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Particle Aggregation versus Cluster Aggregation in High Dimensions

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We distinguish two different types of irreversible aggregation—accretion of individual particles and successive aggregation of clusters of comparable size. In aggregation of particles which follow trajectories of fractal dimension D_1 we show that physical limits on the aggregation rate impose a lower bound on the fractal dimension D_0 of the aggregate. In d-dimensional space, $D_0 \geqslant d - D_1 + 1$. Thus aggregation of ballistic particles, with $D_1 = 1$, is not fractal. By contrast, cluster aggregates appear to attain a finite, limiting D_0 in high dimensions. We present a soluble model with this property, and argue that it should agree with Sutherland's binary aggregation model in high dimensions. For this model, D_0 depends continuously on a parameter; the exponent is not universal.

KEY WORDS: Fractals; aggregation; dendritic growth; critical phenomena; upper critical dimension.

1. INTRODUCTION

One realization of fractal structure in nature seems to be in large aggregates of irreversibly agglomerated particles, such as colloidal particles. The fascinating tenuous quality of such aggregates has been noticed for a long time by colloidal scientists.[1] More recently the interior structure of these aggregates has been studied by direct measurements[2,3] and by computer simulations.[4,5] It appears that the interior correlations of particle density have a scale-invariant form characteristic of a fractal[6] object. In the last few months two distinct classes of fractal aggregates have been identified. Aggregates of the first class are those formed by the successive accretion of independent single particles; we denote such processes as particle aggregation.[4,7-9] The second class of aggregation process is the aggregation

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of aggregates, or cluster aggregation.[5,10] Most colloidal aggregation phenomena appear to belong to this second class. Here the dominant process is the fusion of two aggregates of comparable size, rather than the accretion of small objects onto increasingly large ones.

A particle aggregate assumes a fractal dimension D_0 which depends on how the constitutent particles move. Thus diffusion-limited aggregates,[4] where the constituent particles move in random walks, have a fractal dimension D_0 of about 2.4. In ballistic aggregation, where the particles move in random straight-line trajectories,[7,8] D_0 is larger.

Cluster aggregation has recently been explored entensively by simulation,[5] generalizing Sutherland's original model.[10] These aggregates have a lower fractal dimension than do particle aggregates, with $D_0 \cong 1.7$ in three dimensions. In cluster aggregation, the type of motion of the fusing clusters makes no apparent difference to the fractal dimension. Brownian motion and ballistic motion produce essentially the same structure, in contrast to particle aggregation.

Our approach to understanding these aggregates has been to exploit the simplifying features that appear in high-dimensional space. In high dimensions the two classes of growth emerge as completely different phenomena. Here we present two new results that underline this difference. For particle aggregation we show[11] that the fractal dimension must be nearly equal to the dimension of space d in order to avoid unphysically fast growth. Indeed, the codimension $d - D_0$ must be smaller than the dimension of the particle trajectories, D_1, plus 1. For Brownian particles, this means $d - D_0 \leqslant 1$; for ballistic particles, it means $D_0 = d$. For cluster aggregation the reverse appears to be true: D_0 does not increase indefinitely. We argue[11] that D_0 in the Sutherland model attains a fixed value in high dimensions. In this respect cluster aggregation behaves like classical random fractals such as self-avoiding walks and random animals.[12] But there is a fundamental difference. This asymptotic D_0 is not universal. It depends, e.g., on the ratio of sizes of the fusing constituents.

2. PARTICLE AGGREGATION

We consider first the limitations on D for particle aggregation. We assume that the aggregate consists initially of a seed particle at the origin. The seed particle is immersed in a dilute gas of moving particles of some microscopic radius a. Whenever a moving particle touches the aggregate, it is adsorbed, thus increasing the mass and size of the aggregate. Because of this adsorption, the outer radius R of the aggregate grows in time. Initially, the growth speed dR/dt has some value v_0 proportional to the density u of moving particles. Later, the growth speed is proportional to the flux of

particles onto the outer tips of the aggregate. This flux is partly screened by the rest of the aggregate, and is thus smaller than it was initially. Thus the growth speed can only decrease in time: $dR/dt < v_0 \sim u$. Other characteristic radii, such as the radius of gyration, are necessarily smaller than the outer radius, and thus can grow no faster than this dR/dt.

The flux of particles onto an existing aggregate is related in a simple way to its radius. This may be seen for a variety of types of motion using a geometric picture. We imagine the trajectories of all the moving particles as they would have been in the absence of the aggregate. We suppose that each particle takes one step per unit time. The density of steps after time t is simply ut, and the average number of contacts with the aggregate is Mut. The trajectories which produce these contacts evidently enter the aggregate region, within distance R of the origin. The average number M_{01} of contacts[6,13] of one trajectory with the aggregate obeys

$$M_{01} \sim R^{D_0+D_1-d} + \text{const} \tag{1}$$

In particle aggregation this power is positive; a typical trajectory within the cluster region intersects the aggregate many times. The number C of *first* contacts between trajectories and the aggregate is the total number divided by the number per trajectory:

$$C \sim MutR^{d-D_0-D_1} \sim utR^{d-D_1}$$

The number is thus independent of D_0; since a particle entering the aggregate region has a probability of contact approaching 1, the number of first contacts is the same as for a solid absorbing sphere with radius of order R. The aggregate is "opaque" to the particles, and the actual density within the aggregate is not important.

Each time C increases by 1, a trajectory touches the aggregate and is adsorbed. Thus the flux onto the aggregate is dC/dt. This adsorbed flux increases the mass M of the aggregate: $dM/dt = dC/dt$. This in turn can be related to the growth speed dR/dt: $dM/dt = dM/dR\, dR/dt$. Using our expression for the flux dM/dt, and the power law relation $M \sim R^{D_0}$, this gives[3]

$$uR^{d-D_1+D_0+1} \sim dR/dt$$

Since dR/dt is bounded by $v_0 \sim u$, the exponent of R must be nonnegative—even in the dilute limit $u \to 0$. Thus

$$D_0 \geqslant d + D_1 - 1$$

This is the desired limit on D_0.

[3] This relation for dr/dt was derived for diffusing particles by J. M. Deutch and P. Meakin (Ref. 14) using a more conventional approach.

The limit is consistent with reported simulations of diffusion-limited aggregation.[15] It is also consistent with the Levy-flight aggregation study of Meakin,[9] and with his extensive study of ballistic aggregation. But it disagrees with the reported D_0 of 1.93 for two-dimensional ballistic aggregation by Bensimon *et al.*,[8] and with Henschel's formula[16] for D_0 found via a Flory argument.

3. CLUSTER AGGREGATION

The fractal dimension of cluster aggregates is governed by completely different considerations than those above. To understand the essential features of this process better, we have constructed a solvable variant of the Sutherland model which we call "Sutherland's ghost." In the original Sutherland model,[10] pairs of monomers are assembled to form an ensemble of dimers in random orientations. Two of these dimers are then selected at random and are moved toward each other along arbitrary straight line until they touch, thus forming a tetramer. By taking all possible dimer orientations, one thus constructs an ensemble of tetramers. These are used to make an ensemble of octamers, and so on.

Our ghost model is like Sutherland's model, except that we allow the particles to interpenetrate freely. We also dispense with the trajectories. Our dimers are assembled into tetramers by choosing a monomer of each dimer at random and linking them together in a random direction. Thus the orientation of each dimer and of the connecting link between the chosen monomers are all independent. Octomers are made by taking a monomer from each of two arbitrary tetramers and linking these together at random. The process may clearly be continued indefinitely.

The size of these ghost aggregates can be calculated straightforwardly. We define the average "chemical" distance $Q(M)$ between two arbitrary monomers of a cluster of mass M. The chemical distance between two monomers means the number of connecting links which must be traversed to go from one to the other. The distance $Q(2M)$ is related simply to $Q(M)$. Any $2M$-mer was formed from two M-mers, which we call the A and the B cluster. To find $Q(2M)$, we select two monomers at random on the $2M$-mer. The two belong to the A cluster with probability 1/4. If they do, the average distance between them is $Q(M)$. In the same way the two monomers may both belong to the B cluster. Finally one monomer may belong to each cluster; this occurs with probability 1/2. Then the distance between them is the distance between the first monomer and the connecting link, plus the distance between this link and the second. Since the connecting link itself was arbitrary, each of the two subdistances averages to $Q(M)$. We now find $Q(2M)$ by taking a weighted average:

$$Q(2M) = 1/4\ Q(M) + 1/4\ Q(M) + 1/2\ [Q(M) + Q(M)]$$
$$= 3/2\ Q(M)$$

Thus evidently, $Q(M) = M^X$, where $X = \log(3/2)/\log(2)$.

To determine the fractal dimension D_0, we must relate the chemical distance $Q(M)$ to geometric distance. The displacement between two arbitrary monomers at chemical distance q is the sum of the q connecting link vectors. These are independent, random vectors of unit length. Thus the connecting path is a random walk, and its mean-square end-to-end distance r^2 is q. The average mean square distance $R^2(M)$ is the average of q, viz. $Q(M)$. In view of the scaling of $Q(M)$, we conclude

$$M \sim R^{2/X}$$

Thus the mass M scales with a geometric size R as in a fractal object with $D_0 = 2/X = 2\log(2)/\log(3/2) \cong 3.4$. It seems clear[17] that the scaling of the average mass $M(a)$ within radius a of an arbitrary monomer scales with the same power. In this sense the Sutherland's ghost model produces fractal objects with $D_0 = 2\log(2)/\log(3/2)$.

We expect that this ghost model has the same scaling as the original Sutherland model in sufficiently high dimensions. To see this, we compare the ensemble of ghost aggregates with the ensemble of original Sutherland aggregates. This ensemble is only a subset of the ghost ensemble. In the ghost ensemble each monomer has an equal chance to be linked. Each has equal "exposure." Sutherland aggregates by contrast are made by sliding pairs of M-mers together until they touch; the first touch thus terminates the motion and defines the aggregate. Clearly then, the outer monomers of an aggregate have a greater chance to be linked than do the inner ones. As the cluster grows, the exposed monomers would in general become a smaller and smaller fraction of the total. Since it is the outer monomers that get linked, the size of the linked pair of a given mass tends to be greater than in the ghost ensemble. Thus the fractal dimension of the Sutherland aggregates should be less than or equal to that of the ghost aggregates.

In high dimensions, however, we expect that all monomers are comparably exposed to further growth, even in the original Sutherland model. To see this we consider an arbitrary monomer on the A and the B cluster, each placed randomly in space. The Sutherland model instructs us to move cluster B toward cluster A along the line joining these two monomers, until there is a contact. During this motion there is some probability of a contact before the two chosen monomers touch. Unless that probability is large, the two chosen monomers are exposed. To estimate the probability of contact, we consider the space swept out by the B cluster as it approaches

the A cluster. This is a fractal object of dimension $D_0 + 1$. This B fractal has a certain number of contacts M_{AB} with the A cluster. Since the two objects are uncorrelated fractals, the average number of contacts scales according to Eq. (1) above:

$$M_{AB} \sim R^{2D_0+1-d} + \text{const}$$

The D_0 of Sutherland aggregates should be no greater than the ghost value of about 3.4, as argued above. Thus, for $d > 2D_0 + 1$, the power of R is negative, and the average number of contacts remains limited as R grows to infinity. Evidently the probability of contact does not grow indefinitely large, so that two arbitrary monomers remain exposed, even on the largest clusters. But this means that the Sutherland ensemble does not differ qualitatively from the ghost ensemble, and the two should have the same fractal dimension.

The ghost model may be readily generalized to show that cluster aggregates do not have a universal D_0 values. To this end, we consider the "asymmetric ghost" model. This is identical to the ghost model above, except that the two constituent aggregates do not have equal mass. Instead, an A cluster of mass M is combined with a B custer of mss kM. The mass ratio k is held fixed as the process is repeated. Now when an arbitrary monomer of the combined AB cluster is chosen, it has probability $1/(1 + k)$ of being on the A constituent, and probability $k/(1 + k)$ of being on the B constituent. Our formula for the average chemical distance Q is revised:

$$\begin{aligned} Q(M + kM) = {} & [1/(1 + k)]^2\, Q(M) + [k/(1 + k)]^2\, Q(kM) \\ & + 2k/(1 + k)^2 [Q(M) + Q(kM)] \end{aligned}$$

Now the exponent X must satisfy

$$(1 + k)^{2+X} = 1 + k^{2+X} + 2k(1 + k^X)$$

Evidently X varies with k; hence so does the fractal dimension. Universality is lost.

The dependence of D_0 on k instructive. Clearly, $D_0(k) = D_0(1/k)$, since the same is true for X. One may easily check that for large k, $D_0 \to 2\log(k)$. Thus as the ratio k diverges, $D_0 \to \infty$ in accord with the Eden growth model[13,18] in high dimensions. Further, $D_0(k)$ has a very broad minimum at $k = 1$. Indeed, over the range $0.1 < k < 10$, D_0 increases by less than 50% above the ghost value.

The nonuniversality of cluster aggregation in high dimensions could well be reflected in real three-dimensional aggregation. Any effect which tended to change the typical ratio of two aggregating clusters would be

expected to change the observed D_0 as well. Such an effect would be the mass dependence of the cluster mobility. Meakin[5] has looked for just such effects on D_0 and has seen none. However, the expected changes in D_0 are quite weak, since in our model D_0 depends only weakly on k. Such a weak variation could easily have escaped detection in the simulations.[19] Further simulations, designed to look for this nonuniversality would be important and instructive.

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