Diffusion-controlled cluster formation in two, three, and four dimensions

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Diffusion-controlled cluster formation has been simulated in two-, three-, and four-dimensional space. The radii of gyration (R_g) of the resulting clusters have a power-law dependence on the number of particles in the cluster (N) $R_g = N^{\beta}$. The corresponding Hausdorff dimensionality ($D = 1/\beta$) is related to the Euclidean dimensionality d by the relationship $D \sim \frac{5}{6}d$ for $d = 3$ and 4. For the two-dimensional case we find that D/d has a value about 2% smaller (0.847 ± 0.01). However, a value of $\frac{5}{6}$ (0.833) is only just outside the 95% confidence limits and cannot be completely ruled out. In the two-dimensional simulations β is insensitive to lattice details and in both two- and three-dimensional simulations β is insensitive to the sticking coefficient (S) over the range $1.0 \geq S \geq 0.1$.

INTRODUCTION

The aggregation of small particles to form clusters or flocs is one of the most central problems in colloid science with important implications in a wide range of natural and commercial processes. In addition, the shapes and sizes of clusters near the percolation threshold have become important to our understanding of critical phenomena.[1] In both areas Monte Carlo computer simulations have provided important "experimental" information for comparison with theoretical results and a valuable link between laboratory experiments and theory.

In the 1960s computer simulations of floc formation in colloidal systems were carried out by Vold[2] and Sutherland and co-workers.[3] This early work which did not include the effects of Brownian motion, was reviewed by Medalia.[4] A reasonably complete model of cluster formation in colloidal systems would include the effects of long- and short-range interactions,[5] particle size distribution and irregular shapes, hydrodynamic interactions,[6] clustering of clusters,[3] etc. Because of the complexity of such a model it is important to explore more simple models which contain the most essential elements of the physics of flocculation in real systems. An important step in this direction has recently been made by Witten and Sander.[7]

Witten and Sander start with a single-seed particle at the origin of a lattice. A second particle is added a long distance from the origin and undergoes a random walk on the lattice until it reaches a site adjacent to the seed and becomes part of the growing cluster. A third particle is then introduced at a random distant point and undergoes a random walk until it also becomes incorporated into the growing cluster. The procedure is repeated until a cluster of sufficiently large size is formed.

Witten and Sander[7] showed that the density-density correlation function,

$$C(r) = N^{-1} \sum_{r'} \rho(r')\rho(r+r') \ , \tag{1}$$

obtained in two-dimensional simulations, conformed to a power-law relationship

$$C(r) \sim r^{-\alpha} \tag{2}$$

for distances (r) greater than a few lattice spacings, but significantly less than the size of the cluster. In Eq. (1) the density $\rho(\vec{r})$ at position $\vec{r}$ is defined to be 1 for an occupied site and 0 for an unoccupied site. N is the number of particles in the cluster.

The power-law form of the density-density correlation function [Eq. (3)] is consistent with a fractal[8] (Hausdorff[9]-Besicovitch) dimensionality D_α of $d - \alpha$, where d is the "normal" Euclidean dimensionality of the cluster. The Hausdorff dimensionality can also be obtained from the radius of gyration (R_g) which has a power-law dependence on the number of particles for sufficiently large N:

$$R_g \sim N^{\beta} \ . \tag{3}$$

The Hausdorff dimensionality is given by[10]

$$D_\beta = 1/\beta \ . \tag{4}$$

In this paper the results of computer simulations in two-, three-, and four-dimensional space are presented including some aspects of universality in two- and three-dimensional clusters. Since it has not been possible to generate large enough clusters in three and four dimensions to evaluate the density-density correlation function $C(r)$ over a range of distances

which are both larger than a few lattice spacings and significantly smaller than the "size" of the cluster, we have relied mainly on the radius of gyration to obtain the Hausdorff dimensionality of the cluster. Simulations for clusters of different sizes indicate that the radius of gyration exponent β is much less sensitive to finite-size effects than attempts to obtain the correlation function exponent α.

Two-dimensional simulations

The simulation methods are very similar to those described by Witten and Sander.[7] Since a particle undergoing a random walk starting from a point a large distance from the cluster will intersect a circle enclosing the cluster, for the first time, at a point at random on the circle, we start the particle out at a random point on a circle centered on the "seed" particle with a radius slightly (about five lattice spacings) greater than the distance from the seed to the most distant particle in the cluster (the maximum radius of the cluster). If the particle reaches a point more than three times the maximum radius of the cluster from the origin, it is "killed" and a new particle is started. In the three- and four-dimensional calculations the particle is "killed" if it reaches a point more than two times the maximum radius of the cluster from the origin. A more detailed account of our simulation procedures is planned to be be published later.

Most of the two-dimensional simulations were carried out using a simple square lattice. Six large clusters were generated assuming that the randomly walking particle was incorporated into the cluster every time it reached a nearest-neighbor position. (Each step in the random walk consisted of transferring the particle to one of the four nearest-neighbor positions with respect to the particle.) The density-density correlation function exponent (α) was obtained from $C(r)$ for $5 \leq r \leq 50$ (lattice spacings) for clusters of maximum radius 200 lattice units. The radius of gyration exponent (β) was obtained using the dependence of R_g on N for $0.1N_{\max} \leq N \leq N_{\max}$, where $N_{\max}$ is the maximum number of particles in the cluster. From these six clusters (average size, 9700 particles per cluster) a radius of gyration exponent (β) of 0.595 ± 0.016 was obtained.[11] For four of these clusters a correlation function exponent α of 0.32 ± 0.07 was also obtained. The corresponding Hausdorff dimensionalities are $D_\beta = 1.68 \pm 0.04$ and $D_\alpha = 1.68 \pm 0.07$. These results are in quite good agreement with those of Witten and Sander,[7] but our estimate of uncertainties is much greater despite the fact that our clusters are considerably larger than those of Witten and Sander.

Four clusters (average size, 5900 particles per cluster) were generated in which the particle was incorporated into the growing cluster if it reached a next-nearest-neighbor (NNN) position but was not incorporated if it reached a nearest-neighbor (NN) position. From these four simulations the exponents $\alpha = 0.306 \pm 0.069$, $\beta = 0.589 \pm 0.024$, and the corresponding Hausdorff dimensionalities $D_\alpha = 1.69 \pm 0.07$, $D_\beta = 1.70 \pm 0.07$ were obtained.

The effects of sticking probability were also investigated. Three clusters (average size, 16 300 particles per cluster) were generated in a simulation with a sticking probability of 0.25 at a nearest-neighbor site. The resulting clusters were analyzed giving $\alpha = 0.292 \pm 0.055$, $\beta = 0.579 \pm 0.045$, $D_\alpha = 1.71 \pm 0.055$, and $D_\beta = 1.73 \pm 0.13$. Similar calculations were carried out for NNN capture with a sticking probability of 0.1. The resulting exponents and the corresponding Hausdorff dimensionalities for three clusters with an average of 9800 particles were $\alpha = 0.258 \pm 0.027$, $\beta = 0.577 \pm 0.015$, $D_\alpha = 1.74 \pm 0.03$, and $D_\beta = 1.73 \pm 0.04$.

Two-dimensional simulations were also carried out for a nonlattice model. In this case a step in the random walk consisted of moving the center of a circular "particle" at random to any point in a circle of radius equal to that of the particle. If the "step" causes the particle to overlap the cluster, the particle is moved to the position where it first contacted the cluster and incorporated into the cluster. Three clusters with an average of 8700 particles each were generated leading to the results $\alpha = 0.322 \pm 0.058$, $\beta = 0.584 \pm 0.018$, $D_\alpha = 1.68 \pm 0.06$, and $D_\beta = 1.71 \pm 0.05$.

Figure 1 shows a typical cluster of 10 000 particles obtained in one of the nonlattice simulations, and Fig. 2 shows a plot of the radius of gyration as a function of the number of particles for one of these clusters.

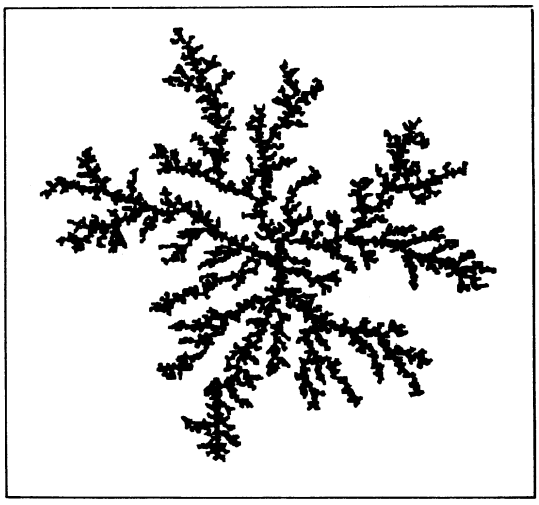

FIG. 1. A two-dimensional cluster of 10 000 particles produced in a simulation of diffusion-controlled cluster formation. No lattice was used in this simulation.

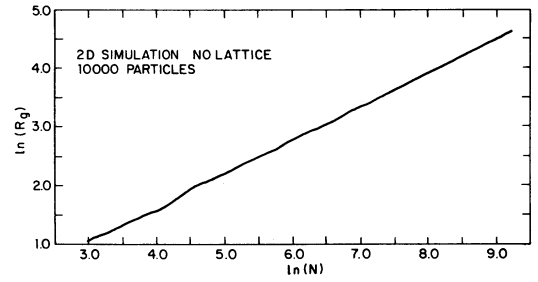

FIG. 2. The radius of gyration as a function of the number of particles obtained during the simulation of the cluster shown in Fig. 1. The last 9000 points can be fitted by $R_g = 0.498N^{0.576}$ with a Pearson product moment correlation of 0.99993.

Clusters grown on three-dimensional cubic lattices

In the three-dimensional simulations clusters were grown until one of the surfaces of a $91 \times 91 \times 91$ simple-cubic lattice was reached. Figure 3 shows projections in three mutually perpendicular directions and a cross section through one such cluster. For a sticking coefficient of 1.0 at nearest-neighbor sites, 11 clusters with an average of 7800 particles per cluster were grown. Attempts to obtain the exponent for the correlation function α indicated that α was sensitive to finite-size effects even for clusters of 5000–10000 particles. Consequently, the Hausdorff dimensionality was obtained from the radius of gyration (R_g) alone. The dependence of R_g on N was analyzed over the range $0.25N_{max} \leq N \leq N_{max}$. From the 11 clusters, β was found to have the value 0.398 ± 0.009. The corresponding Hausdorff dimensionality is 2.51 ± 0.06. Three clusters were also simulated with a sticking coefficient of 0.25. From these three clusters with an average of 11400 particles each, the result $\beta = 0.398 \pm 0.041$ ($D_\beta = 2.51 \pm 0.26$) was obtained.

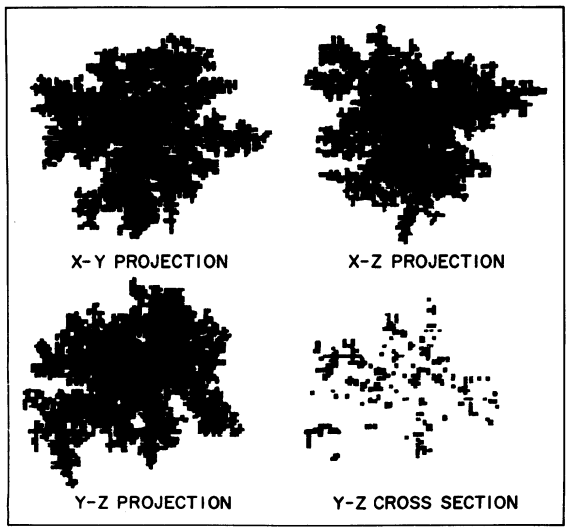

FIG. 3. Three perpendicular projections and a cross section through a typical cluster of 10000 particles formed in a three-dimensional simulation.

Four-dimensional clusters

Similar calculations were carried out using a four-dimensional hypercubic lattice. For 15 clusters with an average of 1600 particles per cluster the result $\beta = 0.304 \pm 0.011$ ($D_\beta = 3.29 \pm 0.12$) was obtained. Somewhat larger clusters could be grown by storing only the coordinates of occupied lattice sites in the computer. Three clusters with 5000 particles each were generated in this way. The radius of gyration exponents (β) obtained from these three clusters had the value $\beta = 0.292 \pm 0.03$ corresponding to a Hausdorff dimensionality of 3.42 ± 0.45. By combining all of our four-dimensional clusters the result $\beta = 0.301 \pm 0.009$, $D_\beta = 3.32 \pm 0.10$ was obtained.

DISCUSSION

One of the most interesting aspects of these simulations is the relationship between the Hausdorff dimensionality D and the Euclidean dimensionality d. For a sticking probability of 1.0 at nearest-neighbor positions, we find $D/d = 0.840 \pm 0.02$ for $d = 2$, $D/d = 0.835 \pm 0.02$ for $d = 3$, and $D/d = 0.830 \pm 0.025$ for $d = 4$. *Preliminary* calculation on a five-dimensional lattice indicates that $R_g \sim N^\beta (\beta \sim 0.24)$. This implies $D/d \sim 0.83$ ($\frac{5}{6}$) for $d = 5$. Calculations are also being carried out using a six-dimensional lattice model. The observation that the Hausdorff dimensionality is independent of lattice details (and independent of whether a lattice is used or not) is not surprising. However, the result that the Hausdorff dimensionality is insensitive to the sticking coefficient (over the range $1.0 \geq S \geq 0.1$) was not anticipated.

In carrying out these simulations we have generated the largest clusters which were practical on our VAX 11-780 computer. Nevertheless, the variability in the results obtained from calculation to calculation was surprisingly large. This may be related to the fact that the calculations described here can be regarded as a simulation of the dendritic growth instability in the limit where fluctuations are dominant.[7,12] Regions of the cluster near the perimeter "shield" the inner portions of the cluster and grow preferentially. Fluctuations in the cluster perimeter are enhanced by the diffusion-controlled growth mechanism and tend to be amplified. For this reason the shape of the cluster at late stages is strongly dependent on the shape at much earlier stages. This is il-

lustrated in Fig. 1 which shows a typical cluster formed by diffusion-controlled aggregation.

If all two-dimensional clusters grown with a sticking probability of 1.0 are included the result $\beta = 0.590 \pm 0.008$, $D_\beta = 1.69 \pm 0.02$ is obtained.

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