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LETTER TO THE EDITOR

Anomalous diffusion on kinetic gelation clusters in three dimensions

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Abstract. Kinetic gelation, the growth model for radical copolymerisation, is investigated for the dynamic properties of its clusters at the gel point. We find that within numerical error bars the fractal dimension d_w of a random walk on a cluster cannot be distinguished from that found for percolation clusters at p_c in three dimensions.

In order to describe the effects of growth on the sol-gel transition, specifically for the mechanism of radical copolymerisation, a model of kinetic gelation was proposed several years ago (Manneville and de Seze 1981, Herrmann *et al* 1982). This model showed differences in the critical behaviour with respect to the model of random percolation, which is the static description of the sol-gel transition (de Gennes 1976, Stauffer 1976). One of the most striking differences was found for the backbone of the incipient infinite cluster (gel) at the transition time. It was found (Chhabra *et al* 1986) that the fractal dimension d_f^B of the backbone is considerably larger ($d_f^B = 2.22$) than that for percolation ($d_f^B = 1.74$) in three dimensions. Since the backbone is responsible for dynamical properties of the gel (diffusion, electrical conductivity, phonon spectrum, elasticity, etc) and since d_f^B is the first exponent from the voltage distribution (de Arcangelis *et al* 1985), it seems interesting to directly investigate dynamical properties at the gelation time in kinetic gelation. We focused on the problem of the diffusion of random walkers on the infinite incipient cluster (IIC) and in the following, after introducing the model and the method used, we will present our results for the fractal dimension $d_w \neq 2$. Thus this problem is also known under the name of anomalous diffusion.

The model of kinetic gelation is defined as follows. At time $\tau = 0$, i.e. the initial state, one places on each site of a simple cubic lattice a functionality and on a fraction c_I of the sites an initiator. The functionality is the maximum number of bonds that one will be allowed to form on the site. Then one starts to grow bonds by executing the following rule over and over again. Randomly choose one of the initiators and one of the six directions of the lattice. Then place a bond in this direction, at the same time shifting the initiator over this bond to the neighbouring site. If the placement of the bond is disallowed because one of the sites has already as many bonds as its functionality, no growth takes place at this time step. Should two initiators come to lie on the same site they annihilate each other. With increasing time more and more bonds will be grown. All sites that are connected to each other via bonds at a given time are said to belong to the same cluster. The sizes of the clusters increase and the

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total number of clusters decreases during the growth. At one critical time τ_g one cluster that spans the lattice from one side to the other will appear for the first time. At τ_g this cluster is called the incipient infinite cluster (IIC) and is known to be a fractal. For $\tau > \tau_g$ an infinite cluster, which is not fractal, will be present. The fractal dimension d_f of the IIC has been calculated in previous papers and it cannot be distinguished numerically from that of percolation, i.e. $d_f \approx 2.5$ and $d = 3$ (Herrmann *et al* 1983, Herrmann 1986, Chhabra *et al* 1986).

Since the IIC is fractal one can expect anomalous diffusion behaviour. Placing a random walker on the cluster we are interested in the average distance, $R(t)$, the walker will have moved from the site on which it was originally placed after having performed t nearest-neighbour jumps, where the walker can only jump to sites belonging to the cluster. We are also interested in the probability $P_0(t)$ that at the tth jump the walker returns to the site on which it was placed in the beginning. Anomalous diffusion is given by the relation

$$t \sim R^{d_w} \tag{1}$$

where the exponent d_w is interpreted as the fractal dimension of the trace of the walker and will, in the anomalous case, be generally larger than two. If $d_w > d_f$ the number $N(t)$ of distinct sites visited by the walker goes like $N \sim R^{d_f}$ and the probability of return is N^{-1}. Thus one finds using (1)

$$P_0 \sim t^{-\tilde{d}/2} \tag{2}$$

where $\tilde{d} = 2d_f/d_w$.

For percolation in $d = 3$ one has the numerical estimates $d_f = 2.53$ (Margolina *et al* 1982) and $d_w = 3.76$ (Derrida *et al* 1983). We only mention that d_w is related to the exponent t describing how the electrical conductivity vanishes at p_c by $t = (d_w - d_f + d - 2)\nu$ and to the exponent $\tilde{d} - 1$ describing how the phonon spectrum vanishes for small frequencies.

To calculate R and P_0 we use the method of exactly solving the probability distribution of a random walker for a given initial site and a given underlying cluster (Ben-Avraham and Havlin 1982, Hong *et al* 1984). We consider only sites with functionality four. Fixing a value for c_I we determine the concentration p_c of bonds at the gel time τ_g via finite-size scaling by methods described in several previous papers (Herrmann *et al* 1982, 1983, Chhabra *et al* 1986). We grow bonds in the way described above until we reach the concentration p_c of bonds and stop the growth there. For $c_I = 3 \times 10^{-3}$, which is the value we used, $p_c = 0.0853$. Having a configuration at p_c we find the largest cluster and then randomly pick a site more or less in the centre of the cluster. From this site we want to let the random walker start. So at time $t = 0$ we put the probability $P(0) = 1$ on this site. At $t = 1$ we put on each nearest neighbour (of this site) that belongs to the cluster the probability $P(1) = 1/q$ where q is the number of these neighbours. We proceed this way so that at each time we have sitting on all sites the exact probability that the random walker is on this site. At a time t the value of $P_0(t)$ is simply read off as the number sitting on the initial site at the tth iteration. The radius $R^2(t)$ is obtained by taking the mean over the squares of the distances of all sites of the cluster from the initial site weighted by the probability sitting on each of these sites at time t.

The results that we obtain for R^2 and P_0 are shown in a log–log plot in figure 1. The data seem to approach straight lines quite well, yielding from R^2 the exponent $d_w = 3.2 \pm 0.2$ (see (1)) and from P_0 the value $d_f/d_w = 0.71 \pm 0.05$ (see (2)). These data

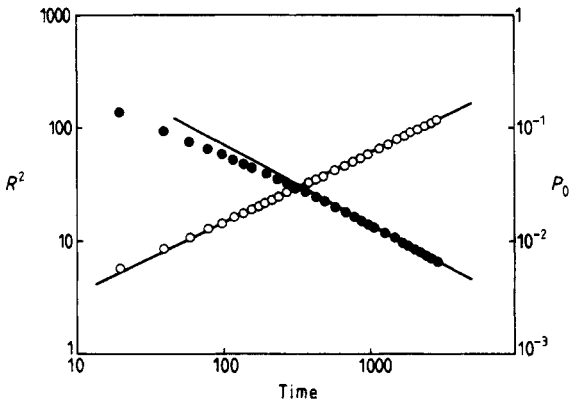

Figure 1. $R^2(t)$ and $P_0(t)$ in a log-log plot as a function of t for $L=60$ and averaged over 100 samples, $p_c=0.0853$.

would seem to give an exponent d_w slightly smaller than the corresponding value for percolation; however, there are two systematic effects that should be taken into account in the extrapolation of the raw data. First of all, there are finite-size effects since we go up to 3000 time steps although our box only has a linear size $L=60$. Secondly, there are corrections to scaling for shorter times which are responsible for the curvature that one can see in figure 1.

To take these effects into account, we make the finite-size scaling assumption

$$\begin{aligned} R^2 &= L^2 f(L^{d_w}/t) \\ P_0 &= L^{-d_f} g(L^{d_w}/t) \end{aligned} \tag{3}$$

where f and g are scaling functions of the scaled variable $x = L^{d_w}/t$ and the corrections to scaling ansatz

$$\begin{aligned} R^2 &\propto t^{2/d_w}(1+At^{\Delta}) \\ P_0 &\propto t^{-d_f/d_w}(1+Bt^{\Delta}) \end{aligned} \tag{4}$$

where Δ is the correction to scaling exponent and A and B are the corresponding amplitudes. Combining (3) and (4) we get

$$\begin{aligned} R^2 &= L^2 \tilde{f}[L^{d_w} t^{-1}(1+At^{\Delta})^{-d_w/2}] \\ P_0 &= L^{-d_f} \tilde{g}[L^{d_w} t^{-1}(1+Bt^{\Delta})^{d_w/d_f}]. \end{aligned} \tag{5}$$

First we investigate only the finite-size effects, i.e. we evaluate (3) alone. We also made calculations for $L=30$ and 40 averaging over 200 samples for each size. In figure 2 we show the finite-size scaling functions f and g of (3) in a log-log plot. The exponents d_w and d_f were chosen so as to produce data collapse onto a single curve for all sizes L. In addition, we should get straight lines in the limit of large $x = L^{d_w}/t$ with slopes $f(x) \propto x^{-2/d_w}$ and $g(x) \propto x^{d_f/d_w}$ in order to regain (1) and (2) for $L \to \infty$. For large times a reasonably good data collapse is found for $d_w = 3.7 \pm 0.1$ and $d_f = 2.5 \pm 0.2$ as seen in figure 2. For large x, i.e. short times, the slopes yield values for d_w around 3.2; that means the picture is not perfectly consistent. The reason for this small inconsistency comes from the corrections to scaling which are responsible for the scattering of the data of different L at small times seen in figure 2. So in figure 3 we

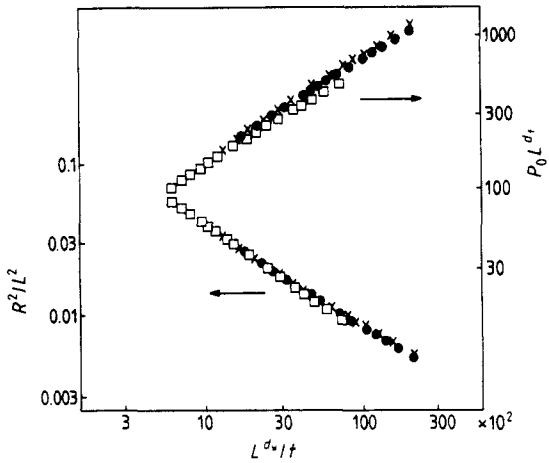

Figure 2. Log-log plot of $f(x) = R^2/L^2$ and $g(x) = P_0 L^{d_f}$ as a function of $x = L^{d_w}/t$ with $d_f = 2.5$ and $d_w = 3.7$; $p_c = 0.0853$. Values of L: □, 30; ●, 40; ×, 60.

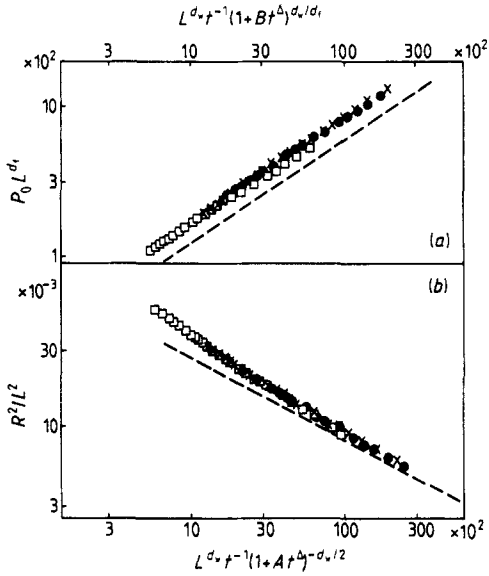

Figure 3. Log-log plot of the scaling functions (*a*) $\tilde{g}$ and (*b*) $\tilde{f}$ according to (5) using $d_f = 2.5$, $d_w = 3.7$, $\Delta = -0.6$, $A = -0.7$, $B = -1.0$, $p_c = 0.0853$. The broken lines are guides to the eye with slopes (*a*) d_f/d_w and (*b*) $-2/d_w$. Values of L: □, 30; ●, 40; ×, 60.

made a scaling plot according to (5) and the parameters Δ, A and B were fitted to have the best data collapse possible. Now the slope in figure 3(*b*) at small times gives an asymptotic value consistent with $d_w = 3.7$ shown in the figure. Also in figure 3(*a*) the asymptotic slope is consistent with the predicted value. Thus, we see that it is important that both finite-size effects as well as limitations due to finite walk time are considered.

Summarising, we find that d_w (and thus t and $\tilde{d}$) for kinetic gelation does not deviate within numerical accuracy from the percolation value in $d = 3$. This suggests

that, although the backbone is different in kinetic gelation, the transport properties on the gel at τ_g might be the same for kinetic gelation and percolation. It would be interesting to see if the same holds for the experimentally important value of the exponent for the elasticity (Adam *et al* 1981).

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