Fractal Aggregation Growth and the Surrounding Diffusion Field

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Abstract

Silver metal trees grow and form a forest at the edge of a Cu plate in the AgNO₃ water solution in a two dimensional (d = 2) cell. The local structure of the forest is similar to that of the diffusion-limited aggregation (DLA), but the whole pattern approaches a uniform structure. Its growth dynamics is characterized by the fractal dimension $D_f$ of DLA. Time-dependence of the tip height is found to satisfy the scaling relation with the solute concentration $c$, and the asymptotic growth velocity $V$ is consistent with the power law $V \sim c^{1/(d-D_f)}$ expected from the theory. The thickness $\xi_c$ of the diffusion boundary layer is measured by the Michelson interferometry, and the scaling relation is also confirmed.

PACS: 05.45.Df, 89.75.Kd, 89.75.Da, 81.10.Dn

1 Introduction

Many fractal objects have been found in nature[1] and their patterns are characterized by the fractal dimension $D_f$. For the diffusion-limited aggregation

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1 Deceased.
(DLA), $D_f = 1.71$ in the two dimensional space $d = 2$ [2]. Despite with many findings, most studies are concerned with the structural aspects of the pattern and little has been said about dynamical aspects of the aggregation processes. An exception is the study of the growth velocity $V$ in a diffusion controlled aggregation from a finite density lattice gas [3,4]. The growth velocity $V$ strongly depends on the gas density $n_g$ in a power law $V \sim n_g^\nu$, where the exponent $\nu$ is determined by the fractal dimension of DLA as $\nu = 1/(d - D_f)$. This theoretical expectation has been confirmed by the Monte Carlo simulation. Although the apparent physical reality of the simulation model, experimental test of the dynamical scaling theory had not been done until we reported our first experiment [5] of electrochemical deposition in a two dimensional geometry[6,7]. In the experiment we grew Ag aggregates on a linear edge of a Cu plate from a AgNO$_3$ solution and confirmed the concentration dependence of the growth velocity. In the present paper, we extend the experiment to study the concentration profile in the solution around the growing aggregate by means of a Michelson interferometry. Thus we prove that the observed phenomenon is really controlled by diffusion and that the fractal dimension of DLA determines the dynamical behavior of the aggregation growth as well as the structure of the aggregate.

2 Theoretical background

When a crystal is growing under the control of diffusive transport, its interface may become unstable to wavy fluctuations and form various growth patterns[8,9]. The surface tension introduces a capillary length $\ell_c$, and the destabilizing diffusive transport introduces the diffusion length

$$\ell_D = D/V$$

(1)

with $D$ being the diffusion constant. The characteristic length of the pattern of unstable crystals, such as the dendritic tip radius, is proportional to the geometrical average of these two lengths, $\sqrt{\ell_c \ell_D}$. If this length is small enough and the crystal anisotropy is negligible, the stochastic noise dominates and irregular ramified solid aggregation emerges. When the system looses any characteristic length, the self-similar fractal structure results.

The DLA [10] is an idealization of the fractal growth in the computer. The fractal structure of the DLA is reflected in the relation of the mass $M$ of the aggregate with the gyration radius $R$ as it grows:

$$M \propto R^{D_f}. \quad (2)$$
For a fractal, $D_f$ is smaller than the dimension $d$ of the space in which the aggregate is embedded. It is 1.71 for a two-dimensional ($d = 2$) DLA. Then the density of the aggregate in a radius $R$ is

$$\frac{M}{R^d} \propto R^{D_f - d}, \quad (3)$$

which decays to zero asymptotically as $R \to \infty$. It is important to note that the DLA is the limit of slow diffusive growth since there is only one mobile atom in the whole system: the growth velocity tends to zero, $V \to 0$. The situation corresponds to the growth from a solution in the limit of zero-density. Thus, the diffusion length $\ell_D$ is infinite, and the DLA has no characteristic length at all.

In the actual aggregation, the aggregate grows from a solution of a finite concentration $c$ with a finite growth rate. If the aggregate grows from a linear seed in a two-dimensional cell, mass conservation in one-dimension requires that the resulting aggregate should have the same density $c$ averaged over a large scale, even though it has a fractal structure at a short scale. We denote by $\xi$ the length which characterizes the crossover of the aggregate from the short-range fractal to the long-range uniform structure. In the fractal region, the density correlation in the aggregate decreases in accordance with the fractal scaling (3) up to a distance $\xi$, whereas in the uniform region, $r > \xi$, it should be the constant $c$. Therefore, the characteristic length is determined by $c \sim \xi^{D_f - d}$.

When the solidification is controlled by the diffusive transport and has the growth rate $V$, the concentration variation in the solution is characterized by the diffusion length $\ell_D$ defined in Eq.(1). We expect that the system has only a single characteristic length, so that $\xi$ is of the order of $\ell_D$. The growth rate $V$ is then related to the concentration $c$ as

$$V \sim D / \xi \sim c^{1/(d-D_f)}. \quad (4)$$

This relation has been proved by the Monte Carlo simulation of a directional aggregation growth from a linear seed in the two dimensions [3,4].

### 3 Experiment

Our experiment involves two-dimensional deposition of Ag from a AgNO$_3$-water solution on a linear edge of a 100 $\mu$m-thick Cu plate. Due to a difference in ionization potential, Ag atoms deposit onto the aggregate while Cu ions dissolve in the solution without applying an external electric field: the solute concentration controls the growth dynamics.
Fig. 1. Aggregation in the experiment: (a) $c = 0.04$ mol/ℓ, and (b) 0.06 mol/ℓ. The width of the image is 12.5mm. Aggregation in the Monte Carlo simulation: (a) $n_g = 0.1$ per lattice site and (b) 0.15. The system size shown is $1024 \times 900$.

The experimental setup is similar to that of [5] except that the doubled thickness of the cell. The thick cell enables us to measure the concentration distribution in the cell. The concentration distribution of the solute around Ag aggregates is measured by a Michelson interferometer adopted to an optical microscope. The interferometer is composed of an objective lens ($\times 2.5$) and an ordinary optical system of the Michelson interferometer [11]. To measure the concentration distribution we coat the back of the growth cell with silver in order to form a sample mirror. Incident beam is reflected by the mirror and it passes through the solution twice. By inclining the reference mirror to the optical axis, interference fringes are superimposed on the image of the object. If the concentration is uniform, fringes are straight. Deviation of a fringe from the straight line measures the concentration inhomogeneity. The shift $\delta$ of the fringe from the straight line is connected to the local decrease in the concentration $\Delta c$ as

$$\delta = \frac{2\ell L}{\lambda} \frac{\partial n}{\partial c} \Delta c,$$

where $\lambda = 547\text{nm}$ is the wavelength of the incident monochromatic light from a halogen lamp through a band pass filter, $\ell$ the spacing of the straight fringes, $L$ the thickness of the solution layer and $n$ the refractive index. In our previous experiment [5] the thickness of the cell was $L = 50\mu\text{m}$ and $\delta$ was
Fig. 2. Density profile of the aggregation at 0.04 mol/ℓ (thick line) and 0.06 mol/ℓ (thin line).

too small for the measurement. As the aggregates grow, concentration around them decreases due to the solute deposition on the aggregates, and the local variation of the concentration builds up.

4 Result

Aggregates grown at 0.04 and 0.06 mol/ℓ are shown in Fig.1(a), (b) in black-and-white images. They look similar to those obtained previously with a thinner ($L = 50 \mu$m) growth cell [5], and have great similarity to those observed in the Monte Carlo simulation [3,4] as shown in Fig.1(c), (d). Numerous silver crystals start growing on the edge of a Cu plate. As the aggregates grow, a tree eats up nearby silver ions in the solution, and the concentration close to it decreases. Within the range of $\ell_D = D/V$ the concentration of silver ions becomes very low, and the situation looks the same as that of the DLA fractal growth. We confirmed the self-similarity by enlargement of the photographs of the “vegetation” at the ground of the “forest”.

As the trees grow, because of the competition for the supply of silver, fewer and fewer trees survive. For the DLA growth the number of trees decreases forever [13,14]. In the growth from a finite concentration gas (or solution) the competition is ended when the distance between the trees (or trunks) becomes about $2\xi$ [4]. As a result the global structure of the aggregate is compact with a finite density, which is the same as the solute density $c$ far from the aggregate. In Fig.2 we show the average density of the pixels occupied by the aggregation along the horizontal position at the same height at two concentrations. They first decrease quite rapidly, and seem to saturate at constant densities corresponding to the solute densities.
In the previous Monte Carlo simulation[3,4], it was shown that the scaling relation (4) is valid in the form
\[ V/D = 5.8 n^{3.50} \approx 1/\xi, \]
which is compatible with the DLA fractal dimension \( D_f = 1.71 \). Therefore, in the present experiment we suppose that the same relation between the crossover length \( \xi \) and the concentration \( c \) holds as
\[ \xi = a_e c^{-3.5} \quad (6) \]
with a constant \( a_e \). Since it is not possible to measure experimentally the crossover length \( \xi \) accurately, here we define \( \xi \) as the half of the average separation between trunks in the steady state. At the concentration \( c = 0.05 \text{ mol/ℓ} \), the separation is 1.1 mm. Then the coefficient is determined as \( a_e = 1.5 \times 10^{-5} \text{ mm(mol/ℓ)}^{3.5} \). This value is consistent with the value \( a_e = 3.0 \times 10^{-5} \text{ mm(mol/ℓ)}^{3.5} \) obtained in the previous experiment with a thinner cell [5]. At concentrations higher than \( c = 0.04 \text{ mol/ℓ} \), the number of trunks saturates during the experiment and the growth seems to become steady. At lower concentrations, on the other hand, we observed that the number of trunks is still decreasing within our cell of height 1cm, and the competition among trunks are still taking place.

The height of the most advanced tip \( h(t) \) of the aggregate within the view of microscope is traced as a function of time in Fig.3(a), which looks similar to that obtained with a thinner cell [5,12]. Since \( \xi \) is the sole macroscopic characteristic length for the diffusion-limited growth, the height scaled by \( \xi \) is expected to be a universal function of the scaled time \( Dt/\xi^2 \):
\[ h/\xi = g\left(Dt/\xi^2\right) \quad (7) \]
where the length \( \xi \) satisfies the relation (6). The scaling plot of the aggregate height versus time is depicted in Fig.3(b). Many curves at various concentra-
Fig. 4. Interference fringes due to the concentration variation obtained by the Michelson interferometer.

tions fall on a universal curve. In the present experiment with the concentration up to \( c = 0.07 \) mol/\( \ell \), the characteristic length \( \xi \) is calculated to be larger than 0.3mm by using the scaling relation (6). Then, \( \xi \) is larger than the thickness of our cell, \( d = 100\mu m \), and the two-dimensional feature of our experiment is guaranteed.

We can make a rough estimation of the diffusion constant \( D \). Fig.1(a) is a pattern at \( t \approx 1020s \) corresponding to \( tc^7 = 1.6 \times 10^{-7}s(\text{mol}/\ell)^7 \). The simulation Fig.1(c) at \( t \approx 3 \times 10^4 \) looks to be at a slightly later scaling stage. If we put \( t \approx 2.5 \times 10^4, D = 1 \) and \( \xi = 2.8 \times 10^{-2}n^{-3.5} \) obtained from the simulation[4,5], we find \( Dt/\xi^2 \approx 3.2 \). Assuming Fig.1(a) corresponds to \( Dtc^7/\alpha^2 = 3.2 \), the diffusion constant is estimated as \( D = 4.3 \times 10^{-3}\text{mm}^2/s \). A similar comparison of Fig.1(b) and (d) gives \( D = 1.6 \times 10^{-3}\text{mm}^2/s \). These values are of the same order as the literature value \( D = 1.7 \times 10^{-5}\text{cm}^2/s \)[15].

We now study the concentration distribution in the solution around the growing aggregate, an example of which is shown in Fig.4. By assuming that the deviation from the straight interference fringe is indiscernible when it decreases by a factor of ten\((\approx e^2)\), we assign a distance between the aggregate tip and the deflection point of a fringe to be \( 2\xi_c \). The arrows in the enlarged picture of Fig.4 indicate the eye guide of the thickness \( 2\xi_c \). It is shown in Fig.5 as a function of the concentration \( c \). The general tendency is that the thickness \( 2\xi_c \) decreases as the concentration increases. The data agree fairly well with the expectation Eq.(6) with the expected value of \( \alpha \).

Some remarks on the measurement of \( \xi_c \) are in order. The thickness \( \xi_c \) is measured when the tip is sufficiently far, namely more than \( \xi \) away, from the Cu edge and when it grows steadily. Since \( \xi \) is expected to be greater than 2.5mm below the concentration \( c = 0.040 \) mol/\( \ell \), our cell size is not large enough. Even if we have large cells, the magnification of the microscope should be low to cover wide area. But then, we cannot detect the small deflection of the interference fringe at low concentrations. Thus, we have to be satisfied
Fig. 5. Measured thickness $2\xi_c$ of the concentration depression layer versus concentration $c$. The curve represents $\xi = a_c e^{-\nu}$.

to depict data at concentrations above $c = 0.045\, \text{mol/ℓ}$. At concentrations higher than $c = 0.060\, \text{mol/ℓ}$, one encounters another difficulty. The thickness $\xi_c$ becomes very small and the data contain large uncertainty. Albeit these restrictions, we may say that the thickness of the concentration boundary layer is strongly correlated with the fractality of the aggregation.

5 Conclusion and discussion

Due to the difference in the ionization potential, Ag metal-leaves aggregate at the edge of a Cu plate from the $\text{AgNO}_3$-water solution. The silver aggregate looks fractal in a short length scale and compact in a large scale. The tip height of a silver aggregate and the concentration depression layer of the solution are found to satisfy the dynamical scaling relation with the scaling exponent determined by the fractal dimension of the DLA. The concentration distribution around the aggregate tip shows that the thickness of the diffusion boundary layer is inversely proportional to the growth velocity. It confirms that the aggregation growth is controlled by the diffusive transport, and that there is an intimate interplay between the growth dynamics and the resulting pattern.

The estimated diffusion constant is consistent with the known value. However, in the present analysis we have neglected Cu diffusion, which can be another rate limiting process. The observed scaling plot Fig.3(b) shows slowdown of the growth in a later stage at high concentrations. We suspect this may be due to the Cu diffusion. Because of this reason and also because of large fluctuation in the growth, the determination of the precise value of the diffusion constant is not possible. Also the crossover length $\xi$ and the diffusion length $\xi_c$ are defined in a rather arbitrary way for experimental convenience. Despite with
these quantitative uncertainty in the prefactors, the exponent in the scaling relation are confirmed with good accuracy.

Acknowledgement

Y. S. and M. U. were supported by the Japan Society for the Promotion of Science through the Grant in Aid. The work was performed as a part of the interuniversity cooperative program of the Institute for Materials Research, Tohoku University.

References

[12] In [3,4] the growth velocity \( V \) is defined through the mass of the aggregate. Experimentally this is very difficult and we define \( V \) by the tip velocity.
[15] The diffusion constant for a AgNO\(_3\) solution of 0.005 mol/\( \ell \) at 25\(^\circ\)C is \( 1.71 \times 10^{-5} \text{cm}^2/\text{s} \) (R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworth, 1959), p. 513).