LETTER TO THE EDITOR

Directed growth in kinetic gelation

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Abstract. A computer simulation study is presented for directed growth in a three-dimensional kinetic growth model for irreversible gelation. Finite size scaling theory is used to extract critical exponents for the gel-sol transition. In contrast to percolation, the exponents for directed and undirected gelation appear to be the same.

The gel-sol transition has been the subject of extensive study for several decades. The gelation process was first described by Flory (1941) and Stockmayer (1943, 1944) in terms of percolation (Fisher and Essam 1961) on a Cayley tree. More recently random percolation of a real lattice was proposed by de Gennes (1976) and Stauffer (1976) as a better description since it included loop formation and excluded volume effects. Although many details of percolation models do not alter the nature of the transition, it is known that directed percolation models have different critical exponents than their undirected counterparts (Redner 1983, Kinzel 1983). Recent computer simulation studies of kinetic growth models by HLS (Hermann *et al* 1982, 1983) have yielded critical exponents for the bulk properties which are indistinguishable from those found for random percolation. In this letter we present results of a computer simulation study of a directed growth model; these results will be compared with those for directed percolation.

We use a kinetic growth model which is similar to that described by HLS. We consider growth on a $L \times L \times L$ simple cubic lattice with periodic boundary conditions. Bifunctional monomers of concentration c_b and tetrafunctional monomers of concentration $c_t = 1 - c_b$ are placed on the lattice randomly. Initiators, each of which have one free bond, are placed on the lattice randomly with concentration c_I and act as the active centres for growth. Note that the definition of initator concentration is different from that of HLS; here c_I = number of initiators/total number of lattice *sites*; in HLS c_I was normalised by the number of *bonds*. An active centre may form a bond to a randomly chosen nearest-neighbour site and the active centre is transferred to the newly bonded site if there is no radical already present; otherwise the two will annihilate each other. Growth thus proceeds by forming bonds along restricted random walk trajectories. In our directed growth model the active centres attempt to move *only* in $+X$, $+Y$, or $+Z$ directions (with equal probabilities) whereas in HLS the active centres attempt to move in all six directions ($\pm X, \pm Y, \pm Z$) with equal probability. Growth proceeds until all the active centres are annihilated or trapped and then another sample is grown. We have obtained data for $L \leq 90$ with up to 500 growth samples.

The data for $p \to p_c$ were analysed using the standard singular forms for the gel fraction G and the second moment of the cluster size distribution χ:

$$G = B\left(\frac{p - p_c}{p_c}\right)^{\beta}, \qquad p > p_c, \qquad \chi = C_{\pm}\left|\frac{p - p_c}{p_c}\right|^{-\gamma} \qquad (1a, b)$$

where C_+ and C_- are the critical amplitudes above and below the gel point respectively. Finite size scaling plots (figure 1) were used to ensure that the best possible exponent estimates were obtained (see HLS for details). In figure 1 we show plots of log $GL^{\beta/\nu}$ and log $\chi L^{-\gamma/\nu}$ against log$[(p - p_c/p_c)L^{1/\nu}]$ which were the best quality we could obtain for $c_b = 0.1$, $c_1 = 10^{-2}$. (The 'tails' which were found for large values of the scaling variable are a consequence of the values of p being outside of the asymptotic critical region.) The exponents obtained for χ were $\gamma = 1.80$, $\nu = 0.90$, and the amplitude ratio $C_-/C_+ \sim 5.0$. The finite size scaling analysis of the gel fraction yielded $\beta = 0.4$, $\nu = 0.90$. These exponents and the ratio C_-/C_+ are (within error bars) equal to those for undirected gelation (see HLS) and β and γ essentially the same as for undirected
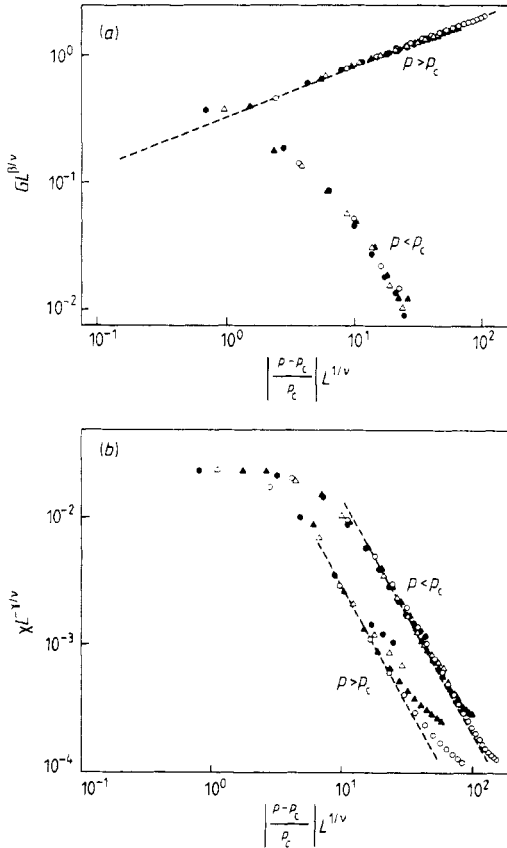

Figure 1. Finite size scaling plots of (a) log $GL^{\beta/\nu}$ and (b) log $\chi L^{-\gamma/\nu}$ against log$[(p - p_c)/p_c]L^{1/\nu}$ for lattices with $L = 30$ (●), 40 (△), 60 (▲), and 90 (○). Averages are taken over growth samples for $L = 90$ and 500 samples otherwise with $c_b = 0.1$, $c_1 = 0.01$. Data are fitted with $p_c = 0.059$ and undirected, random percolation exponents (Stauffer 1984) $\beta = 0.4$, $\gamma = 1.8$, $\nu = 0.9$. The broken lines show the asymptotic slopes equal to β for (a) and $-\gamma$ for (b).

percolation (Stauffer 1985). In contrast we found that finite size scaling plots made using the exponent values $\beta = 0.6$, $\gamma = 1.58$, $\nu_\| = 1.27$ (or with $\nu_\perp = 0.74$ or $\nu_{\text{eff}}^{-1} = (1/\nu_\| + 2/\nu_\perp)/3$] appropriate for directed percolation (Kinzel 1983, Redner 1983) showed distinct *systematic* deviations from scaling behaviour. (In principle, a highly accurate finite size scaling analysis should include two scaling variables representing directions parallel and perpendicular to the directed growth direction.) Within the errors of the analyses we therefore find no difference between the exponents for directed and undirected kinetic gelation models.

As restrictions on growth direction a chain of bonded sites may not fold back on itself and loops may form only when growing chains intersect. The formation of bonds thus tends to enhance the maximum spatial extent of the clusters more rapidly in directed, as opposed to undirected, growth and the gel point is thus reached for smaller values of p. This behaviour seems to be similar to that observed in a recent experiment (Sinclair *et al* 1983) but in a somewhat different context (polydiacetylene 4-butoxycar-bonyl-methylurethane in toluene at low temperatures) where for gelation to occur the polymer must be in its fully extended rod-like conformation. A detailed study of the generalised biased growth and chain/rod preferred reactions in the framework of recent theoretical (Wheeler *et al* 1983) and experimental (Sinclair *et al* 1983, Casalnuovo and Heeger 1984) investigations are in progress and will be published elsewhere.

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