote the probabilities that the centers of exactly no particle, exactly one particle, etc., lie in some region Ω. Here Ω represents some subset of the total volume V. It follows that

$$p_0+\sum_{n=1}^{\infty}p_n=1\ . \tag{A1}$$

This may be written as

$$\begin{aligned}p_0+\sum_{n=1}^{\infty}p_n&=p_0-\sum_{n=1}^{\infty}\{[1+(-1)]^n-1\}p_n\\&=p_0-\sum_{n=1}^{\infty}p_n\sum_{m=1}^{\infty}(-1)^nC_m^n\\&=p_0-\sum_{m=1}^{\infty}(-1)^m\sum_{n=m}^{\infty}C_m^np_n=1\ ,\end{aligned} \tag{A2}$$

where $C_m^n=n!/(n-m)!m!$ are the binomial coefficients. Solving Eq. (A2) for p_0 we have that

$$\begin{aligned}p_0=1&-(p_1+2p_2+3p_3+\cdots)+(p_2+3p_3+6p_4+\cdots)\\&-(p_3+4p_4+\cdots)+\cdots\ .\end{aligned} \tag{A3}$$

The first sum in parentheses in Eq. (A3) represents the average number of individual particles in region Ω. The second sum represents the average number of pairs of particles in region Ω, the third, the average number of tuplets of particles in region Ω, etc. In terms of the s-body distribution functions we have

$$\begin{aligned}p_0(\Omega)=1+\sum_{s=1}^{\infty}\frac{(-1)^s}{s!}\int\cdots\int_{\Omega}\\\times\rho_s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)\,d\mathbf{r}_1\,d\mathbf{r}_2\cdots d\mathbf{r}_s\ ,\end{aligned} \tag{A4}$$

since the volume integral of the quantity $\rho_s(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s)/s!$ over all $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_s$ contained in Ω is, in the thermodynamic limit, the expected number of (unordered) s-tuplets of particles in Ω. In order to make the connection between $p_0(\Omega)$ and S_n we must be more specific about the region Ω. Recall that S_n may be interpreted to be the probability that a region $\Omega^{(n)}$ contains no sphere centers, $\Omega^{(n)}$ being the region of the union volume of n spheres of radius R at positions $\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_n$. It is clear, therefore, that $S_n=p_0(\Omega^{(n)})$. In order to explicitly specify the region of integration we must insert, into the integrand of Eq. (A4), the generalized indicator function, Eq. (28), thus rederiving the result (27).

APPENDIX B: PROBABILITY DENSITY FUNCTIONS

The n-body probability density $P_n(n<N)$ is obtained from P_N by integrating over the remaining $N-n$ particles; we have

$$P_n(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)=\int\cdots\int P_N(\mathbf{r}^N)d\mathbf{r}_{n+1}\,d\mathbf{r}_{n+2}\cdots d\mathbf{r}_N\ . \tag{B1}$$

If we let

$$\rho_n(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_n)\,d\mathbf{r}_1\,d\mathbf{r}_2\cdots d\mathbf{r}_n$$

be the probability that the center of exactly one (unspecified) particle is in $d\mathbf{r}_1$, the center of exactly one other (unspecified) particle is in $d\mathbf{r}_2$, etc., then

$$\begin{aligned}\rho_n(\mathbf{r}^n)&=N(N-1)\cdots(N-n+1)P_n(\mathbf{r}^n)\\&=\frac{N!}{(N-n)!}P_n(\mathbf{r}^n)\ .\end{aligned} \tag{B2}$$

In the case of a homogeneous system (i.e., in the "thermodynamic limit," $N\to\infty$, $V\to\infty$, and $\rho=N/V$ fixed), it is convenient to define another distribution function

$$g_n(\mathbf{r}^n)=[\rho_n(\mathbf{r}^n)]/\rho^n\ . \tag{B3}$$

Note that $g_n(\mathbf{r}^n)\to 1$ for all n as the mutual distances between the n particles increase indefinitely since $\rho_n(\mathbf{r}^n)\to\rho^n$. For an isotropic system and $n=2$, we find that

$$g_2(\mathbf{r}_1,\mathbf{r}_2)\equiv g(r)=V^2p_2(\mathbf{r}_1,\mathbf{r}_2)\ , \tag{B4}$$

where $r=|\mathbf{r}_2-\mathbf{r}_1|$. Here $g(r)$ denotes the well-known radial distribution function of liquid state theory.[15]

In the canonical ensemble of equilibrium statistical mechanics, for a system of rigid particles with potential energy independent of orientation,

$$P_N=Q_N^{-1}\exp-\beta\Phi_N(\mathbf{r}^N)\ , \tag{B5}$$

where Q_N^{-1} is the normalization constant that, from Eq.

(21) must be given by

$$Q_N = \int \exp -\beta\Phi_N(\mathbf{r}^N)\, d\mathbf{r}^N \ . \tag{B6}$$

Here β is $(k_B T)^{-1}$, where k_B is Boltzmann's constant and T is absolute temperature, while Φ_N is the potential energy associated with the N particles. For a system of impenetrable spheres of diameter $2R$ we have (as long as all particles remain in a container or sample of volume V)

$$\Phi_N = \begin{cases} \infty \ , & \text{if } |\mathbf{r}_i - \mathbf{r}_j| < 2R \text{ for any } i \text{ and } j \ , \quad i \neq j \ , \\ & \text{and 0 otherwise} \ . \end{cases} \tag{B7}$$

$$P_N = \begin{cases} 0 \ , & \text{if } |\mathbf{r}_i - \mathbf{r}_j| < 2R \text{ for any } i \text{ and } j \ , \quad i \neq j \ , \\ & \text{and } Q_N^{-1} \text{ otherwise} \end{cases} \tag{B8}$$

For fully overlapping (penetrable) spheres, Φ_N is trivially zero so that $Q_N = V^N$, and

$$P_N = V^{-N} \ . \tag{B9}$$

Because Φ_N and P_N are functions of the $\mathbf{r}_N$ only through the $|\mathbf{r}_i - \mathbf{r}_j|$ (as long as we neglect the potential energy changes associated with particles passing out of the container or sample), the media defined by these hard-sphere ensembles are statistically homogeneous and isotropic. (The neglect of the energy changes associated with interaction between particles and the container boundaries becomes fully justified only when we take the thermodynamics limit $V \to \infty$, $N \to \infty$, ρ fixed.)

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[8] Brown was the first to define n-point matrix functions in Ref. 4.

[9] We note here the relationship between the n-point cumulant functions and the n-point correlation function of the K' field $K'(\mathbf{x}_1)K'(\mathbf{x}_2)\cdots K'(\mathbf{x}_n)$, where K' is the fluctuating part of the bulk property of concern. These correlations arise naturally from the governing differential equations; see, e.g., M. Beran and J Molyneux, Il Nuovo Cimento 30, 1406 (1963), J. Molyneux and M. Beran, J. Math. Mech. 14, 337 (1965). We consider those cases in which the matrix has a constant property value of K_1 and the particle phase has a constant property value of K_2 (e.g., the dielectric constant, magnetic permeability, rigidity, and bulk moduli, etc.). We therefore may express the local property $K(\mathbf{x})$ in terms of the random variable $I(\mathbf{x})$: $K(\mathbf{x}) = K_1 I(\mathbf{x}) + K_2[1 - I(\mathbf{x})] = K_1[(1-\alpha)I(\mathbf{x}) + \alpha]$, where $\alpha = K_2/K_1$. Denoting the fluctuation in the property by $K'(\mathbf{x}) = K(\mathbf{x}) - \langle K \rangle$, one has $\langle K'(\mathbf{x}_1)K'(\mathbf{x}_2)\cdots K'(\mathbf{x}_n)\rangle = K_1(1-\alpha)S_n^*(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_n)$ where S_n^* is given by Eq. (15).

[10] For a two-phase random medium having a particle phase consisting of impenetrable spheres, it is easily seen that the terms associated with $s > n$ are identically zero. Thus for impenetrable spheres, S_2 is given exactly by the exhibited terms of Eq. (25) with the $O(\rho^3)$ term identically zero. This impenetrable-sphere expression for S_2 has already been given by Weissberg and Prager, for the case of a homogeneous system (Ref. 5) who also discuss the expression for S_3 through $O(\rho)$.

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