Research of Pattern Formation, edited by R. Takaki, pp. 169–175.

Experiments on Aggregations

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Abstract. Fundamental processes are first identified in a variety of aggregation phenomena. The aggregation processes are then classified into simple categories. Experiments on aggregations are found to be well-organized in this classification scheme. The experiments reported so far are reviewed according to the classification, and those waiting to be done are also pointed out.

1. Introduction

The irreversible aggregation of small particles to form large clusters is one of the most common phenomena seen in Nature and many areas of science and technology such as food, aerosol and colloid sciences, polymer science and immunology. In a burst of recent developments on their computer simulations, experimental and theoretical investigations, it is this "aggregation" that has been studied in the fullest detail among many phenomena accompanied by growing random patterns. This is because the aggregation processes have been recognized to frequently result in the formation of random and complex materials, which can be well described in terms of the concept of fractal geometry (Mandelbrot, 1982). It is, therefore, of great importance for further development of this field to sum up experiments on aggregations carried out so far and examine the validity of the models to describe them.

2. Classification of Aggregation Phenomena

There are a variety of aggregation phenomena such as cohesion, condensation, coagulation, agglutination and agglomeration. It is, therefore, important to identify

fundamental and characteristic processes in the aggregation phenomena and attempt to classify the aggregation processes. First of all, they can be classified through the form of objects aggregating (whether they are particles or clusters) and the way of their motion before aggregating (whether it is Brownian motion or ballistic such as in an atmosphere of very low pressure).

One can also classify the aggregations from the viewpoint of rate-limiting processes. The mechanisms controlling the growth processes vary widely, but in many cases one can distinguish two basic time scales: (1) The diffusion time τ_D is the typical time needed for particles or clusters to come close together through diffusion, and (2) the reaction time τ_R is the typical time needed for the formation of a bond, e.g., instantaneous bond formation at first contact (high sticking probability) or slow bond formation achieved only after many unsuccessful encounters (low sticking probability). If the two time scales are very different, it is usually possible to find a simplified kinetic description on the time scale of the slow process. For $\tau_D >> \tau_R$ the processes are referred to as diffusion-limited (DL), while for $\tau_D << \tau_R$ the processes are referred to as reaction-limited (RL). Hence, for instance, the interface-controlled process in the area of crystal growth corresponds to RL.

2.1 Particle-cluster aggregation (PA)

Small individual particles move around and aggregate into immobile clusters, which then grow. This group of aggregations is subdivided according to the rate-limiting processes as follows.

2.1.1 Diffusion-limited particle-cluster aggregation (DLPA)

This is the so-called diffusion-limited aggregation (DLA) or Witten-Sander (WS) model, and can describe well the pattern formation in a Laplacian field.

2.1.2 Reaction-limited particle-cluster aggregation (RLPA)

This includes, for instance, the Eden model which was first proposed to model cancer growth, and interface-controlled crystal growth.

2.1.3 Ballistic particle-cluster aggregation (BPA)

This describes the aggregation of particles which have longer mean-free-path than the size of aggregates, e.g., thin-film deposition in a vacuum.

2.2 Cluster-cluster aggregation (CA)

Clusters consisting of particles also move around and collide with individual particles or other clusters to stick each other and grow further. This is also subdivided according to distinct rate-limiting processes as follows.

2.2.1 Diffusion-limited cluster-cluster aggregation (DLCA)

The fast aggregation of colloidal particles which has long been known in colloid science comes under this category.

2.2.2 Reaction-limited cluster-cluster aggregation (RLCA)

The slow aggregation of colloidal particles which has also long been known in colloid science is an example.

2.2.3 Ballistic cluster-cluster aggregation (BCA)

In this case the mean-free-path of clusters should be longer than their maximum size.

Although the classification can be done as described above, it is important to note that in real experiments distinct rate-limiting processes do not always show up, or a crossover from one process to another may be seen.

Computer simulations on idealized models for each case classified above have been performed both intensively and extensively, and the structural properties, growth dynamics and statistics of resultant clusters have been discussed (Meakin, 1988). Here, from the viewpoint of extracting quantitatively in one of the most prominent properties, let us pay attention to fractal dimensionalities D of the resultant clusters. In Table 1 is summed up the results of D obtained by the computer simulations for each case classified above. Careful attention must, however, be paid to the following fact. In general, it is very difficult to determine by the fractal dimensionality alone which model an experiment having been carried out corresponds to. And other, independent experiments that give data characterizing dynamics and/or statistics of the aggregation processes involved are clearly needed. For instance, in the case of cluster-cluster aggregation (CA), One cannot usually draw experimentally a distinction between DLCA, RLCA and BCA by the observed values of D alone, because they usually have large errors. Another example is in the particle-cluster aggregation (PA), in which RLPA cannot be distinguished at all from BPA by D alone.

Table 1. Values of fractal dimensionalities D obtained by computer simulations for various aggregation processes in spatial dimensionalities d = 2 and 3 (Meakin, 1988).

	d	DL	RL	B
		DLPA[a] (or DLA)	RLPA (orEden)	BPA
PA	2	1.71	2.0	2.0
	3	2.50	3.0	3.0
		DLCA	RLCA	BCA
CA[b]	2	1.43	1.55	1.51
	3	1.75	2.07	1.91

(a) There are 2–3% errors. (b) There are 5–6% errors in all (DLCA, RLCA, BCA) cases.

3. Experiments on Aggregations

In this section, we try to arrange recent representative experiments on aggregations according to the classification scheme described in the last section

(Matsushita, 1989). Aggregation phenomena, of course, had long been known. It is, however, since 1984 that they have experimentally been investigated in detail under ideal conditions from the viewpoint of "physics of fractals". Since then the "physics of fractals" has been obtaining ever increasing interest.

3.1 PA

3.1.1 Electrodeposition

A metal-leaf of various metals is a typical example of two-dimensional electrodeposits. This has been known from the end of the last century and used as one of simple and spectacular demonstrations of classroom experiments on electrochemistry. The fact that this metal-leaf exemplifies DLPA or the so-called DLA was shown experimentally for zinc by the group of the present author (1984). This experiment is important in that it was the pioneering work for subsequent bursts of experiments on the "physics of fractals". We showed surprisingly good agreements with two-dimensional DLA of not only the fractal dimensionality but also the existence of screening effect, surrounding potential field and structural stability. Similar electrodeposits grown not from a point electrode like a metal-leaf but from a line electrode may be called a "metal-forest". The entire pattern can be regarded as consisting of individual trees. One can, therefore, discuss not only the fractal structure but also the size distribution of individual "metal-trees". An immediate question is how the statistics of the trees relates to their structures.

3.1.2 Diffusion-limited polymerization

Diffusion-limited two-dimensional polymerization of pyrrole was performed in a thin-layer electrical cell made by two circular glass plates (1986, 1987). Electrical resistivity between two points on a deposit was measured, and the results as well as the fractal dimensionality were reported to be consistent with those of DLA.

3.1.3 Random dendritic crystal growth

Perhaps the most familiar aggregates are various kinds of crystals. The mode of crystal growth is classified roughly into two categories. One is interface-controlled crystal growth, which corresponds to the reaction-limited particle aggregation (RLPA) process and is found for small degrees of supercooling in melt growth or weak supersaturation for solution growth. In this case the crystal morphology is determined mainly by the kinetics of atoms or molecules on crystal surfaces such as surface diffusion or migration. A growing crystal has a simple, non-fractal structure with flat facets such as a cube. The other is diffusion-limited crystal growth, which corresponds to DLPA. In this case, supercooling or supersaturation is so strong that flat facets cannot be maintained when a crystal is growing. This brings about interfacial instability and eventually leads to dendritic crystal growth.

Since crystal growth anisotropy always exists, dendritic growth leads to more or less regular shapes, exemplified by snow crystals. However, if such a strong anisotropy can in some way be substantially reduced, then DLA-like, diffusion-limited random dendritic crystal growth can be realized. This conjecture was

confirmed for the growth of ammonium chloride (NH_4Cl) dendrites from supersaturated aqueous solution (1986) and of succinonitrile from its supercooled melt (1987). This elucidates the important fact that dendritic crystals grow through two competing elements, i.e., regularity coming from crystalline anisotropy and randomness inherent in a diffusion field.

Growth of DLA-like random fractal crystals has also been observed in a solid-solid phase transition of thin film $GeSe_2$ and in a crystallization of monolayer DMPE at an air/water interface.

3.1.4 Thin-film deposition

In usual thin-film depositions particles such as atoms or molecules are deposited on a substrate via trajectories which are more nearly ballistic than Brownian, because the deposition processes are usually carried out in an atmosphere of very low pressure. This means that usual thin-film deposition corresponds to BPA. The internal structure of thin-film deposits is compact except for very small (perhaps atomic) scales. Nevertheless, recent close investigations have been revealing that the thin-film deposits have some characteristic morphologies such as conical inner structure and "cauliflower"-like surface structure for near normal incidence of depositing particles, and columnar structure for oblique incidence.

Two-dimensional structures which are clearly reminiscent of DLA patterns are sometimes observed on the surface of a variety of sputter-deposited thin-films such as $NbGe_2$. Although it is presumed to be due to the diffusion of metallic microstructures on a substrate, the system is so complex that the underlying growth mechanisms are not yet understood.

3.2 Cluster-cluster aggregation (CA)

The growing processes in cluster-cluster aggregation are as follows. Particles which were initially dispersed in some medium at some concentration stick on collision with each other. Resulting clusters also move around with some mobility depending on their size, and repeat colliding with particles or other clusters and sticking together to grow further and irreversibly. These CA phenomena are widely seen in a variety of natural and industrial processes such as soot formation in chimney, mud sedimentation near a river mouth and coagulation of some foods like tofu.

3.2.1 Fast and slow aggregation of colloids

The addition of salt into a colloidal suspension initiates the aggregation process called salting-out. This is why fine mud particles suspended stably in fresh water precipitate sharply near the mouth of rivers. It has been known for a long time that there are at least two distinct regimes of colloidal aggregation for salting-out, fast and slow aggregations, each of which has different rate-limiting physics. This can be understood qualitatively by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of colloidal particle pair interaction potential: In the case of stably dispersed colloids there is a deep "well" at short distances around a colloid particle due to van der Waals attractive interaction, which is combined with a repulsive "barrier" at

longer distances due to the electric double layer. The sufficient reduction of the repulsive barrier caused, e.g., by the addition of sufficient amount of salt brings about the fast aggregation, because there is no obstruction to sticking on collision of two particles. Therefore, the fast aggregation corresponds to DLCA. On the other hand, the slow aggregation is induced by the remaining relatively small barrier which is realized by the addition of insufficient amount of salt. Particles and clusters experience numerous collisions before sticking stably with each other. The slow aggregation, therefore, corresponds to RLCA.

In recent years experiments on aggregation of colloids such as gold, silica and polystyrene have been performed under ideal conditions. Clusters produced by the fast and slow aggregations have been found to possess different fractal dimensions, qualitatively different time-dependence of growth and size distributions for clusters. These are all in fairly nice agreement with the results obtained by large-scale computer simulations for DLCA and RLCA. Such experimental techniques as laser-light scattering, small-angle-neutron and X-ray scatterings (SANS and SAXS) are used for three-dimensional colloidal systems, and in-situ observations through microscopes with digital image processing equipment for two-dimensional colloidal systems.

3.2.2 Ballistic cluster aggregations (BCA)

In an atmosphere of very low pressure and/or very high temperature cluster trajectories are nearly linear rather than Brownian, and BCA processes are more likely to occur. This situation is encountered in practice in the case of various soot aggregates produced by rapid evaporation of metals, combustion of fossil fuels, aerosols, and so on. However, clear and convincing experiments for BCA are still lacking.

4. Concluding Remarks

Aggregation is an important area with a rich phenomenology and a wide variety of applications. So far, it has been found that at least some aggregates can be well described in terms of fractal geometry and that the size distribution of aggregates and the kinetics of their aggregation can also be related to their fractal structure. However, there seem to be many investigations to be done. For instance, DLA-like patterns observed on sputter-deposited film remain mysterious. Diffusion-limited polymerization patterns of pyrrole look rather dense-branching morphology than DLA. Convincing BCA experiments are clearly needed. The surface of vapor-deposited thin film may be self-affine, just the same as the earth's surface. The composite processes of aggregation and other simple processes such as the combination of aggregation and evaporation may also be seen in nature. Let us hope all these interesting problems will be solved in the near future.

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