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LETTER TO THE EDITOR

Computer simulation of chemically limited aggregation

W D Brown and R C Ball

Cavendish Laboratory, Madingley Road, Cambridge, UK

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Abstract. Cluster-cluster aggregation is studied via a computer simulation in the chemically limited regime. True polydisperse flocculation is compared with idealised monodisperse aggregation in two and three space dimensions in terms of fractal dimensions and the exponents associated with the scaling of the reaction rates with cluster size.

Recent interest in aggregation phenomena has been directed towards two classes of problem—cluster-particle and cluster-cluster aggregation. The first of these has been extensively studied via computer simulation (Witten and Sander 1981, Meakin 1983) under a variety of conditions; the most significant variation being the change in the dimension of the trajectory of the incoming particle relative to the seed, d_w , from $d_w = 2$ in diffusion limited aggregation (DLA) to $d_w = 0$ in the Eden model of cancer growth.

The second class of problem, that of cluster-cluster aggregation, has also been studied by computer simulation. When diffusive ($d_w = 2$) and ballistic trajectories were assigned to the flocculating clusters, this was done using monodisperse (Kolb *et al* 1983, Jullien *et al* 1984) and polydisperse (Meakin 1983, 1984, Meakin *et al* 1985) kinetics. The case of chemically limited aggregation (CLA) for which $d_w = 0$ had however been studied only under the constraint that the cluster distribution remained monodisperse (Jullien and Kolb 1984). The extension to polydispersity is both natural and necessary if real flocculation processes are to be understood.

Chemically limited aggregation occurs in the limit where the probability of two clusters sticking on contact is sufficiently low that all physically possible contacts are equally likely. In this limit new clusters will be derived at any stage in the aggregation with equal likelihood from any of the possible cluster-cluster bondings. Furthermore if the cluster concentration is very low we may neglect all bonding configurations that involve more than two clusters.

Our computer simulation represents the distribution of clusters on cubic lattices. Two clusters are chosen and positioned at random in a large box. Only if this results in the clusters being adjacent but not overlapping is this new configuration accepted as a single cluster and the distribution updated. How the clusters are chosen depends upon whether or not we wish the distribution to evolve in a monodisperse or in a polydisperse manner. In the former scheme the distribution begins as 2^q monomers. At each iteration a dimerisation is made until there are no monomers left. Subsequently these dimers are themselves dimerised and so on. In the latter (polydisperse) scheme, however, the choice of clusters is not restricted in any way. The correspondence of this scheme to CLA hinges on our definition of a large box. So long as its size is larger

than twice the size of the largest cluster in the distribution at any stage, then it amounts to an unbiased sampling of all (cluster pair) bonding configurations.

It is however clear that the equal probabilities associated with every possible pairwise bonding will lead to a non-trivial probability of the bond forming between two particular clusters from the distribution. This is of course to be contrasted with the 'polydisperse' scheme of Meakin (1984), in which these probabilities were equal. The study of this was carried out in terms of the reaction surface. If we define $S(1, 2)$ as the number of ways in which cluster 1 and cluster 2 may bond, then the reaction surface $N_c(M_1, M_2)$ is given by the average,

$$N_c = \langle S(i, j) \rangle_{\substack{\text{all clusters } i \text{ of mass } M_1 \\ \text{all clusters } j \text{ of mass } M_2}} \quad (1)$$

Our measurements of the reaction surface N_c relate specifically to the diagonal terms for which $M_1 = M_2$, where the behaviour is found to be given by

$$N_c(M, M) \propto M^\lambda \quad (2)$$

Fractal dimensions were also measured for the clusters evolved by mono- and polydisperse kinetics by investigating the behaviour of cluster radii of gyration with mass.

Some points should be made about these measurements.

(i) The reaction surface is obtained by averaging $S(1, 2)$, (a quantity which may be sampled by observing the number of successful aggregations out of the number of attempts when cluster 2 is positioned at random in a large box containing cluster 1). A simple scheme is employed to obtain S in which cluster 2 is a replica of cluster 1 and no rotations are permitted in the random positioning. The absence of rotations means that the sampling involves only those bonding configurations which are between opposing sides of the identical clusters, and that we are therefore obtaining a reasonable estimate of the full statistical average.

(ii) Logarithmic plots of N_c against M are shown in figures 1 and 2 whilst those of R_g^2 against M are shown in figures 3 and 4. In the monodisperse measurements, the data are gathered across a range of times since there is only one mass at a given time. This is in contrast with the polydisperse measurements which may be carried out at one particular time. Choosing two different times—both when the number of clusters is equal to the square root of the initial number of particles and when the largest cluster mass is equal to the number of clusters in the distribution—gave values of exponents which lay within approximately one standard error of each other.

(iii) The exponents, D and λ , were derived from least square fits to the data and are tabulated for mono- and polydisperse kinetics for two and three space dimensions in table 1. The fits are shown as broken and full lines respectively in figures 1-4.

The effect of the monodisperse constraint is seen to be one of decreasing the fractal dimension, D , and of increasing the reaction surface exponent, λ , relative to the polydisperse process. This is as expected—two clusters of the same size will not be able to penetrate each other as strongly as two of differing sizes. This leads to more compact structures in the polydisperse process ($D_{\text{poly}} > D_{\text{mono}}$) but commensurately fewer bonding configurations become available to clusters of equal size ($\lambda_{\text{poly}} > \lambda_{\text{mono}}$). A point of interest is that as far as processes in which $d_w = 0$ are concerned, monodisperse aggregation has the maximum screening of the centre of clusters whilst the Eden model of deposition has the minimum possible ($D_{\text{Eden}}(d) = d$, $d = 2, 3$). Correspondingly $D_{\text{Eden}} > D_{\text{poly}} > D_{\text{mono}}$, in agreement with our results.

Several physical, as opposed to computational, experiments have been carried out on systems which may be well represented by the model proposed. Slow flocculation

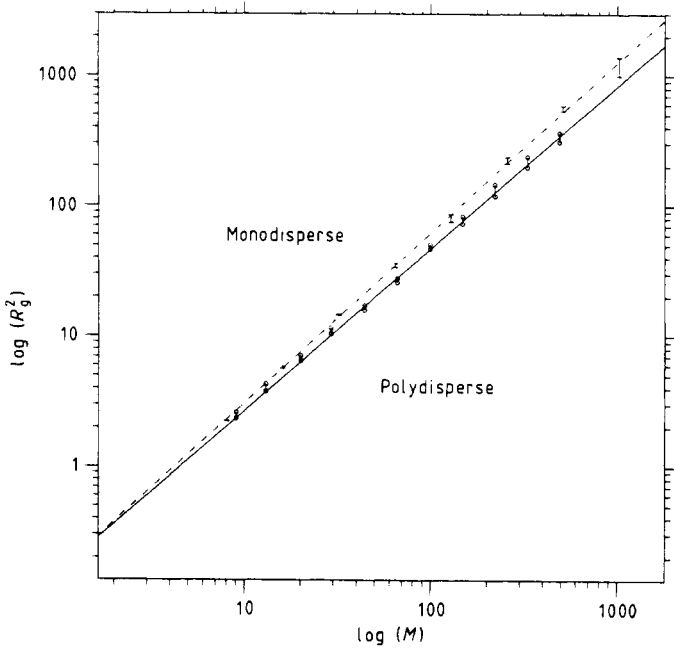


Figure 1. Fractal dimension, $d = 2$, from data of 4 simulations with 1024 particles, each run to completion (monodisperse)—linear error markers show the standard error of the measurement across a set of clusters; and of 30 simulations with 1000 particles, each run to $\sqrt{1000}$ clusters (polydisperse)—circular error markers denote averages over many clusters.

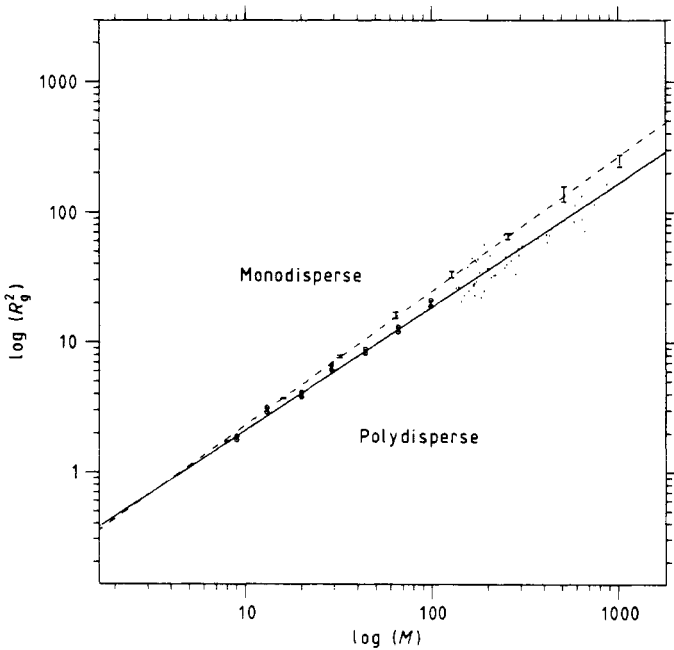


Figure 2. Fractal dimension, $d = 3$, from data of 4 simulations with 1024 particles, each run to completion (monodisperse)—linear error markers show the standard error of the measurement across a set of clusters; and of 6 simulations with 5000 particles, each run until the maximum cluster size equals the number of clusters present (polydisperse)—circular error markers denote averages over many clusters.

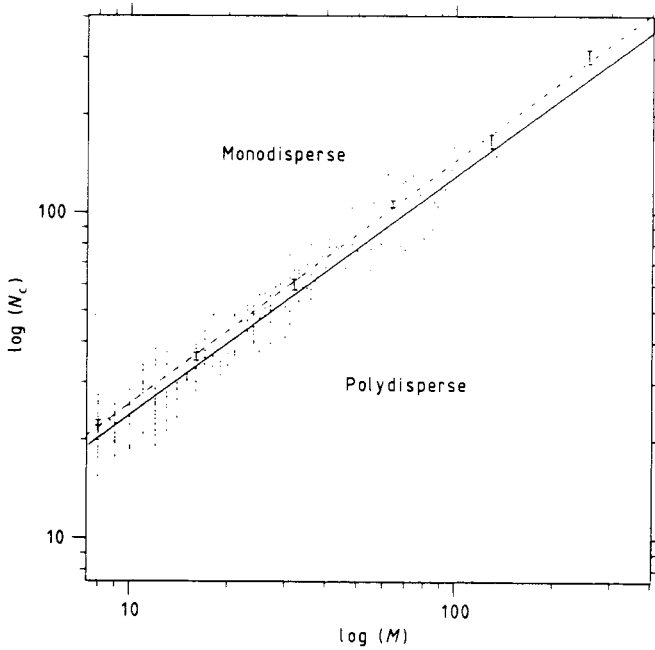


Figure 3. Reaction surface exponent, $d = 2$, from data of 30 clusters each of 2^3 up to 2^8 particles (monodisperse)—linear error markers show the standard error of the measurement across a set of clusters; and of 6 simulations with 1000 particles, each run until the maximum cluster size equals the number of clusters present (polydisperse).

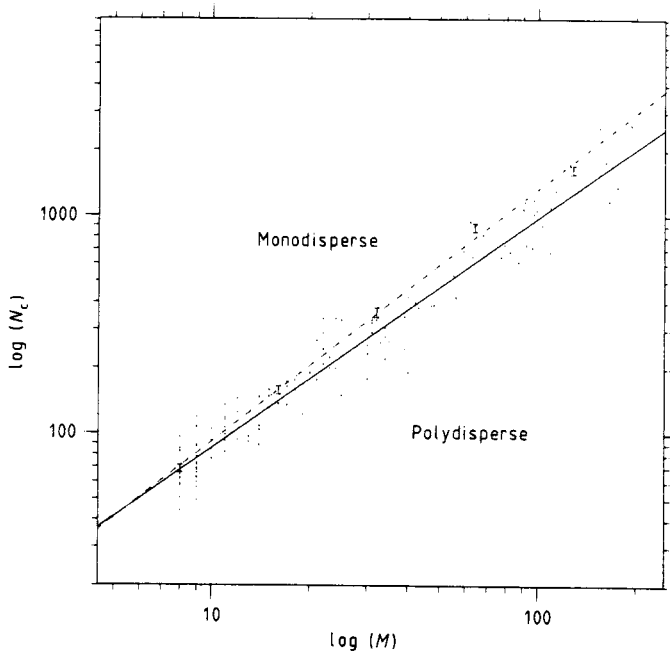


Figure 4. Reaction surface exponent, $d = 3$, from data of 20 clusters each of 2^3 up to 2^7 particles (monodisperse)—linear error markers show the standard error of the measurement across a set of clusters; and of 6 simulations with 1000 particles, each run until the maximum cluster size equals the number of clusters present (polydisperse).

Table 1.

| Model | Exponent | Space dimension | |
|--------------|-----------|-------------------|-------------------|
| monodisperse | λ | 2 | 3 |
| | | 0.75 ± 0.01 | 1.16 ± 0.04 |
| | D | 0.74^a | 1.16^a |
| | | 1.53 ± 0.01 | 1.94 ± 0.02 |
| polydisperse | λ | 1.53 ± 0.04^a | 1.98 ± 0.04^a |
| | | 0.73 ± 0.02 | 1.06 ± 0.02 |
| | D | 1.59 ± 0.01 | 2.11 ± 0.03 |

^a Jullien and Kolb (1984).

of colloidal silica (Schaefer *et al* 1984) produces structures whose measured fractal dimension is higher than those reported in diffusive and ballistic cluster-cluster aggregation computer studies—it is found that $D = 2.12 \pm 0.05$ (cf our result for polydisperse CLA, $d = 3$, for which $D = 2.11 \pm 0.03$). Other experiments have been carried out which look at kinetic rather than structural properties of flocculation clusters (Weitz and Huang 1984, von Schulthess *et al* 1983). The value of λ which we observe in the three dimensional polydisperse case, 1.06 ± 0.02 , is close to the critical value $\lambda = 1$ for which simple scaling predicts exponential kinetics,

$$M(t) \sim e^{t/t_1}$$

where $M(t)$ is a characteristic large cluster mass—a behaviour which is in agreement with the experimental results.

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