LETTER TO THE EDITOR

Clusters and fractals in three-dimensional kinetic gelation in the presence of a mobile solvent

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Abstract. We have analysed the cluster size distribution for three-dimensional kinetic gelation. Our simulations are done on cubic lattices of size up to 45^3 and they include 30% solvent molecules which are capable of diffusing. We observe that the cluster distribution as a function of cluster size is non-monotonic. The peak of this distribution shifts to larger values of s as the reaction proceeds. For fixed extent of reaction the peak shifts to *smaller* values of s as the concentration of initiators is increased and eventually crosses over to random percolation type behaviour. We find that for large s the cluster distribution at p_c behaves as $n_s \sim s^{-\tau}$ with $\tau = 2.3 \pm 0.2$ in agreement with the value for random percolation. We perform a direct measurement of the fractal dimension d_f of the largest cluster at gelation and find that d_f is the same as in random percolation.

The process of free radical initiated irreversible polymerisation in gels such as poly-acrylamide can be simulated by a kinetic gelation model originally proposed by Manneville and de Seze (1981) and developed extensively by Herrmann *et al* (1982, 1983). Bansil *et al* (1984) have incorporated the presence of a mobile solvent to make the computer simulations more realistic. This kinetic gelation model has been shown to be in a different universality class from standard percolation or the Flory theory (Herrmann *et al* 1982). From two-dimensional simulations Jan *et al* (1983a) have shown that the cluster distribution is not a *monotonically* decreasing function of cluster size as it is in percolation. (For a recent review on percolation see Stauffer *et al* 1982.) In this letter we show that a similar non-monotonicity is observed in the cluster distribution as a function of cluster size in three-dimensional simulations.

The calculations reported in this paper use the version of the kinetic gelation model described in Herrmann *et al* (1983) and Bansil *et al* (1984). The basic steps in the simulation are (i) the random distribution of bifunctional (B), tetrafunctional (T) and solvent (S) monomers on the sites of a 3D cubic lattice of size L^3 with the total concentration of monomers satisfying $C_B + C_T + C_S = 1$; (ii) the reaction is initiated by making a fraction C_I of the bonds emanating from the B and T monomers reactive and by drawing one bond from each of the initiated monomers; (iii) growth proceeds by transferring the radical to a randomly chosen nearest-neighbour monomer provided all its functionalities have not been saturated; (iv) growth terminates either by the annihilation of the radicals or the trapping of all radicals (for details, see Bansil *et al*

1984). Mobility of unreacted monomers and solvent molecules is included by permitting nearest-neighbour exchanges between solvent and unreacted monomers.

The simulation keeps track of various parameters of which the one most pertinent for this work is the extent of reaction p, defined as the number of bonds grown up to that step. (For purposes of comparison with laboratory experiments and previous work (Bansil *et al* 1984) we normalise p by dividing by $L^3(C_B+2C_T)$, the maximum possible number of bonds.) For a given value of p we obtain n_s, the number of s-site clusters (normalised per site) as a function of s. Figure 1 shows the cluster size distribution n_s against s at several values of p for a simulation on a 3D cubic lattice with $L=20$, $C_I=0.003$, $C_S=0.3$, $C_B=0.28$, $C_T=0.42$ which corresponds to the fraction of tetrafunctional monomers $f_T=C_T/(C_T+C_B)$ equal to 0.6. The diffusivity D, i.e., the ratio of the number of exchange attempts for solvent molecules to the number of bonds grown between exchange attempts was equal to 160. For these concentrations, gelation occurs at $p_c=0.22$. As can be seen from figure 1, there is a well defined maximum in this distribution. This non-monotonic behaviour persists in the critical region and beyond.
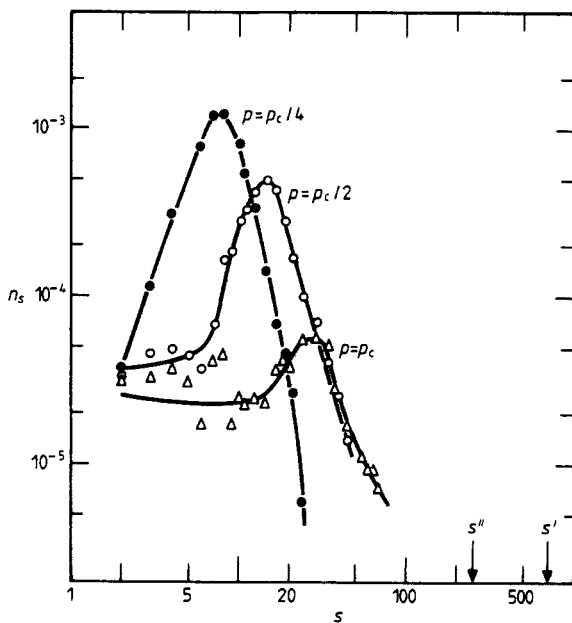
Figure 1. Log–log plot of normalised cluster number n_s (number of clusters per site) against cluster size s for different values of p. The data are obtained by averaging over 50 realisations on a 20^3 lattice with $C_I=0.003$ which corresponds to 72 initiated bonds at the start of the reaction. The sample composition corresponds to $C_S=0.3$ and $f_T=0.6$. Also indicated on the figure is the size of the largest cluster (s') and the second largest cluster (s'') at $p_c=0.22$.

The position of the maximum, s_{max}, which corresponds to the most probable cluster size, increases as the reaction proceeds with $s_{max} \propto p$.

From the cluster distribution at $p=p_c$ we calculate the exponent τ, which describes the dependence of n_s on $s(n_s \sim s^{-\tau})$ for large s. The calculation is done for $s > s_{max}$ and we obtain $\tau=2.3\pm0.2$ in agreement with the result for random percolation. (See

for example Stauffer *et al* 1982.) Thus although the cluster distribution shows a peak, its behaviour for large s at $p = p_c$ is in agreement with random percolation.

From figure 1 we also observe that the peak frequency n_{max} decreases with increasing p and for $p > p_c$ the peak is particularly small because of the rapid decrease in the number of finite clusters. This non-monotonicity in the cluster size distribution is in sharp contrast to the monotonic decrease obtained in standard percolation models. One reason for the non-monotonicity in the cluster distribution is that in kinetic gelation the total number of clusters has an upper limit, being less than $C_I L^3$. If all the bonds were distributed with equal probability among the growing sites then on the average each cluster would have a size proportional to p/C_I. In the absence of coalescence of clusters or annihilation of initiators we expect a Gaussian distribution centred about this typical size. Thus the maximum occurs at larger values of s with increasing p. However clusters can coalesce, giving rise to the long percolation type tail in the distribution as larger clusters have a higher probability of coalescing. Trapping and annihilation of initiators on the other hand contribute to a higher proportion of small clusters than would otherwise be observed. Both factors contribute to a broadening of the distribution and a diminution of the peak—results which are clearly observed from our Monte Carlo experiments.

A similar non-monotonic cluster size distribution was observed in the two-dimensional simulations (Jan *et al* 1983a). However for small values of s there are some differences between the 2D and 3D cluster functions. In 3D there is only one peak whereas in 2D the distribution shows two peaks; one at $s = 1$ and the other at larger s. In 2D simulations because of the finite width of the $s = 1$ peak the number of very small clusters decreases with increasing s (e.g., $n_2 > n_3$) whereas in 3D simulations the reverse is true. This difference in the behaviour for small s between two and three dimensions probably arises because in two dimensions there are fewer ways for small clusters to grow than in three dimensions. Apart from these minor differences it appears that a non-monotonic behaviour is characteristic of the kinetic gelation model irrespective of dimension (other properties of this model have been found to be different in two and three dimensions (Lookman *et al* 1983, Family 1983, Jan *et al* 1983b, Hong *et al* 1984)).

To shed some light on the question of which of the parameters C_I, C_S, f_T influence the characteristic shape of the cluster size function we performed a set of simulations varying one of these parameters at a time. We found the following relations.

(i) For a given C_I and f_T, changing C_S did not produce any significant changes in the characteristic shape and location of s_{max} of the cluster size distribution function.

(ii) For fixed C_S and C_I, s_{max} decreases slightly as f_T increases, with

$$s_{max} \sim f_T^{0.3}. \tag{1}$$

(iii) For fixed C_S and f_T, as C_I increases s_{max} decreases. At $p = p_c/2$ we find

$$s_{max} \sim C_I^{0.6}. \tag{2}$$

Within error bars this relation is also obeyed at other values of p. For a fixed absolute value of p we find that as C_I is increased the position of s_{max} decreases until at $C_I = 0.04$ for small values of p the peak in the cluster size distribution disappears altogether. Thus for $C_I \simeq 0.04$ for the early stages of the reaction ($p < p_c/2$) one crosses over into the percolation regime. For larger extents of reaction the crossover to percolation type behaviour occurs at larger values of C_I. This is shown in figure 2 where n_s is plotted as a function of s for fixed p/p_c and varying C_I.
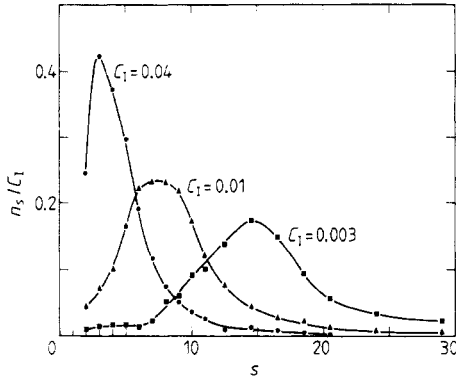
Figure 2. Normalised cluster distribution n_s against s for fixed $p/p_c = 0.5$ and varying initiator concentrations. The other parameters are the same as for the results shown in figure 1.

The strong dependence of s_{max} on C_I is consistent with the explanation that we have proposed for the appearance of a peak in the cluster distribution function. For fixed p, the typical size of a cluster p/C_I will decrease as C_I increases. Also as C_I increases the average separation between locally growing clusters decreases, thus coalescence will begin to occur for clusters of smaller size. Both of these effects cause s_{max} to decrease as C_I increases.

Whereas the cluster distribution function describes the distribution of finite size clusters it says nothing about the infinite cluster formed at p_c. We have calculated the fractal dimension d_f of the incipient infinite cluster in three-dimensional kinetic gelation. All of our calculations for d_f were made at that value of p for which the 'susceptibility' (weight average degree of polymerisation) goes through a maximum and hence are close to p_c but not strictly at $p = p_c$. This may account for the larger scatter in the data. We obtained the fractal dimension by putting grids of different resolution on the incipient infinite cluster and then counting the boxes in which sites are occupied. A log–log plot of the density of occupied boxes against the number of boxes for a given system size gives the slope $d - d_f$. For simulations with $C_I = 0.003$, $C_S = 0.3$ by averaging 50 realisations on a cubic lattice of size 45^3 we obtain $d_f = 2.4 \pm 0.3$. We also found that d_f was unchanged when the fraction of tetrafunctional monomers was decreased from $f_T = 1.0$ to $f_T = 0.6$. We also analysed the incipient cluster for a simulation with a large initiator concentration $C_I = 0.04$. These data are for a smaller system size, $L^3 = 20^3$. However within error bars they also give the same value of d_f. Thus we conclude that unlike the cluster size distribution function, the fractal dimension d_f is independent of C_I or f_T. Furthermore, within error bars the result obtained here for d_f in three-dimensional kinetic percolation agrees with that obtained for random percolation.

The fractal dimension can also be obtained from the relationship $d_f = (\gamma + \beta)/\nu$ where γ, β and ν are the critical exponents for the weight average degree of polymerisation, the gel fraction and the correlation length respectively (see Stauffer *et al* 1982). From the value of γ, β and ν obtained by Herrmann *et al* (1983) in three dimensions one obtains $d_f = 2.5$. Thus our *direct* calculation of d_f is the first independent confirmation of the result obtained previously from the values of the critical exponents and further confirms the validity of the scaling relationship for kinetic gelation. For

two-dimensional kinetic gelation Hong *et al* (1984) also find that d_f is the same for random percolation and kinetic gelation and *independent* of C_I. The apparent dependence of d_f on C_I reported by Family (1983) in two dimensions is probably related to small system size.

To summarise we have shown that the cluster distribution function in three-dimensional kinetic gelation is *non-monotonic* and thus strikingly different from that in random percolation. The location of the peak in this distribution depends on p and C_I, with a cross-over to random percolation type cluster distribution for large C_I ($C_I > 0.04$ for $p < p_{c/2}$). We calculate the cluster size exponent τ for $s > s_{max}$ and find that this exponent is the same as in random percolation. We also obtain the fractal dimension for 3D kinetic gelation and find that d_f is independent of C_I and also that d_f is the same as in random percolation. Our results for three-dimensional kinetic gelation are similar to those reported by Jan *et al* (1983), Lookman *et al* (1984), and Hong *et al* (1984) for two dimensions.

Note added in proof. Recently, Chhabra *et al* (1984) have observed damped periodic oscillations in the cluster size distribution for three-dimensional kinetic gelation simulations. Their simulations were performed for much larger lattices (up to 60^3) and with much greater statistics (1000 to 20 000 samples as compared with 50 samples in our work). Because of the much lower accuracy of our work we do not observe these damped periodic oscillations.

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