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¹³H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford Univ. Press, Oxford, England, 1971), Sec. 6.5.

¹⁴Frustration exists for any even distribution of ξ and η . Use $\text{sgn}(\xi_i)$ and $\text{sgn}(\eta_j)$ instead of the present ξ_i and η_j .

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¹⁶Full details, including the Gaussian interaction, will be given in a paper written in collaboration with A. C. D. van Enter and J. Canisius.

New Universality Class for Kinetic Gelation

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(Received 8 June 1982)

Percolation is often used as a model for critical behavior of the sol-gel transition. A three-dimensional kinetic model for gelation, similar to that of Manneville and de Seze, is investigated with a Monte Carlo method. By looking at the ratios of the critical amplitudes of the "susceptibility" (weight-average degree of polymerization) below and above the percolation threshold, clear evidence is found that this model is neither in the universality class of standard percolation nor in that of classical (Flory-Stockmayer) theory.

PACS numbers: 82.35.+t, 05.70.Jk, 61.40.Km, 64.60.Fr

The sol-gel transition¹ is apparently more complicated than predicted by the current theories. This was first shown in 1976 when Stauffer² and de Gennes³ suggested that percolation on a three-dimensional (3D) lattice is a good model for critical phenomena in gelation, since the classical theory of Flory⁴ and Stockmayer⁵ is identical to percolation on a Cayley tree. As in the case of coagulation⁶ or some other kinetic percolation processes⁷ there has been mounting criticism¹ that standard percolation does not consider the growth process of the gelation, i.e., the kinetics. It has been suggested that a kinetic gelation model might not even be in the universality class of standard percolation.⁸

In this Letter we present Monte Carlo evidence that indeed a rather realistic growth model for the sol-gel transition, similar to that of Manneville and de Seze,⁸ is *not* in the same universality class as percolation.

We want to describe a model of gelation for the irreversible free-radical copolymerization proc-

ess. Here the sol consists of small monomers and the gelation is initiated by radicals. The radicals saturate, opening up a double bond of a monomer and leaving one bond in the monomer unsaturated. This creates a new radical that continues the growth process. We use $L \times L \times L$ simple cubic lattices with periodic boundary conditions containing a concentration c_2 of bifunctional sites and a concentration $1 - c_2$ of tetrafunctional sites. (A bifunctional or tetrafunctional site can have at most two or four occupied bonds incident, respectively.) The initialization is performed by randomly occupying a fraction c_l of bonds. For simplicity, no adjacent bonds are allowed to be occupied. Chemically, an occupied bond means a broken double bond between carbon atoms. The two free ends of an occupied bond are the radicals or "active centers." Now, the growth process is performed as follows: We randomly choose an active center and an adjacent bond of this center. If the other end of this bond is not forbidden, i.e., is not a bifunctional or tetrafunctional site al-

ready having two or four incident occupied bonds, respectively, the bond is occupied and the active center is shifted to the other end of the bond. In this way more and more bonds are occupied. A typical stage of growth where the fraction p of occupied bond is $p=0.17$ is shown in Fig. 1. The active centers can annihilate if there is only one bond between them and this bond becomes occupied. Active centers can become "stuck" if all surrounding sites are forbidden. In summary, we model an irreversible gelation process where the chemical conversion factor p for the bonds increases as a function of time.

We simulated this growth model by a Monte Carlo method. The molecular weight distribution n_s of the macromolecules, i.e., the number per lattice site of clusters containing s sites each, was calculated at different fractions p of occupied bonds. By initiating several hundred independent growth processes we determined the susceptibility $\chi = \sum s^2 n_s$, its statistical error, and the mean gel fraction $G = \text{fraction of sites in the "infinite cluster."}$ ¹¹

The susceptibility is expected to diverge as

$$\begin{aligned} \chi &= C_+ (p - p_c)^{-\gamma} \text{ for } p > p_c, \\ \chi &= C_- (p_c - p)^{-\gamma} \text{ for } p < p_c, \end{aligned} \tag{1}$$

and $R = C_-/C_+$ near the gelation threshold p_c ,

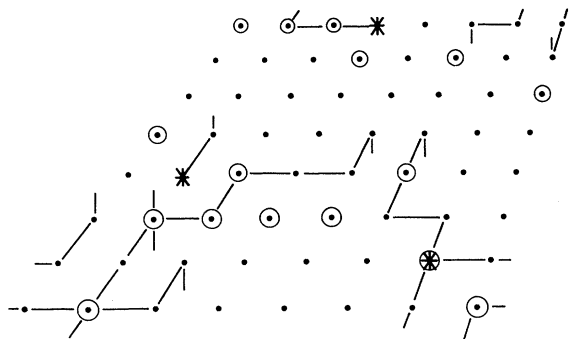


FIG. 1. Top plane of an $8 \times 8 \times 8$ lattice with bifunctional monomers (dots) and tetrafunctional monomers (dots with circles). The occupied bonds (solid lines) can also connect monomers on opposite edges because of the periodic boundary conditions. Only active centers (stars) in the plane are shown. Bonds directed out of this plane, i.e., up or down, connect monomers in the plane above or below and can well end in active centers in these planes. This is the result of a Monte Carlo simulation at a concentration $c_2=0.8$ of bifunctional monomers, after the total number of bonds occupied by radical reactions has increased from an initial value of 10 to 261.

where the infinite cluster first appears producing the gel. (We found p to be a smooth function of time, with no irregularities⁹ apparent at the threshold.)

In Fig. 2(a) we plot χ above and below $p_c=0.074$ logarithmically versus $|p - p_c|/p_c$ for $c_1=0.003$ and $c_2=0$ for different lattice sizes. p_c was determined by the criterion that the slopes γ in this log-log plot should be equal on both sides of p_c as required by scaling.¹⁰ Values for p_c determined in this way are consistent with estimates of the value of p for which the gel fraction goes to zero. We see in Fig. 2(a) that we obtain straight lines for a fair range of values. From these linear regions we obtain

$$\gamma = 1.98 \pm 0.10 \text{ and } R = 2.6 \pm 0.8. \tag{2}$$

For comparison we plot χ for standard bond percolation¹¹ in Fig. 2(b) for comparable lattice size, and using the same method of analysis we find

$$\gamma = 1.74 \pm 0.06 \text{ and } R = 10.0 \pm 1.6. \tag{3}$$

These values agree very well with those obtained by other authors, e.g., $R=8-11$ (see Nakanishi and Stanley¹² and Hoshen *et al.*¹²).

Because the finite-lattice effects in Fig. 1(a) are very strong, we also analyzed our results using finite-size scaling¹⁰ as shown in Fig. 3. p_c , γ , and ν were adjusted in such a way that above and below p_c the points for different lattices sizes collapse onto a single curve. Furthermore, the

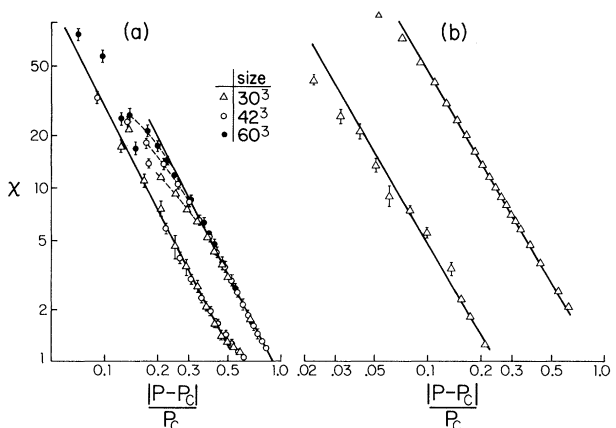


FIG. 2. Susceptibility vs $|p - p_c|/p_c$ for (a) kinetic gelation at $c_1=0.003$, $c_2=0$, and $p_c=0.074$; and (b) bond percolation, $p_c=0.264$. The statistical errors are shown whenever they are larger than the size of the symbols used. The dashed lines are guides to the eye.

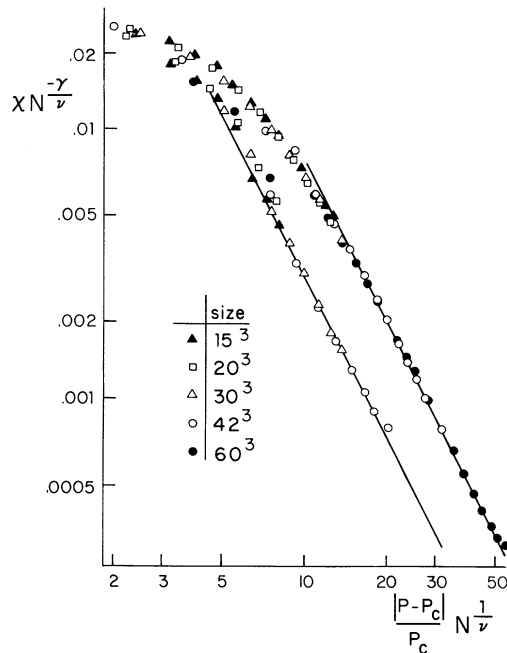


FIG. 3. Finite-size scaling of the susceptibility for $c_1=0.003$ and $c_2=0$ with $p_c=0.074$, $\gamma=2$, $\nu=1$. The straight lines have a slope of -2 ; $R=2.7\pm 0.8$.

linear region of both curves must have slopes equal to $-\gamma$. Within the errors of the individual points the curves scale with $\gamma=2.0\pm 0.1$ and $\nu=1.0\pm 0.2$ yielding $R=2.7\pm 0.8$. Comparing with Eq. (2) we see that a careful finite-size analysis confirms the result obtained from the straightforward log-log plots.

Generally the ratio R is considered to be universal for percolation.¹³ Our value for R in Eq. (2) is clearly different from the standard percolation value in Eq. (3) and also different from $R=1$ which is the ratio predicted by the classical theory of Flory and Stockmayer. Therefore, the kinetic gelation model lies in a different universality class. The exponents γ for our model of kinetic gelation, Eq. (2), and standard percolation, Eq. (3), are too close to reliably state whether or not they are different. The same applies to ν , which we found to be slightly larger in the kinetic model compared to standard percolation.

In Fig. 4 we perform the same analysis as in Fig. 3 for a large concentration of bifunction monomers, $c_2=0.9$. We find essentially the same ratio R and exponents as for $c_2=0$. The same result is obtained for $c_2=0.6, 0.8$, and 0.95 . Thus, the models for all concentrations c_2 appear to lie in the same universality class. This result contradicts a conclusion of Manneville and de Seze⁸

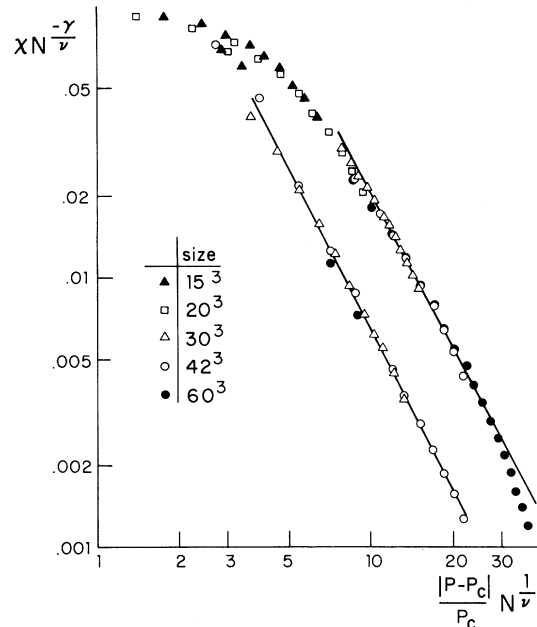


FIG. 4. Finite-size scaling of the susceptibility for $c_1=0.003$ and $c_2=0.9$ with $p_c=0.118$, $\gamma=2$, $\nu=1$. The straight lines have a slope of -2 ; $R=3.2\pm 0.9$.

but is in accord with a recent test of universality for branching chains by Ord and Whittington.¹⁴

If we increase (decrease) c_1 by an order of magnitude, we find $p_c=0.166$ ($p_c=0.0325$) and R increases (decreases). However, the error bars for the increased (decreased) R overlap with the error bars for R in Eq. (2).

In summary, our results confirm our initial expectation that the sol-gel transition is more complicated than currently believed. We find that the kinetic gelation model presented belongs to neither the same universality class as standard percolation nor the universality class of the classical theory. The experimental investigation of R unfortunately is still difficult to interpret⁹ so that a reliable experimental test still needs to be done for R . Presumably the kinetic aspects, not other deviations from random percolation, are responsible for the formation of the new universality class. It remains open whether different kinetic models belong to the same universality class as the present model.

More detailed results and experimentally measurable quantities will be presented elsewhere. As a next step for improving the understanding of the sol-gel transition we suggest the inclusion of mobility^{6,15} and of a solvent,¹⁶ and eventually the removal of the lattice restriction.

We would like to thank L. de Seze for sending a preprint of his work prior to publication. We also wish to thank A. Coniglio, F. Family, P. G. de Gennes, H. Nakanishi, S. Redner, S. Ross-Murphy, H. E. Stanley, B. Souillard, and W. H. Stockmayer for helpful comments and suggestions. One of us (D.S.) wishes to thank the University of Georgia for its hospitality during the final stages of this work. This work was supported in part by the National Science Foundation, the U. S. Office of Naval Research, and the U. S. Army Research Office.

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