                                                            Author's Review

The Application of Fractals to Colloidal Aggregation

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Recent work on understanding colloidal aggregation phenomena using fractal geometry is reviewed. After describing a typical aggregation experiment, the concepts of fractal and fractal dimension are introduced and some simple models fit to describe the mechanism of diffusion-limited aggregation leading to fractal aggregates are presented. The old Smoluchowski's theory for describing the kinetics of colloidal aggregation is revised using fractal concepts.

1. INTRODUCTION

The field of colloidal aggregation is a very old subject whose theory was pioneered by Von Smoluchowski[1] in 1916. However, if a lot of work was devoted to understand the nature of interactions between colloidal particles, the conditions of aggregation and the principles of aggregation kinetics,[2] it is only recently (after the introduction of the concept of fractal by B. Mandelbrot[3] in 1975) that it has become possible to quantitatively describe the structure of colloidal aggregates. These recent studies provide very interesting new insights to old theories. There are a number of books and review papers[4] on this subject but most of them are aimed at physicists. After presenting a typical experimental example, I explain what a fractal aggregate is and I introduce the diffusion-limited aggregation models and their improvements, then I show how the old Smoluchowski's theory can be revised using fractal concepts.

2. AN EXPERIMENTAL EXAMPLE

As a typical example, I have chosen to describe the aggregation of gold colloids. Gold colloids have been known for a very long time. The alchemists of the Middle Age used them to color glasses. These are small spherical solid gold particles, of a diameter of some nanometers, dissolved in a liquid medium. In general, there exists a strong electrostatic long range repulsion between particles, due to the electrical charges located on their surface. This ensures a remarkable stability of the colloidal suspension. Some gold colloids, prepared by Faraday 130 years ago, are still conserved today! The

aggregation phenomenon does not occur as long as this long range repulsion is not suppressed by some suitable experimental procedure. This can be done either by dissolving mobile ions, with a charge opposite to the surface charge, which come near the spheres and produce an efficient electrostatic screening, or by fixing neutral organic molecules on the surface as has been done by David Weitz and collaborators.[5] Under such conditions, short range van der Waals attractive forces are restored and the reversible aggregation phenomenon starts to take place.

As long as a given particle is too far from other particles, it undergoes a random diffusive motion in the suspension (the so-called Brownian motion). But as soon as it approaches another particle, it feels the van der Waals attraction force and it sticks irreversibly to the particle to form a dimer, which can diffuse in the suspension. In turn, this dimer can stick to a particle or to another dimer, and from sticking to sticking, larger and larger aggregates are formed in the solution. Aggregates may eventually contain up to some thousand particles and reach sizes of the order of a micrometer. At this stage, they begin to scatter visible light and the solution exhibits a colored appearance. This irreversible mechanism is called diffusion limited aggregation, since the diffusion of clusters plays an important role in determining the kinetics of the process, as well as the resulting shapes of the clusters.

Similar structures can be obtained with other colloidal suspensions. In a gaseous atmosphere, instead of a liquid, the colloids are called »aerosols«. This is the case of smoke, dust, etc... Until very recently, there was no quantitative analysis of such structures available. By analyzing digitalized photographs, such as the one shown in Figure 1, Forrest and Witten,[6] in 1979, have demonstrated the fractal nature of such aggregates. After this discovery, a great number of quantitative studies have appeared.
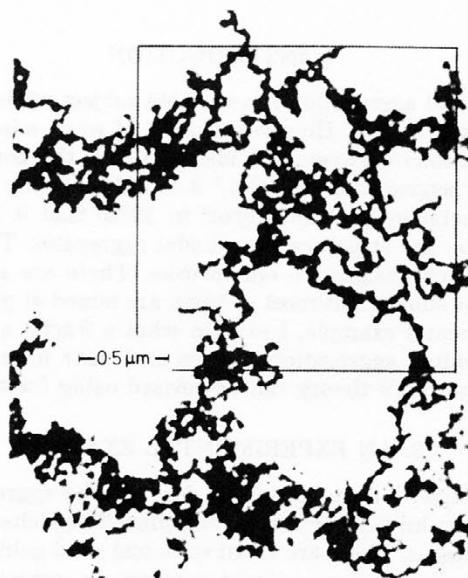

Figure 1. Electron microscope photograph of an aerosol aggregate (iron smoke). By analyzing a digitalized version of this photograph Forrest and Witten[6] have, for the first time, proved the fractal character of aggregates grown by diffusion limited aggregation.

3. WHAT IS A FRACTAL AGGREGATE?

3.1. Self Similarity

The word »fractal« was introduced by Benoit Mandelbrot[3] to describe rugose (wrinkled or corrugated) objects whose rugosities show up in a large range of length scales. The simplest are self-similar fractals whose structure remains invariant under a change of scale. A typical and quite instructive example of a self-similar fractal aggregate built with disc-shaped particles in two dimensions is shown in Figure 2. It is worth noting, as quoted in Mandelbrot's book[3] that such a picture was employed by E.E. Fournier d'Albe[7] in 1907 to describe some hierarchical structure of the world. It is now known as the »Vicsek fractal« since it was used by Tamas Vicsek in the context of aggregation phenomena.[8] This fractal can be built following a precise and deterministic iterative procedure. To begin with, one particle is surrounded with four others to form a cross. Then, this pattern of five particles is treated as a single particle: it is surrounded by the same pattern at each corner, and so on. The object obtained after an infinite number of iterations exhibits fascinating properties. Self-similarity is one of these: here, if a part of the aggregate is enlarged by a power of three, the enlargement is identical to the original structure.

In practice, most of the »natural« fractals, such as the one shown in Figure 1, do not exhibit the regularity and the anisotropy of Vicsek's fractal: they are »disordered« fractals. They can be built by an iterative procedure as before, but introducing some randomness at each iteration. Owing to randomness, enlargement is not strictly identical to the original, like in the case of Vicsek's fractal. The enlargement is, however, statistically equivalent to the original aggregate, in the sense that it could, with equal probability, have been the original aggregate in a similar experiment. Here self-similarity is now only true on average.

3.2. Fractal Dimension

Another remarkable property of self-similar fractal objects appears if one calculates the number of particles N within a circle of radius R around a particle at or near the center of the aggregate. One then discovers a characteristic power-law relationship.

$$N \sim R^D$$

The exponent D is called fractal exponent of fractal dimension.

Fractal dimension can be seen, in a way, to measure the degree of occupation of the embedding space by the particles of the aggregate. If the particles are aligned along a straight line, one trivially recovers $D = 1$. If the particles are placed on a two dimensional array, one has $D = 2$. In fact, for the most compact arrangement, or for any homogeneous disposition, in a space of any number of dimensions, the fractal dimension is equal to the dimension of space ($D = d$). However, for a general fractal aggregate, the fractal dimension D is smaller than the space dimension d and may very well not be an integer. In the case of the aggregate shown in Figure 2, one can easily be convinced that when the radius of the circle is multiplied by a factor 3, the number of particles contained in it is multiplied by a factor 5. The fractal dimension is then $\ln 5/\ln 3 = 1.4649...$ In the case of a disordered fractal, one must calculate an average over many, statistically equivalent, aggregates to get a power law of sufficiently high precision.
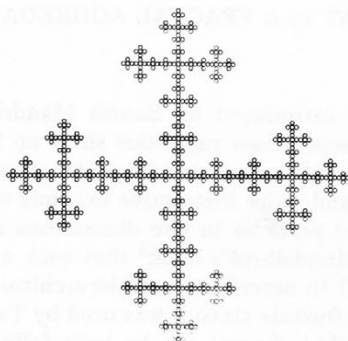
Figure 2. Vicsek fractal built in two dimensions.

3.3. Density and Correlation Function

If one calculates the density of matter within a sphere of radius R, one finds that, for a fractal object, it varies as $R^D/R^d = R^{-(d-D)}$. This is another important characteristic of fractals: the larger the part one considers, the lower is its density. This implies that holes of all sizes are present in its structure.

Another closely related property concerns the particle-particle correlation function $p(r)$, which measures the probability of finding a particle at a distance r from a given particle. This correlation function varies as a power law.

$$\rho(c) \sim r^{-(d-D)}$$

which bears a close resemblance to the laws governing the behaviour of »critical« matter near a second order phase transition.[9]

3.4. The Different Kinds of Fractals

Up to now, I have restricted discussion to the simplest case of self-similar fractals for which there is no ambiguity when defining the fractal dimension. However, much more complicated fractals have been introduced, such as self-affine fractals,[8] for which exist different fractal dimensions along different directions of space. Special attention has also been paid to multifractals,[9] for which one needs an infinite set of independent fractal dimensions to define completely all their properties.

Moreover, fractal aggregates are examples of particular fractal structures called »mass fractals« in contrast to »surface fractals«, where the fractal structure is no more the bulk (which is now compact) but the surface of the considered object.

3.5. Natural Cut-offs

It is important to distinguish between ideal fractal aggregates, which are mathematical objects built of an infinite number of infinitely small particles for which the above properties are exact, and fractal aggregates that are encountered in real world, for which the self-similarity and power-law properties are observed only over a limited range of lengths. The natural cut-offs generally have the typical size, a, of the in-

dividual particles, and the size, L, of the aggregate itself. The aggregate is then considered as a fractal if the characteristic power law behaviour is observed over a wide range of R values between a and L, and if the two cut-offs are sufficiently well separated.

3.6. Experimental Determination of the Fractal Dimension

The most straightforward way to calculate the fractal dimension of a colloidal aggregate is a numerical analysis of digitized images, as it was first done by Forrest and Witten.[6] It can be shown that such a method, which analyzes a two-dimensional projection of a three-dimensional object, gives the right answer for fractal dimensions less than 2. This method has been used to calculate the fractal dimension of gold colloid aggregates,[5] as well as the fractal dimension of aggregates made of polydisperse iron particles.[12]

According to the definition of the fractal dimension, any physical property which is directly linked with the repartition of mass in space can be also used to determine the fractal dimension. One method, which is now commonly used,[13] is the low angle scattering of neutrons, X-ray or light, which gives information on the particle-particle correlations in an aggregate. When one can neglect multiple scattering, the scattered intensity is shown to vary as

$$I(q) \sim q^{-D}$$

where

$$q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$$

is the magnitude of the scattering vector, θ being the scattering angle and λ the wavelength of the incident beam. The range of q-values where this power-law is recovered is limited by the Guinier regime for q of the order of $1/L$ (where the incident beam sees the whole aggregate) and the Porod regime for q of the order of $1/a$ (where the incident beam is scattered by the surface of individual particles).

Special care must be taken when trying the extract the fractal dimension from a given physical property. Many studies have shown that the physics of fractals is quite different than in regular Euclidean spaces.[14] When a physical property on an Euclidean lattice depends explicitly on the dimension d of space, it cannot be trivially extended to fractal structures by simply replacing d by D. Other exponents that also play the role of dimensions must be introduced, and, in general, they are different from the fractal dimension. For example, when studying dynamical properties on fractals, one must introduce the so-called spectral dimension.[14]

4. DIFFUSION-LIMITED AGGREGATION

4.1. Diffusion-Cluster Diffusion-Limited Aggregation

The first simple model for simulating diffusion-limited aggregation phenomena and able of building a fractal structure was that of Witten and Sander (1981).[15] This was the starting point for very many theoretical and experimental studies.

In its original two-dimensional version, particles were disks placed on a square lattice. A seed particle (the first particle of the aggregate) is first placed at the origin. Then a circle, large compared to the size to be attained by the resulting aggregate, centred on the origin, is drawn, and a point is selected at random on the circle. A
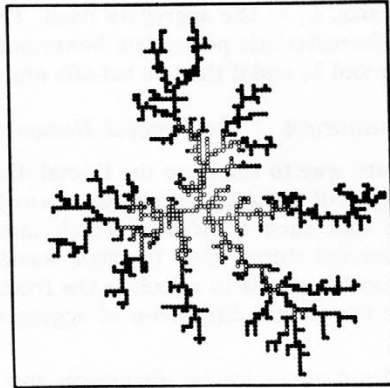
Figure 3. Witten-Sander aggregate built on a square lattice. Gray tones indicate the arrival time of the particles.

second particle is released at the site nearest to this point, which then starts to undergo a random walk on the lattice. If this moving particle goes too far from the origin (say a distance three times the radius of the circle), it is abandoned and a new particle is released again at random, on the circle. When the moving particle reaches a site next to the seed particle, it stops its random walk and sticks permanently to the seed. The aggregate then contains two particles. Then another point is selected at random on the circle and a new particle is released. When it reaches one of the sites nearest to the aggregate, it stays there, and so on.

The aggregate of Figure 3 contains 1024 particles, and even in such a modest simulation, one can already see the fractal character of the Witten-Sander aggregate. The moving particles are most likely to join the aggregate on the tips and, consequently, deep 'fjords' develop in the structure, which are then quickly preserved by the growth of new branches. Thus, holes of all sizes are created. This screening effect can easily be seen in Figure 3, where the gray tones indicate the arrival time for each particle. The fractal character can be quantitatively analyzed by calculating a typical size, the radius of gyration of the aggregate, R which is the standard deviation of the particles from the centre of mass, and by studying its dependence on the total number of particles, N. In doing so, a characteristic power law is recovered:

$$N \sim R^D$$

with $D = 1.70$ in two dimensions. From earlier small scale simulations, it was commonly believed that this number did not depend on the type of lattice used, and the same result was obtained with off-lattice simulations.[16,17] Following the general universality argument of critical phenomena,[9] the fractal dimension of the Witten-Sander model was believed to depend only on the space dimension d. The model can be straightforwardly extended to higher dimensions and the earlier results for the fractal dimension D, as a function of the space dimension d, are given in Table I.

Further numerical and analytical investigations show that the scaling properties of the Witten-Sander aggregate are much more complicated than it was believed initially. First, it was found that there are two different fractal dimensions,[17] one cor-

TABLE I

Fractal dimension D of aggregates obtained by diffusion-limited aggregation as a function of the dimension of space d

d	2	3	4	5	6
Particle-cluster	1.70	2.50	3.33	4.20	5.3
Cluster-cluster	1.44	1.78	2.05	2.27	2.6

responds to radial correlations, the other, which is slightly smaller, corresponds to tangential correlations. As a consequence, the Witten-Sander aggregate is not rigorously self-similar (it is more like a self-affine fractal): the bigger it is, the thinner are its branches. Second, after the large scale simulations of Paul Meakin,[18] it became clear that there was some induced anisotropy arising from the underlying lattice: growth occurs preferentially along some »easy« axis. Third, as first predicted by analytical investigations[19] and confirmed by numerical simulations,[18] the fractal dimension depends on the lattice. All these very exciting results show that the universality arguments, demonstrated for at-equilibrium critical phenomena,[9] do not apply to irreversible processes.

Once three-dimensional simulations had been made using the Witten-Sander model, it was quickly recognized that it could not quantitatively describe colloidal aggregation experiments: the three-dimensional value found for the fractal dimension ($D = 2.5$) is larger than most of the experimental estimates.[5,6,12,13] In fact, a great number of different experimental realizations were found and it became clear that the Witten-Sander model describes what I call »aggregation under field«, typical of electrodeposition and similar situations. In electrodeposition, an electrical current goes through a metallic salt solution, and metallic particles appear on the cathode. If the experiment is performed under the right conditions, metallic particles are more likely to be deposited where the electric field is large, *i.e.* near the tips of the growing aggregate. Such an experiment was first carried out in three dimensions[20] but, since the pattern is probably more spectacular in two dimension, Figure 4 presents the photograph of an aggregate built by a Japanese group.[21] In both cases, however, qualitative as well as
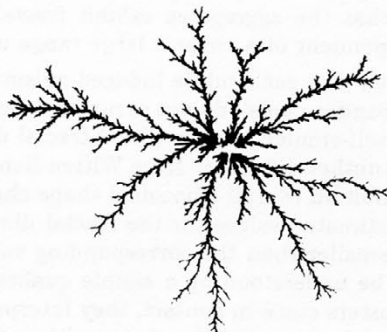

Figure 4. Aggregate obtained in a two dimensional electrodeposition experiment (M. Matsushita et al.).[21]

quantitative agreement with the Witten-Sander model is remarkable. The link with the Witten-Sander model can be understood from the equivalence between microscopic (random walk) diffusion and the macroscopic Laplace equation which governs the distribution of electrical fields in such an experiment.[22] This mathematical equivalence explains why the Witten-Sander model applies to many other situations that are not truly aggregation, such as dielectric breakdown,[23] fluid-fluid displacement (viscous fingering)[24] and the dissolution of porous materials.[25]

4.2. Cluster-Cluster Diffusion-Limited Aggregation

The Witten-Sander model fails to describe correctly the aggregation of colloids because it considers a single immobile growing cluster around which only single particles move, while, in the experiment described in section 2, there is a more democratic system in which all clusters move. To describe this situation more realistically, an extension of the Witten-Sander model, called the cluster-cluster model has been introduced,[26] in which the growth mechanism is now governed by collisions between diffusing clusters of the same mean size.

In its original two-dimensional version,[26] the model starts with a collection of equally sized disc-shaped particles placed randomly on a two-dimensional square lattice in a square box. These particles are then allowed to undergo a random diffusional motion simulated by a pure random walk on the lattice (taking into account the periodic boundary conditions at the edge of the box). When two particles arrive at adjacent lattice sites, they stick together irreversibly to form a rigid dimer which is now also able to diffuse in the box. This dimer, in turn, can stick to other dimers or to single particles, and so on. After each adhesion, the two colliding clusters form a new, rigid, larger cluster. The mechanism can be pursued until a single large aggregate remains in the box. Figure 5 gives a typical case where one can see the aggregates at three different steps of the aggregation process.

In the simulations, a kinetic parameter a is introduced, which determines how the velocity of a cluster, v_i, varies as a function of the number of constituent particles, i:

$$v_i \sim i^\alpha$$

For realistic cases of negative α values, i.e. when small clusters move faster than large clusters, and in the limiting case of a very low initial particle concentration, it can be established numerically that the aggregates exhibit fractal structure and that their fractal dimension is independent of a cover a large range of a values.

Up to now, it appeared that such subtle induced-anisotropy effects, like those encountered in the Witten-Sander model, do not occur, and cluster-cluster aggregates can be considered as 'gentle' self-similar fractals whose fractal dimension depends only on the dimension of space. Another difference from Witten-Sander aggregates is that cluster-cluster aggregates exhibit an overall ellipsoidal shape characterized by quite a large anisotropy ratio.[27] The estimated values for the fractal dimension are given in Table I and can be seen to be smaller than the corresponding values found for the Witten-Sander model. This can be understood by a simple qualitative argument: when two, equally sized diffusing clusters come in contact, they interpenetrate less than a cluster and a single particle do and, consequently, the resulting structure is more open, i.e. has a smaller fractal dimension. The three-dimensional value, $D = 1.78$, appears to be in quite good agreement with the experimental values,[5,6,12,13] at least in the case of rapid aggregation where the electrostatic repulsion between colloids is completely

screened. In contrast to the geometrical characteristics, all the kinetics strongly depend on a, and this will be discussed later in section 6.

An idealized version of the cluster-cluster model, the hierarchical model,[28] has been considered, in which only clusters of exactly the same number of particles are allowed to stick together. This version, which gives the same quantitative results but is less demanding of computer time, has permitted systematic extensions to straightforward simulations, in particular to off-lattice simulations,[29] to reach high space dimensions,[30] to include rotational diffusion,[31] and to take into account polarizability effects.[32] Figure 6a shows an aggregate of 4096 particles built with an off-lattice hierarchical procedure in three dimensions. In comparison, Figure 6b shows a gold-colloid aggregate grown by David Weitz and coworkers.[5]

The hierarchical version has also permitted some interesting analytical investigations. It has been established that, in contrast to the Witten-Sander model, in the cluster-cluster model there is a characteristic upper critical dimension ($d = 8.8$) above which the clusters become transparent to each other and, consequently, their fractal dimension becomes independent of the space dimension.[33]
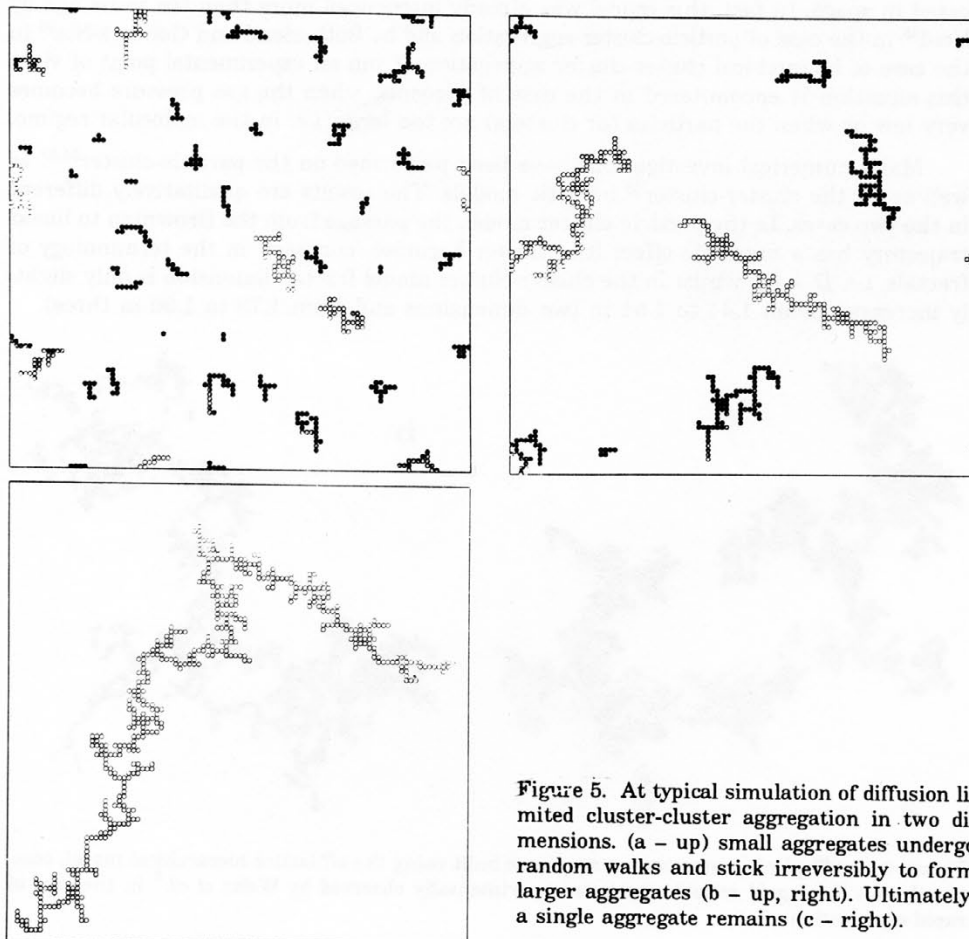

Figure 5. At typical simulation of diffusion limited cluster-cluster aggregation in two dimensions. (a – up) small aggregates undergo random walks and stick irreversibly to form larger aggregates (b – up, right). Ultimately, a single aggregate remains (c – right).

5. OTHER AGGREGATION MECHANISMS

5.1. Ballistic Aggregation

In both particle-cluster and cluster-cluster diffusion-limited aggregation models, the mean-free path of the Brownian diffusion of particles (or clusters) has been chosen, for simplicity, to be exactly equal to the particle diameter, which is the lattice spacing when the model is built on a lattice. This fact was first highlighted by Bensimon et al.[34] in the case of particle-cluster aggregation. In practice, one can easily relax this constraint and choose a larger mean-free path. If this is done, one observes that in both cases, after an intermediate regime where the clusters are more compact, the same results as before with the same fractal dimension are obtained, when the cluster size becomes larger than the mean-free path. An interesting limit is the case where this mean free path is chosen to be quasi-infinite, i.e. when it remains always larger than the cluster size. Within these limits, another model, called ballistic model is defined, in which the particles (or clusters) follow straight-line trajectories randomly located in space. In fact, this model was already introduced more than ten years ago by Vold[35] in the case of particle-cluster aggregation and by Sutherland and Goodarz-Nia[36] in the case of hierarchical cluster-cluster aggregation. From an experimental point of view, this situation is encountered in the case of aerosols, when the gas pressure becomes very low or when the particles (or clusters) are too large, i.e. in the molecular regime.

Many numerical investigations have been performed on the particle-cluster[34,37] as well as on the cluster-cluster[38] ballistic models. The results are qualitatively different in the two cases. In the particle-cluster model, the passage from the Brownian to linear trajectory has a dramatic effect (the cluster becomes 'compact' in the terminology of fractals, i.e. $D = d$), whilst in the cluster-cluster model fractal dimension is only slightly increased (from 1.44 to 1.51 in two dimensions and from 1.78 to 1.90 in three).
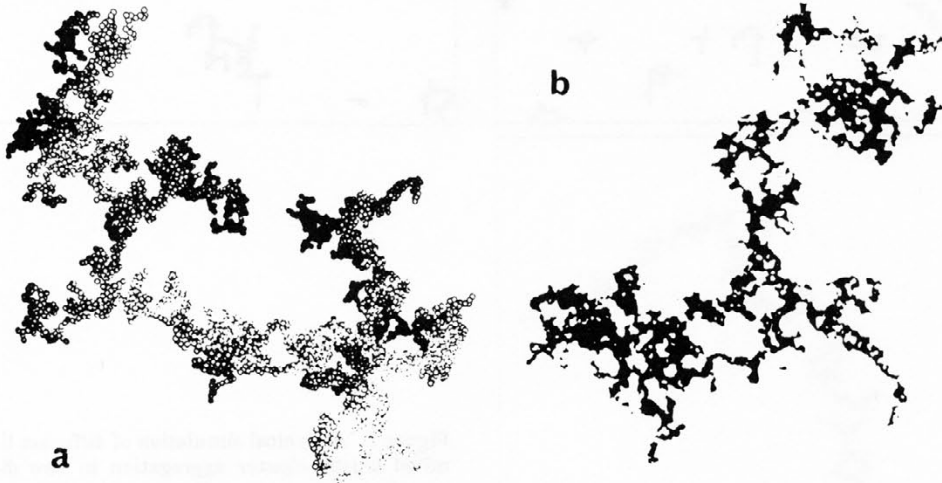

Figure 6. (a) Typical cluster-cluster aggregate built using the off lattice hierarchical model, compared with (b) a gold colloid aggregate experimentally observed by Weitz et al.[5] in the case of rapid aggregation.

Another variant of the ballistic model considers random straight-line trajectories with a zero impact parameter. In this case, the relative trajectory goes through the centres of mass of the two colliding objects. In the case of particle-cluster aggregation, the resulting cluster is again compact ($D = d$), while in the case of cluster-cluster aggregation[39] the fractal dimension is again slightly increased, as compared to the case of non-zero impact parameter (from 1.51 to 1.56 in two dimensions and from 1.91 to 2.06 in three).

5.2. Chemically-Limited Aggregation

Another important constraint of the diffusion-limited aggregation models is that the sticking always occurs on first contact. This constraint can be relaxed by introducing a probability p that when the two colliding objects come into contact they stick together permanently. This is physically justified in the case of partially screened colloids where, due to an electrostatic energy barrier, the aggregates must bounce many times on each other before they finally stick. Again, this modification of the earlier models merely introduces an intermediate regime in which the clusters are apparently more compact, after which the same fractal dimension as that found for $p = 1$ is finally obtained when sufficiently large cluster sizes are reached.[40] The characteristic intermediate regime cluster size tends to infinity when p tends to zero. Thus, one can define another model in the $p = 0$ limit, when the colliding objects have unlimited time to investigate all the sticking possibilities. Clearly, the characteristic of their relative trajectory can no longer play a role in the aggregation mechanism, which is then mostly dependent on the chemical properties of the colliding objects. This is, therefore, called the chemically-limited (or reaction-limited) aggregation model.

In the particle-cluster case one recovers a well-known model, Eden model,[41] which was originally introduced to study biological growth. In this model, particles are added one after another, at random, on the cluster surface. While compact aggregates are produced in this way,[42] their surface exhibits interesting rugosities which have been the subject of many recent numerical investigations.[43]

Although in the cluster-cluster case, this process does not lead to compact aggregates, their fractal dimension is greater than in the ballistic case. The fractal dimensions are found to be 1.55 and 2.04, in two and three dimensions,[44] respectively, which is to be compared with 1.44 and 1.78 in the diffusive case. Soon after the invention of the chemically-limited aggregation model, this change of fractal dimension was verified experimentally by David Weitz et al.,[5] who, in the case of gold colloids, were able to go from rapid aggregation to slow aggregation by increasing the repulsive barrier between particles.

5.3. Aggregation with Restructuring

The last constraint in the earlier aggregation models that I would like to discuss is the rigid character of the clusters throughout the aggregation process. In practice, in all real experiments, restructuring phenomena (i.e. cluster deformations) are always present to some degree. Unless we take into account all the detailed features of the interaction forces between particles, such mechanisms are very difficult to simulate in a simple way. There has, nevertheless, been an attempt to take into account a completely explicit form for the interaction potential in the case of colloidal aggregation by performing molecular dynamics based on the Langevin equation;[45] however, only modest cluster sizes could be reached and no precise conclusion was reached on their

fractal dimension. The only simple large simulations currently available are those taking into account *ad-hoc* restructuring or readjusting mechanisms that are justified by experimental data.

Concerning particle-cluster aggregation, there have been some very interesting extensions of the Witten-Sander model, in which the incoming particle is allowed to diffuse on the cluster surface in order to find a more favourable site where it will adhere more strongly to the aggregate. In this context, surface tension effects[46] and anisotropy effects[47] have been considered in order to model dendritic growth such as observed in the formation of snowflakes.

In the case of cluster-cluster aggregation, a simple readjusting mechanism has been considered in two dimensions: after their first contact, the two colliding clusters are allowed to rotate until a second contact is made.[48] For small clusters (N of order 512), a clear compact ion is evident, as observed, for example, in aggregation experiments of wax balls on water.[49] However, on reaching larger clusters (up to N = 16384), the readjusting effect is less visible and the fractal dimension, measuring long-range correlations, is only slightly increased. Spectacular quantitative experimental confirmation of this has been recently produced by Skjeltorp[50] in an experiment using uniformly sized polystyrene microspheres confined to thin layers. Quantitative comparisons between all the situations encountered in this experiment (including particle-cluster mechanisms) and numerical simulations relating to surface tension and restructuring have been made recently.[51]

Another kind of restructuring permits the particles, or clusters, to escape after sticking. This effect is different from that of considering a sticking probability. Here, some reversibility is allowed, which can be physically justified if the attractive minimum of the van der Waals potential is sufficiently weak. A completely reversible situation, in which a steady-state (or dynamical equilibrium) is reached, making and breaking continuously, has been considered in the particle-cluster[52] as well in the cluster-cluster cases.[53] In both cases, the fractal dimensions of at-equilibrium branched-polymers (or 'lattice animals') are obtained.

6. THE KINETICS OF COLLOIDAL AGGREGATION

6.1. The Smoluchowski Equation

In the preceding sections, we were mainly interested in the geometrical aspects of the aggregates. Other important features of the cluster-cluster aggregation process are the time dependence of the mean cluster size, as well as the knowledge of the cluster size distribution. This was already studied in the past, using a simple formalism based on an equation introduced by von Smoluchowski in 1916.[1] I would like to show how this theory can be revived, taking care of the fractal nature of aggregates.

The Smoluchowski equation can be considered as a standard equation for irreversible chemical reaction kinetics. The reactions are:

$$[i] + [j] \xrightarrow{K_{ij}} [i + j]$$
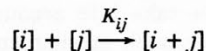
where $[i]$ refers to the chemical species: [ensemble of aggregates containing i particles], and K_{ij} is the kinetic constant (or 'kernel') of the reaction. Note that the $[k]$ species may appear as a result of the reaction between $[i]$ and $[j]$ species, so that $i + j = k$,

but may also disappear to form $[k + i]$ species, by reacting with any $[i]$. Hence, the equation giving the time evolution of the concentration c_k, where c_k is the number of $[k]$ aggregates per unit volume, is given by:

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} K_{ij} c_i c_j - \sum_i K_{ik} c_i c_k$$

Factor $1/2$ is due to the fact that both i,j and j,i events are counted in the double sum.

Quantity $K_{ij}c_ic_j$ is the rate of collisions between $[i]$ and $[j]$ clusters per unit volume or, equivalently, the probability, per unit time and per unit volume, that such an event occurs. The assumption that this probability is proportional to concentrations c_i and c_j is equivalent to neglecting spatial fluctuation of concentrations. This can be considered as an effective medium, or mean-field, approximative treatment, to employ the terminology commonly used in statistical physics.

In the case of colloids, where one initially deals with monodisperse particles, the initial conditions are:

$$c_1 = c$$
$$c_k = 0 \quad \text{for } k > 1$$

where c is the initial particle concentration.

It is sometimes more convenient to write the Smoluchowski equation in terms of the n_k's, where $n_k = Vc_k$ is the number of clusters of k particles and V is the total volume of the solution. The kernel is then $k_{ij} = K_{ij}V$. One can also write the following relations:

$$\sum n_k = V \qquad \sum c_k = N_c$$
$$\sum k n_k = V \qquad \sum k c_k = N$$

where N_c, the number of clusters, is a quantity whose time variations must be studied and where N, the total number of particles, must stay constant if there is no cause of creation or destruction of matter.

6.2. Case of a Constant Kernel

Smoluchowski himself has proposed a solution of this equation in the case where the K_{ij}'s are constant numbers. Considering $\kappa_{ij} = \kappa$, the equation writes:

$$\frac{dn_k}{dt} = \kappa \left(\frac{1}{2} \sum_{i+j=k} n_i n_j - n_k \sum_i n_i \right)$$

Let us write:

$$n_k = \phi(t) \, \psi(t)^{k-1}$$

where we introduce two unknown functions $\psi(t)$ and $\phi(t)$. The initial conditions become:

$$\phi(0) = N \qquad \psi(0) = 0$$

Inserting them in the Smoluchowski equation, one gets a condition to be satisfied, for all k:

$$\psi^{k-1}\frac{d\phi}{dt} + (k-1)\phi\psi^{k-2}\frac{d\psi}{dt} = \kappa\phi^2\psi^{k-2}\left(\frac{k-1}{2} - \frac{\psi}{1-\psi}\right)$$

Identifying terms proportional to $k-1$ and constant terms, one obtains a system of differential equations:

$$\frac{d\phi}{dt} = -\kappa\frac{\phi^2}{1-\psi}$$

$$\frac{d\psi}{dt} = \kappa\frac{\phi}{2}$$

Eliminating dt, one gets:

$$\frac{d\phi}{\phi} + 2\frac{d\psi}{1-\psi} = 0$$

which, taking care of the initial conditions, allows us to express ϕ as a function of ψ:

$$\phi = N(1-\psi)^2$$

Using this expression, the differential equation on ψ writes:

$$\frac{d\psi}{(1-\psi)^2} = \kappa\frac{N}{2}\,dt$$

which, after integrating and taking care of the initial conditions, gives:

$$\frac{1}{1-\psi} = 1 + \kappa\frac{N}{2}t$$

leading to:

$$\psi = \kappa\frac{N}{2}\frac{t}{1+\kappa\frac{N}{2}t}$$

and:

$$n_k = N\frac{(\kappa\frac{N}{2}t)^{k-1}}{(1+\kappa\frac{N}{2}t)^{k+1}}$$

The total number of clusters is then given by:

$$N_c = \frac{N}{1+\kappa\frac{N}{2}t}$$

For very large time, *i.e.* $t >> 2/\kappa N$, n_k takes the following form:

$$n_k = \frac{4}{k^2\kappa^2N}\left(\frac{k}{t}\right)^2 e^{-\frac{2}{kN}\frac{k}{t}}$$

In this large time regime, one observes a data collapse: all the size distribution functions can be superimposed using the reduced variables $k^2 n_k$ and k/t. More generally, it appears to be very useful to write the size distribution function under the following scaling form:

$$n_k = k^{-\tau} f\left(\frac{k}{\tau^\gamma}\right)$$

If this is possible, the γ exponent tells us how the mean cluster size grows with time:

$$\langle k \rangle \sim t^\gamma$$

Correlatively, the total number of clusters N_c decreases as

$$N_c \sim t^{-\gamma}$$

Thus, we have been able to show that, for constant K_{ij}, the solution of the Smoluchowski equation, for sufficiently large times, can be written under the above scaling form as:

$$\tau = 2 \qquad \gamma = 1$$

6.3. The Kernel in the Brownian Case

The explicit form of kernel K_{ij} depends on the considered type of aggregation mechanism. In the Brownian case, the original calculation of Smoluchowski[1] can be straightforwardly extended to the case of fractal aggregates. The rate of collision between a given i aggregate supposed to be fixed, centred on the origin, and all the others j clusters, which is $K_{ij}n_j$, can be calculated assuming that, for sufficiently large times, a steady state is established in which all j aggregates diffuse radially from a region far away from the origin, where concentration c_j is constant and equal to n_j/V (the mean value in the solution) to a region close to the aggregate where they disappear, i.e. $c_j = 0$. Introducing a mean hard core radius R_i for clusters i, and assuming a spherical geometry, this reduces to a trivial steady-state diffusion problem in which c_j depends on the distance r from the origin, with $c_j = n_j/V$ for $r = \infty$ and $c_j = 0$ for $r = R_i + R_j$.

The radial current of j clusters, J_j, is given by:

$$J_j = -\frac{K_{ij}n_j}{4\pi r^2}$$

Introducing the relative diffusion coefficient $\mathcal{D}_{ij}$, the Fick's law writes:

$$J_j = -\mathcal{D}_{ij}\frac{dc_j}{dr}$$

This gives:

$$c_j(r) = c(\infty) - \frac{K_{ij}\, n_{ij}}{4\pi \mathcal{D}_{ij}\, r}$$

Taking care of the limiting conditions on c_j, one obtains:

$$K_{ij} = 4\pi \mathcal{D}_{ij} (R_i + R_j)$$

Using the fact that:

$$\mathcal{D}_{ij} = \mathcal{D}_i + \mathcal{D}_j$$

where $\mathcal{D}_i$ is the absolute coefficient of diffusion for cluster im this relation writes:

$$K_{ij} = 4\pi (\mathcal{D}_i + \mathcal{D}_j) (R_i + R_j)$$

For spherical particles, it is known that the diffusion constant varies as the inverse of the radius. In the case of fractal objects, like our aggregates, this is in principle no longer true. To be general, let us produce an exponent α, which tells how $\mathcal{D}_i$ varies with i:

$$\mathcal{D}_i \sim i^\alpha$$

This is the same a exponent as the one introduced in the first cluster-cluster simulations (see section 4). Using this exponent, extending our reasoning in d dimensions, and assuming the aggregates are self-smiliar fractals with fractal dimension D (this implies that all characteristic lengths, such as R_i, or the radius of gyration, scale as $i^{1/D}$, one finally gets:

$$K_{ij} \sim (i^\alpha + j^\alpha) (i^{1/D} + j^{1/D})^{d-2}$$

Even if this is quite complicated expression, one verifies the following homogeneity property:

$$K_{\lambda i, \lambda j} = \lambda^{2\omega} K_{ij}$$

with:

$$2\omega = \alpha + \frac{d-2}{D}$$

6.4. Form of the Kernel in the Ballistic Case

In the case of random straight line trajectories, the calculation is the same as the one used in the classical theory of the perfect gas. The rate of collision between a given i aggregate, supposed to be fixed, and all the other j clusters is equal to the number of j clusters contained in a cylinder of base area $\pi(R_i + R_j)^2$ and length v_{ij}, where R_i has the same meaning as before and v_{ij} is the mean relative velocity of cluster j compared to cluster i. This reasoning gives:

$$K_{ij} = v_{ij} \pi (R_i + R_j)^2$$

Using

$$v_{ij}^2 = v_i^2 + v_j^2$$

where v_i and v_j are now the mean absolute velocities, and generalizing in d dimensions, one finds:

$$K_{ij} \sim (v_i^2 + v_j^2)^{1/2} (R_i + R_j)^{d-1}$$

Introducing again the exponent α defined by:

$$v_i \sim i^\alpha$$

and assuming that the clusters are self-similar fractals, with fractal dimension D, one finally gets:

$$K_{ij} \sim (i^{2\alpha} + j^{2\alpha})^{1/2} \, (i^{1/D} + j^{1/D})^{d-1}$$

This again leads to homogeneous kernel, whose homogeneity exponent is given by:

$$2\omega = \alpha + \frac{d-1}{D}$$

The same derivation, but assuming a compact spherical shape for the aggregates ($d = D = 3$), and taking $\alpha = -1/2$ for an ideal gas, was already made by Friedlander more than twenty years ago to describe aerosols in a highly rarefied gas atmosphere.[54] His calculation gave $2\omega = 1/6$. Both Brownian and ballistic cases can be summarized in the unique formula:

$$2\omega = \alpha + \frac{d - d_w}{D}$$

where d_w is the fractal dimension of the cluster trajectory: $d_w = 2$ in the Brownian case, $d_w = 1$ in the ballistic case. It has been shown that Smoluchowski's approach, which neglects concentration fluctuations, is justified for space dimensions greater than d_w.[55]

6.5. Scaling Properties of the Smoluchowski Equation

It is generally very difficult to solve the Smoluchowski equation analytically, especially when realistic forms, like the ones derived above, are taken for the kernel. Many efforts have been made[54,56,57] and, using scaling arguments,[57] some general conclusions can be drawn in the case of homogeneous kernel of degree 2ω. The properties of the solution depend on ω. Two cases can be distinguished:

1) $\omega < 1/2$: flocculation regime

This case shows that one can define a regular size distribution function. For large times, the mean cluster size $\langle k \rangle$ varies as a power law:

$$\langle k \rangle \sim t^\gamma$$

with:

$$\gamma = \frac{1}{1 - 2\omega}$$

Considering only the case of large clusters in the large time regime (i.e. $\langle k \rangle > 1$ and $k > \langle k \rangle$), one can even find a reduced form for the size distribution function:

$$n_k \sim k^{-\tau} f\!\left(\frac{k}{\langle k \rangle}\right)$$

with $\tau = 2$ (like in the case of constant K_{ij}'s) and

$$f(x) = x^{-2\omega} \, e^{-(1-2\omega)x}$$

If ω is negative, this distribution function exhibits a maximum at:

$$k_m = \frac{2\omega}{2\omega - 1} \langle k \rangle$$

If $0 < \omega < 1/2$, the size distribution function is always decreasing.

2) $\omega > 1/2$: gelation regime

Let us consider a system of infinite volume containing a given constant number of particles per unit volume. In the case $\omega \geq 1/2$, one finds that, after a finite characteristic time t_g, an infinite cluster appears. By infinite cluster we mean a cluster containing a finite fraction of the total number of particles. At time t_g, a singularity occurs in the solution of the Smoluchowski equation. Above t_g, the total number of particles starts to decrease with time. This can be understood if it is taken that the infinite cluster absorbs more and more other clusters as time goes on. Above t_g, the above scaling form is no longer valid. This change of properties of the solutions of the Smoluchowski equation at $t = t_g$ has been invoked to explain the sol-gel transition observed in some polymeric and colloidal systems.[56] The gelation transition shares some properties with the percolation transition. However, the essential difference is that, while percolation is a static, at equilibrium, phenomenon, obtained by increasing slowly a concentration parameter, gelation is essentially dynamical.

6.6. Connection Between Statics and Kinetics

The connection between the geometry of clusters, characterized by their fractal dimension D, and the kinetics, characterized by exponent ω, is summarized by the formula established above:

$$2\omega = \alpha + \frac{d - d_w}{D}$$

where the other quantities α, d and d_wPv are input parameters of the model. This connection has been fully confirmed by numerical simulations on the cluster-cluster model in the box[58] as well as on direct simulations of the Smoluchowski equation itself.[59] Extensions of the simulations to larger α values show that, beyond a critical α value $\alpha_c = 1 - (d - d_w)/D$ corresponding to the critical value $\omega = 1/2$, the aggregation mechanism becomes dominated by particle-cluster collisions: one large cluster finally dominates by absorbing all other small clusters.[58] This abrupt change from cluster-cluster to particle-cluster aggregation, when increasing α, is related to the change of analytical properties in the solutions of the Smoluchowski equation.[59] While the Brownian case, as well as the ballistic case, are well described by the formalism described above, the case of chemically-limited aggregation is more complicated. A theory has been developed[60] that leads to $\omega = 1/2$ with exponential kinetics ($< k >$ is an exponential function of time).

CONCLUSION

A spectacular progress has recently been made in our understanding of aggregation phenomena owing to the introduction of the Witten-Sander model, different theoretical models have been built. They can be classified according to the nature of the aggregation mechanism, particle-cluster or cluster-cluster, and they correspond to dif-

ferent experimental situations. Agreement between theory and experiment is already very encouraging, but many more studies are still to be made. In particular, one must study the physical properties of aggregates, such as their elasticity, rheology *etc.* One might also hope that the recent studies, which were mainly carried out with the help of numerical methods on large computers, will yield some ideas on how to develop analytical theories and how to make fundamental progress in the understanding of irreversible phenomena.

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SAŽETAK

Primjena fraktala u agregaciji koloida

R. Jullien

Dan jer pregled novijih istraživanja u svrhu razumijevanja pojava kod agregacije koloida primjenom fraktalne geometrije. Nakon opisa tipičnog agregacijskog eksperimenta, uvedeni su koncepti fraktala i fraktalne dimenzije, te prikazani neki jednostavni modeli, koji mogu opisati mehanizam difuzijski-limitirane agregacije, koja prethodi fraktalnim agregatima. Stara teorija Smoluchowskog, koja opisuje kinetiku agregacije, revidirana je uvođenjem (ili upotrebom) fraktalnog koncepta.