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LETTER TO THE EDITOR

# Reversible diffusion-limited cluster aggregation

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**Abstract.** A model of cluster aggregation with and without loops is introduced where clusters can both aggregate and fragment. In the steady state equilibrium, the clusters have a fractal dimension $D = 1.57 \pm 0.06$ ($2.03 \pm 0.05$) in two (three) dimensions. The cluster-size distribution has scaling form and depends on the kinetics. The results are compared with irreversible growth and static cluster models.

The study of irreversible diffusion-controlled aggregation processes (Witten and Sander 1981, Meakin 1983, Kolb *et al* 1983) shows that the kinetics and the irreversibility influence the resulting structures in an important way: the fractal properties in aggregation phenomena are different from purely configurational models such as lattice animals and percolation (Lubensky and Isaacson 1978, Parisi and Sourlas 1981, Glaus 1985, Stauffer 1979, 1985). The theoretical efforts to characterise such growth processes have been hampered by the fact that these processes are far from equilibrium. This motivates one to investigate intermediate situations between growth models and purely static models: here I consider the case of dynamic equilibrium between growth and fragmentation.

A second motivation to study reversible aggregation processes is the observation that in many experiments the growth is not strictly irreversible. Restructuring in some sense needs to be included. Examples where this is important are coagulation and fragmentation of polymers (Blatz and Tobolsky 1945, Nanda and Pathria 1959, Hendriks 1985), restructuring of aggregation clusters (Allain and Jouhier 1983, Richetti *et al* 1985, Meakin and Jullien 1985, Camoin and Blanc 1985), rouleaux formation in red cell aggregation (Herbst and Goldstein 1984) and flocculation/floc dissociation in colloids (Vincent and Whittington 1982).

The model proposed here is the reversible counterpart to diffusive clustering of clusters. It will be shown that the cluster-size distribution in this process is dependent on the kinetics just as in the corresponding growth model, but the geometrical fractal properties appear to be those of statics (animals or branched polymers).

In the *irreversible* cluster aggregation process one considers an assembly of randomly and independently diffusing clusters which stick together by forming rigid permanent bonds whenever they touch each other. Large clusters that form this way have non-trivial scaling properties. In the *reversible* cluster aggregation process studied here, the bonds form in the same way, but they are allowed to break up again, after a characteristic time $\tau$. This way a fragmentation process is introduced. The long time behaviour is characterised by the dynamic equilibrium between aggregation, characterised by the time $\tau_a$ and fragmentation characterised by $\tau_f$. Starting initially with

single particles, aggregation will dominate until the clusters are large enough, such that the bonds formed and the bonds broken balance each other ($\tau_a = \tau_f$). Conversely, if the clusters are initially very large, fragmentation is more important, until the equilibrium cluster size is reached. This characteristic size depends of course on $\tau$. A more quantitative description will be given below.

The model investigated here numerically, both in two and three dimensions, is a lattice version of the above process. On a periodically bounded hypercubic lattice of linear dimension $L$ one places $N_0$ particles at random. No two particles are allowed to occupy the same site, but they can be nearest neighbours. Initially, all the particles (even nearest neighbours) are independent, i.e. no bonds are yet formed. Then, the particles start to perform independent random walks on the lattice (jumping to neighbouring sites). If a particle attempts to move to an already occupied site, it will not be allowed to move; instead, a bond will be placed between the neighbouring particles which have just collided. They form a dimer and diffuse together from now on. A collision between two clusters will be treated in the same way. If any particle of the first cluster attempts to occupy the same site occupied by a particle of the second cluster, the first cluster does not move, but a bond forms between the colliding particles, thus connecting the clusters. On a lattice, it is possible that several particles collide simultaneously, possibly with different clusters. Two alternative procedures have been investigated: either one chooses exactly one pair of colliding particles at random and forms a single bond between them (this imitates off-lattice simulations, where the probability of a multiple collision vanishes), or all possible bonds are formed. The first rule leads to loopless clusters; the second rule allows for loops. The results do not depend on this choice (most of the data presented come from simulating the loopless case). To disaggregate, the bonds are broken randomly and independently with a probability $1/\tau$ per unit time. For a loopless cluster a broken bond necessarily splits a cluster into two smaller clusters, whereas if loops are allowed, a removed bond does not necessarily fragment the cluster. In any case, after a break-up the two clusters diffuse again independently of each other.

A qualitative description of the dynamic equilibrium can be given for the situation with low cluster concentration and a monodisperse cluster-size distribution. Denote by $D$ the fractal dimension of the clusters and by $d$ the Euclidean dimension. The diffusing velocity $v$ of a cluster of mass $m$ (single particles have $m = 1$) is characterised by an exponent $\alpha$ in $v(m) = m^{\alpha}$. Then the time it takes the clusters to pair up is $\tau_a \sim \bar{m}^{1-\alpha-(d-2)/D}/\rho_0$ where $\bar{m} = N_0/N$ is the average mass per cluster, $N$ the number of clusters and $\rho_0 = N_0/L^d$ the initial density (Kolb 1984). For the loopless case the time to pair up is the same as the time to form one bond. In a cluster of mass $m$ a bond breaks on average in a time $\tau_f = \tau/m$. Dynamical equilibrium requires that the aggregation time is equal to the fragmentation time, $\tau_a = \tau_f$, which determines the equilibrium cluster size $m_{eq}$ as a function of $\rho_0$ and $\tau$, $m_{eq}^{2-\alpha-(d-2)/D} = \tau\rho_0$. The corresponding characteristic time $t_{eq} = \tau/m_{eq}$ separates irreversible from reversible steady state aggregation; starting initially with single particles, the growth is irreversible for $t \ll t_{eq}$ and crosses over to the dynamic equilibrium, $t \gg t_{eq}$. It is this latter case that is studied here. Varying $\tau$ (or $\rho_0$) one can change $m_{eq}$ or $\bar{m}$, and a scaling analysis can be performed both for the cluster radius and for the size distribution of the clusters, as a function of $m$.

In figure 1, clusters are shown in two dimensions to illustrate the difference between loopless clusters and clusters with loops. In the second case, not all possible bonds are present, as some have been removed by the bond-breaking mechanism.

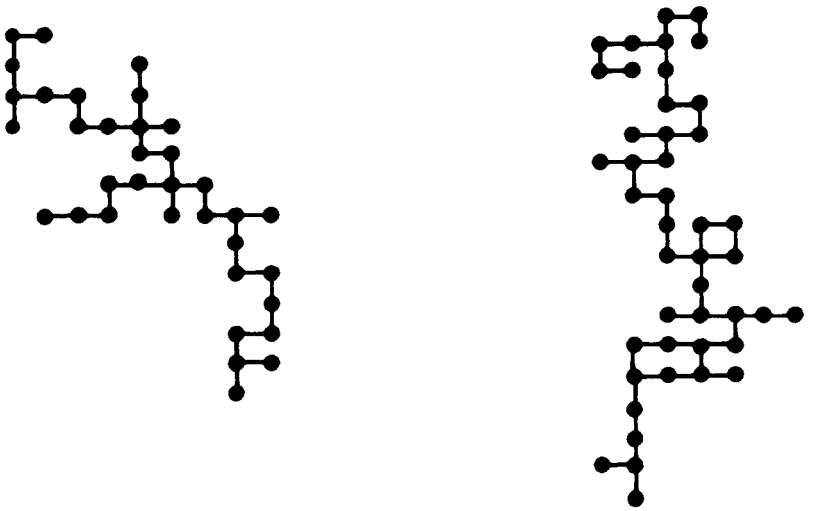

**Figure 1.** Clusters obtained in reversible diffusion-limited cluster aggregation. The difference between loopless clusters (left) and clusters with loops (right) is illustrated ($d = 2$).

In figure 2, the crossover from the growing to the equilibrium regime is shown. The average mass $\bar{m}$ is plotted as a function of time. It is seen to saturate gradually at its equilibrium value. $\bar{m}$ has been normalised by $m_{eq}$, $t$ by $t_{eq}$. The steady state is reached for $t \geq 3t_{eq}$. The curves for $\alpha = -2$ (monodisperse) show that the crossover is practically independent of $\bar{m}$ in normalised units. Most simulations were performed for a system with $L = 100$, $N_0 = 1000$ in two dimensions with $L = 30$, $N_0 = 1000$ in three dimensions. It was checked that the concentration does not influence the results by comparing with a system twice as large. The average number of clusters in equilibrium was kept above ten to keep boundary effects negligible; for $\bar{m}$ large, $L$ was increased at fixed concentration to assure this. Also, in all the simulations, the clusters were not rotated.

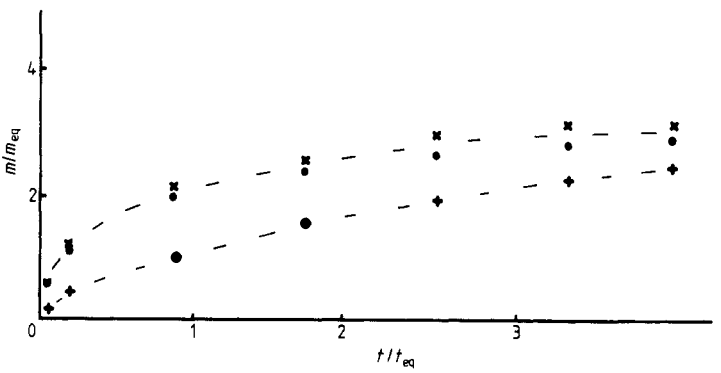


**Figure 2.** Crossover from growth (irreversible clustering) to equilibrium (reversible clustering) aggregation. The average mass $m$ (normalised by $m_{eq}$) is plotted against time $t$ (normalised by $t_{eq}$). For comparison, $\alpha = -2$, $m_{eq} = 6$ (●), $\alpha = -2$, $m_{eq} = 12$ (×) and $\alpha = 0$, $m_{eq} = 12$ (+) are shown. The data are an average over 100 separate simulations in two dimensions.

In figure 3, the fractal properties of the clusters have been collected. The radius of gyration $R$ against the cluster mass $m$ has been plotted both for the largest cluster and for the average over all the clusters, at equilibrium. The points for different values of the cluster mobility, $\alpha$, fall on the same curve (for clusters with and without loops) and the average over all clusters is consistent with the largest cluster alone. Bonding with loops appears to have the same fractal dimension as bonding without loops. The estimated fractal dimension is $D = 1.57 \pm 0.06$ and $D = 2.03 \pm 0.05$ in $d = 2$ and $d = 3$, respectively. Comparing with irreversible cluster formation ($D = 1.42$, 1.78 in $d = 2$, 3) shows a marked difference. The restructuring of the cluster effectively removes the screening which keeps the aggregating clusters at a distance in the irreversible process. The data presented have been measured at intervals of $2t_{eq}$ in equilibrium. The independence of the measurements was monitored by the correlations of $R(t)$ and $R(t+2t_{eq})$.

Finally, in figure 4, the cluster-size distribution $N(m)$ (the number of clusters with $m$ particles) is shown. The scaling function $p(x)$ is defined through $N(m) = m^{-2}P(m/\bar{m})$ where here $m$ is the weight-averaged cluster mass. It is plotted for

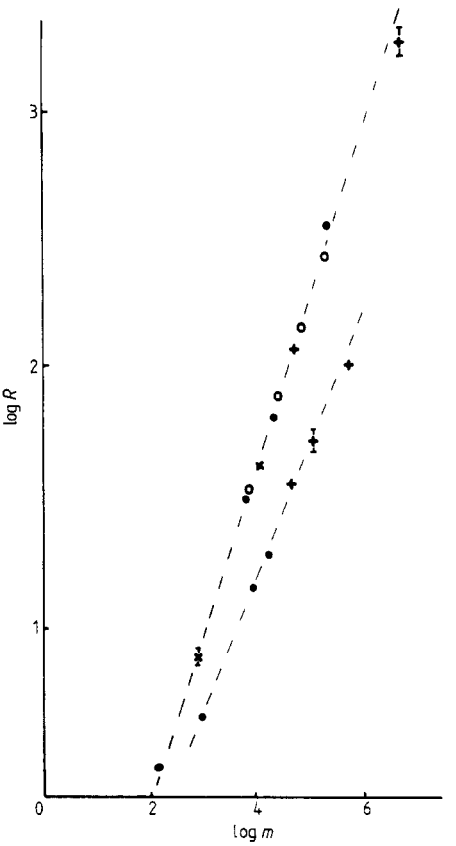


**Figure 3.** A log-log plot of the radius of gyration $R$ against the mass $m$. The upper curve is for $d = 2$, the lower for $d = 3$. Data are shown for $\alpha = -2$ (●) and $\alpha = 0$ (×) for the average over the cluster and for $\alpha = -2$ (+) for the largest cluster, for loopless clusters. Clusters with loops are shown for $\alpha = -2$ (○) (average). The estimated fractal dimension is $D = 1.57 \pm 0.06$ ($2.03 \pm 0.05$) in $d = 2$ (3). The data are an average over 2000 measurements in the steady state regime.

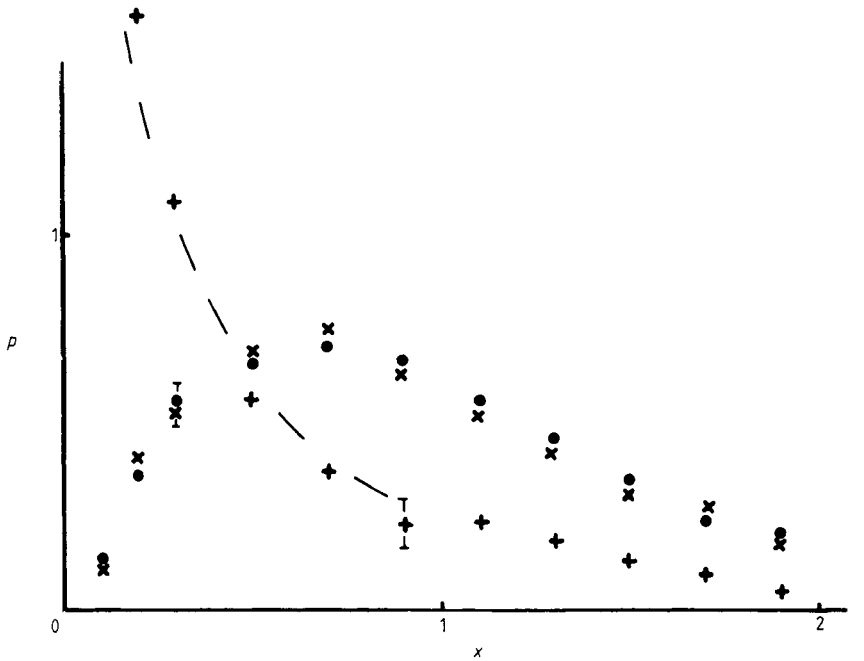


**Figure 4.** Reduced cluster-size distribution $p(x)$ for $d=2$ and loopless clusters. The distribution does not depend on $m_{eq}$ but on $\alpha$. For $\alpha=-2$, $m_{eq}=6$ (●) and $m_{eq}=12$ (×) and for $\alpha=-1$, $m_{eq}=12$ (+) are shown.

different values of $m_{eq}$ and $\alpha$. As in irreversible clustering it does depend on $\alpha$, but the maximum at a finite $\alpha$ value for $\alpha=-2$ is much broader than in irreversible clustering (Kolb 1984). This can be understood from the difference between aggregation and fragmentation. The kinetics is important for aggregation (favouring a monodisperse distribution), but it does not influence the random break-up (which favours a much broader distribution).

The above simulations indicate that the fractal dimension $D$ does not depend on whether one allows loops or not. The steady state also does not depend on the initial cluster-size distribution. The role of $\alpha$ is more interesting, since for irreversible aggregation, $\alpha>1$ corresponds to a different growth process with a different $D$ (Botet *et al* 1984). The present model has been simulated for $\alpha=1$ and does not show any sign of a different $D$. One other way to test if the kinetics is at all important is to consider the reaction-limited instead of the diffusion-limited case. A sticking probability $p=0.05$ has been introduced (a bond between two colliding particles is formed with probability $p$ only). The results indicate that, again in contrast with irreversible growth (Kolb and Jullien 1985, Jullien and Kolb 1984), $D$ is not affected by $p$.

The conclusion from the above calculations is that the steady-state growth is an equilibrium model where the details of how clusters aggregate and fragment is unimportant. Note that the numerical values for $D$ are, within the error bars, the same as the ones for lattice animals. This suggests that, while a particular cluster may have a relative weight that depends on the kinetics, the scaling properties are universal. The statistical weight of individual configurations need not be the same, analogous to branched polymers and lattice animals, which despite different cluster weights belong to the same universality class. One practical difference to the simulation methods for

static models (Glaus 1985) is that there is no detailed balance here. It is interesting to compare the results from diffusive and reactive irreversible growth with the static and dynamic equilibrium results. The exponents suggest that all models have the same fractal properties, except when the process is both diffusive and irreversible.

The reversible cluster aggregation model is the equilibrium counterpart to the usual clustering process. Its geometrical properties are numerically the same as those of lattice animals. One way to change the expected fractal properties would be to choose non-random bond breaking.

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## References

Allain C and Jouhier B 1983 *J. Physique Lett.* **44** L421
Blatz P J and Tobolosky A V 1945 *J. Phys. Chem.* **49** 77
Botet R, Jullien R and Kolb M 1984 *Phys. Rev.* A **30** 2150
Camoin C and Blanc R 1985 *J. Physique Lett.* **46** L67
Glaus U 1985 *Preprint*
Hendriks E M 1985 *Z. Phys.* B **57** 309
Herbst M and Goldstein J H 1984 *Kinetics of aggregation and gelation* ed F Family and D P Landau (Amsterdam: North-Holland) p 53
Jullien R and Kolb M 1984 *J. Phys. A: Math. Gen.* **17** L639
Kolb M 1984 *Phys. Rev. Lett.* **53** 1653
Kolb M, Botet R and Jullien R 1983 *Phys. Rev. Lett.* **51** 1123
Kolb M and Jullien R 1985 *J. Physique Lett.* **45** L977
Lubensky T C and Isaacson J 1978 *Phys. Rev. Lett.* **41** 829
Meakin P 1983 *Phys. Rev. Lett.* **51** 1119
Meakin P and Jullien R 1985 *J. Physique* **46** 1543
Nanda V S and Pathria R K 1959 *J. Chem. Phys.* **30** 27
Parisi G and Sourlas N 1981 *Phys. Rev. Lett.* **46** 871
Richetti P, Prost J and Barois P 1985 *J. Physique Lett.* **45** L1137
Stauffer D 1979 *Phys. Rep.* **54** 1
—— 1985 *Introduction to Percolation* (London: Taylor and Francis)
Vincent B and Whittington S G 1982 *Surf. Colloid Sci.* **12** 1
Witten T and Sander L M 1981 *Phys. Rev. Lett.* **47** 1400