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LETTER TO THE EDITOR

Kinetic gelation with and without initiators: a two-dimensional Monte Carlo study

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Abstract. We simulate a mixture of bifunctional and tetrafunctional molecules which may form bonds, on a triangalar lattice, both with and without the help of free radicals. The model of Herrmann *et al* and normal bond percolation are two special limits of our model. We determine the gel point, the fraction of matter in the infinite network or gel, and the weight-average degree of polymerisation, as a function of time. For radical-initiated gelation, the observed cluster distribution confirms the conclusion of Herrmann *et al*, that this model is different from random restricted-valence percolation. However, the gel point is found to decrease with increasing concentration of bifunctional molecules, quite unlike the behaviour observed in three dimensions.

Flory's theory of gelation (Flory 1953) is based on the approximation that sites on a Bethe lattice are connected by randomly formed bonds; this theory can be regarded as the first percolation theory. If instead the original molecules are placed on a periodic lattice, the lattice structure automatically takes into account the excluded volume effects and also allows for the formation of loops over arbitrary distances. If the permanent bonds between the lattice sites are formed in a random manner as in Flory's theory, then we arrive at bond percolation as a model for the gelation process. The advantages and disadvantages of this well studied model have been recently reviewed by Stauffer *et al* (1982) with particular emphasis on critical phenomena.

Real gelation, however, is not a random process; instead, bonds are formed as a result of chemical reactions which may depend on the previous history of the system. On a lattice this process may be simulated through the use of initiators or free radicals which act essentially as catalysts and whose permitted paths through the lattice lead to trails of permanently formed bonds. This resulting branched network of permanent bonds is then a history of the past movement of initiators.

The model (Manneville and de Seze 1981) has been discussed extensively by Herrmann *et al* (1982, 1983) with respect to computational results near the gel point and by Bansil *et al* (1983) with respect to its chemical justification and limitation. All the previously published work was three-dimensional and also assumed that the growth of the clusters comes exclusively from radical movements, i.e. by the jump of a free radical from one lattice site to a neighbouring site. The present work is two-dimensional; also, to describe more realistically materials like polyacrylamide we now allow our permanent bonds to be formed even without the help of initiators. During the time one radical attempts to jump to a neighbouring site, $n-1$ randomly selected

lattice sites each attempt to form one bond with a neighbour independent of the presence of an initiator. This progress without radicals is much slower; but since there are only few radicals in the system, the overall number of bonds formed without initiators can be appreciable. For example, if $n = 10$, and if, as in our case, only one per cent of the lattice sites carry a radical, then initially about nine out of ten bonds are formed by our newly introduced reaction without radicals. Note, however, that a given lattice site with a radical will only form a bond without the transfer of the radical in one out of ten cases.

Figure 1 shows, at a concentration of 40% tetrafunctional monomers (and thus 60% bifunctional units) how the number of permanent bonds increases with time. Our time unit is one jump attempt per radical; thus for large n, reactions proceed very quickly. The limit $n \to \infty$ corresponds to random restricted-valence percolation since now the radicals have become irrelevant and every bond can be formed with the same probability p. The limit $n = 1$, of course, corresponds to the case discussed by Herrmann *et al* (1982, 1983), Bansil *et al* (1983) and Manneville and de Seze (1981), when reactions proceed exclusively through jumping of radicals. In general we denote by p the conversion factor, i.e. the number of permanent bonds formed, divided by the number $3L^2$ or permissible bonds on the lattice.

A tetrafunctional unit can enter at most four bonds with its six nearest neighbours, a bifunctional unit at most two. It is possible in our model for two nearest-neighbour sites to be connected by multiple bonds. A small fraction (one per cent throughout this work) of tetrafunctional and bifunctional units are marked randomly by radicals, which are essentially unpaired electrons able to break up a carbon double bond (Bansil *et al* 1983). Initially the lattice is free of all bonds; an initiator is then selected

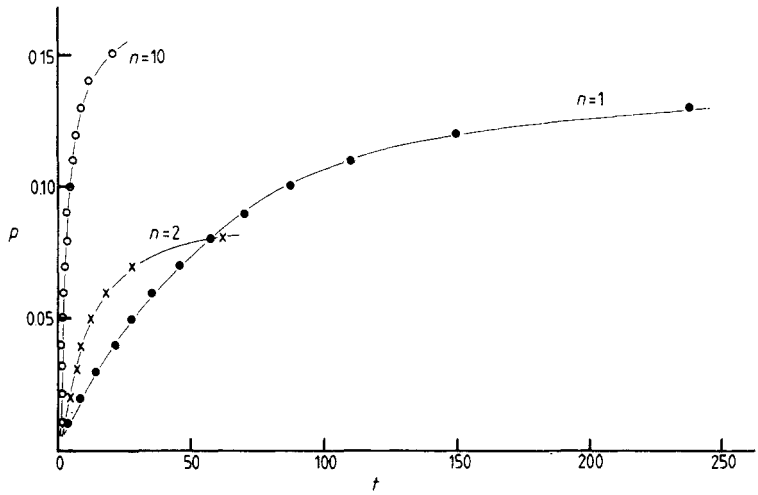

Figure 1. Variation of conversion factor p (fraction of permanently formed bonds) against time t; our time unit is one jump attempt per radical. The number n on each curve gives the number of bond formation attempts made per unit time; e.g. for $n = 2$ one tries to form one bond initiated by a free radical followed by one bond without such help. The initial number of free radicals is one per cent of the total number of lattice sites (also in the later figures). The concentration of bifunctional units is 60%, corresponding to 40% tetrafunctional units; for fewer bifunctional molecules less time is needed to reach the same p. All curves are based on ten runs in a 360×360 lattice and took 4 to 8 minutes on a CDC Cyber 76 computer.

randomly, and the monomer at this site and one at a randomly selected nearest-neighbour site are checked to see if they are saturated. If this is not the case, a bond is formed permanently between the two sites, and the initiator is moved to the new site. If our new parameter n is larger than unity, this step is followed by a random selection of $n-1$ lattice sites (independent of whether they carry a radical or not) each of which tries to form a bond with one of its neighbours; in this case no radical is transferred if a bond is formed. This whole procedure is repeated until all initiators are either trapped or annihilated. (Initiators are annihilated if two happen to be at the same site, and trapped if it is impossible for the initiator to move away as a result of bond saturation in its environment.)

Besides time t and conversion factor p, we measure in our computer experiment the gel fraction G, which is the number of sites belonging to the largest macromolecule or bond cluster divided by the system size L^2, and the 'susceptibility' $\chi = \Sigma s^2 n_s$, where n_s is the number of macromolecules (per lattice site) containing s sites each; the sum excludes the largest cluster. (The unnormalised cluster number $L^2 n_s$ is denoted by N_s.) Here L is the linear dimension of the triangular lattice in units of the nearest-neighbour spacing; thus the lattice contains L^2 sites connected by $3L^2$ bonds. We consider $L = 100$, 200 and 360 with periodic boundary conditions and note that the results for $L = 200$ and 360 are almost identical.

The cluster size distribution N_s in figure 2 shows for $n = 1$ (bonds formed exlusively through radicals) a second maximum as a function of s, besides the trivial maximum at $s = 1$ corresponding to unattached monomers. The second maximum shifts with

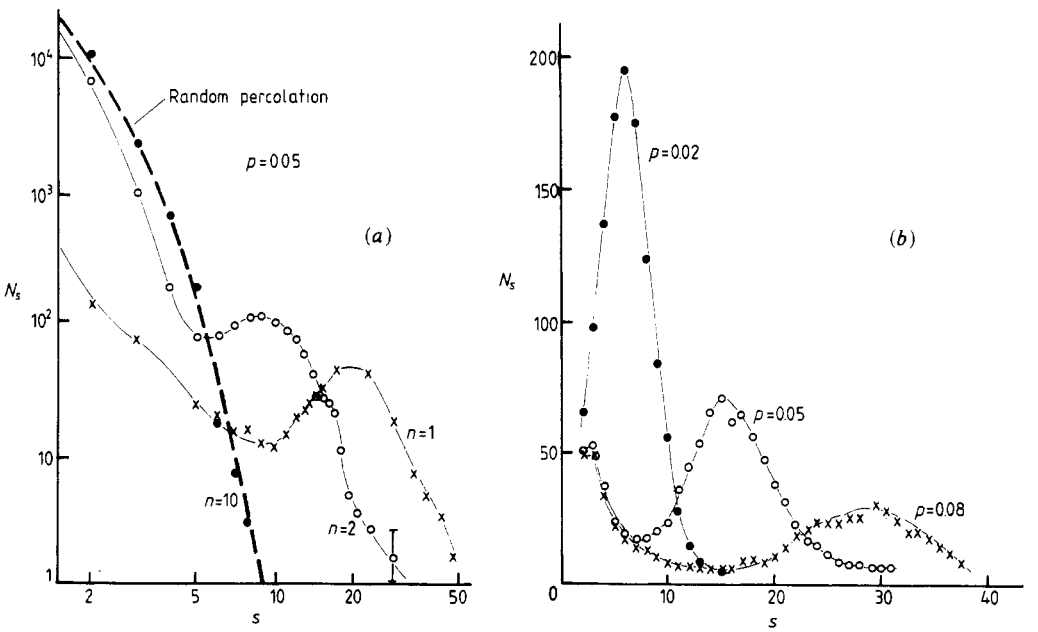

Figure 2. (*a*) Log–log plot of cluster numbers N_s versus cluster size s for $p = 0.05$ at a concentration of 60% bifunctional monomers in a 360×360 lattice (ten runs are added up). The parameter n is defined in figure 1; for $n \to \infty$ we expect the usual random restricted-valence percolation results, indicated here by a broken line. (*b*) N_s against s for various values of p; these results were obtained from ten runs on a 360×360 lattice at a concentration of 20% bifunctional monomers.

time to larger sizes s, and also shrinks with time. At the gel point it is shifted to such large s and shrunk so strongly that it is no longer clearly visible. In the usual random percolation process no such second maximum in N_s as function of s at fixed p appears (see for example the tables of Flammang (1977)); but such maxima are common to phase separation processes if large droplets grow due to condensation and if there is negligible coagulation. Thus the appearance of this second maximum is a clear indication that this kinetic gelation process differs from the essentially static percolation model, in agreement with Herrmann *et al* (1982). On the other hand, large n in our model corresponds to random percolation; and indeed for $n = 2$ the second maximum is much less pronounced, as figure 2 shows, whereas for $n = 10$ it has vanished completely.

As figure 1 already showed, it is difficult in this process for $n > 1$ to reach the gel point. Due to the rapid formation of bonds without the need for initiators, the radicals become trapped before the gel point is reached. From then on the process resembles random percolation, and is therefore not continued in our simulation. Thus from now on we restrict ourselves to the case $n = 1$, where bonds are formed exclusively through radicals.

Figure 3 shows the gel fraction and 'susceptibility' and extends again up to the time when all radicals in the lattice are trapped or annihilated. We determine the gel point from the maximum in χ; this determination is consistent with that from the gel fraction. Finally, figure 4 shows our phase diagram: gel point against ratio of tetrafunctional units to total number of lattice sites.

We point out the differences between this phase diagram and that of Herrmann *et al* (1983) for 3D simple cubic lattices. In both cases the coordination number is six, but the 3D system shows an increase in the gel point p_c with increasing mole fraction of bifunctional units; for the purely tetrafunctional system p_c is about 0.074.

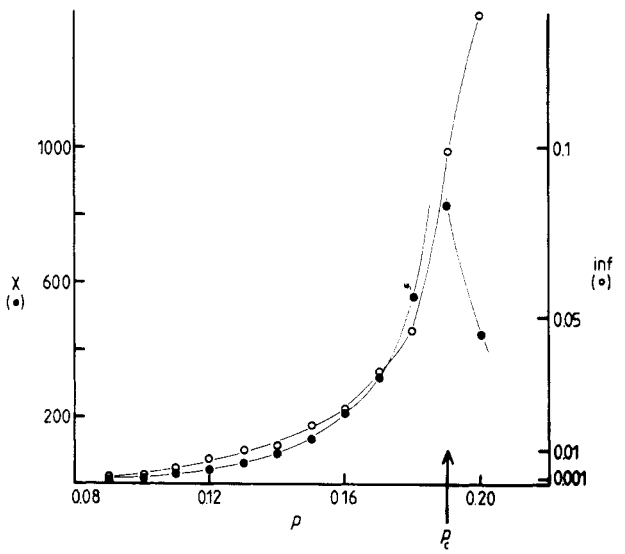

Figure 3. Gel fraction and 'susceptibility' (second moment of cluster size distribution excluding the largest cluster) for $n = 1$, i.e. bonds are formed exlusively through radicals. The statistical error is of the same order as the size of the data points.

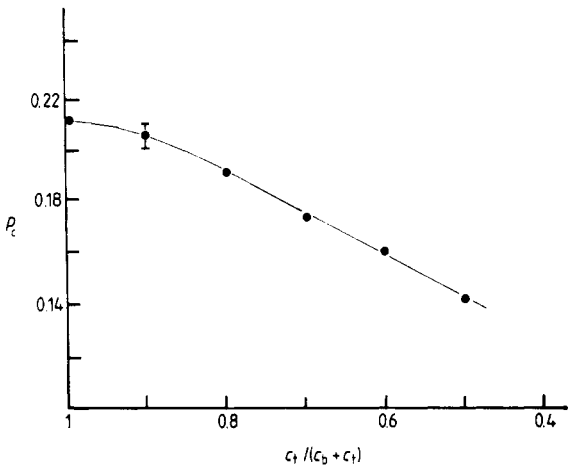

Figure 4. Gel point p_c, for $n = 1$, as function of concentration of tetrafunctional units, in 300×300 lattices. A typical error bar is shown.

In our 2D system we see a decrease in p_c with increasing concentration of bifunctional monomers, with p_c about 0.2 for a purely tetrafunctional system. This strong dimensionality effect is also observed by the formation of an infinite cluster for high concentrations (about 90%) of bifunctionals in 3D, whilst we found it impossible to form infinite 2D clusters for concentration of bifunctionals larger than about $\frac{1}{2}$.

We summarise our result by stating that the kinetic model of Herrmann *et al* can also be simulated in 2D , with results on the whole similar to 3D. Other 2D work is presently in progress (Rushton *et al* 1983, Morgan *et al* 1983). We also generalised the model to incorporate reactions without radicals; the system then becomes more similar to random restricted-valence percolation. Not surprisingly, our 2D gel points are higher than the 3D ones. The gel point in 2D varies in the opposite direction to the 3D case if the ratio of bifunctional to tetrafunctional units is changed.

After this feasibility study, it remains to be seen what the critical behaviour of this system is, and how its behaviour changes if fixed (Morgan and Landau 1983) and mobile (Bansil *et al* 1983) solvent molecules are included in the simulation. It would be nice if the model could be simulated on a continuum without a lattice (Gawlinski and Redner (1983) with earlier literature on continuum percolation). At least in 2D, in the case of reactions occurring both with and without radicals, modifications to the model are necessary if one wants to reach the gel point with untrapped radicals. Further progress in the simulation of 2D gelation could lead to a better theory of antibody–antigen reactions on the surface of lymphocytes in higher vertebrates (Perelson 1978).

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