Clustering properties of d-dimensional overlapping spheres

J. Quintanilla* and S. Torquato†
Princeton Materials Institute and Department of Civil Engineering and Operations Research, Princeton University, Princeton, New Jersey 08544
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Various clustering properties of d-dimensional overlapping (i.e., Poisson distributed) spheres are investigated. We evaluate n_k, the average number of connected clusters of k particles (called k-mers) per unit particle, for $k=2,3,4$ and v_k, the expected volume of a k-mer, for $k=2,3,4$ by using our general expressions for these quantities for $d=1$, 2, or 3. We use these calculations to obtain low-density expansions of various averaged cluster numbers and volumes, which can be obtained from the n_k and v_k. We study the behavior of these cluster statistics as the percolation threshold is approached from below, and we rigorously show that two of these averaged quantities do not diverge for $d \geqslant 2$. [S1063-651X(96)02411-7]

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I. INTRODUCTION

A prototypical model of continuum percolation is a system of spatially uncorrelated, equal-sized spheres in one, two, and three dimensions [1–14]. In this model, spheres of equal size are centered on the points of a stationary Poisson process. Since the spheres are allowed to overlap, clusters of various sizes and volumes are formed, as depicted in Fig. 1. This model has been given a variety of names, including ''fully penetrable spheres,'' ''randomly overlapping spheres,'' the ''Swiss-cheese model,'' and the ''Poisson blob model.'' We shall henceforth refer to this model as *overlapping spheres*. Certain types of ''connectedness'' functions and related quantities have been analytically and numerically determined for this model [3–12,15,16].

In this paper we present integral representations of the average number density n_k of a k-mer (a cluster comprised of k spheres) and the average volume v_k of a k-mer for overlapping spheres in d dimensions. The n_k have been used to estimate the percolation threshold and critical exponent of various overlapping particle systems [1], rigorously bound the mean cluster density [11], and study surface tension in percolation models [17]. We use a constructive paradigm to efficiently evaluate these integral expressions for n_k and v_k. To illustrate this paradigm, we derive exact analytical results for the quantities p_k and v_k in one dimension. In higher dimensions, however, these quantities are integrals that cannot be evaluated analytically and we have to settle for numerical evaluation. We find that the constructive paradigm yields integrals free of the redundancies inherent in previous work [16] and so these integrals can be numerically evaluated more efficiently. The effort to perform these numerical integrations increases as k and the number of dimensions increase, and therefore efficient computation of these integrals becomes imperative. With this approach, we are able to compute n_4 and correctly evaluate v_2, v_3, and v_4 for any sphere number density ρ. Our evaluations of these quantities are in excellent agreement with Monte Carlo simulations that we also perform.

We also will study various cluster statistics related to the average number of particles and average volume of the clusters within the system. We will consider Q, the average number of particles contained in a cluster chosen at random, S, the average number of particles in the cluster of a particle chosen at random, V_Q, the average volume of a randomly chosen cluster, and V_S, the average volume of the cluster containing a randomly chosen particle. The ''particle-averaged cluster number'' S and the ''particle-averaged cluster volume'' V_S both diverge at the percolation threshold (the minimum density at which a cluster of infinite size and volume exists [15,16]). However, the ''average cluster number'' Q and ''average cluster volume'' V_Q remain finite at the percolation threshold for spatial dimension $d \geqslant 2$. The cluster statistic S, sometimes called the mean cluster size, is a well-known quantity in percolation theory and has been studied

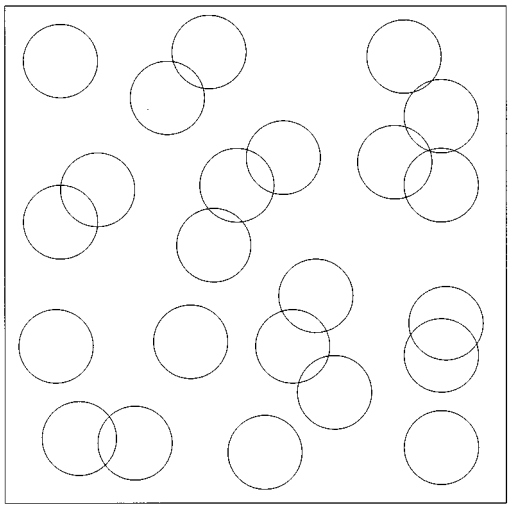

FIG. 1. Schematic of fully penetrable disks. There are five monomers, four dimers, two trimers, and a 4-mer.

*Present address: Department of Mathematics, University of North Texas, Denton, TX 76203.
Electronic address: johnq@cardinal.math.unt.edu
†Corresponding author.
Electronic address: torquato@matter.princeton,edu

extensively for overlapping spheres in two and three dimensions [1–6]. Also, V_S has been approximated by Fanti, Glandt, and Chiew [8] for overlapping spheres in three dimensions. To our knowledge, the average cluster number Q and the average volume volume V_Q have heretofore not been evaluated. Using our exact low-density expansions of n_k and v_k, we compute low-density expansions of Q, V_Q, and V_S for any dimension d.

It is believed that S and V_S obey a power law near the percolation threshold. Under this assumption, the low-density expansion of S has been used to estimate the percolation threshold and critical exponent [1]. Based on our study of Padé approximants of these cluster statistics, we suggest that a similar analysis may also be applicable to V_S.

In Sec. II we define the quantities that will be used throughout this report. In Sec. III we discuss the asymptotic behavior and certain inequalities involving the cluster statistics Q, S, V_Q, and V_S. In Sec. IV we consider the calculations of the expected number of k-mers in the system; we obtain exact analytical results in one dimension and integral expressions in higher dimensions that require numerical evaluation for arbitrary density ρ. In Sec. V we calculate the expected volume of a k-mer for any dimension d. Finally, in Sec. VI we discuss how cluster statistics derived from the n_k and v_k may be used to estimate the percolation threshold and critical exponents for overlapping disks ($d=2$) and spheres ($d=3$).

II. DEFINITION OF CLUSTERING QUANTITIES

We now define the quantities that will be investigated in this article. Our model is a system of overlapping equal-sized spheres, i.e., spheres whose centers are determined by a Poisson process with given rate ρ. The common diameter of the spheres will be denoted by σ. The reduced density is defined in terms of the sphere number density ρ by

$$\eta=\rho V_1, \tag{1}$$

where

$$V_1=\frac{\pi^{d/2}}{\Gamma(1+d/2)}\left(\frac{\sigma}{2}\right)^d \tag{2}$$

is the volume of a sphere of diameter σ in d dimensions. Finally, the volume fraction of the void phase and particle (sphere) phases are respectively given by

$$\phi_1=e^{-\eta}, \quad \phi_2=1-\phi_1. \tag{3}$$

We now define the statistics describing clusters, which will be evaluated in this article. A cluster is defined to be a complete set of particles which are connected, that is, for any two particles in the set, a path can be drawn between their centers that lies entirely within the particles, and no such path can be drawn between any particle center in the set and any particle center outside the set. The probability that a given particle is part of a k-mer (a cluster containing k particles) is denoted by p_k, so that

$$\sum_{k=1}^{\infty} p_k=1. \tag{4}$$

The probability that a given particle is the leftmost [18] particle of a k-mer is denoted by n_k. We can also interpret n_k to be the average number of leftmost spheres of k-mers per unit number of particles or, equivalently, the average number of k-mers per unit number of particles. The two quantities p_k and n_k are related by

$$p_k=kn_k. \tag{5}$$

In this paper, we consider these quantities to be *ensemble averages*, that is, they are averaged over all realizations of the ensemble.

The average number of k-mers per unit volume is given by

$$\rho_k=\rho n_k \tag{6}$$

and the average number of clusters per unit volume is therefore

$$\rho_c=\sum_{k=1}^{\infty} \rho_k. \tag{7}$$

Also, it is clear that

$$\rho=\sum_{k=1}^{\infty} k\rho_k. \tag{8}$$

The probability that a randomly chosen *cluster* is a k-mer is denoted by q_k, which is given by

$$q_k=\frac{n_k}{\sum_{i=1}^{\infty} n_i}. \tag{9}$$

The average cluster number Q is the average number of particles in a randomly chosen cluster. Using the above definitions, it is given by

$$Q=\sum_{k=1}^{\infty} kq_k=\frac{\sum_{k=1}^{\infty} kn_k}{\sum_{k=1}^{\infty} n_k}=\left(\sum_{k=1}^{\infty} n_k\right)^{-1}. \tag{10}$$

This quantity also can be related to the number of particles N and the number of clusters M for a given realization under the thermodynamic limit:

$$Q=\lim_{M,N\to\infty} N/M. \tag{11}$$

We also consider the particle-averaged cluster number S (also referred to as the mean cluster size), which is the average number of particles in the cluster containing a randomly chosen *particle*. This cluster property is given by

$$S=\sum_{k=1}^{\infty} kp_k=\frac{\sum_{k=1}^{\infty} k^2n_k}{\sum_{k=1}^{\infty} kn_k}=\sum_{k=1}^{\infty} k^2n_k \tag{12}$$

for densities below the percolation threshold.

The expected volume of a k-mer is denoted by v_k and so the fraction of space occupied by the particles is given by

$$\phi_2=\sum_{k=1}^{\infty}\rho_k v_k \tag{13}$$

below the percolation threshold. We also define the analogs of Q and S for the cluster volume

$$V_Q=\frac{\sum_{k=1}^{\infty}n_k v_k}{\sum_{k=1}^{\infty}n_k} \tag{14}$$

and

$$V_S=\frac{\sum_{k=1}^{\infty}kn_k v_k}{\sum_{k=1}^{\infty}kn_k}=\sum_{k=1}^{\infty}kn_k v_k. \tag{15}$$

The first cluster statistic V_Q is the average cluster volume or the average volume of a randomly chosen cluster. On the other hand, V_S is the particle-averaged cluster volume, defined to be the average volume of the cluster containing a randomly chosen particle.

III. CRITICAL BEHAVIOR AND INEQUALITIES

It is well known that the particle-averaged cluster number is given in terms of the pair-connectedness function $P_2(\mathbf{r})$ for any statistically homogeneous system via the relation [19]

$$S=1+\rho\int P_2(\mathbf{r})d\mathbf{r}. \tag{16}$$

The quantity $\rho^2P_2(\mathbf{r})d\mathbf{r}_1d\mathbf{r}_2$ is the probability of finding any pair of particles of the same cluster in the volume elements $d\mathbf{r}_1$ and $d\mathbf{r}_2$ centered on $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively, where $\mathbf{r}=\mathbf{r}_2-\mathbf{r}_1$. Relation (16) is the connectedness analog of the compressibility equation of equilibrium statistical mechanics. We will directly verify (16) for fully penetrable rods in the Appendix.

Since $P_2(\mathbf{r})$ becomes long ranged at the percolation threshold ϕ_2^c, it follows that S diverges to infinity as $\phi_2\to\phi_2^c$. Indeed, it is believed that S obeys the power law

$$S\propto(\phi_2^c-\phi_2)^{-\gamma},\quad \phi_2\to\phi_2^c \tag{17}$$

in the immediate vicinity of the percolation threshold. In this expression, γ is a universal exponent for both lattice and continuum percolation dependent on the spatial dimension d. For example, $\gamma=43/18$ for $d=2$ and $\gamma=1.8$ for $d=3$; see Refs. [1,2,20] and references therein.

The definition (10) of the average cluster number Q weighs clusters of large size less heavily than the definition (12) and so

$$Q<S=1+\rho\int P_2(\mathbf{r})d\mathbf{r}. \tag{18}$$

This relation implies that Q cannot grow as rapidly as S at the percolation threshold. In fact, we can show that Q does not diverge at the percolation threshold for d-dimensional overlapping spheres when $d\geq 2$. This is proved simply by observing that

$$\sum_{k=1}^{\infty}n_k>n_1=\phi_1^{2^d}>0 \tag{19}$$

for any $\phi_2<1$, where we have used (29). Therefore, in view of (10), Q does not diverge at the percolation threshold unless it is equal to unity, which is true only when $d=1$. Therefore, since $\phi_2^c<1$ for $d\geq 2$, Q cannot diverge as ϕ_2 approaches ϕ_2^c. Physically, this means that at any density, including above the percolation threshold, the number of clusters M is proportional to the number of particles N in the thermodynamic limit for $d\geq 2$, given in (11).

The particle-averaged cluster volume V_S also becomes infinite as the percolation threshold is approached from below, and we assume that it has the asymptotic form

$$V_S\propto(\phi_2^c-\phi_2)^{-\omega},\quad \phi_2\to\phi_2^c. \tag{20}$$

Assuming the validity of power laws (17) and (20), we can relate the critical exponents γ and ω to one another, as we now describe. By comparing (12) with (15), we observe that $V_S\leq SV_1$ since $v_k\leq kV_1$. Therefore, if the critical exponents exist, we conclude that

$$\omega\leq\gamma. \tag{21}$$

We also notice the inequality

$$V_Q<V_S, \tag{22}$$

which is similar to (18) for the cluster numbers. Finally, since $V_Q\leq QV_1$, V_Q remains finite as percolation threshold is approached from below for $d\geq 2$. This also has a physical interpretation similar to the above argument that was applied to Q.

In order to study the behavior of Q, S, V_Q, and V_S, we will obtain low-density expansions of these cluster statistics. To do this, we discuss in Secs. IV and V how the individual n_k and v_k can be evaluated.

IV. PROBABILITY OF FINDING A k-MER n_k

In this section we calculate the probability n_k related to finding a k-mer in the system. This probability can be computed rather handily in one dimension. We also write a formal integral expression for calculating this probability in two or more dimensions; however, these integrals cannot be calculated analytically and hence require numerical evaluation. This expression is somewhat simplified by a constructive paradigm, viewing the model as an arrival process. These simplifications allow us to numerically evaluate the probabilities more efficiently.

A. Exact results in one dimension

Consider a system of overlapping rods with density ρ such that each rod has length σ. We will often refer to a given rod by the position of its center or midpoint. Then the probability that a given particle is the leftmost particle in a k-mer is given by

$$n_k = \phi_1^2(1-\phi_1)^{k-1}. \tag{23}$$

To prove this, suppose the center of a given particle is located at r_1. Then this particle is the leftmost particle of a k-mer exactly when the region $[r_1-\sigma, r_1)$ is empty of centers, the next center after r_1, denoted by r_2, occurs somewhere in $(r_1, r_1+\sigma]$, the next center after r_2, denoted by r_3, occurs somewhere in $(r_2, r_2+\sigma]$, ... , the next center after r_{k-1}, denoted by r_k, occurs somewhere in $(r_{k-1}, r_{k-1}+\sigma]$, and, finally, the region $(r_k, r_k+\sigma]$ is empty of centers. These events are independent since the positions of the centers are generated by a Poisson process. Since this process has density ρ, we conclude that

$$\begin{aligned} n_k &= e^{-2\rho\sigma}\int_{r_1}^{r_1+\sigma} dr_2 \rho e^{-\rho(r_2-r_1)} \int_{r_2}^{r_2+\sigma} dr_3 \\ &\quad \times \rho e^{-\rho(r_3-r_2)} \cdots \int_{r_{k-1}}^{r_{k-1}+\sigma} dr_k \rho e^{-\rho(r_k-r_{k-1})} \\ &= e^{-2\rho\sigma}\int_{r_1}^{r_1+\sigma} dr_2 \int_{r_2}^{r_2+\sigma} dr_3 \cdots \int_{r_{k-1}}^{r_{k-1}+\sigma} dr_k \\ &\quad \times \rho^{k-1} e^{-\rho(r_k-r_1)} = \phi_1^2(1-\phi_1)^{k-1} \end{aligned} \tag{24}$$

by induction.

Using Eqs. (5), (6), (9), (10), and (12), we obtain the following cluster statistics for overlapping rods on the line:

$$p_k = k\phi_1^2(1-\phi_1)^{k-1}, \tag{25}$$

$$\rho_k = \rho\phi_1^2(1-\phi_1)^{k-1}, \tag{26}$$

$$q_k = \phi_1(1-\phi_1)^{k-1}, \tag{27}$$

$$Q = S = 1/\phi_1. \tag{28}$$

Comparing Eq. (28) with (17), we see that $\phi_2^c = \gamma = 1$. We also see that Q diverges at the percolation threshold; this is consistent with (10) since $n_k = 0$ at $\phi_1 = 0$. We can use (28) to directly verify the equality of (16) for fully penetrable rods; this is shown in the Appendix.

Formulas (25)–(28) are in agreement with the results of Roach [21], who obtained p_k by considering a sequence of Bernoulli trials. Such an argument, however, cannot be rigorously applied to the formation of k-mers in higher dimensions, which we now consider.

B. Extension to higher dimensions

We have illustrated the constructive paradigm by calculating n_k for overlapping rods. We now extend this paradigm to calculate n_k in higher dimensions. The expressions we obtain cannot be evaluated analytically, so we will use numerical means to evaluate them.

In d dimensions, a given sphere is a monomer exactly when the sphere of *radius* σ centered at the given sphere contains no other sphere centers, so

$$p_1 = n_1 = \exp[-2^d\rho V_1] = \phi_1^{2^d}. \tag{29}$$

For $k \geq 2$, Given *et al.* [11] claimed and Penrose [16] later rigorously proved, in any dimension, that

$$\begin{aligned} p_k &= \frac{\rho^{k-1}}{(k-1)!}\int d\mathbf{r}_{12}\int d\mathbf{r}_{13}\cdots\int d\mathbf{r}_{1k} \\ &\quad \times \exp[-\rho V_k(\mathbf{r}^k;\sigma)] I(\mathbf{r}^k;\sigma/2), \end{aligned} \tag{30}$$

where $V_k(\mathbf{r}^k;\sigma)$ is the union volume of k spheres with radius σ centered at $\mathbf{r}^k = \mathbf{r}_1\cdots\mathbf{r}_k$ and $I(\mathbf{r}^k;\sigma/2)$ is the indicator function for k spheres with centers at $\mathbf{r}_k$ and radius $\sigma/2$ forming a single cluster. (Given *et al.* suppressed all prefactors and the indicator function in their expression.)

The previous integral evaluation (24) is equivalent to Penrose's expression in one dimension; this can be shown by ordering the arrivals of the rod centers. In other words, by considering the centers of the rods as an arrival process, we were able to evaluate this integral expression and hence determine p_k analytically. We now use this arrival method to calculate p_k in higher dimensions, which again will yield an expression equivalent to Penrose's, but this expression will be more efficient for numerical integration. We find that

$$p_k = \sum_{1=k_0<\cdots<k_i=k} p_k(k_0,\ldots,k_i), \tag{31}$$

where

$$\begin{aligned} p_k(k_0,\ldots,k_i) &= c(k_0,\ldots,k_i)\int_{B_1^{k_1-k_0}} d\mathbf{r}_{12}\cdots d\mathbf{r}_{1k_1}\int_{C(k_0,k_1)^{k_2-k_1}} d\mathbf{r}_{1(k_1+1)}\cdots d\mathbf{r}_{1k_2}\cdots\int_{C(k_{i-2},k_{i-1})^{k_i-k_{i-1}}} d\mathbf{r}_{1(k_{i-1}+1)}\cdots d\mathbf{r}_{1k} \\ &\quad \times \exp[-\rho V_k(\mathbf{r}^k;\sigma)] \end{aligned} \tag{32}$$

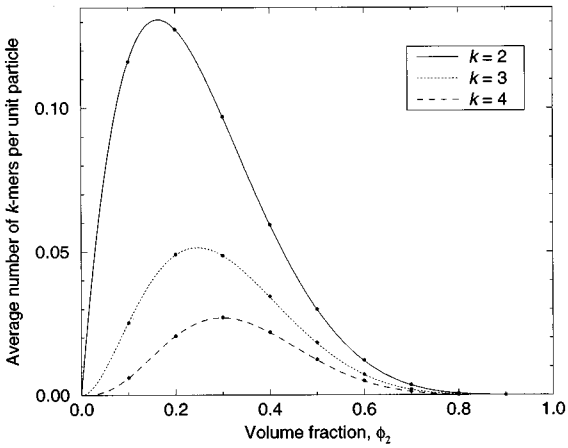

FIG. 2. Average number of k-mers per unit particle (i.e., n_k) in two dimensions. The solid dots are simulation data.

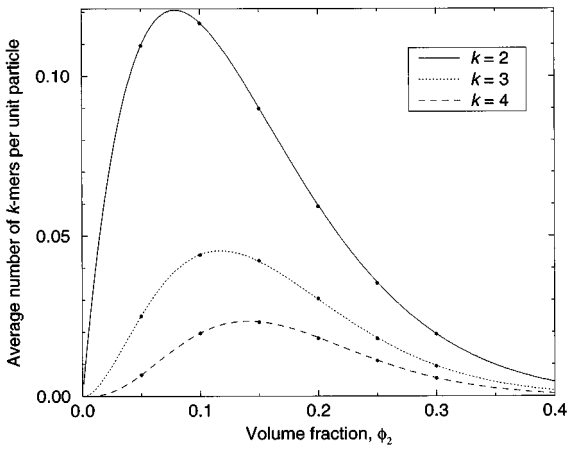

FIG. 3. Average number of k-mers per unit particle (i.e., n_k) in three dimensions. The solid dots are simulation data.

and

$$c(k_0,\ldots,k_i)=\frac{\rho^{k-1}}{(k_1-k_0)!\cdots(k_i-k_{i-1})!}. \tag{33}$$

In this expression $k_0=1$, $k_i=k$,

$$B_i=B_\sigma(\mathbf{r}_i), \tag{34}$$

the sphere with radius σ centered at $\mathbf{r}_i$, and

$$C(k,l)=(B_{k+1}\cup\cdots\cup B_l)\backslash(B_1\cup\cdots\cup B_k). \tag{35}$$

We present the proof of (31) elsewhere [22], but we will illustrate the proof by considering p_3. There are two ways that a cluster containing a particle centered at $\mathbf{r}_1$ could exist. The two centers $\mathbf{r}_2$ and $\mathbf{r}_3$ could both lie in B_1, or only one center $\mathbf{r}_2$ in B_1 and one more center in $B_2\backslash B_1$. To ensure that the cluster has only three particles, the region $V_3(\mathbf{r}^3;\sigma)$ must be otherwise empty for both cases. We conclude that

$$p_3=\frac{\rho^2}{2!}\int_{B_1}d\mathbf{r}_{12}\int_{B_1}d\mathbf{r}_{13}\exp[-\rho V_3(\mathbf{r}^3;\sigma)] + \rho^2\int_{B_1}d\mathbf{r}_{12}\int_{B_2\backslash B_1}d\mathbf{r}_{13}\exp[-\rho V_3(\mathbf{r}^3;\sigma)]. \tag{36}$$

Similarly, we find that p_4 is given by

$$\begin{aligned}p_4=&\frac{\rho^3}{3!}\int_{B_1}d\mathbf{r}_{12}\int_{B_1}d\mathbf{r}_{13}\int_{B_1}d\mathbf{r}_{14}\exp[-\rho V_4(\mathbf{r}^4;\sigma)]\\&+\frac{\rho^3}{2!}\int_{B_1}d\mathbf{r}_{12}\int_{B_1}d\mathbf{r}_{13}\int_{(B_2\cup B_3)\backslash B_1}d\mathbf{r}_{14}\exp[-\rho V_4(\mathbf{r}^4;\sigma)]\\&+\frac{\rho^3}{2!}\int_{B_1}d\mathbf{r}_{12}\int_{B_2\backslash B_1}d\mathbf{r}_{13}\int_{B_2\backslash B_1}d\mathbf{r}_{14}\exp[-\rho V_4(\mathbf{r}^4;\sigma)]\\&+\rho^3\int_{B_1}d\mathbf{r}_{12}\int_{B_2\backslash B_1}d\mathbf{r}_{13}\int_{B_3\backslash(B_1\cup B_2)}d\mathbf{r}_{14}\\&\times\exp[-\rho V_4(\mathbf{r}^4;\sigma)].\end{aligned} \tag{37}$$

With sufficient patience one can obtain similar expressions in terms of these subintegrals for the higher p_k. The inherent difficulty with this procedure is parametrizing the domains of integration. Once this is accomplished, however, this expression eliminates all redundancies and hence lends itself to more efficient numerical integration.

1. Two-dimensional results

The integrals determining n_k require knowledge of $V_k(\mathbf{r}^k;\sigma)$, the union area of k circles of equal radius. To calculate V_k, it is sufficient to obtain expressions for the *intersection* of j circles for $j\leqslant k$. Kratky [23] showed that the area of intersection of four or more circles can be reduced to a linear combination of the areas of intersection of two and three circles. Using this result, we can evaluate the integrands of the above integrals exactly and then use numerical integration to finally obtain the n_k.

Figure 2 shows theoretical predictions of n_2, n_3, and n_4 and direct Monte Carlo simulation of these quantities. As we see, simulation and theory are in excellent agreement.

Using heuristic reasoning, Roach suggested that n_k can be approximated by

$$n_k\approx\frac{p_1(1-p_1)^{k-1}}{k}, \tag{38}$$

where p_1 is given in (29). This formula indeed provides a good approximation to n_2, n_3, and n_4 for small to medium values of ϕ_2, but does not estimate n_k well for large ϕ_2.

2. Three-dimensional results

Kratky [24] also stated that the intersection volumes of five or more spheres of equal radius can be expressed as a linear combination of intersection volumes of two, three, and four spheres. The volume of the intersection of three spheres [25–28] and four spheres [29] are known analytically. Using these results, we can again evaluate the integrands of the above integrals analytically and then numerically obtain the n_k. A graph comparing the theoretical predictions of n_2, n_3, and n_4 in three dimensions to computer simulations is shown in Fig. 3.

Roach's heuristic argument can also be applied to this three-dimensional model and so (38) can be used as an approximation of n_k. This turns out to be an excellent approximation of n_2, n_3, and n_4 for $\phi_2 < 0.05$; however, its accuracy diminishes as ϕ_2 increases above this value.

V. AVERAGE VOLUME OF A k-MER v_k

We now consider the average volume of a given k-mer. In any dimension, the expected union volume of a k-mer can be expressed in terms of a conditional expectation on the positions of its k constituent spheres. After giving the general expression for any dimension, we directly calculate the average volume of a k-mer v_k in one dimension. We then numerically evaluate the lower v_k in two and three dimensions.

The average volume of a k-mer is the conditional expectation of the volume of k spheres, given that the k spheres indeed form a cluster. From (30), given that k particles form a k-mer, the conditional probability density function of the locations of the k particles is given by

$$f(\mathbf{r}_{12},\ldots,\mathbf{r}_{1k}) = \frac{\frac{\rho^{k-1}}{(k-1)!}\exp[-\rho V_k(\mathbf{r}^k;\sigma)]I(\mathbf{r}^k;\sigma/2)}{\frac{\rho^{k-1}}{(k-1)!}\int d\mathbf{x}_{12}\int d\mathbf{x}_{13}\cdots\int d\mathbf{x}_{1k}\exp[-\rho V_k(\mathbf{x}^k;\sigma)]I(\mathbf{x}^k;\sigma/2)}. \tag{39}$$

Since

$$v_k = \int d\mathbf{r}_{12}\cdots\int d\mathbf{r}_{1k} V_k(\mathbf{r}^k;\sigma/2) f(\mathbf{r}_{12},\ldots,\mathbf{r}_{1k}), \tag{40}$$

from the definition of conditional expectation, we conclude that

$$v_k = \frac{\int d\mathbf{r}_{12}\cdots\int d\mathbf{r}_{1k} V_k(\mathbf{r}^k;\sigma/2)\exp[-\rho V_k(\mathbf{r}^k;\sigma)]I(\mathbf{r}^k;\sigma/2)}{\int d\mathbf{r}_{12}\cdots\int d\mathbf{r}_{1k}\exp[-\rho V_k(\mathbf{r}^k;\sigma)]I(\mathbf{r}^k;\sigma/2)}. \tag{41}$$

This is somewhat different from the expression described by Given *et al.* [11], which suppresses the indicator functions and ignores the conditional expectation and hence the denominator.

We now directly calculate v_k in one dimension by using the arrival process paradigm described in Sec. IV. We find that

$$v_k = \frac{\int_{r_1}^{r_1+\sigma} dr_2 \int_{r_2}^{r_2+\sigma} dr_3 \cdots \int_{r_{k-1}}^{r_{k-1}+\sigma} dr_k (\sigma + r_k - r_1) e^{-\rho(2\sigma + r_k - r_1)}}{\int_{r_1}^{r_1+\sigma} dr_2 \int_{r_2}^{r_2+\sigma} dr_3 \cdots \int_{r_{k-1}}^{r_{k-1}+\sigma} dr_k e^{-\rho(2\sigma + r_k - r_1)}} = \sigma\left(\frac{k\phi_1 - 1}{\phi_1 - 1} + \frac{k-1}{\eta}\right). \tag{42}$$

As expected, this expression is consistent with the known cumulative distribution function of the length of a k-mer in systems of overlapping rods [21].

As the density ρ tends to zero, the expected length of a one-dimensional k-mer tends to $\sigma(k+1)/2$. This may be surprising at first glance; after all, at very low densities, k-mers will not exist for $k \geqslant 2$. However, we are not now calculating the probability that k-mers exist; instead, *we are calculating the expectation of the volume of a k-mer given that the k-mer exists*.

In higher dimensions, we again must settle for numerical evaluation of the v_k. To do so, we use the same decomposition scheme underlying (31) of Sec. IV to break both the numerator and denominator of (41) into subcases. These subexpressions are then integrated numerically to obtain the v_k.

In Figs. 4 and 5, we plot the lower v_k in two and three dimensions, respectively. As we see, the v_k decrease to V_1 as the inclusion (cluster) volume fraction ϕ_2 increases to 1. This is not surprising: as the volume fraction of the spheres increases, we would expect the separation distances of a k-mer to decrease.

From the graphs of the v_k for $k \leqslant 4$ and computer simulations for larger k, a decent empirical approximation for v_k at small volume fractions appears to be

$$v_k(0) \approx \frac{1 + k(2^d - 1)}{2^d} V_1, \tag{43}$$

where d is the number of dimensions. However, this does not provide a rigorous upper bound on the v_k. A precise determination of v_k and its derivative at $\eta = 0$ should provide an excellent upper bound and approximation of v_k for even intermediate values of η.

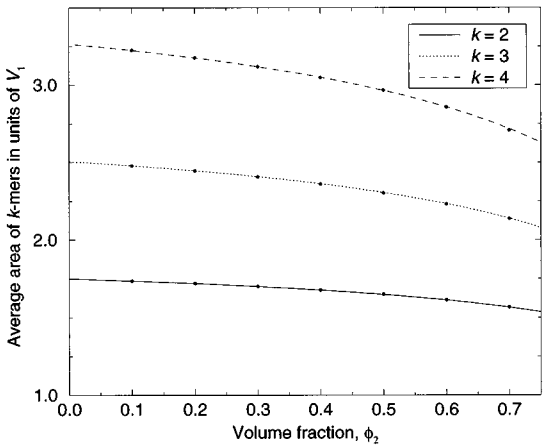

FIG. 4. Expected area of a k-mer in units of V_1 in two dimensions. The solid dots are simulation data.

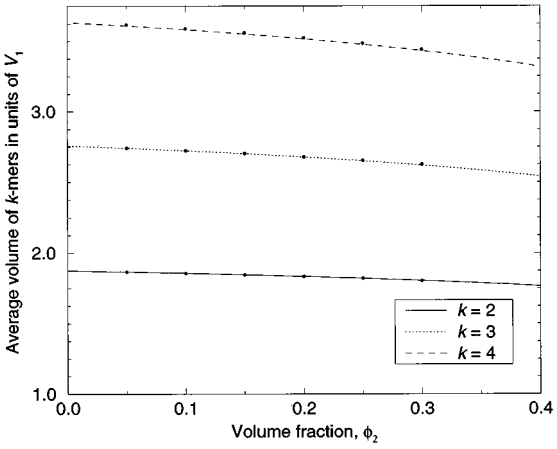

FIG. 5. Expected volume of a k-mer in units of V_1 in three dimensions. The solid dots are simulation data.

VI. LOW-DENSITY EXPANSIONS OF CLUSTER STATISTICS

In the previous sections, we have considered a procedure to numerically evaluate the n_k and v_k in any dimension d. We will now use this procedure to obtain low-density expansions of the cluster statistics Q, S, V_Q, and V_S, which were defined in Sec. II. Our approach is similar to that of Haan and Zwanzig [1], who obtained the low-density expansions of the n_k from the virial theory of the equation of state of a hard-sphere fluid and then obtained the low-density expansions of $1/Q$ and S. Such low-density expansions are important since they are exact to an accuracy of the above numerical integrations and hence can be used as a benchmark for approximate approaches.

In one dimension, Q and S were given by (28). Using (24) and (42), we also obtain

$$V_Q=\frac{\phi_2\sigma}{\phi_1\eta}=-\frac{\phi_2\sigma}{\phi_1\ln(1-\phi_2)} \tag{44}$$

and

$$V_S=\frac{2\phi_2\sigma}{\phi_1\eta}-\sigma=-\frac{2\phi_2\sigma}{\phi_1\ln(1-\phi_2)}-\sigma. \tag{45}$$

Notice that V_Q diverges at the percolation threshold for this one-dimensional system; this is consistent with the discussion of Sec. III. Also, there is a logarithmic contribution in the denominator of V_S. Therefore, in one dimension, V_S does not obey a power law as ϕ_2 approaches the percolation threshold. The presence of η in the denominator, however, would not preclude power-law behavior in higher dimensions, since $\eta^c<\infty$ for $d\geq 2$.

Haan and Zwanzig [1] used the coefficients in the low-density expansion of S to estimate the percolation threshold and critical exponent for S. They did this by using (12) and by obtaining the low-density expansions of the n_k from the virial theory of the equation of state of a hard-sphere fluid. In principle, the same analysis could be performed, using the above integral expressions, on the particle-averaged cluster volume V_S. This would be done by using the Taylor-series expansion

$$n_k=\sum_{j=0}^{\infty}(-1)^j\frac{\rho^{k-1+j}}{k!\,j!}\int d\mathbf{r}_{12}\int d\mathbf{r}_{13}\cdots\int d\mathbf{r}_{1k}\times[V_k(\mathbf{r}^k;\sigma)]^j I(\mathbf{r}^k;\sigma/2). \tag{46}$$

The integrals of (46) can be decomposed in a fashion similar to (31) and then numerically evaluated. Similarly, the expansions of the $n_k v_k$ can be obtained from the numerator of (41). The evaluation of each coefficient will require approximately the same computational effort as the computation of n_k itself. Finally, these coefficients can be used to obtain the low-density expansions of the cluster statistics Q, S, V_Q, and V_S. We present these expansions in Table I for $d=2$ and in Table II for $d=3$. As expected, our expansions for the n_k are in agreement with the expansions obtained by Haan and Zwanzig [1].

TABLE I. Coefficients in the expansions of n_k, v_k, Q, S, V_Q, and V for fully penetrable disks. Recall that $n_1=e^{-4\eta}$ from (29), and that $v_1=V_1$ trivially. The series expansions for v_k, V_Q, and V_S are expressed in units of V_1, the area of a single disk. The expansions for Q, S, V_Q, and V_S are derived from (10), (12), (14), and (15), respectively.

	η^0	η^1	η^2	η^3	η^4
n_2		2	−11.3079	32.2915	−62.0415
n_3			4.8720	−35.3346	129.6895
n_4				13.022	−114.823
n_5					36.728
v_2	1.75	−0.1295	−0.0273	0.0028	
v_3	2.5071	−0.257	−0.055		
v_4	3.268	−0.4			
Q	1	2	2.436	2.432	2.2
S	1	4	6.616	8.834	11
V_Q	1	1.5	1.603	1.5	
V_S	1	3	4.548	5.9	

TABLE II. Same as in Table I, except for fully penetrable spheres. For this system, $n_1 = e^{-8\eta}$ from (29).

	η^0	η^1	η^2	η^3	η^4
n_2		4	−49	302.2238	−1250.5030
n_3			22	−359.4203	2959.1209
n_4				139.7867	−2842.60
n_5					964.68
v_2	1.875	−0.1574	−0.1025	−0.0270	
v_3	2.7578	−0.3080	−0.2073		
v_4	3.64	−0.5			
Q	1	4	11	26.7432	61.6
S	1	8	34	125.3660	436
V_Q	1	3.5	9.1667	21	140
V_S	1	7	29.0048	102	800

Taking the Padé approximants [30] in η for these low-density expansions, we can obtain estimates of the percolation thresholds of overlapping disks and spheres, which are roughly 0.68 and 0.30, respectively, from computer simulations. We show the singularities of the [0,1], [1,1], and [2,1] approximants of Q, S, V_Q, and V_S in Table III for $d=2$ and in Table IV for $d=3$. We notice that the singularities of Q and V_Q occur *above* the percolation threshold in three dimensions. This is not surprising since Q and V_Q do not diverge at the percolation threshold, as discussed in Sec. III. We also notice that the estimates of η^c from V_S are somewhat larger than the estimates from S, as expected, since $V_S < SV_1$, which was also discussed in Sec. III.

Fanti, Glandt, and Chiew [8] obtained a series expansion for V_S for three-dimensional overlapping spheres in terms of the one-point–one-particle connectedness function. They then evaluated V_S to account for binary overlaps under the superposition approximation. They were not, however, concerned with the individual n_k and v_k. Their expression is

$$V_S = \frac{V_1 S \phi_2}{\eta}. \tag{47}$$

If we generalize this expression to d dimensions, we obtain

$$V_S = \frac{S\phi_2}{\eta} \frac{\pi^{d/2}}{\Gamma(1+d/2)} \left(\frac{\sigma}{2}\right)^d \tag{48}$$

after using (2). We see from (28) and (45) that this expression, generalized to one dimension, is off by a factor of 2.

TABLE III. Roots of Padé approximants of Q, S, V_Q, and V_S for fully penetrable disks. For S and V_S, this provides an estimate on the reduced density percolation threshold η^c. The approximate correct value is $\eta^c = 1.13$.

	[0,1]	[1,1]	[2,1]
Q	0.500	0.82	1.00
S	0.250	0.60	0.75
V_Q	0.667	0.94	1.05
V_S	0.333	0.66	0.77

TABLE IV. Same as in Table III, except for fully penetrable spheres. The approximate reduced density percolation threshold is $\eta^c = 0.35$. The roots of the [2,1] approximants of Q and V_Q are greater than η^c.

	[0,1]	[1,1]	[2,1]
Q	0.143	0.363	0.41
S	0.125	0.235	0.27
V_Q	0.286	0.38	0.43
V_S	0.143	0.24	0.28

To our knowledge, the asymptotic behavior of V_S near the percolation threshold has not been studied quantitatively with high precision. It would be useful in future studies to determine if V_S shares the same critical exponent as S (that is, if $\omega = \gamma$).

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APPENDIX: COMPRESSIBILITY EQUATION FOR FULLY PENETRABLE RODS

In (16) we stated the compressibility equation, which in dimensionless units can be stated as

$$S = 1 + \eta \int_0^\infty P_2(z)\, dz, \tag{A1}$$

where P_2 is the pair-connectedness function and $z = r/\sigma$ is dimensionless distance. We now directly verify this result. For fully penetrable rods, P_2 is simply

$$P_2(z) = \begin{cases} 1, & z < 1 \\ C_2(z-1), & z \geq 1, \end{cases} \tag{A2}$$

where C_2 is the two-point cluster function [7]. For fully penetrable rods, this function is given by [12,31]

$$C_2(x) = 1 + \sum_{k=1}^{m} (-1)^k \phi_1^k \times \left(\frac{[\eta(z-k+1)]^{k-1}}{(k-1)!} + \frac{[\eta(z-k+1)]^k}{k!} \right), \tag{A3}$$

where m is the positive integer that satisfies $m-1 \leq x < m$. We recall that $\phi_1 = e^{-\eta}$ for fully penetrable rods. We also note that the n-point connectedness function for this system can be expressed as

$$P_n(x_1, \ldots, x_n) = \prod_{i=1}^{n-1} P_2(x_{i+1} - x_i), \tag{A4}$$

where $x_1<x_2<\cdots<x_n$.

Direct integration of P_2 shows that

$$\int_0^\infty P_2(z)dz=\frac{\phi_2}{\phi_1\eta} \tag{A5}$$

and so we obtain (49) upon comparison with (28). To obtain this integral, we have used the identity

$$e^{\eta}=1+\lim_{n\to\infty}\sum_{k=0}^{n-1}\frac{(-1)^k\eta^{k+1}}{(k+1)!}[(n-k+1)^{k+1}e^{-k\eta} -(n-k)^{k+1}e^{-(k+1)\eta}] \tag{A6}$$

for $x>0$. This identity can be derived using the method of subtracted singularities [32,33] and the generating function

$$f(z)=\frac{\phi_1\exp(-z\eta\phi_1)-\exp(-2z\eta\phi_1)}{\eta\phi_1[1-z\ \exp(-z\eta\phi_1)]}+\frac{1-\phi_1}{\eta\phi_1(1-z)}. \tag{A7}$$

We also notice that we have directly verified that the integral of C_2 diverges at the percolation threshold, as expected [7].

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