Self-Similarity of Diffusion-Limited Aggregates and Electrodeposition Clusters

F. Argoul, A. Arneodo, and G. Grasseau
Centre de Recherche Paul Pascal, Domaine Universitaire, 33405 Talence CEDEX, France

Harry L. Swinney
Department of Physics and the Center for Nonlinear Dynamics,
The University of Texas, Austin, Texas 78712
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We report experimental evidence indicating that two-dimensional zinc electrodeposition clusters in the limit of small ionic concentration and small voltage are self-similar with generalized dimensions $D_q = 1.66 \pm 0.08$. Small-mass clusters obtained in a numerical simulation of diffusion-limited aggregation in a strip geometry are also found to be self-similar, with $D_q = 1.60 \pm 0.02$. These results suggest that electrodeposition and diffusion-limited clusters have a similar geometrical structure.

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The fundamental and practical importance of diffusion-limited growth processes has motivated extensive experimental, numerical, and theoretical studies in the past few years.[1] Electrochemical metallic deposition[2] is particularly well suited for studies of the transition from directional to "random" growth phenomena since one can vary independently two parameters, the concentration of metal ions and the cathode potential.

Experimental studies[3] of fractal properties of electrochemically deposited two-dimensional metallic aggregates have yielded values of the fractal dimension D_0 varying from 1.66 ± 0.03 [3a] to 1.75 ± 0.03.[3b] This variation could be a consequence of the narrow range of length scales available in the experiments; however, a similar range of dimension values has also been obtained in numerical studies of diffusion-limited aggregation (DLA).[4] Witten and Sander[4] found that the dynamical dimension D_d describing the dependence of the weight of a cluster (number of occupied sites) on its average radius of gyration *during the growth process* was 1.70 ± 0.02,

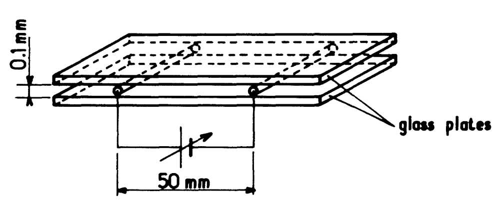

FIG. 1. The system consists of two parallel zinc electrodes (0.1-mm diam) separated by a distance of 50 mm and contained between two glass plates ($100 \times 25 \times 1$ mm^3). The space between the electrodes is filled by capillarity with an aqueous solution of $ZnSO_4$ ($0.15M$). A constant potential of 12 V is imposed across the electrodes. The system is illuminated with white light from below and photographed (at intervals of 20 s) from above with a 35-mm camera (magnification from $1\times$ to $10\times$).

while the dimension D_2 extracted from the density-density correlation function of the cluster *at the end of the growth* was smaller, 1.66 ± 0.01. Subsequent numerical simulations[5] have corroborated the result that D_d is larger than D_2.

We compute not only the fractal dimension D_0 and the correlation dimension D_2 (as in previous work[3,6]) but also the whole spectrum of generalized dimensions,[7] D_q, and we find that within the uncertainties the D_q are the same. We first consider aggregates generated by electrodeposition of zinc in the apparatus shown in Fig. 1. We consider here only a highly ramified cluster, obtained in the asymptotic limit of low voltage and low zinc sulfate concentration. Zinc trees grow in the cathode for 10 to 15 min without any abrupt change in geometrical properties of the cluster; see Fig. 2(a). We analyze clusters at a late stage of growth, but before a transition to a more directional dendriticlike growth.[2] Photographs of the clusters are digitized (512×512) and intensity levels above a threshold are taken to define the boundary of a cluster. The cluster boundaries are quite sharp, and the results for D_q are insensitive to the arbitrarily chosen threshold.

The values of D_q for $q \geq 0$ are estimated with use of a box-counting algorithm. The cluster is covered with a grid of square boxes of size ϵ, which varies from 2^{-9} to 2^0. The D_q are then obtained from the scaling of the partition function,[8] $Z_q \sim \epsilon^{(q-1)D_q}$, as $\epsilon \rightarrow 0$, where $Z_q = \sum_{(i=1,\ldots,N)} p_i^q$, p_i is the relative portion of the cluster boundary in cell i (with $\sum_{(i=1,\ldots,N)} p_i = 1$), and N is the total number of boxes that cover the cluster boundary. (For $q=1$, $Z_1 = \sum_{(i=1,\ldots,N)} p_i \log p_i$.) Thus the D_q are given by the slopes of graphs of $\log Z_q/(q-1)$ vs $\log\epsilon$ for small ϵ. Then the $f(\alpha)$ spectrum of singularities can be computed from a Legendre transform.[8]

Two factors have proved to be crucial in obtaining robust estimates of D_q. First, since the estimates of D_q depend on the location of the grid with respect to the

(a)

(b)

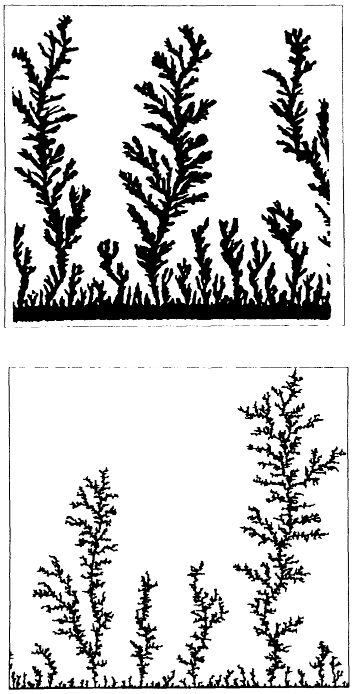

FIG. 2. (a) Electrodeposited clusters (about 5 mm long), photographed 15 min after the beginning of the growth. (b) A diffusion-limited aggregate computed with the random-walker model of Witten and Sander (Ref. 4) in a strip geometry. The digitized images in both (a) and (b) have about 1.6×10^4 boundary sites.

fractal cluster, we average $\log Z_q/(q-1)$ for fifty different randomly distributed locations of the origin of the grid for each value of ϵ. Second, the boundary is defined by elementary cells centered at each boundary site, and the values of p_i are calculated from the portion of *area* of these cells in each box of the grid (so $D_q\rightarrow 2$ rather than 1 as $\epsilon\rightarrow 0$); this contrasts with previous studies, which counted the number of *points* in a box.

The determination of D_q (for $q\geq 0$) from slopes of graphs of $\log Z_q/(q-1)$ vs $\log\epsilon$ for electrodeposited clusters is illustrated in Figs. 3(a) and 3(b). For ϵ smaller than the plate separation, projection effects become important and the slopes decrease before ultimately approaching the limiting value 2. This decrease in the slope towards unity at small ϵ may also result from the crossover from a ramified to a smooth boundary that occurs for experimental conditions that are a finite distance from the limit of small ionic concentration and small voltage. However, for larger ϵ there is a range of scales, $2^{-6}<\epsilon<2^{-3}$, for which the slopes (local dimensions[9]) depend only weakly on both ϵ and q. The results for different q are all approximated by $D_q=1.66\pm0.04$.

For $q<0$ the values of D_q cannot be determined reliably with a box-counting algorithm because of its inefficiency in handling spurious small p_i. However, a nearest-neighbor algorithm can be used to extract D_q^{-1} from the slopes of graphs of $-\tau^{-1}\log\langle R(M)^{-\tau}\rangle$ vs $\log M$, where $R(M)$ is the radius of a disk containing M boundary sites, centered at random on the boundary of

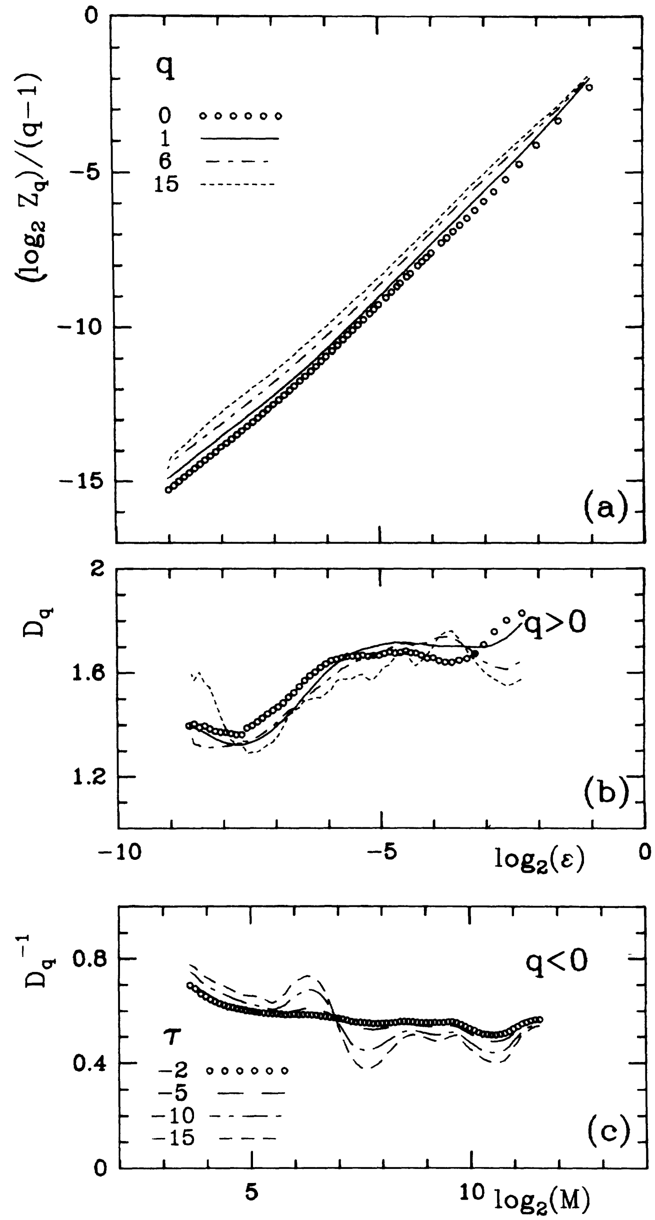

FIG. 3. These graphs illustrate the determination of the generalized dimensions D_q for the electrodeposition clusters shown in Fig. 2(a). (a) Box-counting computation of $\log_2 Z_q/(q-1)$ vs $\log_2\epsilon$ for $q\geq 0$. (b) Values of D_q given by the local slopes of the curves in (a), obtained from linear-regression fits for the range $\Delta\log_2\epsilon=1$. (c) Fixed-mass dimensions D_q^{-1} for $q<0$, obtained from the local slopes of graphs of $-\tau^{-1}\log_2\langle R(M)^{-\tau}\rangle$ vs $\log_2 M$, where $R(M)$ is the radius of a disk centered at random on the boundary of the cluster and containing M boundary sites. These local measurements yield $D_q=1.66\pm0.08$ for $-15\leq q\leq 15$.

the cluster.[10] The estimation of the local dimensions obtained by averaging over 400 centers is illustrated in Fig. 3(c) for several values of $\tau < 0$, where $q = 1 + \tau/D_q$. The values for D_q for all q are consistent with $D_q = 1.66 \pm 0.08$, suggesting that the electrodeposition clusters observed at low ionic concentration and low voltage are self-similar with a singularity of strength $\alpha = 1.66$ and density $f(\alpha) = D_0 = 1.66$.

We have conducted a similar analysis of D_q for clusters obtained in a simulation of a realistic model[4] of diffusion-controlled deposition. The DLA cluster shown in Fig. 2(b) was computed for a strip geometry with use of an on-square lattice algorithm with periodic boundary conditions. In order to avoid anisotropic growth[5,11] induced by the underlying lattice, we study only clusters of height less then the finite width of the strip. Like small-mass aggregates in a circular geometry, these clusters are expected[5,12] to be of the same nature as those computed with use of off-lattice algorithms where disks of elementary size diffuse in a continuous medium. As in our analysis of electrodeposition clusters, the boundary of the DLA clusters is taken to be given not by a discrete set of points but by elementary square cells centered at each border point. The analysis for $q \gtrsim 0$ yields $D_q = 1.60 \pm 0.02$, independent of q for an ϵ range of nearly two decades. Moreover, the values of D_q for $q < 0$ [see Fig. 4(c)] are in excellent agreement with the D_q values for $q \gtrsim 0$, and these values are independent of the mass of a cluster for clusters of 3000 to 30000 particles. Simulations for a circular geometry[13] yield the same result as those for the strip geometry, and, furthermore, the same result is obtained for a triangular lattice as well as a square lattice. Therefore, we conclude that small DLA clusters are self-similar with $D_q = \alpha = f(\alpha) = 1.60 \pm 0.02$.

Our value of D_q and previous box-counting[14] and pointwise[12] computations of D_0 are significantly smaller than numerical estimates[4,5,12] and theoretical predictions[15] for the dynamical dimension D_d deduced from the evolution of the radius of gyration during cluster growth. The possible reason[16] that D_d is greater than the fractal dimension D_0 is that in computing the dependence of the gyration radius R as a function of the mass of the growing cluster, one underestimates the number of sites that will be contained in a disk (centered on the original seed) of radius R at the end of the growth. In fact, D_d has been found to decrease during the early stages of growth.[17] The use of D_d instead of D_0 is perhaps the reason that a previous study[18] did not reveal the self-similar structure of DLA clusters.

In conclusion, these experimental and numerical results provide evidence that two-dimensional clusters formed in electrodeposition in the limit of low ionic concentration and low voltage and in DLA simulations are self-similar. The value of D_q from the experiment (1.66 ± 0.08) is slightly larger than D_q for small-mass DLA aggregates (1.60 ± 0.02), presumably because of projection effects that are important for small ϵ where the electrodeposition clusters are three (rather than two) dimensional; nevertheless, the D_q for the electrodeposition and DLA clusters are the same within the experimental uncertainty. On the other hand, previous studies

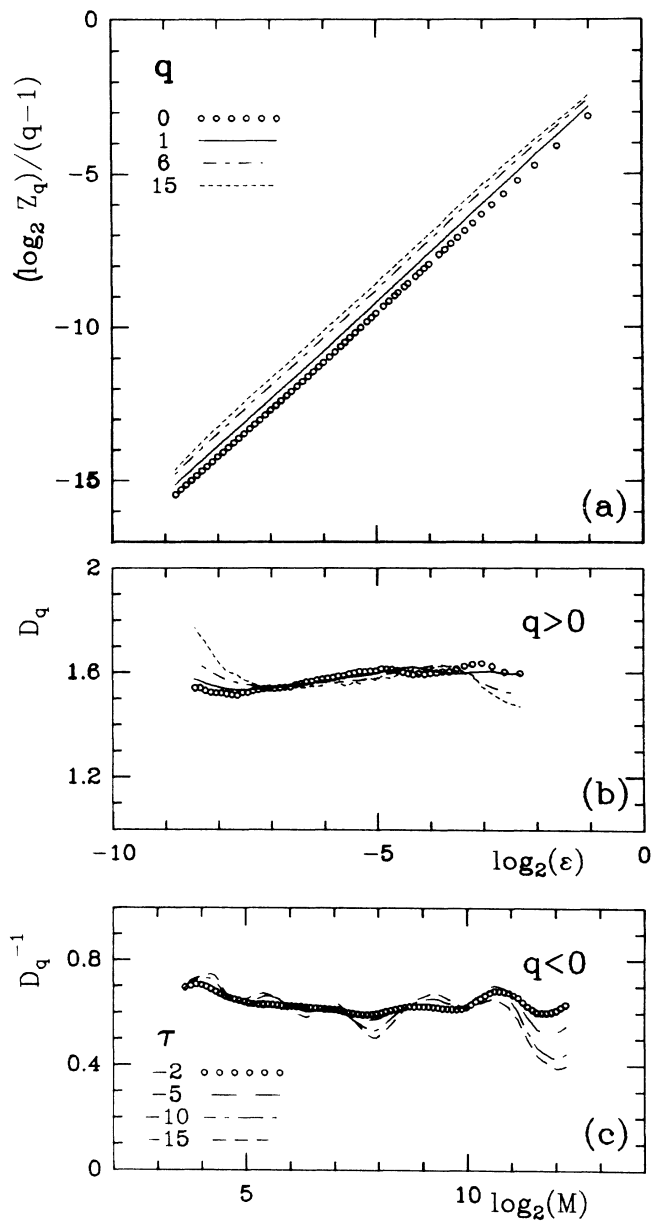

FIG. 4. These graphs illustrate the determination of the generalized dimensions D_q for the diffusion-limited aggregation clusters shown in Fig. 2(b). (a) Box-counting computation of $\log_2 Z_q/(q-1)$ vs $\log_2 \epsilon$ for $q \gtrsim 0$. (b) The local dimensions D_q, given by the slopes of the curves in (a) obtained from linear-regression fits for the range $\Delta \log_2 \epsilon = 1$. (c) Fixed-mass dimensions D_q^{-1} for $q < 0$, obtained from the local slopes of graphs of $-\tau^{-1} \log_2 \langle R(M)^{-\tau} \rangle$ vs $\log_2 M$, as in Fig. 3(c). The plateau in the slopes in (b) and (c) has a magnitude that is independent of q, $D_q = 1.60 \pm 0.02$. [These dimension estimates were made for a strip twice as large as in Fig. 2(b)].

indicate that the growth process is not self-similar for DLA clusters[15,19]—the growth probability measure has a finite range of scaling indices, and the $f(\alpha)$ spectrum is a convex function similar to those found for other multifractal systems.[8] Does the chemical electrodeposition mechanism display the same multifractal properties? The experimental answer to this question would help in the understanding of electrochemical deposition processes in terms of diffusion-limited aggregation. More generally, it is not clear how a non-self-similar growth process can generate self-similar fractal objects. The use of new techniques (e.g., the wavelet transform[13]) for characterizing multifractals may provide insight into the growth mechanism of clusters and lead to the development of a complete theory.

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