Fractal Structures of Zinc Metal Leaves Grown by Electrodeposition

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(Received 28 March 1984)

Zinc metal leaves are grown two-dimensionally by electrodeposition. The structures clearly remind us of the random patterns simulated by computer according to the Witten-Sander diffusion-limited-aggregation model. The scale invariance is tested by computing the density-density correlation function for the digitized patterns of the photographs. The Hausdorff dimension averaged over many examples is $D = 1.66 \pm 0.03$, which is in excellent agreement with that of the two-dimensional diffusion-limited-aggregation model ($D \cong \frac{5}{3}$).

PACS numbers: 61.50.Cj, 05.40.+j, 61.90.+d

The irreversible aggregation of many separate small elements to form large clusters is one of the most common phenomena which can be seen in many fields such as aerosol and colloidal physics, polymer science, material science, immunology, phase transitions, critical phenomena, etc. Recently much attention has been paid to the diffusion-limited aggregation [hereafter abbreviated as (DLA)] processes[1] which idealize the irreversible aggregation and, in particular, model smoke- and colloid-particle aggregates. Many computer simulations[1,2] suggest that the patterns produced by the DLA processes are characterized by the open, random, and chainlike structures; seem to have no natural length scale and thus exhibit scale invariance; and can be well described as fractals.[3] Hence the density-density correlation function $C(r)$ for such a pattern obeys $C(r) \sim r^{-A}$, where the exponent A is related to the fractal (Hausdorff) dimension D which characterizes the random pattern by $D = d - A$ (d is the Euclidean dimension).[1] The analytical derivation of the relation between D and d is one of the most challenging problems in the DLA. In the case of the DLA grown from a seed particle two attempts have appeared so far,[4,5] both of which give the relation

$$D = (d^2+1)/(d+1), \tag{1}$$

which is in excellent agreement with the computer-simulation results.[1,2]

So far there have been very few experimental studies[6,7] of real physical systems which may realize the theoretically proposed DLA model. Such studies surely contribute to deeper understanding of both theoretical and experimental aspects of more general aggregation processes. In this Letter we present a simple experimental system, i.e., the irreversible two-dimensional growth of a metal cluster which has long been known as a metal leaf,[8] and investigate the structural characteristics of the clusters. We show that the resulting metal leaves which really remind us of the DLA patterns[1,2] indeed exhibit scale invariance with fractal dimension $D \sim \frac{5}{3}$, in excellent agreement with that of two-dimensional DLA obtained by many computer simulations[1,2] and from Eq. (1).

Two-dimensional zinc metal leaves are grown by electrolytic deposition. The experimental procedures are as follows: A vat of diameter 20 cm and depth 10 cm is filled with $2M$ zinc sulfate ($ZnSO_4$) aqueous solutions (depth ~ 4 mm), on which n-butyl acetate [$CH_3COO(CH_2)_3CH_3$] is poured to make an interface. A carbon (pencil core with diameter ~ 0.5 mm) cathode with a flat tip polished perpendicular to the axis is set near the center of the vat so that the flat tip is placed just at the interface. The electrodeposition is initiated by applying the dc voltage between the carbon cathode and a zinc ring-plate anode with diameter 17 cm, width 2.5 cm, and thickness 3 mm placed in the vat. Then a zinc metal leaf grows two dimensionally along the interface from the tip of the cathode toward the outside with an intricately branched random pattern. Usually metal leaves are grown to the size of several centimeters for about 10 min by applying constant dc voltage of several volts. The temperature of the system is fixed at 15 °C. Photographs are taken either during or after their growth. An example is shown in Fig. 1.

The photographs are analyzed by computer to evaluate the fractal dimension of the zinc metal leaves from the density-density correlation function. The procedures used are as follows: An enlarged black-and-white photograph of a metal leaf is printed with clear constrast. It is then recorded into the imaging data memory of a computer through a television camera which consists of 512×512 pixels, the size of each of which is enough for the resolution of the thickness of the branches. Each pixel is registered in the memory in such a way that the density $\rho(\vec{r})$ of a pixel ($\vec{r}$ the position vector) is 1 if any part of the metal leaf pattern is on the

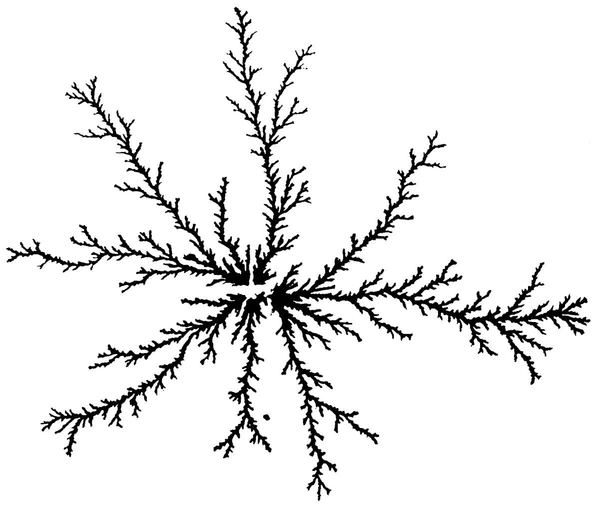

FIG. 1. A typical example of zinc metal leaves.

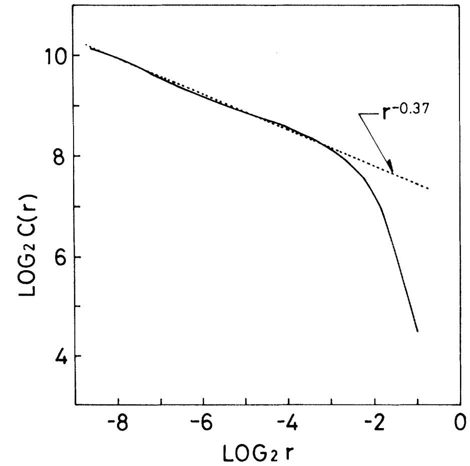

FIG. 2. Density-density correlation function obtained by digitizing the photo of the metal leaf shown in Fig. 1. The unit of distance r is given by the length of 512 pixels. The exponent A obtained from the linear part of $C(r)$ in this case is $A = 0.37$, which yields the fractal dimension $D = 1.63$.

pixel, and 0 otherwise. The density-density correlation function defined by

$$C(r) = N^{-1} \sum_{\vec{r}'} \rho(\vec{r} + \vec{r}') \rho(\vec{r}') \qquad (2)$$

is computed as follows: The density profile of the pattern stored in the imaging data memory of the computer is two-dimensionally Fourier transformed by a fast Fourier-transform technique, the power spectrum obtained, and the transform inverted and averaged over directions. An example of $C(r)$ thus obtained is shown in Fig. 2 in the form of log-log plot. As described before, an inclination of the linear part ($r < R_g$, R_g the radius of gyration) of the curve $C(r)$ yields the exponent A and the fractal dimension $D = 2 - A$. This method was tested within the accuracy of 1% by applying it to one of the Koch curves with a known value of D. We also confirmed the consistency of the values of fractal dimension for several metal leaves by means of the evaluation of D from the log-log plot of N (number of occupied pixels) versus R_g ($N \sim R_g^D$) for photographs taken successively from an as-grown metal leaf.

The values of the fractal dimension D thus obtained for many zinc metal leaves which are grown independently at various applied voltages of V of electrodeposition are plotted in Fig. 3. When V is less than some threshold value V_c (in the case of our experimental setup, $V_c \sim 8$ V) the values of D look constant, and the average for $V \leq V_c$ gives 1.66 ± 0.03. The values of D then increase linearly when the applied voltage is increased.

First of all we would like to point out that as seen in Fig. 1 the patterns of the zinc metal leaves clearly remind us of those of two-dimensional DLA obtained by computer simulations.[1,2] Their structures were found to exhibit scale invariance and their fractal dimension was also found to be constant ($D = 1.66 \pm 0.03$) for $V < V_c$, in excellent agreement with that of two-dimensional DLA ($D \sim \frac{5}{3}$). Moreover another feature is seen in Figs. 4(a)–4(d), in which photographs taken in time sequence for a typical as-grown zinc metal leaf are shown. The significant feature is that although the inner part has an open structure, branches there stop growing at pretty early stages and outer protruding

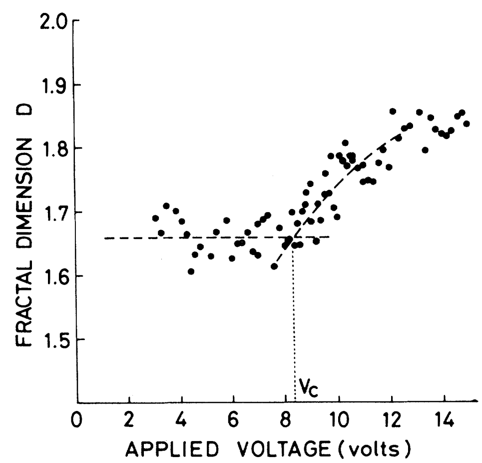

FIG. 3. Values of the fractal dimension of many zinc metal leaves grown independently at various electrodeposition voltages. The solution depth and temperature are always fixed as 4 mm and 15 °C, respectively.

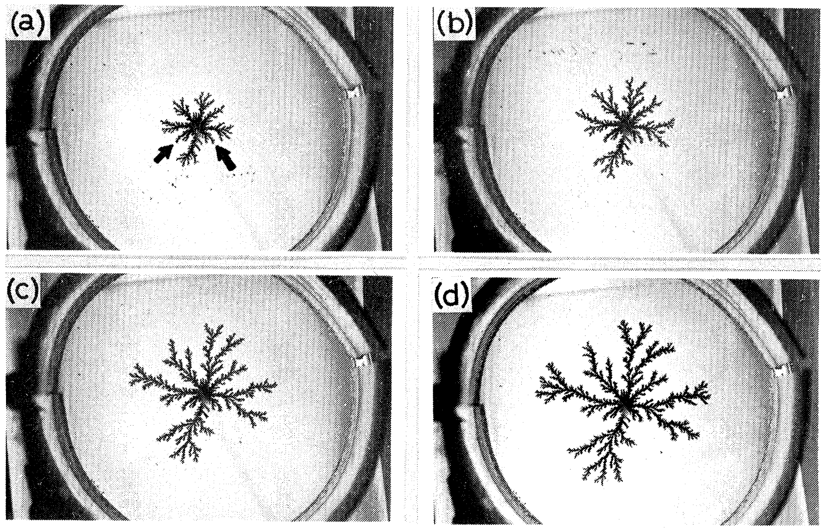

FIG. 4. Screening effect during growth of a metal leaf. Photographs (a)–(d) were taken 3, 5, 9, and 15 min after initiating the electrolysis, respectively. Branches shown by arrows in (a), e.g., are seen to stop growing afterwards in spite of their open neighborhood.

arms grow more and more, leaving the open structure in the interior. This screening effect, which is also a prominent feature of DLA found by computer simulations,[1,2] clearly indicates that metal leaves grow primarily along the interface two-dimensionally, and not from below.

The electric current under constant applied voltage of electrodeposition increases very gradually, almost linearly in time, after the very steep increase at the earliest stage of deposit growth. Preliminary measurement of the electric potential distribution ϕ near the interface suggests that it satisfies the Laplace equation with the boundary condition consistent with our experimental setup ($\phi \sim \log r$) not near the metal leaf deposit under low applied voltage and after the earliest stage of deposition. This means the metal leaves grow almost stationary with the diffusion-controlled processes. Let us consider the increase of the two-dimensional area A of a metal leaf. Assuming that transport of metal ions (or ion clusters) is governed by the potential gradient $\nabla\phi(\sim 1/r)$, we have $dA/dt \sim R\nabla\phi(r\sim R) \sim \text{const}$, where R is the effective radius of the metal leaf. Since $A \sim R^D$, we obtain $R \sim t^\eta$ (t is the deposition time), where $\eta = D^{-1}$. Preliminary results of the dependence of the radius of gyration of a few metal leaves on the deposition time give the D values consistent with those shown in Fig. 3 for $V < V_c$. This argument may be valid only when deposits grow purely two dimensionally. But since the present metal leaves are thin vertically compared with the horizontal thickness of the main branches and the screening effect is prominent as seen in Fig. 4, we think these preliminary results suggest that zinc metal leaves are formed nearly two-dimensionally by the diffusion-limited processes.

Taking all these detailed and preliminary results into account, we would like to conclude that the zinc metal leaves grown for $V < V_c$ provide a real experimental demonstration of the two-dimensional DLA.

The innermost part of the deposits always looks rather regular with dense radial structure. It may be because at the earliest stage of the deposit growth the particle drift inside the electrolytic solution contributes mainly to the growth, i.e., the initial steep increase of the electric current described above corresponds to the drift current. After the transient stage the rearrangement of both positive and negative ions (or ion clusters) takes place inside the solution, and then the metal ions (or ion clusters) move by means of diffusion only. In fact, applying higher voltage ($V > V_c$) gives rise to a larger inner core with dense radial structure, which causes larger Hausdorff dimension, as seen in Fig. 3. Recent computer simulations[9] demonstrate that the particle drift really entails uniform structures ($D \sim 2.0$) on the cluster formation. We conjecture, therefore, that the crossover at $V \cong V_c$ in Fig. 3 comes from the dominance of the drift effect.

So far we do not know why the metal leaves grow two-dimensionally at the solution–organic-solvent interface and their fractal dimension D abruptly increases at V_c when the applied voltage is increased. In the future one should certainly investigate the microscopic mechanism electrochemically. The dependence of V_c on the depth of the electrolytic solution and temperature should also be studied. Doing the same experiments for various metals like copper is interesting. We can also attempt to grow metal leaves from a linear carbon cathode placed horizontally at the interface to obtain the DLA growth from a "surface" (line) in the two-dimensional space.[2]

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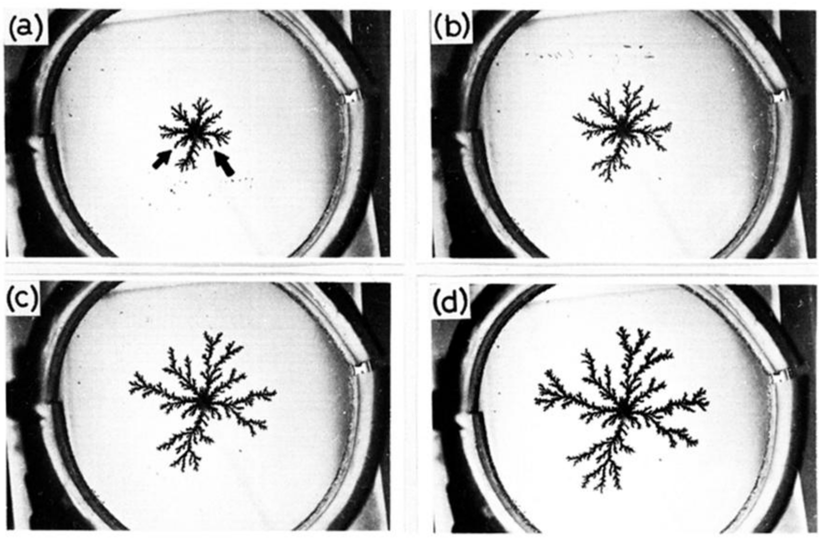

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