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LETTER TO THE EDITOR

Fractal dimensionality for kinetic gelation with conserved initiators §

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Abstract. A kinetic gelation model is developed for which the number of active initiator molecules is conserved. For this reason this model exhibits a gelation threshold even for very small values of c_1 , the concentration of initiator molecules, in contrast to the conventional model of kinetic gelation with non-conserved initiators. This model is studied by Monte Carlo analysis for a two-dimensional triangular lattice with a sequence of lattice sizes up to 900×900 sites. We use finite-size scaling to study the dependence of y_h (the fractal dimension) and $y_T (= 1/\nu)$ upon c_1 . We find that y_T depends weakly on c_1 , but that the fractal dimension y_h is *independent* of c_1 . This is in accord with the most recent work for the conventional kinetic gelation model with non-conserved initiators.

How does one describe the phenomenon of addition polymerisation in which multifunctional monomers are irreversibly linked by the movement of free radicals ('initiators')? Flory was the first to address this question (see the review of Herrmann 1984), and recently considerable interest has arisen due to the formulation of the problem as a lattice model (Manneville and de Seze 1981, Herrmann *et al* 1982, 1983, Jan *et al* 1983, Bansil *et al* 1984).

It is now widely believed that the irreversible kinetic nature of the growth process in this 'kinetic gelation model' leads to novel features. In particular, the kinetic gelation model may not be in the same universality class as percolation. For example, in three dimensions the critical amplitude ratio for the mean cluster size above and below the gelation threshold varies significantly as c_1 , the concentration of initiators, decreases. For $d = 2$, even the critical exponents seem to change as c_1 decreases. Family (1983) and Hong *et al* (1984) have reported Monte Carlo data on the field-like scaling power y_h (which equals the fractal dimension d_f , as shown by Stanley 1977), but they reach opposite conclusions on the important question of whether d_f changes from its percolation value $\frac{91}{48} = 1.89$ as c_1 decreases. Also, Lookman *et al* (1984) have extended to kinetic gelation the large-cell position space renormalisation group (PSRG) methods of Reynolds *et al* (1980) and found that d_f does not decrease when c_1 does. However they *did* find that the thermal scaling power, $y_T = 1/\nu$, increases as c_1 decreases; here ν is the exponent characterising the divergence of the connectedness length at the gelation threshold.

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The unique critical properties of the kinetic gelation model occur only in the limit of low c_1 , where severe initiator reduction occurs during the growth process due to the two phenomena of (i) trapping (the initiator is unable to move because of a saturation of the monomers on the neighbouring sites) and (ii) annihilation (two initiators arrive on the same site). Indeed, for $c_1 \leq 0.006$, the $d = 2$ system is unable to reach the gel point as all initiators are rendered inactive by one of the above mechanisms. But in real free radical polymerisation processes, the rate of creation and annihilation of initiators is the same in steady state and the initiator concentration does not change much during the growth process (Flory 1953). Thus the conventional kinetic growth model of Manneville and de Seze (1981) and others miss the important feature of real free radical polymerisation by allowing the initiator concentration to constantly decrease during the growth process.

Here we introduce a variation of the conventional kinetic gelation model by conserving the number of initiators during the growth process. This model is not only closer to real free radical polymerisation but allows one to study in detail the question of how y_h and y_T depend on c_1 , *even for very small values* of c_1 where the conventional kinetic gelation model can say nothing. This model simulates more realistically ultra-violet initiated polymerisation where initiators may be formed during the gelation process. It is also appropriate to the case of polyacrylamide where the dissociation of more complex molecules such as ammonium persulphate into two ammonium sulphate molecules is relatively slow so that, again, initiators may be formed during the gelation process. This is in contrast to the case where all initiators are produced at the beginning of the reaction (this 'fast' limit has hitherto been adopted in the conventional gelation model). In our model we avoid the problems caused by (i) trapping and (ii) annihilation by adding a new initiator to a randomly chosen location of the lattice whenever trapping occurs, and by adding two initiators if annihilation takes place. Pandey and Stauffer (1983) and Pandey (1983) have *independently* considered a somewhat analogous model but replaced only those initiators that were annihilated; they limited their investigation to $d = 3$ where trapping is not an important issue.

Finite-size scaling predicts that right at the gelation threshold, the fraction of sites $\rho(L)$ in the incipient infinite cluster (iic) decreases with system size L as

$$\rho(L) \sim L^{d_f - d} \quad (1)$$

Of course, we do not know p_c in advance so that determining d_f from (1) is not so straightforward. Figure 1(a) shows our data for $\rho(L)$ for several trial choices of p_c . The data suggest that $p_c = 0.21$ might be the straightest line, but due to correction-to-scaling effects one cannot rule out other choices of p_c such as $p_c = 0.22$. Therefore we also consider the prediction

$$|p_c(\infty) - p_{\max}(L)| \sim L^{-1/\nu} \quad (2)$$

where $p_c(\infty)$ is the gelation threshold of the infinite system, and $p_{\max}(L)$ is that of a finite system. We determined $p_{\max}(L)$ by the maximum value of the mean cluster size. In figure 1(b), we clearly see deviations from a straight line for large values of L with the choice $p = 0.21$, but not with the choice $p = 0.22$ which leads to the prediction

$$d_f = 1.89, \quad 1/\nu = 0.70 \quad (c_1 = 0.001), \quad (3)$$

from figures 1(a) and 1(b) respectively. Thus d_f is the same as for random percolation, while $1/\nu$ is about 7% smaller. We also cross checked $p_c(\infty)$ by plotting $|p_c(\infty) - p_{\max}(L)|$ against $L^{-1/\nu}$. We had a straight line with the choice $p_c = 0.22$ but not the choice

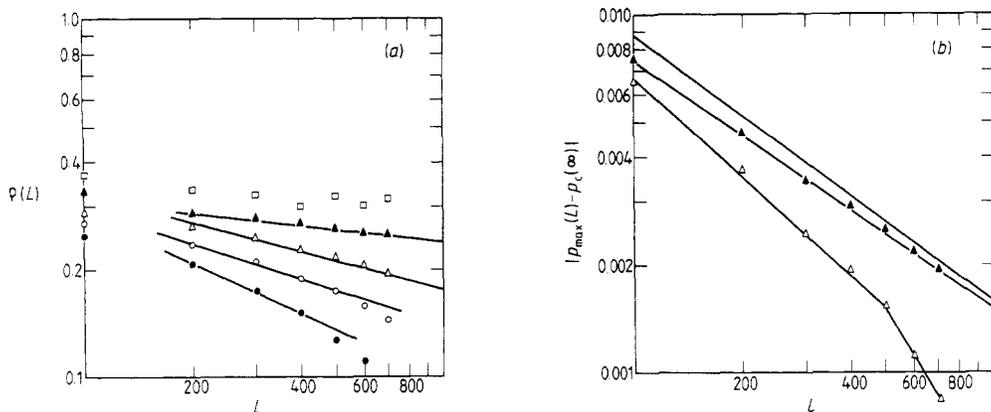


Figure 1. (a) Dependence on $\log L$ of the fraction of sites of $\rho(L)$ belonging to the largest cluster for $c_1 = 0.001$. By equation (1), the limiting slope should be $d_f - d$ if $p = p_c$, so several trial values are used: $p_c^{\text{trial}} = 0.19$ (●), 0.20 (○), 0.21 (△), 0.22 (▲), and 0.23 (□). From this graph it is not clear whether 0.21 or 0.22 gives the straighter line, so in (b) we show the function $|p_{\max}(L) - p_c^{\text{trial}}|$ for $p_c = 0.21$ (△) and 0.22 (▲). It is clear that 0.22 is considerably straighter than 0.21 for L larger than about 500, so we use $p_c = 0.22$ and hence find $d_f = 1.89$ from figure 1(a). From the limiting slope in (b) we also estimate $y_T = 1/\nu = 0.70 \pm 0.05$; the straight line at the top has slope $\frac{3}{4}$, corresponding to y_T for random percolation.

$p_c = 0.21$. Here we are tempted to assume $1/\nu = 0.75$ because from figure 1(b) we can guess that if p_c is slightly lower than 0.22, we easily pass the slope of $\frac{3}{4}$ of random percolation.

It is interesting to note that had we not simulated systems with L larger than 400 then we could not have easily concluded that $p_c = 0.22$, and a small error in p_c would lead to a large error in d_f ; e.g., if p_c were 0.21, then d_f would be 1.74.

Since our system size is so large, it was possible to study even smaller values of c_1 . Thus, e.g., we show in figure 2(a) the analogue of figure 1(a) but with $c_1 = 0.0004$. Similarly, figure 2(b) is the analogue of figure 1(b) from which we estimate $p_c = 0.205$. Combining both graphs, we estimate.

$$d_f = 1.89 \quad 1/\nu = 0.64 \quad (c_1 = 0.0004). \quad (4)$$

Thus for this low value of c_1 , we can clearly rule out the possibility $1/\nu = 0.75$.

In summary, we have developed a kinetic gelation model which differs from the standard model (Herrmann 1984) in that the number of initiator molecules is conserved. This model is much closer to real free radical polymerisation. We study this model in the limit of low initiator concentration c_1 , which cannot be probed using the standard model since there is no gelation below $c_1 = 0.006$. Our estimates for the magnetic field scaling power $y_h = d_f$ suggest independence on c_1 , while our estimates for the thermal scaling power $y_T = 1/\nu$ suggest a slight decrease as c_1 is lowered to extremely small values. Clusters seem to be more and more expanded ('swollen') as c_1 is lowered, but the self-similarity or 'fractal' nature of the cluster remains unchanged. Our findings are reminiscent of the observations of Suzuki (1974) that y_h is 'more universal' (less dependent on details) than y_T . We note that critical properties substantially different from random percolation occur now only at much lower initiator concentrations when compared with the model with non-conserved initiators. This is in agreement with the

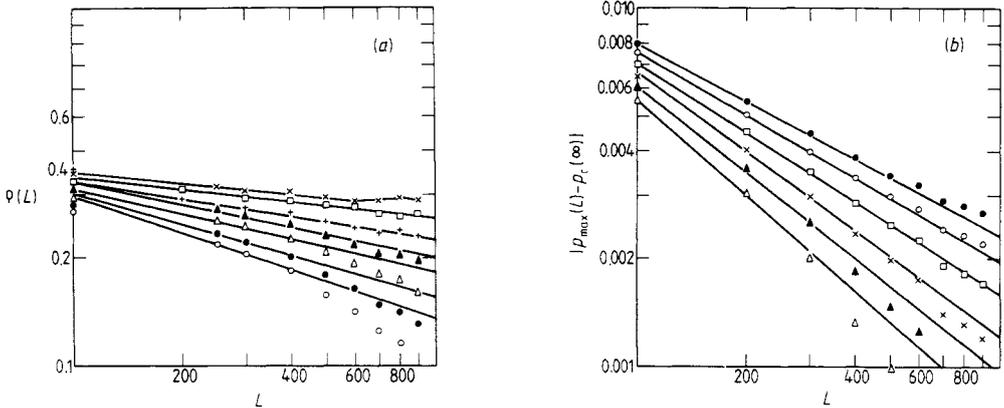


Figure 2. Same as figure 1 except that $c_1 = 0.0004$ now. The trial values of p_c^{trial} used in part (a) are $p_c^{\text{trial}} = 0.185$ (\circ), 0.190 (\bullet), 0.195 (\triangle), 0.200 (\blacktriangle), 0.205 ($+$), 0.210 (\square) and 0.215 (\times). (b) is the analogue of figure 1(b), with $p_c^{\text{trial}} = 0.195$ (\triangle), 0.200 (\blacktriangle), 0.205 (\times), 0.210 (\square), 0.215 (\circ) and 0.220 (\bullet). We estimate that the best p_c^{trial} is 0.210 , and hence conclude that $d_f = 1.89$ as before but now $\nu_T = 1/\nu = 0.64$, about 15% smaller than in random percolation.

main conclusion of Pandey and Stauffer (1983) and Pandey (1983). Our findings for the conserved initiator model are also consistent with recent MC results on the non-conserved initiator model (Hong *et al* 1984), which suggest that the apparent dependence of d_f on c_1 reported recently by Family (1983) may be due to a system size that was not large enough.

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