Universality of an irreversible kinetic gelation model

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We present Monte Carlo results for the critical exponents γ and β and the amplitude ratio R of percolation susceptibilities for kinetic gelation model. The values of γ and ν for the kinetic gelation model have been reported to be roughly the same as the standard percolation values, but the amplitude ratio R has been found to differ strongly from the percolation value, implying that the kinetic gelation model might be in a different universality class from that of the standard percolation model. However, our estimates exhibit that both γ, β and R are similar to the corresponding percolation values within the statistical errors, and thus, we are not able to rule out the possibility of strong universality between the two systems. We point out that the cause of this difference may be the different sampling technique used for measuring the percolation susceptibilities. [S1063-651X(97)06509-4]

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I. INTRODUCTION

The ''kinetic gelation'' is the irreversible growth model designed to investigate the formation of an infinite macromolecule, i.e., gelation [1]. The first study of the sol-gel transition was carried out by Flory [2] and Stockmayer [3] by a simple model which was later identified as a percolation on a Bethe lattice. Manneville and de Seze [4] have developed a more realistic model of additive copolymerization by radicals. In such a model, initially all sites are assumed to be in a sol phase, which consists of small monomers of multiple functionalities. The gelation is initiated by radicals which saturate, opening up a double bond of a monomer and leaving one bond in the monomer unsaturated. This unsaturated bond acts as a new radical which, in turn, opens up another double bond of the neighboring monomer. As this process continues, an infinite macromolecule occurs at a certain fraction of the polymerized sites, i.e., at gel-point p_c.

The universality of the kinetic gelation model has been intensively studied via Monte Carlo simulations. Herrmann *et al.* [5,6] carried out simulations in three dimensions (3D) and found that the critical exponents γ and ν, which characterize, respectively, the susceptibility and the correlation length, are roughly the same as the corresponding percolation values; however, the amplitude ratio R of susceptibilities, which is supposed to be universal, has been found to be considerably smaller than that of a percolation model. Based on this, they claimed that the kinetic gelation model belongs to a universality class different from that of the lattice percolation. Similar conclusion was also drawn in 2D by Rushton *et al.* [7], who obtained both the exponents and the amplitude ratio considerably different from the percolation counterparts. Family [8] also estimated the fractal dimension d_F of an infinite network of gel phase in 2D and found that d_F depends upon the concentration of initiators c_I and is smaller than that of a percolation network. Since the fractal dimension of an infinite percolation cluster is related to the static critical exponents β and ν via $d_F = d - \beta/\nu$ [9], d being the embedding lattice dimensionality, the different estimates of d_F imply that at least one of the critical exponents is different from the percolation value, suggesting a different universality between kinetic gelation and percolation models. This conclusion, however, was ruled out by more elaborate calculations and the fractal dimension was found to be similar to the percolation value, independent of c_I [10]. Considering these works, it seems that various critical exponents for the kinetic gelation model are similar to the corresponding percolation values, while the amplitude ratio still remains unresolved. This raises us the suspicion for a ''strong'' universality between the two systems, leaving the possibility of unusual ''weak'' universality in the sense that only the static exponents are the same while the amplitude ratio differs.

Recently, similar results have been reported for various percolation models for which the critical exponents are the same but the amplitude ratio is found to be considerably different from the lattice percolation value. Kim *et al.* [11] have carried out simulations for randomly bonded percolation and obtained the exponent γ close to the lattice percolation value, while they estimated R to be at least one order in magnitude smaller than the percolation value. In their discussions on this ''unusual'' behavior, they have referred to the kinetic gelation model as a similar example. Motivated by their work, simulations for continuum percolations of various objects, such as overlapping spheres, capped cylinders, widthless sticks, overlapping disks, and penetrable-concentric-shell (PCS) model, were also carried out and the results obtained were, in principle, similar to those of the randomly bonded percolation model [12,13].

More recently, Lee and his collaborator [14–16] studied, in a series of works, the continuum percolations of overlapping disks and spheres and of PCS model and the randomly bonded percolation both in 2D and 3D, devoting for accurate determinations of R. He found several possible sources of errors occurring in estimating R which were mostly caused by the finite size effect. After the finite size effect carefully taken into account, he showed that the values of R were similar to the percolation values for all models he studied, indicating a *strong* universality among the off-lattice, continuum percolations of such models and the standard lattice percolation model. In this line of study, it is natural to make clear whether or not the kinetic gelation model is also in this vein.

In this paper, we study by Monte Carlo simulation the critical behavior of the kinetic gelation model both in 2D and 3D. We estimate the exponents γ and β characterizing, respectively, the susceptibility and the gel fraction (which is equivalent to the order parameter in critical phenomena) given as

$$\chi(p)=\sum_s{}' n_s s^2 \sim \begin{cases} C_-(p_c-p)^{-\gamma} & \text{for } p<p_c \\ C_+(p-p_c)^{-\gamma'} & \text{for } p>p_c, \end{cases} \quad (1)$$

with $\gamma=\gamma'$, and

$$G(p)=p-\sum_s{}' n_s s \sim (p-p_c)^{\beta} \quad \text{for } p>p_c, \quad (2)$$

where n_s denotes the density of clusters of size s and the prime implies that the spanning cluster should be excluded in the sum. The parameter p, corresponding to the probability of occupation in the percolation, is defined as the concentration of the polymerized sites [7], or often as the fraction of the polymerized bonds [5,6]. The amplitude ratio $R=C_-/C_+$, which is known to be universal for standard percolation model [17] and is believed to be so for other percolation models as well while the amplitudes C_- and C_+ themselves are nonuniversal, is intensively studied for various values of c_I and for various size system.

We have calculated $\chi(p)$ and $G(p)$ for various size systems. The largest cluster has been eliminated only above p_c for the implication of the prime on the sums in Eqs. (1) and (2). (Note that since we do not know accurate values of the gel point we estimate χ both with and without the largest cluster for all p and select appropriate data to use for analyses.) We found that the values of both γ and β are within the errors of less than 10% from the corresponding percolation values both in 2D and 3D. This agreement is even better than the agreement of the previous results with the percolation values. Our estimates of R are also within the error bounds of the percolation values for all cases of c_I, suggesting a *strong* universality between percolation and kinetic gelation.

II. MONTE CARLO PROCEDURE

Our simulation methods are basically similar to those of the previous works of Ref. [7] for 2D and of Ref. [6] for 3D simulations. At the beginning of each simulation, all lattice sites are assumed to be in the sol phase with the fractions of the tetrafunctional units c_t and the bifunctional units c_b, with $c_t+c_b=1$ (no solvent molecule is assumed).

A. Two dimensions

Since the monomers of a bifunctional unit contribute only on a linear link, all sites on a square lattice are initially assumed to be occupied by tetrafunctional units, i.e., $c_t=1$ and $c_b=0$. The $c_I L^2$ initiators of concentration c_I are randomly distributed in a given system, assuming that each initiator acts as an active center for polymerization. Then, one of those active centers and its neighboring bond are selected randomly. If the new site connected by that bond is yet unsaturated (i.e., has less than four incident bonds), the bond is completed and the active center is moved to a new site. If the bond cannot be completed, another attempt is made with a different active center. We keep track of the positions of all active centers and, when an antive center is trapped by being surrounded by closed sites or any two active centers happen to meet and annihilate, we eliminate such active centers from the list. This allows us to continue the simulations until either all active centers are trapped or the desired values of p are achieved. This way of checking the trapping of the system is different from the previous works in which the simulation is terminated if a certain number of attempts of polymerization are failed by selecting either a trapped active center or an already completed bond.

The degree of polymerization can be determined in two ways. First, we take the statistics whenever the desired number of monomers are polymerized, and second, the statistics is sampled after a certain number of bonds are completed. The former provides us with data at exact concentration, while the latter allows us to sample the data at a certain interval of polymerization time. We, however, found that both methods yield essentially the same results within the statistical errors. In this paper, we present our simulation data obtained by the latter method so that our data can be utilized for comparison with those of the previous works.

B. Three dimensions

In 3D, the simulation method is basically similar to that in 2D, except that the algorithm is designed to describe the physical situation better than in 2D. Each site of simple cubic lattice is initially occupied by either a tetrafunctional unit with concentration c_t or a bifunctional unit with concentration c_b $(=1-c_t)$. Initially a fraction c_I of $3L^3$ links (bonds) connecting nearest neighbors are assumed to be occupied randomly by initiators, each end of those links carrying an active center. Since the number of bonds in a simple cubic lattice of side L is $3L^3$ and since each initiator contributes two active centers, the total number of active centers is $6c_I L^3$. The sampling and averaging procedures are essentially the same as those in 2D.

III. RESULTS AND DISCUSSIONS

We have carried out simulations for various values of c_I and L for both 2D and 3D, and the results were averaged over 100–5000 realizations, depending on the values of c_I and L. (Note that the number of active centers is initially $c_I L^2$ in 2D while that in 3D is $6c_I L^3$.)

Data are analyzed in a usual way. We plot on a double logarithmic scale the susceptibilities calculated excluding the largest cluster for $p>p_c$ and without excluding the largest cluster for $p<p_c$. We then measure accurate values of p_c^{eff}, assuming the same power law below and above it. This value of p_c^{eff} is considered to be an effective gel point for the given size of system and might be (slightly) different from the true p_c. It should be noted that the parameter p is defined as the concentration of the polymerized sites in 2D and the fraction of the polymerized bonds in 3D. We defined it as this so that one can compare our data with those of the previous works. (Note that our definition of p in 2D is identical to that in Ref. [7] and that in 3D is identical to that in Refs. [5,6].) The values of γ and R can be obtained, respectively,

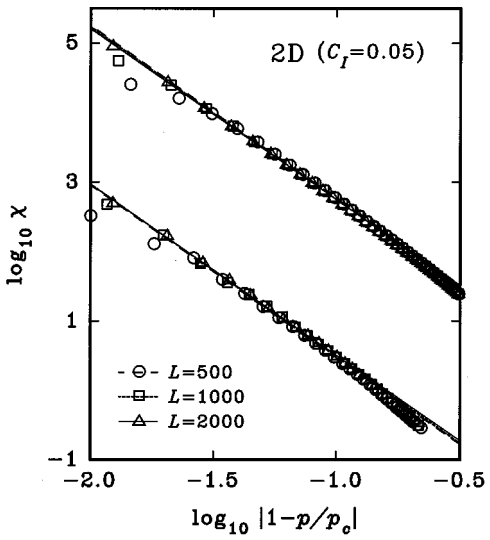

FIG. 1. Monte Carlo data of χ for 2D kinetic gelation model for $c_I=0.05$ for three typical values of L, plotted on a double logarithmic scale. The dashed, dotted, and solid lines are the regression fits obtained assuming the same power-law behavior below and above p_c.

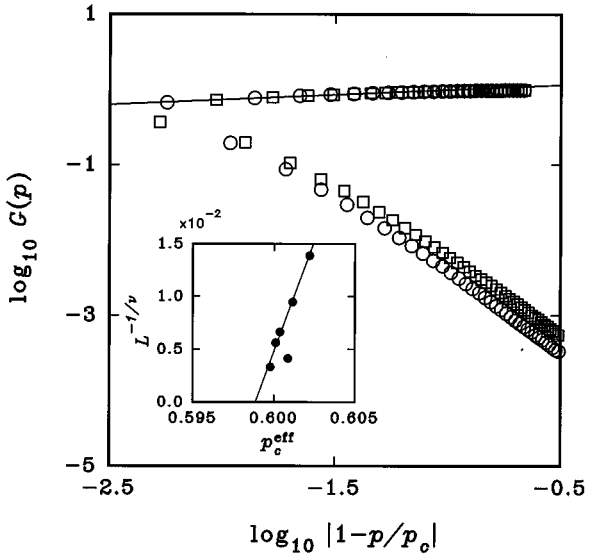

FIG. 2. Monte Carlo data of $G(p)$ for 2D kinetic gelation model for $c_I=0.05$ for two typical values of L, $L=1500$ (square) and $L=2000$ (circle). The solid line on the upper set of data is the regression fit using $p_c=0.5989$, obtained from the scaling relation of Eq. (3) as shown in the inset.

from the slope of the power-law fits and from the displacement between the fits below and above $p_c^{\rm eff}$.

A. Critical exponents and amplitude ratio for various size systems

In order to investigate how the size of system affects the critical behavior, we have carried out extensive simulations for a selected value of c_I in each dimension and for various size systems, i.e., $c_I=0.05$ for $L=300$, 500, 800, 1000, and 2000 in 2D, and $c_I=0.003$ (with $c_t=0.4$) for $L=40$, 60, 80 100, 150, and 200 in 3D.

Plotted in Fig. 1 on a double logarithmic scale is the 2D Monte Carlo data of χ (for $c_I=0.05$) for three typical values of L, $L=500$, 1000, and 2000. Clearly, data for all selected values of L exhibit reasonably good power-law fits. The estimates of γ from the plot are $\gamma=2.49\pm0.05$ for $L=500$ and $L=1000$ and $\gamma=2.46\pm0.06$ for $L=2000$. (Note that the errors listed are the regression errors and there might be additional statistical errors not taken into account.) These values are slightly larger than the known percolation value $\gamma=\frac{43}{18}$ [18]. However, considering that the errors of χ are typically of the same order as the value of susceptibility itself, they are considered to be similar to the percolation value. Results for other values of L not shown in the figure are basically similar to those in Fig. 1.

The exponent β can be obtained from the power-law plot of the gel fraction $G(p)$, given in Eq. (2). However, we found from numerical investigation that the estimate of β is very sensitive to the choice of p_c. Thus, without accurate value of p_c, it is not simple to estimate β from the power-law plot, unlike for γ. In order to resolve such a difficulty, we estimate p_c, in a way similar to the renormalization calculations, by extrapolating the values of $p_c^{\rm eff}(L)$ in the $L\to\infty$ limit, using the scaling relation

$$|p_c-p_c^{\rm eff}(L)|\sim L^{-1/\nu}. \tag{3}$$

We obtained $p_c\simeq0.5989$ for $c_I=0.05$, using the values of $p_c^{\rm eff}$ obtained from the power-law fits of χ. Plotted in Fig. 2 are the fractions of the largest cluster for the two largest systems we used in the simulation, i.e., for $L=1500$ and 2000. The inset shows the extrapolation of $p_c^{\rm eff}$; the intercept on the abscissa is the gel-point. Since the gel fraction is the fraction of the largest cluster above p_c, the exponent β can be obtained from the slope of the plot for $p>p_c$ (upper sets of data). The regression fit (solid line) gives $\beta\simeq0.13\pm0.01$, which is close to the percolation value $\beta=\frac{5}{36}$ [9].

We also estimated from our data the amplitude ratio of susceptibilities. By numerical investigation, we found that the reliable data of R for small c_I, such as $c_I\leqslant0.05$, can only be obtained for sufficiently large L. For example, for $c_I=0.05$, the estimates for $L\leqslant500$ vary significantly depending on how the fitting region of the power-law is selected; however, for L beyond $L=500$, data yield consistent values of R. We found that the estimates of R for $500\leqslant L\leqslant2000$ appear to decrease slightly as L increases and all estimates lie between 173 and 198 which are close to the percolation value $R=196\pm40$ [19,20]. However, the size dependence of R for the gelation model is not as significant as that for the continuum percolations of the PCS model and for the randomly bonded percolations. All estimates of R for various L are within the error bounds of the percolation value.

From these estimates, we assert that the amplitude ratio as well as the various critical exponents for the kinetic gelation model is similar to the corresponding percolation value in 2D, suggesting a strong universality between percolation and gelation models, unlike the previous work [7]. The estimates of γ, p_c, and R for various values of L are summarized in Table I.

Results in 3D are qualitatively similar to those in 2D. Plotted in Fig. 3 are the data of χ for $c_I=0.003$ and $c_t=0.4$ for selected values of L: $L=60$, 100, and 200. The values estimated from the plot are $\gamma=1.87\pm0.06$ for $L=60$, $\gamma=1.84\pm0.02$ for $L=100$, and $\gamma=1.81\pm0.03$ for

TABLE I. The estimates of $p_c^{\rm eff}$, γ, and R for various L from the power-law fits for 2D kinetic gelation model for $c_I=0.05$.

L	$p_c^{\rm eff}(L)$	$\gamma(L)$	$R(L)$
300	0.60221	2.53 ± 0.10	211 ± 45
500	0.60116	2.49 ± 0.05	198 ± 30
800	0.60038	2.48 ± 0.07	183 ± 20
1000	0.60014	2.49 ± 0.05	183 ± 20
1500	0.60088	2.49 ± 0.08	187 ± 20
2000	0.59979	2.46 ± 0.06	173 ± 15

$L=200$, all of which are consistent with the percolation value $\gamma\simeq1.80$ [9].

The values of R estimated from the displacements between the power-law fits for $p<p_c$ and $p>p_c$ were found to be $R\simeq6.8$ for $L=60$ and $L=100$ and $R\simeq7.0$ for $L=200$. These values appear to be similar to (although slightly smaller than) the known percolation value (known to be between 8 and 11 [19]), but considerably larger than the previous estimate $R=2.8\pm1.0$ for the same values of c_I and c_t [5,6]. The cause of such a large difference is due to the different sampling technique of $\chi(p)$. Although the authors of the previous works did not mention how they sampled for χ, we found by numerical investigation that they have measured χ excluding the largest cluster both below and above p_c. As an evidence, we found the peak of $\chi(p)$ for $L=60$ (for $c_I=0.003$) to be 1.45×10^3 at $p\simeq0.083$ which is nearly 7 times larger than that obtained in the previous work in [6] for the same parameters. Such an underestimation of $\chi(p)$ close to (but still less than) p_c appears to have yielded an underestimation in R.

Shown in Fig. 4 is the gel fraction plotted on a double logarithmic scale for $L=150$ and 200, using $p_c=0.0838$ obtained from the scaling relation in Eq. (3). The regression fit

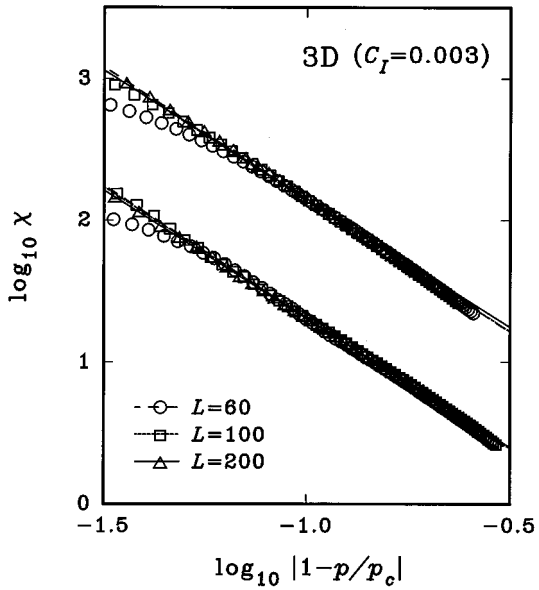

FIG. 3. Monte Carlo data of χ for 3D kinetic gelation model for $c_I=0.003$ and $c_t=0.4$ for three typical values of L, plotted on a double logarithmic scale.

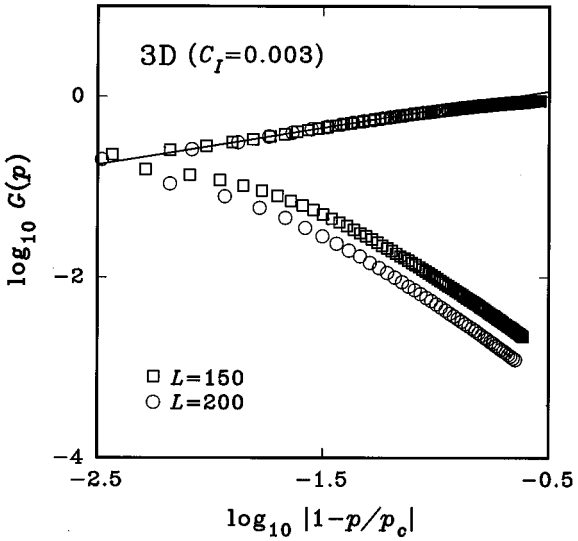

FIG. 4. Monte Carlo data of $G(p)$ for 3D kinetic gelation model for $c_I=0.003$ for two typical values of L, $L=150$ (square) and $L=200$ (circle), plotted using $p_c=0.0838$ obtained from the scaling analysis.

(solid line) yields $\beta\simeq0.42\pm0.03$, which is again consistent with the percolation value $\beta\simeq0.4$ [9].

B. Finite size scaling analyses

In the previous subsection, we have presented the critical exponents and the amplitude ratio for various size systems. In many instances, researchers employ the finite size scaling analyses of the susceptibilities and the order parameters to verify the estimates of the critical exponents and to estimate the infinite system results of R. However, Lee has recently shown that there are subtleties for the finite size scaling analyses if the estimates of R depend upon the size of the system. He showed that such scaling analyses failed to provide an infinite system result of R for the cases of the continum percolation of PCS model and the randomly bonded percolation model. However, we have seen that the amplitude ratio for the kinetic gelation model does not depend strongly on the size of system. It is, therefore, interesting to study the finite size scaling analyses with our Monte Carlo data for kinetic gelation model.

The susceptibility defined in Eq. (1) for any finite system, $\chi(p,L)$, can be written as a function of two competing lengths L and ξ ($\sim|p-p_c|^{-\nu}$):

$$\chi(p,L)=|p-p_c|^{-\gamma}f(L,\xi). \tag{4}$$

Since, according to the universality, there should be only one relevant length, one can write $f(L,\xi)$ as a function of the ratio of two lengths, i.e., as a function of $L/\xi\propto L|p-p_c|^{\nu}$ near p_c. After a change of variables, one can write the scaling relation as

$$\chi(p,L)=L^{\gamma/\nu}g(L^{1/\nu}|p-p_c|), \tag{5}$$

with the extreme conditions of the scaling function given as

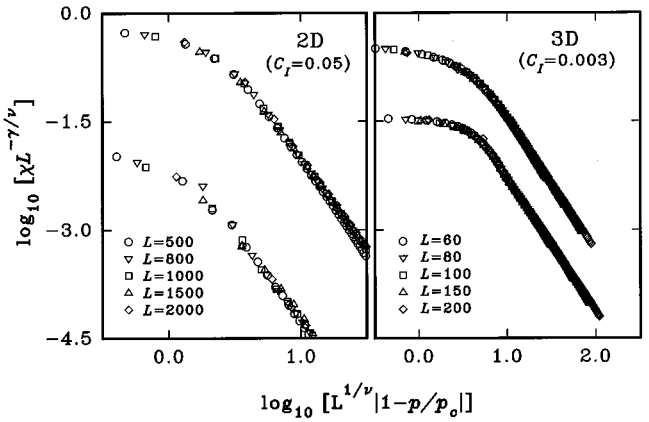

FIG. 5. Scaling function of Eq. (5) plotted for 2D kinetic gelation model using $\gamma=\frac{43}{18}$, $\nu=\frac{4}{3}$, and $p_c=0.600$ (left), and for 3D model using $\gamma=1.8$, $\nu=0.88$, and $p_c=0.0839$ (right). Monte Carlo data show fairly good data collapsing for both cases.

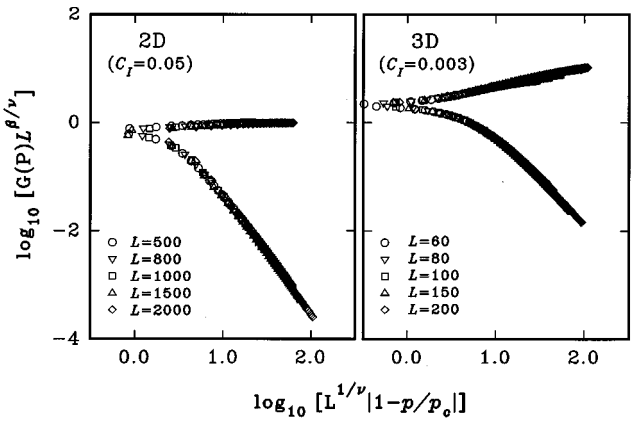

FIG. 6. Scaling function of Eq. (7) plotted for 2D kinetic gelation model using $\beta=\frac{5}{18}$ and $\nu=\frac{4}{3}$ (left) and for 3D model using $\beta=0.4$ and $\nu=0.88$ (right).

$$g(x)=\begin{cases}\text{const} & \text{for } x\ll 1,\\ x^{\beta} & \text{for } x\gg 1.\end{cases} \tag{6}$$

This implies that the data of $\chi(p,L)L^{-\gamma/\nu}$ for various L and p plotted against $x\equiv L^{1/\nu}|p-p_c|$ collapse onto a single curve.

We plotted the scaling function for various L, using the percolation values of ν and γ, i.e., $\nu=\frac{4}{3}$ and $\gamma=\frac{43}{18}$ for 2D and $\nu\simeq 0.88$ and $\gamma\simeq 1.8$ for 3D. Figure 5 is the scaling function for $c_I=0.05$ in 2D (left) and $c_I=0.003$ in 3D (right) kinetic gelation models, obtained using, respectively, $p_c=0.600$ and 0.0839. It should be noted that these values of p_c are those which were obtained by extrapolating $p_c^{\text{eff}}(L)$ using the scaling relation in Eq. (3). Clearly data show good collapsing in the critical region where $|p-p_c|\ll 1$ and $L\gg 1$ hold. This is a good indication that the values of ν and γ for the kinetic gelation model are similar to the corresponding percolation values. If one measures the slopes and the displacements of the fits, one would get γ and R similar to those we presented earlier. We have also studied similar scaling analyses with the different sets of γ and ν, such as those obtained in the previous works [5–7]; however, we were not able to observe the data collapsing better than those in Fig. 5.

Similar analysis can also be made for the gel fraction to verify our estimates of β. The scaling function of $G(p,L)$ can be written, in a similar way to the susceptibility, as

$$G(p,L)=L^{-\beta/\nu}h(L^{1/\nu}|p-p_c|). \tag{7}$$

Plotted in Fig. 6 are the data for $G(p,L)L^{\beta/\nu}$ against the scaling variable $x\equiv L^{1/\nu}|p-p_c|$ for 2D (left) and 3D (right) kinetic gelation models for the same parameters as in Fig. 5. The values of p_c used in the plot are $p_c=0.6022$ for 2D and $p_c=0.084$ for 3D, the former of which is slightly larger than that we used for the scaling of $\chi(p,L)$. (We have tested with other values of p_c, but these values yielded the best data collapsing.) Clearly data show good collapsing for both dimensions, implying that the exponent β for the kinetic gelation model is also similar to the percolation value. For p far away from p_c (rightmost region in the plots), data for smaller L deviate slightly from those of larger L. We believe this behavior to be due to that the data for those values of p are out of the scaling region.

The degrees of data collapsing for the scaling relations in Eqs. (5) and (7) are much better than the previous works of this kind, particulary in the region of $|p-p_c|\ll 1$. This leads us a conclusion that the values of the universal critical exponents and the amplitude ratio for the kinetic gelation model are similar to the corresponding percolation values.

C. Simulations for various initiator concentrations

Since the exponent γ in 2D were found to vary depending on the values of c_I [7] and since slightly different values for different c_I were also reported in 3D [21], it is interesting to carry out simulations for other values of c_I to see whether or not c_I is relevant. We thus carried out additional simulations for $c_I=0.01$, 0.02, 0.1 and 0.2 in 2D, each for $L=300$–2000, and for $c_I=0.0003$ and 0.03 in 3D, for $L=40$–200. (Note that these values of c_I are identical to those used in the earlier works.)

Results of χ for $c_I=0.1$ and 0.2 for $L=1500$ and those for $c_I=0.02$ for $L=2000$, all in 2D, are plotted in Fig. 7. Estimates of (γ, p_c^{eff}) from the plot are (2.43 ± 0.03, 0.6709), (2.45 ± 0.04, 0.7528), and (2.49 ± 0.05, 0.5187) for $c_I=0.1$, 0.2, and 0.02, respectively. The errors are again the regression errors. The values of γ for all three cases are considered to be consistent with one another and are again close to the percolation value. Results for $c_I=0.01$ are also similar; the estimates are $\gamma=2.40\pm 0.10$ and $p_c^{\text{eff}}=0.4628$ for a system of $L=2500$. These results, together with the previous result for $c_I=0.05$, imply that the value of c_I is irrelevant as long as the exponent γ is concerned.

Our work is contrasted to the previous work, where considerably different values of γ have been obtained depending on c_I: $\gamma=5.3\pm 0.8$ for $c_I=0.01$, $\gamma=3.8\pm 0.5$ for $c_I=0.05$ and $\gamma=2.6\pm 0.4$ for $c_I=0.2$ for systems of size up to $L=400$. These estimates are unusual because, according to the universality concept, the value of c_I is believed to be irrelevant as long as it is not extreme, i.e., $c_I\neq 0$ and $c_I\neq 1$. The primary cause of such strange results is again due

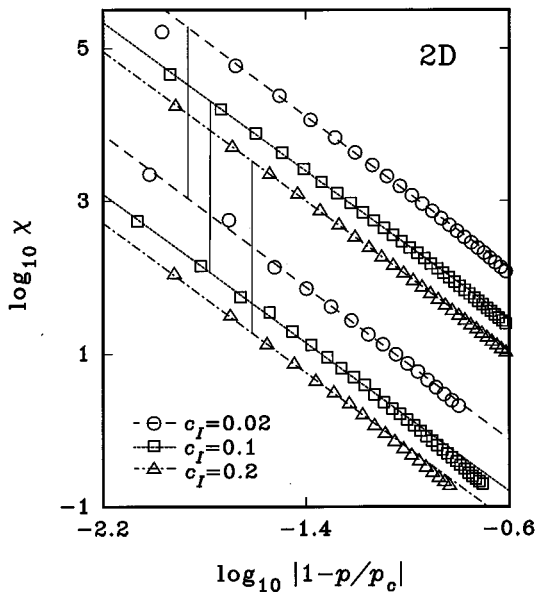

FIG. 7. Monte Carlo data of χ for 2D kinetic gelation model for three different values of c_I. The vertical displacements of the power-law fits (solid lines) are similar for all cases, exhibiting that the amplitude ratio does not depend strongly on c_I.

to that the largest cluster has been excluded in the sum in Eq. (1) *both* below and above p_c, in that work (while we have eliminated it only above p_c), similar to the 3D case that we discussed before. (We, in fact, estimated χ in a way similar to the previous work and obtained essentially the same results as those in Ref. [7].) Since the prime in the sums of Eqs. (1) and (2) implies that *the spanning cluster should be excluded* and since the spanning cluster exists above p_c, we believe that the largest cluster should be excluded only above p_c. Although the largest cluster is small enough and it appears to be reasonable to ignore it for $p<p_c$, we believe that exclusion of it near p_c causes significant errors on the measurements of $\chi(p)$. Since the power-law behavior in Eq. (1) is expected to hold close to p_c, an exclusion of the largest cluster results in the power-law region shifted away from p_c. Such a shift may possibly yield the estimates of γ and R significantly deviated from the true values, as it was already pointed out by Lee [16] for different models. It should also be noted that our systems are much larger and the statistics is also at least one order in magnitude better than the previous work of Ref. [7].

Our estimates of R are also very different from those of the previous work. While the previous authors reported $R=250\pm70$, 140 ± 45, and 80 ± 20 for $c_I=0.01$, 0.05, and 0.2, respectively, we obtained R similar to the percolation value for all selected values of c_I. As we have seen in Fig. 1, the estimates of R for $c_I=0.05$ were between 173 and 198 (see Fig. 1), depending on L. For other values of c_I, i.e., $c_I=0.01$, 0.02, 0.1, and 0.2, the estimates are not very different from that for $c_I=0.05$ (Fig. 7). For the latter two cases, i.e., for $c_I=0.1$ and 0.2, we obtained R between 175 and 190 depending on the values of c_I and L. On the other hand, for the former case of $c_I=0.01$, we attempted to sample the data for the concentration of polymerized sites p as large as possible. However, we were not able to sample sufficient data for $p\geqslant0.49$ due to the trapping of the systems; all active centers are either trapped or annihilated before the desired value of p is achieved. With the sampled data, we estimate R between 150 and 170 for various L, which are slightly smaller than those of our earlier estimates for other values of c_I, but are still within the error bounds of the percolation value. From these estimates, we are not able to rule out the possibility of a *strong* universality between the percolation and the kinetic gelation models, ''strong'' in the sense that the amplitude ratio as well as the critical exponents is the same for two models.

Similar results for β were also observed. For all cases of c_I, we obtained β between 0.11 and 0.14 (not shown). The estimates of γ, β, R, and p_c in 2D are summarized in Table II, in comparison with the previous estimates (numbers in parentheses). It shoud be noted that the values in the table were calculated considering the results for various size systems, and they are slightly different from those which were presented before for a given size system.

Results for 3D are not different from those in 2D. For $c_I=0.0003$ and 0.03 with $c_t=1.0$, results were basically similar to the case for $c_I=0.003$; the estimates of γ for various L are between 1.8 and 1.9 depending on the size of system. These estimates are slightly smaller than (although consistent, within the errors, with) the previous estimates in Refs. [5] and [6] and are closer to the known percolation value, particularly for $c_I=0.0003$.

The amplitude ratio for the selected cases of c_I, were between 8 and 9, as long as the size of system is not too small. Considering these values and the statistical errors of $\chi(p)$, it seems that the amplitude ratio of susceptibilities for the kinetic gelation model is also similar to the percolation

TABLE II. The estimates of γ, β, R, and p_c for 2D kinetic gelation model for various values of c_I, in comparison with the results in Ref. [7] (in parentheses). The errors listed are the regression errors and there might be additional statistical errors.

c_I	γ	β	R	p_c
0.01	2.40±0.10	0.14±0.01	160±30	0.4618
	(5.3±0.8))	(0.15±0.04)	(250±70)	(0.43±0.005)
0.02	2.49±0.10	0.12±0.02	175±30	0.5188
0.05	2.49±0.05	0.13±0.01	185±30	0.5989
	(3.8±0.5)	(0.16±0.04)	(140±45)	(0.568±0.05)
0.1	2.45±0.03	0.11±0.02	180±25	0.6709
0.2	2.47±0.06	0.12±0.02	185±20	0.7525
	(2.6±0.4)	(0.14±0.04)	(80±20)	(0.732±0.005)

TABLE III. The estimates of γ, β, R, and p_c for 3D kinetic gelation model for various values of c_I, in comparion with the results in Refs. [5,6] (in parentheses).

c_I	γ	β	R	$100\times p_c$
0.0003	1.85 ± 0.10	0.33 ± 0.04	8.4 ± 1.7	3.485
	(2.3 ± 0.4)		(1.7 ± 0.6)	(3.2)
0.003	1.84 ± 0.06	0.42 ± 0.03	6.9 ± 1.2	8.384
	(1.98 ± 0.10)	(0.37 ± 0.09)	(2.8 ± 1.0)	(8.35 ± 0.05)
0.03	1.81 ± 0.05	0.40 ± 0.01	8.3 ± 1.0	14.020
			(4.2 ± 1.2)	(16.6)

value, implying that both models might belong to the same universality class as long as our simulations are carried out. The estimates of γ, β, R, and p_c for 3D kinetic gelation model are compared with the previous estimates in Table III.

IV. SUMMARY AND CONCLUSIONS

We have studied by Monte Carlo methods the statistical properties of the irreversible kinetic gelation model in both 2D and 3D. We have estimated the exponents γ and β and the amplitude ratio R from the Monte Carlo data of the susceptibility and the gel fraction. Results for γ and R in 2D are very different from those of the previous work. While in the previous work considerably different values have been observed depending on the values of c_I, we obtained consistent values, within the statistical errors, for all selected values of c_I. The estimates of R in 3D are also very different from the previous work. Whereas they obtained R considerably smaller than the known percolation value, we obtained it rather close to the percolation value. From these estimates, we are not able to rule out the possibility of strong universality between the kinetic gelation and the standard percolation models.

We found that such a different conclusion for the universality of kinetic gelation model is a consequence of the different sampling technique of $\chi(p)$, as Lee [16] has already pointed out for off-lattice percolation models. While the largest cluster has been excluded in the sum for the susceptibility both below and above p_c in the previous works, we have excluded it only above p_c. Such a different sampling method affects only the susceptibility and, accordingly, the estimates of γ and R, leaving the gel fraction unaffected. We believe this to be the reason that our estimates of β are similar to the previous estimates, which were found to be close to the percolation values in both 2D and 3D.

Our work, together with the previous works of Lee and his collaborator [14–16], thus resolves the unusual critical behavior of the amplitude ratio of percolation susceptibilities. The previously reported nonuniversal behaviors for various off-lattice percolation models and for the kinetic gelation model appear to have been caused artificially from the approximate method of sampling $\chi(p)$ in the Monte Carlo procedure. With the more elaborate technique, R has been found to be universal as it is expected from the field theoretical calculations.

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[1] H. J. Herrmann, Phys. Rep. **136**, 153 (1986); D. Stauffer, A. Coniglio, and M. Adam, Adv. Polym. Sci. **44**, 103 (1983).
[2] P. J. Flory, J. Am. Chem. Soc. **63**, 3083 (1941).
[3] W. H. Stockmayer, J. Chem. Phys. **11**, 45 (1943).
[4] P. Manneville and L. de Seze, *Numerical Methods in the Study of Critical Phenomena*, edited by I. Della Dora, J. Demongeot, and B. Lacolle (Springer, Berlin, 1981).
[5] H. J. Herrmann, D. P. Landau, and D. Stauffer, Phys. Rev. Lett. **49**, 412 (1982).
[6] H. J. Herrmann, D. Stauffer, and D. P. Landau, J. Phys. A **16**, 1221 (1983).
[7] A. F. Rushton, F. Family, and H. J. Herrmann, J. Polym. Sci. Polym. Symp. **73**, 1 (1985); also see A. F. Rushton, M.S. thesis, Emory University, 1984 (unpublished).
[8] F. Family, Phys. Rev. Lett. **51**, 2112 (1983).
[9] D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor and Francis, London, 1992).
[10] D. C. Hong, H. E. Stanley, and N. Jan, Phys. Rev. Lett. **53**, 509 (1984).
[11] D. Y. Kim, H. J. Herrmann, and D. P. Landau, Phys. Rev. B **35**, 3661 (1987).
[12] I. Balberg, Phys. Rev. B **37**, 2391 (1988).
[13] S. B. Lee and S. Torquato, Phys. Rev. A **41**, 5338 (1990).
[14] S. B. Lee, Phys. Rev. B **42**, 4877 (1990).
[15] S. B. Lee and J. H. Ahn, J. Korean Phys. Soc. **26**, S438 (1993).
[16] S. B. Lee, Phys. Rev. E **53**, 3319 (1996).
[17] A. Aharony, Phys. Rev. B **22**, 400 (1980).
[18] B. Nienhuis, Phys. Rev. Lett. **49**, 1062 (1982).
[19] J. Hoshen, D. Stauffer, G. H. Bishop, R. J. Harrison, and G. D. Quinn, J. Phys. A **12**, 1285 (1979).
[20] One of us (S.B.L.) has also calculated R for standard percolation model with the finite size effect fully taken into account and obtained $R=180\pm40$; see, e.g., [16].
[21] The exponent γ for 3D gelation was estimated to be 1.98 ± 0.10 for $c_I=0.003$ and $c_t=0.4$ and 2.3 ± 0.4 for $c_I=0.0003$ [6], the latter of which is rather close to 2D percolation value.