

## Spatial correlations in kinetic gelation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1986 J. Phys. A: Math. Gen. 19 L1209

(<http://iopscience.iop.org/0305-4470/19/18/017>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 31/05/2010 at 19:25

Please note that [terms and conditions apply](#).

## LETTER TO THE EDITOR

### Spatial correlations in kinetic gelation

R Bansil<sup>†</sup>, M Willings<sup>†</sup> and H J Herrmann<sup>‡</sup>

<sup>†</sup> Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215, USA

<sup>‡</sup> Service de Physique Theorique, CEN Saclay, 91191 Gif-sur-Yvette Cedex, France

Received 3 September 1986

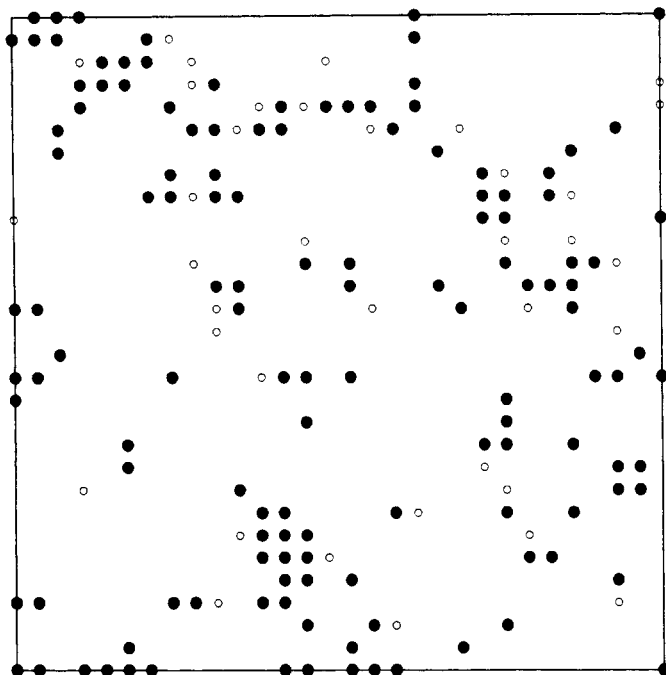
**Abstract.** We report here a calculation of the spatial correlation function of the fully polymerised four-functional units in the kinetic gelation model in three dimensions. The results indicate that the fully polymerised four-functional units form small correlated regions in space. This is in sharp contrast to normal percolation where the spatial distribution of fully polymerised units is uniform. The size of these clusters of crosslinks depends on the extent of reaction, the concentration of initiators and the solvent diffusivity. The results suggest a picture of the microscopic structure of a gel as consisting of bundles of chains linked by clusters of crosslinks in agreement with electron microscopic studies of polyacrylamide gels.

The process of free-radical-initiated irreversible polymerisation in gels such as polyacrylamide can be simulated by a kinetic gelation ( $\kappa G$ ) model originally proposed by Manneville and de Seze (1981) and developed extensively by Herrmann *et al* (1982). Bansil *et al* (1984) incorporated the presence of a mobile solvent to make the computer simulations more realistic. The  $\kappa G$  model differs from standard percolation in producing a cluster size distribution which is non-monotonic (Jan *et al* 1983a, b, Bansil *et al* 1984).

Chhabra *et al* (1985) showed the existence of oscillations in the cluster size distribution. Since the cluster size distribution is very difficult to measure experimentally in a gel we have simulated the spatial distribution of crosslinks, i.e. the fully polymerised four-functional (FP4) units.

Several experiments suggest that the distribution of crosslinks in polyacrylamide (PA) gels prepared by free radical polymerisation is not homogeneous. On the basis of optical turbidity and swelling equilibrium measurements in high crosslink content polyacrylamide gels, Richards and Temple (1971) suggested that the crosslinking monomer (i.e. the four-functional monomer) forms clusters. This suggestion is also consistent with electron microscopic studies (Ruchel *et al* 1978, Hsu and Cohen 1984) of PA gels which show the existence of bundles of chains and clusters of crosslinks. Direct evidence for the formation of small clusters of four-functional monomers was seen in Raman spectra of high crosslink content gels (Gupta and Bansil 1983). The purpose of this letter is to see whether such spatial inhomogeneities are observed in simulations by the kinetic gelation method.

A typical slice from a three-dimensional cubic box (size  $30^3$ ) of a simulated gel showing the distribution of fully polymerised two-functional and four-functional monomers is shown in figure 1. This picture suggests that the distribution of FP4 units may indeed be inhomogeneous in this model. To describe the spatial inhomogeneity



**Figure 1.** A typical slice from a simulation of the KG model on a cube of size  $30^3$  at an extent of reaction  $p = 0.36$ . The extent of reaction,  $p$ , is defined as the total number of bonds grown up to that step normalised by  $3L^3(1 - C_S)$ , the maximum number of bonds possible on this lattice. This simulation was for  $C_B = 0.28$ ,  $C_T = 0.42$ ,  $C_S = 0.3$ ,  $C_I = 0.03$ , and diffusivity = 159. Under these conditions  $p_c = 0.24$ . Open circles represent fully polymerised two-functional units and filled circles represent fully polymerised four-functional units. Clustering of FP4 is clearly observed.

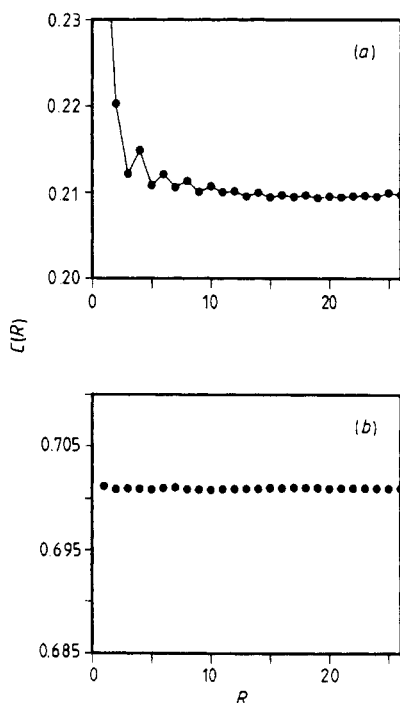
seen in figure 1, we calculate the density-density or pair correlation function,  $C(R)$  of the FP4.

The calculations reported in this letter use the version of the kinetic gelation model described in Herrmann *et al* (1983) and Bansil *et al* (1984). In this letter we analyse the spatial correlation of FP4 using periodic boundary conditions. The basic steps in the simulation are (i) the random distribution of bifunctional (B), tetrafunctional (T) and solvent (S) monomers on the sites of a 3D cubic lattice of size  $L^3$  with the total concentration of monomers satisfying  $C_B + C_T + C_S = 1$ ; (ii) the reaction is initiated by making a fraction  $C_I$  (radicals) of the bonds emanating from the B and T monomers reactive and by drawing one bond from each of the initiated monomers; (iii) growth proceeds by transferring the radical to a randomly chosen nearest-neighbour monomer provided not all its functionalities have been saturated; (iv) growth terminates either by the pairwise annihilation of radicals when they meet each other or by the trapping of all radicals (for details, see Bansil *et al* 1984). Mobility of unreacted monomers and solvent molecules is included by permitting nearest-neighbour exchanges between solvent and unreacted monomers.

The spatial correlation function  $C(R)$  of FP4 is calculated by going to the site of an FP4 and building a set of concentric spheres with unit increase in radius around the FP4. The largest sphere encloses the cubic lattice, i.e. for a cubic lattice of size  $L^3$  the largest sphere has a radius equal to  $\sqrt{3}L/2$ . The number of FP4 within the unit

shell at distance  $R$  from the centre FP4 is summed, and then normalised by the total number of sites in the shell of radius  $R$  to give the local density at a distance  $R$  from the central FP4 unit. The average value of  $C(R)$  is obtained by repeating this process over each of the FP4 in the lattice. Apart from a normalisation constant,  $C(R)$  is proportional to the probability of finding a pair of FP4 a distance  $R$  apart and thus could be measured directly in a neutron or x-ray scattering experiment. Periodic boundary conditions were implemented such that any point within a unit shell which lies  $n$  units outside the lattice would reflect to a point  $n$  units inside the opposite face of the cube, using mirror images of the system. Thus effectively the correlations are calculated inside a cube of length  $3L$ .

A plot of the spatial correlation function  $C(R)$  against  $R$  obtained from a distribution at a late stage of the growth process ( $p > p_c$ ) is shown in figure 2(a). For comparison we also show (figure 2(b)) the correlation function  $C(R)$  calculated from a standard percolation on the same lattice at  $p = 0.7$  (much greater than  $p_c$ ). A comparison of figures 2(a) and (b) clearly shows that in kinetic gelation the density-density correlation is non-uniform; in sharp contrast to standard percolation where  $C(R)$  is a constant independent of  $R$ . (Note that  $C(R)$  is not the connectivity function usually calculated in percolation theory but rather a spatial correlation function.) This implies that the full polymerised units are distributed uniformly in standard percolation whereas they

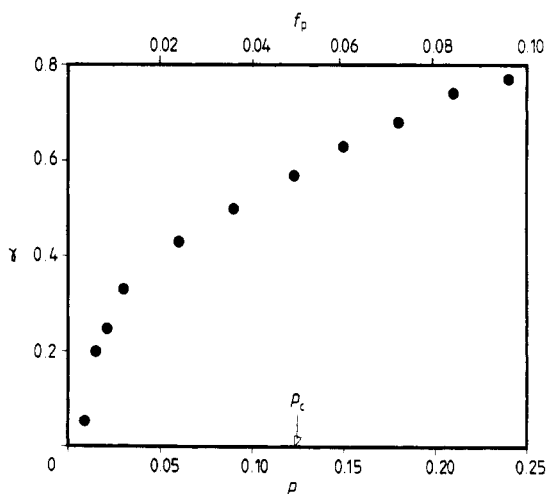


**Figure 2.** (a) The spatial correlation function  $C(R)$  plotted against  $R$  for kinetic gelation calculated on a  $30^3$  lattice at  $p = 0.36$  using periodic boundary conditions as described in the text. The results are for  $C_B = 0.28$ ,  $C_T = 0.42$ ,  $C_S = 0.3$ ,  $C_I = 0.03$  and diffusivity = 159.  $C(R)$  was averaged over five realisations. Note that the local density fluctuation at small  $R$  is about 10%. (b) The spatial correlation function  $C(R)$  plotted against  $R$  for a simulation of standard percolation on a  $30^3$  lattice at  $p = 0.7$ . In contrast to the results shown in (a) the density fluctuation is less than 1%.

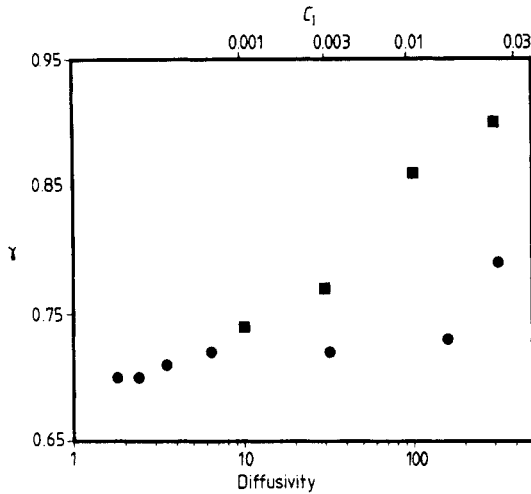
are distributed non-uniformly in kinetic gelation. The sharp peak at small  $R$  represents the structure factor of these clusters, the width of this peak being a measure of the characteristic size of the cluster. We have found that the height and width of this peak depends on the parameters of the simulation. For a given initiator concentration and solvent mobility the size of the aggregates of FP4 is small at the beginning of the reaction and increases as the reaction proceeds. At the same extent of reaction, larger clusters are produced when the concentration of initiators is small. These observations are consistent with a picture of local growth around initiator sites followed by merging of clusters at late stages. To quantify these clustering effects we calculate the ratio,  $\gamma$ , of the probability of finding an FP4 at a distance of two units to the probability of finding an FP4 at a distance of one unit. We investigate the dependence of  $\gamma$  as a function of four parameters: monomer and solvent diffusivity, number of steps, concentration of initiators and concentration of bifunctional monomers.

In figure 3 we show how  $\gamma$  depends on the degree of polymerisation  $p$ . In the early stages FP4 are mostly nearest neighbours so that  $\gamma$  is very small. In the post-gel phase,  $\gamma$  seems to saturate against a number between 0.9 and 0.7. For increasing  $C_1$ , as shown in figure 4,  $\gamma$  increases which means that the distribution of FP4 gets more homogeneous at late times for larger  $C_1$ . This corresponds to the well known observation that this model crosses over the percolation if  $C_1 \approx 1$ . In figure 4, we also show the dependence of  $\gamma$  on solvent and monomer mobility defined as the ratio of the number of exchange attempts to the number of bonds grown between exchange attempts. Increasing diffusivity also leads to producing a more homogeneous distribution, implying that clustering is related to localised growth around initiator sites. The ratio  $\gamma$  was essentially independent of the ratio of two- and four-functional monomers in the initial mixture.

In conclusion, we have found that in kinetic gelation the fully polymerised units form interesting non-trivial structures. As a consequence of the fact that in this model growth is localised to the vicinity of initiators the crosslinks form spatially correlated



**Figure 3.** The dependence of  $\gamma$  (defined in the text) on the extent of reaction,  $p$ . The critical extent of reaction at which gelation occurs,  $p_c$ , is indicated on the figure. Also indicated is  $f_p$ , the fraction of FP4 units normalised by  $L^3$  corresponding to each value of  $p$ . The results are obtained by averaging over five realisations with  $C_B = 0.28$ ,  $C_T = 0.42$ ,  $C_S = 0.3$ ,  $C_1 = 0.003$  and diffusivity = 159 on a  $30^3$  lattice.



**Figure 4.** The dependence of  $\gamma$  on diffusivity (●) and  $C_1$ (■). The results are at  $p = 0.24$  (greater than  $p_c = 0.12$ ). All the other parameters are same as in figure 3.

regions. Thus the gel produced in  $\kappa G$  has a 'microscopic' structure of bundles of chains linking small aggregates of crosslinks. This is qualitatively similar to the structure observed in electron micrographs of polyacrylamide gels. A direct measurement of the spatial correlation function (or the structure factor) by an appropriate scattering technique such as neutron or x ray would be very informative in this context. Also, oscillations were found by Savits *et al* (1986) in a different model. It remains to be seen if the oscillations observed in the  $\kappa G$  model as a function of cluster size (Chhabra *et al* 1985) are related to the oscillations in the spatial pair correlation function.

This research was supported by grants from the NSF and Gillette Corporation.

## References

- Bansil R, Herrmann H J and Stauffer D 1984 *Macromol.* **17** 1004  
 Chhabra A, Matthews-Morgan D, Landau D P and Herrmann H J 1985 *J. Phys. A: Math. Gen.* **18** L575  
 Gupta M K and Bansil R 1983 *J. Polym. Sci.* **21** 969  
 Herrmann H J, Landau D P and Stauffer D 1982 *Phys. Rev. Lett.* **49** 412  
 Herrmann H J, Stauffer D and Landau D P 1983 *J. Phys. A: Math. Gen.* **16** 1221  
 Hsu T P and Cohen C 1984 *Polymer* **25** 1419  
 Jan N, Lookman T and Hunter D L 1983a *J. Phys. A: Math. Gen.* **16** L757  
 Jan N, Lookman T and Stauffer D 1983b *J. Phys. A: Math. Gen.* **16** L117  
 Manneville P and de Seze L 1981 *Numerical Methods in the Study of Critical Phenomena* ed I Della Dora, J Demongeot and B Lacolle (Berlin: Springer)  
 Richards E G and Temple C J 1971 *Nature Phys. Sci.* **230** 92  
 Ruchel R and Brager M D 1978 *Anal. Biochem.* **68** 415  
 Ruchel R, Steere R L and Erbe E F 1978 *J. Chromatogr.* **166** 563  
 Savit R *et al* 1986 *J. Phys. A: Math. Gen.* to be submitted