

Real-space renormalization group for kinetic gelation

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We investigate percolation of branching monomers by computer simulation. A Monte Carlo renormalization scheme similar to that of Reynolds *et al.* gives effective critical exponents ν for the correlation length. We compare the behavior of that exponent in two and three dimensions. Also, the exponent ratio γ/ν is estimated from finite-size scaling.

In kinetic gelation, the formation of bonds between neighboring monomers is controlled, at least partly, by the motion of initiators (radicals) which move between the two-functional and multifunctional polymerizable molecules. Once a bond is formed, it can never be destroyed in irreversible gelation; the functionality of a molecule is the maximum number of bonds it can form with its neighbors.

This irreversible kinetic gelation process has been recently investigated with the help of computer simulation by several groups.¹⁻⁷ One of the results was that in three dimensions the critical exponents seemed^{2,5} roughly consistent with those of random percolation theory,⁸ whereas in two dimensions the exponent γ for the "susceptibility" χ (i.e., the second moment of the cluster size distribution, related to the so-called mean cluster size or weight-average degree of polymerization) seemed to change drastically.^{4,6} The aim of the present work is to check these results by using the same method and the same model in both two and three dimensions.

Our method is analogous to the large-cell real-space renormalization-group (RSRG) Monte Carlo simulations of Reynolds and co-workers.⁹ We made, however, some changes to adjust it to the present kinetic gelation model. For random percolation,⁹ one has large lattices with up to 10^{10} independently occupied or empty sites. Thus one changes the concentration p of occupied sites (or bonds) until one has found the percolation threshold p_c with the desired accuracy. (At p_c an infinite cluster appears, and χ diverges.) For kinetic gelation, one has to take into account memory effects and thus needs to construct one bond after the other in the system. Then it is more convenient to monitor the variation of the mean cluster size χ during this process and to determine the gel time t_c as that time at which χ has reached its maximum value. This method of determining p_c may, in fact, have certain advantages over the spanning cluster check used in previous applications of the Monte Carlo renormalization group. Several rules were used by Reynolds *et al.*⁹ to detect a spanning cluster and the RG yielded results (for a given cell size) which were dependent on the rule. Here, as in the case of the Monte Carlo simulation of the Ising model with periodic boundary conditions (where the magnetization is always nonzero), we monitor the susceptibility and use its peak to determine p_c . This rule is independent of the direction in which the largest cluster spans the cell. To each time t_c there corresponds a critical concentration p_c . (In order to ensure observation of

the maximum χ and rule out spurious fluctuations we have waited until χ has decreased by at least 15% from its maximum value in three dimensions while in two dimensions the process was continued until no further growth was possible.)

From then on our method is completely analogous to that of Reynolds *et al.*⁹ From about 10^3 runs we determine the average threshold $\langle p_c \rangle$ and its fluctuation $W_L^2 = \langle p_c^2 \rangle - \langle p_c \rangle^2$, both of which depend on the linear dimension L of the lattice. For large systems, the distribution of the threshold values approaches a Gaussian¹⁰ proportional to $\exp[-(p_c - \langle p_c \rangle)^2/2W_L^2]$, with a maximum approaching $(1/\sqrt{2\pi}W_L)$. Renormalization-group arguments then give⁹

$$1/\nu(L) = \ln(\sqrt{2\pi}W_L)^{-1}/\ln L \quad (1)$$

for the effective size-dependent correlation-length exponent. Moreover, one expects^{9,11}

$$1/\nu(L) = 1/\nu(\infty) + \text{const}/\ln L + O(L^{-\omega}) \quad (2)$$

Thus in a plot of $1/\nu(L)$ vs $1/\ln L$ one expects the data to follow *asymptotically* a straight line with an intercept equal to the true exponent $\nu = \nu(\infty)$. This relation can also be made plausible by finite-size scaling: If the width W_L of the threshold distribution varies as $L^{-1/\nu}$ apart from corrections to scaling, then $\ln(\text{const} \times W_L)/\ln L$ has to follow Eq. (2).

We used a triangular lattice in two and a simple cubic lattice in three dimensions considering only monomers with functionality four. In addition, a fraction c_l of lattice sites was occupied by radicals which could diffuse randomly among the lattice sites if bonds were possible. Each radical formed a string of permanent bonds along its track. More details of the model and its chemical applications are given in Refs. 2, 3, and 5.

Table I gives details of our computer runs on a Control Data Corporation Cyber 76 computer and an IBM 3081 computer. Figure 1 shows the effective reciprocal exponents $1/\nu(L)$ in two and three dimensions for various c_l .

We see that the data do not follow a straight line for the lattice sizes L investigated; but there is some evidence to suggest a monotonic decrease of $1/\nu(L)$ with increasing L . The three-dimensional ν may approach the random percolation value 0.88 ± 0.01 ⁸ for $L \rightarrow \infty$. The two-dimensional results are ambiguous: For $c_l = 0.3$ and 0.2 the extrapolation to large L indicates a value near that for random percolation ($\nu = \frac{4}{3}$). For smaller initiator concentration c_l the

TABLE I. Details of computer runs. One sample for $L=200$ and $c_I=0.01$ in two dimensions took about 1.5 sec on the Control Data Corporation Cyber-76 computer. N is the number of statistically independent runs made for each L and each initiator concentration c_I .

$d=2$		$d=2$		$d=3$		$d=3$	
$c_I=0.01$		$c_I=0.2$		$c_I=0.01$		$c_I=0.005$	
L	N	L	N	L	N	L	N
30	5000	30	1000	10	3000	10	3000
50	5000	50	1000	15	3000	15	3000
70	5000	70	1000	20	2000	20	3000
100	1500	100	500	25	2000	25	2000
150	1500	150	250	30	800	30	1500
200	1000	200	135	35	800	35	1000
250	1700	300	110	40	500	40	800
300	1000			50	500	50	800
400	900			60	300	60	800
600	352					75	800
700	720					90	765
900	200						

same possibility is not ruled out but the data suggest some deviations ($\nu \approx 1.4$ for $c_I=0.1$ and $\nu \approx 1.6$ for $c_I=0.01$) if we treat the last few data on the largest samples as asymptotic. We have also analyzed our data through finite-size scaling,

$$\Delta p_c(L) = |p_c(L) - p_c(\infty)| \sim L^{-1/\nu} f(L/\xi).$$

Thus, (i) for ν_t (trial value) $= \nu$, a plot of $\Delta p_c(L)$ vs $L^{-1/\nu}$ should yield a straight line; (ii) a graph of $\ln \Delta p_c(L)$ vs $\ln L$ is drawn for various trial values [$p_c^t(\infty)$] of $p_c(\infty)$. A straight line, whose slope is $-1/\nu$, is obtained for $p_c^t(\infty) = p_c(\infty)$.

Analysis of the three-dimensional results with these methods indicates that ν is 0.90 ± 0.03 while in two dimensions we find that $\nu = 1.56 \pm 0.05$ for $c_I=0.01$. These results are compatible with our Monte Carlo renormalization group. One may have, however, a complicated crossover,

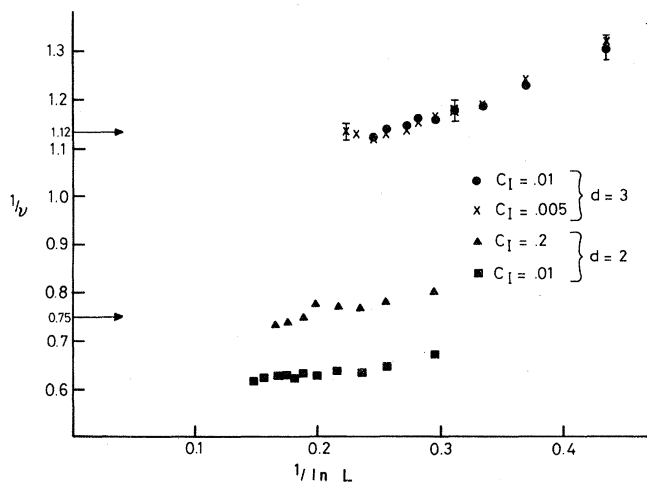


FIG. 1. Variation of the effective correlation length exponent $1/\nu(L)$ with $1/\ln L$, where L is the linear dimension of the lattice. The number on each set of data is the initiator concentration c_I . The asymptotic value for random percolation is marked by arrows in two (bottom) and three (top) dimensions. Error bars \sim symbol size.

as function of c_I , between the universality class of random percolation for large c_I and a single-cluster growth process for small c_I . The accuracy of the present data is not good enough to allow a quantitative study of such a crossover, as was done, for example, by Gouker and Family for another percolation problem.¹² We have not ruled out that ν may be

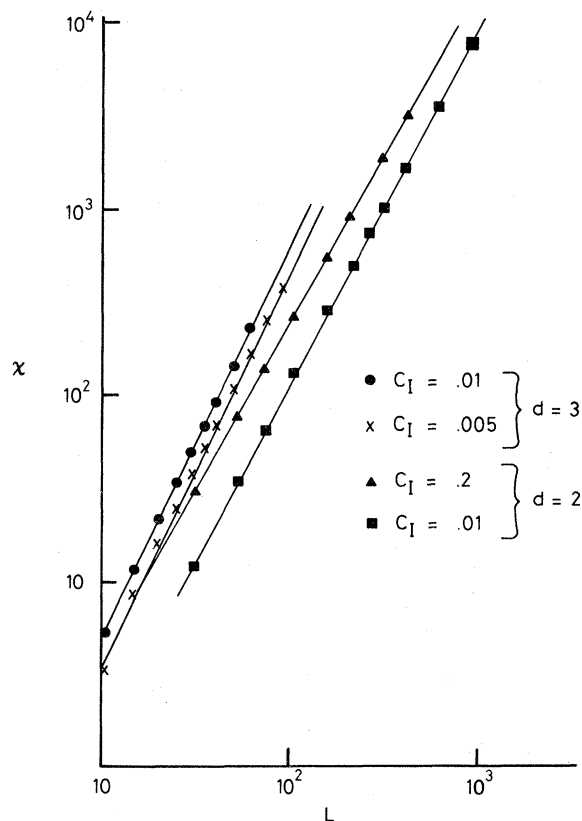


FIG. 2. Variation of the "susceptibility" χ with system size L at the size-dependent gelation threshold; the symbols correspond to the same c_I as in Fig. 1. The slope in this log-log plot gives γ/ν ; for random percolation its values are 1.792 in two and about 2.0 in three dimensions.

a continuously varying function of c_I ; thus careful, accurate calculations of ν for various values of c_I are required to answer this question.

We also looked at the value of χ as a function of L at the percolation threshold of the finite sample. It should vary as $L^{\gamma/\nu}$ according to finite-size scaling. Figure 2 shows χ , in accord for three dimensions ($\gamma/\nu \approx 2.1$) with the results of Herrmann, Lander, and Stauffer,² while in two dimensions γ/ν is 1.79 at $c_I=0.2$ to about 1.83 at $c_I=0.01$. We, therefore, conclude that although ν and hence y_p is a function of c_I (the nature of the function to be determined), y_h and hence the fractal dimensionality appears to be independent of c_I for the range of c_I investigated.

To summarize: Our results are in accord with random percolation exponents for the three-dimensional kinetic

gelation model but allow for nonrandom percolation values in two dimensions for small initiator concentrations c_I .

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