

Measure of clustering in continuum percolation: Computer-simulation of the two-point cluster function

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The two-point cluster function $C_2(\mathbf{r}_1, \mathbf{r}_2)$ is determined for a D -dimensional interpenetrable-sphere continuum model from Monte Carlo simulations. $C_2(\mathbf{r}_1, \mathbf{r}_2)$ gives the probability of finding two points, at positions \mathbf{r}_1 and \mathbf{r}_2 , in the same cluster of particles, and thus provides a measure of clustering in continuum-percolation systems. A pair of particles are said to be "connected" when they overlap. Results are reported for $D = 1, 2$, and 3 at selected values of the sphere number density ρ and of the impenetrability index λ , $0 \leq \lambda \leq 1$. The extreme limits $\lambda = 0$ and 1 correspond, respectively, to the cases of fully penetrable spheres ("Swiss-cheese" model) and totally impenetrable spheres.

I. INTRODUCTION

As is well known, the overall (or effective) transport, mechanical, and electromagnetic properties of a disordered heterogeneous medium, such as a composite, porous material, micellar dispersion and colloidal suspension, depend in a complex fashion upon the morphology¹⁻⁴ of the medium. In particular, it is important to ascertain morphological information regarding the degree of clustering in the heterogeneous material since it can dramatically influence the effective property; the most notable state being when an infinite cluster forms, i.e., at the percolation transition. Some examples of problems in which clustering plays a major role is the conduction of electricity or heat through a composite, chemical reactions among reactive sinks, flow in porous media, breakdown phenomena (e.g., dielectric, mechanical strength), particle aggregation in microemulsions and colloids, and conductor-insulator transition in liquid metals.

Rigorous relations for effective properties¹⁻³ are expressible in terms of various types of correlation functions.⁴ A commonly employed correlation function is the so-called n -point probability function $S_n(\mathbf{r}_1, \dots, \mathbf{r}_n)$, which gives the probability of finding n points at positions $\mathbf{r}_1, \dots, \mathbf{r}_n$ all in one of the phases.⁴ Unfortunately, only the lower-order correlation functions can be determined in practice and these quantities do not contain information about clustering in the random medium. Recently, Torquato *et al.*⁵ introduced a correlation function, referred to as the two-point cluster function $C_2(\mathbf{r}_1, \mathbf{r}_2)$, that reflects information about clustering in general continuum-percolation models. Specifically, for any two-phase random medium, $C_2(\mathbf{r}_1, \mathbf{r}_2)$ gives the probability of finding two points, at positions \mathbf{r}_1 and \mathbf{r}_2 , in the same cluster of one of the phases. Unlike other commonly employed lower-order correlation functions, such as the

two-point probability functions $S_2(\mathbf{r}_1, \mathbf{r}_2)$,⁴ the two-point cluster function becomes long ranged as the percolation threshold is approached from below, thus providing a better signature of the microstructure. Moreover, incorporation of such information in rigorous theories for effective properties of continuum systems, could lead to sharp estimates of the properties even near the percolation point.

Torquato *et al.*⁵ also obtained an integral representation of C_2 for the continuum model of a distribution of inclusions. Using this series representation, they were able to study some general asymptotic properties of C_2 . For example, it is rigorously shown that $C_2(r)$ becomes long ranged for large r . In the case of impenetrable particles which form clusters only as the result of interparticle contacts, it is shown that the second derivative of $C_2(r)$ with respect to r is related to the average coordination number (i.e., average number of particles touching each particle). They then evaluated C_2 for a continuum model of a distribution of "sticky" spheres in the Percus-Yevick approximation.

In this paper, we shall obtain the two-point cluster function from computer simulations for isotropic distributions of D -dimensional spheres in the penetrable concentric-shell (PCS)⁶ model. This is a useful and versatile model for which to study clustering in continuum systems.⁷ In this model, each D -dimensional sphere of diameter σ is composed of an impenetrable core of diameter $\lambda\sigma$, encompassed by a perfectly penetrable shell of thickness $(1 - \lambda)\sigma/2$ (cf. Fig. 1). The extreme limits $\lambda = 0$ and 1 correspond, respectively, to the cases of fully penetrable (i.e., randomly centered) and totally impenetrable spheres. (The instance of fully penetrable spheres is sometimes referred to as the "Swiss-cheese" model.) A pair of particles are said to be "connected" when they overlap.

In Sec. II we shall briefly describe the integral representation of C_2 and analytically evaluate it for $D = 1$ up to two-body graphs. In Sec. III we discuss our simulation procedure. In Sec. IV we present and discuss computer-simulation results for C_2 for $D = 1, 2$, and 3 in the PCS model for various

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$$C_2(r) = \begin{cases} \rho(\sigma - 4) + \rho^2 \left[\sigma r(1 - \lambda) - \frac{\sigma^2}{2}(1 - \lambda)^2 \right], & 0 < r < \sigma, \\ \rho^2 \left[\sigma r(\lambda - 1) + \frac{\sigma^2}{2}(3 - 2\lambda - \lambda^2) \right], & \sigma < r < (1 - \lambda)\sigma, \\ \frac{\rho^2}{2}(r - 2\sigma)^2, & (1 - \lambda)\sigma < r < 2\sigma, \\ 0, & r > 2\sigma. \end{cases} \quad (9)$$

Note that $C_2(r) = 0$ for $r > 2\sigma$ since clusters of size three (trimers) or more are being ignored in the calculation. We shall use result (9) to test our computer simulation results given in Sec. IV.

III. SIMULATION DETAILS

We consider obtaining from computer simulations the two-point cluster function $C_2(r)$ for the model of an isotropic distribution of D -dimensional spheres in the PCS model; each sphere of diameter σ possesses an inner impenetrable core of diameter $\lambda\sigma$, $0 \leq \lambda \leq 1$. This task involves: (1) generating configurations of the random medium, and (2) sampling for C_2 .

The first step of this process for fixed impenetrability parameter λ and reduced number density $\eta (= \rho V_1$, where $V_1 = \sigma$, $\pi\sigma^2/4$, and $\pi\sigma^3/6$ are the volumes of a 1D, 2D, and 3D sphere, respectively) is carried out using a standard Metropolis algorithm.⁹ A total of N particles are initially placed, with no inner hard core overlaps, in a cubical cell of volume L^D on the sites of a regular lattice (square and simple cubic lattice for $D = 2$ and 3, respectively). Each particle is then randomly moved by a small distance to some new position which is accepted or rejected according to whether or not the inner hard cores overlap. This process is repeated until equilibrium is achieved. Each of our simulations consist of 2400 moves, the first 400 of which are discarded before sampling for equilibrium properties. $C_2(r)$ is sampled at intervals of 20 moves per particle.

Sampling for $C_2(r)$ is equivalent to sampling for the two-point probability function $S_2(r)$,⁴ with the important additional feature of having to check whether the two points are connected to each other (i.e., whether they are in the same cluster of one of the phases). Here we shall consider clustering among the penetrable particles. $C_2(r)$ may be found by tossing a large number of line segments of length r at random orientations onto the penetrable images generated for a large number of representative configurations and measuring what fraction of time both ends of the line segments fall in the inclusion phase and are connected to each other. A faster way of obtaining $C_2(r)$ is to employ a "sampling template" technique developed by Smith and Torquato¹⁰ to sample for $S_2(r)$. Each D -dimensional template (for $D \geq 2$) contains 36 points (76 points for 3D) arranged uniformly on a ring (a spherical surface is used in 3D) at a distance r from a central point, with a radial increment of $\Delta r = \sigma/n$ (where $n = 15$ was used both for two and three dimensions). A large number of sampling templates are used to test each configuration.

In order to check whether a point falls in the inclusion phase, one could in principle check whether each D -dimensional sphere in the system is within a distance $\sigma/2$ of the point. This, however, is computationally too time consuming. We instead use the "digitized GRID" method¹¹ employed by us to measure the porosity; this technique was used here to significantly reduce the computing time required to check whether a point lies in the included phase. This method essentially involves subdividing the system into square (cubical) pixels which have sides of length much smaller than a particle diameter. One determines the pixels which lie entirely in the included phase, those which lie entirely outside the included phase, and those which lie in both phases. One then need only check the neighboring pixels about the random point of interest.

Checking connectivity. An important aspect of the simulation procedure is the determination of whether the pair of points in the included phase lie in the same cluster. Before computing $C_2(r)$ one must first identify the clusters in the system. In order to accomplish this we employ a modified Hoshen-Kopelman¹² cluster labeling algorithm. In order to check the connectivity of the pair of points we employ so-called "free boundary" conditions over the central and replicated cells (i.e., periodic images). This algorithm was successfully employed by us elsewhere¹³ to sample for the pair-connectedness function and the results obtained were found to approach infinite-system behavior much more rapidly than algorithms which used "standard" periodic boundary conditions over the central cell, even near the percolation transition. (For further details we refer the reader to Ref. 13.)

The central points of the templates are always randomly chosen to be in the central cell. When the central point falls near the central cell boundaries, some of the points on the rings will lie in the nearest replicated cells. Checking to see whether such points fall within the included phase can be determined from the image points in the central cell, while the connectedness algorithm is applied to the central point of the template and those in the replicated cell (i.e., the original points of the ring) for reasons mentioned above.

IV. RESULTS AND DISCUSSION

A. Simulations of $C_2(r)$ in one dimension

We have carried out Monte Carlo simulations of $C_2(r)$ for the 1D PCS model under very dilute conditions in order to test our algorithm. Specifically, we only considered realizations consisting of clusters of at most size two (i.e.,

dimers). Hence, we attempted to choose η small enough ($\eta = 0.001$) so that no clusters of more than two particles can appear. For $\eta = 0.001$, however, it is still possible to have "unwanted" realizations with small probability. When such clusters appeared, we simply discarded that realization and attempted to generate a new one. Since the probability of having such unwanted clusters is expected to be small at very low densities, we believe that elimination of such realizations does not affect the statistics of $C_2(r)$.

Simulations were carried out for $\lambda = 0$ and $\lambda = 0.5$. For each realization, $C_2(r)$ was calculated for 200 000 templates (each of which contains 2 points for each r) and results were averaged over 3000 realizations. Simulation results for $\lambda = 0$ are compared in Fig. 2 with the exact low-density calculation given in Eq. (9). Monte Carlo data are seen to be in excellent agreement with the theory over the range of r , $0 < r < 2\sigma$. This validates our sampling method for $C_2(r)$. We also performed simulations for $\lambda = 0.5$ and for the same η , and results were found to be in good agreement with the exact relation (9) (not shown).

B. Simulations of $C_2(r)$ in two and three dimensions

Following the procedure described in Sec. III we have carried out simulations of $C_2(r)$ for the PCS model at selected values of the reduced number density η ($= \rho\pi\sigma^2/4$ for $D = 2$ and $\rho\pi\sigma^3/6$ for $D = 3$) and impenetrability index λ . Figure 3 shows the two-point cluster function for fully penetrable disks ($\lambda = 0$) at $\eta = 0.7, 1.0$, and 1.125 . (Note that this system percolates at the critical value of $\eta_c = 1.128$; see Ref. 13 and references therein. Thus, the value $\eta = 1.125$ reported here is very close to η_c .) In order to study how $C_2(r)$ converges to the infinite-system limit as the system size increases, we have selected system sizes, for $\eta = 1.0$ and

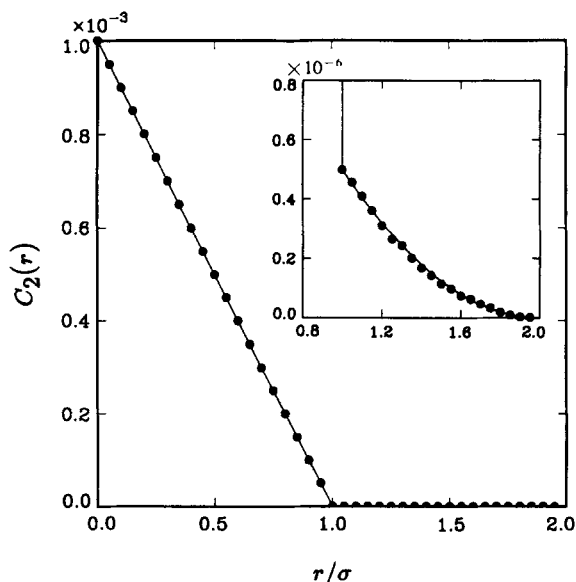


FIG. 2. The two-point cluster function $C_2(r)$ of the 1D PCS model for $\lambda = 0$ (fully penetrable rods) and $\eta = 0.001$. Points are computer-simulation results with the number of particles $N = 100$, and solid line is obtained from the exact low-density relation (9).

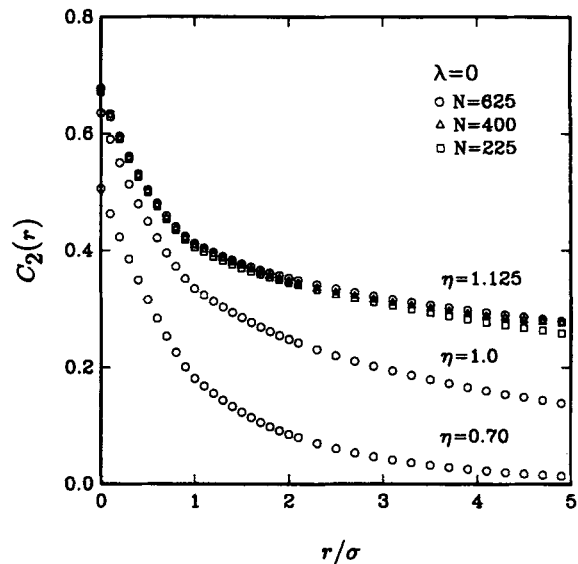


FIG. 3. The two-point cluster function $C_2(r)$ from computer simulations of the 2D PCS model for $\lambda = 0$ (fully penetrable disks) and $\eta = 0.7, 1.0$, and 1.125 for various system sizes. Here the critical reduced density $\eta_c \cong 1.128$.

1.125 , in which the number of particles $N = 225, 400$, and 625 . Simulation results are generally insensitive to the size of the system. Data for $N = 225$ are slightly smaller than those for $N = 400$ and 625 , indicating that finite-size effects result in a slight underestimation of $C_2(r)$, similar to what was found in our study of the pair-connectedness function and mean cluster size.¹³ Results for $N = 400$ are not appreciably different from those of the 625 particle system. For $\eta = 1.0$, the differences essentially disappear (not shown), indicating that finite-size effects are negligible for η below η_c .

$C_2(r)$ at $r = 0$ is generally the inclusion volume fraction, ϕ_2 , which in the case $\lambda = 0$ is equal to $1 - \exp(-\eta)$. (For $0 < \lambda < 1$, the relationship between ϕ_2 and η is nontrivial.^{11,14}) As r increases, $C_2(r)$ generally monotonically decreases for all η and goes to zero for large r (even at $\eta = \eta_c$). As η increases and approaches η_c , $C_2(r)$ becomes progressively longer ranged, as expected. For $\eta = 1.125$, $C_2(r)$ at $r = 5\sigma$ is about 41% of ϕ_2 [i.e., $C_2(r)$ at $r = 0$], indicating the presence of clusters which are substantially larger than for the case of $\eta = 0.7$.

Simulation data for $\lambda = 0.7$ and 0.9 are shown in Figs. 4 and 5, respectively. Although in these instances $C_2(r)$ decays to zero as r increases (as for the case $\lambda = 0$), the two-point cluster function exhibits damped-oscillatory behavior [as does $S_2(r)$, the two-point probability function studied by Torquato and Stell and by Torquato and Lado⁴] due to exclusion-volume effects associated with the nonzero hard core radii ($\lambda > 0$). This behavior is apparent already for $\lambda = 0.7$ and $\eta = 0.65$ and becomes more pronounced for higher η and λ , as it does in the case of $S_2(r)$.¹⁰ This is expected since for higher densities, more particles are connected to one another than at lower densities and thus $C_2(r)$ becomes closer to $S_2(r)$.

Simulation results for the 3D case are plotted in Figs. 6–8. Figure 6 shows $C_2(r)$ for fully penetrable spheres. For $\eta = 0.34$, a value near the percolation-threshold value

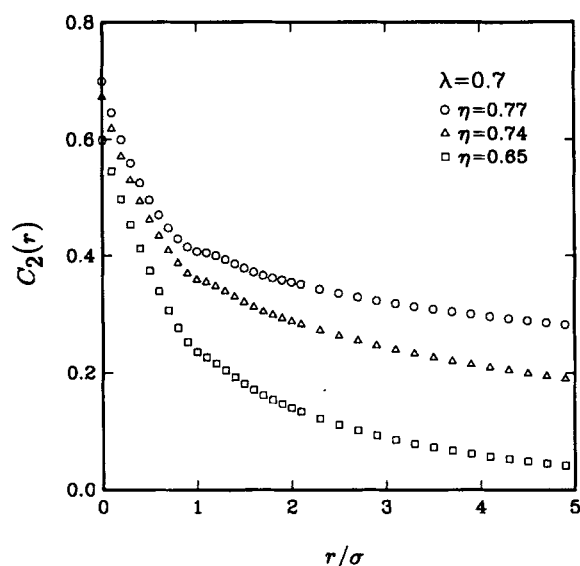


FIG. 4. The two-point cluster function $C_2(r)$ from computer simulations of the 2D PCS model for $\lambda = 0.7$ and $\eta = 0.65, 0.74, 0.77$. Here $N = 625$.

$\eta_c \cong 0.35$ (see Refs. 7 and references therein), simulations were performed for systems in which $N = 125, 216$, and 512). As for fully penetrable disks, data are again relatively insensitive to the system size. As in the 2D case, $C_2(r)$ for fully penetrable spheres monotonically decreases with increasing r . However, for large r there is an important distinction between the 2D and 3D instances. This point shall be touched upon shortly.

For $\lambda = 0.8$ (cf. Fig. 7), results for $C_2(r)$ are not different from $\lambda = 0$, except for small oscillations. The two-point cluster function at fixed η decreases more rapidly for $\lambda = 0.9$ (cf. Fig. 8) than for $\lambda = 0.8$, except near the percolation point ($\eta_c = 0.41$, see Sevick *et al.*⁷). For example, for $\eta = 0.3$, $C_2(r)$ for $\lambda = 0.9$ is negligibly small at $r = 2.5\sigma$,

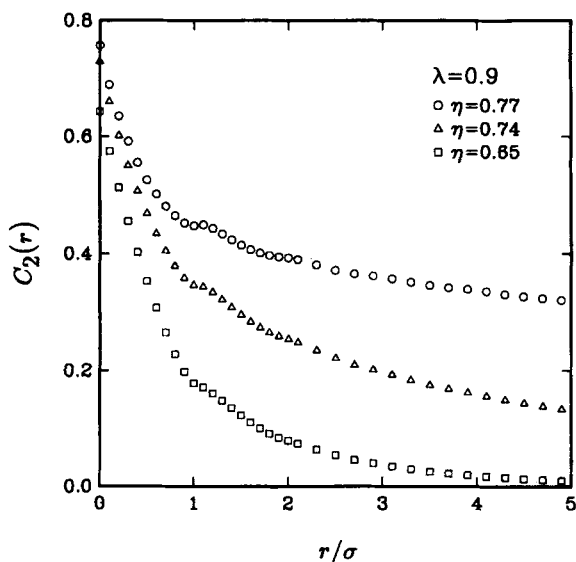


FIG. 5. As in Fig. 4 for $\lambda = 0.9$ and $\eta = 0.65, 0.74, 0.77$.

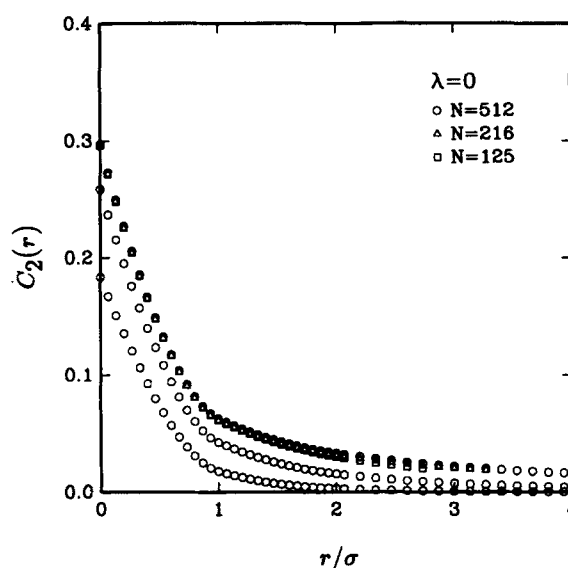


FIG. 6. The two-point cluster function $C_2(r)$ from computer simulations of the 3D PCS model for $\lambda = 0$ (fully penetrable spheres). Data are from bottom to top for $\eta = 0.20, 0.30$, and 0.34 , respectively. Here the critical reduced density $\eta_c \cong 0.35$.

whereas for $\lambda = 0$ and $\lambda = 0.8$, $C_2(r)$ is *not* negligibly small. This can be understood by examining the extreme case of totally impenetrable spheres ($\lambda = 1$): a system for which $C_2(r) = 0$ for all $r \geq \sigma$, for any $\eta < \eta_c$. As λ approaches unity, clustering becomes increasingly inhibited, thus explaining the observation noted immediately above. Of course, at the percolation point, $C_2(r)$ will be long ranged, even when $\lambda = 1$.

We now return to the consideration of the large r behavior of $C_2(r)$ for the 2D and 3D cases when η is near η_c . Under such conditions, $C_2(r)$ for 3D systems decreases more rapidly with increasing r than does $C_2(r)$ for 2D systems. (This is most easily seen by appealing to Figs. 3 and 6

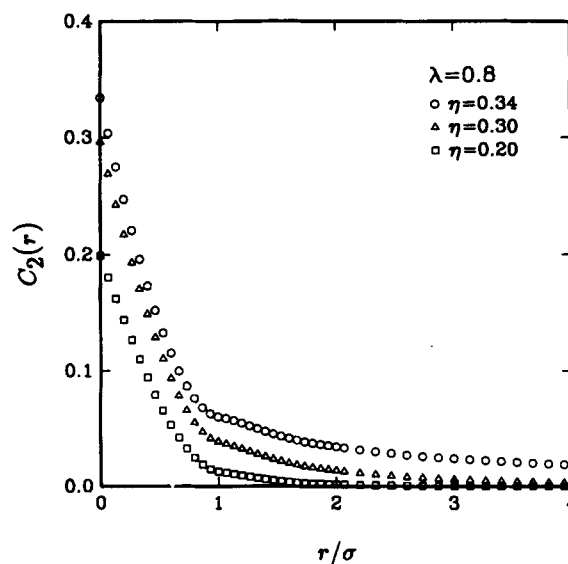


FIG. 7. The two-point cluster function $C_2(r)$ from computer simulations of the 3D PCS model for $\lambda = 0.8$ and $\eta = 0.20, 0.30$, and 0.34 . Here $N = 512$.

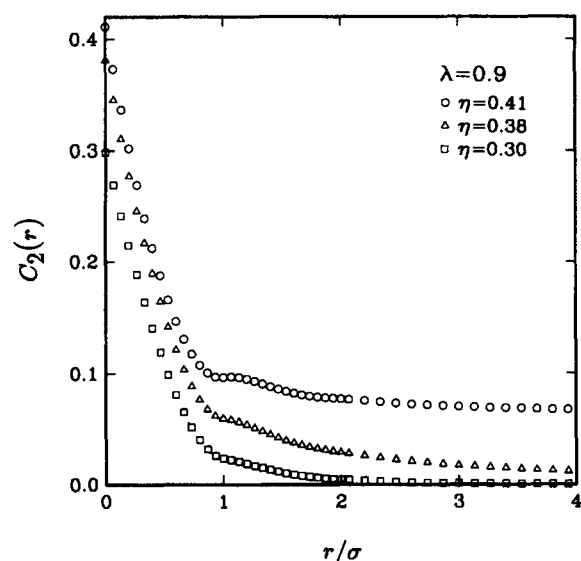


FIG. 8. As in Fig. 7 for $\lambda = 0.9$ and $\eta = 0.30, 0.38,$ and 0.41 .

which describe fully penetrable particle systems.) The reason for this involves the critical behavior of percolation clusters. As $\eta \rightarrow \eta_c$, the major contribution to the long-range behavior of $C_2(r)$ is from the infinite cluster (or the largest cluster). Now if $r \gg \sigma$, $C_2(r)$ will be proportional to the volume fraction of inclusions (which is part of the infinite cluster) in the concentric D -dimensional spherical shell of radius r and thickness Δr which is centered on the infinite cluster. We denote this D -dimensional volume fraction, in the limit $\Delta r \rightarrow 0$, by $\phi_2^{\text{inf}}(r)$. The infinite cluster is a fractal object and possesses a volume in the D -dimensional sphere which obeys the equation

$$V(r) \sim r^{D_f}, \quad (10)$$

where D_f is the fractal dimension. Hence, the D -dimensional volume fraction ϕ_2^{inf} decreases as r increases in the following manner:

$$\phi_2^{\text{inf}}(r) \sim \frac{\Delta V(r)}{r^{D-1} \Delta r} = r^{D_f - D}, \quad (11)$$

where $\Delta V(r)$ is the volume of the inclusions in the shell of radius r and thickness Δr . Thus, with D_f known for lattice percolation,¹⁵ we find

$$C_2(r) \sim r^{-0.5}, \quad (12)$$

in 3D, and

$$C_2(r) \sim r^{-0.1}, \quad (13)$$

in 2D. Hence, this shows that $C_2(r)$ for the 3D case decays more rapidly than the corresponding 2D counterpart.

V. CONCLUSIONS

We have derived an efficient algorithm to obtain, for the first time, the two-point cluster function $C_2(r)$ of continuum models of random media from computer simulations. In particular, we consider the D -dimensional PCS model for various values of the impenetrability index λ . It is shown that $C_2(r)$ becomes long ranged at the percolation transition, thus confirming the theoretical results of Torquato *et al.*⁵ As $\eta \rightarrow \eta_c$, it is demonstrated that $C_2(r)$, for large r , decays more rapidly in three than in two dimensions.

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