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LETTER TO THE EDITOR

Oscillations and scaling in the cluster size distribution for kinetic gelation

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Abstract. We have studied the distribution of cluster sizes n_s in an irreversible kinetic gelation model using Monte Carlo simulations on a simple cubic lattice. We find quite surprising, pronounced oscillations in the distribution n_s , with cluster size s . The variation of n_s with s and the fraction p of bonds formed is described by unconventional scaling behaviour.

The initial description of the sol-gel transition in terms of a simple classical approach [1] has often been replaced by percolation theory [2, 3][†]. Recently, however, Herrmann *et al* [5, 6] (HLS) used a kinetic growth model [7] to show that gelation by additive polymerisation belongs to a different universality class than percolation. (Although the critical exponents associated with bulk properties appeared to be the same, a universal amplitude ratio turned out to be different.) In this letter we examine the cluster size distribution for the model studied by HLS. If we define n_s as the number of clusters of size s , we would expect that, at least for large s , the general shape and form for the distribution and scaling laws for n_s would be the same for gelation and percolation. At the same time, because of the upper bound which exists [5] for the number of initiators (and hence the number of clusters) we might expect to see fewer clusters of small size for gelation as opposed to percolation [8]. In the following we report results for the quite unexpected behaviour which we actually observed.

Our model consists of tetrafunctional monomers on each site of an $L \times L \times L$ simple cubic lattice [5]. A small randomly selected number of the sites ($3c_1L^3$) are occupied by isolated initiators attached to the monomers[‡]. These initiators form the growth centres: an initiator may be transferred to a randomly chosen nearest neighbour by the formation of a bond between them. (The bond may be formed, of course, only if the monomer is not already saturated.) If a bond is formed to a site which is already occupied by an initiator the two initiators annihilate each other. An initiator may also be 'trapped' if all its nearest-neighbour sites are saturated. The number of 'active' initiators may therefore decrease substantially with time, where time is defined as being proportional to the number of attempts to grow a bond. Individual clusters will not

[†] A clear and complete comparison and description of classical and percolation theories is given in [4].

[‡] The present model differs from that studied in [5] only in that isolated initiators are formed instead of pairs as in [5]. Some results for bulk properties of the present model are given in [6].

only grow but will also merge to form larger clusters until an infinite cluster is formed at the gel point.

We have studied the cluster distribution function n_s as a function of cluster size s for different lattice sizes and initiator concentrations. In figure 1 we show results obtained for $L = 60$, $c_1 = 0.0003$ averaged over 1.5×10^4 growth samples. This damped, oscillatory behaviour is in striking contrast to the simple monotonically decreasing variation found for percolation [9]. In fact, the monotonic decrease which we see at very small s is completely unrelated to percolation behaviour but arises instead due to initiator annihilation. Hence this 'maximum' at $s = 1$ is not related to the oscillations which occur at larger s and we have seen that it can be eliminated by suppressing annihilation. The cluster size distribution for this model was previously studied by Manneville and de Seze [7] but with large c_1 and statistics which were more than an order of magnitude worse than ours; they did not recognise oscillatory behaviour. (Jan *et al* [8] simulated the equivalent model in two dimensions, but also with too few samples, and hence did not notice this oscillatory behaviour.) Although the current study is for tetrafunctional monomers only, it is straightforward to extend the investigation to include bifunctional monomers as well. The data for $L = 20$ and $L = 40$ are qualitatively similar but show an increase in the maxima for large s due to finite size effects. A large number of clusters are formed at characteristic cluster size s^* ; additional maxima are found at $\sim 2s^*$, $3s^*$, $\dots ms^*$ where multiple clusters of size s^* have paired together. s^* varies only slightly with L but has a strong dependence on the number of bonds grown in the system. The number of bonds is proportional to p which is equal to the fraction of all possible bonds which has been formed. We find that $s^* \sim p^\rho$ with $\rho = 1$. At p_c the first 7-8 maxima decay as $\sim m^{-2.5}$ and then the decay begins to slow. In contrast the minima decay as m^{-x} where $x < 2$, but x changes with s and apparently approaches ~ 2.2 . We have also determined the fraction of sites which are bonded \bar{s} as a function of p . Defining

$$\bar{s} = \sum_{s \geq 2} n_s s \quad (1)$$

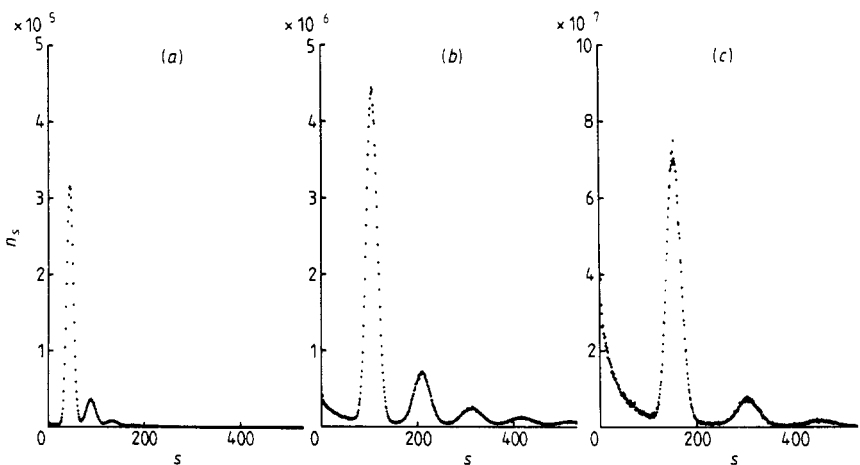


Figure 1. Distribution of clusters (see (6)) as a function of cluster size s for $L = 60$, $c_1 = 0.0003$: (a) $p = 0.016$; (b) $p = p_c = 0.037$; (c) $p = 0.053$. Note the different scales for each plot.

we find for $0.016 \leq p \leq 0.08$

$$\bar{s} = Ap^{0.89} \quad (2)$$

with $A \approx 1$; there is no noticeable change in behaviour at p_c . Having found a cluster size distribution distinctly different from percolation, we are faced with the question of whether or not the scaling form used for percolation can apply [4]:

$$n_s = s^{-\tau} f[(p - p_c)s^\sigma]. \quad (3)$$

From an analysis of our data we have concluded that it is not possible to describe the cluster distribution by (3).

From our previous discussion of the location of the peaks of the oscillations it is evident that for this model (s/s^*) is a natural scaling variable. In addition, any form which we use for the cluster size distribution must yield power law behaviour for the bulk properties with critical exponents which are essentially the same as for percolation [4], e.g.

$$\chi = \sum n_s s^2 \left(\sum n_s \right)^{-1} \sim |1 - p/p_c|^{-\gamma} \quad (4)$$

where the infinite cluster is excluded from the summations. We have found empirically that it is possible to satisfy these concerns and to describe our data by the unusual scaling form

$$n_s = (s/s^*)^{-\tau} \exp[-b(s/s^*)^\sigma |p - p_c|] f(s/s^*) \exp[a(p - p_c)] \quad (5)$$

where a and b are constants. Here the dependence upon τ is the same as in (3), with the redefinition of the scaling variable. If one inserts (5) into (4), it is easy to see that σ and τ defined in (5) are the 'droplet exponents' [4] which appear in (3). The data analysis is relatively insensitive to the choice of σ and τ , so we fixed them at the percolation values [4, 10]. Since s^* is proportional to p we can use s/p as the scaling variable and can rearrange the terms in (5) to solve for $f(s/p)$:

$$f(s/p) = n_s (s/p)^\tau \exp[b(s/p)^\sigma |p - p_c|] \exp[-a(p - p_c)]. \quad (6)$$

In figure 2 we show scaling plots for our data using (6). The best choices for a and b are quite different above and below p_c ; using these values we are able to obtain good scaling over a wide range of $|p - p_c|$ and s . The first two factors in (5) are essentially the same as those which appear in the asymptotic (large s) region [4] for the usual scaling relation (3). The last two factors contain (s/s^*) and $(p - p_c)$ dependence respectively; the function $f(s/s^*)$ (defined by figure 2) is highly non-trivial and describes the explicit shape of the damped oscillations, whereas the factor $\exp[a(p - p_c)]$ is essentially a scale factor whose mathematical form could be different without having any impact on the critical behaviour. A reasonable extrapolation suggests that the minima and maxima do not meet even at $s = \infty$. This would mean that we have qualitatively different behaviour than droplet scaling since $f(s/s^*)$ could not be treated as a correction. But even if the maxima and minima do converge at $s = \infty$ for finite c_1 , there is strong evidence that the damping of the oscillations disappears altogether in the limit $c_1 \rightarrow 0$. Therefore, at least for $c_1 \rightarrow 0$ a totally new scaling behaviour is found.

In conclusion it has previously been shown that the behaviour of the bulk properties for kinetic gelation in three dimensions differs from that of percolation in a subtle way: the critical exponents appear to be the same although the critical amplitude ratios

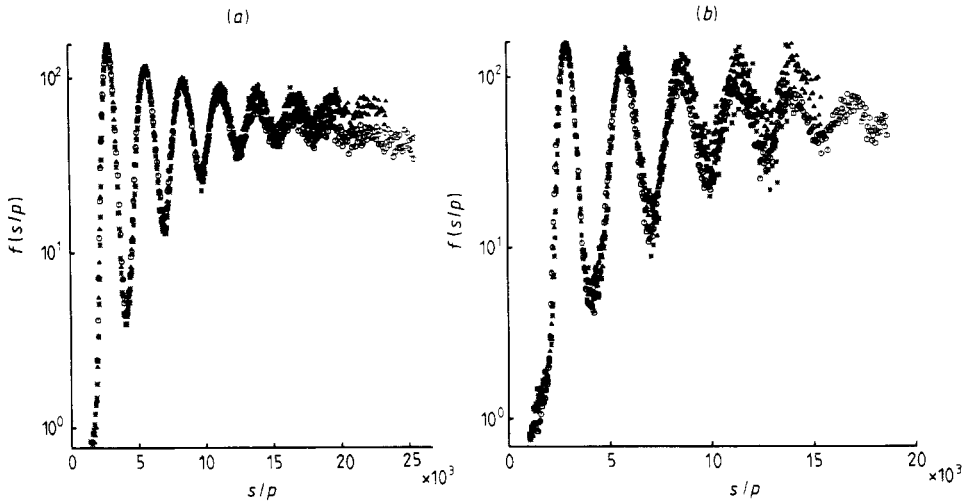


Figure 2. Scaling behaviour of the cluster size distribution as a function of (s/p) for $L=60$, $c_f=0.003$ (see (6)): (a) $p < p_c$, $a=100$, $b=0.1$ (p : \circ , 0.0267; Δ , 0.0307, $*$, 0.0360); (b) $p > p_c$, $a=0$, $b=2.6$ (p : \circ , 0.0386; Δ , 0.0467, $*$, 0.0520).

are different [5]. In this letter we have shown that there are dramatic, qualitative differences in the cluster size distributions for the two models although the corresponding 'droplet exponents' are apparently the same.

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