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Experimental Investigations on the Fractality and Kinetics of Aggregation

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We show two kinds of experiments on the fractal properties and kinetics of aggregation; electrodeposition and colloidal particle aggregation. In the first experiment zinc electrodeposits are grown two-dimensionally from a line electrode. The fractal structure and size distribution of the deposits (trees of zinc metal-forest) are investigated. In the second experiment static and dynamic light scattering measurements are performed on the colloidal aggregates of polystyrene uniform latex particles. The fractal dimension of the aggregating clusters and the dynamic exponent of the mean cluster size are determined. All the results are discussed by comparison with theoretical predictions and computer simulations available.

INTRODUCTION

Nonequilibrium growth of random patterns or clusters has recently been attracting much interest since those produced by computer simulations for various models of, e.g., colloid-particle aggregation, dielectric breakdown and polymerization were found to exhibit self-similarity (Family & Landau;1984). In particular, the aggregation of small particles to form larger clusters is very important in many natural and industrial processes.

There are two prototypic models proposed so far to describe complicated kinetic aggregation processes; (1) particle- cluster diffusion-limited aggregation (hereafter abbreviated as DLA) model (Witten & Sander:1981), and (2) kinetic cluster-cluster aggregation (abbreviated as KCA) model (Meakin:1983d, Kolb et al:1983). Both models are now well-known to yield characteristic self-similar patterns: Their fractal dimensions d_f depend only on the Euclidean dimensionality d of the space in which the aggregation takes place, but are widely different from each other. This means that the two models constitute their own universality classes among those of various models which produce self-similar random patterns.

DLA describes the growth of an immobile cluster in the diffusion field, because the cluster grows from a seed by means of

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successive sticking of Brownian (diffusing) particles launched, one at a time, far from the cluster. It can, therefore, be applicable, with the appropriate modification if necessary, to the pattern formation of many seemingly unrelated phenomena such as dielectric breakdown (Niemeyer et al:1984), electrodeposition (Matsushita et al:1984, Brady & Ball:1984), dendritic crystal growth (Vicsek:1985), and viscous fingering instability (Nittmann et al:1985, Ben-Jacob et al:1985). They are all characterized by the pattern formation in a field (electrostatic potential, concentration, temperature and pressure, respectively) which satisfies a Laplace equation, hence, is equivalent to the diffusion field.

KCA involves, on the other hand, irreversible cluster formation by the homogeneous aggregation of mobile clusters starting from a collection of Brownian particles. It is, therefore, a model much more relevant to phenomena associated with colloidal particle aggregation widely seen in Nature such as soot, smoke and aerosol clusters and colloid flocs and aggregates.

Recent computer simulation studies disclosed that KCA clusters are of almost the same size (nearly monodisperse) during the aggregation and have much more ramified structures, i.e., smaller fractal dimension ($\underline{d}_f \cong 1.45$, 1.75 for $\underline{d}=2$, 3, respectively) than DLA ($\underline{d}_f \cong 1.67$, 2.50 for $\underline{d}=2$, 3, respectively). The latter feature comes from the fact that in KCA a cluster cannot penetrate into another when they collide and stick rigidly via particle-particle contact. Hence the Brownian motion of the KCA clusters is not much relevant to their fractal structure (Meakin:1984a), in contrast to the case of DLA in which particles can to some extent diffuse into the cluster and their Brownian motion is essential to the fractal structure. This means that the fractal dimension alone is insufficient to characterize the KCA model: One needs an additional quantity such as dynamic scaling exponent $\underline{z}$ in the mean cluster size at time $\underline{t}$ after the initiation of aggregation; $\overline{R}(t) \sim t^{1/z}$ (Matsushita:1985).

In contrast to the wealth of recent computer simulations only several experimental studies have begun to be reported on DLA and KCA. In fact, from the viewpoint of Science on Form it is more interested whether and how these idealized models relate to real systems. Here we would like to present our recent experimental investigations on the fractal structure and kinetics of two kinds of aggregation relevant, respectively, to DLA and KCA; electrodeposition and colloidal particle aggregation.

EXPERIMENT ON DLA -- METAL-TREES

Recently we have shown that a zinc metal-leaf grown two-dimensionally from the tip of a needle-like electrode seems to be particularly relevant to two-dimensional DLA (Matsushita et al: 1984): Not only is its fractal dimension constant and very close to 5/3, consistent with the results of simulations (Witten & Sander:1981,1983, Meakin:1983a,b) and mean-field theories (Muthukumar:1983, Tokuyama & Kawasaki:1984, Honda et al:1986), but it has also been directly observed that the fractal structure emerges due to screening by protruding outer branches which seem to interrupt the diffusion of metal ions into the interior and prevent inner branches from growing larger, just as in DLA (Witten & Sander:1983).

We have extended this metal-leaf experiment to that of two-

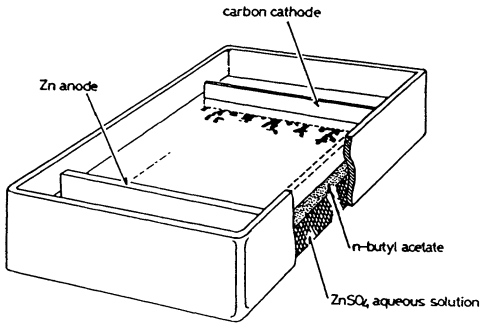


Fig. 1 Experimental setup.

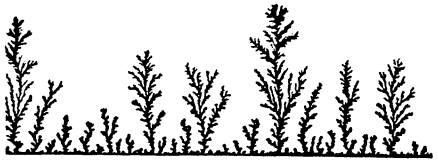


Fig. 2 A typical example of a forest of zinc metal-trees.

dimensional zinc metal deposits grown from a line electrode (Matsushita et al:1985b). This can be regarded as the experimental realization of diffusion-limited deposition, computer-simulated first by Meakin (1983c). Our experimental setup is shown in Fig. 1. The bottom side of a long carbon cathode with rectangular section is placed just on the interface between $ZnSO_4$ aqueous solution and immiscible organic liquid. The application of a dc voltage between a zinc anode plate and the cathode brings about the two-dimensional growth of zinc metal deposits just along the interface from the edge of the cathode toward the anode. One can obtain a little more detailed information on the procedures of the experiment and the data analysis through references by Matsushita et al (1984, 1985b). Here we briefly present the results of this experiment. In Fig. 2 is shown a typical example of the electrodeposits obtained. Let us call the individual deposits metal-"trees" and the whole a metal-"forest" in order to distinguish them from usual metal-leaf which grows from the tip of a needle-like electrode. In fact, as seen in Fig. 2, they really look like trees, and the overall view looks like a forest.

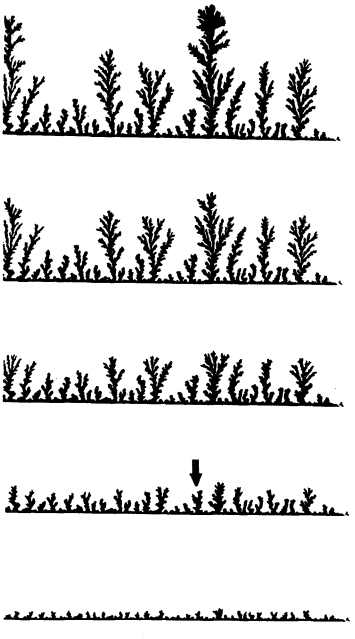


Fig. 3 The growth process of zinc metal-trees.

The growth process of the zinc metal-trees is shown in Fig.3. One can again clearly see the screening effect for, e.g., the tree indicated by arrow. It just stops growing after then, although it has still quite an open environment. One can find many other examples. This means that the fractal structure of the zinc metal-forest comes from the screening effect of protruding larger trees by preventing smaller trees of tardy growth from becoming larger, just as in the case of branches of a metal-leaf.

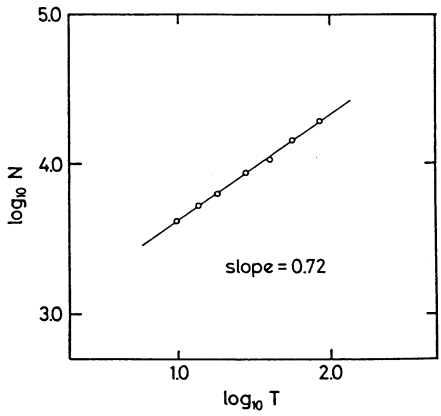


Fig. 4 A typical experimental result of the relation between $\underline{N}$ and $\underline{T}$ for zinc metal-forest.

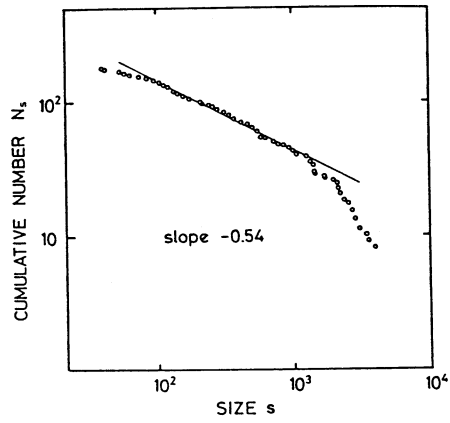


Fig. 5 Log-log plot of the dependence of $\underline{N}_S$ on $\underline{s}$.

The fractal dimension $\underline{d}_{ff}$ of the metal forest is defined as $N \sim T^{d_{ff}}$, where $\underline{T}$ is the rms thickness (or height) of the forest and $\underline{N}$ is the number(per unit length of linear cathode)of occupied pixels of the forest pattern in the imaging data memory. A typical example of the log-log plot of $\underline{N}$ on $\underline{T}$ is shown in Fig.4. One can see $\underline{T}$ scaled by $\underline{N}$ quite well. The fractal dimension for this example is $d_{ff}=0.72$. The average value of $\underline{d}_{ff}$ obtained is

$$d_{ff}=0.70\pm0.06$$

for the ten independent trials performed. This is in excellent agreement with Tokuyama-Kawasaki(1984)'s mean-field theory and Meakin(1984b)'s large-scale computer simulation result.

As seen in Fig. 1, one can regard metal-trees grown from a line electrode as individual clusters and the number of pixels, $\underline{s}$, constituting one tree as its size. Hence one can now discuss cluster statistics of the metal-forest. We counted cumulative number $\underline{N}_S$ which is the total number of metal-trees of more than $\underline{s}$ pixels, and then averaged it over several examples of forests of approximately the same size. The result is shown in Fig.5. It also exhibits the scaling behavior, $N_S \sim s^{-0.54}$, in the middle of the available values of size $\underline{s}$. The deviation from the scaling behavior for the small values of $\underline{s}$ clearly comes from the ambiguity of counting small trees, and that for the larger $\underline{s}$ from the finite size effect. One can conclude from the result that the number density $\underline{n}_S$ of the zinc metal-trees of size $\underline{s}$ is also scaled as

$$n_S \sim N_S' \sim s^{-\tau}, \quad \tau=1.54.$$

On the other hand, Rácz and Vicsek (1983) predicted the scaling behavior $n_S \sim s^{-\tau}$ with $\tau=1+1/d_f=1.60$ for d=2, and Meakin (1984b) confirmed it by large-scale computer simulation. Our experimental result agrees quite well with theirs. This means that one can now relate the fractal structures of deposits to the nonequilibrium

cluster statistics.

From a viewpoint of the close resemblance to Fig.1, natural dendrites of MnO_2 found on the cleaved surface of shale or limestone may be relevant to the diffusion-limited deposition described in this section.

EXPERIMENT ON KCA -- LIGHT SCATTERING OF POLYSTYRENE COLLOIDAL AGGREGATES

Simulation rule of KCA model is very simple (Fig.6): One starts with an assembly of Brownian particles as in Fig.6(1). They stick together upon contact to form rigid clusters. The newly formed clusters also diffuse with their "mobility", and continue to grow by aggregation when they meet other clusters or particles as in Fig.6(2)-(4). One finally obtains a large, very ramified cluster. As is easily imagined from the figure, KCA model is much more relevant to phenomena associated with colloidal particle aggregation widely seen in Nature described before. It is, therefore, very interesting and important to obtain the information of both fractal structure and kinetics of colloid aggregation by using ideal monodisperse colloidal particles such as aqueous gold (Weitz & Oliveria:1984, Weitz et al:1984,1985) and silica (Schaefer et al :1984, Martin & Schaefer:1984) colloids.

Here we present our recent results of *in situ* measurements on fractal structures and dynamics of polystyrene colloidal aggregates by means of light scattering technique (Matsushita et al:1985a). Our experimental setup is shown in Fig.7. For this purpose laser-light scattering technique is very powerful: First of all, from static measurements one obtains scattered light intensity $\underline{I}(\underline{k})$ which is proportional to the structure factor $\underline{S}(\underline{k})$ of colloidal aggregates, where $\underline{k}$ is the scattering wavevector. If the aggregates have self-similar structure with the fractal dimension $\underline{d}_f$ then it can be easily verified that $S(k) \propto k^{-d_f}$. Hence, if the log-log plot of the scattered intensity $\underline{I}$ vs. $\underline{k}$ is linear the slope gives the

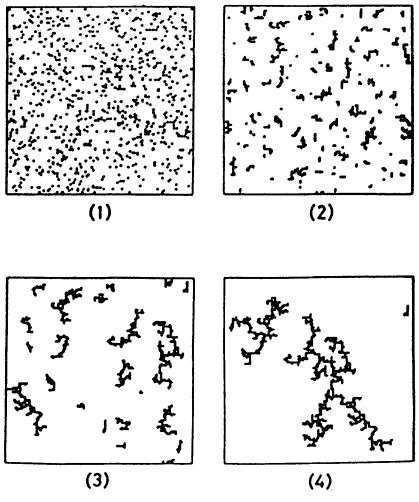


Fig. 6 Simulation of KCA model performed by a personal computer.

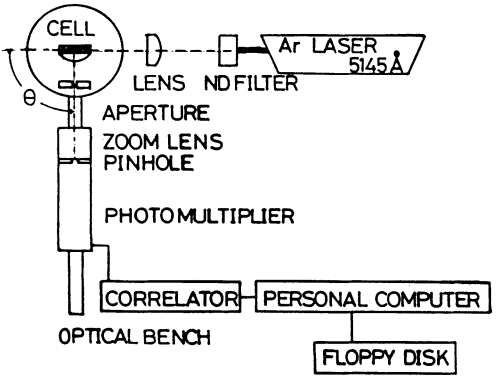


Fig. 7 Experimental setup.

fractal dimension $\underline{d}_f$ of the colloid aggregates. Next, dynamic measurement of scattered light, i.e.,photon correlation technique gives average value of the radius of gyration of the colloidal aggregates.

We used as the sample commercial polystyrene uniform latex particles of 0.038 μm diameter. For more detailed information on the procedures of the experiments and the data analysis see Matsushita et al (1985a). First we determined the fractal dimension $\underline{d}_f$ of the colloidal particle aggregates from the light scattering structure factor $\underline{S}(\underline{k})$. We measured the scattered-light intensity before and about 30 min. after the initiation of the aggregation. In Fig.8 is shown a typical example of the logarithmic plot of the scattered light intensity. Closed and open circles indicate, respectively, the data measured before and after the aggregation. This figure clearly shows that $\underline{S}(\underline{k})$ of the aggregating clusters exhibits power-law behavior, and hence they are of a fractal nature. We repeated the measurements more than ten times, observed the power-law behavior every time, and obtained the fractal dimension of the aggregates as

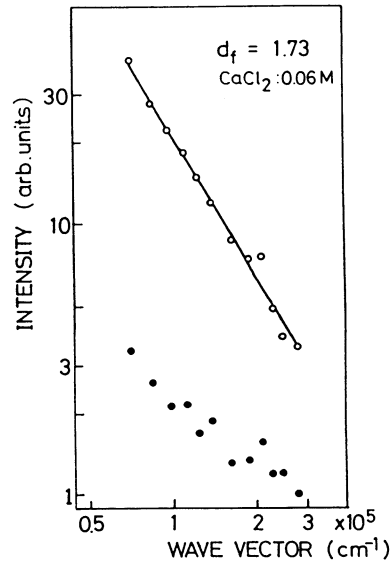


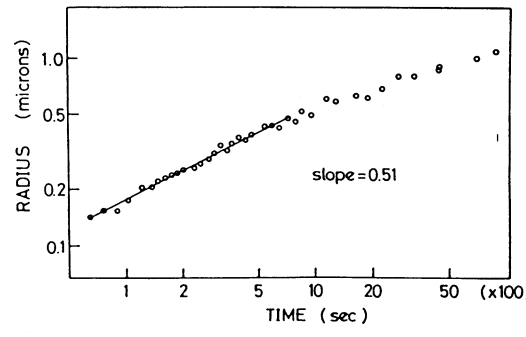
Fig. 8 Typical example of a log-log plot of the scattered-light intensity from aggregating clusters of polystyrene uniform latex particles.

$$d_f = 1.70 \pm 0.10 \ .$$

The agreement with the computer simulations (Meakin:1984a) and the value obtained from simple geometric model (Matsushita:1985) is very good, although somehow the data yield rather large standard deviation.

Next we investigated the aggregation dynamics by measuring autocorrelation functions of quasi-elastically scattered-light by means of homodyne technique. In Fig.9 we show a typical example

Fig. 9 Typical example of a log-log plot of the mean cluster radius as a function of time after initiation of aggregation.



of a log-log plot of the measured $\bar{R}$ as a function of time for aggregating clusters of polystyrene particles with 0.038 μm diameter. The data again indicate a scaling behavior of the mean cluster radius in time, $\bar{R}(t) \sim t^{1/z}$, at least until it reaches about 1 μm. Repeated measurements showed the scaling behavior every time and gave the value of the dynamic scaling exponent z

$$z^{-1}=0.54\pm0.02 \ .$$

The standard deviation is a little smaller in this case. This result is also in good agreement with the simple scaling prediction (Weitz et al:1984,1985, Matsushita:1985).

Before concluding this section we would like to point out one more interesting problem. It has been known for a long time that there are two typical but different kinds of coagulation; slow and fast. It is, therefore, of great interest and importance to elucidate what is essential difference between the two and whether they have different fractal nature and kinetics of the cluster aggregation from each other. The aggregation rate (or speed) can be controlled by the amount of appropriate salt added, such as $CaCl_2$, which we always used for the initiation of aggregation. If the concentration of the salt is very high the aggregation takes place very quickly, i.e., the reaction (cluster-cluster sticking) time is very short compared with the cluster diffusion time. This means that the structural properties and dynamics of the aggregation in this case is governed by the cluster diffusion processes. Hence this is called diffusion-limited cluster aggregation (DLCA). All the data presented so far in this section were obtained in the regime of this DLCA (or fast coagulation). On the other hand, if the salt concentration is very low the aggregation is very slow. This means that the reaction time necessary for the rigid contact between two clusters is much longer than the cluster diffusion time and the reaction processes govern the aggregation mechanism. Hence one can call this case reaction-limited cluster aggregation (RLCA), which corresponds to the slow cagulation.

We measured the dependence of the fractal dimensionality d_f of the colloidal particle aggregates on the concentration of added salt $CaCl_2$, which is shown in Fig.10. This figure indicates that if the salt concentration is decreased very much the values of the fractal dimension of the aggregates tend to increase: As is easily understood, the longer the reaction time takes the more compact the clusters become. The limiting state may, therefore, correspond to RLCA or slow coagulation.

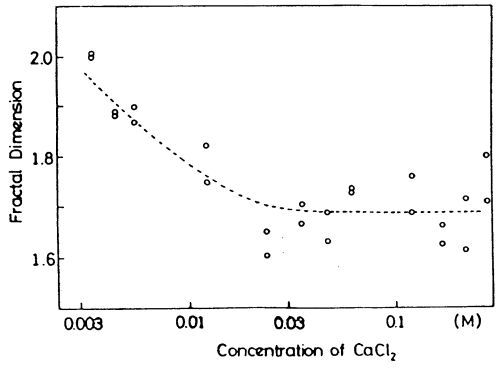


Fig. 10 Dependence of the fractal dimension d_f of colloidal aggregates on the concentration of salt added.

CONCLUSION

In summary, we have shown that zinc metal-forest offers very good experimental realization of two-dimensional diffusion-limited deposition on a one-dimensional substrate, and confirmed that both the values of the fractal dimension and the scaling exponent of the cluster-size distribution are in excellent agreement with theoretical values and computer simulation results. The chemical deposition known as chemical garden and the electrodeposition or dendritic crystal growth on a fiber may also be very interesting.

We have also confirmed that polystyrene colloidal aggregates have self-similar structure and show the dynamic scaling behavior for the radius of gyration in the fast coagulation regime. We have observed a sign of the existence of slow coagulation regime by decreasing the concentration of salt added and measuring the cluster fractal dimension. But it is necessary to extend the measurement to much lower salt concentration region and, in addition, to perform dynamic measurements all over the slow coagulation regime.

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1-3
Q: You've mentioned the influence of solute concentration on the KCA patterns. How about the dependence of DLA on D.C. voltage? I expect, the pattern would become more regular with decreasing D.C. voltage. (T. Kuroda)

A: Very surprizingly the answer is the opposite. Recent experiment performed by Prof. Sander and his collaborator at Michigan University indicates the pattern is DLA-like when the voltage is low, and it becomes regular dendritic when the voltage is over some critical value. Our data also show almost the same behavior.

Q: A general question: When you compare two random patterns and say that they are statistically the same, is it sufficient to characterize these patterns only by a single parameter, the fractal dimension? I suspect that two patterns with same fractal dimension may look different. (K. Kitahara)

A: You are certainly right. That's why we are always trying to obtain additional information to characterize the pattern formation mechanism, in addition to the fractal dimension, such as the screening effect for the metal-leaf experiment and dynamic scaling exponent for the colloidal aggregation experiment.