RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 29, NUMBER 3 MARCH 1984

Flory-type approximation for the fractal dimension of cluster-cluster aggregates

H. G. E. Hentschel and J. M. Deutch
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 19 December 1983)

We consider the structure and fractal dimension of aggregates formed by cluster-cluster diffusional encounters. Both the fractal dimensions and symmetry properties of these aggregates are found to differ significantly from those found in the case of a single aggregating cluster. We find for the fractal dimension $D(d)=d(4d+3)/(9d-2)$ for $d<d_c=8$ and $D(d)=d/2$ for $d>d_c$.

Witten and Sander[1] have introduced a model for single aggregates formed by the irreversible clustering of individual particles: These particles execute isotropic random walks on a lattice toward the origin where a seed particle has been placed. If the random walker reaches a nearest-neighbor site, it becomes part of the growning cluster; if not, it is killed off. These clusters can be characterized in part by the scaling behavior of the number of particles in the aggregate N with its radius of gyration R as $N\sim(R/a)^{\hat{D}(d)}$, where a is the length scale of the diffusing single particle, $\hat{D}$ is the fractal dimension,[2] and d is the Euclidian dimension of the space in which the walk is occurring. Meakin[3] carried out computer simulations in two to six dimensions which suggested $\hat{D}\approx 5d/6$. While theoretically using a Flory-type argument we have found[4]

$$\hat{D}(d)=(8+5d^2)/(6+5d) \quad . \tag{1}$$

$\hat{D}(d)=(d^2+1)/(d+1)$ has also been suggested[5,6] by making different assumptions about the structure of the aggregate.

However, for coagulation, precipitation, and flocculation one expects that growth by cluster-cluster aggregation is of importance. This suggests a model where an initial concentration of particles moves on a lattice according to some given kinetics; encounters lead to growing clusters, and any time two clusters touch they become part of a larger cluster until a single network forms.

Recently, simulations have been undertaken for this model.[7–9] Here we present an argument for the fractal dimension $D(d)$ and structure of the resulting aggregates.

Examination of the simulation results shows the aggregates formed by cluster encounter to be much more "stringy"[9] than those formed by single-particle addition. Their fractal dimensions are much smaller: $D(2)=1.38\pm0.06$ (Ref. 9), $D(2)=1.45\pm0.05$ (Ref. 8) compared with $\hat{D}(2)=1.67\ \pm0.05$ (Ref. 3); $D(3)\approx1.82$ (Ref. 10), $D(3)\approx1.85$ (Ref. 7) compared with $\hat{D}(3)=2.49\pm0.06$ (Ref. 3); and $D(4)\approx2.7$ (Ref. 11) compared with $\hat{D}(4)=3.34\pm0.01$ (Ref. 3) for the case of single-particle diffusion. In addition, the results for $D(d)$ seem to be independent of the kinetics.[7–9]

These simulation results become understandable when we recognize that essentially the aggregate is growing by the addition of pairs of equal-sized clusters. Sutherland and Goddarz-Nia[7] introduced exactly this model which they called the maximum chain model where N particles collide to form doublets, all doublets collide to form quadruplets, and so in a hierarchial manned (i.e., N of size $1\rightarrow N/2$ of size $2\rightarrow N/4$ of size $4\ldots$). Computer simulations on this model[7] agree with the quite different kinetic model of Kolb, Botet, and Jullien[9] and Meakin.[8]

This explains why the fractal dimension D is found in the simulations to be independent of the kinetics. Irrespective of how clusters move between collisions, when two clusters collide the only relevant length scale l is the average interpenetration distance of the clusters. We estimate l by considering the probability that any lattice point in the overlap region is occupied by particles from both encounter clusters. By smearing out particles over their respective volumes we see this probability $\sim[N/(R/a)^d]^2$. So that for the entire overlap volume the total probability of contact is $\sim(l/a)^d[N/(R/a)^d]^2$. The scale l is determined by requiring that this total probability is of order unity or

$$l\sim a[N(R/a)^{-d}]^{-2/d}\sim a(R/a)^{2(d-D)/d} \quad . \tag{2}$$

The kinetics do not appear in this derivation. This is very different from the case of single-particle diffusion-limited clusters where the relevant length scale[4] is $l'\sim a(R/a)^{(d-\hat{D})/d_w}$ and the fractal dimension of the particle's walk d_w makes a specific appearance. From Eq. (2) we can immediately see that there exists an upper critical dimensionality d_c given by

$$D(d_c)=d_c/2 \quad . \tag{3}$$

For $d<d_c$ the clusters cannot interpenetrate macroscopically, i.e., as $R\rightarrow\infty$, $l/R\rightarrow0$. While for $d>d_c$ we shall argue $D(d)=d/2$ and complete interpenetration occurs, i.e., l/R is finite as $R\rightarrow\infty$. This excluded volume effect for $d<d_c$ will also have important consequences for the macroscopic structure of the aggregate, which we shall consider first.

In this paper we argue that the stringy appearance of the clusters and their fractal dimensions can be estimated from the hierarchical process shown in Fig. 1. We assume that *on a large enough scale, $r\gg l$*, the properties of the cluster can be understood in terms of the "macroscopic collision process," whereby at each collision the clusters are replaced by spheres of the average maximum radius R. This assumption can be justified in a "mean-field" way by arguing that on a large enough scale one may replace the average of many two-cluster collisions by a single collision between rotationally averaged clusters. Thus, in contrast to the case of single-particle cluster formation, the aggregates here are anisotropic, at least for $d<d_c$. What do we mean by this

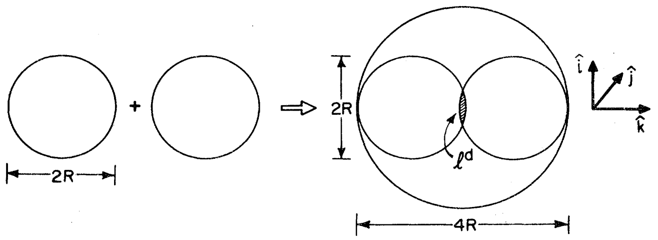

FIG. 1. Macroscopic collision process for cluster-cluster aggregation.

statement? Consider first the case of single-particle diffusion-limited clusters. We say that they are isotropic because when we calculate the radius of gyration tensor

$$(R^2)_{\alpha\beta}=1/N \sum_{i=1}^{N} r_i^\alpha r_i^\beta \ ,$$

where $\vec{r}_i$ is the position vector of the ith particle from the center of mass of the aggregate; then on averaging over many clusters as $N\rightarrow\infty$ we expect $(R^2)_{\alpha\beta}\rightarrow R_g^2(N)\delta\alpha\beta$. In the case of cluster-cluster aggregation, however, if we calculate $(R^2)_{\alpha\beta}$, in the limit $N\rightarrow\infty$, and if we average the principle moments, we expect that

$$(R^2)_{\alpha\beta}\rightarrow R_\perp^2\delta\alpha\beta+(R_\parallel^2-R_\perp^2)\hat{k}_\alpha\hat{k}_\beta \ ,$$

where $\hat{k}$ is a unit vector along some unique symmetry axis. In order to estimate the relative sizes of $R_\parallel^2$ and $R_\perp^2$, we argue that the anisotropy of the principal radii of gyration $R_\parallel$ and $R_\perp$ is the same as that between maximum distances between parts of the cluster according to the macroscopic collision encounter shown in Fig. 1. In this case $R_\parallel/R_\perp=2$ which agrees very well with the results of Sutherland and Goodarz-Nia[7] who found, for clusters of 256 particles, that $R_\parallel/R_\perp=2.04\pm0.15$. The anisotropy is also apparent in Fig. 2. In this sense the cluster-cluster aggregates have a limiting behavior $(R^2)_{\alpha\beta}\rightarrow R_\perp^2(N)(\delta\alpha\beta+3\hat{k}_\alpha\hat{k}_\beta)$, which also accounts for the stringy appearance of the clusters. For $d>d_c$, on the other hand, if complete interpenetration does occur the aggregate should be isotropic.

To estimate the fractal dimension of the cluster, we employ the length scale l given by Eq. (2). We divide a typical aggregate into blobs of size l^d and look on length scales $r<<l$ and $r>>l$. We assume that a typical blob on a length scale $r<<l$ behaves like a fractal of dimension D_1. In other words, the number of particles n_l of size a^d in a typical blob of size l^d scales like $n_l\sim(l/a)^{D_1}$. On the scale $r>>l$ we assume that the blobs of size l^d form a fractal of dimension D_2. In other words, an aggregate of size R^d will be covered by N_l blobs where $N_l\sim(R/l)^{D_2}$. Since the number of particles in the aggregate obeys the relation $N=N_l n_l\sim(R/a)^D$ we have, employing Eq. (2), a self-consistent equation $D=D_2+2(d-D)(D_1-D_2)/d$ or

$$D=\frac{d(2D_1-D_2)}{d+2(D_1-D_2)} \ . \tag{4}$$

Note that the reason the new fractal dimension D appears is that l scales with R. If l had been a constant then we would simply have found a crossover in behavior on scales $r<<l$ and $r>>l$.

Next, we estimate D_1 and D_2. One consequence of the macroscopic encounter process, assuming no interpenetration as $R\rightarrow\infty$, is that an aggregate of size R can be covered by two blobs of size $R/2$, four blobs of size $R/4$, etc. This should continue down to length scales l where the aggregate would be covered by a chain of (R/l) blobs of size l. Thus $D_2=1$. This scale invariance appears on the aggregate of 5000 particles in Fig. 2. The maximum end-to-end distance of the cluster ≈ 440 lattice units. Thus $l\sim 39$ lattice units. We have drawn blobs of radius 220, 110, and 55 lattice units and see that a chain appears.

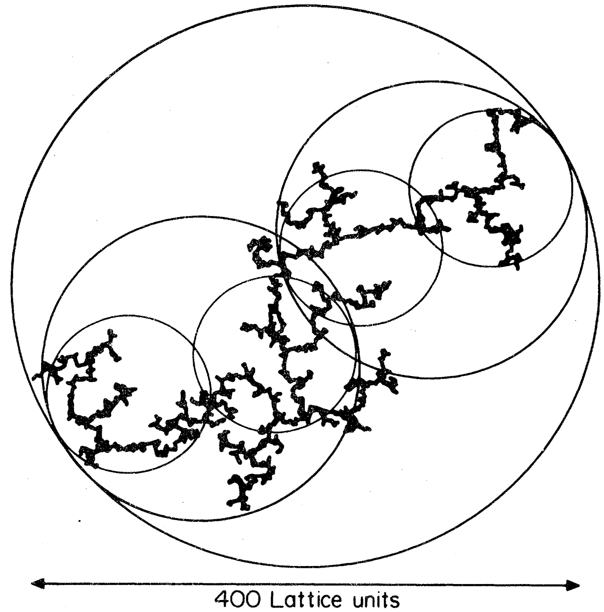

FIG. 2. An aggregate of 5000 particles from Ref. 11 formed by cluster-cluster addition for $d=2$. $R\sim440$ lattice units. Since $l\sim a[N(R/a)^{-d}]^{-2/d}$, one has $l/a\sim39$. Drawn also are covering circles of radii $R=220$, 110, and 55 lattice units.

However, the linear shape will break down for length scales $r<<l$, and a single blob appears like a branched object as on these scales interpenetration can occur. To obtain its dimension D_1, we appeal to the concept of universality. Two choices for the universality class spring to mind: first, randomly branched polymers[12,13] and, second, single-particle diffusion-limited aggregates.[4] Initially, the second choice appears tempting. After all, the aggregate is formed by a diffusion process. However, the aggregate is not formed in the manner of single-particle diffusion-limited aggregation. Even the small scale structure is formed by the interpenetration of large clusters. Thus the reasonable assumption is to treat every configuration on the small scale as equally likely. But this is just the definition of the lattice animal or randomly branched polymer problem; and, accordingly, we assume that on the small scales we have its fractal dimension $D_1=2(d+2)/5$ for $d<d_c'=8$ and $D_1=4$ for $d>d_c'$, where d_c' is the branched polymer upper critical dimensionality. Substituting these values for D_1 and D_2 in Eq. (4) we obtain $D(d)=d(4d+3)/(9d-2)$ for $d<8$ and $D(d)=7d/(d+6)$ for $d>8$. Using these values in Eq. (3), we see that $d_c=8$ and that while $D(d)>d/2$ for $d<8$, and therefore self-consistently no interpenetration occurs; for $d>8$ the value for $D(d)$ given above obeys

$D(d) < d/2$, which is not self-consistent, and interpenetration does occur for $d > 8$. At low dimensionalities

$$D(d) = d(4d+3)/(9d-2), \quad d < 8 \ . \tag{5}$$

From Eq. (5) we find $D(1) = 1$, which is an exact result, $D(2) = 1.375$, $D(3) = 1.80$, and $D(4) = 2.24$. These values are in excellent agreement with the simulation results quoted earlier.

At high dimensionalities complete interpenetration does occur. Thus we take $D_2 \to \infty$ in Eq. (4) and find, independently of D_1, that

$$D(d) = d/2, \quad d > 8 \ . \tag{6}$$

Equation (6) can also be derived from Eq. (2) by noting that as interpenetration occurs $l \sim R$.

Equation (6) is derived on the implicit assumption that, though clusters interpenetrate, they cannot simply pass through each without touching like ghosts. We can see that this is the case and gives us the lower bound $D \geq d/2$, for during the process of forming the aggregate the initial small clusters are of high density. Thus interpenetration is small and a more tenuous object appears after the collision process. However, when the aggregate gets too tenuous, interpenetration again occurs during collisions forming a more compact object. Thus there exists a stabilizing mechanism which will ensure that $l \lesssim R$ and therefore $D \geq d/2$.

In summary, we have argued that the cluster-cluster aggregates belong to a different universality class from single-particle aggregates and have determined their structure and and fractal dimension. We are now considering the dynamics of this model and the properties of the infinite network.

ACKNOWLEDGMENT

This work is supported in part by the Defense Advanced Research Projects Agency and the National Science Foundation.

[1]T. A. Witten and L. M. Sander, Phys. Rev. Lett. 47, 1400 (1981).
[2]B. B. Mandelbrot, *The Fractal Geometry of Nature* (Freeman, San Francisco, 1982).
[3]P. Meakin, Phys. Rev. A 27, 1495 (1983).
[4]H. G. E. Hentschel, Phys. Rev. Lett. 52, 212 (1984).
[5]M. Muthukumar, Phys. Rev. Lett. 50, 839 (1983).
[6]M. Tokuyama and K. Kawasaki (unpublished).
[7]D. N. Sutherland and I. Goodarz-Nia, Chem. Eng. Sci. 26, 2071 (1971).
[8]P. Meakin, Phys. Rev. Lett. 51, 1119 (1983).
[9]M. Kolb, R. Botet, and R. Jullien, Phys. Rev. Lett. 51, 1123 (1983).
[10]P. Meakin (unpublished).
[11]P. Meakin (private communication).
[12]J. Isaacson and T. C. Lubensky, J. Phys. (Paris) Lett. 41, L469 (1980).
[13]P. G. DeGennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979).