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Ramified Polymerization in Dirty Media: A New Critical Phenomenon

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We simulate $d=2$ polymer growth by allowing for a branching probability b and an impurity concentration c ($0 \le b,c \le 1$). In the (b,c) space we find a critical line (locus of vanishing order parameter and diverging correlation length) which separates *infinite* from *finite* growth regimes; in particular, a *nonzero* critical value for b exists even for $c=0$.

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Polymerization is an extremely important phenomenon which, during the last decades, has been modeled and studied in a variety of manners. The simplest, of course, is the *random walk*. The first nontrivial complexity arrives when the polymer is not allowed to cut itself, i.e., *the self-avoiding random walk* [1,2]. In this case, growth stops whenever the randomly chosen growth direction leads onto an already occupied site. More realistic models have been introduced in which the growing end tries to avoid occupied regions; in this category falls the so-called *kinetic growth model* [3-5]. However, even in these models unavoidably occurs the *steric hindrance* effect [5]; i.e., the growth necessarily stops because the polymerization has occurred in a narrow "cul de sac." This effect determines the nature of polydispersion (hence of the viscoelastic properties [6]), the consequences being particularly dramatic in two dimensions, in which case the growth stops with probability 1. Nevertheless, the statistical relevance of this hindrance effect has never been focused in detail, as far as we know. In the present Letter, we generalize the kinetic growth model by allowing for *branching* (or *ramification*) of the polymer as well as for *impurities* (see, for instance, [7,8] for relevant features about branching). We show with the help of simulation that the competition between hindrance (due to both self-avoiding growth and impurities) and branching will bring up interesting phenomena associated with a new kind of phase transition. This type of critical phenomenon should be relevant in the discussion of real ramified polymers [1,9]; the inclusion of impurities in the model can be useful in the discussion of a variety of substances (e.g., commercial polymer paints, in which the color is obtained through addition of chemically inert pigments). Also there is a general scientific interest in this kind of problem. In a recent review paper, Derrida [10] emphasizes the importance of studying *branched polymers in disordered media*, especially because of the possible connections with other fundamental problems like spin glasses, and expected differences in behavior from the simple linear polymer case. He says that "little is known on this problem, even at the mean field level." The present model has allowed us to make some progress in this complex problem.

This model can still be considered as belonging to the general class of models displaying kinetic phase transitions, such as Schlogl's model [11], although it differs essentially from that one. We are going to comment on this subject.

Let us consider an $L \times L$ square lattice in the center of which we start, at $t=0$, growing a polymer. The growth direction is randomly chosen among the four possible first neighbors. At $t=1$, the growing end might *bifurcate* with probability b or remain linear with probability $(1-b)$. The succesive growth directions are, in all the cases, randomly chosen among the *available* ones. The process recursively goes on in a *self-avoiding* manner. Successive bifurcations will of course generate a great number of growth ends. At *every* time step t, *each one* of those ends is sequentially visited (in a clockwiselike manner following the sequence of births) and can bifurcate with probability b. For a particular growth end, bifurcation can effectively occur only if at least *two* first neighbors are unoccupied. If only one first neighbor is available, it necessarily grows in a linear manner. If no first neighbor is available, that particular end stops growing. The process is continued as long as at least one end keeps growing, or until at least one end touches the contour of the $L \times L$ square lattice. The entire experiment is then repeated $N_{\exp} \gg 1$ times; this constitutes the ensemble over which we perform the averages (denoted by $\langle \cdots \rangle$).

We note N the number of occupied bonds (linking first-neighboring sites), i.e., the number of connected monomers; in a real polymer, N is proportional to its total mass. If $b=0$, then $N=t$. If $b=1$, then $N \le 2^t - 1$. If $0<b<1$, N becomes a random variable satisfying $\langle N \rangle \le [(1+b)^t - 1]/b$; the equality holds for arbitrary t if the self-avoiding restriction is either relaxed (i.e., random walk branched polymerization) or inoperative (e.g., on a Cayley tree, or on a $d \to \infty$ d-dimensional Bravais lattice). In the thermodynamic limit ($L \to \infty$), $\langle N \rangle$ can, in principle, either indefinitely grow with t (*infinite growth* regime) or stop at a certain range of t (*finite growth* regime). In practice, once the growth has stopped, a polymer will be called "infinite" if at least one of its growing ends touched the $L \times L$ contour; otherwise,

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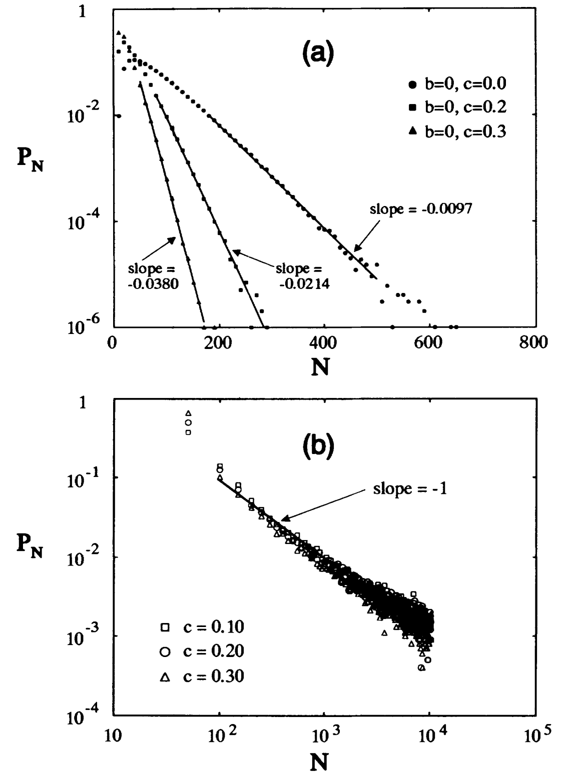

FIG. 1. Polydispersion distribution law: (a) finite growth phase (semi-log representation, $L=1000$ and $N_{\mathrm{exp}}=10^6$); (b) on the critical line, i.e., for $(b_c(c),c)$ (log-log representation, $L=1000$ and $N_{\mathrm{exp}}=20000$).

it will be called "finite." We denote by P_∞ the fraction of polymers that are infinite, and by $P_N(N)$ the distribution law of N, corresponding to finite polymers.

In addition to the "mass," it is interesting also to measure the (linear) size s of the polymer. This was done as follows. Once a particular experiment stops growing (either because it touched the $L\times L$ contour or because steric hindrance stopped all the growing ends), we determined the smallest rectangle (parallel to the $L\times L$ square) and denoted by s_x and s_y the lengths of its two sides. We define $s\equiv\sqrt{s_x s_y}$ (this choice preserves the area) and denote by $P_s(s)$ the distribution law associated with finite polymers; the mean size $\xi\equiv\langle s\rangle$ plays an important role, namely, that of the correlation length in standard phase transitions. The fractal dimension d_f of the branched polymer is defined through $\langle N\rangle\propto\xi^{d_f}$.

To the best of our knowledge, branched polymerization in the presence of impurities has never been studied. To do this, we shall extend the model we have just introduced. More precisely, let us assume that, when growth starts, a concentration $c\in[0,1]$ of site impurities has already been randomly frozen in the lattice. The growing branched polymer must now avoid, besides itself, these obstacles. The influence of impurities on the quantities of interest (e.g., P_∞ and ξ) is followed. A particularly interesting question is to see whether impurities introduce a new universality class in the problem. Indeed, it must be noticed that, in this extended model, steric hindrance will be due to two different sources, namely self-avoidance and impurities, which can or cannot be overcome by branching.

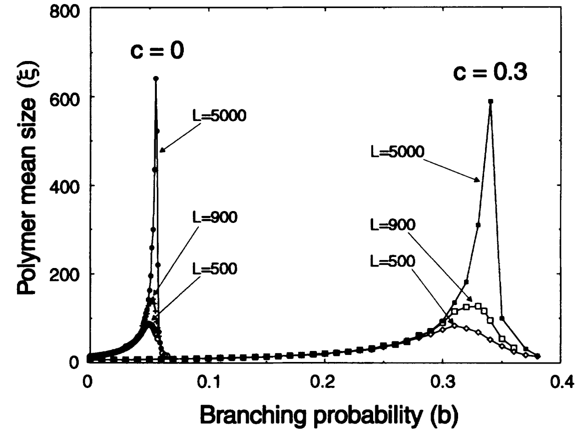

FIG. 2. Typical results for the b dependence of the mean size ξ ($1000\leq N_{\mathrm{exp}}\leq 20000$).

Let us now present our results. We have typically worked with $300\leq L\leq 5000$ and $200\leq N_{\mathrm{exp}}\leq 10^6$. Some polydispersion curves $P_N(N)$ are shown in Fig. 1. We verified that, in almost all points of (b,c) space, $P_N(N)$ decays exponentially with N [Fig. 1(a)]. There is, however, a (critical) line on which the decay becomes a power law [Fig. 1(b)]. We can see [in Fig. 1(b)] that, for $c=0$, the critical value for b is $b_c(0)\cong 0.055$. On the other hand, we see, in Fig. 1(a) that $\langle N\rangle\cong 1/0.0097\cong 100$ for $b=c=0$. Consequently, on a basis of Flory-like arguments [1], one would expect $b_c\cong 1/\langle N\rangle\cong 0.0097$, much lower than 0.055. Indeed, the fact that the $c=0$ threshold $[b_c(0)\cong 0.055]$ is about $5\frac{1}{2}$ times larger than the slope indicated in Fig. 1(a) ($\cong -0.01$) reflects the *nonlinear* nature of the present geometrical effects. More explicitly, increase of the branching in order to compensate the excluded volume further increases the amount of excluded volume to be compensated. We can also check that the discrepancy with Flory's arguments increases (i.e., $\langle N\rangle b_c$ increases) with increasing c.

In Fig. 2 we exhibit typical results for the polymer mean size ξ as a function of (b,c) as well as of the square-lattice size L. In Fig. 3 we present the order parameter $P_\infty(b,c)$ as well the phase diagram in the (b,c) space. Finally we present, in Fig. 4, a typical example of M vs R, where M is the polymer mass contained in a square box (centered at the origin of growth) with linear size R, in an $L\times L$ lattice. This log-log representation yields the fractal dimensionality d_f. From this type of construction we extracted $d_f\cong 2\pm 0.004$ for the points inside the infinite growth region [e.g., $(b,c)=(0.1,0)$]. On the critical line we obtained values for d_f monotonically varying from 1.83 [at $(b,c)=(0.055,0)$] to 1.76 [at

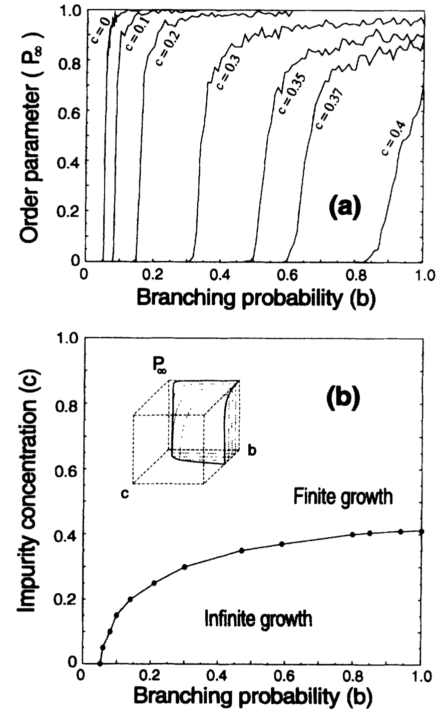

FIG. 3. (a) Typical results for the order parameter as a function of (b,c); we used $L=300$ (the small tails at $P_\infty \cong 0$ disappear with increasing L). (b) Phase diagram; we used $300 \le L \le 5000$ (the full line is a guide to the eye); the inset schematically represents $P_\infty(b,c)$.

$(b,c)=(1,0.4072)$]. This slight variation is judged to be consistent with a single universality class (characterized by $d_f \cong 1.8$). Nevertheless, to definitely exclude a nonuniversal behavior along the critical line, more extensive simulations should be cone. The point $(b,c)=(1, 0.4072)$ corresponds to percolation (the critical value $1-0.4072=0.5928$ is the site percolation threshold [12]). Indeed, the polymer can grow only in the subset of points which are *not* occupied by the impurities. Figure 5 shows a typical growth at this point: Note the existence of regions belonging to the infinite vacant cluster that will never be occupied. To make this point obvious we have also run *trifurcating* (instead of bifurcating) polymers, and have obtained *full occupancy* of the infinite vacant cluster. For this case we have consistently obtained $d_f=1.896$, which precisely recovers the value [12] associated with (site) percolation. Since this value is definitely different from $d_f \cong 1.76$ corresponding to bifurcations, we believe we are herein exhibiting a new universality class, clearly related to the incomplete filling of the infinite vacant cluster.

The phase transitions experienced by this system exhibit some analogy with those shown by Schlogl's model [11] in the sense that both are kinetic. There are, however, essential differences: (1) Our model represents a growth of a molecule and is therefore highly dependent on

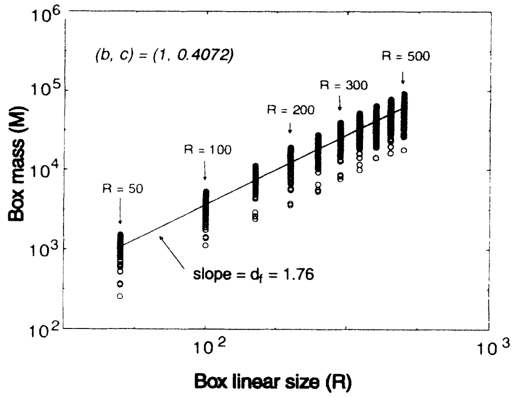

FIG. 4. Log-log determination of d_f for the critical point $(b,c)=(1, 0.4072)$ ($L=5000$ and $N_{\mathrm{exp}}=1000$) using the standard box method. All data points are displayed to show the experimental scatter. The slope is obtained by linear regression.

geometry; (2) in the present model there are explicit *memory* effects (i.e., the polymerization steps having occurred at previous times) and quenched noise due to impurities. The quenched distribution of impurities is consistent with the fact that we do not allow a relaxation of the steric hindrance in the course of the polymerization. In this sense our model corresponds to a "low temperature" regime.

To conclude, let us remark that the model introduced herein presents a rich phenomenology which mimics real branched polymerization in clean or dirty media. In particular, it gives us some insight on how impurities can affect technologically important properties such as polydispersion. Other studies of this new model would be welcome. For example, the triangular lattice enables the

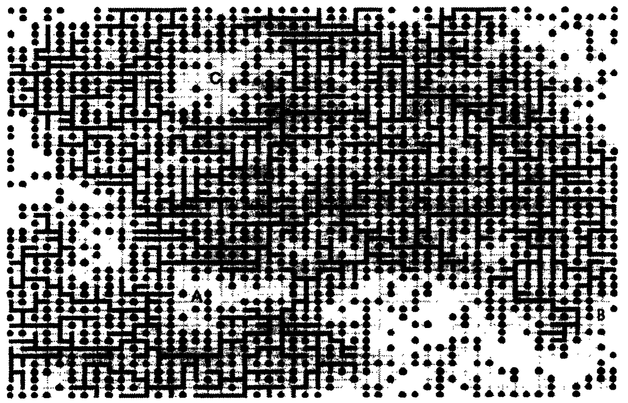

FIG. 5. Typical fragment of a polymer (shaded structure) grown in a 50×50 lattice with a particular random realization for the impurity sites (filled dots), and for the critical point $(b,c)=(1, 0.4072)$. The regions A and B belong to the *infinite* cluster of vacancies but have not been occupied by the bifurcating polymer; region C is a *finite* cluster of vacancies (and is, consequently, inaccessible to the growing polymer).

easy realization of higher-order branching (trifurcations, tetrafurcations, etc). Also, it seems intuitive that, for $d > 2$, $b_c(0)$ should be smaller than 0.055 because the steric hindrance effect would be less efficient. Finally, one could consider anisotropic or directional growth, anisotropic or directional branching, changes in the growth fronts, and polymers growing (from the very beginning) from both ends or from various seeds, or even growing on preexisting nontrivial networks or in their interstitial regions.

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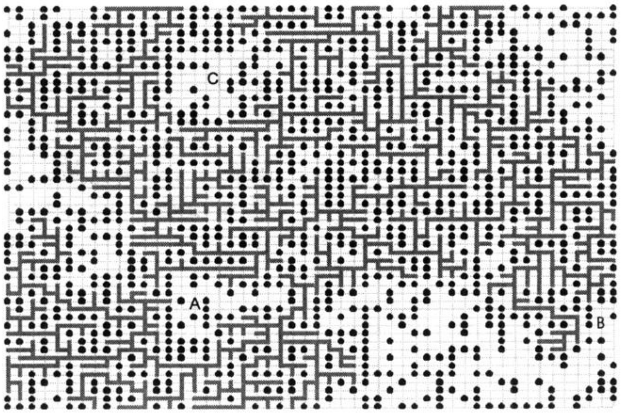

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