

Are Branched Polymers in the Universality Class of Percolation?

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We study the model for branched polymers recently introduced by Lucena *et al.* [Phys. Rev. Lett. **72**, 230 (1994)]. Our calculations of the three exponents d_ℓ , d_{\min} , and τ for large systems suggest that the model belongs to the universality class of percolation. This is in contrast with the common belief that branched polymers belong to the universality class of lattice animals.

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In the last decades, the polymerization process has become an important topic in both applied and basic research [1–5]. It is commonly believed that in dilute solutions [6], where interactions between different polymers can be neglected, linear polymers can be modeled by self-avoiding walks (SAWs) [1,2,5] and branched polymers are in the universality class of lattice animals (LAs) [7–9]. The SAW ensemble consists of all configurations of non-intersecting random walks (of N steps), while the LA ensemble consists of all configurations of N -site clusters. In recent years it became clear that asymptotically SAWs can be generated by a kinetic growth walk (KGW), where at each step the random walker can move only to those neighboring sites that have not been visited before [10–12]. Very recently, in order to generate branched polymer structure, Lucena *et al.* [13] generalized the KGW to include branching [branched polymer growth model (BPGM)] [14]. They found the interesting phenomenon that at a (small) finite probability of branching, b_c , that increases monotonically with the concentration q of impurities in the system, a transition occurs from SAW-type structures at small branching probability b to compact structures at large b . The important question, however, to which universality class the structures at the critical line $b_c(q)$ belong to has not been resolved.

In this Letter we show that the branched polymers at the critical line are *not* of LA type as would have been expected, but most probably belong to the universality class of percolation. Our results are based on extensive numerical studies of the fractal dimension d_{\min} of the minimum path between two cluster points, of the chemical dimension d_ℓ and of the exponent τ characterizing the distribution of clusters of given size.

The BPGM generates polymer structures from a seed in a self-avoiding manner similar to the KGW, but allows for the possibility of branching with bifurcation probability b . To be specific, consider a square lattice where at $t = 0$ the center of the lattice is occupied by a polymer “seed.” There are four empty nearest-neighbor sites of the seed, where the polymer is allowed to grow. At step $t = 1$, two of these four growth sites are chosen randomly: One of them is occupied by the polymer with probability 1, the other is occupied with probability b .

This process is continued. At step $t + 1$, the polymer can grow from each of the sites added at the foregoing step t to empty nearest-neighbor sites (growth sites) either in a linear fashion or by bifurcation with probability b , provided there are enough growth sites left; otherwise, the polymer stops growing. If a certain concentration q of the lattice sites are occupied by impurities and cannot serve as growth sites, large polymers can be generated only below the percolation threshold q_c of the considered lattice ($q_c \approx 0.40723$ on the square lattice). According to Lucena *et al.* [13] the critical line $b_c(q)$ separates a phase that belongs to the universality class of SAWs at small b from a phase belonging to the universality class of compact Eden clusters at large b , with $b_c(0) \cong 0.055$ and $b_c(q_c) = 1$. The universality class at the critical line could not be identified by Lucena *et al.* [13] when calculating the fractal dimension d_f of the clusters in Euclidean space.

To determine the universality class of the BPGM at the critical line we have studied the growth process in chemical ℓ space and determined the critical exponents d_{\min} , d_ℓ , and τ [14]. The chemical distance ℓ between two cluster points separated by Euclidean distance r is defined as the length of the shortest path between them on the cluster, and the fractal dimension d_{\min} describes how ℓ scales with r , $\ell \sim r^{d_{\min}}$. The chemical dimension d_ℓ describes how the cluster mass within chemical distance ℓ scales with ℓ , $M \sim \ell^{d_\ell}$. The conventional fractal dimension d_f , defined by $M \sim r^{d_f}$, is related to d_ℓ and d_{\min} by $d_f = d_\ell d_{\min}$. For SAW structures, $d_\ell = 1$ and $d_{\min} = d_f$, while for Eden clusters $d_{\min} = 1$ and $d_\ell = d_f = d$. For percolation clusters in $d = 2$ at criticality, we have $d_{\min} \cong 1.13$, $d_f = 91/48$, and $d_\ell \cong 1.68$ [15]. The exponent τ describes the cluster size distribution. We have found that direct numerical calculations of d_f by the mass-radius relation are not conclusive due to the existence of strong boundary effects. In contrast, calculations in chemical space do not have any boundary effect, since the branched polymers are *grown in chemical space*: At step $t = 1$ the first shell in ℓ space is completed, at $t = 2$ the second shell, and so on. Hence the chemical space is the natural metric for calculating the critical exponents of the BPGM.

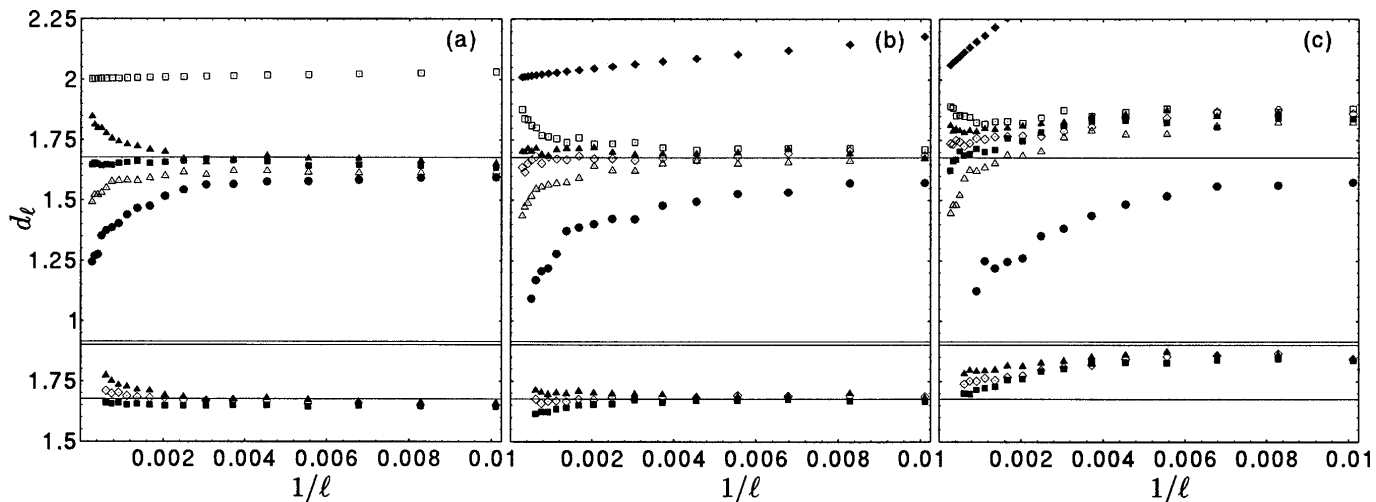


FIG. 1. Plot of the chemical dimension d_ℓ as a function of $1/\ell$ [obtained from the successive slopes of $\log M(\ell)$ vs $\log \ell$] for (a) $b = 1$ and $q = 0.2$ (square), 0.4030 (full triangle), 0.4045 (diamond), 0.4040 (full square), 0.4050 (triangle), and 0.4072 (full circle); (b) $b = 0.5$ and $q = 0.2$ (full diamond), 0.34 (square), 0.3410 (full triangle), 0.3415 (diamond), 0.3420 (full square), 0.3430 (triangle), and 0.35 (full circle); (c) $q = 0$ and $b = 0.04$ (full circle), 0.0550 (triangle), 0.0565 (full square), 0.0570 (diamond), 0.0575 (full triangle), 0.0580 (square), and 0.1 (full diamond). The upper plots of the figures show a broad regime around criticality and are based on averages of $M(\ell)$ over 4000 configurations, with a maximum chemical distance $\ell_{\max} = 4000$. The lower parts concentrate on the immediate vicinity of the critical points, with 20 000 configurations and $\ell_{\max} = 2000$. The horizontal lines represent the known value $d_\ell \cong 1.68$ for percolation. The simulations were performed on a square lattice.

Figures 1 and 2 show the fractal dimensions d_ℓ and d_{\min} in the vicinity of three representative points at the critical line: (a) around ($b = 1$, $q \cong 0.4037$), (b) around ($b = 0.5$, $q \cong 0.3415$), and (c) around ($b \cong 0.0567$, $q = 0$). The symbols are from our simulations, and the horizontal lines represent the known values for percolation. We expect three types of behavior for $\ell \rightarrow \infty$: compact structures with $d_\ell \rightarrow 2$ and $d_{\min} \rightarrow 1$ below the critical line, SAWs with $d_\ell \rightarrow 1$ and $d_{\min} \rightarrow \frac{4}{3}$ above the critical line, and critical branched polymers with different exponents at the critical line. These features are clearly seen in the figures and the values of the fractal dimensions at the three points on the critical line are in

very good agreement with the known values for percolation. The results are particularly convincing for $b = 1$ [Figs. 1(a) and 2(a)] and $b = \frac{1}{2}$ [Figs. 1(b) and 2(b)], where the critical regime is reached already for small ℓ . For $q = 0$ [Figs. 1(c) and 2(c)], however, there exist large crossover phenomena due to initial exponential growth in the absence of impurities, which yields too large values of d_ℓ . This is clearly seen in Fig. 1(c) for $b = 0.1$, where d_ℓ approaches 2 from above. From Figs. 1(c) and 2(c) we conclude that the critical point for $q = 0$ is between $b = 0.0565$ and 0.0575 , and the exponents are $d_\ell = 1.70 \pm 0.05$ and $d_{\min} = 1.1 \pm 0.05$ which are consistent with percolation. For obtaining more accu-

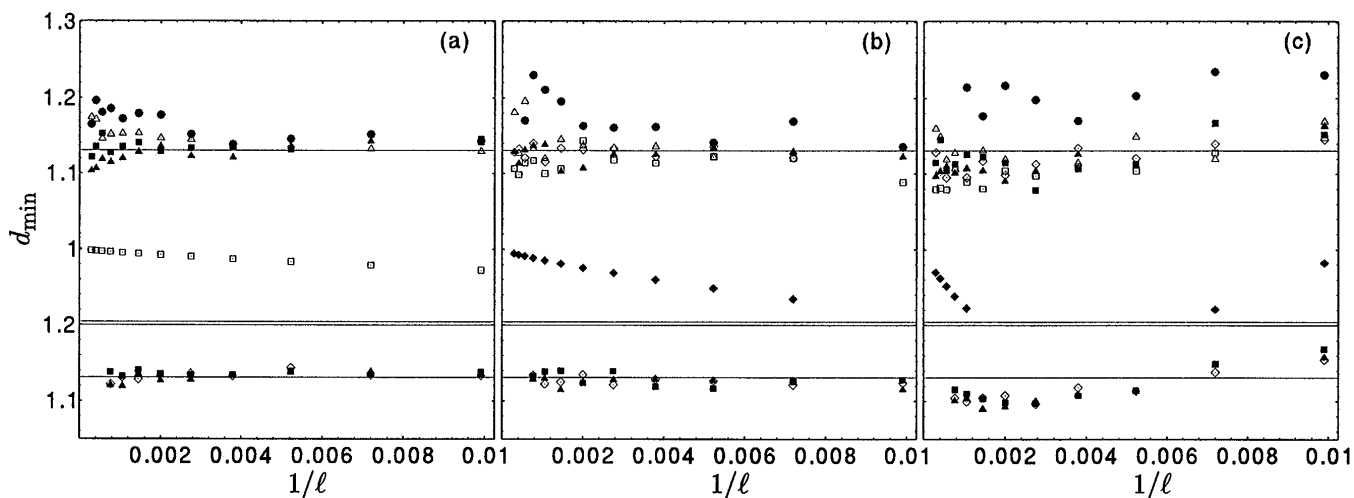


FIG. 2. Plot of d_{\min} as a function of $1/\ell$ [obtained from the successive slopes of $\log r(\ell)$ vs $\log \ell$] for the parameters described in Fig. 1. The horizontal lines represent the known value $d_{\min} \cong 1.13$ for percolation.

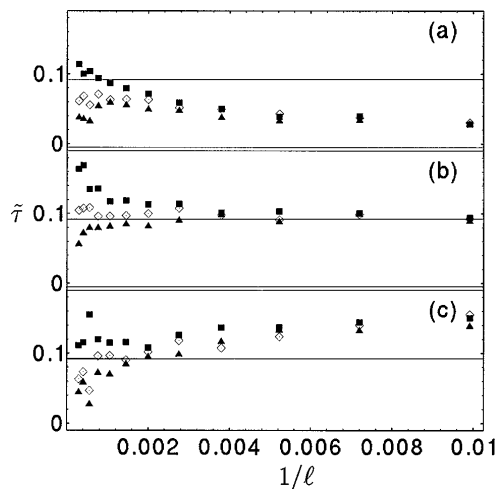


FIG. 3. Plot of the exponent $\tilde{\tau}$ as a function of $1/\ell$ [obtained from the successive slopes of $\log N(\ell)$ vs $\log(\ell)$] in the vicinity of the critical points, for the same parameters as in the upper parts of Figs. 1 and 2. The horizontal lines represent the known value $\tilde{\tau} = (\tau - 2)d_\ell = (d/d_f - 1)d_\ell \cong 0.092$ for percolation.

rate results for $q = 0$, one needs to study much larger systems (with $\ell_{\max} \gg 10^4$) which is beyond the capacity of present computers. From Figs. 1(a) and 1(b) and 2(a) and 2(b), on the other hand, we conclude $d_\ell = 1.68 \pm 0.02$ and $d_{\min} = 1.13 \pm 0.02$ already for $\ell_{\max} = 4000$. These values are in excellent agreement with known percolation values, but are significantly different from the values known for lattice animals, $d_\ell \cong 1.33$ and $d_{\min} \cong 1.17$ [9].

For obtaining further information on the exponents we calculated the number $N(t)$ of surviving polymers as a function of the number of growth steps t . For compact structures we expect $N(t) \rightarrow N(\infty) > 0$ for $t \rightarrow \infty$, while for SAWs $N(t)$ should decay exponentially. At criticality, we expect power-law behavior, $N(t) \propto t^{-\tilde{\tau}}$ or, since in the BPGM $t = \ell$, $N(\ell) \propto \ell^{-\tilde{\tau}}$. For percolation structures one has $\tilde{\tau} = (\tau - 2)d_\ell = (d/d_f - 1)d_\ell \cong 0.092$. Figure 3 shows $\tilde{\tau}$ vs $1/\ell$ in the vicinity of the above three critical points. Again, the symbols are from our simulations, and the horizontal lines represent the percolation value for $\tilde{\tau}$. The results are consistent with our conclusion from Figs. 1 and 2 that the BPGM belongs to the universality class of percolation.

Figures 1(a), 2(a), and 3(a) show that for $b = 1$ (full bifurcation) the critical q value for the square lattice is $q^*(b = 1) = 0.4040 \pm 0.0005$, which is well below the percolation threshold $q_c \approx 0.40723$. The reason for the difference between q^* and q_c is that higher-order branching (trifurcation, tetrafurcation, etc.) is forbidden,

which effectively decreases q_c . From this follows the surprising observation that even on the infinite percolation cluster below q_c , which is compact on large length scales, branched polymers with bifurcation probability $b = 1$ will also end up as SAW-type polymers, as long as $q > q^*(b = 1)$.

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