Diffusion-Limited Aggregation, a Kinetic Critical Phenomenon

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A model for random aggregates is studied by computer simulation. The model is applicable to a metal-particle aggregation process whose correlations have been measured previously. Density correlations within the model aggregates fall off with distance with a fractional power law, like those of the metal aggregates. The radius of gyration of the model aggregates has power-law behavior. The model is a limit of a model of dendritic growth.

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Gold black, Cab-o-Sil™, and coagulated aerosols[1] are aggregates of solid particles distinguished by their wispy appearance. The size of these aggregates far exceeds the range of forces holding them together[2]; it seems likely that the aggregation process can be understood without reference to the details of these forces. A class of aggregates were shown by Forrest and Witten[3] to have density correlations of a power-law form. We show here that the formation conditions of these objects suggest a model which we simulate on a computer; the model is a discrete version of dendritic growth.[4] The simulation produces model aggregates which also have power-law correlations. We compare the behavior of the model to other models which produce low-density object: the Eden growth model,[5] random animals,[6] self-avoiding walks,[6] and percolating clusters.[5,7]

The aggregates which were studied by Forrest and Witten[3,8] were formed when a metal vapor produced by heating a plated filament was quench condensed. Metal particles of average radius 40 Å condensed near the filament and streamed outward. The particles accumulated in a thin spherical shell (the "puff ball") of roughly a centimeter radius. In this region the particles are thought to coalesce. Then they drifted down to an electron microscope slide. The aggregates found on the slides contained on the order of 10^5 metal particles in a low-density mass. The particles appeared to coalesce *irreversibly* to form the aggregates, since these maintained their wispy shape even after drifting through the gas. We suppose that two particles in the puff ball stick together whenever their thermal motion brings them into contact.

The simplest model for the growth of such a cluster of particles is the Eden model,[5] a lattice model in which particles are added one at a time at random to sites adjacent to occupied sites. This process produces a relatively compact cluster whose density correlations are independent of distance in the limit of large size. The metal aggregates, by contrast, were reported[3] to have correlations which fall off as a fractional power of distance. Thus they resemble random walks, percolating clusters, and other density profiles associated with critical phenomena.[5-7] We present here a model for the observed aggregation which also exhibits fractional power-law behavior of the correlation function.

Our model is a variant of the Eden model whose initial state is a seed particle at the origin of a lattice. A second particle is added at some random site at large distance from the origin. This particle walks randomly until it visits a site adjacent to the seed. Then the walking particle becomes part of the cluster. Another particle is now introduced at a random distant point, and it walks randomly until it joins the cluster, and so forth. If a particle touches the boundaries of the lattice in its random walk it is removed and another introduced. A similar process was studied by Rosenstock and Marquardt.[9] The exposed ends of our clusters tend to grow more rapidly than other perimeter sites because perimeter sites near the center are "shadowed"; our aggregates should be less compact than the Eden clusters.

Figure 1 shows a 3600-particle aggregate on a square lattice. Aggregates on a triangular lattice have the same general appearance. One may obtain information about the particle distribution from the density correlation function. The density $\rho(\vec{r})$ is defined to be 1 for the occupied sites

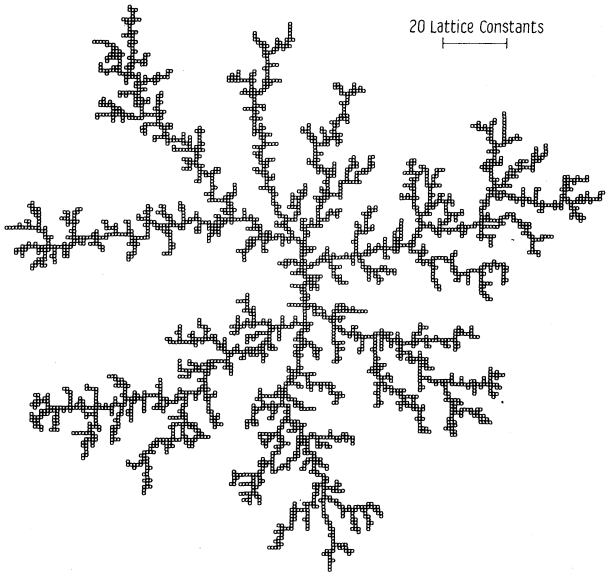

FIG. 1. Random aggregate of 3600 particles on a square lattice.

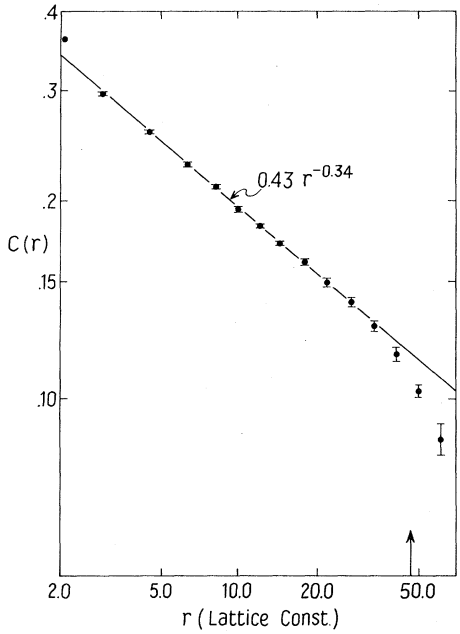

FIG. 2. The density correlation function averaged over six aggregates as a function of distance measured in lattice constants. The arrow marks the average radius of gyration. The solid line is a least-squares fit over the range $r=3$ to $r=27$. The error bars represent the spread of values among the six aggregates.

and 0 for the others. The correlation function in an N-particle aggregate,

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

is an approximation to the ensemble average correlation function $\langle\rho(\vec{r}')\rho(\vec{r}'+\vec{r})\rangle/\langle\rho(\vec{r}')\rangle$. This function is assumed to depend only on the distance r separating the two sites. Of course, this can only be true for r much less than the size of the aggregate. Figure 2 shows $C(r)$ averaged over directions and over six aggregates of roughly 3000 particles. It is clear from the fitted line that the data are consistent with a power law over distances from a few lattice spacings to the size of the cluster:

$$C(r)\sim r^{-0.343\pm0.004}. \tag{2}$$

The same exponent describes clusters on a triangular lattice; see Table I.

To check our computations we have measured[3] $C(r)$ for a certain Koch curve, a geometric construction which is a Hausdorff set with a Hausdorff dimension[10] D of $\ln3/\ln2 = 1.585$. One expects the density of points in a Hausdorff set to have correlations of the form

$$\langle\rho(\vec{r}')\rho(\vec{r}'+\vec{r})\rangle\sim r^{D-d}\equiv r^{-A}. \tag{3}$$

By definition, a Hausdorff set can be covered by a number of neighborhoods of radius a, $K(a)$, which varies as a^{-D}. The average number of points $N(a)$ within such a neighborhood must then vary as a^D. Assuming that the neighborhoods may be chosen with arbitrary centers, one may relate the behavior of $N(a)$ to that of the correlations:

$$a^D\sim N(a)=\int_0^a d^dr\langle\rho(\vec{r})\rangle_{\text{origin occupied}}$$
$$=\int_0^a d^dr\langle\rho(\vec{r})\rho(0)\rangle/\langle\rho(0)\rangle, \tag{4}$$

where d is the dimension of space. To yield this behavior the correlation function must obey Eq. (3).

To test the accuracy of our sampling procedure we generated images of the Koch curve and analyzed them with the same program used for the model aggregates. The resulting power-law fit confirms Eq. (3) as reported in Table I.

For the Koch curves and the model aggregates the measured $C(r)$ fall below the power-law line as r becomes comparable to the size of the aggregate. At short distances r the correlations of the model aggregates also differ from the power-law prediction. We believe this is a nonuniversal feature associated with the lattice.

The size R of a model aggregate should scale with the number of particles. Indeed, for neighborhoods of radius of order R, the contents $N(R)$

TABLE I. Values of the correlation exponent A for diffusion-limited aggregation model and other systems.

	A	
	Two dimensions	Three dimensions
Diffusion-limited aggregation:		
Square lattice, average of six clusters of 2079–3609 particles in size (Fig. 2).	0.343 ± 0.004[a]	
Triangular lattice, average of three clusters of 1500–2997 particles.	0.327 ± 0.01[a]	
Radius of gyration, weighted average of A values inferred for six clusters of 999–3000 particles, Eq. (5).	0.299 ± 0.02[a]	
Koch curve with $A = 2D = 0.416$, measured average correlation function of seven curves, translated and rotated at random.	0.42	
Metal-particle aggregates, correlations of particle density from micrographs, Ref. 3.	0.32 ± 0.01[b]	1.32 ± 0.01[c]
Self-avoiding walk (flight), correlations of step density, Ref. 6.	0.667	1.33
Percolation, from radius of gyration of clusters at threshold, Eq. (5), Refs. 5 and 7.	~ 0.2	0.9
Random animals from radius of gyration, Eq. (5), Ref. 5.	0.46	1.18

[a]Error range indicates statistical error only.
[b]Here we interpret the measured two-dimensional density literally.
[c]Here we interpret the measured density profile as the two-dimensional projection of a three-dimensional profile and infer the A value for the three-dimensional density.

must approach N. Since $N(a) \sim a^D$ for $a \lesssim R$, we expect

$$N \sim R^D = R^{d-A}. \tag{5}$$

Measurements of the radii of gyration of our aggregates support this prediction, as indicated in Table I.

Figure 2 suggests[3] that our model aggregates are "critical" objects, having scale-independent correlations over an arbitrarily large range of distances. They are thus akin to self-avoiding walks, percolating clusters and order-parameter fluctuations near a phase transition. But in an important respect the model is different: The critical correlations here do not arise from an equilibrium ensemble but from an irreversible growth process. Indeed, our model is the discrete counterpart of the dendritic growth model of Langer and Muller-Krumbhaar.[4] In this continuum model a substance (e.g., one species in a two-component solution) diffuses from infinity to an absorbing surface. The density $u(\vec{r},t)$ of the substance is constant on the surface (neglecting surface-tension effects) and zero at infinity. The rate of growth of the surface at r is proportional to the flux density ∇u there.

In our model the probability that a perimeter site at $\vec{x}$ gains a particle at step n of the walk may also be expressed as a gradient of a quantity $u(\vec{r},n)$, which gives the probability (in the ensemble of all random walks of length n) that there is an nth step and that it is at $\vec{r}$. The probability $u(\vec{r},n)$ is proportional to the number of walks, $Z_n(\vec{r})$ arriving at $\vec{r}$ in n steps. This $Z_n(\vec{r})$ satisfies the relation

$$Z_{n+1}(\vec{r}) = \sum_{\alpha=1}^{c} Z_n(\vec{r}+\vec{\alpha}), \tag{6}$$

where $\vec{\alpha}$ is one of the "c" nearest-neighbor vectors. To obtain the number of walks which have not visited perimeter sites $\vec{x}$, one sets $Z_n(\vec{x}) = 0$

on the right side of Eq. (6), for these sites. This equation for Z_n implies a discrete diffusion equation for $u(\vec{r},n)=Z_n(\vec{r})/c^n$:

$$u(\vec{r},n+1)-u(\vec{r},n) = c^{-1}\sum_{\alpha=1}^{c}[u((\vec{r}+\vec{\alpha}),n)-u(\vec{r},n)], \quad (7)$$

with the boundary condition that $u=0$ on perimeter sites. The left side of Eq. (7) is a discrete derivative in n and the right-hand side is the discrete Laplacian operator. The probability $v_{n+1}(\vec{x})$ that the perimeter site at $\vec{x}$ grows in the $(n+1)$th step is

$$v_{n+1}(\vec{x}) = \sum_{\alpha=1}^{c} u_n(\vec{x}+\vec{\alpha})/c = c^{-1}\sum_{\alpha=1}^{c}[u((\vec{x}+\vec{\alpha}),n)-u(\vec{x},n)]. \quad (8)$$

This is a discrete gradient at $\vec{x}$. Thus our model is a discrete version of the dendritic growth model described above.

In the study of this system by Langer and Muller-Krumbhaar,[4] they discovered that a smooth interface is unstable against wrinkling at all length scales; its growth depends on fluctuations in the diffusing field. Our findings describe the limit where these fluctuations are dominant.

The Monte Carlo study reported here may be extended to three or higher dimensions. We can study the effects of extending the size of the seed to simulate a finite tip radius of a dendrite. Realistic dendritic growth with surface tension can be simulated by making the sticking probability of particles smaller or larger for perimeter sites with fewer or more neighbors. Finally, the model can be used to predict the time-dependent growth rate of real random aggregates, as well as their mechanical and transport properties. The predicted features may appear in many processes, including gelation, condensation polymerization, and agglutination of biological molecules.

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[1]S. K. Friedlander, *Smoke, Dust, and Haze* (Wiley, New York, 1977).

[2]We neglect long-range electrostatic and magnetic forces.

[3]S. R. Forrest and T. A. Witten, Jr., J. Phys. A 12, L109 (1979).

[4]J. S. Langer and H. Muller-Krumbhaar, Acta Metall. 26, 1081, 1689 (1978); H. Muller-Krumbhaar and J. S. Langer, Acta Metall. 26, 1697 (1978).

[5]H. P. Peters, D. Stauffer, H. P. Hölters, and K. Loewenich, Z. Phys. B 34, 399 (1979).

[6]D. S. McKenzie, Phys. Rep. 27C, 37 (1976).

[7]H. E. Stanley, J. Phys. A 10, L211 (1977).

[8]S. Forrest, thesis, University of Michigan, 1979 (unpublished).

[9]H. B. Rosenstock and C. L. Marquardt, Phys. Rev. B 22, 5797 (1980). See also Z. Alexandrowicz, Phys. Lett. 80A, 284 (1980); P. Manneville and L. de Seze, to be published.

[10]B. Mandelbrot, *Fractals, Form, Chance, and Dimension* (Freeman, San Francisco, 1977).

Spontaneous Decay of High-Frequency Acoustic Phonons in CaF_2

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The decay of high-frequency acoustic phonons in CaF_2 at low crystal temperature is studied with use of an optical technique of tunable phonon detection. A strongly frequency-dependent lifetime is found for phonons at frequencies $\nu > 10^{12}$ Hz. The lifetime decreases proportionally to ν^{-5}, indicating spontaneous phonon decay by anharmonic three-phonon processes. These results suggest that nonlinear elasticity theory is applicable to describe anharmonic interactions of high-frequency acoustic phonons.

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Anharmonic lifetimes of high-frequency acoustic phonons at low crystal temperature were first studied by Slonimskii[1] using nonlinear elasticity theory. He performed calculations for an isotropic dispersionless solid, which has a longitudinal phonon branch and a degenerate transverse pho-

