Two-point cluster function for continuum percolation

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We introduce a two-point cluster function $C_2(\mathbf{r}_1,\mathbf{r}_2)$ which reflects information about clustering in general continuum–percolation models. Specifically, for any two-phase disordered medium, $C_2(\mathbf{r}_1,\mathbf{r}_2)$ gives the probability of finding both points $\mathbf{r}_1$ and $\mathbf{r}_2$ in the same cluster of one of the phases. For distributions of identical inclusions whose coordiantes are fully specified by center-of-mass positions (e.g., disks, spheres, oriented squares, cubes, ellipses, or ellipsoids, etc.), we obtain a series representation of C_2 which enables one to compute the two-point cluster function. Some general asymptotic properties of C_2 for such models are discussed. The two-point cluster function is then computed for the adhesive-sphere model of Baxter. The two-point cluster function for arbitrary media provides a better signature of the microstructure than does a commonly employed two-point correlation function defined in the text.

I. INTRODUCTION

Transport and mechanical properties of two-phase composite media have been expressed in terms of the n-point probability function S_n:[1–4] quantities which statistically characterize the microstructure. The $S_n(\mathbf{x}^n)$ give the probability of simultaneously finding n points with positions $\mathbf{x}^n \equiv \{\mathbf{x}_1,...,\mathbf{x}_n\}$, respectively, in one of the phases. Employing the formalism of Torquato and Stell,[5] lower-order S_n (such as S_1,S_2, and S_3) have recently been computed for various models[6,7] of random two-phase media and, as a result, rigorous bounds on bulk properties (e.g., conductivity, elastic moduli, and fluid permeability), which depend upon such information, have been calculated.[7] On the experimental side, Berryman[8] has shown that image processing techniques can be employed to effectively measure lower-order S_n from samples of the material.

Unfortunately, lower-order S_n do not reflect information about percolating clusters within the system. (This point is elaborated upon in the subsequent section.) In the study of disordered media, it would be highly desirable to define and employ correlation functions, analogous to the S_n, which reflect information about clustering in the system, thus providing a better signature of the microstructure. Incorporation of such information in rigorous bounds on transport and mechanical properties of two-phase media would lead to very sharp bounds.

In Sec. II we define the two-point cluster function C_2 for arbitrary two-phase media. This is followed by a formulation of a series representation of C_2 for a distribution of identical inclusions whose coordinates are fully specified by center-of-mass positions. In Sec. III we discuss some general properties of C_2 for such suspensions. In Sec. IV we compute C_2 in the adhesive-sphere model of Baxter.[9] Finally, in Sec. V we make some concluding remarks.

II. DEFINITION AND REPRESENTATION OF THE TWO-POINT CLUSTER FUNCTION

A. Definition of the two-point cluster function

The random medium is a domain of space $D(\omega)$ (where the realization ω is taken from some probability space Ω) of volume V which is composed of two regions: a phase 1 region D_1 of volume fraction ϕ_1 and a phase 2 region D_2 of volume fraction $\phi_2 = 1 - \phi_1$. A cluster of phase i is defined as that part of phase i which can be reached from a point in phase i without passing through phase j, $i \neq j$. It is important to realize that this definition of a cluster is perfectly general: it is not restricted to clusters of "connected" particles or inclusions. In Fig. 1 a general situation is depicted.

The two-point probability function $S_2(\mathbf{r}_1,\mathbf{r}_2)$ gives the probability of finding the two points $\mathbf{r}_1$ and $\mathbf{r}_2$ in one of the phases, say phase 2. Note that when $\mathbf{r}_1$ and $\mathbf{r}_2$ coincide, $S_2 = S_1$ (which is simply equal to the volume fraction ϕ_2 of phase 2) and when $\mathbf{r}_1$ is far from $\mathbf{r}_2$, $S_2 \to S_1^2$ (assuming no long-range order). The two-point probability function may be written as a sum of two contributions:

$$S_2(\mathbf{r}_1,\mathbf{r}_2) = C_2(\mathbf{r}_1,\mathbf{r}_2) + D_2(\mathbf{r}_1,\mathbf{r}_2)\,, \qquad (2.1)$$

where

$$C_2(\mathbf{r}_1,\mathbf{r}_2) = \textit{Probability of finding both points } \mathbf{r}_i \textit{ and } \mathbf{r}_2 \textit{ in the same cluster of phase } i, \qquad (2.2)$$

and

$$D_2(\mathbf{r}_1,\mathbf{r}_2) = \textit{Probability of finding both points } \mathbf{r}_i \textit{ and } \mathbf{r}_2 \textit{ in phase } i \textit{ such that each point is in a different cluster.} \qquad (2.3)$$

We term C_2, the quantity of interest here, the "two-point cluster function."[10,11] Definition (2.2) applies to two-phase random media of arbitrary microstructure.

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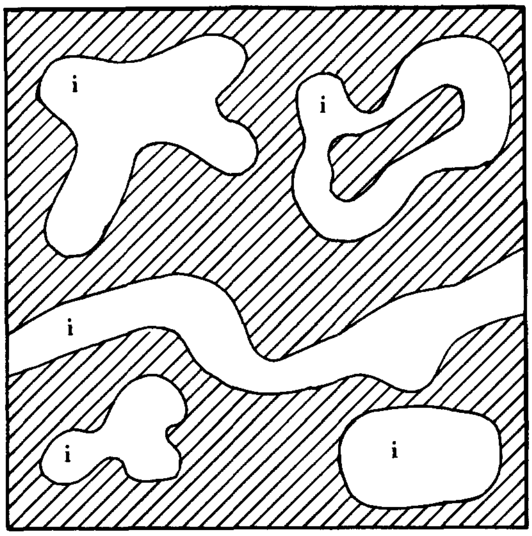


FIG. 1. Schematic of a general two-phase disordered system. According to the definition given in the text, there are a total of five clusters of phase i.

B. Representation of C_2 for distributions of inclusions

We now focus our attenion on obtaining a representation of the two-point cluster function C_2 for a distribution of identical inclusions such that the coordinate of each inclusion i is fully specified by a center-of-mass position $\mathbf{r}_i$ (e.g., spheres, disks, oriented squares, cubes, ellipsoids, or ellipses, etc.). We shall be interested in physical clusters of inclusions which may form, for example, as the result of interparticle overlap or as the result of particles coming in contact with one another. Torquato and Stell[5] have obtained a series representation of the general n-point probability function S_n (for the aforementioned system) in terms of the n-particle probability density function $\rho_n(\mathbf{r}_1,...,\mathbf{r}_n)$ associated with finding any n inclusions with configuration $\mathbf{r}_1,...,\mathbf{r}_n$. In particular, the probability of finding two points with positions $\mathbf{r}_1$ and $\mathbf{r}_2$ anywhere in the particulate phase is given by[5,12,13]

$$S_2(\mathbf{r}_1,\mathbf{r}_2) = \sum_{k=1}^{\infty} \frac{(-1)^k}{k!} \int \rho_k(\mathbf{r}_3,...,\mathbf{r}_{2+k}) \times F(\mathbf{r}_1,...,\mathbf{r}_{2+k}) d\mathbf{r}_3 \cdots d\mathbf{r}_{2+k}, \qquad (2.4)$$

where

$$F = \prod_{j=3}^{2+k} m^{(2)}(\mathbf{r}_{1j},\mathbf{r}_{2j}) - \prod_{j=3}^{2+k} m(\mathbf{r}_{1j}) - \prod_{j=3}^{2+k} m(\mathbf{r}_{2j}), \qquad (2.5)$$

$$m^{(2)}(\mathbf{x},\mathbf{y}) = m(\mathbf{x}) + m(\mathbf{y}) - m(\mathbf{x})m(\mathbf{y}), \qquad (2.6)$$

and $m(\mathbf{x})$ is an inclusion indicator function defined by

$$m(\mathbf{x}) = \begin{cases} 1, & \mathbf{x} \textit{ is interior to the inclusion} \\ 0, & \textit{otherwise} \end{cases}. \qquad (2.7)$$

In Eq. (2.5), $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, and in Eq. (2.7), $\mathbf{x}$ is measured with respect to the center-of-mass of an inclusion. For a sphere or disk of radius R, the indicator function is simply

$$m(r) = \begin{cases} 1, & r<R \\ 0, & \textit{otherwise} \end{cases}, \qquad (2.8)$$

where r is the distance from the center of the particle.

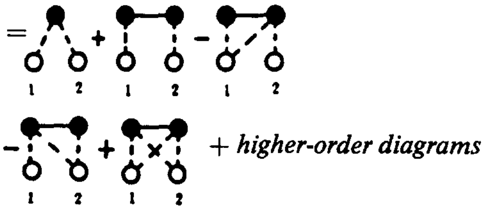
For statistically homogeneous media, ρ_n depends only upon the relative positions $\mathbf{r}_{12},...,\mathbf{r}_{1n}$ (e.g., ρ_1 is simply the number density ρ) and hence S_2 depends upon the relative position $\mathbf{r}_{12}$. In such instances, it is convenient to introduce the n-particle distribution functions g_n defined by $\rho_n = \rho^n g_n$, which when substituted into Eq. (2.4) yields

$$S_2(\mathbf{r}_{12}) = \sum_{k=1}^{\infty} \frac{(-1)^k \rho^k}{k!} \times \int g_k(\mathbf{r}_3,...,\mathbf{r}_{2+k}) F(\mathbf{r}_1,...,\mathbf{r}_{2+k}) d\mathbf{r}_3 \cdots d\mathbf{r}_{2+k}. \qquad (2.9)$$

Note that the volume integral of m [Eq. (2.7)] over the position of the inclusion is an excluded volume, namely, the volume excluded to an inclusion by a "point" particle which is simply equal to the volume of an inclusion, V_1. Similarly, the volume integral of $m^{(2)}$ [Eq. (2.6)] over the position of the inclusion gives $V_2(\mathbf{x}-\mathbf{y})$, the union volume of two such excluded volumes whose center-of-mass coordinates are separated by the relative displacement $\mathbf{x}-\mathbf{y}$.

Before obtaining C_2 from Eq. (2.4), it is necessary to examine S_2 a little further. Expanding (2.4) up to two-body terms using the diagrammatic notation of Torquato and Stell[14] yields

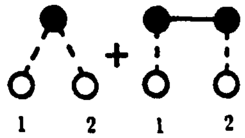
$S_2(\mathbf{r}_1,\mathbf{r}_2) =$



(2.10)

where - - - is an m bond and — is a g_2 bond. For the case of totally impenetrable inclusions, the two-point probability function is exactly given by

$S_2(\mathbf{r}_1,\mathbf{r}_2) =$



(2.11)

because of the conflicting demands of the indicator function m and the n-particle probability densities g_n. By "totally impenetrable inclusions" we mean inclusions which are completely impenetrable to one another; the inclusions are not impenetrable to the probing points, however. The first diagram of (2.11) is the probability of finding both points in the same particle. For statistically homogeneous media, it is equal to $\rho V_2^{\text{int}}(\mathbf{r}_{12})$, where $V_2^{\text{int}}(\mathbf{r}_{12})$ is the intersection volume of two "point-particle" exclusion volumes whose center-of-mass coordinates are separated by the relative distance $\mathbf{r}_{12}$. The second diagram is the probability of finding a point in one inclusion and the second point in another inclusion. Therefore, for the general case described by (2.10), the terms beyond the first two diagrams account for overlap between the inclusions.

For the case of "fully penetrable" particles (i.e., randomly centered and thus spatially uncorrelated particles), $g_n = 1$ and, hence, Eq. (2.9) readily gives

$$S_2(\mathbf{r}_{12}) = \sum_{s=1}^{\infty} \frac{(-1)^s \rho^s}{s!} [V_2^s(\mathbf{r}_{12}) - 2V_1^s]$$
$$= 1 - 2\exp[-\eta] + \exp[-\eta V_2(\mathbf{r}_{12})/V_1], \tag{2.12}$$

where $\eta = \rho V_1$ is a reduced density. From Eq. (2.12) it is seen that $S_1 = \phi_2 = 1 - \exp[-\eta]$ and hence Eq. (2.12) attains its proper asymptotic value for large separations. Figure 2 depicts a distribution of fully penetrable disks. In Fig. 3, $S_2(r)$ for distributions of fully penetrable spheres[15] is plotted as a function of r at sphere volume fractions below, at, and above the percolation threshold value (equal to about 0.3[16]). Note that $S_2(r)$ at the percolation threshold is not singularly different than $S_2(r)$ at other volume fractions. This statement will apply to other models as well and hence one concludes that S_2 for general microstructures is incapable of reflecting information about percolating clusters within the system.

By decomposing Eq. (2.4) or (2.10) according to Eq. (2.1), we can obtain a series representation of C_2 for the aforementioned distribution of inclusions. Therefore, we must identify those graphs of Eq. (2.10) in which the points $\mathbf{r}_1$ and $\mathbf{r}_2$ are contained in the same cluster. For simplicity, we shall first consider statistically homogeneous media and hence Eq. (2.9). The g_n of Eq. (2.9) may be decomposed into contributions involving clusters of different sizes:

$$g_n(\mathbf{r}_1,...,\mathbf{r}_n) = \sum_{\{\gamma\}} P_n(\{\gamma\}), \tag{2.13}$$

where $\{\gamma\} = \{\gamma_1|\gamma_2|\cdots|\gamma_k\}$ denotes the unordered partitioning of the set $\{\mathbf{r}_1,...,\mathbf{r}_n\}$ into k disjoint, unordered subsets and

$\rho^n P_n(\{\gamma\})$ = *Probability density associated with finding n_1 particles with positions γ_1 which are members of the same cluster, n_2 particles with positions γ_2 which are members of the same cluster,...,and n_k particles with positions γ_k which are members of the same cluster, such that the clusters associated with each subset are different and* $\sum_{i=1}^{k} n_i = n$. (2.14)

The sum of Eq. (2.13) is over all partitions of $\{\gamma\}$. For $n = 2$ and $n = 3$, Eq. (2.13) yields

$$g_2(\mathbf{r}_{12}) = P_2(\mathbf{r}_1,\mathbf{r}_2) + P_2(\mathbf{r}_1|\mathbf{r}_2), \tag{2.15}$$

$$g_3(\mathbf{r}_{12},\mathbf{r}_{13},\mathbf{r}_{23}) = P_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) + P_3(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3) + P_3(\mathbf{r}_1,\mathbf{r}_3|\mathbf{r}_2) + P_3(\mathbf{r}_2,\mathbf{r}_3|\mathbf{r}_1) + P_3(\mathbf{r}_1|\mathbf{r}_2|\mathbf{r}_3). \tag{2.16}$$

The first term on the right hand side of Eq. (2.15), $P_2(\mathbf{r}_1,\mathbf{r}_2)$ is the pair-connectedness function.[17] The quantity $\rho^2 P_2(\mathbf{r}_1,\mathbf{r}_2)$ is the probability density associated with finding two particles centered at $\mathbf{r}_1$ and $\mathbf{r}_2$ which are connected, i.e., which are members of the same cluster of size at least two. The next term $P_2(\mathbf{r}_1|\mathbf{r}_2)$ is the pair-blocking function.[17] The quantity $\rho^2 P_2(\mathbf{r}_1|\mathbf{r}_2)$ is the probability density associated with finding two particles centered at $\mathbf{r}_1$ and $\mathbf{r}_2$ which are disconnected, i.e., which are members of different clusters each of size at least one. The terms of Eq. (2.16) have similar interpretations. For example, $\rho^3 P_3(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_3)$ is the probability density associated with finding a pair of connected particles at $\mathbf{r}_1$ and $\mathbf{r}_2$ and a particle at $\mathbf{r}_3$ which is not connected to the particles at $\mathbf{r}_1$ and $\mathbf{r}_2$.

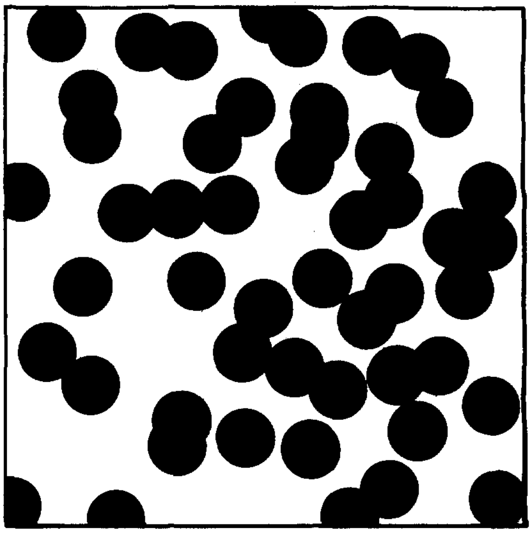


FIG. 2. A two-dimensional distribution of equisized, fully penetrable (i.e., randomly centered) disks at a disk area fraction of about 0.35.

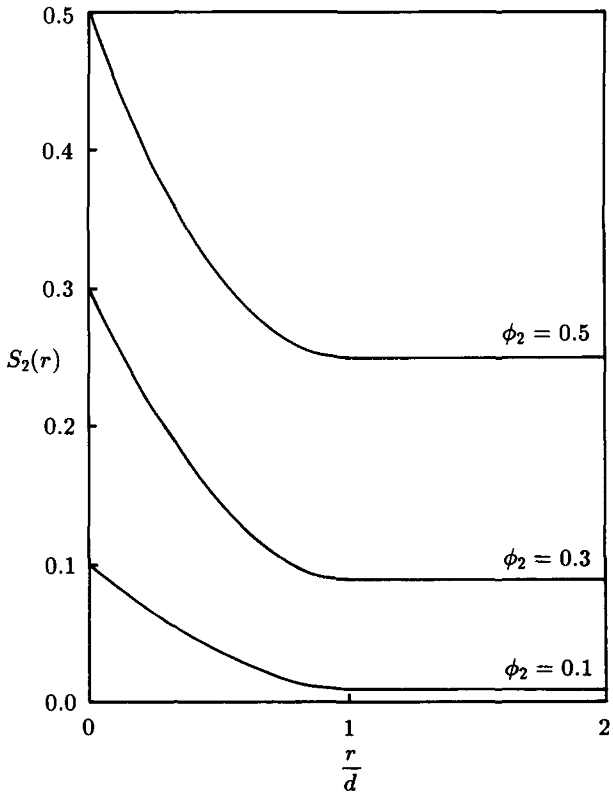
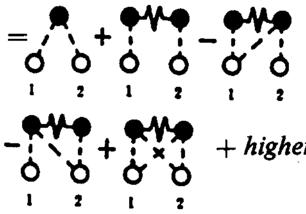


FIG. 3. The two-point probability function $S_2(r)$ associated with the particle phase for a system of equisized, fully penetrable spheres (Ref. 15) of unit diameter at $\phi_2 = 0.1$, 0.3, and 0.5, where ϕ_2 is the particle-phase volume fraction (Ref. 12). The percolation threshold occurs at approximately $\phi_2 = 0.3$ (Ref. 16).

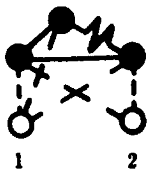
Substitution of Eq. (2.13) into Eq. (2.9) leads to a series representation of S_2 in terms of the P_n; associated with each graph involving a g_n bond are L graphs involving the $P_n(\{\gamma\})$ corresponding to the possible partitions of $\{\gamma\}$. In accordance with Eq. (2.1) the prescription for obtaining C_2 from this series of S_2 is as follows:

$C_2(\mathbf{r}_{12}) -$  = *graphs containing $P_n(\{\gamma\})$ in which at least one black circle is attached to a white circle labeled 1 by an m bond and another black circle is attached to a white circle labeled 2 by an m bond such that both black circles belong to a subset of $\{\gamma\}$.* (2.17)

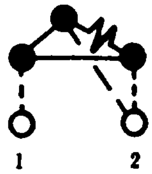
Through terms involving two-body graphs, Eq. (2.17) gives

$C_2(\mathbf{r}_{12}) =$  + *higher-order graphs,* (2.18)

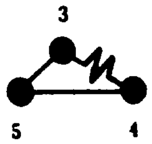
where higher-order graphs, is a $P_2(\mathbf{r}_1,\mathbf{r}_2)$ bond, i.e., a pair-connectedness bond. The higher-order graphs involve three or more inclusions. For example, the graph



is one of the three-body contributions to Eq. (2.18), whereas the graph

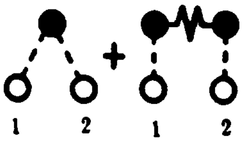


does not contribute to C_2 but rather is a contribution to D_2 of Eq. (2.1). Here the subgraph



is a $P_3(\mathbf{r}_3,\mathbf{r}_4|\mathbf{r}_5)$ bond.

In general, totally impenetrable inclusions need not be in strict contact to form a bounded pair; each graph in Eq. (2.18) will generally be nonzero. However, if one restricts oneself to totally impenetrable inclusions in which clusters form only as the result of interparticle contacts, then Eq. (2.11) along with Eqs. (2.1) and (2.18) lead to the exact relation

$C_2(\mathbf{r}_{12}) =$  . (2.19)

The first graph of Eq. (2.19) gives the contribution to C_2 when both points land in a single inclusion. The second graph of Eq. (2.19) accounts for cases in which one point lands in one inclusion and the other point lands in a different inclusion such that both incusions are members of the same cluster.[18] The only way that the second graph can be nonzero is for the inclusions to form clusters as the result of interparticle contacts.

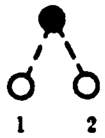
Note that the generalization of the above arguments for inhomogeneous media is achieved by replacing in Eq. (2.17) $C_2(\mathbf{r}_{12})$ with $C_2(\mathbf{r}_1,\mathbf{r}_2)$ and P_n with G_n, where the latter quantity is defined through a relation like Eq. (2.13) but with g_n and P_n replaced by ρ_n and G_n, respectively. Finally, we remark that since there exists a cluster which spans the entire macroscopic sample at the percolation point, C_2 must become long ranged as the percolation threshold is approached from below. This last assertion is proved in the subsequent section.

III. SOME GENERAL ASYMPTOTIC PROPERTIES OF C_2 FOR DISTRIBUTIONS OF INCLUSIONS

We obtain some general results for the two-point cluster function C_2 of statistically homogeneous distributions of identical inclusions such that the coordinate of each inclusion is fully specified by a center-of-mass position. Thus, we focus our attention on Eq. (2.18), in general. We first study the asymptotic behavior of $C_2(\mathbf{r})$ for large r as the percolation point is approached. This is followed by an examination of the asymptotic behavior of $C_2(\mathbf{r})$ for small r, for a distribution of totally impenetrable spheres.

A. Asymptotic behavior of C_2 near the percolation point

Consider the distribution of identical inclusions described above. The first diagram of Eq. (2.18), as noted earlier, is given by

 $= \rho V_2^{\text{int}}(\mathbf{r}_{12})$, (3.1)

where $V_2^{\text{int}}(\mathbf{r})$ is the intersection of two point-particle exclusion volumes. Therefore, V_2^{int} is a short-ranged function. For the special case of spheres of diameter d,

$$V_2^{\text{int}}(r) = \frac{\pi d^3}{6}\left[1 - \frac{3}{2}\left(\frac{r}{d}\right) + \frac{1}{2}\left(\frac{r}{d}\right)^3\right] H(d-r)\,, \tag{3.2}$$

where $H(x)$ is the Heaviside step function defined to be zero if $x<0$ and unity if $x>0$, and $r=|\mathbf{r}_{12}|$. The second diagram of Eq. (2.18), which we denote by $C_2^*(\mathbf{r})$, can be expressed as

$$\tilde{C}_2^*(\mathbf{k}) = \rho^2 \tilde{m}^2(\mathbf{k}) \tilde{P}_2(\mathbf{k})\,, \tag{3.3}$$

where generally $\tilde{f}(\mathbf{k})$ is the Fourier transform of some function $f(\mathbf{r})$ and $k = |\mathbf{k}|$. For the instance of spheres,

$$\tilde{m}(k) = \frac{4\pi d^3}{(kd)^3}\left[\sin\left(\frac{kd}{2}\right) - \frac{kd}{2}\cos\left(\frac{kd}{2}\right)\right]. \qquad (3.4)$$

Note that for arbitrary-shaped particles $\tilde{m}(0) = V_1$ where V_1 is the volume of an inclusion.

We shall now prove that $C_2(\mathbf{r})$ must become long ranged at the percolation threshold. The mean cluster size S is generally defined by[17]

$$S = 1 + \rho \int P_2(\mathbf{r})d\mathbf{r}$$
$$= 1 + \rho\tilde{P}_2(0) . \qquad (3.5)$$

Combination of Eq. (2.18) and Eqs. (3.3)–(3.5) yields

$$S = 1 + \frac{\rho}{\eta^2}\tilde{C}_2^*(0) + \cdots$$
$$= 1 + \frac{\rho}{\eta^2}\int C_2^*(\mathbf{r})d\mathbf{r} + \cdots . \qquad (3.6)$$

Since the percolation threshold corresponds to the limit $S \to \infty$, $C_2^*(\mathbf{r})$ and, thus, $C_2(\mathbf{r})$ must be long ranged at this critical point. For totally impenetrable inclusions, the mean cluster size is exactly given by

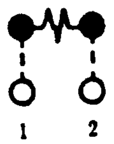
$$S = 1 + \frac{\rho}{\eta^2}\int C_2^*(\mathbf{r})d\mathbf{r},$$
$$= \frac{\rho}{\eta^2}\int C_2(\mathbf{r})d\mathbf{r}. \qquad (3.7)$$

B. Small r behavior of C_2 for totally impenetrable spheres

Here we determine the asymptotic behavior of $C_2(r)$ for small r, for isotropic distributions of totally impenetrable spheres of diameter d which can only form clusters as the result of interparticle contacts. Therefore, we are interested in Eq. (2.19), which in the notation of the present section is expressed as

$$C_2(r) = \rho V_2^{\text{int}}(r) + C_2^*(r) , \qquad (3.8)$$

where $V_2^{\text{int}}(r)$ is given by Eq. (3.2) and

$C_2^*(\mathbf{r}) =$  . (3.9)

For $r > d$ in the vicinity of $r = d$, $P_2(r)$ must be of the form

$$P_2(r) = \frac{\bar{Z}}{\rho 4\pi d^2}\delta(r-d) + P_2^C(r) , \qquad (3.10)$$

where $P_2^C(r)$ is the continuous part of $P_2(r)$ for r just larger than d and

$$\bar{Z} = \rho\int_0^d 4\pi r^2 P_2(r)dr \qquad (3.11)$$

is the average coordination number. Note that for an equilibrium distribution of hard spheres the probability of finding pairs of particles in contact at $r = d$ is zero and so $\bar{Z} = 0$.

By substituting Eq. (3.10) into Eq. (3.9) and employing a bipolar coordinate system, we find

$$C_2^*(r) = \frac{\bar{Z}\eta}{4}\left(\frac{r}{d}\right)^2 + O(r^3) . \qquad (3.12)$$

Hence, $C_2^*(0) = 0$. Combining Eq. (3.12) with Eq. (3.2) in Eq. (3.8) yields

$$C_2(r) = \eta - \frac{3}{2}\eta\left(\frac{r}{d}\right) + \frac{\bar{Z}\eta}{4}\left(\frac{r}{d}\right)^2 + O(r^3) . \qquad (3.13)$$

When $r = 0$, $C_2 = \eta$, i.e., when the two points coincide, C_2 equals the probability of finding one point in a single particle $\eta = \phi_2$. Note that the linear term of Eq. (3.13) is proportional to the specific surface (interfacial surface area per unit volume) $s = \rho\pi d^2 = 6\eta/d$:

$$\left.\frac{dC_2(r)}{dr}\right|_{r=0} = -\frac{s}{4}. \qquad (3.14)$$

The quadratic term of Eq. (3.13) is the first term to provide information about the average number of particle contacts.

IV. EVALUATION OF THE TWO-POINT CLUSTER FUNCTION FOR ADHESIVE SPHERES

Here we evaluate Eq. (3.8) for totally impenetrable spheres of diameter d in the adhesive-sphere model due to Baxter.[9] Before computing C_2, we first describe the model.

A. Adhesive-sphere model

The adhesive-sphere model is defined by a pair potential $u(r)$ given by

$$\beta u(r) = \begin{cases} \infty, & 0 < r < \sigma \\ -\ln\left[\dfrac{d}{12\tau(d-\sigma)}\right], & \sigma < r < d, \\ 0, & r > d \end{cases} \qquad (4.1)$$

in the limit $\sigma \to d$, where the parameter τ is equivalent to a dimensionless temperature. The quantity τ^{-1} is a measure of the stickiness of the particles, with $\tau^{-1} \to 0$ corresponding to nonsticky hard spheres. The Boltzmann factor develops a Dirac delta contribution at contact:

$$\exp[-\beta u(r)] = \begin{cases} \dfrac{d}{12\tau}\delta(r-d), & r \leqslant d \\ 1, & r > d \end{cases}. \qquad (4.2)$$

Baxter[9] analytically obtained the radial distribution function (and the equation of state) for the adhesive-sphere model in the Percus–Yevick (PY) approximation. Chiew and Glandt[16] obtained the pair-connectedness function $P_2(r)$ for the same model in the PY approximation by defining bound and unbound pairs of particles through a decomposition of the Boltzmann factor[17]

$$\exp[-\beta u(r)] = \exp[-\beta u^+(r)] + \exp[-\beta u^-(r)] , \qquad (4.3)$$

where

$$\exp[-\beta u^+(r)] = \frac{d}{12\tau}\delta(r-d) , \qquad (4.4)$$

$$\exp[-\beta u^-(r)] = \begin{cases} 0, & 0 < r < d \\ 1, & r > d \end{cases}. \qquad (4.5)$$

Clearly, $u^+(r)$ and $u^-(r)$ are the interaction potentials for bound and unbound pairs, respectively.

For the range $0<r\leqslant d$,

$$P_2(r)=\tfrac{1}{12}\lambda d\delta(r-d)\,, \tag{4.6}$$

where the dimensionless parameter λ is related to τ and to the reduced density $\eta=\phi_2=\rho\pi d^3/6$ by

$$\frac{\eta}{12}\lambda^2-\left(\frac{\eta}{1-\eta}+\tau\right)\lambda+\frac{1+\eta/2}{(1-\eta)^2}=0\,. \tag{4.7}$$

Chiew and Glandt obtained the following analytical expression for the Fourier transform of the PY pair-connectedness function:

$$1+\rho\tilde{P}_2(k)=\left[1-2\lambda\eta\frac{\sin(kd)}{kd}+2\left(\frac{\lambda\eta}{kd}\right)^2[1-\cos(kd)]\right]^{-1}. \tag{4.8}$$

The average coordination number is calculated using Eq. (3.11), with the result that

$$\bar{Z}=2\lambda\eta \tag{4.9}$$

for adhesive spheres in the PY approximation. Note that when there is no stickiness ($\lambda=0$), $\bar{Z}=0$, as expected.

Finally, we point out that Chiew and Glandt found the mean cluster size to be given by

$$S=\frac{1}{(1-\lambda\eta)^2}\,, \tag{4.10}$$

and so the percolation threshold η_p corresponds to

$$\eta_p=1/\lambda\,. \tag{4.11}$$

Equation (4.11) combined with Eq. (4.7) yields the locus of the percolation line on the τ–η plane:

$$\tau=\frac{19\eta^2-2\eta+1}{12(1-\eta)^2}\,. \tag{4.12}$$

B. Calculation of C_2 in the adhesive-sphere model

Through order η^3, the double convolution integral (3.9) can be evaluated exactly:

$$C_2^*(\mathbf{r})=A\eta^2+B\eta^3+O(\eta^4)\,, \tag{4.13}$$

where

$$A=\frac{1}{12}\lambda\begin{cases}6r^2-6r^3+\frac{6}{5}r^4, & 0<r<1\\ -\frac{48}{5r}+24-12r-6r^2+6r^3-\frac{6}{5}r^4, & 1<r<2\\ 0, & r>2\end{cases} \tag{4.14}$$

and

$$B=\frac{1}{12}\lambda\begin{cases}\frac{3}{2}r^3-\frac{6}{5}r^4+\frac{1}{5}r^5, & 0<r<1\\ -\frac{3}{10r}+\frac{18}{5}-12r+18r^2-12r^3+\frac{18}{5}r^4-\frac{2}{5}r^5, & 1<r<2\\ -\frac{243}{10r}+\frac{162}{5}-18r^2+\frac{21}{2}r^3-\frac{12}{5}r^4+\frac{1}{5}r^5, & 2<r<3\\ 0, & r>3.\end{cases} \tag{4.15}$$

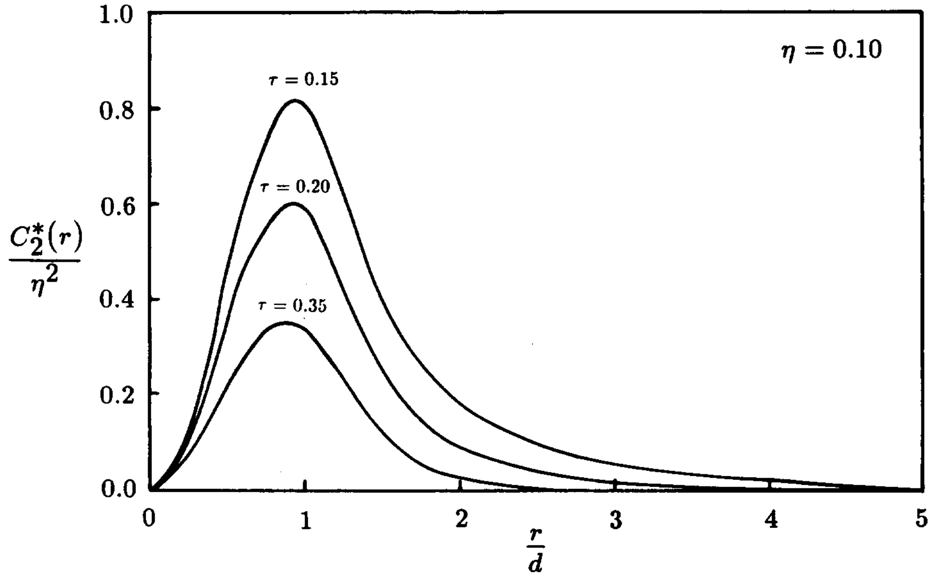


FIG. 4. The scaled two-point cluster function $C_2^*(r)/\eta^2$ for spheres of unit diameter [defined by Eq. (3.9)] for an adhesive-sphere system at $\eta=0.1$ for $\tau=0.15$, 0.20, and 0.35. At this density, the system percolates when $\tau=0.102$.

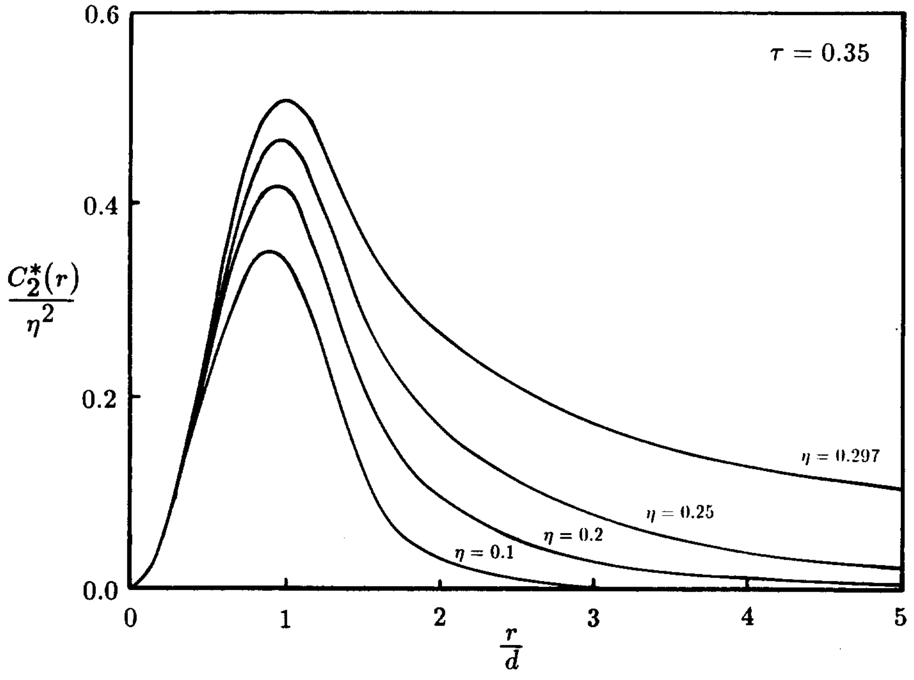


FIG. 5. The scaled two-point cluster function $C_2^*(r)/\eta^2$ for spheres of unit diameter for an adhesive-sphere system at $\tau = 0.35$ for $\eta = 0.1, 0.2, 0.25$, and 0.297. The system percolates at $\eta = 0.297$.

Here we have taken the diameter to be unity. Equation (4.13) combined with Eq. (3.2) and (3.8) gives $C_2(r)$ exactly through order η^3.

For arbitrary density, we evaluate the integral (3.9) by inverting Eq. (3.3), using the numerical Fourier-transform technique given by Lado,[19] and employing the PY expression (4.8) for $\tilde{P}_2(k)$. In Fig. 4 we plot $C_2^*(r)/\eta^2$ as a function of r at $\eta = 0.1$ for $\tau = 0.15, 0.20$, and 0.35. The percolation threshold for this case corresponds to $\tau = 0.102$ and so for the values of τ described in the figure, the system does not percolate. In accordance with Eq. (3.12), $\tilde{C}_2^*(0) = 0$. As r is increased, C_2^* increases until it attains a maximum value, and then decays rapidly to zero after several diameters. Since the system is always below the percolation transition, C_2^* and, thus, C_2 are short ranged.

In Fig. 5 we present $C_2^*(r)/\eta^2$ at $\tau = 0.35$ for four different values of η: $\eta = 0.1$, 0.2, 0.25, and 0.297. The last value of η corresponds to the percolation transition. As the density approaches the predicted percolation threshold ($\eta_p = 0.297$), $C_2^*(r)$ becomes progressively longer ranged, unlike the two-point probability function $S_2(r)$ described in Sec. II. For $\eta = 0.25$, $C_2^*(r)/\eta^2$ becomes negligibly small after nine diameters, indicating the presence of clusters which are considerably larger than for the case $\eta = 0.1$. At the PY percolation threshold, $C_2^*(r)$ of course is long ranged.

V. CONCLUDING REMARKS

The two point cluster function $C_2(r)$ defined and studied here clearly reflects information about clustering in the system and hence provides a better signature of the microstructure than does the two-point probability function $S_2(r)$ which does not contain such information. In future work on the determination of bounds on transport and mechanical properties of disordered media, it would be highly desirable to incorporate n-point cluster functions rather than n-point probability functions. Such bounds typically involve certain integrals over the correlation functions[1–5] and use of the n-point cluster functions here would result in divergent integrals at the percolation threshold. Rigorous bounds on bulk properties of this type would be able, for the first time, to predict criticality in percolative systems.

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[11]In Ref. 10 Torquato defines a different two-point cluster function; this is described in footnote 17.
[12]The S_n in Ref. 5 are defined in terms of the matrix phase (i.e., the phase outside the particles), while those contained herein are defined in terms of the particle phase. The relationship between the n-point probability functions associated with the matrix and particle phases is described in Ref. 5.
[13]Note that Eq. (2.4) can be easily generalized to particles of arbitrary shape. In such instances, the quantity $\mathbf{r}_i$ would describe the center-of-mass coordinate as well as the orientation of the inclusion.
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[18]The two-point cluster function defined in Ref. 10 is given by the second diagram of Eq. (2.17) only, even in cases when the particles can overlap. Although this is a perfectly valid theoretical quantity to study and compute, it is not a practically useful quantity to measure since one must necessarily overcount successes when the particles can overlap. However, if the particles are impenetrable, then the two-point function defined in Ref. 10 is exactly the same as C_2^* given by Eq. (3.9) in the present work.
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