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LETTER TO THE EDITOR

The sol–gel transition modelled by irreversible aggregation of clusters

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Abstract. Irreversible aggregation of clusters leads in a natural way to the formation of large ramified structures. We investigate this growth process close to the sol-gel transition, where for the first time an infinite spanning cluster appears, and find scaling behaviour. The kinetics of the model leads to properties which are distinct from standard percolation. Two critical exponents are determined numerically. The fractal dimension of the clusters is $D_g = 1.75 \pm 0.07$ in two dimensions.

It has been suggested that the sol-gel transition can be described by standard percolation (De Gennes 1976, Stauffer 1979, Stauffer *et al* 1982). This approach, however, considers neither the growth nor the mobility of the macromolecules (clusters). The approach using kinetic equations (Cohen and Benedek 1982, Leyvraz and Tschudi 1983, Ziff *et al* 1982, Ziff 1980) does consider the growth but takes the limit of infinite mobility. Hence it loses information about the local environment and thus it is a mean field theory which neglects spatial correlations. The real (experimental) situation with a finite mobility depends very much on the growth mechanism. If the growth is governed by initiators (additive polymerisation) (Manneville and de Seze 1981, Herrmann *et al* 1982), one knows that the sol-gel transition has universality properties of its own (sensitive to the initiator concentration). If the growth is not induced by initiators the most common mechanism is polycondensation, which has been studied experimentally on macromolecules (Adam *et al* 1981, Schmidt and Burchard 1981), on coagulation (Wiltzius *et al* 1982) and on experimental models (Allain and Jouhier (1983) with wax balls on water; Von Schulthess *et al* (1980) with latex spheres).

Here we propose a model for irreversible polycondensation. The growth mechanism is that of kinetic clustering of clusters (Meakin 1983, Kolb *et al* 1983) which has been used to describe flocculation. We have determined the scaling properties numerically and conclude that they are distinct from flocculation and from standard percolation.

The model of kinetic clustering of clusters is defined as follows: N_0 particles (clusters of unit mass and diameter) are distributed randomly (no overlap) in a volume $V_0 = L^d$ in d-dimensional space (density $\rho_0 = N_0/V_0$). If any of these particles touch each other, they stick together rigidly and permanently. These clusters now start to move randomly and independently (Brownian motion). Each cluster of mass m is assumed

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to have an average velocity

$$v = m^{\alpha} \tag{1}$$

where the parameter α can be chosen at will. A strong short range attraction then lets the clusters grow: whenever two clusters of mass m_1 resp. m_2 touch each other, they irreversibly form a bond at the point(s) of contact and thus build a new cluster of mass $m_1 + m_2$, now diffusing with velocity $v(m_1 + m_2)$, etc.

In the past, this model has been extensively studied for the case when the distance between clusters is much larger than the radius of the clusters (flocculation). Asymptotically this corresponds to $\rho_0 \to 0$. In this paper we will study the opposite limiting case: the process is so advanced that the clusters interpenetrate each other and eventually an infinite spanning cluster appears.

Starting with a finite initial density ρ_0 there will always be a time t_g when such an infinite cluster appears. This is because the clusters have a fractal dimension D smaller than the spatial dimension d and therefore asymptotically the density of each single cluster goes to zero. Two cases are possible: $t_g = \infty$ (no gel) or t_g finite (gel) depending on α. It is the aim of this letter to study the critical behaviour of our model around t_g and to compare it with flocculation on one hand and standard percolation on the other.

The only true parameter in the model then is α, and it influences the growth in an important way. In particular it controls the relative size of the aggregating clusters. It is illustrative to consider the limiting situations: for $\alpha \to -\infty$ aggregation of equally sized clusters is favoured whereas for $\alpha \to \infty$ only the largest cluster moves and grows.

To better understand the role of α it is useful to recall the mean field approach to cluster aggregation: it is given by the Smoluchowski equations

$$\frac{\mathrm{d}}{\mathrm{d}t} N(m, t) = \tfrac{1}{2} \sum_{i+j=m} K_{ij} N(i, t) N(j, t) - N(m, t) \sum_i K_{mi} N(i, t) \tag{2}$$

where $N(m, t)$ is the number of clusters of size m at time t and the kernel K_{ij} is the probability that two clusters of masses i and j aggregate. If one supposes $K_{ij} = (ij)^{\omega}$ it is known that (2) has qualitatively different asymptotic solutions for $\omega < \frac{1}{2}$ and $1 > \omega > \frac{1}{2}$. For $\omega < \frac{1}{2}$ (Lushnikov 1973) one has $t_g = \infty$, and $N(m, t)$ scales as

$$N(m, t) = m^{-2} p(m / t^{\theta}) \tag{3}$$

where θ is related to ω through

$$\theta^{-1} = 1 - 2\omega. \tag{4}$$

For $\omega < 0$ the scaling function $p(x)$ has a peak and vanishes for small x. For $1 > \omega > \frac{1}{2}$ (Hendriks *et al* 1983) one has $t_g < \infty$, the scaling behaviour is different and has a monotonically decreasing scaling function.

For the case of flocculation numerical evidence has been given in Kolb (1984) that the Smoluchowski approach describes the scaling behaviour of $N(m, t)$ obtained in the simulation in $d = 2$ if one sets

$$2\omega = 1 - \alpha \tag{5}$$

for $\omega < 0$. However, as the Smoluchowski equation neglects spatial structure, it cannot yield the fractal dimension of the clusters.

In this letter we want to determine the fractal dimension in the gelation regime and investigate if the scaling behaviour of $N(m, t)$ is also described by the Smoluchowski equation.

We present a simulation of the model under the same conditions as in Kolb *et al* (1983), considering growth on a square lattice with periodic boundary conditions. The clusters move one lattice spacing at a time and stick together when they are nearest neighbours. Rotation of the clusters is neglected as seems justified for the asymptotic exponents for slow enough rotations (Meakin, unpublished). In figure 1 snapshots of the system at $\rho_0 = 0.25$ are shown for different stages of the growth (or times).

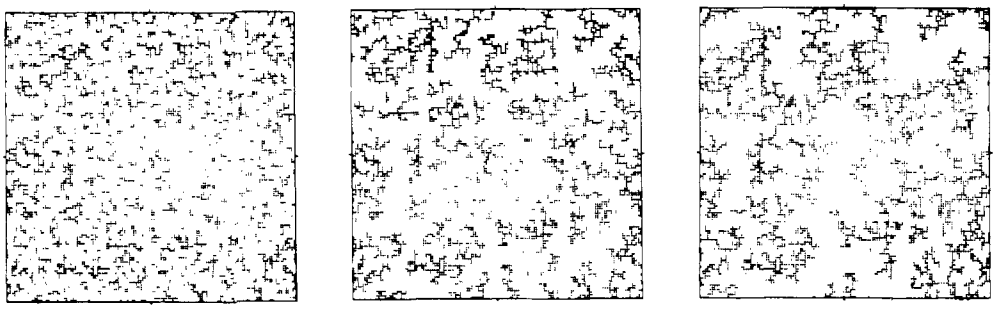

Figure 1. Simulation of kinetic cluster growth at different stages ($L = 128$, $\rho_0 = 0.25$); (*a*) initial stage, (*b*) scaling region, and (*c*) past the gel point (when the largest cluster spans the system).

We will define the time t as follows: at the beginning we set $t = 0$. We randomly choose a cluster and move it with a probability proportional to $v = m^{\alpha}$, where m is the mass of the chosen cluster. Simultaneously we increment the time by $\Delta t = N^{-1}(t)$, where $N(t)$ is the actual number of clusters in the box before the move. Thus one time unit is one Monte Carlo step per cluster.

First we want to show the results for the effective fractal dimension D_g of the clusters in the asymptotic region close to t_g (see, e.g., figure 1(*b*)). Numerically we define the gel time as the moment when the largest cluster attains the system size in either the x or the y direction.

At a given time we pick out the largest cluster in the box and calculate its radius of gyration R and its mass m. By doing this for 20 samples an average R and m are obtained for each time. In figure 2 we plot R logarithmically against m for $t < t_g$ and several choices of ρ_0 and α. Irrespective of the exponent α, equation (1), to within the error bars the points lie on straight lines of equal slope 0.57. This yields $D_g = 1.75 \pm 0.07$. The dependence on ρ_0 is slight for the large ρ_0 that we have chosen. If $\rho_0 \ll 1$ one would expect to see a crossover phenomenon to flocculation, where $D_f = 1.42 \pm 0.05$. The remarkable feature of our result is that the fractal dimension D_g is noticeably distinct not only from that of flocculation clusters but also from $D_g = \frac{91}{48} \approx 1.89$ the fractal dimension of the percolation clusters at the percolation threshold $p_c = 0.592\,75$.

For the present model, the density ρ_0 cannot exceed p_c, as for $\rho_0 = p_c$ the initial configuration already contains on average a percolating cluster whose properties are not determined by the kinetic process any longer.

Three technical points concerning figure 2 are interesting to note.

(1) The finite size effects at $L = 150$ are not very strong as can be seen from figure 2 where the results for $L = 90$ are also shown.

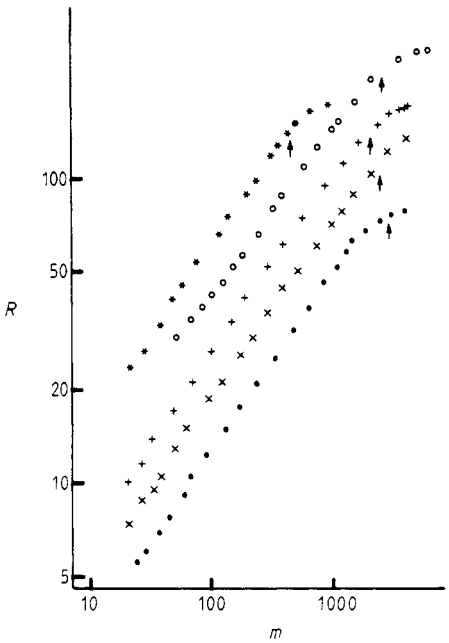

Figure 2. Radius R against mass m (log-log) of the largest cluster for $\alpha = -4$ (●), $\alpha = -2$ (×) and $\alpha = 0$ (+), all for $L = 150$ and $\rho_0 = 0.25$. The conclusions are insensitive to L and ρ_0, as illustrated by the results for $\alpha = -2$, $L = 150$ and $\rho_0 = 0.37$ (○) resp. $\alpha = -2$, $L = 90$, $\rho_0 = 0.25$ (*). The arrow indicates gelation (the largest cluster spans the system). For better distinction, the curves are shifted vertically.

(2) It is also possible to obtain D_g not only through the largest cluster but also by looking at the relation between the average radius and average mass of all the clusters at a given time, giving each cluster the same weight. We have also analysed this second method. The D_g obtained in this way is the same as the one obtained in figure 2.

(3) We also distributed the initial particles not randomly but in a regular way (on equidistant sites). This does not change the results either.

Next, we will analyse the cluster size distribution function $N(m, t)$ which tells how many clusters there are of mass m at time t. Previous work on flocculation (Kolb 1984) has shown that $N(m, t)$ scales as

$$N(m, t) = N^2(t)/N_0 p(m/\bar{m}) \tag{6}$$

where $\bar{m} = N_0/N(t)$ is the average mass of a cluster.

This scaling behaviour is also valid here as we can see from figure 3 where the scaling function $p(x)$ is shown as a function of $x = m/\bar{m}$ for several values of ρ_0 and α.

The curves are obtained just before the gel point t_g, i.e. before the largest cluster spans the system. They depend on α but not on ρ_0. For $\alpha = -2$ and -4, the functions $p(x)$ peak at finite values $x_{max} \approx 0.50$ and $x_{max} \approx 0.68$ respectively and fall off very rapidly as $x \to 0$. The vanishing of $p(x)$ for $x \to 0$ is very different from two dimensional percolation. As will be discussed below, this result can be understood when comparing the present model with the mean field approach using the Smoluchowski equation (equation (2)) (Kolb 1984).

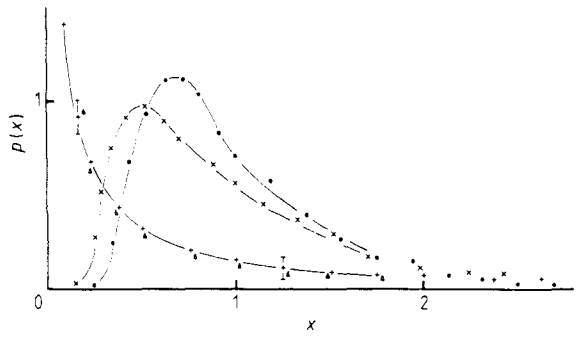

Figure 3. Scaling function of the cluster size distribution $p(x) = \bar{m}/N\,N(x\bar{m})$ in the scaling region where it is time independent. The curves correspond to $\alpha = -4$ (●), $\alpha = -2$ (×) and $\alpha = 0$ (+) and $L = 150$, $\rho_0 = 0.25$. For $\alpha = 0$ we show also $\rho_0 = 0.50$ (△).

The moments of $N(m, t)$ are expected to show some singular behaviour at t_g. We analyse the first moment $\bar{m}(t)$. For $t_g = \infty$ (no gelation), we expect

$$\bar{m}(t) \propto t^{\theta} \tag{7}$$

with $\theta \geqslant 0$ and for t_g finite we expect

$$\bar{m}(t) \propto |t_g - t|^{\theta} \tag{8}$$

with $\theta \geqslant 0$. We call θ the dynamic exponent (because of the time t involved). This dynamical exponent is more difficult to determine than the exponent D_g due to the difficulty of reliably estimating the gel time t_g. For the values of $\alpha = 0$, -2 and -4 we always find $\theta > 0$, i.e. $t_g = \infty$. We have analysed the average mass $\bar{m}(t)$ and the mass of the largest cluster $m(t)$ as a function of t and found that $\bar{m}$ and m are proportional to each other for $t \to \infty$. In figure 4 we show the mass m of the largest cluster double logarithmically as a function of t. We find a power law dependence like that of (7) and the exponents are: $\theta = 1.55 \pm 0.15$ for $\alpha = 0$, $\theta = 0.42 \pm 0.07$ for $\alpha = -2$ and $\theta = 0.21 \pm 0.03$ for $\alpha = -4$. The α dependence of θ can be described within our error bars by

$$\theta^{-1}(\alpha) = \theta^{-1}(\alpha = 0) - \alpha. \tag{9}$$

If we set in the Smoluchowski approach

$$2\omega = 1 + (\alpha - \alpha_0) \tag{10}$$

in analogy to (5), we obtain (9) from (4) if α_0 is chosen to be $\alpha_0 = \theta^{-1}(\alpha = 0)$. The case $\theta \geqslant 0$ corresponds to $\alpha < \alpha_0$. We find numerically $\alpha_0 = 0.61 \pm 0.12$ by localising the value of $\alpha_0 - 1$ for which the scaling function $p(x)$ changes its behaviour from a divergence at small x to zero at small x.

The description of our process by the Smoluchowski equation (2) is reinforced by the study of the form of the scaling function $p(x)$ (figure 3). We find that for $\alpha < \alpha_0 - 1$, i.e. $\omega < 0$, $p(x)$ is bell shaped while for $\alpha > \alpha_0 - 1$, i.e. $\omega > 0$ the function $p(x)$ is monotonic. This agrees with the results from the Smoluchowski equations. In addition

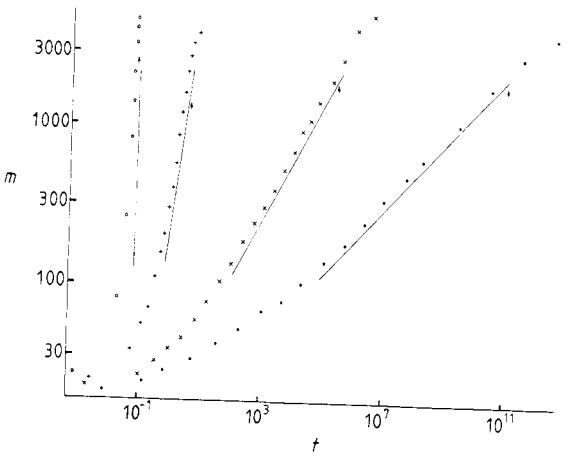

Figure 4. Plot of m against t for the largest cluster (log-log) from which the α-dependent dynamic scaling exponent $m \sim t$ (7) is determined. The parameters are $\alpha = -4$ (●), $\alpha = -2$ (×), $\alpha = 0$ (+) and $\alpha = 1$ (○) with $L = 150$, $\rho_0 = 0.25$. Gelation is indicated by the arrows. The results suggest that gelation occurs in a finite time for $\alpha = 1$.

we find that for $\alpha = 1$ the behaviour of the growth is qualitatively different from the case $\alpha \leqslant 0$: t_g is finite as illustrated in figure 4. This is consistent with the prediction of the Smoluchowski equation that for $\omega > \frac{1}{2}$ (i.e. $\alpha > \alpha_0$, (10)) a different, percolation-type behaviour is expected.

Unfortunately, for $\alpha \geqslant 1$ the analysis is numerically more difficult. Still we can establish the result that the mean mass $\bar{m}$ and the mass of the largest cluster m are no longer proportional to each other as a function of time. This resembles the behaviour of random percolation.

The present model which is based on irreversible cluster-cluster aggregation has been used to describe the sol-gel transition of polycondensation type. The scaling behaviour of the cluster-size distribution (figure 3) and the value of the fractal dimension of the gel are clearly distinct from random percolation for $\alpha < \alpha_0$. Based on our numerical results, we suggest that the asymptotic behaviour of the cluster size distribution $N(m, t)$ and its moments (say the average mass $\bar{m}(t)$) can be described qualitatively by the Smoluchowski equation: for $\alpha < \alpha_0 (\omega < \frac{1}{2})$ one finds that the gel time is infinite and the scaling properties of the average over all clusters and of the large clusters are the same (Kolb 1984). In this case $p(x)$, (6), vanishes at zero argument as for aerosols and one-dimensional percolation (Stauffer 1979). For $\alpha > \alpha_0$, gelation occurs in a finite time and averages over all the clusters behave differently from averages over the large clusters (percolation).

It is now very interesting to investigate to what extent the experiments can reproduce the exponents and scaling laws predicted by our kinetic model. For instance our models may describe to a good extent the macroscopic experiment of Allain and Jouhier (1983); this connection is supported by the agreement in the fractal dimensions.

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