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## LETTER TO THE EDITOR

# Monte Carlo simulations for a kinetic growth model

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**Abstract.** We simulate a kinetic growth model on the square lattice using a Monte Carlo approach in order to study ramified polymerization with short-distance attractive interactions between monomers. The phase boundary separating finite from infinite growth regimes is obtained in the  $(T, b)$  space, where  $T$  is the reduced temperature and  $b$  is the branching probability. In the thermodynamic limit, we extrapolate the temperature  $T^* = 0.102 \pm 0.005$  below which the phase is found to be always infinite. We also observe the occurrence of a roughening transition at the polymer surface.

Since a single polymer chain was originally idealized by a random walk [1] on a periodic lattice, more and more complex models for the polymerization phenomenon have arisen in the literature. The *self-avoiding random walk* [2, 3] describes a chain which can never intersect itself. It models a linear polymer in dilute solution with a good solvent.

An alternative model which describes a linear polymer chain is the *kinetic growth walk* [4–6]. In this model, the tip of the chain grows, at each time unit, toward one of the nearest-neighbour *unvisited* sites and stops if all the surrounding neighbours are occupied. This model was generalized to incorporate the *branching* possibility and also the presence of *impurities* [7]. It exhibits a finite–infinite transition due to competition among ramification and hindrances. Recently, the topological and dynamical aspects of this generalized kinetic growth model have been investigated [8]. In this study, a kind of roughening transition at the polymer surface was also detected.

In the present letter, we study the polymerization on the square lattice in an even more realistic way. For this purpose, we include, in the kinetic growth model, short distance attractive forces between the monomers. At a fixed time of the polymer growth we employ a Monte Carlo method for sampling the configuration space. So the evolution of the system is quasi-static and is always in a thermal bath equilibrium. Besides the reduced temperature  $T$ , the other relevant parameter is the branching probability  $b$  (we only study the case in which the impurity concentration  $c$  is zero). We find a critical line in the  $(T, b)$  plane which separates the finite from infinite phase. At low temperatures, due to the presence of attractive forces, the cluster structure gets more compact with a decreasing occurrence of steric hindrances, as will be explained below. We also detect a secondary transition occurring at all temperatures, which is related to the roughness of the polymer surface.

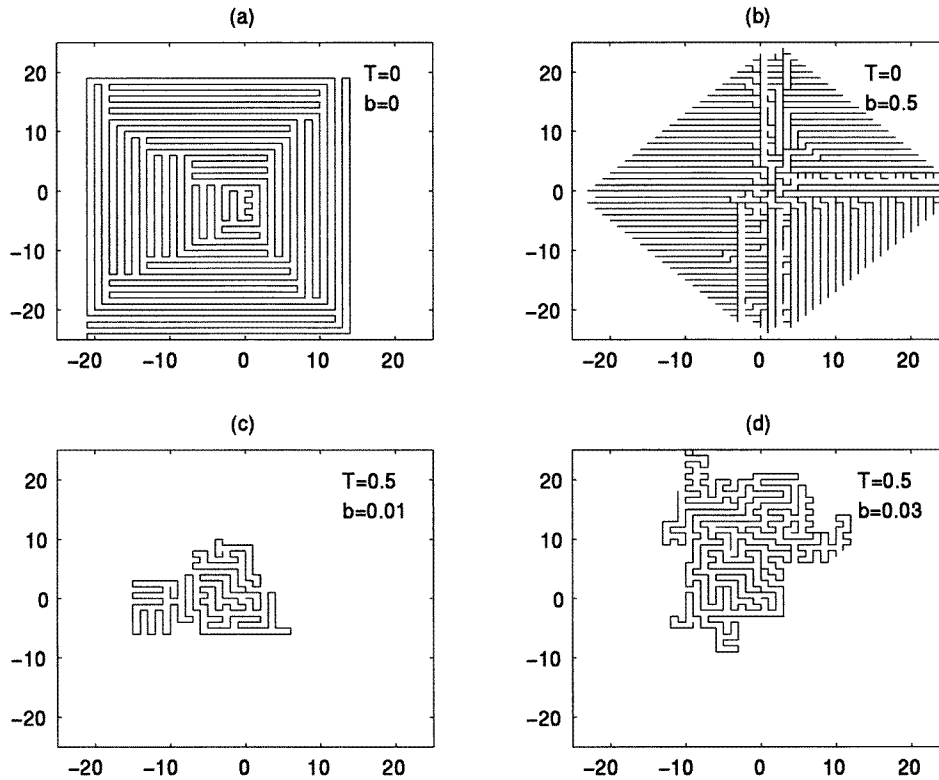
Let us now briefly review the kinetic growth model. Each site  $i$  of an  $L \times L$  square lattice may be empty or occupied by a monomer. Initially, only the centre is occupied. At time  $t = 0$ , the polymer starts growing from the origin towards a randomly chosen adjacent site. At  $t = 1$ , this site is filled and becomes the new growing end which now

may bifurcate with probability  $b$  or keep its linear growth with probability  $1 - b$ . Over each new growing tip, this process is applied recursively always respecting self-avoidance. All available growth directions are equally probable. At each time  $t$ , *all* current growing ends are sequentially visited in a clockwise manner following the order of births. All tips are connected to the origin by  $t$  bonds. The tip always tries to avoid filled regions, but sometimes may find itself in a trap without exit, i.e., in a ‘cul de sac’. Then it stops. The experiment finishes when either the cluster touches the lattice boundary (infinite polymer) or all tips are dead ends (finite polymer).

We consider the kinetic growth model as treated in [7, 8] but now modified in order to include an attractive energy,  $\epsilon$  ( $\epsilon < 0$ ), for *each* pair of nearest-neighbour monomers. The reduced temperature  $T$  is defined by  $T = 1/\beta|\epsilon|$ . We now describe how we developed the Monte Carlo method. Consider every pair of sites formed by a growing tip at time  $t$  and an occupied adjacent site. Let  $N_t$  be the total number of such pairs. Using the growth mechanism explained above, there are, at each stage  $t$ , many different configurations toward which the system can evolve. Let  $C_1$  be the first configuration at time  $t + 1$  generated by applying the growth rules at time  $t$ . This adds an energy  $E_1 = \epsilon N_{t+1}(C_1)$  to the total energy. A second configuration  $C_2$  will always be accepted if  $E_2 < E_1$ , otherwise a random number  $r$  is drawn and the new configuration is only accepted if  $r < e^{-\beta(E_2 - E_1)}$ . This process is repeated  $N_M$  (a previously fixed number of Monte Carlo steps) times. Observe that our prescription resembles the algorithms of Swendsen–Wang [9] or Wolff [10] in the sense that the *whole* perimeter is flipped when passing from a configuration  $C_k$  to  $C_{k+1}$ . In general, this kind of dynamics reduces harmful effects such as the critical slowing down. Finally, we must point out that, at a *fixed* time, the number of bifurcations occurring in the *first* configuration is kept constant along *all*  $N_M$  Monte Carlo steps. If this were not so, certainly the transition from one configuration to another would systematically favour those with more bifurcated sites (once they have smaller energies). This care avoids a biased simulation that might corrupt the meaning of  $b$  as an external parameter. Of course, this number changes with time.

The *order parameter* of the system is defined as the fraction of the polymers which are *infinite* [7]. The locus of the vanishing order parameter defines a critical line in the  $(T, b)$  space. We can measure the *correlation length*  $\xi$  of the system through [7]:  $\xi \equiv \langle (l_x l_y)^{1/2} \rangle$ , where  $l_x$  and  $l_y$  are the sizes of the smallest rectangle which contains a *finite* polymer when a particular experiment finishes. With this definition the correlation length has the following behaviour: at high temperatures,  $\xi$  is small because there is a large number of hindrances hampering the polymer growth and, at small temperatures, this number diminishes due to the presence of attractive forces. This means that most of the polymers are infinite, so, in order for a cluster to remain finite, it must die quickly or it never will and  $\xi$  is again small. The maximum of  $\xi$  locates the bulk phase transition which separates finite from infinite growth regimes. At this point,  $\xi$  grows with the lattice size  $L$ . Of course, in the limit  $T \rightarrow \infty$ , the bond energy between monomers is irrelevant and we should reproduce previous results [7, 8].

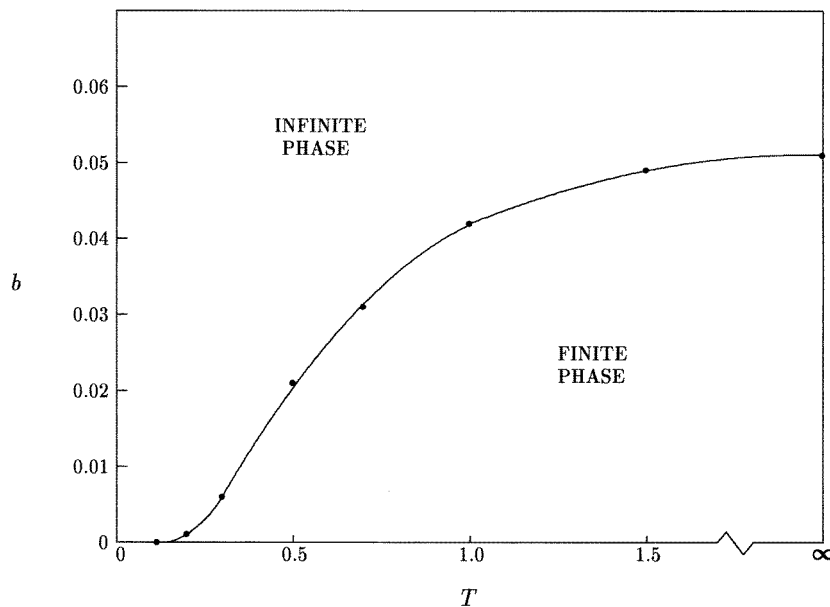
To show some typical graphs is both illustrative and instructive. The first graph (figure 1(a)) is a linear chain ( $b = 0$ ) which is *infinite* at  $T = 0$ . This result is completely different from that of the original kinetic model (without attractive interactions) where, for  $b = 0$ , the system is in the *finite* phase! The cluster is compact and displays a bond parallelism. The reason is as follows. When the unique growing tip bends, the minimum energy criterion obliges it to turn again following a path which is parallel to its own structure. This behaviour precludes the appearance of vacancies, compacts the system and keeps the tip growing indefinitely. One should also mention that, at  $T = 0$ , the phase is infinite



**Figure 1.** Typical graphs simulated on a square lattice of size  $L = 51$ , with  $N_M = 400$ .

for every  $b \geq 0$ . In figure 1(b), we show a simulated cluster for  $T = 0$  and  $b = 0.5$ . The surface acquires the shape of a lozenge and becomes smooth thus indicating that a roughening transition is occurring. In fact, for a determined temperature, we can observe that as  $b$  increases, the mean number of threefold sites  $\langle N_3 \rangle$  passes through a *maximum* which is a clue to the roughening transition (see [8]). This phenomenon happens at all temperatures. The peak of  $\langle N_3 \rangle$  occurs at  $b \approx 0.20$  at low temperatures ( $T < 0.5$ ) and tends to  $b \approx 0.15$  at high temperatures. The other two graphs were simulated with  $T = 0.5$ . The cluster is finite at  $b = 0.01$  (figure 1(c)) whereas it is infinite at  $b = 0.03$  (figure 1(d)).

We now present the *phase diagram* of the system in the  $(T, b)$  plane (figure 2). The critical line is the locus of diverging correlation length. A second-order phase transition separates finite from infinite growth regimes. This line touches the axis  $T$  at  $T = 0.115 \pm 0.005$  (this point was particularly obtained by looking for the peak of  $\xi$  at constant  $b = 0$ ). All other points were determined by fixing the temperatures. They carry an uncertainty of order  $\Delta b \sim 10^{-3}$  and were smoothly connected as a guide to the eyes. In our simulations, the thermal equilibrium (measured by the stabilization of the system energy) is attained around 400 Monte Carlo steps for *each* time interval  $[t, t + 1]$ . We simulate systems of size  $L = 1501$ , average over 100 experiments, and the results are presented in figure 2. Although we have not extrapolated to the thermodynamical limit ( $L \rightarrow \infty$ ) we believe that our results are very close to the real phase diagram since simulations that we have also performed for systems of size  $L = 1001$  differ less than 3% in respect to the  $L = 1501$  case.



**Figure 2.** The phase diagram in the  $(T, b)$  space corresponding to  $L = 1501$ .

Let us now discuss the phase diagram. In the limit  $T \rightarrow \infty$ , our estimate  $b_c \approx 0.051$  is in good agreement with previous results [7, 8]. In this high-temperature regime, the phase transition results from the competition between hindrances and branching. The attractive energy between monomers does not play any role. On the other hand, at low temperatures, the steric hindrance effect is so reduced (due to the presence of the attractive forces) that even the finite phase disappears!

On the axis  $b = 0$ , we have determined the critical temperatures  $T^*(L)$  for systems of sizes  $L = 501, 1001$  and  $1501$  and extrapolated the value  $T^* = 0.102 \pm 0.005$  using the Bulirsch–Stoer (BST) algorithm [11, 12]. At this point, the order parameter seems to approach a step function, indicating that a first-order phase transition is perhaps taking place. We do not discard the possibility that  $T^*$  may correspond to a tricritical temperature where the second-order line ends. It would be interesting to study this point further and also to obtain some thermodynamic properties of this system such as, for example, the specific heat. Then the question of universality along the critical line could be addressed.

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