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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  $900 \times 900$  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  $\nu$  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

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

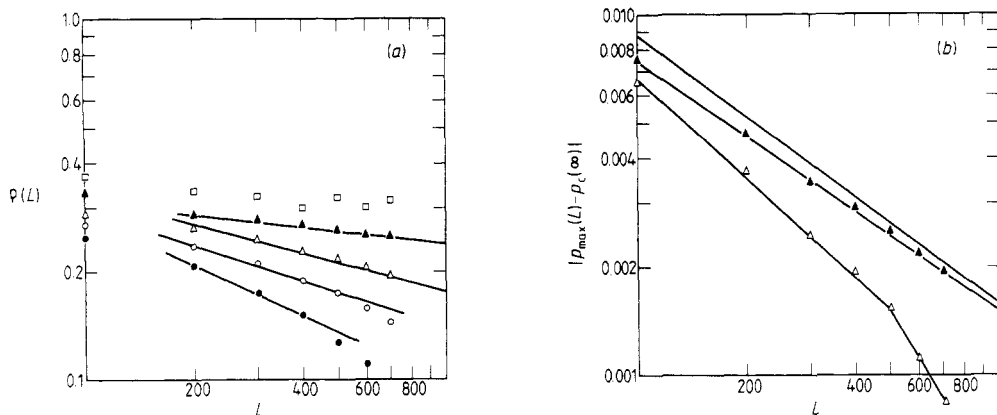
Of course, we do not know  $p_c$  in advance so that determining  $d_f$  from (1) is not so straightforward. Figure 1(a) shows our data for  $\rho(L)$  for several trial choices of  $p_c$ . The data suggest that  $p_c = 0.21$  might be the straightest line, but due to correction-to-scaling effects one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

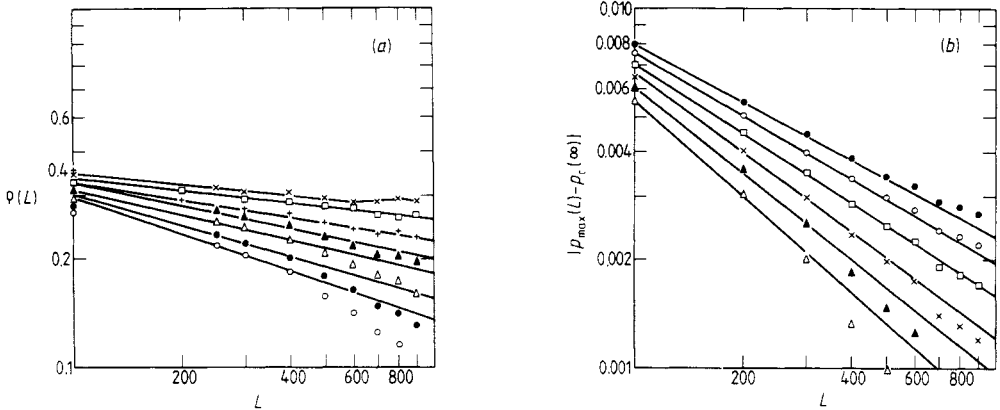
It is interesting to note that had we not simulated systems with  $L$  larger than 400 then we could not have easily concluded that  $p_c = 0.22$ , and a small error in  $p_c$  would lead to a large error in  $d_f$ ; e.g., if  $p_c$  were 0.21, then  $d_f$  would be 1.74.

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  $p_c^{\text{trial}}$  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  $p_c^{\text{trial}}$  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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## References

- Bansil R, Herrman H J and Stauffer D 1984 *Macromolecules* in press  
 Family F 1983 *Phys. Rev. Lett.* **51** 2112  
 Flory P J 1953 *Principles of polymer chemistry* (Cornell: Cornell University Press) pp 113, 124  
 Herrmann H J 1984 *Phys. Rep.* In press  
 Herrmann H J, Landau D P and Stauffer D 1982 *Phys. Rev. Lett.* **49** 412  
 Herrmann H J, Stauffer D and Landau D P 1983 *J. Phys. A: Math. Gen.* **16** 1221  
 Hong D C, Stanley H E and Jan N 1984 preprint  
 Jan N, Lookman T and Stauffer D 1983 *J. Phys. A: Math. Gen.* **16** L117  
 Lookman T, Pandey R B, Jan N, Stauffer D, Moseley L L and Stanley H E *Phys. Rev.* 1984 B **29** to appear  
 Manneville P and de Seze L 1981 in *Numerical Methods in the Study of Critical Phenomena* ed I Della Dora, J Demongeot and B Lacolle (Berlin: Springer)  
 Pandey R B 1983 *Phys. Lett.* **95A** 551  
 Pandey R B and Stauffer D 1983 *J. Stat. Phys.* in press  
 Reynolds P J, Stanley H E and Klein W 1980 *Phys. Rev.* B **21** 1223  
 Stanley H E 1977 *J. Phys. A: Math. Gen.* **10** L211  
 Suzuki M 1974 *Prog. Theor. Phys.* **51** 1992