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LETTER TO THE EDITOR

On the relation of kinetic gelation and percolation

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Abstract. We analyse the results of kinetic gelation and propose a diagram compatible with the existing data. We introduce the concept of 'limited' and 'full' universality. The former refers to systems with an identical *subset* of critical exponents; the latter refers to systems with an identical *set* of critical exponents. The evidence suggests that kinetic gelation and random percolation are in the same limited universality class. It appears that the concentration of initiators plays the role of an active parameter, similar to that of the interplane coupling in quasi-two-dimensional Ising models.

A complete understanding of the properties of the gelation process is a challenge to polymer scientists (see, e.g., the articles in Stanley and Ostrowsky (1985)). Recently the kinetic aspects of the growth of polymers during gelation has become the focus of considerable interest (Manneville and de Sèze 1981). A model for the process of additive copolymerisation, which is commonly referred to as kinetic gelation, has been studied extensively in several variations (Herrmann *et al* 1982, 1983, Bansil *et al* 1984, 1985, Chhabra *et al* 1984, 1985a, b, 1986, Hong *et al* 1984a, b, Pandey 1984, Herrmann 1984, 1985, 1986). Compared to percolation, the static model for gelation, kinetic gelation, has shown some subtle peculiarities. If we assume that the concepts of universality classes and critical crossover remain valid for irreversible growth models like kinetic gelation, several questions arise. What is the universality class of kinetic gelation? Is there some crossover between kinetic gelation and percolation? Is the kinetic aspect of kinetic gelation responsible for a more limited universal behaviour than the usual one? It is the aim of this letter to use the existing results to formulate answers to some of the above questions and to suggest further work to help resolve ambiguous situations.

We consider the lattice version of the model. Each lattice site is occupied by a monomer of functionality f, which is a measure of the maximal number of bonds the monomer can form with its neighbours. Additionally, radicals are randomly placed on a fraction c_I of the lattice sites. The radicals are allowed to diffuse randomly to neighbouring sites provided that the monomers concerned have formed fewer bonds than their initial functionality. The movement of radicals leads to the formation of chain-like structures and crosslinks. If two radicals are at the same site at the same time then they annihilate each other. All monomers that are connected to each other through bonds belong to the same cluster. The gel point is reached when for the first time a cluster spanning the whole lattice appears. It is found that the number of s-site clusters, n_s, scales close to the gel point. Since the number of bonds formed increases monotonically with time, the total number of steps made by all the radicals at any instant per unit volume, called the concentration p, is a reasonable measure of time. The gel point is given by a critical value p_c. For a more detailed description of the model, see e.g. Herrmann (1985, 1986).

Some parameters that can be varied in this model are:

(i) the relative concentrations of monomers of different functionalities c_2, c_4, etc, . . . ,

(ii) the concentration of radicals c_I,

(iii) the dimension of the system d.

Critical properties are expected to be dependent, at the very least, on dimension and we consider the pertinent results for d equal to two and three. Most computer experiments investigated the variation of the critical properties with c_I for systems consisting exclusively of tetrafunctional monomers ($f = 4$).

Quantities of interest are the critical exponents ν, which describes the divergence of the pair connectedness length, and γ, which describes the divergence of the mean cluster size $\chi = \Sigma\, s^2 n_s$ as a function of $\varepsilon (= p - p_c)$. Also of interest is the ratio R of the mean cluster size at a fixed value of ε below p_c to the corresponding mean cluster size above p_c.

In two dimensions, Hong *et al* (1984a, b) looked at the critical properties of kinetic gelation with a constant amount of initiators. Their main conclusion is that γ and ν are indistinguishable from their classical percolation values for $c_I > 0.005$. For very low $c_I (\sim 0.0004)$, Hong *et al* found an effective exponent $\nu_{\text{eff}}^{-1} \sim 0.64$ (as opposed to $\nu^{-1} = 0.75$ in percolation) although there is no evidence that the fractal dimension, d_f, has changed. However this change from percolation exponents may be due to finite-size effects, as the lower length cutoff is not the lattice spacing, but the length $l = c_I^{-1/d}$, i.e. the average distance between initiators.

For system size $L \sim l$ one therefore finds an effective exponent ν_{eff} given by the usual finite-size scaling relation

$$|p_c(L) - p_c| \sim L^{-1/\nu_{\text{eff}}} \tag{1a}$$

where $p_c(L)$ is the 'bond percolation threshold' for a finite size L, and $p_c = p_c(\infty)$ the true bond percolation threshold. For such small values of initiators, $p_c \simeq 0$ and $p_c(L) \sim N/L^d$ where N is the number of bonds in a chain generated by the walk of a single initiator. This walk, which has the property of avoiding itself and of being terminated only when self-trapped, for small concentrations of tetrafunctional units barely differs from the kinetic growth walk (KGW) recently introduced (Majid *et al* 1984, Family 1984, Hemmer and Hemmer 1984, Lyklema and Kremer 1984, Havlin *et al* 1984) to describe the growth of a polymer chain. Since the fractal dimension of the KGW, d_{KGW}, is given by $N \sim L^{d_{\text{KGW}}}$, from (1*a*)

$$\nu_{\text{eff}}^{-1} = d - d_{\text{KGW}}. \tag{1b}$$

For $d = 2$, the values of d_{KGW} range from 1.47 for small N to the self-avoiding walk value 4/3 for large N (Peliti 1984), and $\nu_{\text{eff}}^{-1} \simeq 0.53$–$0.66$. This explains the result of Hong *et al* (1984a, b). For $d = 3$ d_{KGW} has an effective value of $d_{\text{KGW}} \simeq 1.9$ for $N \leqslant 5000$ (Majid *et al* 1984, 1985) with a very slow crossover to the self-avoiding walk value leading to $\nu_{\text{eff}}^{-1} \sim 1.1$, which coincides with the percolation critical exponent ν. Therefore for $d = 3$ one does not expect any apparent change from percolation exponents, and this expectation is confirmed numerically.

For $d = 3$, numerical results show that the exponents β, ν and γ are independent of c_I, but R was found to decrease from the random percolation value of ~ 10 at high c_I to about 4 for $c_I = 0.003$. In addition, the numerically observed fractal dimension of the backbone, $d_f^{\text{BB}} = 2.22 \pm 0.10$ was found to be about the same as the fractal dimension of the entire incipient infinite cluster (Chhabra *et al* 1985a, 1986). This is in marked contrast to percolation, where $d_f = 2.53 \pm 0.03$ whereas $d_f^{\text{BB}} = 1.74 \pm 0.04$ (Herrmann and Stanley 1984).

The variation of p_c reported in the literature (Jan *et al* 1983a, b, Herrmann *et al* 1983) shows the expected crossover behaviour of a system in the presence of an active parameter (Harbus and Stanley 1973) where we anticipate a new universality class in the limit $c_I \to c^*$. Here c^* is defined as that concentration of initiators below which the formation of an infinite network is suppressed by the self-trapping of the radicals; c^* can, for all practical purposes, be assumed to be zero in three dimensions. The slope of $p_c(c_I) - p_c(c^*)$ against c_I indicates a crossover exponent, $1/\phi \simeq 0.2$ ($d = 2$) and $1/\phi \simeq 0.3$ ($d = 3$) (see figure 1). If the new universality class, with exponents different from those of percolation, is indeed the limit $c_I \to c^*$, then the critical amplitudes $A_\pm$ are expected to vary as (Harbus and Stanley 1973)

$$A_\pm(c_I) \sim c_I^{(\gamma_{\text{perc}} - \gamma(c^*))/\phi} \tag{1c}$$

where γ_{perc} is the percolation value of the susceptibility exponent and $\gamma(c^*)$ the exponent of the new class. This behaviour will be tested in subsequent work.

Another feature of kinetic gelation which is different from lattice percolation is the presence of oscillations in the cluster size distribution n_s as a function of s (Chhabra *et al* 1984, 1985b, 1986, Herrmann 1985, 1986). This anomalous feature may seem to imply the existence of novel universal features, especially if the *relative* amplitude of

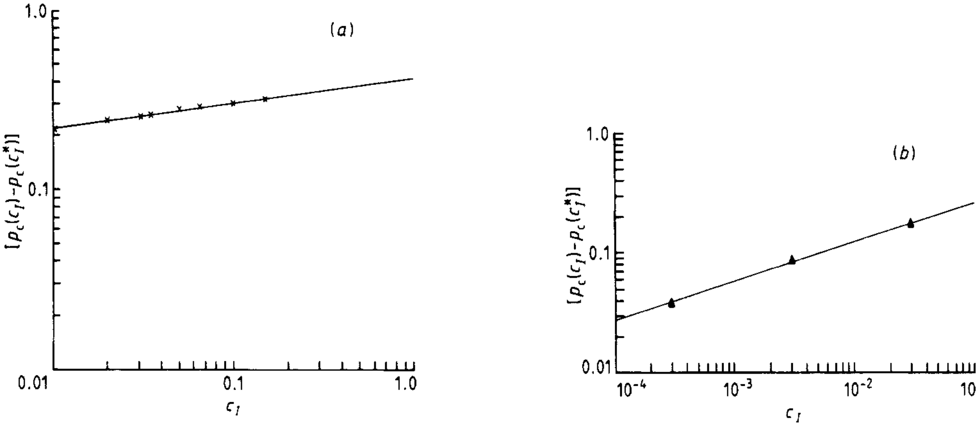

Figure 1. Log-log plot showing the dependence on the concentration of initiators c_I of the percolation threshold p_c. The linearity of the plots for $d = 2, 3$ supports the analogy with the crossover problem in which the role of the parameter is played by c_I and the role of the critical temperature $T - T_c$ is played by $p - p_c$. (*a*) $[p_c(c_I) - p_c(c_I^*)]$ against c_I for $d = 2$ kinetic gelation for c_I in the range 0.01–0.16. The crossover exponent, $1/\phi$, is ~ 0.2. (*b*) Specifically, $[p_c(c_I) - p_c(c_I^*)]$ is plotted against c_I for $d = 3$ kinetic gelation for c_I in the range 3×10^{-2} to 3×10^{-4}. The crossover exponent, $1/\phi$, is approximately 0.3.

the oscillations remains finite as $s \to \infty$, i.e., if $s^\tau n_s$ does not reach a limit as $s \to \infty$. We now show that an amplitude ratio different from that of percolation cannot be explained by the presence of oscillations in the cluster size distribution n_s alone. The size of the critical region, however, may be influenced by the presence of such oscillations. For percolation one has asymptotically

$$n_s = q_0 s^{-\tau} F(\varepsilon s^\sigma) \tag{2}$$

where now $\varepsilon \equiv q_1(p - p_c)$, q_0 and q_1 are non-universal constants, F is a universal scaling function and τ and σ are universal exponents. For the 'susceptibility' (or mean cluster size) one gets, with $\gamma = (3-\tau)/\sigma$ (Herrmann 1985):

$$\chi = \sum_{\text{finite clusters}} s^2 n_s = q_0 \int_0^\infty s^{2-\tau} F(\varepsilon s^\sigma)\, \mathrm{d}s. \tag{3}$$

Let now x be εs^σ. One then obtains (Herrmann 1985, 1986)

$$\begin{aligned} \chi_- &= \frac{q_0}{\sigma}\varepsilon^{-\gamma} \int_{-\infty}^0 |x|^{-1+\gamma} F(x)\, \mathrm{d}x \qquad \text{for } p < p_c \\ \chi_+ &= \frac{q_0}{\sigma}\varepsilon^{-\gamma} \int_0^\infty x^{-1+\gamma} F(x)\, \mathrm{d}x \qquad \text{for } p > p_c. \end{aligned} \tag{4}$$

Thus χ_-/χ_+ is a universal quantity since both q_0 and q_1 cancel out.

Now postulate that the cluster size distribution n_s for *kinetic gelation* is

$$n_s = \alpha_0 s^{-\tau} F(s^\sigma \varepsilon) g(s, \varepsilon) \tag{5}$$

where now $\varepsilon = \alpha_1(p - p_c)$. Further, we assume that $F(x)$ is the *same* scaling function as percolation and $g(s, \varepsilon)$ embodies the oscillatory behaviour. As $\varepsilon \to 0$, we assert that $g(s, \varepsilon)$ tends to some limiting function $g(s)$. The assumption that $F(x)$ is the same function as for percolation is motivated by the fact that the exponents for both systems are identical, and this places severe constraints on the scaling function (Reatto 1970). Now let us substitute $x = s^\sigma \varepsilon$ into equation (5)

$$\chi_\pm = \frac{\alpha_0}{\sigma}[\alpha_1(p - p_c)]^{-\gamma} \int |x|^{\gamma - 1} F(x) g\left[\left(\frac{x}{\varepsilon}\right)^{1/\sigma}\right] \mathrm{d}x \tag{6}$$

where α_0 and α_1 are non-universal quantities and the integrals run from $-\infty$ to 0 for $p < p_c$ and from 0 to ∞ for $p > p_c$. We replace $g[(x/\varepsilon)^{1/\sigma}]$ by its average value $\bar{g}$, since for small ε the function g is rapidly oscillating compared to the function $F(x)$. Thus

$$R = \chi_-/\chi_+ = \frac{\int_{-\infty}^0 |x|^{\gamma-1} F(x)\, \mathrm{d}x}{\int_0^\infty x^{\gamma-1} F(x)\, \mathrm{d}x}. \tag{7}$$

Thus R is predicted to be the same as in percolation, since $\bar{g}$ has also cancelled out.

The main conclusion from the above argument is that if the scaling function $F(x)$ is the same for kinetic gelation as for percolation, the critical amplitude ratios for both systems are the same but the critical region for kinetic gelation is likely to be smaller, dictated by the fact that ε should be small enough for $g(s)$ to be replaced by its average value. This means that the typical cluster size in the critical region must be much larger than the period of the oscillations. Since this period becomes quite large as c_I becomes small, this may become a severe requirement. Indeed, it is possible that this small critical region was in fact not reached in some of the numerical studies of the amplitude ratio.

The measured fractal dimension of the backbone of the incipient infinite cluster of lattice kinetic gelation appears to be quite distinct from the fractal dimension of the backbone of the incipient infinite cluster in lattice percolation. This reflects the fact that biconnected paths are quite common in kinetic gelation, due to the growth process from the restricted random walk of the radicals. As observed by de Arcangelis *et al* (1985) and Meakin *et al* (1985), an infinite number of exponents must be used to completely characterise some fractals, specifically the percolation backbone and the DLA surface. In the past, the rule of thumb was that the critical exponents (γ, ν, β) and critical amplitude ratios characterise the universality class. It is possible therefore to have 'limited' universality in that the usual critical exponents (β, γ, ν, etc) are identical, but others, e.g. the backbone dimension, the fracton dimension and others may be different. This feature is also noticed in the forest fire model (MacKay and Jan 1984) where the fractal and chemical dimensionalities are identical to those of percolation, but the absence of loops leads to backbone and fracton dimensionalities different from those observed for percolation.

In conclusion, we propose that kinetic gelation and percolation may be in the same *limited* universality class: namely the exponents y_T and y_h are identical but other exponents describing the geometric properties may be different. The numerically observed differences in the amplitude ratios could be ascribed to the fact that kinetic gelation may have a rather small critical region due to the presence of a large but finite intermediate length scale on which such structures as oscillations in the cluster size distribution are observed. An analysis of the crossover behaviour of kinetic gelation for $c_I \to c^*$ seems to indicate that the limit $c_I \to c^*$ may in some sense be a multicritical point having the characteristics of kinetic gelation, i.e. a value of R smaller than that of percolation. Thus we expect that in this limit the scaling function $F(x)$ may well be different from that of percolation. A possibility is that for any finite c_I kinetic gelation is described by percolation in a sense that some of the geometrical properties of the incipient infinite cluster, such as the fractal dimension of the backbone, appear to be different. The limit $c_I \to c^*$ may indicate a specific new universality class and we observe its presence through the existence of characteristic crossover phenomena, as in the classical theory of thermal critical phenomena. More accurate measurements are required to check the expected crossover behavior for the critical amplitude ratio. We also propose that other 'dynamic' exponents such as d_w should be measured, since both d_w and d_f^{BB} are physically relevant in the description of transport phenomena.

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