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1984 J. Phys. A: Math. Gen. 17 L639

(http://iopscience.iop.org/0305-4470/17/12/003)

J. Phys. A: Math. Gen. 17 (1984) L639–L643. Printed in Great Britain

LETTER TO THE EDITOR

Hierarchical model for chemically limited cluster–cluster aggregation

R Jullien and M Kolb

Laboratoire de Physique des Solides†, Bât. 510, Université Paris-Sud, Centre d'Orsay, 91405 Orsay, France

Received 20 June 1984

Abstract. A hierarchical model is introduced to describe chemically limited cluster–cluster aggregation. The fractal dimension of the clusters, D, as well as an exponent characterising the number of active sites per cluster are evaluated numerically for $d = 2, 3, 4$. The relevance of the model to realistic physical situation is discussed.

Several theoretical models have been introduced to describe aggregation phenomena. The prototype is particle–cluster (PCI) aggregation model of Witten and Sander (1981) in which single brownian particles stick, one by one, to an immobile growing cluster. In the alternative cluster–cluster (CICI) aggregation model (Meakin 1983a, Kolb *et al* 1983), clusters of particles as well as single particles, are allowed to diffuse together and the growth process is dominated by the sticking of clusters of almost the same size. The common feature of both models is that they describe the physical situation of 'diffusion limited aggregation' in the sense that sticking occurs at the first contact. As a consequence, the structure of the clusters is directly connected to the nature of the diffusion process. In particular the fractal dimension of the cluster, D, depends on the fractal dimension, d_w, of the diffusive trajectory. As observed both in PCI (Meakin 1984b) and in CICI (Meakin 1984a), D increases (the clusters become more compact) when d_w decreases. However, in several experimental situations, it is more reasonable to assume that the clusters (or particles) stick only after a large number of contacts. This occurs when a chemical reaction is responsible for the sticking. Hence this is called 'chemically limited' aggregation in contrast with 'diffusion limited' aggregation. This situation has already been studied in the context of particle–cluster aggregation, when a sticking probability has been introduced for the Witten–Sander model (Meakin 1983b). It has been found that, for finite sticking probability, a crossover takes place between a small size (compact) and a large size (Witten and Sander) regime. In the limit of infinitesimally small sticking probability, the Eden model, with $D = d$, is recovered, since, in this limit the added particle can reach any point of the surface with an equal probability. To our knowledge, the same limiting situation has not yet been considered in the case of cluster–cluster aggregation. It is the purpose of this letter to introduce a model from chemically limited cluster–cluster aggregation in which, clusters of the same size stick, after a quasi-infinite number of trials. This is the analogue of the Eden model for cluster–cluster aggregation but due to obvious

† Laboratoire associé au CNRS.

0305-4470/84/120639+05$02.25

steric constraints, the clusters cannot become compact as in the Eden model. Since each cluster can reach any point of space with the same probability before sticking, the model can also be viewed as the $d_w = 0$ limit of cluster–cluster aggregation. The non-trivial fractal dimension of the clusters in this model should provide an upper bound for the fractal dimension of any physical process involving cluster-cluster aggregation (as long as the clusters stay rigid and do not rotate).

Let us present here a hierarchical version of this chemically limited cluster–cluster aggregation model, similar, in spirit, to the hierarchical version for diffusion limited aggregation (Botet *et al* 1984a). Direct simulation of cluster aggregation with a finite sticking probability and the crossover from chemically to diffusion limited aggregation have been considered by Kolb and Jullien (1984). Clusters are built on a square (hypercubic) lattice in two (d) dimensions. Successive collections of clusters of the same size $2, 4, 8 \ldots$ are built iteratively starting from a collection of N_0 individual particles. Given the $(k-1)$th collection of clusters, of $N = 2^{k-1}$ particles, these old clusters are grouped into pairs to generate the clusters of the new collection. A new cluster is built as follows. Let us consider one pair, say cluster (1) and cluster (2). We consider all the possibilities for cluster (1) to stick to cluster (2), provided there is no double occupancy and that the new cluster is entirely connected by nearest-neighbour bonds. This can be done, for example, by moving cluster (1) around cluster (2) as shown in figure 1. (Note that no rotation is allowed.) All these distinguishable possibilities have the same probability and we choose one of these configurations, at random, as the new cluster. To estimate the size of a N-particle cluster, we have averaged the square of the radius of gyration:

$$R_N^2 = \frac{1}{2N^2} \sum_{i,j} (\boldsymbol{r}_i - \boldsymbol{r}_j)^2$$

over all the clusters of one collection. The fractal dimension of the clusters, defined by

$$R_N \sim N^{1/D} \qquad \text{for } N \to \infty$$

is estimated by extrapolating to $N \to \infty$ an effective fractal dimension D^* obtained when comparing two successive collections

$$D^* = \ln 4 / \ln [(R_{2N}^2 - \tfrac{1}{4})/R_N^2].$$

A corrective term $\frac{1}{4}$ has been added to kill small size R^{-2} corrections (Ball and Jullien 1984).

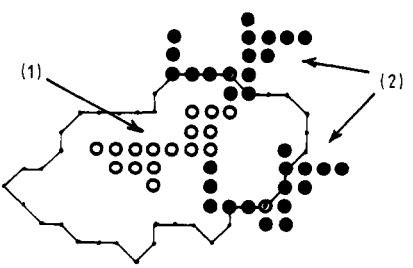

Figure 1. Aggregation of two clusters (1) and (2) of N particles to form a new cluster of $2N$ particles. All possibilities with one or several connecting nearest-neighbour bonds between the two clusters are equiprobable, provided there is no overlap. Two such possibilities are shown. When all the possibilities are considered, a given fixed point of cluster (2) follows the curve shown, whose number of points C_N is calculated (see text).

We have considered 1024 trials, all starting with $N_0 = 512$ particles, stopping after 6 iterations, so that 8192 independent clusters of 64 particles were generated. The results for D^* as a function of N^{-1} are reported in figure 2. The extrapolated fractal dimension is estimated to be $D = 1.53 \pm 0.04$, 1.98 ± 0.04, 2.32 ± 0.04 respectively for $d = 2, 3, 4$. As expected these values are larger than all the values found previously in cluster–cluster aggregation models, either with brownian ($d_w = 2$) (Jullien *et al* 1984) or with linear ($d_w = 1$) (Meakin 1984a) trajectories.

We have also calculated the number of possibilities, C_N, for two clusters of size N to stick, by simply averaging the number of possible configurations for each pair over all pairs of the collection. The results for C_N as a function of N are given in a log–log plot (figure 3). A very linear behaviour is found such that

$$C_N \sim N^{2\delta}$$

with $\delta = 0.37$, 0.58, 0.72 for $d = 2$, 3, 4 respectively. The quantity $C_N^{1/2} = N^{\delta}$ is the number of sticking points per cluster. It is obvious that δ must be smaller than one since only a fraction of all the points can be a sticking point. However it is expected that the upper found $\delta = 1$ must be recovered exactly above upper critical dimensions, when the clusters become transparent. For the present model, where $d_w = 0$, the condition of transparence gives $d_c = 2D_c$, where $D_c = \ln^4/\ln\frac{3}{2}$ is the fractal dimension of the ghost model (Ball and Witten 1984). Our results for δ plotted as a function of d (figure 4) are consistent with the theoretical prediction that $\delta = 1$ for $d > 6.8$. Note also that the following inequality is satisfied

$$\delta D > D - 1.$$

This means that the sticking points are localised in a volume which cannot be smaller than the volume of the surface.

One must be careful when applying the above results, obtained in a, monodisperse, hierarchical model, to the real, polydisperse, physical situations. In the case of diffusion limited aggregation, the hierarchical model has recently been extended to polydisperse

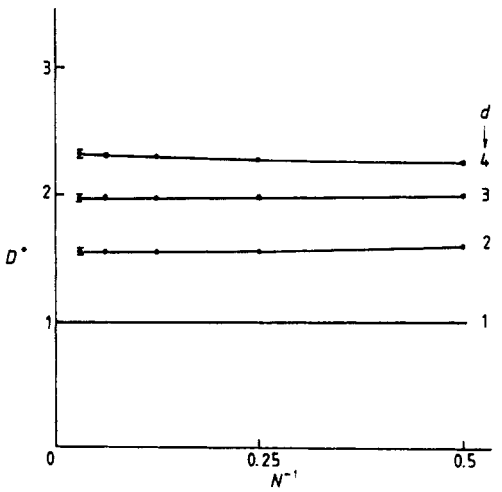

Figure 2. Plot of the effective exponent D^* for the hierarchical model against N^{-1} for dimensions $d = 2$, 3, 4.

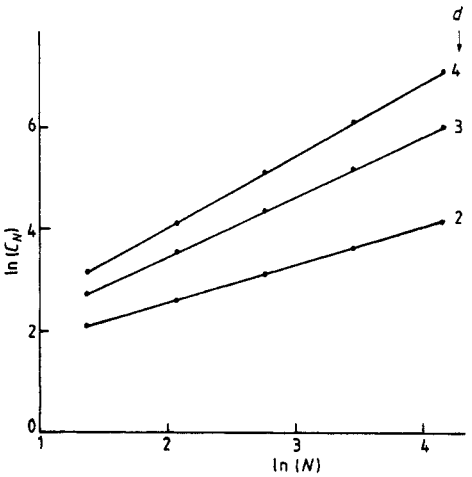

Figure 3. Log–Log plot of the number of sticking possibilities C_N against N for $d = 2, 3, 4$.

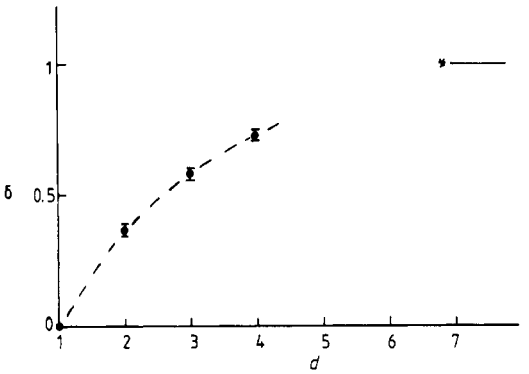

Figure 4. Plot of the exponent δ defined in the text as a function of d. The point (*) indicates the dimension above which one expects $\delta = 1$.

situations by choosing the two coalescing clusters with some probability depending on their numbers of particles i and j. The case where this probability varies as $(ij)^{\omega}$ has been considered (Botet *et al* 1984b). It was found, numerically, that the results of the hierarchical model are valid for all ω smaller than $\frac{1}{2}$. For $\omega > \frac{1}{2}$, one cluster becomes larger than all the others and has a different fractal dimension, characteristic of particle–cluster aggregation. This effect corresponds to the gelation phenomenon predicted by the Smoluchowski equation (Leyvraz and Tschudi 1981, Ernst *et al* 1982, Hendriks *et al* 1983, Spouge 1983, 1984). Let us consider a real physical situation of chemically limited cluster–cluster aggregation in which the clusters have a mobility depending on their number of particle i as i^{α}. Usually the diffusion constant varies as the inverse of the radius so that $\alpha = 1/D$ but let us consider any α for generality. The origins of the size dependence of the kernel K_{ij} entering the Smoluchowski equation are twofold: one is the relative velocity of the coalescing clusters, $(i^{2\alpha} + j^{2\alpha})^{1/2}$, the other is proportional to the number of possibilities of sticking which can be written as $C_{ij} \sim (ij)^{\delta}$, when δ is defined as above. Thus one finds

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

with

$$2\omega = \alpha + 2\delta.$$

Considering the δ values calculated above the condition for gelation $\omega > \frac{1}{2}$ is given by

$$\alpha > 0.26 \qquad \text{for } d = 2$$

$$\alpha > -0.17 \qquad \text{for } d = 3.$$

Note that these conditions are not satisfied in realistic cases where $\alpha = -1/D$, when taking the D values reported above. Thus, we think that the results found in this letter can be applied reasonably to physical situations. The results of the direct simulations of chemically limited aggregation depending on the mobility exponent α (Kolb and Jullien 1984) are consistent with this inequality.

The value $D = 2$, found for $d = 3$ could perhaps explain the result $D = 2.1$ of Schaeffer *et al* (1984), who considered the aggregation of small silica particles. However, one must note that other effects, such as restructuring of clusters, can also explain an effective exponent larger than that predicted by diffusion limited aggregation ($D \sim 1.78$).

We have benefited from interesting discussions with R Ball and R Botet. We thank D Taupin and J Noguès (service de microdensitometrie du CNRS, Orsay, France) and also the CCVR (Centre de Calcul Vectoriel pour la recherche) Ecole Polytechnique, Palaiseau, France for providing computing facilities.

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