Clustering and percolation in assemblies of anisotropic particles: Perturbation theory and Monte Carlo simulation

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We present a theoretical approach for describing clustering and percolation phenomena in an assembly of nonspherical particles. The theory is based upon calculations of an orientation-dependent pair connectedness function. We show how this function may be approximated using a perturbation expansion in which the reference system is an assembly of spherical particles. The reference system is treated via the connectivity Ornstein-Zernike equation in the Percus-Yevick approximation. Although such an approach might appear to be limited to particles of small anisotropy, we find that as the particle anisotropy increases, the regime of interest (i.e., densities below percolation) moves to lower densities where the theory is increasingly accurate. Results are presented for systems of randomly distributed ellipsoids with aspect ratios varying from unity to 5:1 and are compared with Monte Carlo simulations. The approach successfully describes the pair connectedness function, mean cluster size, and percolation threshold. In principle, the formalism is capable of describing the connectivity of randomly distributed particle systems over a wide range of particle anisotropy, including the limiting cases of randomly distributed spheres and infinitely extended rods.

I. INTRODUCTION

The description of cluster statistics in an assembly of particles in which each particle may reside at any point in space and not necessarily on a site of a lattice has important applications in a variety of problems such as continuum percolation. The clustering of continuum particles can be used to mimic the domain structure in composite materials and the appearance of percolating clusters may be associated with drastic changes in the material properties or performance. Examples include the permeability or conductivity of composite systems, such as fiber-polymer[1,2] and polymer-polymer blend[3] systems, flow through porous media,[4] and the sol-gel transition in polymerizing systems.[5] The clustering phenomena, as well as the percolation threshold, depend upon the nature of the particles, i.e., their shape, dimension, and their interaction with other particles or an external field. There is a variety of situations where departures from spherical particle shape can be expected to play a determining role in percolation. However, such a three-dimensional treatment of anisotropic particle systems has received only limited attention in experiment,[6] simulation,[7] and theory[8,9] even though a generalized theoretical description of clustering in continuum systems has been available for some time.[10]

Such a generalized description of clustering is based upon the pair connectedness function, which measures the probability that a pair of particles have a given separation and are also members of the same physical cluster. The range of the pair connectedness function reflects the size of clusters present in the system and the function becomes long ranged as the density approaches the percolation threshold. Such a function can in principle be obtained for any monodisperse or polydisperse collection of particles of arbitrary shape and potential. Coniglio *et al.*[10] derived an Ornstein-Zernike-like integral equation (the connectivity Ornstein-Zernike or COZ equation) for the pair connectedness function, and showed that solutions to this equation could be obtained via a closure approximation. The COZ equation has been solved using the Percus-Yevick (PY) approximation[11] for a number of models; these include randomly centered spheres,[12,13] adhesive spheres,[12] concentric shell,[14,15] and attractive square-well particles.[16] The theoretical predictions of these models have been shown to compare favorably with Monte Carlo simulation.[17–20] Most recently Xu and Stell[21] obtained analytic solutions to the COZ equation in the mean spherical approximation for spherical hard-core particles with an attractive Yukawa tail. Solution of the COZ equation for nonspherical particle systems is a formidable task and has not been attempted.

In this paper we extend the Coniglio description of clustering to assemblies of anisotropic particles. The extension is accomplished by defining an orientation-dependent pair connectedness function. We develop an

approximation scheme for calculating this function using a perturbation theory, similar to the treatment originally developed in the statistical mechanics of molecular fluids.[22] This method seeks to account for particle anisotropy starting from a known reference system of spherical particles. Using this theoretical formalism and Monte Carlo simulation, we investigate the role of particle anisotropy in the clustering and percolation of randomly distributed ellipsoids. Other more complicated assemblies, as for example partially penetrable ellipsoids, can be investigated using the techniques described here.

Prior to this work, the principal focus of theoretical investigations has been the conjecture that the percolation threshold of randomly distributed objects scales with the average excluded volume of particles.[7] Using the cluster expansion of Coniglio *et al.*,[10] Bug *et al.*[8] recently showed that this conjecture is exact to lowest order in density, and provides an appropriate percolation description only in the limit of infinite particle extent or aspect ratio. The theoretical formalism presented here allows us to bridge the available descriptions of randomly distributed spheres[12] and infinitely extended particles,[8] and describe the clustering and percolation over the entire range of particle anisotropies.

The remainder of the paper is outlined in the following manner. In the next section we briefly review the general formalism of part connectedness in continuum models. In Sec. III we extend the formalism to isotropic assemblies of nonspherical particles. Sections IV and V describe the model system studied, its numerical implementation in the theory, and the Monte Carlo simulation. Section VI gives a comparison of the theoretical predictions and Monte Carlo results, and we conclude in Sec. VII with a summary of the results and a discussion of the theory in the context of previous investigations.

II. GENERAL THEORY OF PAIR CONNECTEDNESS

The pair connectedness function $P(1,2)$ for a system of number density ρ is defined[10] such that the quantity $\rho^2 P(1,2)\,d1\,d2$ measures the probability that a pair of particles possess a configuration lying between 1,2 and $1+d1,2+d2$, and are members of the same cluster. The coordinates 1 and 2 denote positions of the particle centers, say, $\mathbf{r}_1$ and $\mathbf{r}_2$, as well as the particle orientations Ω_1 and Ω_2, where Ω denotes a set of angular coordinates, depending upon the dimension of the system and the particle symmetry. In the case of a translationally invariant, isotropic system, the pair-connectedness function is more simply expressed for spherical particles as $P(r)$, and for nonspherical particles as $P(r,\Omega_1,\Omega_2)$, where r represents the interparticle separation.

The pair-connectedness function can be described within the context of the statistical theory of physical clusters set forth by Hill.[23] The connectivity of particle pairs is described by separating the Mayer function into two contributions: $f^+(1,2)$, corresponding to bound or connected particle pairs, and $f^*(1,2)$ for unbound pairs, such that $f(1,2)=f^+(1,2)+f^*(1,2)$, where $f(1,2)=\exp[-\beta u(1,2)]-1$ and $u(1,2)$ is the interparticle potential. By introducing this notation into the cluster expansion of the pair correlation function $h(1,2)$, Coniglio *et al.*[10] identified a subset of graphs at each order in density corresponding to contributions to the pair correlation function from particles which are members of the same cluster. Each graph in this subset has at least one continuous path of $f^+(1,2)$ bonds between the root points. The sum of these contributions over all orders in density is the pair connectedness function. In complete analogy with the pair correlation function, the pair connectedness function is governed by an Ornstein-Zernike-like integral equation, to which we refer as the connectivity Ornstein-Zernike (COZ) equation,

$$P(1,2)=c^+(1,2)+\rho\int c^+(1,3)P(2,3)\,d3\ , \tag{2.1}$$

where $c^+(1,2)$ is the direct-connectedness function, analogous to the direct correlation function $c(1,2)$. The functions $c(1,2)$ and $c^+(1,2)$ correspond graphically to the subset of diagrams in $h(1,2)$ and $P(1,2)$, respectively, having no nodal points. Solution of Eq. (2.1) requires a second independent relation between $P(1,2)$ and $c^+(1,2)$. A simple and often used closure is the Percus-Yevick approximation,[13] written in terms of the connectedness functions as

$$c^+(1,2)=y(1,2)f^+(1,2)+y^+(1,2)f^*(1,2)\ , \tag{2.2}$$

where $y(1,2)$ is the cavity distribution function, defined via

$$g(1,2)=[1+f(1,2)]y(1,2)\ , \tag{2.3}$$

and $y^+(1,2)$ is its connectedness counterpart, defined via

$$P(1,2)=[1+f^*(1,2)]y^+(1,2)+f^+(1,2)y(1,2) \tag{2.4}$$

such that $y(1,2)=y^+(1,2)+y^*(1,2)$ and where the functions $y(1,2)+1$ and $y^+(1,2)$ correspond to the subsets of diagrams in $h(1,2)$ and $P(1,2)$, respectively, with at least one nodal point. The mean cluster size can be obtained from $P(1,2)$ or $c^+(1,2)$ using[10]

$$S=1+\rho\int P(1,2)\,d1\,d2 = \left[1-\rho\int c^+(1,2)\,d1\,d2\right]^{-1}\ . \tag{2.5}$$

For some models of spherical particles, $P(1,2)$ can be solved from Eqs. (2.1) and (2.2) analytically,[12–14,21] using the factorization techniques developed by Baxter, or numerically.[16] However, for the case of anisotropic particles, Eq. (2.1) becomes very complex because of the orientation dependence. One could follow a strategy used in the study of molecular fluids where the angle-dependent correlation functions are expanded in spherical harmonics.[24] However, this is still a relatively complex procedure, even for simple specifications of particle shape and potential. Thus as an initial effort we take a somewhat simpler approach where we employ a perturbation approach to the COZ formalism.

III. PERTURBATION THEORY

A well-known method used to calculate the structure and thermodynamic properties of fluids in statistical mechanics is thermodynamic perturbation theory. The basis of this approach is the relation of the Helmholtz

free energy or pair distribution function of a complex fluid to that of a simple reference fluid. Such a relation is accomplished via a perturbation expansion in terms of a parameter describing the change in the intermolecular forces in passing from the reference fluid to the fluid of interest. It is common to express the perturbation by parametrizing either the intermolecular potential or the Mayer function, as for example

$$f(1,2)=f_0(1,2)+\lambda[f(1,2)-f_0(1,2)] , \tag{3.1}$$

where the subscript 0 denotes the reference system and λ varies from zero to unity. In treating slightly anisotropic particles, it is common to include the anisotropy only in the perturbation, so that Eq. (3.1) becomes

$$f(1,2)=f_0(r)+\lambda[f(1,2)-f_0(r)] . \tag{3.2}$$

A variety of choices for $f_0(r)$ are available but the most appropriate appears to be

$$f_0(r)=\langle f(1,2)\rangle_{\Omega_1,\Omega_2} , \tag{3.3}$$

where the angular brackets indicate an orientation average. This approach ensures that the first-order term in the Helmholtz free-energy expansion vanishes and that the zeroth-order theory is exact in the limit of low density. The pair distribution function or the cavity distribution function, written as a Taylor series expanded about the reference system, can then be used to construct the perturbation theory. Even at zeroth order in perturbation, the approach yields reasonable results for the pair correlation function in systems of slightly anisotropic particles with repulsive interparticle forces. However, for systems of large particle anisotropy, the perturbation is very large and the approach generally fails.

At first glance it might appear that an analogous approach applied to the percolation description of anisotropic particles would not have much merit. It turns out, however, that the limitations of the perturbation approach are suppressed in the percolation problem since as the anisotropy increases, the regime of interest in describing percolation moves to progressively lower densities where the theory is more accurate.

To apply this Mayer function perturbation expansion to the percolation problem we write, in addition to Eq. (3.2),

$$f^+(1,2)=f_0^+(r)+\lambda[f^+(1,2)-f_0^+(r)] , \tag{3.4}$$

where $f_0^+(r)$ is given by

$$f_0^+(r)=\langle f^+(1,2)\rangle_{\Omega_1,\Omega_2} \tag{3.5}$$

and the relation

$$f_0(r)=f_0^+(r)+f_0^*(r) \tag{3.6}$$

still holds. The cavity distribution functions $y(1,2)$ and $y^+(1,2)$ can be written as Taylor series,

$$y(1,2)=y_0(r)+y_1(1,2)+y_2(1,2)+\cdots , \tag{3.7a}$$

$$y^+(1,2)=y_0^+(r)+y_1^+(1,2)+y_2^+(1,2)+\cdots , \tag{3.7b}$$

where $y_k(1,2)$ denotes the kth perturbative term. As an initial approximation, we implement the expansions at zeroth order, hence we have

$$g(1,2)=[1+f(1,2)]y_0(r) \tag{3.8}$$

and

$$P(1,2)=[1+f(1,2)]y_0^+(r)+f^+(1,2)y_0^*(r) . \tag{3.9}$$

The orientation average pair connectedness function is obtained by removing the angular dependence of the right-hand side of Eq. (3.9) or, equivalently, substituting the expressions (3.3) and (3.5) for $f(1,2)$ and $f^+(1,2)$. Thus it is easy to see that, to zeroth order in the perturbation scheme, the orientation average pair connectedness function of the anisotropic system is simply the pair connectedness function of the spherical reference system,

$$\langle P(1,2)\rangle_{\Omega_1,\Omega_2}=P_0(r) . \tag{3.10}$$

In the zeroth-order perturbation approximation, the mean cluster size of the anisotropic particle assembly also corresponds to the mean cluster size of the spherical reference system. For the remainder of the paper we will denote the orientation average of the pair connectedness function as $P(r)$.

IV. APPLICATION TO RANDOMLY DISTRIBUTED PARTICLES

A. Model

The preceding formalism is in principle applicable to any anisotropic particle model, e.g., spherocyclinders, rods, etc. However, in the present work we choose a model that can be easily tested in Monte Carlo simulations. This model is that of fully permeable or randomly distributed ellipsoids with aspect ratios L/σ ranging from 1.0 to 5.0. The particle pair configuration is defined by the separation vector $\mathbf{R}$, and the particle axial unit vectors $\mathbf{u}_1$ and $\mathbf{u}_2$ or, equivalently, by r, θ_1, θ_2, and ϕ_{12}, Fig. 1. The overlap or connectedness of particle pairs at discrete orientations is determined using the criteria specified by the Gaussian overlap model (GOM) of Berne and Pechukas,[25] i.e.,

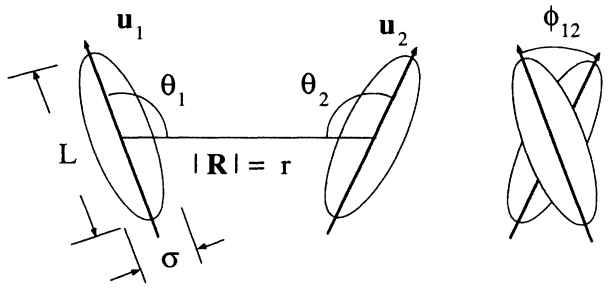

FIG. 1. Representation of ellipsoids of aspect ratio L/σ with particle pair configuration described by the interparticle separation r and the set of angles (θ_1, θ_2 and ϕ_{12}). Parameters in the Gaussian overlap model are $\mathbf{u}_1$ and $\mathbf{u}_2$, the axial vectors of particles 1 and 2, and $\mathbf{R}$, the separation vector.

$$\lambda(\Omega_1,\Omega_2)=\sigma\left[1-\tfrac{1}{2}\chi\left[\frac{(\mathbf{R}\cdot\mathbf{u}_1+\mathbf{R}\cdot\mathbf{u}_2)^2}{[1+\chi(\mathbf{u}_1\cdot\mathbf{u}_2)]}+\frac{(\mathbf{R}\cdot\mathbf{u}_1-\mathbf{R}\cdot\mathbf{u}_2)^2}{[1-\chi(\mathbf{u}_1\cdot\mathbf{u}_2)]}\right]\right]^{-1/2}, \quad (4.1)$$

where $\chi=[(L/\sigma)^2-1]/[(L/\sigma)^2+1]$ and particles 1 and 2 are directly connected if by this expression $r\le\lambda(\Omega_1,\Omega_2)$. This potential has been used successfully in the Monte Carlo simulation to describe the thermodynamics of systems of hard-core ellipsoids of small particle anisotropy, both prolate ($L/\sigma>1$) and oblate ($L/\sigma<1$).[26] The GOM collision diameter does not exactly mimic ellipsoids, but it gives a qualitatively similar angle-dependent connectivity.

B. Numerical solutions of the integral equation

The pair connectedness of randomly centered ellipsoids is obtained from a numerical solution of the COZ integral equation using the perturbation formalism described in Sec. IV A. The functions $f^+(r,\Omega_1,\Omega_2)$ and $f^*(r,\Omega_1,\Omega_2)$ are determined from the GOM connectedness criteria, Eq. (4.1), as

$$f^+(r,\Omega_1,\Omega_2)=-f^*(r,\Omega_1,\Omega_2)=\begin{cases}1 & \text{for } r\le\lambda(\Omega_1,\Omega_2)\\ 0 & \text{for } r>\lambda(\Omega_1,\Omega_2)\end{cases}. \quad (4.2)$$

The spherical reference Mayer functions $f_0^+(r)$ and $f_0^*(r)$ are found by Eqs. (3.3) and (3.5) using a Simpson's rule integration evaluated over 300 or more discrete orientations, depending on the value of L/σ, in intervals of $r=0.025\sigma$. Figure 2 displays the functions for ellipsoidal particles of aspect ratio $L/\sigma=2.0$. The interpretation of the Mayer function $f_0^+(r)$ is apparent: $f_0^+(r)$ is the probability that two reference particles separated a distance r are directly connected. In this sense the particle described by these reference Mayer functions is a randomly centered sphere with a "connectedness-in-probability" criteria similar to that proposed by Coniglio, Stanley, and Klein (CSK) for lattices[5] and used most recently in a continuum context by Xu and Stell.[21]

The tabulated reference Mayer functions serve as initial guesses to the direct connectedness functions $c_0^+(r)$ and $c_0^*(r)$ in an iterative solution of the COZ equation coupled with the PY closure, Eq. (2.2). The solution of these equations is obtained using an adaptation of the method of Gillan,[27] and yields directly $y_0(r)$ and $y_0^+(r)$, and the zeroth-order perturbation to the orientation-average pair connectedness function and inverse mean cluster size, via Eq. (2.5). The orientation-dependent pair

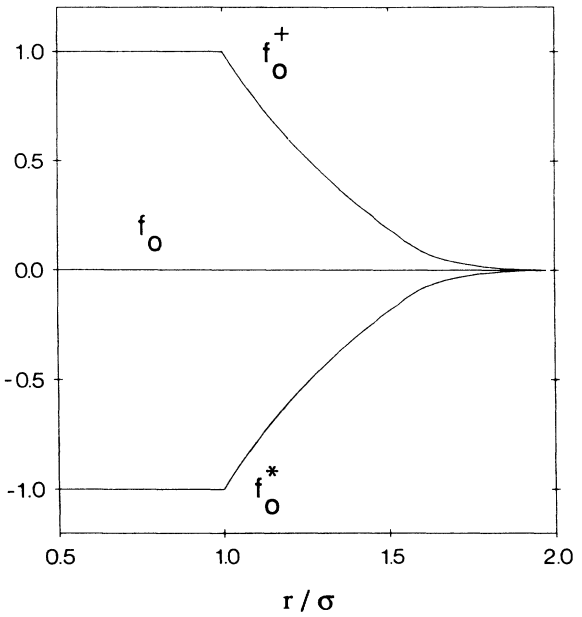

FIG. 2. Spherical reference Mayer functions for randomly distributed GOM particles of aspect ratio $L/\sigma=2.0$. The full Mayer function, $f_0(r)$ is zero for all r, indicative of randomly centered particles. The connectedness Mayer function $f_0^+(r)$ may be interpreted as the probability that two reference particles separated a distance r are directly connected. In the zeroth-order approximation, the complete connectivity of an assembly of spherical reference particles is taken to be the connectivity of an assembly of anisotropic particles.

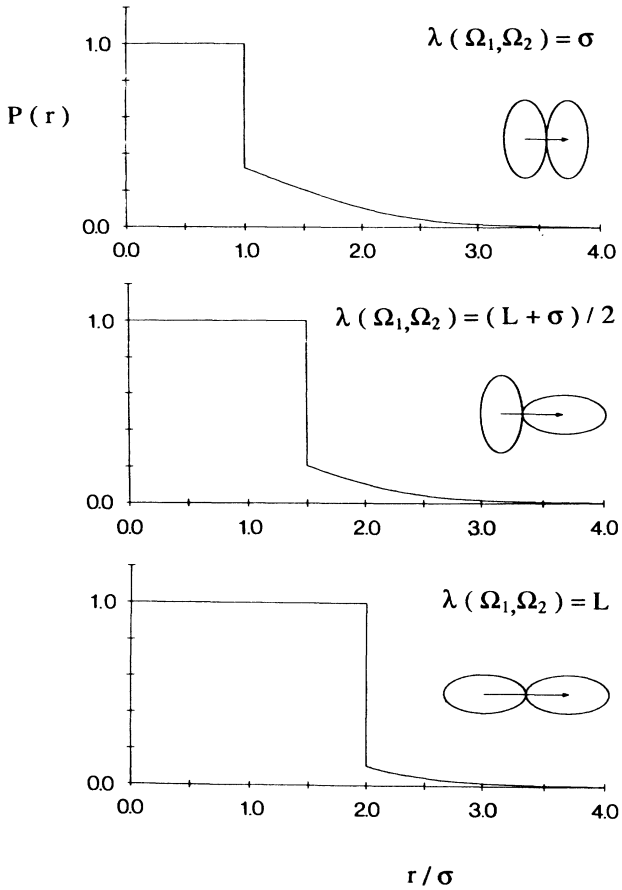

FIG. 3. Orientation-dependent pair connectedness function $P(r,\Omega_1,\Omega_2)$ for randomly distributed GOM particles of $L/\sigma=2.0$ at $\phi=0.20$ with fixed orientation, as pictured in insets. As a consequence of the truncation of the perturbation at zeroth order, $P(r,\Omega_1,\Omega_2)$ is independent of particle orientation for $r>\lambda(\Omega_1,\Omega_2)$.

connectedness is found by substitution of $y_0^+(r)$ and $y_0^*(r)$ into Eq. (3.9). Figure 3 displays $P(r,\Omega_1,\Omega_2)$ for GOM particles of $L/\sigma=2.0$ at specific particle pair orientations. Note that $P(r,\Omega_1,\Omega_2)$ is independent of the relative orientation of the particle pair for $r>\lambda(\Omega_1,\Omega_2)$, where $\lambda(\Omega_1,\Omega_2)$ is the maximum separation for which two particles of fixed relative orientation may be directly connected. This is a direct consequence of the zeroth-order approximation made in Eqs. (3.7a) and (3.7b).

V. MONTE CARLO SIMULATIONS

Assemblies of randomly distributed ellipsoids were simulated using the Monte Carlo method.[28] The simulations were initialized with the ellipsoidal particles aligned on the sites of a simple cubic lattice with periodic boundary conditions and were carried out for various value of ϕ below the percolation threshold, where ϕ is defined as the product of ρ and the volume of an ellipsoid. At each value of ϕ, the simulations were carried out using several different numbers of particles, $N=125$, 216, 512, and 1000, in order to estimate finite size effects. Each simulation consisted of 10 000 moves per particle, where a move constitutes a translation and rotation of arbitrary magnitude. Equilibration was considered complete after 500 moves per particle. Correlation and connectedness statistics, as well as cluster characteristics, were compiled at intervals of 5 moves per particle.

The cluster statistics, namely, the pair connectedness function, mean cluster size, and particle coordination number, were found using the cluster counting algorithm of Sevick *et al.*[18] This algorithm can be applied to the simulation of particles of any dimension, shape, or interparticle potential with arbitrary criteria for direct connectedness. The algorithm uses direct connectedness information, or in this case, the overlap of all particle pairs, to detect clusters of particles and construct the pair connectedness function. To obtain the orientation average pair connectedness function and the mean cluster size, we recorded particles "overlapping" according to Eq. (4.1).

As discussed elsewhere,[18] simulations of percolation phenomena are plagued by finite size effects, particularly near the percolation threshold. To reduce the impact of using a finite number of particles, we extrapolated the mean-cluster-size results to infinite system size. Additionally, the pair connectedness functions were recorded for the largest system size explored (usually 1000 particles). Nevertheless, for periodic boundary conditions and for densities approaching the percolation threshold, we can expect finite size effects to falsely increase the value of the pair connectedness function for $r>L/\sigma$. However, the magnitude of this error is relatively small, even for the most extreme system studied, $L/\sigma=5.0$ at $\phi=0.12$, or $\phi/\phi_p=0.86$, where ϕ_p is the volume fraction at the percolation threshold, and is not readily apparent on the scale of the figures presented in this paper. As demonstrated in simulations of the connectivity of spherical particles,[29] alternative boundary conditions can further diminish the magnitude of the finite size results.

VI. COMPARISON OF THEORY AND SIMULATION RESULTS

Figures 4 and 5 compare the orientation averaged pair connectedness function $P(r)$ predicted by the perturbation theory and obtained from simulation over various ϕ for $L/\sigma=2.0$ and 5.0, respectively. These figures show that larger aspect ratios increase the range of connectedness, both direct connectedness (trivially by definition) and indirect connectedness (for $r>L/\sigma$); the perturbation theory successfully mimics this trend. At small L/σ, Fig. 4, the theory describes connectivity reasonably well at small ϕ but increasingly underestimates $P(r)$ as ϕ approaches the percolation threshold ϕ_p. The connectedness of randomly centered spheres, predicted by the Percus-Yevick approximation, is qualitatively similar.[12,18] In contrast, at intermediate L/σ, Fig. 5, the theory overestimates $P(r)$. From the range of ϕ studied, it is not apparent that this overestimation becomes more dramatic as ϕ approaches ϕ_p.

Figure 6 displays the corresponding inverse mean cluster size versus ϕ for $L/\sigma=2.0$, 3.0, and 5.0. Also included in this figure are the randomly centered sphere results, i.e., $L/\sigma=1.0$, obtained from an analytic solution using the PY approximation.[12] Consistent with an underestimation of connectivity at larger densities, the theoretical predictions of S^{-1} for $L/\sigma=1.0$ and 2.0 are larger than the Monte Carlo results, particularly at densities close to the percolation threshold. At $L/\sigma=3.0$, the perturbation theory predicts mean cluster sizes quite well

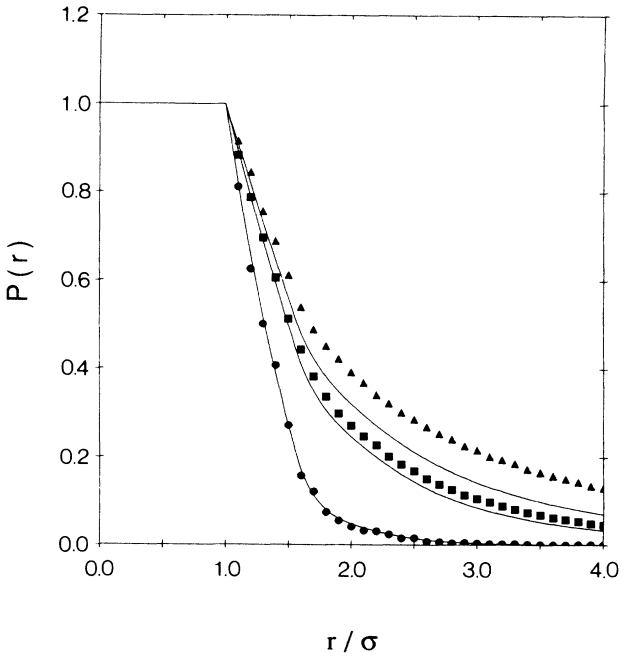

FIG. 4. Orientation average pair connectedness function $P(r)$ for $L/\sigma=2.0$ found from Monte Carlo simulation (symbols) and the perturbation theory (lines). $\phi=0.05$ (●), 0.20 (■), and 0.25 (▲) corresponding to $\phi/\phi_p=0.17$, 0.68, and 0.85, respectively. Note that the theory underestimates the connectivity, particularly for densities approaching ϕ_p.

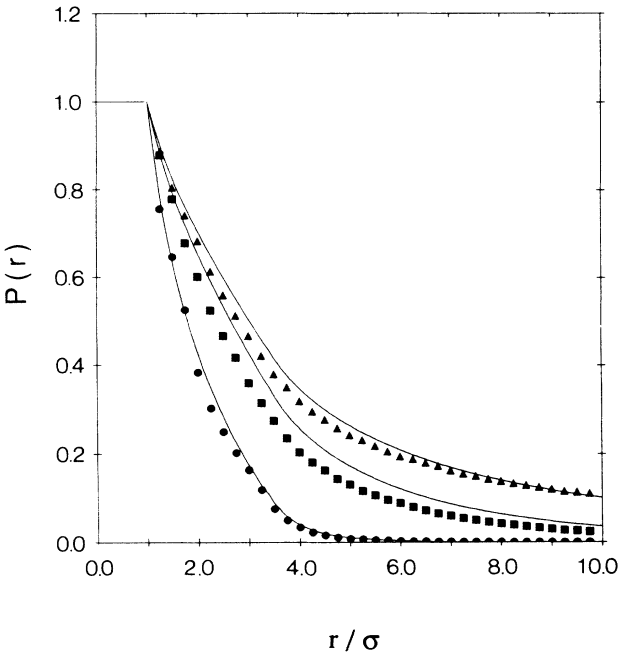

FIG. 5. Orientation average pair connectedness function $P(r)$ for $L/\sigma=5.0$ found from Monte Carlo simulation (symbols) and the perturbation theory (lines). $\phi=0.025$ (●), 0.100 (■), and 0.120 (▲) corresponding to $\phi/\phi_p=0.18$, 0.72, and 0.86, respectively. Note that the theory overestimates the connectivity.

over the subpercolation regime; however, for larger anisotropy, $L/\sigma=5.0$, the theory slightly underestimates S^{-1}, again consistent with the pair connectedness results.

Table I lists the percolation thresholds ϕ_p found by extrapolating the numerical predictions and simulation results of S^{-1} for $L/\sigma=1.0$, 1.5, 2.0, 3.0, and 5.0. Despite

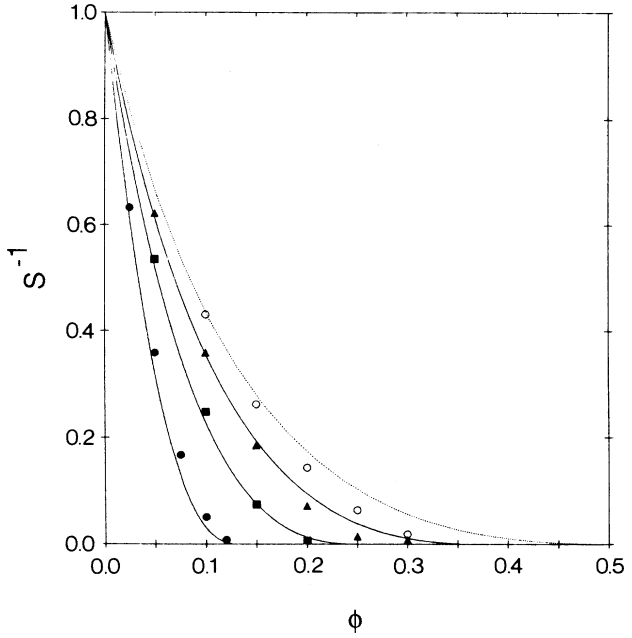

FIG. 6. Inverse mean cluster size S^{-1} vs ϕ found from Monte Carlo simulation (symbols) and the perturbation theory (lines). $L/\sigma=1.0$ (○), 2.0 (▲), 3.0 (■), and 5.0 (●).

TABLE I. Percolation threshold of GOM particles of variable aspect ratio predicted by perturbation theory and simulation. Results are obtained by extrapolating plots of $S^{-1/2}$ vs ϕ to $S^{-1/2}=0.0$.

Aspect ratio	Perturbation theory	Simulation
5.0	0.13	0.139
3.0	0.245	0.228
2.0	0.37	0.294
1.5	0.45	0.339
1.0	0.50[a]	0.361

[a] Analytic solution of PY approximation of randomly centered spheres Ref. 12.

the zeroth-order approximation, which suggests that the theory becomes less appropriate as particle anisotropy increases, the perturbation prediction of percolation threshold compares more favorably with the simulation results as the aspect ratio increases. This is because as the particle anisotropy increases, the regime of interest moves to progressively lower densities, where the theory is more accurate. Thus the success of the approach is based upon the degree to which particle anisotropy lowers the percolation threshold.

VII. SUMMARY AND DISCUSSION

We have presented a theory, based upon a perturbation expansion and the Percus-Yevick approximation, capable of describing the connectivity of a random assembly of anisotropic particles. Using this formalism, we can predict the clustering of anisotropic particles, specifically, the mean cluster size and the pair connectedness function, evaluated for a specific particle pair orientation or, alternatively, averaged over all orientations. Using this procedure we have investigated assemblies of randomly centered ellipsoids and compared theoretical results with that of Monte Carlo simulation. Although the theory in its present form is relatively crude, the quality of the predictions is quite encouraging. It is nevertheless worthwhile to reflect more closely upon the behavior of the theory, particularly as a function of particle anisotropy.

Difficulties encountered in numerical solution of the integral equation and the finite size effects in Monte Carlo simulations prevent us from investigating the performance of the perturbation approach for much larger anisotropies than those considered here. Nevertheless, within the range investigated, $1.0<L/\sigma<5.0$, we find that the theoretical underestimation of connectivity at small anisotropy and overestimation at larger anisotropy may be explained in terms of the impact of introducing the zeroth-order perturbation assumption and the PY approximation.

The perturbation theory description of assemblies of particles of small anisotropy (i.e., $L/\sigma=2.0$ of Fig. 4) is consistent with the Percus-Yevick description of randomly centered spheres.[12,18] Both theories predict the pair connectedness function quite well at low densities, but underestimate connectivity at densities approaching the

percolation threshold. This underestimation is attributed, in the case of spherical particle assemblies, to an incomplete cancellation of parallel and bridge diagrams in the cluster expansion of $P(1,2)$, since such a cancellation to all orders in density is assumed in the PY approximation.[14] We might expect this incomplete cancellation to also yield an underestimation of connectivity in anisotropic particle assemblies. However, as the anisotropy increases, the low-density limit, correctly accounted for in the PY approximation, increasingly becomes a dominant contribution to the pair connectedness function. In the limit of infinite L/σ, the pair connectedness function is given exactly by $f^+(1,2)$ (Ref. 8) and the PY approximation is essentially exact. Thus it does not appear possible to explain in a simple way the accuracy of the PY approximation over a range of particle anisotropy; at the very most we can say that the PY approximation underestimates connectivity, and that its behavior with increasing L/σ depends upon a competition between an increasingly incomplete diagrammatic cancellation and the growing contribution of the exact low-density result.

In contrast, the perturbation theory consistently overestimates connectivity of systems with large aspect ratio (i.e., $L/\sigma=5.0$), even at low densities, e.g., $\phi/\phi_p=0.18$ in Fig. 5. Since the zeroth-order perturbation approximation in Eqs. (3.7a) and (3.7b) becomes more severe as L/σ increases, it seems reasonable to attribute this connectivity overestimation to the perturbation assumption. Given the lack of orientational dependence for $r>\lambda(\Omega_1,\Omega_2)$ in Fig. 2, it appears that the zeroth-order perturbation term alone cannot accurately account for the propagation of the orientation-dependent indirect connectivity. However, in the limit of infinite L/σ, the zeroth-order approximation becomes exact since the pair connectedness function is given exactly by $f^+(1,2)$, and the reference spherical system then becomes an exact representation of the orientation average $L/\sigma\rightarrow\infty$ system.[30] We thus expect that the zeroth-order assumption becomes less accurate as slightly anisotropic particles become more anisotropic, and becomes more accurate as highly anisotropic particles approach infinite extent.

Thus we have demonstrated that the theory can, in principle, bridge the regime between randomly centered spherical particles (described in the PY context) and particles of infinite extent. We have not identified the range of L/σ where the zeroth-order and PY approximations combine to be more or less accurate. However, the formalism does appear to assess the connectivity and percolation threshold of randomly distributed ellipsoidal particles of $L/\sigma=5.0$ more correctly than in the case of spheres or $L/\sigma=1.0$.

Another issue which we hope to address in future work is the particle anisotropy dependence of the exponent γ defined through

$$S^{-1}\sim|\phi-\phi_p|^{\gamma}. \tag{7.1}$$

For the case of randomly centered spheres γ is thought to be close to 2, as predicted by the PY theory.[12] For very long rods, γ should approach unity.[8] Our present simulation results for the mean cluster size were not sufficiently close to the percolation threshold to permit the accurate determination of γ. However, a more detailed study of the predictions from our perturbation theory should provide some useful information in this context.

We are presently investigating other model systems which are solvable for larger ranges of L/σ. One possible model is an assembly of spherocyclinders for which the zeroth-order contribution to S^{-1} is analytically known.[8] In order to more fully assess the utility of the approach, we are currently applying the perturbation theory to other models for which connectedness solutions have been found by other methods such as the randomly distributed interaction site models.[9]

Application of the formalism might be extended to particles with various interparticle potentials. As an example, increasing the hard-core content might improve the perturbation results at low anisotropy, since the cancellation of bridge and parallel diagrams is more complete in the PY approximation.[14] However, because of the isotropic nature of the theory and the zeroth-order perturbation assumption, the range of densities for which the theory will be accurate is questionable. Nevertheless, particle assemblies with anisotropic hard cores provide the possibility of orientational ordering and perhaps liquid crystallinity. The coupling of such effects with percolation phenomena presents an interesting theoretical challenge.

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[1]See, for example, D. M. Bigg, Polym. Eng. Sci. **19**, 1188 (1979).

[2]I. Balberg and S. Bozowski, Solid State Commun. **44**, 551 (1982).

[3]J. E. Sax and J. M. Ottino, Polymer **26**, 1073 (1985).

[4]*Physics and Chemistry of Porous Media* (Schlumberger-Doll Research, Ridgefield, CT), Proceedings of a Symposium on the Physics and Chemistry of Porous Media, AIP Conf. Proc. No. 107, edited by D. L. Johnson and P. L. Sen (AIP, New York, 1983).

[5]A. Coniglio, H. E. Stanley, and W. Klein, Phys. Rev. B **25**, 6805 (1982).

[6]F. Carmona, P. Prudhon, and F. Barreau, Solid State Commun. **51**, 255 (1984).

[7]I. Balberg, N. Binenbaum, and N. Wagner, Phys. Rev. Lett. **52**, 1465 (1984); I. Balberg, C. H. Anderson, S. Alexander, and N. Wagner, Phys. Rev. B **30**, 3933 (1984).

[8]A. L. R. Bug, S. A. Safran, and I. Webman, Phys. Rev. B **33**,

4716 (1986); Phys. Rev. Lett. **54**, 1412 (1985).
[9]M. Lupkowski and P. A. Monson, J. Chem. Phys. **89**, 3300 (1988).
[10]A. Coniglio, U. DeAngelis, A. Forlani, and G. Lauro, J. Phys. A **10**, 219 (1977); A. Coniglio, U. DeAngelis, and A. Forlani, *ibid.* **10**, 1123 (1977).
[11]J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958).
[12]Y. C. Chiew and E. D. Glandt, J. Phys. **16**, 2599 (1983).
[13]Y. C. Chiew, G. Stell, and E. D. Glandt, J. Chem. Phys. **83**, 761 (1985).
[14]T. DeSimone, S. Demoulini, and R. M. Stratt, J. Chem. Phys. **85**, 391 (1986).
[15]S. Torquato, J. Chem. Phys. **81**, 5079 (1984).
[16]S. C. Netemeyer and E. D. Glandt, J. Chem. Phys. **85**, 6054 (1986).
[17]G. O. Williams and G. Stell (unpublished).
[18]E. M. Sevick, P. A. Monson, and J. M. Ottino, J. Chem. Phys. **88**, 1198 (1988).
[19]N. A. Seaton and E. D. Glandt, J. Chem. Phys. **86**, 4668 (1985).
[20]A. L. R. Bug, S. A. Safran, G. S. Grest, and I. Webman, Phys. Rev. Lett. **55**, 1896 (1985); S. A. Safran, I. Webman, and G. S. Grest, Phys. Rev. A **32**, 506 (1985).
[21]J. Xu and G. Stell (unpublished).
[22]C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Oxford University Press, Oxford, 1984), Vol. 1.
[23]T. J. Hill, J. Chem. Phys. **23**, 617 (1955).
[24]W. A. Steele, J. Chem. Phys. **39**, 3197 (1963).
[25]B. J. Berne and P. Pechukas, J. Chem. Phys. **56**, 4213 (1972).
[26]P. A. Monson and K. E. Gubbins, J. Phys. Chem. **87**, 2852 (1983).
[27]M. J. Gillan, Mol. Phys. **38**, 57 (1979).
[28]N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. N. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).
[29]S. B. Lee and S. Torquato (unpublished).
[30]This also suggests that simulations of assemblies of particles of effectively infinite extent can be carried out using the CSK or "connectedness-in-probability" criteria, i.e., randomly centered points (where a point represents the center of mass of a particle of infinite extent) where connectedness between points depends upon distance between the points and a random number.

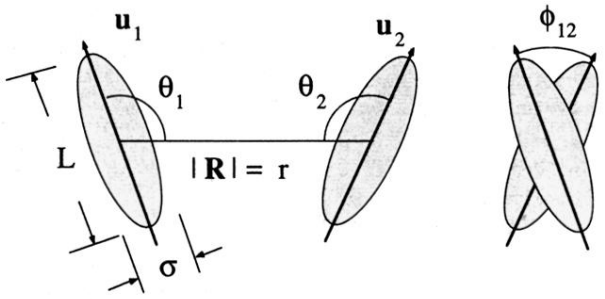

FIG. 1. Representation of ellipsoids of aspect ratio L/σ with particle pair configuration described by the interparticle separation r and the set of angles (θ_1, θ_2 and ϕ_{12}). Parameters in the Gaussian overlap model are $\mathbf{u}_1$ and $\mathbf{u}_2$, the axial vectors of particles 1 and 2, and $\mathbf{R}$, the separation vector.