Monte Carlo calculations of connectedness and mean cluster size for bidispersions of overlapping spheres

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(Received 21 May 1990; accepted 5 July 1990)

The pair-connectedness function and mean cluster size are computed from Monte Carlo simulations for the continuum-percolation model of overlapping spheres with two different diameters. The percolation threshold of the spheres is found to be independent of the distribution (for the cases examined) and slightly higher than that for equisized spheres. Our simulation results are used to assess the accuracy of the Percus–Yevick approximation for the aforementioned cluster statistics.

I. INTRODUCTION

There has been a recent upsurge of interest in the subject of the physical clustering of particles in *continuum* (off-lattice) models of disordered many-body systems (see Refs. 1–14 and references therein). A singularly important case of physical clustering occurs at the percolation transition, i.e., the point at which a cluster becomes infinite in size. The study of the clustering behavior of particles in continuum systems is of importance in phenomena such as conduction (thermal or electrical) in dispersions,[15] sol–gel transition in polymer systems,[4] aggregation of colloids and microemulsions,[10] and the structure of liquid water,[9] to mention but a few examples.

A quantity of key fundamental interest in the study of continuum percolation is the *pair-connectedness* function $P(r)$ which, for statistically isotropic distributions of particles, is proportional to the probability that two particles, with relative position r, are connected (or in the same cluster).[1] From $P(r)$ one can obtain other useful quantities, such as the mean cluster size, percolation threshold, and mean coordination number.

Theoretical techniques used to obtain $P(r)$ focus on solving the "connectedness" Ornstein–Zernike integral equation as described by Coniglio *et al.*[1] Closure of the integral equation requires one to employ an approximation for the "direct" connectedness function. A commonly employed closure is the Percus–Yevick (PY) approximation. This approximation was used by Chiew and Glandt[6] and by DeSimone *et al.*[9] to study equisized spheres in the permeable-sphere model and penetrable-concentric-shell model, respectively. Subsequently, Chiew *et al.*[8] conducted an analogous investigation for permeable spheres with a size distribution. All of these interpenetrable-sphere models are parametrized by an impenetrability index λ, $0 \leqslant \lambda \leqslant 1$. The special case of $\lambda = 0$ corresponds to randomly centered spheres or spatially uncorrelated spheres and is sometimes referred to as "overlapping spheres," "fully penetrable spheres," or the "Swiss-cheese" model.

Although computer simulations of the pair-connectedness function has been carried out for various distributions of *equisized* spheres,[11,12,14] to our knowledge, such computations have not been carried out for systems of spheres with a size distribution. One of the purposes of this paper is to compute the pair-connectedness function for binary mixtures of randomly centered spheres (i.e., overlapping spheres having two different diameters) from Monte Carlo simulations. The mean cluster size S is also determined independently from the simulations for such models. From S the percolation thresholds are estimated. Our simulation results are compared to the theoretical results of Chiew *et al.*[8] in the PY approximation. Thus, we study the effect of polydispersity in particle size on the clustering of overlapping spheres.

II. SIMULATION PROCEDURE

Obtaining statistical measures, such as the pair-connectedness function and mean cluster size, from computer simulations is a two-step process. First, one generates realizations of the medium of interest. Second, one samples each realization for the desired quantity and then averages over a sufficiently large number of realizations. In the ensuing discussion, we describe the details of our simulation methods to obtain the aforementioned cluster measures for binary mixtures of randomly centered (i.e., spatially uncorrelated) spheres.

A simple and efficient means of generating realizations of randomly centered or overlapping spheres is to randomly and sequentially place each sphere of diameter σ_i ($i = 1$ or 2) in a cubical cell until the desired density ρ_i for each species is reached. This procedure, subject to periodic boundary conditions, is the one employed in the present study.

In order to compute cluster measures, one needs to be able to distinguish between the various clusters in the system. By definition, two particles of diameter σ_i and σ_j are assumed to be "directly" connected if the interparticle distance r satisfies the relation

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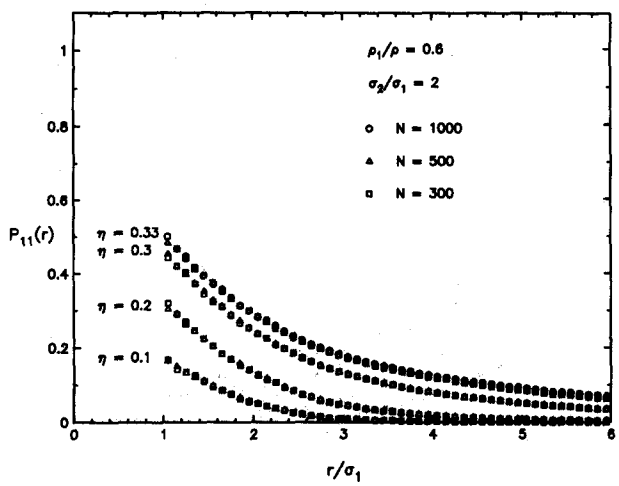

FIG. 1. Comparison of the simulation results for the pair-connectedness function $P_{11}(x)$ at various system sizes for bidispersed overlapping spheres at $\eta = 0.1$, 0.2, 0.3 and 0.33. Here $\rho_1/\rho = 0.6$ and $\sigma_2/\sigma_1 = 2$.

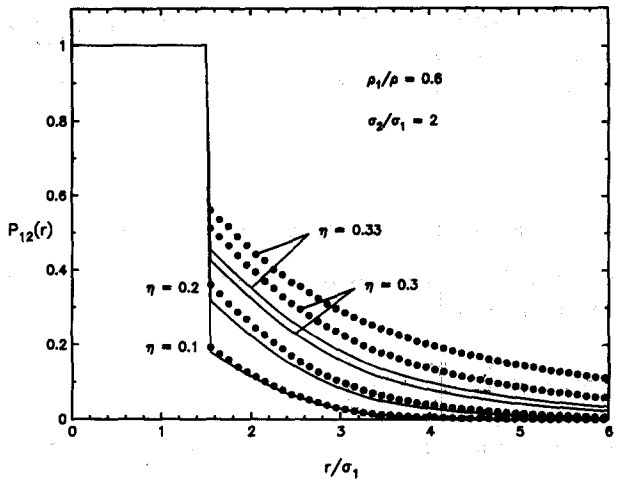

FIG. 3. As in Fig. 2 for the pair-connectedness function $P_{12}(x)$.

$$r \leqslant \frac{\sigma_i + \sigma_j}{2}. \tag{1}$$

Pairs of particles can be "indirectly" connected, however, through chains of other particles. Existing cluster-counting algorithms which are able to distinguish particles of different clusters include the "cluster-labeling method"[16] and the "connectivity matrix method."[12] In this study, we employ a modified cluster-labeling method used by Lee and Torquato.[14]

A. Pair-connectedness function

In a bidispersed, isotropic system of generally interacting particles, the pair-connectedness function $P_{ij}(r)$ $(i, j = 1,2)$ is defined such that the quantity $\rho_i \rho_j P_{ij}(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2$ is the joint probability of finding particles of species i and j, centered in volume elements $d\mathbf{r}_1$ and $d\mathbf{r}_2$ about $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively, and that these two particles are physically connected, i.e., belong to same cluster. Computing $P_{ij}(r)$ from computer simulations is relatively straightforward. First one constructs concentric shells of radii

$$r_k = k\Delta r, \qquad k = 1,2,3,... \tag{2}$$

up to $r = L/2$ around each particle of diameter σ_i in the system (where Δr is a distance which is small compared to σ_i). One then counts the number of particles of diameter σ_j in each shell which are connected to each of the central particles. The pair-connectedness function $P_{ij}(r)$ is readily obtained from the number of the connected particles for each value of k.

In order to minimize the effect of system size in simulations of $P_{ij}(r)$, the central cell is surrounded with replicas of itself. Cluster identification depends upon the type of boundary conditions employed. The standard practice has been to use "simple" periodic boundary conditions over the central cell. Lee and Torquato[14] have shown that "free" boundary conditions over the *central* and *replicating* cells lead to a pair-connectedness function which converges

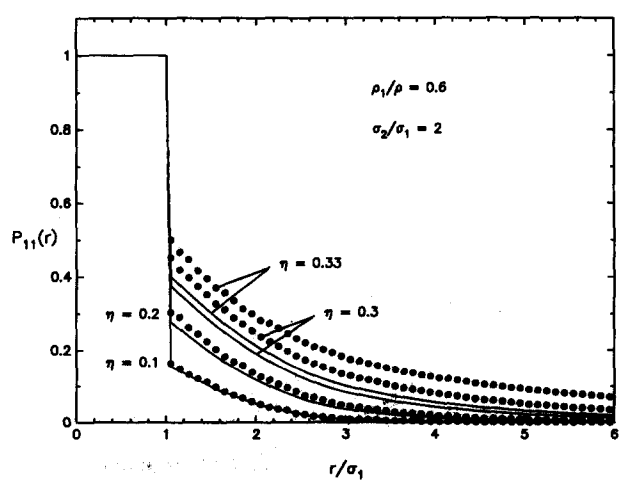

FIG. 2. Pair-connectedness function $P_{11}(x)$ for bidispersed overlapping spheres at $\rho_1/\rho = 0.6$ and $\sigma_2/\sigma_1 = 2$. The solid lines are the PY results (Ref. 8).

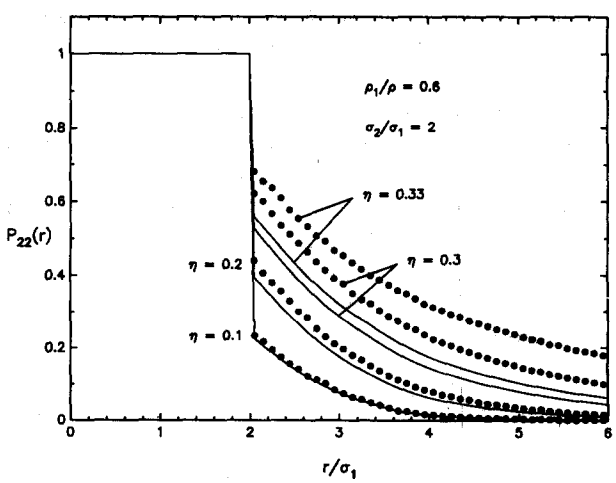

FIG. 4. As in Fig. 2 for the pair-connectedness function $P_{22}(x)$.

to the infinite-system behavior much more rapidly than the application of simple periodic boundary conditions. We therefore apply free boundary conditions to compute $P_{ij}(r)$.

B. Mean cluster size and percolation threshold

Given $P_{ij}(r)$, one can determine the mean cluster size S from the relation[8]

$$S=1+\rho \sum_i \sum_j x_i x_j \int P_{ij}(r)dr, \tag{3}$$

where $\rho=\Sigma_i \rho_i$ and $x_i=\rho_i/\rho$ or from an alternative definition

$$S=\frac{\Sigma_s s^2 n_s}{\Sigma_s s n_s}, \tag{4}$$

where n_s is the mean number of clusters of size s. Note that the size of a cluster s is simply the number of particles in that cluster, regardless of the species of the constituent particles. We employ the latter definition (4) to compute S from our simulations. Unlike the determination of $P_{ij}(r)$, the values of the mean number of clusters of size s, n_s, and hence S are the same for both free boundary conditions and simple periodic boundary conditions. We therefore utilize the latter to compute S since use of simple periodic boundary conditions is much less computer intensive. Note that mean cluster size S becomes infinite at the sphere volume fraction $\phi=\phi_c$, the percolation threshold. Thus, we estimate ϕ_c by extrapolating the data for the inverse mean cluster size S^{-1} as a function of ϕ to the $S^{-1}\to 0$ limit. Extrapolation is achieved by employing the least-squares fit equation of the data for S^{-1} in the range of ϕ from about 0.25 to 0.3.

III. RESULTS AND DISCUSSION

We have carried out computer simulations of the pair-connectedness function $P_{ij}(r)$ and the mean cluster size S for bidispersions of overlapping spheres for selected values of the sphere volume fraction ϕ. Such calculations require substantially more CPU time than corresponding computations for monodispersed systems of particles since in the former roughly twice as many total particles (up to 1000 particles) are needed to obtain sufficient accuracy. Two different distributions are examined: (i) one in which $\rho_1/\rho=0.2$ and $\sigma_2/\sigma_1=2$ and (ii) the other in which $\rho_1/\rho=0.6$ and $\sigma_2/\sigma_1=2$. Recall that ρ_i and σ_i are the density and the diameter of species i, respectively, and $\rho=\Sigma_i \rho_i$. It is useful to introduce the reduced number density η defined by

$$\eta=\frac{\pi}{6}\rho_1\sigma_1^3+\frac{\pi}{6}\rho_2\sigma_2^3. \tag{5}$$

The sphere volume fraction is then given by

$$\phi=1-e^{-\eta}. \tag{6}$$

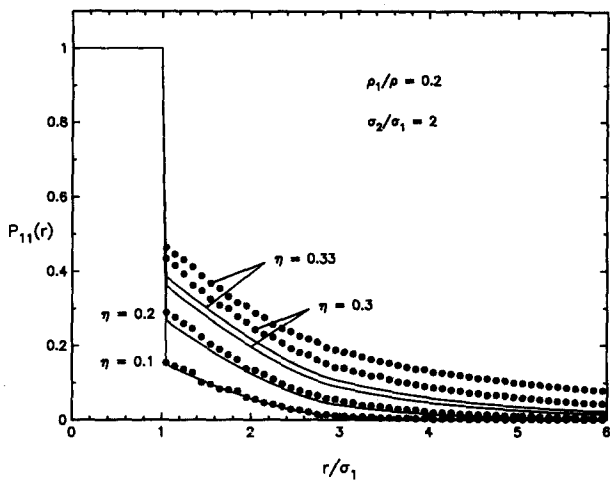

FIG. 5. Pair-connectedness function $P_{11}(x)$ for dispersed overlapping spheres at $\rho_1/\rho=0.2$ and $\sigma_2/\sigma_1=2$. The solid lines are the PY results (Ref. 8).

A. Pair-connectedness function

We first studied the effect of system size on our results for $P_{ij}(r)$ by computing it for N, total number of particles, equal to 100, 200, 300, 500 and 1000. It is found that in all cases systems with $N=500$ or $N=1000$ are sufficiently large to neglect finite-size effects. To illustrate this point we depict, in Fig. 1, $P_{11}(r)$ for selected values of the reduced number density η at several different system sizes for the case $\rho_1/\rho=0.6$ and $\sigma_2/\sigma_1=2$. Here we see that a system as small as $N=300$ is sufficiently large to yield $P_{11}/(r)$ accurately. Beyond the discontinuity which occurs at $r=\sigma_1$, $P_{11}(r)$ decreases monotonically as r increases, as expected. Note that $P_{ij}(r)$ is trivally equal to unity for $r<\sigma_{ij}$.

Displayed in Figs. 2–4 are the functions $P_{11}(r)$, $P_{12}(r)$ and $P_{22}(r)$, respectively, at selected values of η for the case $\rho_1/\rho=0.6$ and $\sigma_2/\sigma_1=2$. Here $N=500$ for $\eta=0.1$, 0.2, and 0.3 and $N=1000$ for $\eta=0.33$. In Figs. 5–7 we depict corresponding plots for the case $\rho_1/\rho=0.2$ and $\sigma_2/\sigma_1=2$.

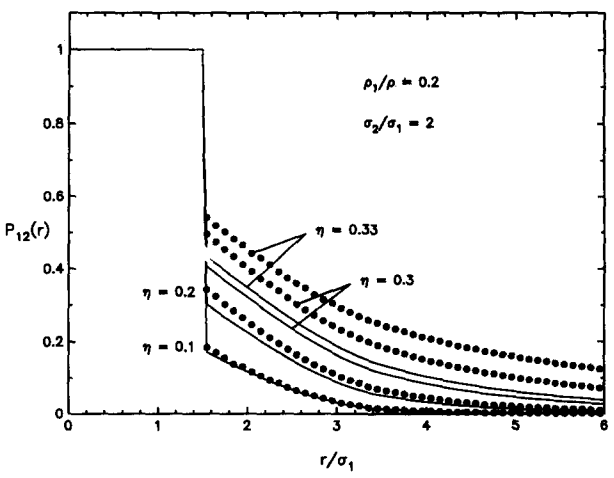

FIG. 6. As in Fig. 5 for the pair-connectedness function $P_{12}(x)$.

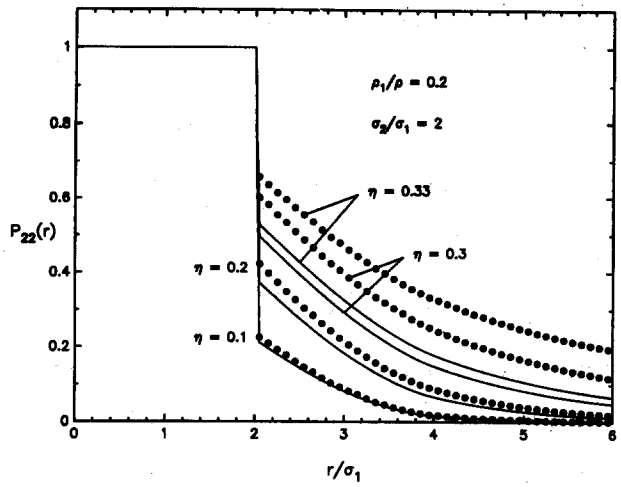

FIG. 7. As in Fig. 5 for the pair-connectedness function $P_{22}(x)$.

Here $N = 1000$. It is seen that $P_{ij}(r)$ at fixed η and σ_2/σ_1 is not very sensitive to changes in the density of species 1. Included in Figs. 2–7 are the Percus–Yevick (PY) theoretical results of Chiew *et al.*[8] Their theoretical results are generated by numerically computing the factorized form of the mixture Ornstein–Zernike equation using the algorithm of Perram.[17] As in the case of monodispersed systems of overlapping spheres, the agreement between our simulations and the PY approximation is generally poor, except at low reduced number densities. As the percolation threshold is approached from below, the PY approximation considerably underestimates $P_{ij}(r)$ and hence significantly overestimates the percolation transition density. This is due to the well-known fact that the PY approximation leaves out important cluster integrals from the exact expression for $P_{ij}(r)$.[1,7,9] However, as shall be shown, the PY approximation does capture another important feature regarding the percolation threshold of such systems.

B. Mean cluster size and percolation threshold

We present results for S as a function of ϕ and estimate ϕ_c for the two bidispersed systems of overlapping spheres (i.e., $\rho_1/\rho = 0.6$, $\sigma_2/\sigma_1 = 2$ and $\rho_2/\rho = 0.2$, $\sigma_2/\sigma_1 = 2$). The data are obtained by extrapolating S^{-1} for various system sizes ($N = 100$, 140, 200, 300, 500, 1000) to the $N^{-1} \to 0$ limit. (Such extrapolations are necessary since, for any finite system, the mean cluster size will be underestimated.) We then estimate ϕ_c by extrapolating these data to $S^{-1} \to 0$ limit. Table I shows our results for S^{-1} as a function of the reduced number density η and of the volume fraction of the particle phase ϕ. The volume fraction ϕ and the reduced number density η are related by Eq. (6). The error bounds given in the table are determined from errors associated with the linear regression. For the two different bidispersions examined here, we find that $\phi_c \simeq 0.32$ which is

TABLE I. The inverse mean cluster size S^{-1} for bidispersed overlapping spheres extrapolated to the $N^{-1} \to 0$ limit. The parameter values for the two cases examined are: (i) $\rho_1/\rho = 0.6$ and $\sigma_2/\sigma_1 = 2$ and (ii) $\rho_1/\rho = 0.2$ and $\sigma_2/\sigma_1 = 2$. The error bounds are determined from the linear regressions. From these data, the critical reduced density η_c is estimated to be 0.38 for both distributions and hence, from Eq. (6), the critical particle volume fraction ϕ_c is estimated to be 0.32.

		S^{-1}	
η	ϕ	$\rho_1/\rho = 0.2$	$\rho_1/\rho = 0.6$
0.10	0.095 16	0.439 17±0.000 65	0.447 69±0.001 00
0.14	0.130 64	0.295 68±0.001 68	0.300 98±0.001 71
0.18	0.164 73	0.188 57±0.001 74	0.186 25±0.000 82
0.22	0.197 48	0.109 37±0.001 48	0.105 96±0.000 59
0.25	0.221 20	0.064 13±0.001 55	0.062 26±0.000 92
0.28	0.244 22	0.031 29±0.000 98	0.032 25±0.001 21
0.30	0.259 18	0.017 51±0.001 19	0.015 85±0.000 69
0.31	0.266 55	0.011 29±0.000 55	0.012 44±0.001 09
0.32	0.273 85	0.007 58±0.000 41	0.010 70±0.000 88
0.33	0.281 08	0.004 50±0.000 52	0.005 71±0.000 60
0.34	0.288 23	0.002 63±0.000 44	0.004 35±0.000 29
0.35	0.295 31	0.001 96±0.000 31	0.002 75±0.000 29
0.36	0.302 32	0.001 12±0.000 24	0.001 73±0.000 17
0.37	0.309 27	0.000 63±0.000 07	0.001 04±0.000 17
0.38	0.316 14	0.000 44±0.000 16	0.000 68±0.000 17

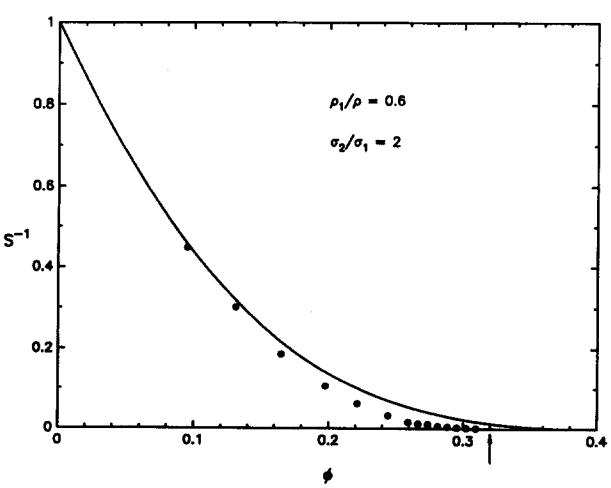

FIG. 8. Mean cluster size S^{-1} for bidispersed overlapping spheres. Here $\rho_1/\rho = 0.6$ and $\sigma_2/\sigma_1 = 2$. The solid line is the PY result. The arrow indicates the percolation threshold.

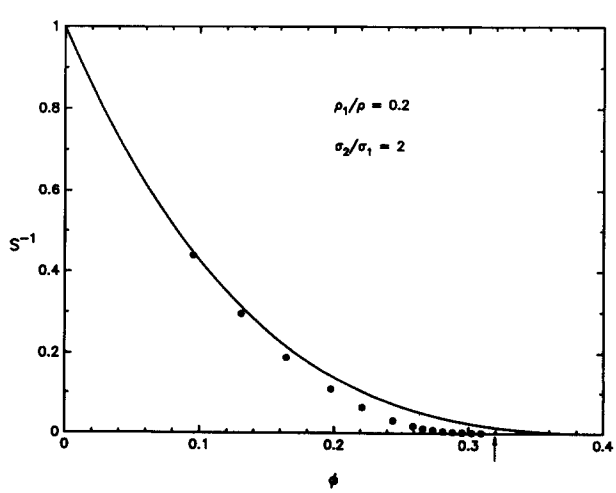

FIG. 9. Mean cluster size S^{-1} for bidispersed overlapping spheres. Here $\rho_1/\rho = 0.2$ and $\sigma_2/\sigma_1 = 2$. The solid line is the PY result. The arrow indicates the percolation threshold.

slightly higher than the value $\phi_c \simeq 0.29$ for monodispersions of overlapping spheres.[2,12,14] This finding is consistent with the Monte Carlo results of Kertesz and Vicsek[5] who find that ϕ_c for *two-dimensional* distributions of overlapping disks with a polydispersity in size is slightly larger than ϕ_c for monodispersed overlapping disks.

In Figs. 8 and 9, our extrapolated results for S^{-1} are plotted versus ϕ and compared with PY approximation which is seen to overestimate S^{-1} or underestimate S. This observation is consistent with the fact that the PY approximation underestimates the pair-connectedness function. At any rate, the PY approximation is known to predict $\phi_c = 0.39$, regardless of the values of ρ_1/ρ and σ_2/σ_1, and hence overestimates the percolation threshold. Nonetheless, the PY approximation does, in fact, appear to capture the important feature that the percolation theshold is not very sensitive to particle size distribution.

The procedure used here to estimate the percolation thresholds has been shown to yield results accurate to within two significant figures.[12,14] More accurate estimates of the thresholds could have been obtained by using the scaling law for the mean cluster size and finite-size scaling analysis.[18] Such an analysis is considerably more complex[19] and will be carried out in a future study.

[1] A. Coniglio, U. DeAngelis, and A. Forlani, J. Phys. A: Math, Nucl. Gen. **10**, 1123 (1977).
[2] S. W. Haan and R. Zwanzig, J. Phys. A: Math, Nucl. Gen. **10**, 1547 (1977).
[3] E. T. Gawlinski and H. E. Stanley, J. Phys. A: Math, Nucl. Gen. **14**, L291 (1981).
[4] A. Coniglio, H. E. Stanley, and Klein, Phys. Rev. B **25**, 6805 (1982).
[5] J. Kertesz and T. Vicsek, Z. Phys. B **45**, 345 (1982).
[6] Y. C. Chiew and E. D. Glandt, J. Phys. A: Math, Nucl. Gen. **16**, 2599 (1983).
[7] G. Stell, J. Phys. A: Math, Nucl. Gen. **17**, L855 (1984).
[8] Y. C. Chiew, G. Stell, and E. D. Glandt, J. Chem. Phys. **83**, 761 (1985).
[9] T. DeSimone, S. Demoulni, and R. M. Stratt, J. Chem. Phys. **85**, 391 (1986).
[10] R. F. Berg, M. R. Moldover, and J. S. Huang, J. Chem. Phys. **87**, 3687 (1987).
[11] N. A. Seaton and E. D. Glandt, J. Chem. Phys. **86**, 4668 (1987).
[12] E. M. Sevick, P. A. Monson, and J. M. Ottino, J. Chem. Phys. **88**, 1198 (1988).
[13] S. Torquato, J. D. Beasley, and Y. C. Chiew, J. Chem. Phys. **88**, 6540 (1988).
[14] S. B. Lee and S. Torquato, J. Chem. Phys. **89**, 6427 (1988).
[15] S. Torquato, Rev. Chem. Eng. **4**, 151 (1987).
[16] J. Hoshen and R. Kopelman, Phys. Rev. B **28**, 5323 (1983).
[17] J. W. Perram, Mol. Phys. **30**, 1505 (1975).
[18] Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).
[19] S. B. Lee and S. Torquato, Phys. Rev. A **41**, 5338 (1990).