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Self-organization in growth of branched polymers

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Abstract

We propose a growth mechanism for branched polymers where self-organization leads the system to criticality. By incorporating a dynamical rule which simply regulates the flux of monomers available for aggregation, the system is spontaneously driven to the critical branching probability which separates the finite from infinite growth regimes. The fact that the system reaches and maintains itself close to a critical state without the need of a fine tuning of the parameters is thus discussed in terms of the self-organized criticality (SOC) concept. Finally, we also demonstrate the feasibility of the method in association with a practical implementation of the theoretical model.

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1. Introduction

The growth of branched polymers in disordered media is complex problem which still presents a real challenge to the physicists nowadays [1]. In spite of its intricate nature, the phenomenon has attracted the attention of many researchers in the past years [2–6]. Recently, a new branched polymer growth model (BPGM) has been proposed by Lucena et al. [7] to describe this process. The results from computational simulations using this idealized model clearly indicate that it embodies a very rich phenomenology (non-linear behaviour, diverse criticality and fractality, kinetic phase transitions, etc.) as a consequence of the competition between several effects including branching, self-avoidance, the complex morphology of long chains and the disorder of the medium. The two relevant parameters in the model are the branching probability b and the impurity concentration c . In the (b, c) space, Lucena et al. [7] found a critical line, locus of a diverging correlation length, which separates the infinite from finite growth

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regimes. Also at the critical line, the polydispersion distribution follows a power law and the polymer cluster has a fractal structure.

An interesting result of the BPGM was presented by Bunde et al. [8] in a recent study, namely that the critical polymer cluster belongs to the same universality class of percolation. Apparently, this is in contradiction with the common belief that branched polymers are in the universality class of lattice animals.

Another surprising feature of this model concerns the time evolution of the growth fronts, where the occurrence of a roughening transition was detected [9]. For sufficiently large values of b and small values of c inside the infinite growth region, the fronts are faceted in shape similar to a growing crystal, in contrast with other situations in which the fronts can be very rough.

The concept of self-organized criticality (SOC) has been introduced by Bak et al. [10] as a plausible explanation for the tendency of large and complex systems to drive themselves to critical states. As a consequence, an authentic SOC system would naturally display spatial and temporal correlations with all sizes and durations. Common features to SOC systems are the presence of thresholds and opposing mechanisms that prevent accommodation in any sort of equilibrium [10–14]. Accordingly, the critical behaviour would have to be dynamically achieved without the need of imposing a fine tuning to a given parameter. Such a situation is clearly different from typical second order phase transitions, where scaling can only be observed when a parameter is tuned close to a critical point. Nevertheless, this self-tuning condition for the occurrence of SOC behaviour is still a very controversial issue. For instance, it has been the theme of ample discussions regarding whether the characterization of an SOC system by means of a simple mean-field description could provide a physical rationale for a spontaneous organization towards the critical state. Very recently, this apparent paradox has been solved by Zapperi et al. [15] with the introduction of a new mean-field model, the self-organizing-branching-process (SOBP). The essence of their model is based on a sandpile paradigm where open boundary conditions are explicitly incorporated to allow for energy dissipation. In addition, local dynamical rules are conveniently coupled to a global condition which is analogous to inducing a constant energy flux throughout the system. As a result, the system organizes itself into a stationary state described by a critical branching process.

In the present paper, we show that self-organization can be achieved, leading and maintaining the system close to criticality during the growth of branched polymers. We perform numerical simulations with the BPGM to demonstrate how a simple and feasible feedback mechanism can systematically drive the aggregation process to the vicinity of the transition line between the finite and infinite regimes of growth [7].

2. The model

In the BPGM, we consider an $L \times L$ square lattice with the center cell occupied by a polymer *seed* at the initial time, $t = 0$. In the next time step, there are four directions

for growth available in the lattice. At this point, the polymer can bifurcate with probability b (which means taking randomly two directions and occupying two neighbour sites), or only one direction is selected with probability $(1 - b)$, corresponding to the formation of a linear chain. Following the same rule in each subsequent time step, the active sites (chain tips) have a probability b to bifurcate and a probability $(1 - b)$ of remaining linear. Again, the directions of growth are chosen among the available ones (now, less than four directions for growth can be available due to the previous occupation of neighbour sites by polymer or by impurities). In a real polymerization experiment, linear or branched chains can be obtained if two types of monomers are used, one with coordination number 2 and the other with coordination number 3. We will show later that the branching or bifurcating probability b can be controlled by changing the relative concentration of these monomers. Obviously, this is only a nominal probability because the bifurcation process will only be effective if there are at least two unoccupied neighbours of the active site. The chain will remain linear in the case of only one unoccupied site. Also the active site can be completely surrounded by impurities or by the polymer itself. In this case, the chain stops growing and this front site becomes inactive.

One important question is how one can guarantee that the polymer never stops growing and also that it never “explodes” in an exponential form. In other words, the idea is to maintain the polymer growing indefinitely, but under limited branching conditions. This problem can be solved if we note that the necessary condition for the polymer to keep growing is the existence of at least one active tip at a given time. However, this is not a sufficient growth condition because a fluctuation can easily kill a single tip in the next time step. A safer criterion would be to sustain the number of active tips in the growth front close to a constant value, arbitrarily chosen, N_T (for instance, $N_T = 100$ or $N_T = 200$). This can be achieved if we introduce a control rule in which the branching probability is allowed to vary in order to compensate the increase or decrease in the number of active tips, compared with the threshold N_T . This feedback mechanism should then have the effect of increasing the branching probability if the number of alive tips at a given time, $N(t)$, falls below N_T and decreasing b if $N(t)$ becomes larger than N_T . A possible control mechanism is given by the following recurrence relationship:

$$b(t+1) = b(t) + k[N_T - N(t)], \quad (1)$$

where k is a kinetic coefficient. Obviously, $0 \leq b \leq 1$, so that we have to impose $b(t+1) = 1$ if Eq. (1) gives a nonphysical value greater than one. Also we impose $b(t+1) = 0$ if Eq. (1) results in a value less than zero. By means of Eq. (1), a stochastic restoring force is imposed to the system so that the branching probability b is regulated to ensure the continuity of the growth process at a lower rate.

Unlike the problem studied by Zapperi et al. [15], the boundary condition in the BPGM is not only *open* in the sense that energy (in the BPGM case, mass) can freely leave or penetrate in the system, but it is also *mobile* since the active sites in

the polymer growth frontier are the only ones available for monomer aggregation at a given time step.

3. Results

In Fig. 1 we show a typical realization of a polymer cluster grown subjected to the feedback mechanism given by Eq. (1). This particular picture has been generated with an initial branching probability $b_0 = 1$ assuming that there are no impurities present in the system ($c = 0$). Therefore, the polymer initially grows as a compact object (the central region in the cluster) changing gradually to a ramified peripheral structure as a result of the variation in parameter b . This spontaneous evolution corresponds to a trajectory in the (b, c) plane where the system crosses the roughening transition line [9] and later reaches the finite-infinite critical line [7]. Fig. 2 shows that, after this transient period and independent of the initial conditions, the time evolution of the branching probability $b(t)$ reaches a self-organizing state characterized by an average value $\langle b \rangle$ which precisely recovers the critical probability $b_c \approx 0.056$ at $c = 0$ separating infinite from finite growth regimes [7,8]. Although self-organized in a critical state, the cluster grown under these conditions is not a genuine fractal. The generation of a real

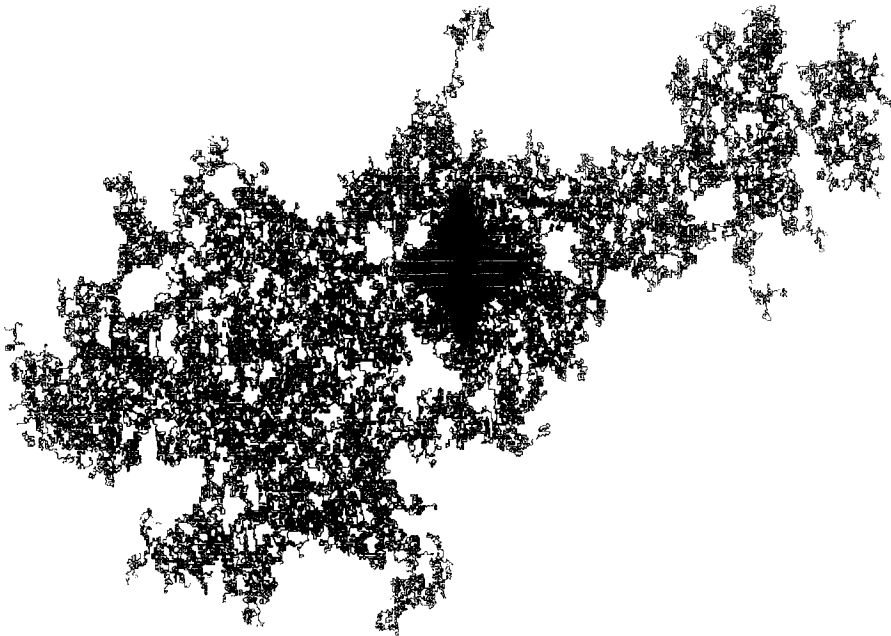


Fig. 1. Typical realization of a branched polymer grown under the controlling rule given by Eq. (1). In this particular simulation, there are no impurities in the system, $c = 0$, the initial branching probability is $b_0 = 1$, the kinetic coefficient is $k = 10^{-3}$, the threshold for the number of active sites is $N_T = 80$, and the final time is $t = 1000$. The cluster initially grows as a compact object and eventually becomes a *fractal-like* structure.

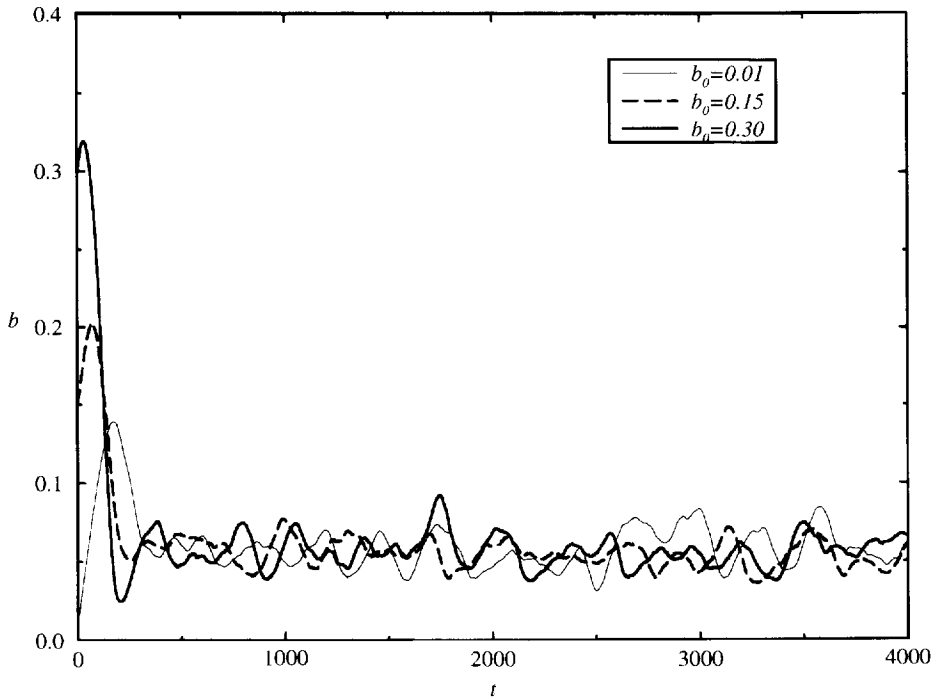


Fig. 2. Plot of the branching probability b as a function of time for three different initial conditions b_0 in a lattice without impurities ($c=0$, $k=10^{-5}$ and $N_T=100$). After a short transient, $b(t)$ achieves a critical state and fluctuates around it with short range correlations.

self-similar structure is impaired in the process by the fluctuations of $b(t)$ around the critical value b_c . On the other hand, this also means that the system remains close to a fractal structure, since it executes small oscillations around the critical line, performing small excursions inside the finite region of the phase diagram and thus going back and forth into the infinite (compact structure) region too.

An entirely similar behaviour is shown in Fig. 3 where an arbitrarily chosen concentration of impurities, $c=0.3$, is present in the lattice acting as obstacles for polymer growth. However, in order to compensate this additional growth limitation, the self-organized system is now spontaneously driven to another critical state of increased bifurcation probability ($b_c \approx 0.342$, $c=0.3$). This result is also in perfect agreement with previously performed simulations [7]. As a consequence, the present method enable us to readily and accurately obtain the entire critical line in the (b, c) phase space. We emphasize that in this approach the system itself seeks criticality, while in Ref. [7,8] the critical line is located by procedures in which fixed parameters are utilized, so that particular points in the (b, c) plane are probed at each tentative.

In Fig. 4, the time dependence of the variable N is shown for different values of the parameters k and N_T . Expectedly, the threshold N_T merely determines the average

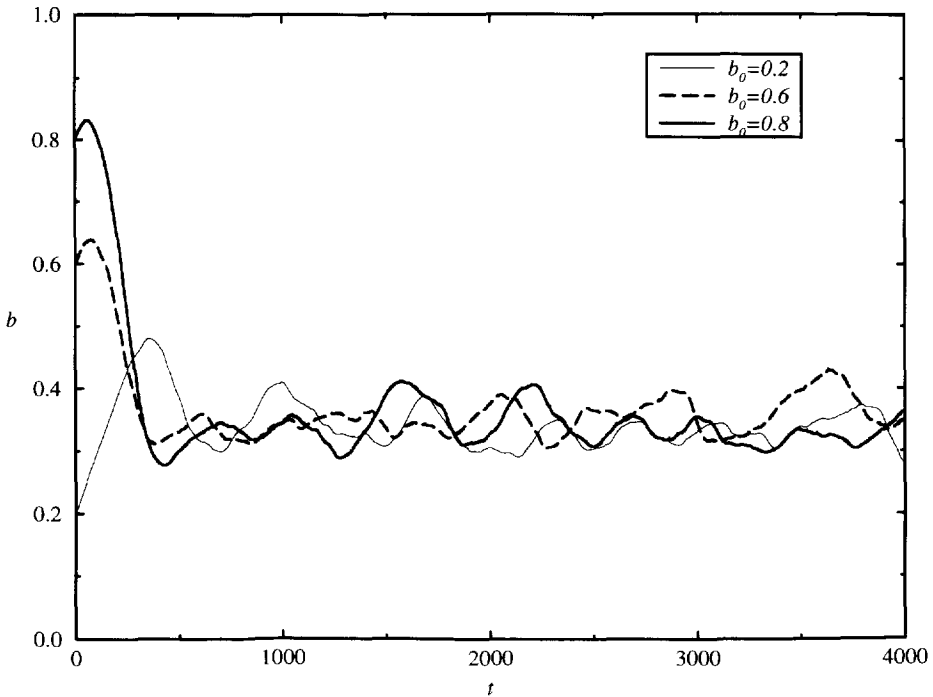


Fig. 3. Plot of the branching probability b as a function of time for three different initial conditions b_0 in a lattice with some degree of impurity ($c=0.3$, $k=10^{-5}$ and $N_T=100$). As in Fig. 2, $b(t)$ reaches a corresponding fixed-point value (critical state) after a transient period and fluctuates around it with short range correlations.

value around which the number N of active sites fluctuates in time when the system becomes self-organized or, in other words, reaches stationarity. Keeping the number of active sites close to the threshold N_T is equivalent to ensure the survival of the growing polymer near the critical state. The parameter k , on the other hand, seems to exert a strong influence on the time series characteristics of $N(t)$. This behaviour can be further understood if we analyse a mean-field representation for the system where self-avoiding effects induced by topological correlations in the lattice are not explicitly taken into consideration. We then propose the following expression to describe the growth of a branched polymer:

$$N(t+1) = [1 - a(t)][1 + b(t)]N(t), \quad (2)$$

where $a(t)$, $0 \leq a(t) \leq 1$, is the *annihilation or death probability* of a polymer chain tip caused by steric hindrance effects. In this way, exclusion mechanisms leading to deactivation (e.g. self-avoidance and impurities) can be approximately incorporated to

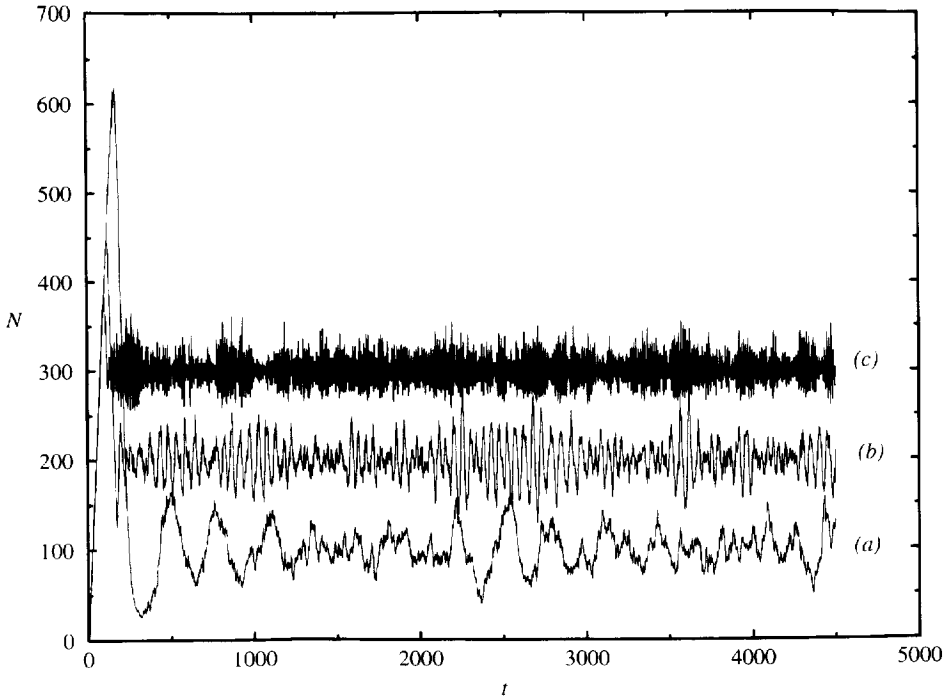


Fig. 4. Dependence on time of the number of active sites $N(t)$ calculated at distinct threshold positions N_T for different values of the parameter k : (a) $N_T = 100$ and $k = 10^{-5}$; (b) $N_T = 200$ and $k = 10^{-4}$; (c) $N_T = 300$ and $k = 10^{-3}$. As mentioned in the text, the parameter N_T just sets the average value $\langle N \rangle$ around which the number of active sites $N(t)$ will fluctuate in time. The parameter k , on the other hand, is intrinsically related to the oscillatory behaviour of the system. As large k is, larger are the frequencies dominating the time evolution of $N(t)$.

the model. Taking the continuum time limits of Eqs. (1) and (2), we obtain

$$\frac{db}{dt} = k[N_T - N], \tag{3}$$

$$\frac{dN}{dt} = [b(1 - a) - a]N. \tag{4}$$

For simplicity let us assume that the probability a is roughly constant for a given lattice topology at the stationary phase of the dynamical process. Differentiating Eq. (4) with respect to time and inserting Eq. (3) into the resulting expression gives

$$\frac{d^2N}{dt^2} = k(1 - a)N_T N - k(1 - a)N^2 + \frac{1}{N} \left(\frac{dN}{dt} \right)^2. \tag{5}$$

The presence of the middle term in the right side of Eq. (5) provides a convincing explanation for the diversity in the oscillatory behaviour of $N(t)$ when computed with distinct values of k , as shown in Fig. 4. Correspondingly, a large value of k should be directly associated with the occurrence of high frequency oscillations in the function

$N(t)$, a response which is clearly consistent with the results of our simulations. The remaining terms are related to the increasing tendency to grow of the polymer cluster if there were no restoring mechanisms always driving the system back to the threshold value N_T .

4. Discussion

As already mentioned, we expect the feedback mechanism expressed by Eq. (1) to be experimentally feasible due to the observability of the variable N and controllability of the probability b during the process. As an illustration, let us examine this problem in the context of a typical polymerization experiment, for example, a continuously stirred tank reactor. In this type of reacting unit, the monomer solution is constantly fed and removed at the same volume flow rate Q . We can also assume that, under efficient mixing conditions, the diffusional resistance to mass transfer of the bulk fluid phase enclosing the polymer aggregate can be regarded as negligible. The variation with time of the total polymer mass M can then be effectively measured from a simple material balance of the monomer species

$$\frac{dM}{dt} = Q(C_{in} - C_{out}), \quad (6)$$

where C_{in} and C_{out} would be the total monomer concentrations at the reactor inlet and outlet, respectively. It turns out that the instantaneous mass growth rate dM/dt can be directly related to the actual number of active sites N present in the branched polymer cluster,

$$\frac{dM}{dt} = N. \quad (7)$$

In addition, if we consider that bi- or tri-functional monomer molecules (but having equal masses) are the only reagent species added to the system at a given time, the parameter b can then be interpreted as the instantaneous fraction of trifunctional species in the monomer feeding solution

$$b = \frac{C_t}{C_b + C_t}, \quad (8)$$

where C_b and C_t are the monomer concentrations of bi- and tri-functional species, respectively. Hence, a device to monitor and control these concentrations at the inlet and the total concentration of monomers at the outlet solution from the polymerization reactor, would be the single requirement to implement the dynamical rule given by Eq. (1).

Summarizing, in this paper a growth mechanism for branched polymers is investigated where self-organization and criticality are intrinsic components of the same dynamics. We demonstrate that an SOC state can be readily and spontaneously achieved by coupling the BPGM to a simple dynamical rule which tacitly regulates the flux

of monomers available for chemical reaction in the fluid phase surrounding the growing polymer cluster. It is under these circumstances that the practical implementation of the controlling rule Eq. (1) also appears to be a conceivable experimental task. We strongly believe that the modelling technique presented here represents a convincing example where there is a true connection between criticality and self-organization.

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