LETTER TO THE EDITOR

Phase diagram, critical properties and dimensional effects of the kinetic gelation model

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Abstract. We simulate the formation of a gel from a mixture of bifunctional and tetrafunctional monomers which may form bonds with the help of initiators on the triangular lattice. Our Monte Carlo results for the average-weight degree of polymerisation exponent, γ, substantiate the conclusion that this model has distinct critical properties from other models of branched polymers. We observe a crossover to normal bond percolation as the concentration of initiators is increased. However, the cluster number ratio appears to be a universal quantity. We offer an explanation for the differences in phase diagrams of the two- and three-dimensional systems in terms of restricted random walkers.

Recently, a new model was proposed to simulate the growth of a strong gel in which covalent bonds were formed between monomers through the presence of free radicals or initiators (Manneville and de Seze 1981). This model, which is referred to as kinetic gelation through additive copolyprisation, was shown to be in a different universality class from that of random percolation (Herrmann *et al* 1982), primarily on the evidence of the critical amplitude ratio. A brief description of the model is given below but the interested reader should consult Herrmann *et al* (1983) for more details and Bansil *et al* (1983) for its chemical justification and limitations. Tetrafunctional or bifunctional monomers are placed at each lattice site (the numerical results presented here are for the two-dimensional (2D) triangular lattice) and a relatively small number of initiators are sprinkled on randomly selected lattice sites. The tetrafunctional monomers can form at most four bonds with their nearest neighbours whilst the bifunctional monomers can form at most two. We allow the formation of multiple bonds between nearest neighbours. An active initiator and a nearest neighbour of the site on which the initiator resides are selected at random. If the monomers at these selected sites are not saturated, a bond is formed and the initiator moves to the nearest neighbour, but if either monomer is saturated, growth of the cluster is not possible at that instant and the initiator does not move. Initiators may be deactivated by annihilation (two found at the same site), trapping (the initiator surrounded by saturated monomers) or poisoning (the monomer on the site of the initiator is saturated). Clusters are formed by the movement of the initiators which may be considered as restricted random walkers (RRW).

The critical properties of the 3D cubic lattice were determined by Herrmann *et al* (1982) who found that R, the critical amplitude ratio of the weight-average degree of polymerisation ('susceptibility'), is approximately 3 for a concentration of initiators, C_I, of 0.003. This ratio is approximately 10 for random percolation (Stauffer *et al*

1982) and 1 for the classical Flory–Stockmayer theory (Flory 1953). Thus this model is in a distinct universality class as the critical amplitude ratio is expected to be a universal quantity. However, the 'susceptibility' exponent, γ, was found to be indistinguishable from that of random percolation. Rushton *et al* (1983) simulated the model on the 2D square lattice and reported values of 3.8 ± 0.5 for γ and 140 ± 45 for R from an analysis of their Monte Carlo data, thus further substantiating the conclusion reached by Herrmann *et al* (1982) that this model is distinct from other models of branched polymers. Jan *et al* (1983) have shown that the cluster distribution is not a monotonically decreasing function of cluster size as it is in percolation, thereby shedding some light on why this model may be in a different universality class. In this letter we investigate the variation of the exponent, γ, and the cluster ratio number with C_I and offer an explanation for the strong dimensional effects observed in the phase diagrams.

The phase diagram of the variation of p_c, the bond fraction at which the sol–gel transition occurs, with C_I is shown in figure 1. The concentration of tetrafunctional monomers, C_t, is 1 and we observe that the infinite or spanning cluster is not found for values of C_I less than 0.006. p_c is determined from the maximum value of the 'susceptibility' and varies from 0.192 for C_I equal to 0.006 to 0.280 at C_I equal to 0.06 but shows smaller increases for larger values of C_I. The corresponding 3D phase diagram (Herrmann *et al* 1983) shows that the spanning cluster is formed for much smaller values of C_I, and in addition p_c is smaller for a given value of C_I, e.g. at $C_I = 0.01$, p_c is ~ 0.11 whilst the corresponding 2D value is ~ 0.21. The coordination number in both cases is 6. We sketch in figure 2 the variation of p_c with varying concentration of bifunctional monomers (C_b) for the 2D and 3D systems and again observe rather strong dimensional effects. These results may be understood by assuming properties for the RRW compatible with the known properties of a random walker in 2D and 3D. In the limit of infinite functionality the RRW becomes a random walker.

A random walker returns with certainty to the origin in 2D but has a finite probability of not returning in 3D. We assume, and this is substantiated by our numerical work, that for a given number of steps a RRW will be nearer the origin for a 2D walk than for the 3D walk. For a given number of steps the spatial extent of a cluster will be greater in 3D and furthermore, trapping is enhanced in 2D where there is a greater tendency for the RRW to return to previously visited sites. The growth of a cluster is localised to the vicinity of the initiator; thus a trapped initiator or a cluster of small spatial extent has a much smaller probability to coalesce with others to form a spanning cluster, and these properties are reflected by the lower value of p_c for the 3D systems when compared with the equivalent 2D system for a given value of C_I. A saturated monomer may be called upon to perform two functions: (i) to limit the paths available to the initiator (a blocker); (ii) trapping of the initiator. The addition of bifunctional monomers allows for the easy formation of saturated monomers and in 2D these saturated monomers primarily function in the role of blockers. Again, numerical results show that the average radius of gyration of a cluster for fixed p is 1.33 larger for C_b equal to 0.2 than it is for C_b equal to 0. As we have already noted, large clusters have a greater probability to coalesce, thus a larger portion of the bonds formed contribute to the spanning cluster, hence the decrease in p_c with increase of C_b for the 2D system. At C_b equal to 0.5 the competition from trapping is too great and the growth process is frustrated before the gel transition. The RRW is not severely hampered by blockers in 3D (the random walker has a finite probability of diffusing away), and as such there is small change in p_c for C_b in the range from 0 to 0.5.
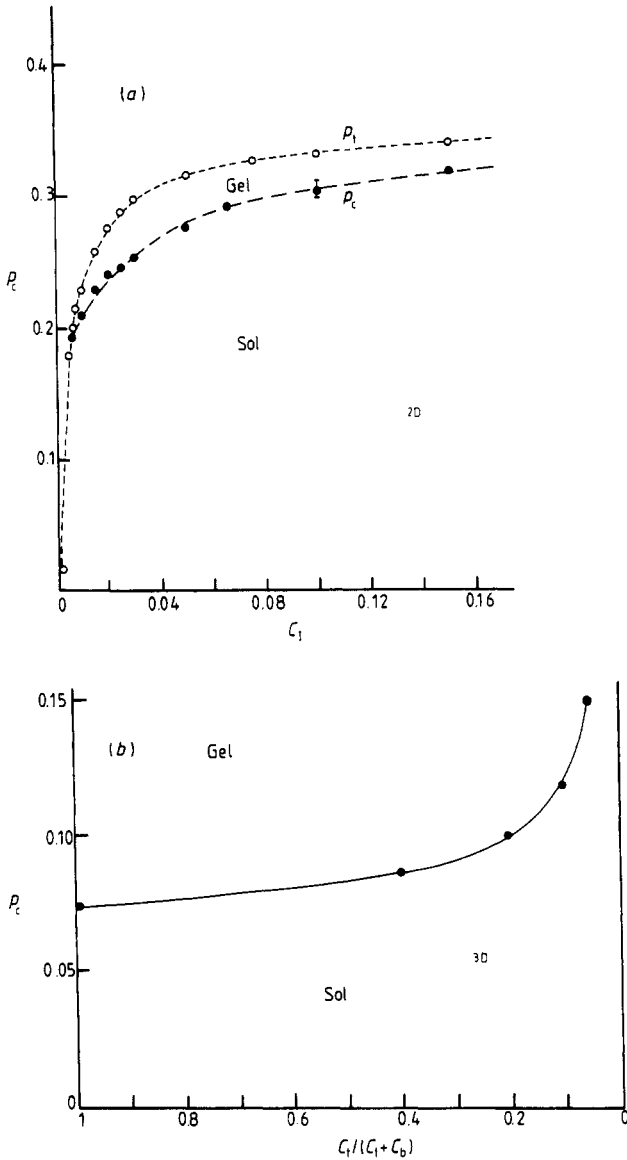
Figure 1. The variation of p_c, the critical bond concentration, with C_I, concentration of initiators, for the 2D triangular lattice (a) and 3D cubic lattice (b) (from Herrmann *et al* (1983)). p_t is the concentration at which complete trapping occurs.

However, large values of C_b lead to trapping which in turn implies an increase in p_c as a larger fraction of bonds have to be added before the spanning cluster is formed.

Restricted valence percolation is recovered in the limit of large C_I for in this region all the sites have the potential to form bonds. The critical properties are, therefore, expected to cross over from kinetic gelation to those of restricted valence percolation as C_I is increased. We have calculated the 'cluster number ratio', the ratio of s-clusters at p_c to the number of s-clusters at the concentration of bonds $p_{max}(s)$ where the
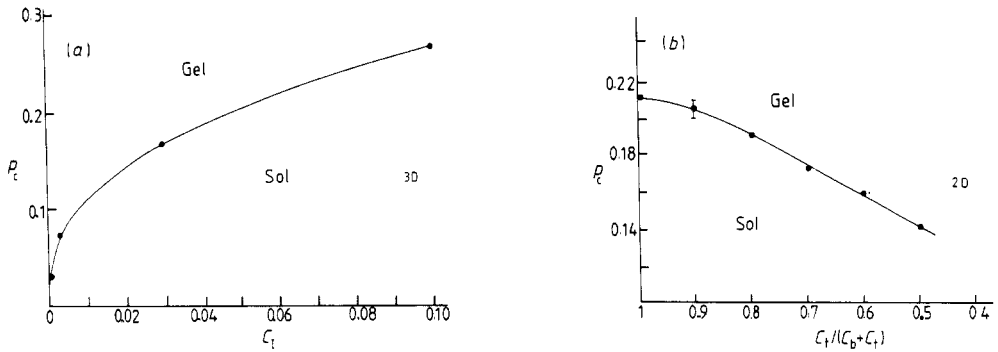
Figure 2. The variation of p_c with varying concentration of tetrafunctional monomers. The phase diagram for the 2D system is from Jan *et al* (1983) whilst the 3D diagram is from Herrmann *et al* (1983).

number of s-clusters is a maximum, as a function of C_I. The results, shown in table 1, suggest that this is a universal quantity (i.e. independent of C_I) and may have the same value as random percolation (~ 5; Jan and Stauffer (1982)). Preliminary analysis of the susceptibility exponent γ on the 450×450 triangular lattice indicates that there is a strong dependence on C_I for values of C_I up to 0.15. In fact, we see γ decrease from approximately 5 for the two small values investigated to approximately 2.5 at $C_I = 0.15$. The actual values of γ observed here are less important than the variation itself and the fact that for a relatively low concentration of initiators γ tends to the random percolation value. A more detailed investigation of the critical exponents involving finite size scaling and renormalisation group analysis is in progress to ascertain whether the exponents are continuously varying with C_I or if there is a sharp crossover from kinetic gelation to restricted valence percolation. This question cannot be answered with our present work.

To summarise, we have determined the phase diagram for the kinetic gelation model (p_c against C_I for $C_t = 1$) and have interpreted this phase diagram and also the phase diagram (p_c against $C_b/(C_t + C_b)$) for the 2D and 3D systems in terms of restricted random walkers. The 'susceptibility' exponent confirms that this model is distinct from random percolation and the evidence strongly suggests that there is a crossover from kinetic gelation to random percolation as C_I is increased. However, the cluster number

Table 1. The variation of the cluster number ratio (the number of s-clusters at that concentration $p_{max}(s)$ where the number of s-clusters is a maximum to the number of s-clusters at p_c for a fixed s) with C_I. Note the strong variation for small values of initiators. The random bond percolation value is approximately 5.

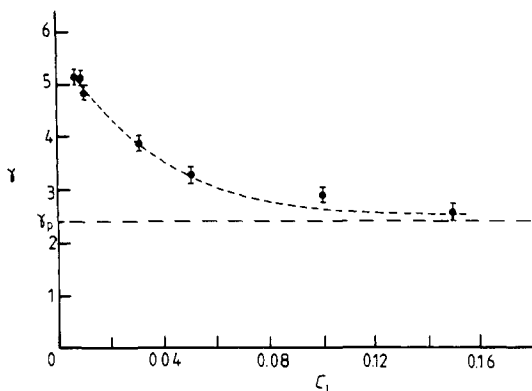| Concentration of initiators C_I	Bin 1 s 16–31	Bin 2 s 32–63	Bin 3 s 64–127	Bin 4 s 128–255	Bin 5 s 256–512
0.0075	23	15	7	5	4
0.01	23	12	6	4	3
0.075	7	5	5	5	3
0.10	7	6	5	4	4
0.15	5	5	6	4	3

Figure 3. The variation of γ, the average-weight degree of polymerisation exponent, as a function of C_I. The straight broken line represents the random bond percolation value, the broken curve is a guide to the eye. The error bars are obtained from an analysis of the Monte Carlo data and do not take into account systematic deviations like finite size effects.

ratio appears to be a universal quantity, i.e. independent of C_1, and our numerical results do not rule out that this quantity may have the *same* value as that of random percolation.

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