The Strange Behavior of Critical Branched Polymers

H. H. Aragão-Rêgo¹, J. E. de Freitas¹,², Liacir S. Lucena¹, G. M. Viswanathan¹,³

¹International Center for Complex Systems and Departamento de Física Teórica e Experimental, Universidade Federal do Rio Grande do Norte, 59078–970 Natal–RN, Brazil
²Departamento de Matemática, Universidade Federal do Rio Grande do Norte, 59078–970 Natal–RN, Brazil
³Departamento de Física, Universidade Federal de Alagoas, 57072–970 Maceió–AL, Brazil

(March 21, 2022)

We find that 2-dimensional (2-D) critical branched polymers with no impurities conclusively belong to the same universality class as 2-D random percolation clusters, although pure critical 3-D branched polymers do not belong to the 3-D percolation universality class. We find, moreover, that the fractal dimension $d_f$ of critical branched polymers is independent of the presence of a random environment in 2-D, but not in 3-D. We also report that when there are no impurities the critical branching probability in 3-D is $b_c = 3.34 \times 10^{-4} \pm 0.16 \times 10^{-4}$.

Polymerization has been an important topic of recent interest in the physics community [1,3]. Polymers are extensively studied complex systems, and can be either linear or branched [1,6,11]. In spite of being simpler, linear polymers (LP) present physical features such as non-Markovian growth and nontrivial scaling. For several decades it has been known that linear polymers in diluted solutions can be successfully modeled using self-avoiding walks (SAW). More recently it was found that large SAW chains can be more easily constructed by kinetic growth walks (KGW) [11] that belong to the same universality class as SAW chains [3]. Branched polymers (BP) have a larger degree of complexity and exhibit an astonishingly rich phenomenology [1,6,11,12,13]. In the 1990’s, the KGW approach was generalized to describe the growth of BP in disordered media [1,6,11,12,13]. Such BP are typically grown when polymerization occurs in a solution with two types of units: (i) monomers with two chemically active molecular sites (“tips”) that lead to branching; and (ii) three-tipped monomers that lead to branchings (i.e., bifurcations). Many important physical properties of the resulting BP depend on the probability $b$ for branching to occur and the concentration $c$ of impurities [12] that can block or slow the polymerization.

Here, we first address the controversial question: to which universality class does the critical polymer ($b = b_c$) belong for $c = 0$? A typical phase diagram [1,10] (Fig. 1(a)) for BP consists of several distinct regions. For large $b$ and small $c$, the polymer is compact and grows indefinitely (i.e., is “infinite”) with a smooth (faceted) growth surface, while for smaller values $1 > b > b_c$ closer to the critical line $b_c(c)$ the resulting polymer grows indefinitely but with a rough growth surface [13]. For yet smaller values of $b < b_c$ the resulting polymer is finite, due to termination of polymerization at all active growth sites. Along the critical line $b = b_c(c)$, the polymer is fractal (Fig. 1(a)) and has a diverging correlation length.

The commonly held belief that BP belong to the lattice animals [14] universality class was based on the assumption that there is no random environment ($c = 0$) and that there are only repulsive forces between chains [13]. It was thus a remarkable finding when Bunde et al. [1] showed, using the branched polymer growth model (BPGM), that critical BP in random environments in 2-D belong to the same universality class as 2-D random percolation clusters. One conceivable explanation for this interesting result is that in 2-D such behavior is induced by the random impurity obstacles that, indeed, form real percolation clusters with site occupation probability $p = c$. Hence, it can be argued that the polymer grows as if constrained by the random obstacles, and this effect can generate an effective attraction between chains (Fig. 1(b)). For the special case $c = 0$, however, there are no such impurities, hence this physical argument becomes irrelevant. The study by Bunde et al. [1] is conclusive all along the critical line $b = b_c(c)$ for $c \neq 0$, but the important special case of pure BP ($c = 0$) still remains unconfirmed [1], and both the percolation as well as the lattice animals universality classes remain plausible. An additional controversy surrounding the special case $c = 0$ arises because in many systems [13] the introduction of disorder is sufficient to modify the universality class (and sometimes even to destroy the ordered phase). The Harris criterion [15] predicts that the critical BP in 2-D is a candidate for experiencing a change of universality class when going from $c = 0$ to $c \neq 0$.

We investigate this problem by using simulations of the BPGM [10]. BPGM is a generalization of KGW [11] which is able to capture the essential dynamics of branched polymerization. We briefly describe the model here (Fig. 1(b)). The BP is generated from an initiating seed at time $t = 0$ located at the center of a $d$-dimensional lattice. At time step $t = 1$, one of the vacant nearest-neighbor sites of the seed is chosen randomly and occupied to become the next active growth tip, and the seed ceases to be an active growth tip. At each step $t$ of the growth process, a branching also can occur at every such growth tip, by occupation of an additional (second) site with probability $b$. A fraction $c$ of randomly chosen sites is not available for growth. Hence, at time $t + 1$, the poly-
mer can grow from any of the active tips added at the previous step \( t \) to empty neighboring sites (Fig. 1(b)).

Our extensive 2-D simulations, discussed below, leave no doubt that, surprisingly, random percolation is indeed the correct universality class even for \( c = 0 \). We simulate critical polymers for \( c = 0 \) and \( b = b_c(0) \approx 0.056 \) and find that the fractal dimension \( d_f \) in 2-D is 1.37 (Fig. 2(a)) and the chemical dimension \( d_c \) (Fig. 2(b)) are in strong agreement with the known values for a 2-D critical percolation cluster \([14]\). These dimensions are defined by the relations \( M \sim r^{d_f} \), \( M \sim \ell^{d_c} \), and \( \ell \sim r^{d_{\text{min}}} \), where \( r \) is the radius and \( \ell \) is the chemical distance (\( \ell = \ell \) in BPGM). Clearly \( d_f = d_c \cdot d_{\text{min}} \approx 1.89 \). We conclude that the critical 2-D random percolation cluster and the critical polymer generated by BPGM unmistakably belong to the same universality class. Therefore the fractal dimension of the critical BP in 2-D is independent of the presence of a random environment—in apparent violation of the Harris criterion.

We further investigate this “paradoxical” result by performing similar 3-D simulations of pure \( (c = 0) \) critical BP, because the Harris criterion favors a little more the irrelevance of the quenched disorder in 3-D. Until now, such 3-D simulations have not been possible because the precise value of \( b_c(0) \) in 3-D was unknown.

So we now determine the value of \( b_c(0) \) in 3-D for \( c = 0 \). The fundamental difficulty of finding a precise value for \( b_c(0) \) in 3-D is that the value is extremely small, \( b_c(0) < 10^{-3} \) (i.e., on average more than \( 10^5 \) monomer units between successive branchings), making it computationally expensive to pinpoint it using traditional numerical approaches that involve tuning \( b \). We overcome this difficulty by mapping BPGM to the computationally less intensive fixed number of tips model (FNTM) \([17]\) that has been shown \([17,18]\) to generate phase diagrams identical to BPGM. FNTM differs from BPGM as follows: rather than fixing the branching probability \( b \), instead FNTM dynamically attempts to fix the number \( N \) of active polymerization growth tips. Hence, the branching process does not occur with an \textit{a priori} fixed value \( b \), but rather branchings occur whenever one or more of the \( N \) existing active tips “die,” either because of impurities or due to other steric hindrance effects. We can be certain that the value of \( b_c \) found using FNTM is identical to the one found from BPGM simulations because FNTM generates polymers in which the number of active growth tips neither vanishes nor explodes exponentially, i.e., corresponding to the critical line at \( b = b_c \) in BPGM simulations \([17,18]\). FNTM greatly reduces the computational burden of generating critical polymers because it automatically generates critical polymers with \( b = b_c(c) \) and, moreover, it has only one free parameter, namely the impurity concentration \( c \). (The arbitrary value of \( N > 1 \) chosen is irrelevant in the large mass limit, as seen in Fig. 3(a)) The effective critical branching probability \( b_{\text{eff}} = B/M \) is found by dividing the total number \( B \) of branchings of active tips by the total number \( M \) of occupied polymer sites. Most importantly, FNTM goes spontaneously to the critical line without the need of parameter tuning (of \( b \), as with BP growth models that exhibit self-organized criticality (SOC) \([18]\).

We simulate FNTM for \( c = 0 \) in 3-D and \( N = 5, 10, 20, 30, 50, 80 \) and 100 tips as a function of polymer mass \( M \). In the limit \( M \to \infty \), we find that the values of \( b_{\text{eff}} = B/M \) converge towards an identical point independently of \( N \) (Fig. 3(a)). The uncertainty for a typical point in Fig. 3(a) is \( \Delta b_{\text{eff}} \approx 10^{-5} \). This remarkably small error bar is made possible only because FNTM dynamically seeks the fixed point attractor near \( b \approx b_c \), such that the effective critical branching probability \( b_{\text{eff}} = B/M \) fluctuates around \( b_c \). By extrapolating \( b_{\text{eff}} \) for \( 1/M \to 0 \) we find that \( b_c(0) = 3.34 \times 10^{-4} \pm 0.16 \times 10^{-4} \).

Since it is not altogether inconceivable that the value of \( b_c(0) \) obtained from FNTM will not carry over to BPGM, we check the above conclusions by simulating BPGM with \( 2.9 \times 10^{-4} < b < 4.0 \times 10^{-4} \). We find (Fig. 3(b)) that the number of active tips either grows or decays much faster than a power law except in the approximate range \( 3.3 \times 10^{-4} < b_c(0) < 3.4 \times 10^{-4} \). This value obtained for \( b_c(0) \) is not inconsistent with the value \( b_c = 3.34 \times 10^{-4} \pm 0.16 \times 10^{-4} \) found using FNTM.

Using this result, we are able to perform 3-D BPGM simulations of pure critical BP. We find that \( d_f \approx d_{\text{min}} \approx 2 \) and \( d_c \approx 1 \) in 3-D for \( b = b_c(0) \) and \( c = 0 \) (Figs. 2(c), (d)), definitely ruling out the 3-D random percolation universality class. Although this is the expected field theoretical result (see ref. \([18]\) for 3-D polymers, the Harris criterion indicates a relevant disorder and a change in the value of \( d_f \) (because \( d_f = 1.5 < 2 \) for \( d = 3 \) BP). This prediction is confirmed by the finding of Bunde et al. \([18]\), that \( d_f \approx 2.53 \) for \( b_c = 1 \), consistent with 3-D random percolation.

Somewhat surprising is our confirmation that in 2-D the fractal dimensions of the critical BP are identical for the pure case \( c = 0 \) and the maximally disordered case \( b = 1, c = 1 − p_c \) (see Fig. 1(a)), where \( p_c \approx 0.59 \) is the critical site occupation probability in random percolation for a square lattice. For \( b = 1 \) the critical polymer grows in a vacant space that is itself almost a critical percolation cluster (Fig. 1(a)). Since there is no random environment for \( c = 0 \), a larger fractal dimension had been conceivable in principle. Our findings indicate, strangely, that the fractal dimension (but not the lacunarity) of the critical polymer in 2-D is independent of the growth environment. Why this is so is indeed an interesting question that merits further investigation, and seems to be related to a self-organizing process \([18]\). Criticality occurs only when there is a delicate balance between the rates of tip deaths and branchings—a dynamic not unlike the one used in the self-organized generation of infinite 2-D percolation clusters \([19]\).
We now comment briefly on our finding that, strangely, pure critical BP fall into the percolation universality class in 2-D but not in 3-D. The deeper reason behind this mysterious behavior is possibly related to the well known fact that in 2-D, encounters between different branches of a BP can result either in “trapping” of a polymer chain or else in “scattering” (bending) of the chains. In 3-D a completely different effect becomes important in the large-scale growth dynamics: interpenetration and “entanglement” of BP chains—not by independent linear parts of a BP that act independently at criticality, because the chemical distance between successive branchings is much larger than the persistence length. In 2-D, there is no entanglement (for topological reasons), but in 3-D such effects can counteract the excluded volume repulsion, so that the mean square displacement of the tips grows linearly with mass (as with polymer melts, see Ch. 2 and 8 of ref. [6]), leading to power law scaling equivalent to ideal Gaussian chains, but by linear parts of a BP that act independently large-scale growth dynamics: interpenetration and “entanglement” of BP chains [6]—not by independent linear tanglement” of BP chains [6]—of BP growth in the realistic case of no impurities governed by a branching probability \( b \) when \( c=0 \). When the impurity concentration \( c \) is nonzero, then the random obstacles (circles) can sometimes cause an effective attraction between chains (see branches on the right), but this effect disappears when \( c=0 \).

Finally, one hint for the cause of the observed change in the universality class (when we vary \( b \) from \( b=b_c(0) \) to \( b=1 \)) in 3-D becomes evident by comparing the two situations with zero and maximum disorder: for \( b_c(0) = 3.3 \times 10^{-4} \) the “freedom” of motion of the tips is limited only by the sparse steric hindrance due to the polymer chains, while for \( b=1 \) the behavior is dictated by the interstitial percolation cluster available for BP growth. The arguments presented above raise new questions, such as whether other critical exponents vary along the critical line \( b=b_c(c) \).

We thank U. L. Fulco, H. J. Hilhorst, M. L. Lyra, S. Roux, and L. R. da Silva for discussions; CNPQ, PRONEX, the Projeto Nordeste de Pesquisa & FINEP for support.

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[1] A. Bunde, S. Havlin and M. Porto, Phys. Rev. Lett. 74, 2714 (1995).
[2] P. De los Rios, Phys. Rev. Lett. 82, 4236 (1999).
[3] M. Myllys et al., Phys. Rev. Lett. 84, 1946 (2000).
[4] R. Du et al., Phys. Rev. Lett. 84, 2417 (2000).
[5] P. J. Flory, Principles of Polymer Chemistry (Cornell University Press, Ithaca, 1953).
[6] P. G. de Gennes, Scaling Concepts in Polymer Physics (Cornell University Press, Ithaca, 1979).
[7] M. Doi and S. F. Edwards, The Theory of Polymer Dynamics (Oxford University Press, Oxford, 1986).
[8] T. C. Lubensky and J. Isaacson, Phys. Rev. Lett. 41, 829 (1978).
[9] G. Parisi and N. Sourlas, Phys. Rev. Lett. 46, 871 (1981).
[10] L. S. Lucena, J. M. Araújo, D. M. Tavares, L. R. da Silva and C. Tsallis, Phys. Rev. Lett. 72, 230 (1994).
[11] I. Majid, N. Jan, A. Coniglio and H. E. Stanley, Phys. Rev. Lett. 52, 1257 (1984).
[12] L. Peliti, J. Phys. (Paris) Lett. 45, L925 (1984).
[13] M. Porto, A. Shechter, A. Bunde and S. Havlin, Phys. Rev. E 54, 1742 (1996).
[14] A. Bunde and S. Havlin, Fractals and Disordered Systems (Springer, Berlin, 1991).
[15] J. Cardy, Scaling and Renormalization in Statistical Physics (Cambridge University Press, Cambridge, 1997), and references therein.
[16] L. S. Lucena, L. R. da Silva and S. Roux, Physica A 266, 81 (1999).
[17] H. H. Aragão-Rêgo et al., in Computer Simulation Studies in Condensed Matter Physics XII, eds. D. P. Landau, S. P. Lewis and H.-B. Schüttler, 85, 223 (Springer, Berlin, 1999).
[18] J. S. Andrade Jr., L. S. Lucena, A. M. Alencar and J. E. Freitas, Physica A 238, 163 (1997).
[19] A. M. Alencar, J. S. Andrade Jr. and L. S. Lucena, Phys. Rev. E 56, R2379 (1997).

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FIG. 1. (a) schematic phase diagram for BP (see text). We focus exclusively on the critical point at \( b = b_c(0) \) that corresponds to BP growth in the realistic case of no impurities. (b) the branched polymer growth model (BPGM) assumes that growth takes place only at active growth tip sites located on a lattice. The seed (cross) initiates polymerization governed by a branching probability \( b \). When the impurity concentration \( c \) is nonzero, then the random obstacles (circles) can sometimes cause an effective attraction between chains (see branches on the right), but this effect disappears when \( c=0 \).
FIG. 2. (a) double-log plot of the polymer mass in units of monomers (mass axis label at left) and chemical distance (label at right) as a function of radius for BP with critical branching probability $b_c(0)$ in the absence of impurities in 2-D. We have used 100 samples with mass $M = 5 \times 10^5$ monomers. The fractal dimension $d_f$ and the minimum dimension $d_{\text{min}}$ (the slopes) are those of a 2-D critical percolation cluster (straight lines). (b) double-log plot of the polymer mass as a function of the chemical distance for the identical simulations, showing that the chemical dimension is also consistent with the universality class of 2-D random percolation. (c) polymer mass and chemical distance vs. radius and (d) polymer mass vs. chemical distance in 3-D, showing that the behavior is definitely different from 3-D random percolation ($d_f = 2.52$, $d_\ell = 1.84$, $d_{\text{min}} = 1.37$ [14]). We have averaged over 900 samples. We find that 3-D critical BP scaling is more reminiscent of polymer melts [1] than random percolation.

FIG. 3. (a) $b_{\text{eff}}$ as a function of $1/M$ and the number $N$ of active growth tips for FNTM in 3-D. The solid lines are fitted curves, by which we are able to extrapolate for arbitrarily large masses. The values shown for $1/M = 0$ are the extrapolated results. We are thus able to estimate the value of $b_c(0) = 3.34 \times 10^{-4} \pm 0.16 \times 10^{-4}$. (b) double log plot of $N$ as a function of chemical distance $\ell$ for BPGM, with $N_0 = 2$ tips initially at $t = 0$. For values $b$ larger than the estimated value of $b_c(0)$, we find that $N$ tends to explode exponentially, while for $b < b_c(0)$ we find $N$ decays. For $3.3 \times 10^{-4} < b < 3.4 \times 10^{-4}$, however, we obtain power law growth for $N$, indicating critical branching.