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A new model of cluster aggregation

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Abstract. An extension of the model of diffusion-limited cluster-cluster aggregation, which emphasises sticking by tips, is numerically investigated. It is argued that the model can be physically justified in the case of polarisable clusters. A quantitative agreement is found with a recent experiment of aggregation of silica microspheres in two dimensions. The particle-cluster counterpart of the model is also studied.

1. Introduction

Several theoretical models have been recently introduced to describe the geometry of clusters obtained by aggregation of particles (Family and Landau 1984). The prototype is the diffusion-limited particle-cluster (PCI) aggregation model of Witten and Sander (1981), in which single Brownian particles stick one after another on to an immobile cluster. It quantitatively describes several experiments such as electrodeposition (Brady and Ball 1984, Matsushita *et al* 1984) and filtration (Houi and Lenormand 1984), as well as others which are not truly aggregation, such as dielectric breakdown (Niemeyer *et al* 1984) and the motion of fluids in porous and viscous media (Patterson 1984, Nittmann *et al* 1985, Kadanoff 1985). An alternative model is the clustering of clusters (CICI) model (Meakin 1983, Kolb *et al* 1983) in which clusters, as well as particles, are allowed to diffuse and stick together when they come in contact. This model is better adapted to truly aggregation experiments. In the case of the aggregation of smoke particles (Forrest and Witten 1979) or colloids (Weitz and Oliveria 1984) the experimental fractal dimension has been quantitatively recovered ($D \sim 1.75$ in three dimensions). Many extensions of CICI have recently been introduced to apply to various peculiar experimental situations (Botet *et al* 1985). In particular, it has been shown that, in the molecular regime, when Brownian motion is replaced by random straight-line trajectories, the fractal dimension is slightly increased (Meakin 1984, Ball and Jullien 1984). More generally, in CICI (as well as in PCI) decreasing the fractal dimension of the cluster trajectory implies stronger penetration effects and thus leads to a resulting larger fractal dimension of the clusters. In this paper I would like to describe an alternative extension of CICI which, in contrast to the previous ones, considers *smaller penetration*. The present model systematically emphasises sticking on tips and consequently leads to a smaller fractal dimension of the clusters. I argue that this is physically justified when considering electrostatic forces in the case of polarisable clusters. The creation of this model was mainly motivated by the recent experiment by Hurd and Schaeffer (1985) on aggregation of silica microspheres in two dimensions. Hurd and Schaeffer (HS) obtained very 'stringy' clusters with a fractal dimension $D = 1.20 \pm 0.15$, much smaller than the one found by two-dimensional simulations on

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CICI ($D \simeq 1.40$ in $d = 2$ (Meakin 1983, Kolb *et al* 1983)). The model has been sketched and a few results already announced in a short comment on the HS paper (Jullien 1985) and here I present further details and results.

2. The model and its physical interest

The model is a 'hierarchical' version of CICI (Botet *et al* 1984a, b) in which successive collections of clusters of the same number of particles, 2, 4, 8, ..., 2^k, ..., are built, iteratively, starting from an initial set of individual particles. Moreover, it is 'off-lattice' in the sense that, in d-dimensional space, the particles are hard d-dimensional hyperspheres of unit diameter which irreversibly stick when in contact. At step k, a collection of clusters of 2^k particles has been generated. These clusters are grouped into pairs. Each pair generates a cluster of 2^{k+1} particles which becomes a member of the new collection. Here the model essentially differs in the way a new cluster is built. I consider the two clusters of a pair, say C_1 and C_2. I first choose a random direction in space: this defines a randomly oriented z axis. C_1 and C_2 are placed far apart, at abscissae $-\infty$ and $+\infty$, respectively, on this axis. I determine the particles P_1 (of C_1) and P_2 (of C_2) such that the distance P_1P_2 is a minimum. Then, C_2 is rigidly translated, without rotation, to a position C_2' where these two particles come in contact aligned along the z direction. The reunion of C_1 and C_2' forms the new cluster. Practically, as shown in figure 1, given the two clusters, anywhere in space (not necessarily far apart), the sticking points on each cluster C_1 (C_2) can easily be found by determining the point of contact with the $(d-1)$-dimensional hyperplane, tangent to the cluster, perpendicular to the z axis, with the highest (lowest) abscissa. Note that the only source of randomness in the model comes from the choice of the z axis.

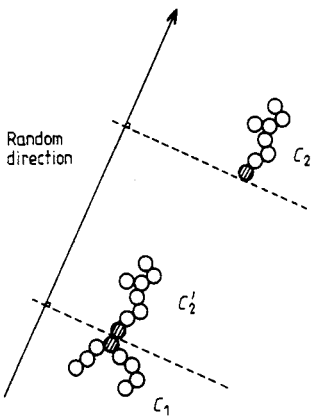

Figure 1. Sketch of the collision process (see text).

This procedure can be physically justified in the case of polarisable clusters as follows. I shall consider, in the low concentration limit, two clusters, far apart from each other, before they collide. If they are polarisable, opposite charges appear on their nearest tips, which are the points P_1 and P_2 defined above. Then, I assume that the electrostatic attraction between P_1 and P_2 is so strong that it biases the random diffusion of the clusters and that they will finally stick on these tips.

As presented here the model has the great advantage of being very simple but it obviously gives a sketch of the physical situation. In practice, the electrostatic interactions are not so strong and are probably partially screened so that the resulting penetration would in fact be intermediate between the one obtained with pure Brownian motion and the one defined here. Moreover, I have neglected the repulsion between a given tip and the opposite part of the other cluster. This could be justified since for large clusters this repulsion, acting on larger distances, is of smaller intensity. Indeed, as already noticed by Hurd and Schaeffer (1985) taking this repulsion into account would induce some rotation tending to align the clusters. Note that the two modifications suggested here (not completely biased diffusion and rotational alignments) act in opposite ways and could compensate themselves in the final result for the fractal dimension. Further works are in progress to quantitatively appreciate these effects. Finally, I would like to restate that the hierarchical model is only justified in the low concentration regime (Botet *et al* 1984a). The quantitative results could be modified for larger concentrations near the gel condition (Botet *et al* 1984b, Kolb and Herrmann 1985).

3. Results

Using the procedure defined in § 2 I have generated 100 independent clusters of 8192 particles, up to dimension $d = 30$. Typical clusters of 1024 particles in $d = 2$ and $d = 3$ are shown in figure 2. Note the resemblance of our two-dimensional cluster with those of Hurd and Schaeffer (1985). The fractal dimension has been determined from the variation of the averaged radius of gyration with the number of particles:

$$R(N) \sim N^{1/D} \qquad N \to \infty.$$

This dimension D can only be defined in the asymptotic limit of very large clusters. Practically, D can be estimated by extrapolating to $N \to \infty$, an effective N-dependent fractal dimension (Botet *et al* 1984a)

$$D_1 = \ln 2[\ln(R(2N)/R(N)]^{-1}$$

which is obtained by comparing the relative radii of gyration of the clusters between two successive collections. I have also calculated another finite-size estimate

$$D_2 = \ln 4\{\ln[(R(2N)^2 - \tfrac{1}{4})/R(N)^2]\}^{-1}.$$

Obviously, this estimate has the same limit for $N \to \infty$ but, as shown recently (Ball and Jullien 1984) the approach of D_2 to its limiting ($N \to \infty$) value at small cluster sizes is much closer.

Figure 3 shows a plot of D_1 and D_2 against $1/N$ for $d = 2$. As in Ball and Jullien (1984), the convergence of D_2 is very good, giving here $D = 1.28 \pm 0.03$.

Despite the low value found for D in $d = 2$, I consider that figure 3 strongly supports an asymptotic value definitely different from 1. This value is in good agreement with the experimental result $D = 1.20 \pm 0.15$ of Hurd and Schaeffer (1985).

The same analysis can be done in higher dimension and the results are reported in table 1.

Figure 4 shows a plot of D as a function of d. For large d, D increases very slowly with d and might saturate to the fractal dimension of the 'ghost' model of Ball and Witten (1984), $D_g = \ln 4/\ln \frac{3}{2} \simeq 3.42$ when $d \to \infty$. This suggests that the present model

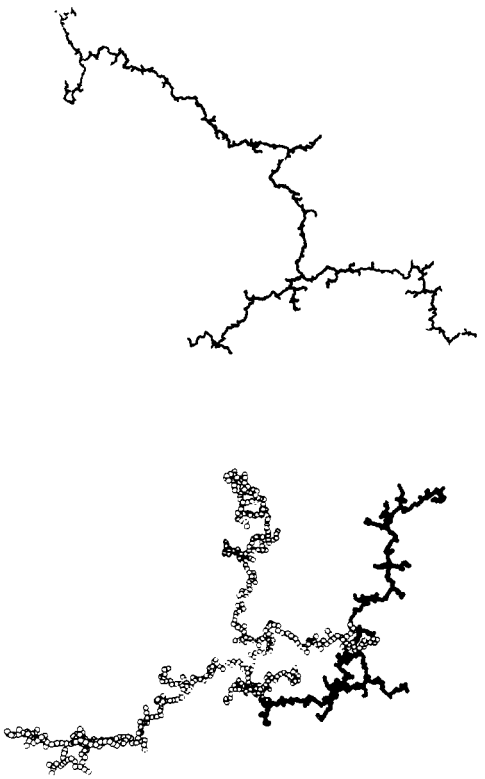

Figure 2. Typical clusters of $N = 1024$ particles in $d = 2$ (top) and $d = 3$ (bottom) obtained with the cluster-cluster version of the model. (In the $d = 3$ picture the different grey tones indicate the depth.)

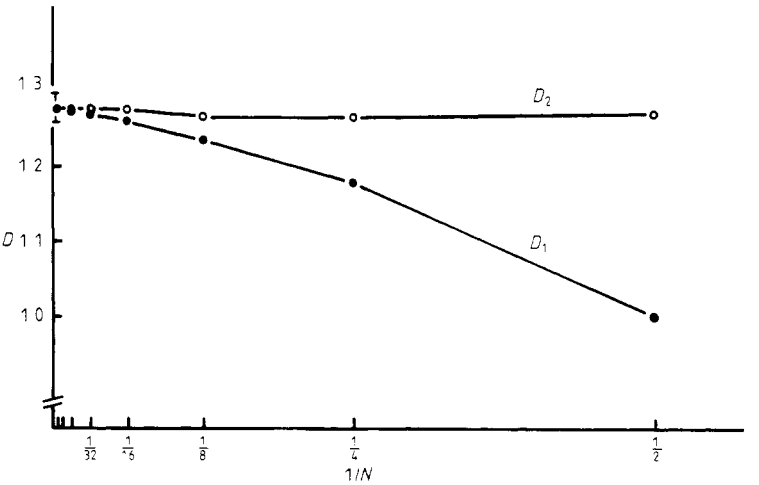

Figure 3. Plot of the effective (size-dependent) fractal dimensions D_1 and D_2 against $1/N$ in the case of the two-dimensional cluster-cluster version of the model.

Table 1. Numerical values obtained for the fractal dimension in the cluster-cluster version of the model.

d	2	3	4	10	20	30
D	1.28 ± 0.03	1.42 ± 0.06	1.55 ± 0.06	2.00 ± 0.08	2.3 ± 0.1	2.5 ± 0.1

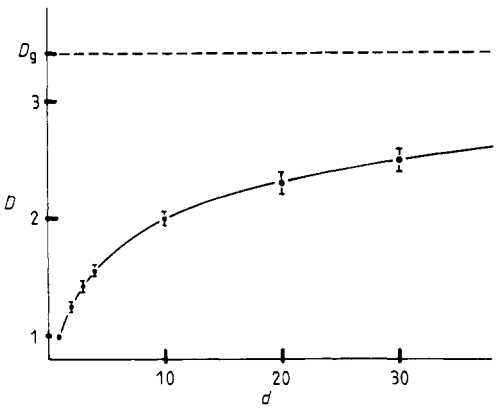

Figure 4. Plot of the fractal dimension D against the space dimension d, in the case of the cluster-cluster version of the model.

does not have any upper critical dimension. This is reasonable since, due to the procedure itself, no transparency is allowed in any finite dimension.

4. The particle–cluster counterpart

Although I have not yet found any experimental realisation, I consider it instructive to study the PCI counterpart of the present model. Now, as in the original model of Witten and Sander (1981), single particles are added, one after another, on to an immobile cluster. The above procedure is thus straightforwardly extended by considering that C_2 is always a single particle. After choosing the random direction, the $(d-1)$-dimensional hyperplane of the largest abscissa tangent to the cluster is determined and the extra particle is added on its contact point. In figure 5, I show typical clusters of $N = 1024$ particles, in $d = 2$ and $d = 3$. They look like stars with only a few stick-shaped arms. However randomness is still present and one observes some kind of screening effect, as in the original PCI model. When two large arms exist near each other, extra arms between them have difficulty in growing and show fewer fluctuations (they are more linear). When studying the radius of gyration as a function of the number of particles it appears that a linear behaviour is always recovered for a sufficiently large size, suggesting that the fractal dimension is trivially equal to 1 in this model. This is quantitatively illustrated in figure 6 where I have plotted N/R against $\ln N$, up to $d = 6$. In this series of calculations 500 independent clusters of 4096 particles have been generated and the square of the radii of gyration has been averaged over all the clusters of the same number of particles. On this figure, one always observes a saturation of N/R with increasing N. However, it is necessary to

Figure 5. Typical clusters of $N = 1024$ particles in $d = 2$ (top) and $d = 3$ (bottom) obtained with the particle-cluster version of the model. (In the $d = 3$ picture the different grey tones indicate the depth.)

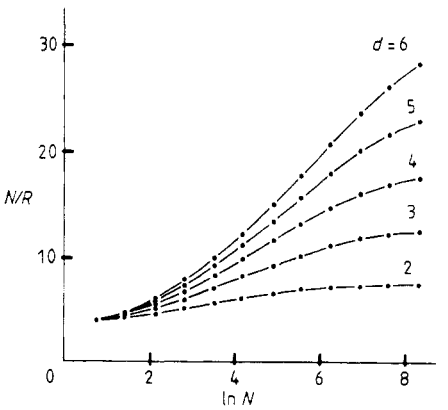

Figure 6. Plot of N/R against ln N for different d values, in the case of the particle-cluster version of the model.

reach larger sizes to effectively see this saturation when reaching larger dimensionalities. Moreover this figure suggests that, if the fractal dimension remains equal to 1 for any finite d, logarithmic corrections could appear in the limit of infinitely large d (R behaving as $N/\ln N$).

It is interesting to note that the fractal dimension decreases when going from CICI to PCI, while this is not the case with pure Brownian trajectories (Botet *et al* 1984b).

5. Conclusion and discussion

I have presented a very simple extension of previous diffusion-limited aggregation models, which takes into account electrostatic interactions in the case of polarisable clusters. While I do not believe that the PCI version of this model has any experimental realisation, the CICI version could quantitatively apply well to the experiment by Hurd and Schaeffer (1985) on silica microspheres. As already proposed by HS, the electrostatic interactions are certainly present and are able to reduce the cluster penetration and decrease the fractal dimension. Moreover, much more recently, a 3D aggregation experiment on aluminium hydroxide $Al(OH)_{2.5}$ has been reported by Axelos *et al* (1985) with a fractal dimension $D \sim 1.4$, much lower than the 3D value of the original CICI model. Since their value is comparable with that obtained in 2D simulations on CICI, these authors concluded that they had an effective 2D aggregation mechanism. One could imagine instead that the present model could apply, since here $D = 1.42 \pm 0.06$ in 3D. However, it is essential to understand why polarisation effects are so strong in such experiments. Further work is thus needed to improve and justify the present model.

Acknowledgments

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