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COMMENT

The effect of randomness on the critical behaviour of kinetic gelation

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Abstract. The behaviour of a three-dimensional kinetic gelation model with regularly placed initiators is determined from Monte Carlo simulations. We find marked differences with the behaviour observed when initiators are placed on the lattice randomly. We also look at the effect of introducing repulsion between initiators.

1. Introduction

Kinetic gelation [1-5] is a model for addition polymerisation which has been studied extensively via computer simulation. Growth occurs by the addition of bonds through modified random walks (kinetic growth walks) which eventually join to form a gel. In all of our previous studies we have placed the starting points for these random walks (initiators) at random locations on the lattice. It has been shown [6] that for the problem of random walks with traps the resulting probability of hitting a trap is strongly dependent on whether the distribution of traps is regular or random. As we shall show shortly, our model is similar except that we have time reversal: our initiators play the role of the traps. It is, therefore, interesting to determine whether or not the critical behaviour of the kinetic gelation model is dependent upon whether the initiators are placed randomly or periodically. We shall also use this model to study growth in a system where the initiators are anionic or cationic rather than radicals. The result of this is that the initiators are charged and thus repel each other [7]. As a first step towards understanding what effects this produces we shall consider cases where the initiators are subject to hard-core repulsion. A particular limiting case occurs when the initial spacing between initiators is equal to the minimum distance allowed by the hard-core repulsion; growth can then occur only if all initiators grow bonds simultaneously and in the same direction. As a result all clusters are the same size at all times and they all join together at a single time to form a gel in a first-order transition.

2. Model and method

We have considered $L \times L \times L$ simple cubic lattices with periodic boundary conditions in which each site contains a four-functional monomer and initiators are placed on sites at regular intervals with concentration c_1. Growth begins with a randomly chosen

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initiator attempting to form a bond to a nearest neighbour, transferring the 'active centre' to that site in the process. (This model is explained in detail in reference [2].) The number of bonds grown up to a given time can be determined from the conversion factor p (which is simply the number of bonds formed divided by $3L^3$). As the random walks emanating from each initiator grow, they form clusters of increasing size due to the joining of individual walks. The effect of the hard-core repulsion between the active centres is included by defining a distance of minimum approach Δ and checking at each growth step to ensure that the movement of an active centre does not bring it closer to any of the other active centres than Δ. This is a very time-consuming task and hence the statistics which we could obtain for Δ greater than zero were not as great as for the case of no repulsion, i.e. $\Delta = 0$. The fraction of the lattice which is occupied by the largest cluster is called the gel fraction and the second moment of the cluster size distribution n_s is called the susceptibility:

$$\chi = \sum s^2 n_s \tag{1}$$

where s is the size of a cluster, n_s is the number of clusters of size s divided by L^3, and the sum excludes the largest cluster. As p approaches the gel point χ is expected to diverge as

$$\chi = C_{\pm} \not{p}^{-\gamma} \tag{2}$$

where C_- is the amplitude below p_c, C_+ is the amplitude above p_c, the ratio $C_-/C_+ = R$ and $\not{p} = (p - p_c)/p_c$ if $p > p_c$ and $\not{p} = (p_c - p)/p_c$ if $p < p_c$. Because finite-size effects are so important for the lattice sizes which we can study, we shall extract the infinite lattice critical behaviour using finite-size scaling. In the critical region the susceptibility for the finite lattice is given by

$$\chi L^{-\gamma/\nu} = f(x) \tag{3}$$

where $f(x) \to x^{-\gamma}$ as $x \to \infty$ and $x = \not{p} L^{1/\nu}$ if the correct infinite-lattice singularity is to be obtained. In order to properly test finite-size scaling it is important that we be able to analyse data over a wide range of the finite-size scaling variable x. If corrections to scaling are important the analysis of finite-size effects will be limited by deviations from the simple asymptotic power laws. To reduce such effects we analysed the susceptibility using the following form:

$$\chi = \chi_0 (1 + D \not{p}^{\omega}) \tag{4}$$

where

$$\chi_0 = C_{\pm} \not{p}^{-\gamma} \tag{5}$$

is the dominant singularity and D and ω are the amplitude and exponent of the lowest-order correction to scaling term. Equation (4) can be rewritten as

$$\ln(\chi/\chi_0 - 1) = \ln D + \omega \ln \not{p}. \tag{6}$$

Thus by estimating $C_{\pm}$ and γ we can use (5) in (6) to extract values of D and ω from the data. These values may then be used to eliminate the correction from the data, i.e.

$$\chi' = \chi_{\text{meas}} - D \chi_0 \not{p}^{\omega} \tag{7}$$

where χ_{meas} is the value of χ measured by the simulation. χ' should then be described by (5) for the infinite lattice, and finite-lattice data should obey (3) over a wider range of χ than before.

For the gel fraction G, i.e. the fraction of sites that belong to the largest cluster, a similar correction to scaling analysis and subsequent finite-size scaling can be performed and one obtains

$$G' = G_{\text{meas}} - EG_0 \not{p}^{\omega}$$
$$G' = L^{-\beta/\nu} g(\not{p} L^{1/\nu}) \tag{8}$$

where g is a scaling function, E a correction to scaling amplitude and β is the critical exponent for the gel fraction.

3. Results

All of the qualitative features of the data for periodic initiators are the same as for random [2, 3] initiator placement; we shall, therefore, not show raw data but shall go directly to the analysis. In figure 1 we show a finite-size scaling plot for the susceptibility for both cases with $c_1 = 3 \times 10^{-4}$. In addition to the difference in p_c, the ratio $R = 9.5$ is much larger for regular initiator placement. This value for R is close to that for standard percolation ($R = 10$) and substantially greater than that for kinetic gelation with random initiators [3] ($R = 2.6$) and $c_1 = 3 \times 10^{-4}$. The critical exponents themselves appear to be about the same in both cases.

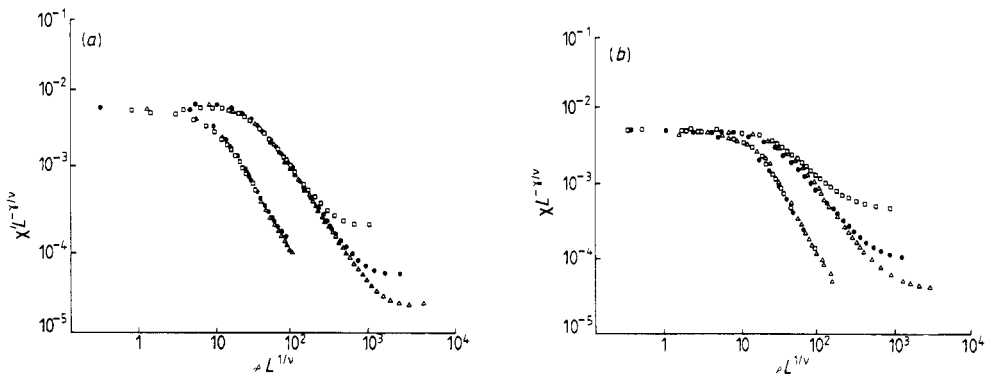

Figure 1. Finite-size scaling plot for the susceptibility for (*a*) regular placement ($p_c = 0.046$) and (*b*) random placement ($p_c = 0.040$) of initiators with $c_1 = 3 \times 10^{-4}$, $\gamma = 1.8$, $\nu = 0.8$. $L = 30(\square)$, $60(\bullet)$, $90(\triangle)$.

In figure 2 we also show finite-size scaling plots for the gel fraction and for the susceptibility for regular initiators where the corrections to scaling have been taken into account as described in (7). There is a small systematic shift in critical exponents β and γ to smaller values compared to those obtained with random initiators. However, because the difference is within our error bars we cannot say for certain that a real difference exists. Finite-size scaling plots for $c_1 = 3 \times 10^{-4}$ with $\Delta = 5.0$ and $\Delta = 8.0$ are shown in figures 3 and 4. For this value of c_1 the spacing between initiators is ten lattice spacings. Apart from the shift of p_c to higher values with increasing Δ, there is no apparent change in the critical exponents or in the critical amplitude ratio R as compared to the results for $\Delta = 0$. Therefore we see no indication of crossover behaviour associated with the eventual first-order transition which would occur for $\Delta = 10$. (In this case all initiators would have to form a bond in the same direction at the same

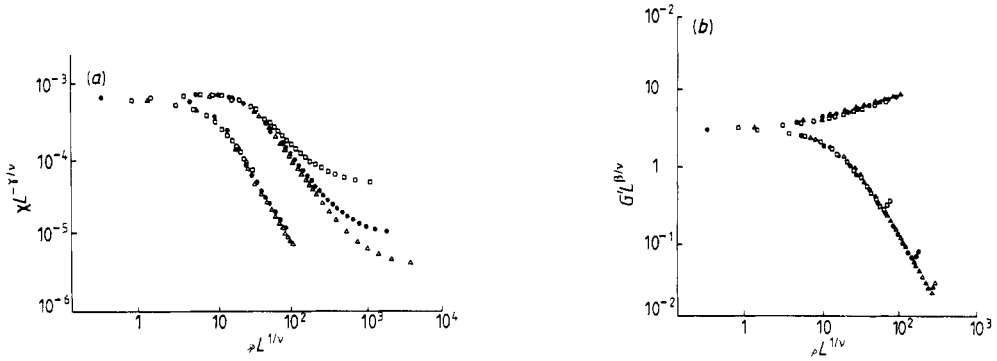

Figure 2. Finite-size scaling plots of periodic initiator placement with $c_1 = 3 \times 10^{-4}$ and with corrections to scaling removed according to equations (7) and (8), $\omega = 1.6$, $D = 0.3$, $E = -0.5$. (*a*) Susceptibility. (*b*) Gel fraction (no repulsion). $p_c = 0.046$, $\gamma = 1.8$, $\beta = 0.35$, $\nu = 0.8$.

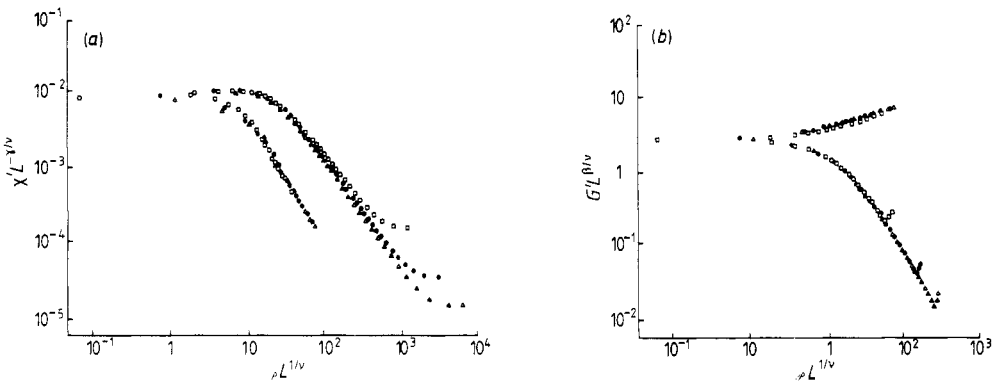

Figure 3. Finite-size scaling plots for periodic initiator placement with $c_1 = 3 \times 10^{-4}$ and repulsion distance $\Delta = 5$. Corrections to scaling have been removed according to equations (7) and (8), $\omega = 1.6$, $D = 0.3$, $E = -0.5$. (*a*) Susceptibility. (*b*) Gel fraction. $p_c = 0.054$, $\gamma = 1.75$, $\beta = 0.35$, $\nu = 0.8$.

time since the repulsion would prevent any initiator from moving individually. The result is that all clusters would always be the same size and when a gel forms all clusters join simultaneously to give a gel fraction of unity.) It is perhaps worthwhile to point out that since we only allow growth of one bond at a time, it is not possible for us to observe the first-order transition directly.

4. Conclusions

From a comparison of the results for the cases of periodic and random initiation we conclude that the randomness of the distribution of initiators is crucial. It is possible that this effect is a more general property of percolation on a random lattice [8] and that the change in amplitude ratio (and possibly exponents) is due to some sort of singular behaviour such as the one found by Griffiths [9]. If this is true, this result is particularly interesting also because for percolation α is less than 0. Further work in

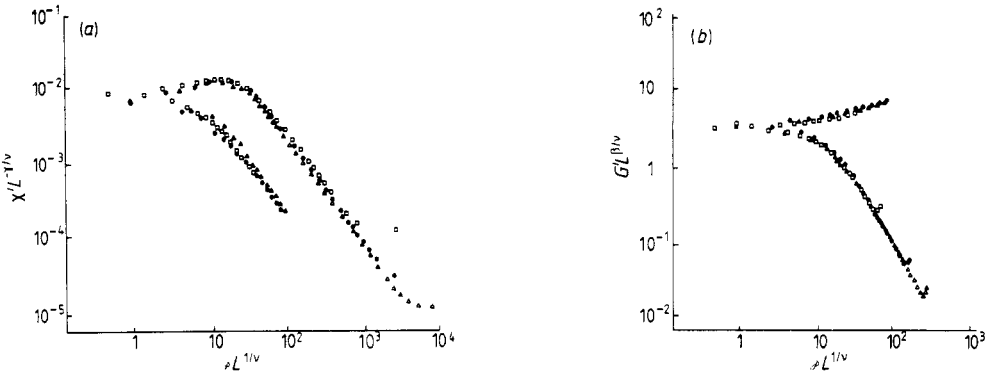

Figure 4. Finite-size scaling plots for periodic initiator placement with $c_i = 3 \times 10^{-4}$ and repulsion distance $\Delta = 8$. Corrections to scaling have been removed according to equations (7) and (8), $\omega = 1.6$, $D = 0.3$, $E = 0.5$. (*a*) Susceptibility. (*b*) Gel fraction. $p_c = 0.065$, $\gamma = 1.7$, $\beta = 0.35$, $\nu = 0.8$.

this direction would be most welcome. In contrast there is no apparent change in the critical behaviour when hard-core repulsion between the active centres is added.

Acknowledgment

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