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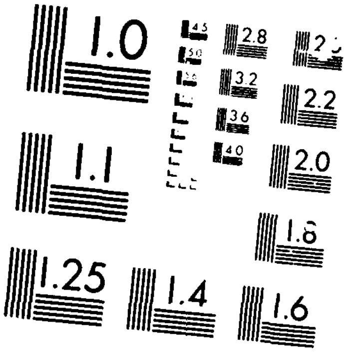
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40% larger for the observed pattern. This results from the fact that the observed pattern has more radial symmetry than the calculated one. This implies that the chemical length from the center to the perimeter of the pattern is minimized during the growth. Possible causes for the observed deviation are discussed.

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TECHNICAL REPORT NO. 47

# "Comparison between Electrodeposited Aggregates in Two Dimensions and the Fractal Pattern Calculated by the Witten-Sander Model"

by

P. Evesque, C. L. Yang and M. A. El-Sayed

J. Phys. Chem. 90, 2519 (1986)

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# COMPARISON BETWEEN ELECTRODEPOSITED AGGREGATES IN TWO DIMENSIONS AND THE FRACTAL PATTERN CALCULATED BY THE WITTEN-SANDER MODEL

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Copper metal leaves are experimentally grown in two dimensions by its electrodeposition in a field of circular symmetry from a solution of small thickness. The determined fractal (D) and spectral ($\bar{\bar{d}}$) dimension of the deposited aggregates is compared with that determined for the simulated pattern calculated by using the diffusion limited aggregation method of Witten and Sander using a square lattice. Good aggreement is found for the fractal dimension but the value of the spectral dimension, $\bar{\bar{d}}$, is found to be 40 % larger for the observed pattern. This results from the fact that the observed pattern has more radial symmetry than the calculated one. This implies that the chemical length ~~form~~ from the center to the perimeter of the pattern is minimized during the growth. Possible causes for the observed deviation are discussed.

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## INTRODUCTION

The Witten and Sander model of diffusion limited aggregates (DLA)[1] is found to be useful in describing the dendritic growth phenomena. The aggregates which are grown in this manner are fractal[2], with fractal dimension D which depends only on the Euclidean dimension d of the growth. It has been shown that this model can be applied under certain circumstances not only to the solidification of a pure or a binary liquid[3], but also to the diffusion[4] of nonviscous liquid into a viscous one. It has also been applied to describe the electrodeposition process[5]. Indeed, Matsushita et al.[6] have demonstrated that electrodeposition of zinc metal can grow aggregates, the fractal dimension of which corresponds to the value expected from the Witten Sander model.

This letter is aimed at reporting experimental results on copper electrodeposition which tends to confirm the generality of the shape of the aggregates grown by this method. However, it turns out that a careful analysis of the electrodeposited pattern demonstrates that this aggregate exhibits a more radial symmetry than that calculated using the DLA theoretical model on the square lattice. We interpret this feature in terms of a process which tends to minimize the chemical length[7] connecting the center and the circumference of the pattern, and the effect of the geometric lattice model (i.e., square lattice for DLA) where the aggregation processes are carried out.

## EXPERIMENTAL SET UP AND RESULTS

A brass cathode (5 mm) diameter with an emmersed tip of 2 mm diameter located at the center of a circular copper anode electrode of a diameter of

14 cm and 5 mm high. Both electrodes are emmersed in an electrolyte $CuSO_4$ solution. The whole setup is contained in a glass container having a flat and horizontal bottom. The tip of the cathode confines the initiation of the growth of the aggregate from the exact contact point between the glass vessel and the tip of the cathod. The centering of the cathod in order to have the circular symmetry was made by hand and its precision was better than 1 mm. The electrolyte was a water solution of cupric sulfate ($CuSO_4$), the concentration of which has been varied from 0.1 to 1.0 M. The thickness of the electrolyte in the vessel has been also varied from 3 mm to 7 mm, so that the liquid sometimes covered the anode and sometimes did not. More importantly, we expect that the aggregation process is a 2 dimensional process for length scales larger than this thickness and 3 dimensional one on the contrary. Neither the thickness of the electrolyte nor the salt concentration is found to have observable effect on the shape of the aggregate at large length scale. The electrical potential difference between the electrodes was kept constant during any growth experiment and was varied from 2 V to 15 V.

At the beginning of the experiments we have checked the variation of the potential inside the solution and measured the resistance of the electrode as a function of the salt concentration, of the applied voltage and of the thickness of the solution. These dependences were normal. Pictures of growing aggregates have been recorded during the growth using a video camera placed below the vessel. They have been digitized and analyzed using a computer (VAX 11/780). The analyzing procedure is similar to that used in the zinc case[6].

## RESULTS

The picture of a typical copper aggregate is given in Fig. 1a to 1d for different stages of the growth. The observed pattern is formed from branches of characteristic width, $R_0$ of the order of 1 - 5 mm. It looks very much like the leaves of electrodeposited zinc observed by Matsushita et al.[6] for radii larger than $R_0$. It is found experimentally that $R_0$ depends on the thickness of the electrolyte and on the applied potential. $R_0$ also is found to fluctuate from pattern to pattern so that no predeterminated pattern can be obtained. Moreover, slight non-linearity in the digitization process shows relatively more copper in the center than it is observed. Following the method used by these authors to analyze their pattern[6], we have computed the variation of the integrated dark zone in the pattern as a function of the distance R from the electrode center. Assuming that the integrated intensity of the dark zone at distance R is proportional to the mass of the copper at that distance, a best fit procedure has been used to determine the fractal dimension of the aggregate:

$$M(R) \sim R^D \qquad (1)$$

in the range of interest $(R > R_0)$ (cf. Fig. 2).

The average value of D obtained for the different aggregates is found to be 1.6 0.2. This reproducibility in copper deposition is poorer than the 5 % found in the case of the electrodeposition of Zinc[6] and is in agreement with previous results[8]. It might result from the fact that a mixture of two substance seems to be deposited in the case of copper, most likely copper and copper oxide. In spite of this difference from the Zink case, D seems to be similar and both seem to show a more centrally symmetric pattern than that was calculated with diffusion limited aggregation model (Fig. 1e) on a square lattice.

## DISCUSSION

We will assume that: 1) There is neither a charge accumulation in the electrolyte nor a potential drop at the interface; and 2) the current density at the interface should be proportional to the electric field. If we now assume that the copper leaves are perfect conductors, the equation governing the motion of a random walker in the Witten-Sander model can be used to describe the change in the electrical potential inside the electrolyte during the growth out of the electrolyte solution. This model yields fractal dimension consistent with the experimentally determined value.

However our experiments have detected some difference between the model and the experiment. Before giving a physical meaning to this difference, it is first necessary to quantify it. This requires to introduce the notions of chemical length[13] $L_c$, between the origin and a point at a distance R. This is simply the length of the actual path that connects this point to the origin. According to this definition, the shorter the chemical length $L_c$ is, the less tortuous the path is and more radial the pattern looks. Measuring the statistics of the chemical length $L_c(R)$ as function of the Euclidean distance R between the center of the pattern to another point for both the experimental aggregate and the simulated one should enable us to quantify their difference in the following manner. It is shown[13] that $L_c(R)$ obeys a power law $R^\alpha$ ;

$$L_c(R) \sim R^\alpha \qquad (2)$$

since the space is fractal, $\alpha$ depends on the geometry of the fractal and can take any value larger than 1 (it cannot be smaller than 1 since the smallest distance between any two point is the straight line which lead to $L_c \sim R$). By measuring $\alpha$ for both the experimental and simulated aggregates we may quantify the difference between them.

In order to relate the $\alpha$ exponent to other exponent already defined in the case of a fractal space, let us first notice that in the computer simulated and the experimental patterns, there is generally only one path which connects two points (i.e., there is no circle or closed loop existed); also recall that in a fractal space the spectral dimension[9], $\bar{\bar{d}}$, governs the number of distinct sites N(t) that a random walker has visited from time 0 to time t:

$$N(t) \sim t^{\bar{\bar{d}}/2} \qquad (3)$$

Under these circumstances and when $\bar{\bar{d}}$ is smaller than 2, the exploration can be considered as compact[10] which means that any point separated (i.e., from the center) by a chemical distance $L_c$ smaller than $l_{c_0}$ has been reached by the random walker. $L_{c_0}$ is proportional to the square root of the ellapsed time as in a classical one dimensional diffusion problem. Combining the definitions of the fractal dimension (Eq. 1) and spectral dimension (Eq. 3) together with this consideration leads to

$$N(t) = t^{\bar{\bar{d}}/2} = (L_c)^{\bar{\bar{d}}} \sim R^D \qquad (4)$$

Comparing this equation to the definition of the exponent $\alpha$ (Eq. 2) leads to:

$$\alpha = D/\bar{\bar{d}} \qquad (5)$$

One way to compute the exponent $\alpha$ is then to determine $\bar{\bar{d}}$ through a random walk problem (Eq. 3). This was the approach we have used. We first began with the DLA model in order to check the accuracy of our program. We get $\bar{\bar{d}} = 1.1 \pm 0.2$ for the Witten Sander model. This result is in agreement with previous determinations[11]. The large fluctuation we get are mostly due to the small number (1000) of sites which constitute our aggregate. In the case of the experimental pattern, we get $\bar{\bar{d}} = 1.5 \pm 0.2$. These values of $\bar{\bar{d}}$, from Eq. 5 with $D = 1.7$, leads to a value of the exponent $\alpha$ :

$\alpha_{DLA} = 1.5$

$\alpha_{electrodeposition} = 1.1$

which are very different from one another. This result confirms that the experimental pattern has more radial symmetry than that predicted by the DLA model calculated on a square lattice.

There are several reasons that might account for the difference between the calculated and the observed $\bar{\bar{d}}$. The DLA model is an ideal model for describing electrodeposition. It does not consider any transport properties which could be very important for the real physical systems. For example, in the electrodeposition process, the Cu aggregates have loose, porous structure instead of compact, crystalline structure. This might increase its resistance. Since the resistance within the aggregate is determined by the chemical length $L_C$ of the aggregate branches, for a certain radius from the center of the patt~~en,~~ern radial branches are expected to have lower resistance than branched ones. This leads to higher current density, and thus faster rate of deposition at the end of radial branches than at the end of more tortuous branches having the same distance from the center. Other possible causes for the more radial appearance of the observed pattern could simply be an inhomogeneous depletion of the $Cu^{+2}$ concentration during the deposition process. Due to the fragile nature of the two dimensional pattern, stirring was not carried out.

While we have blamed the disagreement between the observed and calculated spectral dimension on deviation of the deposition process from the DLA model, some of the deviation might actually result from the use of a square lattice in the simulation calculation of the pattern according to the DLA model. It has already been pointed out[12] that the value of the fractal dimension, D, depends on the type of lattice used in these types of calculations. It might be that the value of the spectral dimension is also sensitive to the type of the lattice used.

Studies are now in progress and aimed at examining the sensitivity of the observed fractal and spectral dimension to variation in the different experimental conditions. We are also examining the sensitivity of the spectral dimension of the calculated pattern on the type of lattice used in the calculation.

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## Figure Caption

Fig. 1: Digitized form of the observed electrodeposited copper aggregate at four different stages of the growth: voltage used is 2.0 volt, copper ion concentration is 0.5 M, the complete time of growth is 50 minutes. Fig. 1e is the simulation of a aggregate grown by diffusion limited aggregation model. The first four patterns exhibit a more radial symmetry than the simulated one.

Fig. 2: A Plot of ln (N(R)) vs. ln R for different observed electrodeposited copper patterns. It is assumed that N(R) is proportional to the area of the dark area of the digitized form of the pattern in a circle of radius R. From the slope of the line, the fractal dimension D is determined.

Fig. 3: The determination of the spectral dimension for the observed (a) and the calculated (b) patterns.

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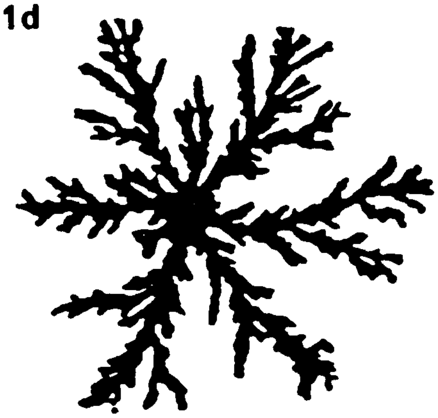
1b

1c



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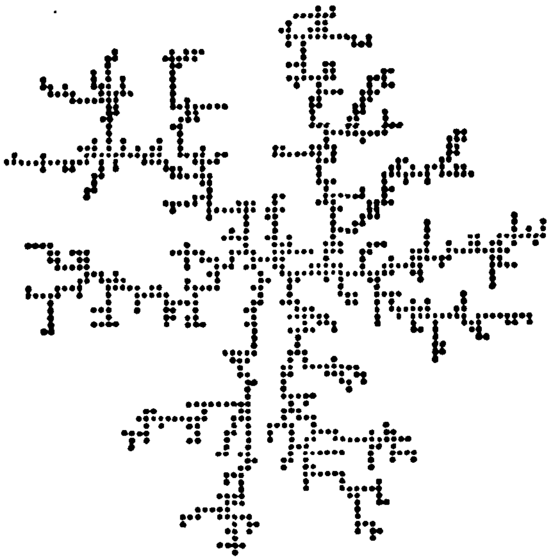

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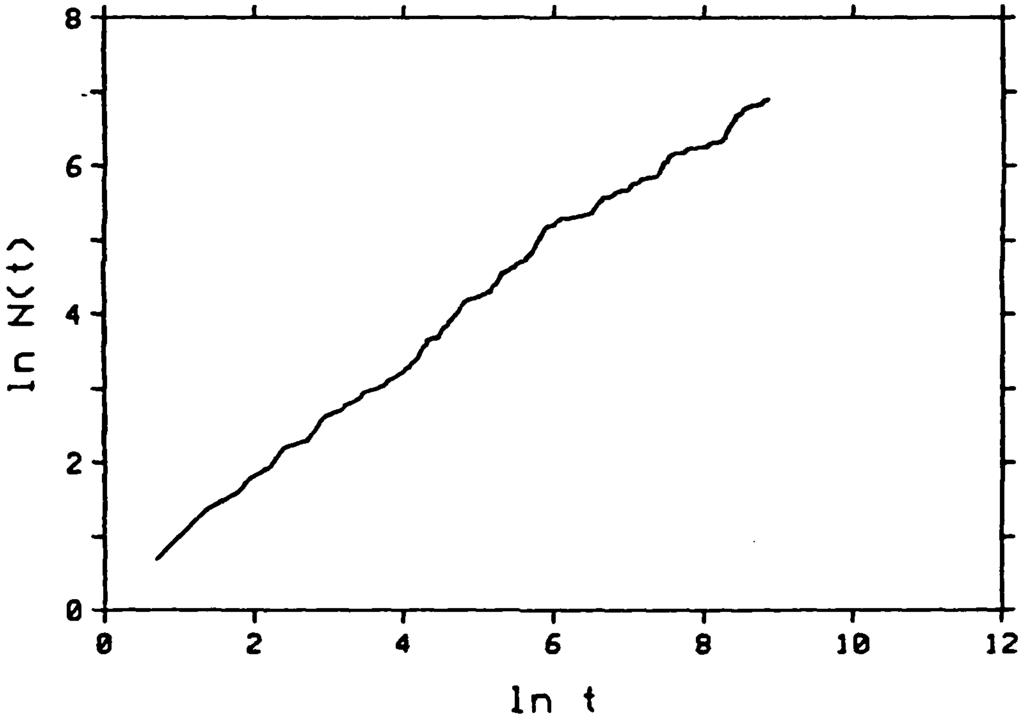

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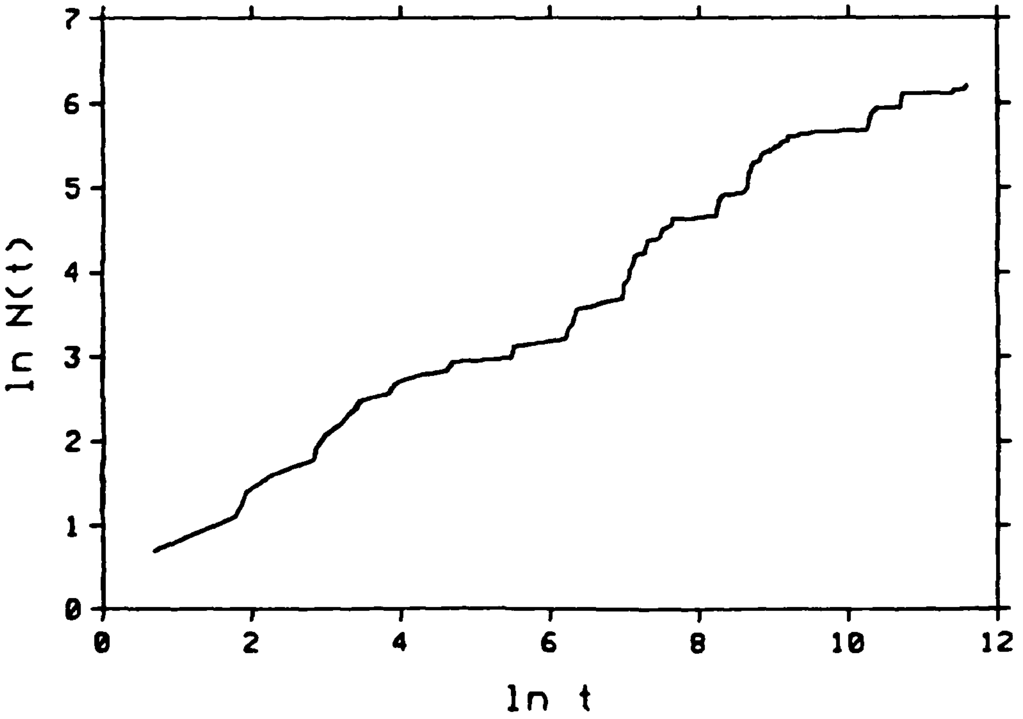

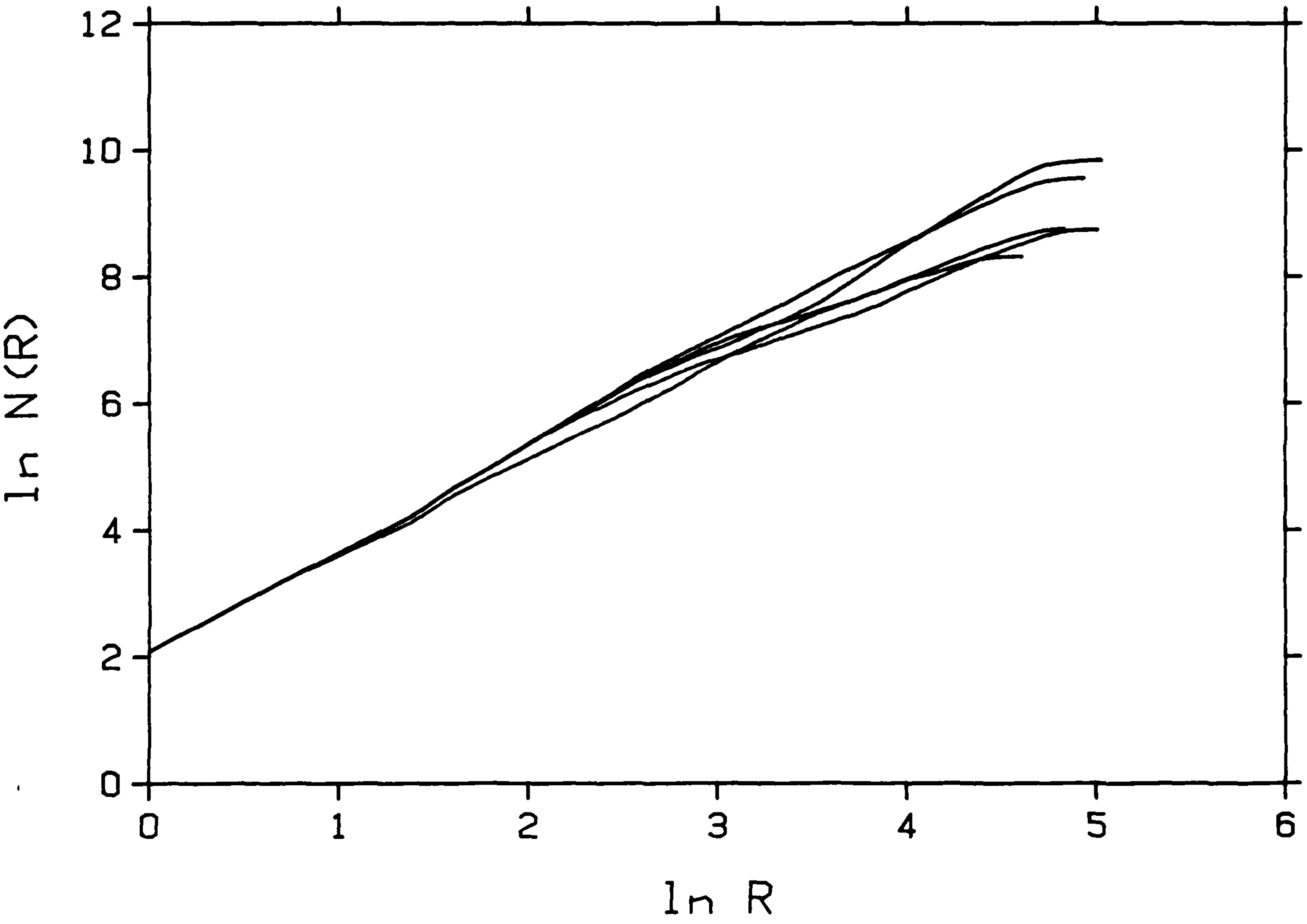
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