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LETTER TO THE EDITOR

Percolation on a randomly expanded lattice: a model of polymer gels

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Abstract. We discuss a random expansion of a lattice in which a series of 2-valent vertices are inserted between the original vertices of the lattice. The critical exponents do not change under this expansion but the critical region narrows. The relevance of these results to percolation models of gelation in polymerisation reactions is also considered.

There are two competing models for the sol–gel phase transition which occurs in systems such as polyfunctional condensation reactions. The classical approach (Flory 1941, Stockmayer 1943, Gordon 1962) can be cast in terms of the theory of branching processes or, alternatively, as a percolation process in the interior of a Bethe lattice. The second model which has been used is percolation on a regular lattice (Broadbent and Hammersley 1957, Frisch and Hammersley 1963). The predictions of these two models, close to the sol–gel transition, are quite different (Stauffer 1981) and, in particular, the predicted values of the critical exponents are different. Although there have been several experimental studies of the critical exponents in gelation (e.g. Whitney and Burchard 1980, Schmidt and Burchard 1981) there is no clear-cut agreement with predictions of either model (Stauffer 1981) though Schmidt and Burchard (1981) favour the mean field values predicted by the classical approach of Flory (1941).

Stauffer (1981) has discussed a number of reasons why percolation theory may not be a good model of these polymer gels. The one which we shall consider here is that simple bond percolation processes might apply to a condensation of q-functional monomers ($q \geq 3$) but that many experimental situations involve both q-functional and 2-functional monomers. For instance, Whitney and Burchard (1980) studied the radical polymerisation of methyl methacrylate and ethylene dimethacrylate in which the 2-functional monomer accounts for about ninety mole percent of the reaction mixture. Similarly, Schmidt and Burchard (1981) studied the anionic copolymerisation of styrene and divinylbenzene. These processes involve addition rather than condensation reactions and will have a distribution of numbers of 2-functional units between the branch points in the polymer molecules formed in the reaction. Two possibilities arise: (i) that the exponents are changed by the inclusion of a distribution of 2-functional units, or (ii) that the size of the critical region is changed. In this paper we shall discuss a simple model of this situation, involving a random expansion of a lattice, and show that for this model the critical exponents are not changed by the expansion but that the critical region shrinks as the proportion of 2-functional units increases. These

arguments apply equally to a Bethe lattice and to a lattice embeddable in a d-dimensional Euclidean space. The related problem of vulcanisation has been discussed by de Gennes (1977), Daoud (1979) and Coniglio and Daoud (1979).

We consider a q-coordinate lattice L and construct an expanded *stochastic* lattice L^S, as follows. We replace the jth bond in L by a set of n_j bonds in series, where the n_j are discrete random variables independently distributed with density $\{g(n), n = 0, 1, \ldots\}$. The original sites on L correspond to q-functional units and the added $(n_j - 1)$ sites between a pair of sites on L correspond to 2-functional units in L^s. The mean number of 2-functional units on L^s between a pair of q-functional units which were adjacent on L is

$$\bar{n} = \sum_n ng(n). \tag{1}$$

In the following we restrict our attention to the case $g(0) = 0$ so that L and L^s are homeomorphic. If $g(0) \neq 0$ then lattice defects are introduced and the topological equivalence is destroyed. The arguments can be extended to this case provided that the defects do not eliminate the percolation singularity.

If we consider bond percolation on this pair of lattices we can map any configuration on L^s onto a corresponding (unique) configuration on L by occupying a bond on L (between a pair of vertices A and B) if and only if all bonds are occupied in the simple chain joining the vertices A and B on L^s. This surjection of configurations on L^s onto configurations on L preserves percolation since a configuration on L^s percolates iff its image on L also percolates. If the bond density on L^s is w then the bond density (p) on L is given by

$$p = \sum_n g(n)w^n. \tag{2}$$

If p_c is the critical bond density for bond percolation on L, the corresponding critical bond density (w_c) on L^s will be the real positive root in $(0, 1)$ of the equation

$$\sum_n g(n)w_c^n = p_c. \tag{3}$$

To investigate the n_0 dependence of w_c we note that

$$\bar{n} = (dp/dw)|_{w=1} \tag{4}$$

and expand (2) about $w = 1$. This yields

$$w_c \simeq 1 - (1 - p_c)/\bar{n} \tag{5}$$

for $\bar{n}$ large. As expected, the critical bond density increases as the system is 'diluted' with 2-functional units. We note that the functional form (5) is the same for percolation on regular lattices and in the branching process models.

Suppose that $P(p)$ is the percolation probability on L and $F(w)$ is the percolation probability on L^s. We assume the usual functional form for $P(p)$,

$$P(p) \sim B(p - p_c)^\beta \tag{6}$$

which describes the behaviour in the critical region $p_c \leqslant p \leqslant p + \varepsilon$. Since the coefficients of $g(n)$ are all non-negative, $p(w)$ is strictly increasing on $(0, 1]$. Expanding $p(w)$ about w_c and inserting the result into (6) gives

$$F(w) \sim P(p(w))$$

$$\sim B[(dp/dw)|_{w=w_c}(w - w_c)]^\beta \tag{7}$$

with $(dp/dw)|_{w=w_c} > 0$. The critical exponent characterising the percolation probability is unchanged by the stochastic expansion of the lattice.

Equation (7) will apply in the critical region $w_c \leq w \leq w_c + \delta$ where δ and ε, the widths of the critical regions on L^s and L, are related by

$$\delta \leq \varepsilon w_c \Big/ \sum_n ng(n)w_c^n, \tag{8}$$

where equality holds if a linear approximation is adequate. The denominator in (8) is the mean number of occupied bonds, at bond density w_c, between a pair of vertices on L^s which were adjacent vertices on L. Since the mean number of bonds which we inserted in the lattice expansion is $\bar{n}$, and the bond density is w_c, we obtain

$$\delta \leq \varepsilon/\bar{n} \tag{9}$$

so that the lattice expansion leads to a narrowing of the critical regime.

We wish to emphasise that the two principal results of this Letter—the invariance of the critical exponent and the narrowing of the critical regime after a stochastic expansion of the lattice—have been established for any lattice and for (practically) any distribution, $g(n)$. These results suggest that the lattice models of gelation preserve their non-classical behaviour near criticality even when the system is diluted with bifunctional units. This is in agreement with the field theory predictions of Lubensky and Isaacson (1978, 1979). Indeed, the lack of restrictions on the distribution $g(n)$ allows considerable distortion of the underlying 'regular' lattice, without apparent change in the critical exponent.

On the other hand, the shrinkage of the critical region due to increased concentration of 2-functional units could in practice be so great as to render the critical region inaccessible experimentally. This suggests that attempts to measure critical exponents should ideally be carried out in the low bifunctional unit concentration regime.

References

Broadbent S R and Hammersley J M 1957 *Proc. Camb. Phil. Soc.* **53** 629
Coniglio A and Daoud M 1979 *J. Phys. A: Math. Gen.* **12** L259
Daoud M 1979 *J. Physique Lett.* **40** 201
de Gennes P G 1977 *J. Physique Lett.* **38** 355
Flory P J 1941 *J. Am. Chem. Soc.* **63** 3083, 3091, 3096
Frisch H L and Hammersley J M 1963 *J. Soc. Indust. Appl. Math.* **11** 894
Gordon M 1962 *Proc. R. Soc.* A **268** 240
Lubensky T C and Isaacson J 1978 *Phys. Rev. Lett.* **41** 829
—— 1979 *Phys. Rev.* A **20** 2130
Schmidt M and Burchard W 1981 *Macromolecules* **14** 370
Stauffer D 1981 *Physica* **106A** 177
Stockmayer W H 1943 *J. Chem. Phys.* **11** 45
Whitney R S and Burchard W 1980 *Makromol. Chem.* **181** 869