Formation of Fractal Clusters and Networks by Irreversible Diffusion-Limited Aggregation

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(Received 21 June 1983)

A model for diffusion-controlled aggregation in which growing clusters as well as individual particles are mobile has been investigated. Two versions of the model in which the cluster diffusion coefficient is either size independent or inversely proportional to number of particles (mass) give very similar results. In the limit of low concentration and large system size both models lead to structures with a fractal (Hausdorff) dimensionality of about 1.45–1.5 in two-dimensional lattice-based simulations.

PACS numbers: 05.40.+j, 64.60.Cn, 82.70.Dd

Witten and Sander[1] have recently developed a model for diffusion-limited aggregation which produces complex random dendritic structures. Numerical simulations using the Witten-Sander (WS) model indicate that these structures have remarkable scaling and universality properties.[1,2] In particular, the fractal[3] (Hausdorff[4]-Besicovitch) dimensionality D is distinctly smaller than the ordinary Euclidean dimensionality d (for $d = 2$, $D \approx \frac{5}{3}$).

These results have stimulated considerable theoretical[5-10] and experimental interest in diffusion-limited aggregation and other growth processes. The Witten-Sander model provides a basis for obtaining a better understanding of a variety of diffusion-limited processes such as random dendritic growth and the flocculation of colloidal systems. In the original Witten-Sander model all growth originates from a single immobile growth site and only one particle is allowed in the vicinity of the growing cluster at any time. These features are unrealistic for many real colloidal systems.

In this paper, I investigate a related model in which clusters of particles as well as single particles are allowed to "diffuse" and in which clusters of all sizes (including single particles) stick together on contact.

The two-dimensional simulations are carried out on a simple square lattice with periodic boundary conditions. At the start of the simulation, a fraction (ρ) of the lattice sites are picked at random and occupied (avoiding multiple occupancy). Sites (particles) at nearest-neighbor positions are considered to belong to the same cluster. Clusters (including single-particle clusters) are then picked at random and moved with a probability proportional to their "mobility" by one lattice spacing in one of four equally probable directions ($\pm x$, $\pm y$ also picked at random). If a cluster contacts other clusters (via nearest-neighbor occupancy), the contacting clusters are "merged" to form a single cluster. In this manner, the clusters grow larger and larger until only one large cluster remains. Two simple versions of the model have been investigated; in model A the cluster mobility is the same for all clusters and in model B the mobility is inversely proportional to the size (number of occupied sites) of the cluster. Other models which may be more relevant to specific physical systems could easily be implemented.

Figure 1 shows the final stage for several simulations carried out with a constant (mass-independent) mobility on 400×400 lattices. The densities are 0.0625 [Fig. 1(a)], 0.093 75 [Fig. 1(b)], 0.125 [Fig. 1(c)], and 0.156 particle per lattice site [Fig. 1(d)]. Density-density correlation functions obtained from these simulations are shown in Fig. 2 in the form of log-log plots. At short distances the plots of $\ln[C(r)]$ vs $\ln(r)$ are essentially linear with a slope which appears to approach a value of about $-\frac{1}{2}$ in the limit of low initial particle concentrations.

For a structure with a fractal[3] (Hausdorff[4]) dimensionality of D and a Euclidean dimensionality of d, we expect that the density-density correlation function $[C(r)]$ will have the form $C(r) \sim r^{-\alpha}$ where the exponent α is given by $\alpha = d - D$, i.e., α is the Hausdorff codimension. Many structures have a fractal geometry over a limited range of length scales with "cutoffs" at long and/or short lengths.[3] In this case, it appears that the lower cutoff length is a few lattice units and the upper cutoff length is determined by the average particle density $\langle\rho\rangle$. In other words there is a crossover from a fractal structure ($\alpha \approx -\frac{1}{2}$) on short length scales to a structure with uniform density

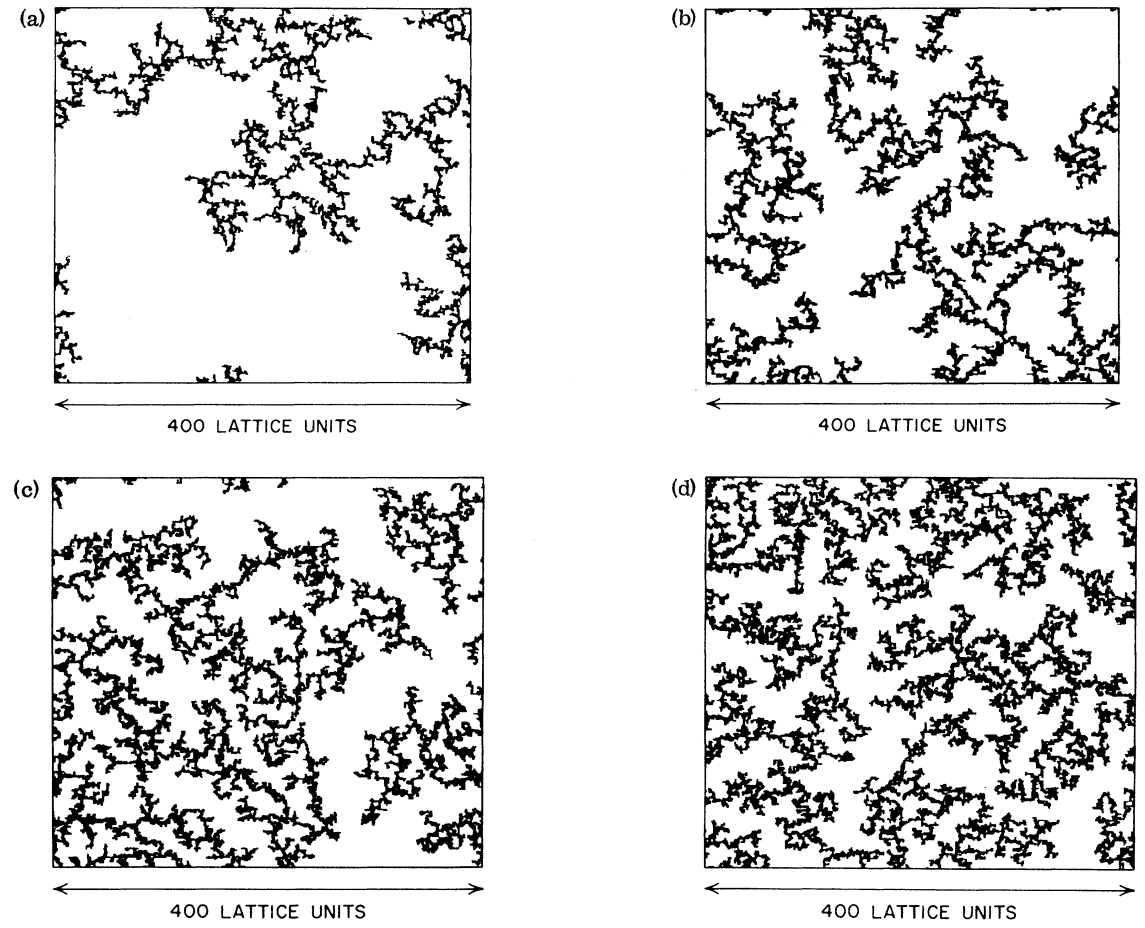

FIG. 1. The final stage of simulations carried out with a size-independent diffusion coefficient on a 400×400 lattice. In (a) the cluster contains 10 000 particles ($\rho = 0.0625$ particle per lattice site); for (b), $N = 15\,000$ ($\rho = 0.093\,75$); for (c), $N = 20\,000$ ($\rho = 0.125$); and for (d), $N = 25\,000$ ($\rho = 0.156\,25$).

on long length scales ($\alpha = 0$) with a crossover length l given by

$$C_0 l^{-\alpha} \approx \langle\rho\rangle \text{ or } l \approx (\langle\rho\rangle/C_0)^{-1/\alpha},$$

where $C_0 \approx 1.0$. As $\langle\rho\rangle \to 0$, $l \to \infty$ and the resulting structures have a fractal geometry on essentially all length scales, if the present picture is correct.

In addition to the simulations used to obtain the results shown in Figs. 1 and 2, simulations have also been carried out at a lower concentration (5000 particles on a 400×400 lattice or $\rho = 0.031\,25$). From seven such simulations I find that $\alpha = 0.516\pm0.029$[11] ($1 \leq r \leq 25$ lattice units), $\alpha = 0.530 \pm 0.033$ ($5 \leq r \leq 25$), $\alpha = 0.491 \pm 0.009$ ($1 \leq r \leq 5$), and $\alpha = 0.524 \pm 0.028$ ($2 \leq r \leq 20$). A summary of these results is shown in Fig. 3.

Results very similar to those shown in Figs. 1 and 2 were obtained from simulations in which the cluster diffusion coefficient was inversely proportional to the cluster size (number of particles in the cluster). Figure 3 shows the density-density correlation function obtained from simulations carried out at a density of 0.031 25 particle per lattice site on a 400×400 lattice. The results shown in this figure represent the average of seven simulations. The Hausdorff codimension α is $\alpha = 0.519\pm0.014$ ($1 \leq r \leq 25$ lattice units), $\alpha = 0.519\pm0.037$ ($5 \leq r \leq 25$), $\alpha = 0.493 \pm 0.018$ ($1 \leq r \leq 5$), and $\alpha = 0.531\pm0.013$ ($2 \leq r \leq 20$). From these results I conclude that the limiting (low-density) Hausdorff dimensionality is 1.45–1.5 for both versions of the model. In Fig. 2 the dashed line with a slope of $-\frac{1}{3}$ represents the behavior expected for a very large object with a fractal dimensionality of (about) $\frac{5}{3}$ (such as a WS cluster). The dashed line with a slope of $-\frac{1}{2}$ represents the limiting (low-density,

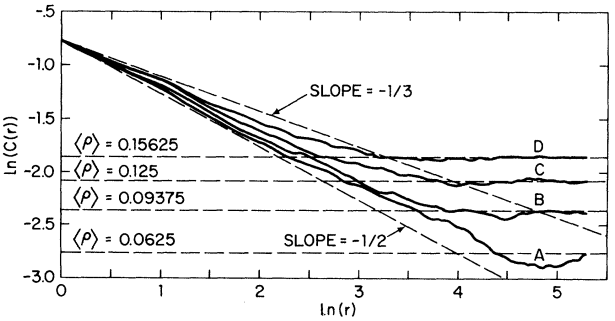

FIG. 2. The density-density correlation functions obtained from the structures shown in Fig. 1. Curve *A* is obtained from Fig. 1(a), curve *B* from Fig. 1(b), etc.

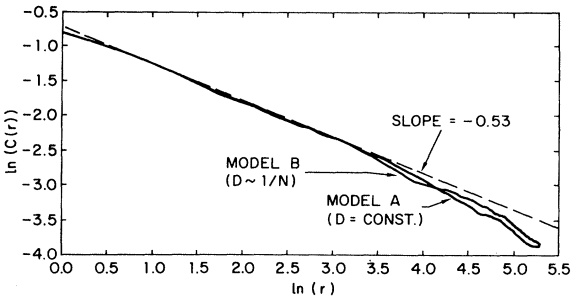

FIG. 3. Density-density correlation functions obtained from the final (single-cluster) stage of aggregation in simulations carried out at a density of 0.031 25 particle per lattice site. Curve *A* was obtained from model A (size-independent diffusion coefficient) and curve *B* from model B (diffusion coefficient proportional to 1/mass). Both curves represent the average of seven simulations carried out with 5 000 particles on 400×400 lattices. The dashed line has a slope of -0.53 and represents the correlation functions for a structure with a Hausdorff dimensionality of 1.47 on all length scales. The deviation of the correlation functions from the dashed line at large distances (r) is due to finite-size effects.

large-size) behavior suggested by our results. The fractal dimensionality has also been estimated from the dependence of the cluster radius of gyration R_g on cluster size N from the relationship $R_g \sim N^{1/D}$. Results obtained from fitting a straight line to the dependence of $\ln(R_g)$ on $\ln(N)$ for intermediate clusters formed during the course of the simulations described above indicate that $D \approx 1.4$–1.5 for both models A and B.

A few simulations have also been carried out with other similar models. If only the *smallest* cluster(s) are allowed to move, results very similar to those obtained with models A and B (above) were obtained ($D \approx 1.5$ in the small concentration limit). In this model, single particles are removed during the early stages of the simulation and the smallest clusters become doublets which in turn are rapidly removed leaving only larger clusters in the system. If only the *largest* cluster is allowed to move the model becomes equivalent to the Witten-Sander model of diffusion-limited aggregation in the limit $\rho \to 0$ (i.e., $D \approx \frac{5}{3}$ for $d = 2$). If ρ is finite a crossover from $D \approx \frac{5}{3}$ on short length scales to $D \approx 2.0$ on long length scales is observed. This crossover effect is similar to that found with models A and B. Similar behavior has also been observed in computer simulations using a modified Witten-Sander model[12] and has been predicted theoretically by Nauenberg, Richter, and Sander[10] for large aggregates grown at a finite density of diffusing particles.

The fractal dimensionalities of the structures generated using these models are distinctly different from the dimensionalities of most other random structures in two dimensions such as percolation clusters at the percolation threshold ($D \approx 1.9$),[13] self-avoiding random walks ($D \approx 1.33$),[14,15] and Witten-Sander clusters ($D \approx 1.67$).[1] However, two-dimensional lattice animals do have a fractal dimensionality which is quite close (≈ 1.56).[16]

The models described in this paper seem to have the same sort of universality properties as the WS model[1,2] of diffusion-limited aggregates. The fractal dimensionality is insensitive to the sticking probability and the effective dimensionality obtained from a nonlattice version of the model[17] is equal to that obtained from the lattice models described above (within the accuracy of the simulations). I am presently in the process of carrying out very similar simulations using three-dimensional lattices and related nonlattice simulations in two and three dimensions. The model described in this paper includes translational but no rotational diffusion. A nonlattice model will allow both effects to be included. Sutherland and Goodarz-Nia[18] have investigated three-dimensional nonlattice models in which clusters aggregate via linear (rather than Brownian) trajectories. Their results may be interpreted in terms of an effective dimensionality of about 1.85. Using a two-dimensional version of the Sutherland–Goodarz-Nia model, I have generated fractal aggregates with a dimensionality similar to that associated with the present model.

The process(es) simulated in this paper are closely related to spinodal decomposition with

very deep quenches. Under these conditions Heerman and Klein[19] have found evidence that nucleating droplets formed during Monte Carlo simulations of nucleation and growth in Ising systems with Glauber dynamics have noncompact (fractal) structures during the initial stages of growth.

The model described in this paper has been discussed with many colleagues during the past year or so. The author would like to thank them for their suggestions and encouragement. In particular helpful discussions with T. A. Witten are acknowledged.

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