Surface Fractals in Irreversible Aggregation

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We introduce a mechanism to model irreversible aggregation of clusters at high concentration and investigate it by Monte Carlo simulations. Depending on the cluster diffusivity the aggregates are surface fractals, volume fractals, or nonfractal objects. Our results are compared with experiments on colloidal aggregation where, depending on concentration, either volume or surface fractals are observed. The model also provides a new, kinetic interpretation of random percolation.

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Irreversible aggregation of clusters at low concentration experimentally leads to beautiful, tenuous structures of considerable size—volume fractals.\(^{1,2}\) Most remarkably, the fractal properties can be directly related to the growth mechanism.\(^{3,4}\) A consequence of the fractal nature of these irreversible colloidal growth processes is that the volume occupied by the clusters increases with time until the fractals fill the whole space.\(^{5}\) How does the aggregation process change with time and what do the aggregates look like at high concentration? Experimentally, it has been observed that the aggregates change from volume to surface fractals when the concentration is varied.\(^{6}\)

It can be seen easily that irreversibly aggregating clusters must crowd space as they grow larger and as a consequence the growth mechanism must change with time. Let \(N_0\) particles aggregate irreversibly. At a given moment there are \(N\) clusters each of average mass \(M = N_0 \rho / n\) and radius \(R = M^{1/3}\) where \(D\) is the fractal dimension. Together, the \(N\) clusters occupy a volume \(V = N R^D = N_0 M^{(D-D)/D}\) which increases monotonically with mass or time as \(D < d\) (\(d\) is the spatial dimension). When \(V\) is equal to the total available volume the system suddenly gels. This argument neglects, however, the fact that \(D\) changes with increasing cluster density.\(^{5}\) To describe the aggregation process for low and for high concentration, we suggest that two separate modelizations are necessary. The low-concentration regime is well understood.\(^{3,4}\) Here we introduce a model describing the high-concentration regime and analyze it by Monte Carlo simulations. Strictly speaking, the two models have to be considered at concentration zero or unity; the crossover between these extremes takes place when the distance between neighboring clusters is of the order of the cluster radius.

Our model is an assembly of rigid clusters. Each cluster is surrounded by other clusters such that it has little room to move. The clusters jitter randomly with a rate that depends on their size. Growth is introduced by the rule that whenever two clusters touch each other (they can never overlap) a rigid bond will connect them permanently—they from then on form a single larger cluster.

We have investigated the following lattice version of this aggregation process. Initially, place one particle on every site of a square (cubic) lattice of side length \(L\) and consider each particle to be an independent cluster. Now the following growth process is repeated indefinitely: (i) Choose a cluster at random, with a probability (cluster diffusivity) proportional to

\[
D(M) = M^a,
\]

where \(M\) is its mass or number of particles (\(a\) is a parameter that can be chosen to match the diffusivity observed in experiments\(^{1,2}\)); (ii) select one of the four (six) lattice directions, also at random; (iii) pick at random one of the particles which are nearest neighbors of the cluster in the selected direction (these are the particles the cluster would collide with if we tried to move it in this direction); (iv) merge the cluster to which this particle belongs with the chosen cluster to form one larger cluster. In this lattice model, the concentration is always unity. The clusters jitter according to \(D(M) = M^a\) but their positions never change.

We have performed Monte Carlo simulations of this model for \(d = 2,3\). The results show that the structure of the clusters and the distribution of cluster sizes depends on the parameter \(a\). The four qualitatively different possibilities are illustrated in Fig. 1. From left to right, as \(a\) increases, the aggregates can either be compact surface fractals, porous surface fractals, volume fractals, or nonfractal objects. Experimentally \(a < 0\) (surface fractals) seems the most realistic, as large clusters diffuse more slowly than small ones.

A _volume fractal_ has an internal density that becomes arbitrarily low with increasing cluster size. Its mass scales with its radius like

\[
M = R^0, \quad 1 < D < d.
\]

For a volume fractal, the number of surface points \(M_s\) as a function of \(R\) necessarily scales with the same power \(D\). For fractals with holes on all scales, the hull (the _external_ surface) may scale with a different exponent.\(^{8}\)

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For a surface fractal, the exponent $D$ is simply $D = d$. But its surface scales with a nontrivial exponent $D_s$:

$$M_s = R^{D_s}, \quad d - 1 < D_s < d. \quad (3)$$

Common examples of surface fractals are shore lines of continents or islands. Our examples, shown on the left in Fig. 1, visually seem to resemble rugged islands.

The results of the simulations are given in Figs. 2 and 3. In Fig. 2, the mass of the largest cluster and its hull are plotted against its radius, for $d = 2$. On the left, for $a = -2$, the clusters are compact with $D = 2 \pm 0.06$, but they have a fractally rough surface with $D_s = 1.60 \pm 0.08$. In this case the hull is equal to the surface as the clusters are compact. The same results are obtained for all negative values of $a$ up to $a = 0$. As $a \rightarrow 0$, the clusters become porous but hull and total surface still scale with the same $D_s$. Past $a = 0.5$ the measured $D_s$ increases, and for $a = 1.0$ the clusters have a different structure: They are volume fractals with $D = 1.85 \pm 0.09$, with a hull that scales with $D_s = 1.51 \pm 0.15$. Finally, for $a > 1.0$ ($a = 2$ in Fig. 2) the aggregates are nonfractal with $D = 2 \pm 0.10$ and $D_s = 1 \pm 0.12$.

For $d = 3$, the results are qualitatively the same as in two dimensions: One also distinguishes a surface fractal, a volume fractal, and a nonfractal regime. In Fig. 3 the results for the negative-$a$ region are shown. Within statistical errors, $a = -2$ and $a = 0$ have the same fractal dimensions $D = 3 \pm 0.07$ and $D_s = 2.52 \pm 0.09$ indicating that for all $a < 0$ the clusters are surface fractals.

The cluster size distribution (the number $n$ of clusters of mass $M$) can be cast in a scaling form with $M/M^*$ as scaling variable. $M^*$ is the typical cluster size, or the size of the largest cluster. The precise scaling form for $n(M)$ depends on $a$. For $a < a_1 = -0.3 \pm 0.1$ ($-0.7 \pm 0.2$) in $d = 2$ ($d = 3$), the scaling function is bell shaped ("monodisperse"), for $a_1 < a < a_2 = 0.85 \pm 0.1$ ($0.5 \pm 0.2$) it is "weakly polydisperse" [it diverges as $(M/M^*)^{a-1}$ with $\tau < 2$ for $M/M^* \to 0$], and for $a > a_2$ it is "strongly polydisperse" ($\tau > 2$). The data from the simulations over a range of $10^2 \leq M^* \leq 10^4$ collapse according to these scaling forms. An analogous distinction between monodisperse and polydisperse regimes characterizes cluster aggregation at low concentration, and the mechanism can be understood in the context of the Smoluchowski equation.

For cluster aggregation at low concentration, the growth mechanism, diffusive or reactive, influences the structure of the aggregates, notably the fractal dimension. For our model at concentration unity, this difference disappears, as for a sticking probability less than 1 the probability for an open bond to close still is proportional to the collision rates of the clusters it links. However, the aggregation time does depend on the sticking probability.

Irreversible cluster aggregation can lead to a gelation phenomenon. How does it compare with percolation where a gel is grown by random and uncorrelated placing of bonds on the lattice? We argue that—while in general the kinetics dominates the gelation process.
FIG. 2. Mass and hull of largest cluster as functions of the radius of gyration $R$ (log-log) for $L=200$ in $d=2$ (from left): For $a=1$ the mass scales with $D=2\pm0.06$ and the hull (surface) with $D_S=1.60\pm0.08$ (circles, plusses show data from $L=100$); for $a=1$, $D=1.85\pm0.09$ and $D_S=1.51\pm0.15$ (circles, plusses show data from bond percolation); and for $a=2$, $D=2\pm0.10$ and $D_S=1\pm0.12$. The arrows indicate the finite-system gel points.

(sometimes with infinite gel time)—for the special case $a=1$ our model is equivalent to random bond percolation. If an aggregate is a fractal, the number of surface sites is on average proportional to the total number of particles, and there are on average the same number of surface sites in all directions. The number of bonds in a given direction is also proportional to the number of surface sites in the same direction. This means that for $a=1$, each bond is chosen with the same probability on average (in bond percolation each bond has exactly the same probability). The data of Fig. 2 confirm this connection. For $a=1$ each open bond between two clusters has a probability to close that depends on the size of the clusters. For $a<1$ this probability is determined mainly by the kinetics of the smaller of the two clusters; for $a>1$, by the larger of the two.

Gelation for irreversible clustering does not always occur in a finite time (in the thermodynamic limit). For the present model the growth is exponential for $a_1>a>a_2$ (as observed experimentally and the gel time is finite for $a>a_2$. This is due to the polydispersity of the cluster size distribution. If the distribution were monodisperse, the gel time would be finite for all $a>0.15$.

Recent experiments on silica colloids yield either volume or surface fractals depending on the concentration. Our model can explain the appearance of surface fractality in colloids. In fact, the experimentally and numerically measured values for $D_S$ are surprisingly close to each other. Nevertheless, a direct comparison should not be taken too seriously, as in experiments the concentration is not unity, which leads to a concentration dependence for the measured $D_S$. Furthermore, the comparison with experiments has to be limited to sizes for which the clusters can still be considered to be rigid.

Let us give some arguments to explain our results. The relevance of $a$ for $D$ is due to the fact that it determines how deeply clusters are interpenetrated. In this sense $a$ is similar to the dimension $d_w$ of the trajectory in diffusion-limited aggregation, where it is known that $D$ depends on $d_w$. Why do surface fractals appear? Aggregation usually leads to volume fractality, where $D=D_S<d$. If, however, $a$ is negative, small clusters attach fast
and fill up holes in the larger clusters, compactifying them and leaving behind only the surface fractality.

In conclusion, we found for the first time surface fractals in an irreversible cluster aggregation process, as has been observed experimentally. The necessary conditions to get surface fractals are high cluster concentration and negative $\alpha$ (i.e., small clusters are more agitated than large ones). Under these conditions it takes an infinite time to grow an infinitely large cluster—in contrast to gelation.

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15Details will be presented elsewhere.