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Living polymers in random media: a 2D Monte-Carlo investigation on a square lattice

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Abstract. The evolution of the mean chain length $\langle L \rangle$ and mean end to end square radius $\langle R_e^2 \rangle$ of a two dimensional system of living polymers at constant monomer concentration is studied as a function of the obstacle density ρ. The fact that the system adapts the mean chain length $\langle L \rangle$ in order to reduce the entropic constraint does not lead to a different asymptotic dependence of $\langle R_e^2 \rangle$ on ρ than what is observed for dead polymers. The change of the molecular weight distribution form in the presence of obstacles suggests that a Levy flight could appear in system of wormlike micelles in a porous medium.

PACS. 36.20-r Macromolecules and polymer molecules – 82.35+t Polymers reactions and polymerization – 61.43.Bn Structural modeling: serial-addition models, computer simulation

Introduction

The so-called "living polymers" are systems in which polymerization is believed to take place under condition of chemical equilibrium between the polymers and their respective monomers. These long (one dimensional) aggregates break and recombine reversibly. Therefore, they are seen as linear macromolecules in equilibrium with respect to their molecular weight distribution.

A number of examples have been studied, including liquid sulfur [1–3] and selenium [4], poly (α-methylstyrene) [5], polymer-like micelles [6,7] and protein filaments [8].

Many theoretical works within the mean field approximation describe the dependence of the length and distribution with temperature and concentration [7,9–13] while others show that reversible aggregation of monomers into linear polymers exhibits critical phenomena which can be described by the $n \to 0$ limit of the n-vector model of magnetism for linear chains [3,14].

Due to experimental difficulties [7] the properties of living polymers still pose a number of questions. Controversial results about the extent of the growth in micelles with decreasing temperature or rising density are reported [15–18] and no direct measurements of the molecular weight distribution have been published yet .

Up to now only a small number of simulational studies [19–28] have been carried out. Indeed, while the connectivity of polymer chains and the resulting slow dynamics render computer simulations a demanding task in its own terms, the scission-recombination processes, which are constantly under way in living polymers, impose additional problems on computational algorithms.

Until now, most of the computational research was focused on the transition between an oriented ordered phase and a disordered state [1,19–24] although numerous static properties are still unexplained.

At the same time, the behavior of polymers in constrained geometry such as polymers in a slit or in random media has found a growing interest both from a theoretical and practical point of view and theoretical predictions have been confirmed by numerical results [29–34].

In the case of living polymers, however, only few works deal with constrained systems [35,36]. In the present communication, some results on living polymers in a random medium in two dimension are reported and discussed. For dead polymers, the simulation of a two dimensional system is studied by varying the obstacle density at various chain length [37–39]. In the case of living polymers, the chain length is not fixed but both the mean chain length and the chain length distribution adapt themselves to minimize the free energy of the system. The behaviour of a dead polymer in a random medium made of quenched obstacles depends at high obstacle concentration, but still below the percolation threshold, only on the density of obstacles [40,41].

A high obstacle density below the percolation threshold ρc is better found in two dimension since $\rho c = 0.593$ on the square lattice instead of only 0.311 on the cubic lattice [42].The non-ergodicity of the reptation algorithm, which may influence the results [38], disappears completely for living polymers when a non-conserving chain length procedure is added [43].

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Simulation method

The reader can find a detailed description of the algorithm in reference [27]. The principal features of the algorithm are just recalled here for sake of clarity.

Only one monomer at a time may be present on a lattice site (excluded volume interaction between monomers). Those sites of the lattice which are not occupied by monomers or obstacles are considered empty (vacancies) and contribute to the free volume of the system. An energy $-V$ ($V > 0$) is set for the creation of a bond between monomers. The value of V/k_BT (here set to 7.4, a value found to be optimal in preceding studies [27, 28,35]), in absence of any other type of interaction between the monomers but the excluded volume interaction, defines the probability of the creation of a bond.

In the present study the ends of a given polymer chain are not allowed to bind together. This last condition avoids the formation of rings [19,20] which gives a different length distribution for even and odd chain length (in monomer units) with temperature. This is not really a constraint if we consider micellar systems in which rings are not likely to occur [7].

A MCS (Monte-Carlo Step) is organized as follows:
(i) The chains are allowed to perform a reptation move.
(ii) A monomer is chosen at random. If the monomer happens to be at the end of a chain, an attempt is made to create a bond with another monomer which might be present on any one of the four neighboring sites also chosen at random. If the end of another polymer is present on the chosen neighboring site, the Metropolis algorithm [44] is applied, that is, a new bond is created if the value of a random number between 0 and 1 is smaller than Min $\left(1, \exp\left(\frac{-V}{k_BT}\right)\right)$.
(iii) Finally, a monomer is chosen at random. If a bond on the right of the current monomer exists, it attempts to break, also according to the Metropolis rule. During one MCS one carries out (ii)–(iii) as many times as there are monomers in the system.

The algorithm was adapted to the simulation of random media by forbidding the occupancy of a given fraction ρ of randomly chosen lattice sites. The start configuration for the monomers is made of randomly distributed unbounded monomers placed on the lattice once the forbidden sites have been generated. The monomer density was fixed at 0.25 and the obstacle density ρ varied from 0 to 0.65. Hence the density of occupied sites on the lattice increases with the obstacle concentration. The time relaxation in Monte-Carlo steps (MCS) increases strongly at high value of ρ so that as much as 10^6 MCS are necessary to reach equilibrium. Such a relaxation slowing down has been already observed with different algorithms for living polymers in slits and stripes [35].

A number of structural properties are sampled during the simulation by averaging over the various system configurations and different realizations of the porous medium and randomly distributed monomers at given ρ: mean average values like the mean average contour length $\langle L\rangle$ and the mean average square end-to-end distance $\langle R_e^2\rangle$ (an average over all the chains) which can be estimated experimentally, and more precise data, like the distribution of chain lengths which has not been yet given experimentally. The simulations have been carried out on a 100×100 square lattice with periodic boundary conditions. A snapshot of the system is shown in Figure 1.

Brief theoretical summary

At the level of mean-field approximation in the absence of closed rings, one can write the free energy for a system of linear chain as:

$$\frac{F}{k_BT} = \sum_L c(L,T)\left[\ln c(L,T) - (L-1)\frac{V}{k_BT}\right] \qquad (1)$$

where $c(L,T)$ is the molecular weight distribution for chain length L. Minimization of equation (1) with respect to $c(L,T)$, subject to the condition:

$$\phi = \sum_L Lc(L,T) \qquad (2)$$

with ϕ the density of the system yields:

$$c(L,T) = \exp\left(-\left(\frac{V}{k_BT}+1\right)\right)\exp\left(-\frac{L}{\langle L\rangle}\right) \qquad (3)$$

$$\langle L\rangle = \sqrt{\frac{\phi}{e}}\exp\left(\frac{V}{2k_BT}\right).$$

This result should be valid when correlations, brought about by the mutual avoidance of the chain, are negligible.

In fact, the distribution takes a Schultz-Zimm like form for $L > 1$ as suggested by more recent analytical and numerical works [28,45–47]

$$c(L,T) = \left(\frac{L}{\langle L\rangle}\right)^{\gamma-1}\exp\left(-\frac{L}{\langle L\rangle}\right)\cdot \qquad (4)$$

Some experiments [48] suggest that the distribution can decay more fastly than in equation (3).

Simulation results

Figures 2 and 3 show the dependence of the mean chain length $\langle L\rangle$ and the mean end to end radius $\langle R_e^2\rangle$ as a function of the obstacle density ρ respectively. In this simulation, the number of sites occupied by the polymer units is kept constant and the effective monomer density, defined by the fraction of sites occupied by a polymer unit on available sites ($\phi_{\text{eff}} = \phi/(1-\rho)$), increases with the obstacle concentration. According to equation (3), an increase of $\langle L\rangle$ with increasing ρ would not be at first sight ruled out [49]. However, the opposite behaviour is observed.

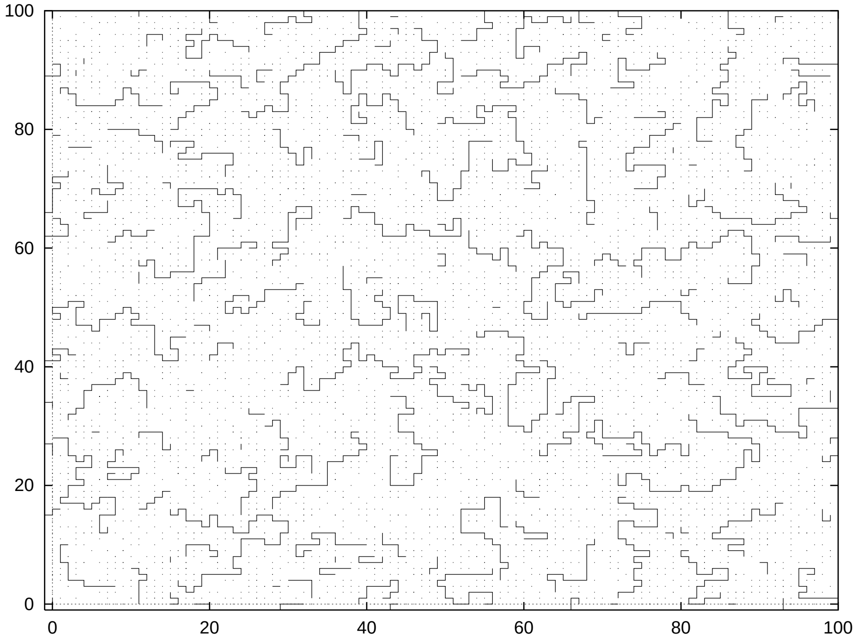

Fig. 1. Snapshot of the system for $\rho = 0.495$.

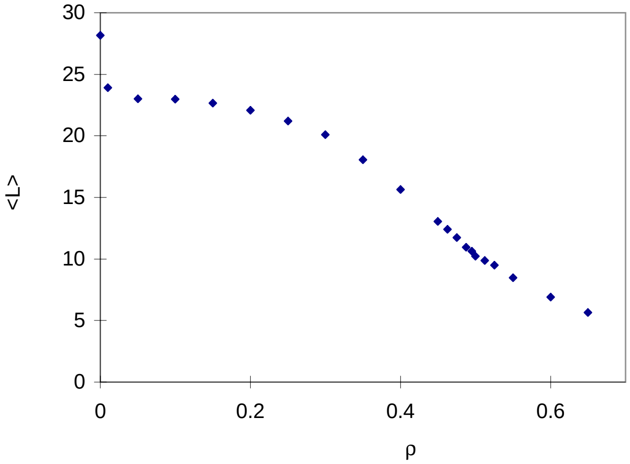

Fig. 2. Plot of the mean chain length $\langle L \rangle$ *versus* obstacle density ρ.

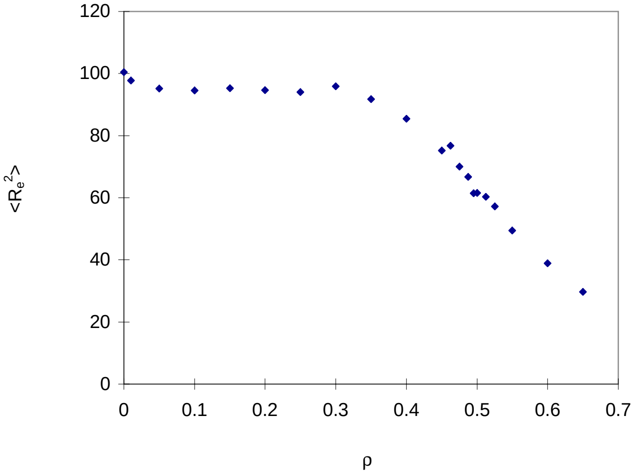

Fig. 3. Plot of the mean end to end square distance $\langle R_e^2 \rangle$ *versus* obstacle density ρ.

Unlike dead polymers, living polymers can adapt their size to minimize the perturbation exerted by an imposed constraint [35,36]: a balance is established between a reduction of the entropical energy cost through a decrease of $\langle L \rangle$ and the corresponding loss of bonds.

Hence, in addition to the natural decrease in polymer size R_e^2 due to the presence of obstacle for a given contour length L observed for dead polymers [32–34], a part of this decrease is induced by the decrease of the mean contour length $\langle L \rangle$. The system does not seem to feel as a high perturbation the percolation of the quenched obstacles since both $\langle L \rangle$ and $\langle R_e^2 \rangle$ smoothly change around ρc. This is quite not surprising if the closed domains formed above ρc are still rather large. Attempts to study the system far above the percolation threshold lead to a great fluctuation of the mean values: the formation of small closed domains of different monomer densities (see Eq. (3)) gives rise to this effect.

Figure 4 displays the scaling plot $\ln(\langle R_e^2 \rangle) = f(\ln(\langle L \rangle - 1)$. Two regimes can be distinguished below and above a cross-over value of $\rho = \rho_{\text{cross}} \sim 0.3$: For the greater values of $\langle L \rangle$ (low value of ρ), the mean end to end radius $\langle R_e^2 \rangle$ reaches smoothly and asymptotically the value of $\langle R_e^2 \rangle$ at $\rho = 0$. For the smaller values of $\langle L \rangle$ corresponding to high values of ρ, the curve is a straight line of slope 1 ± 0.05, an indication that the chains have an almost Gaussian behavior. Hence, the predictions made for Gaussian dead polymers in reference [34] could apply for living polymers for this range of value of ρ. In the limit $\rho\langle L \rangle \to \infty$ the dependence $\langle R_e^2 \rangle \sim \rho^{-2/(4-d)}$ for $d < 4$ should be observed. Indeed, the plot of $\langle R_e^2 \rangle$ as a function of ρ^{-1} (Fig. 5) displays at low value of ρ^{-1} a straight line as awaited.

The molecular weight distribution (MWD) at $\rho = 0.495$ is shown in Figure 6. Disregarding the particular value for the chain of one monomer length which needs

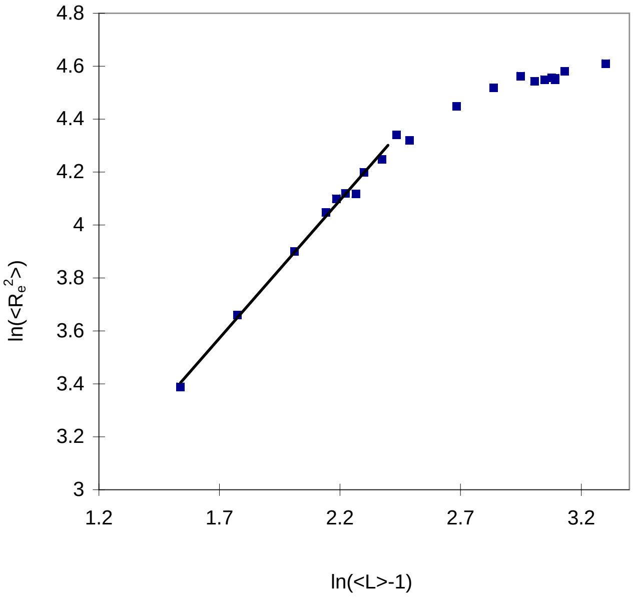

Fig. 4. Scaling plot of the mean end to end square distance $\langle R_e^2 \rangle$ *versus* mean chain bond number $\langle L \rangle^{-1}$.

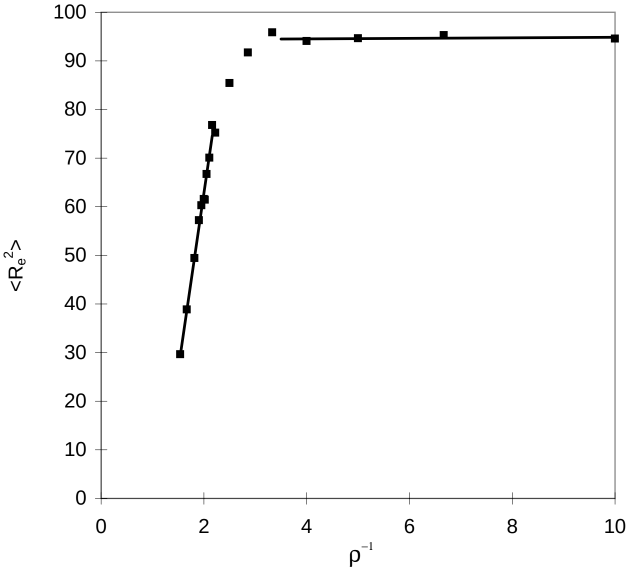

Fig. 5. Plot of the mean end to end square distance $\langle R_e^2 \rangle$ *versus* inverse obstacle density ρ^{-1}.

a specific treatment as in the case of a system without obstacle [28], the MWD is clearly not a Schultz-Zimm like distributions but can be fitted by a function of the form [48,50]

$$c(L,T) \sim L^{-2\sigma} \exp\left(-\frac{l}{\langle L \rangle}\right) \qquad (5)$$

with $2\sigma \approx 0.6$ numerically in this present case. Such a law is common in the physic of clusters: a well known example is the cluster size distribution in percolation below threshold for which $\sigma \approx 1$ [51].

This MWD form deserves some comments. In case of wormlike micelles moving by a reptation process, such kind of distribution leads to the observation of an hyperdiffusive behavior of the surfactants [48,50]: the mean square displacement scales like $\overline{R^2}(t) \sim t^{2/\mu}$ with $\mu < 2$. Hence, in one hand, the random medium decreases the diffusion of the chains [31,33] but in the other hand modifies the distribution so that a Levy flight can take place. This effect should even be enhanced in the random medium case since the inverse dependence of the chain diffusion coefficient on chain length is stronger than in the reptation case [33]. These dynamic properties should be studied numerically with other algorithms (*e.g.* Bond Fluctuation Model) but it has been shown that such kind of numerical study implies non trivial difficulties [52] that are still not solved. Following reference [48], the value of the exponent $\sigma \approx 0.3$ deduced from the present distribution leads to $\mu \approx 1.4$ which should be compared to the experimental values $\sigma \approx 0.25$ and $\mu \approx 1.5$. We must however be extremely cautious, the experiment and the present simulation are not directly comparable in their form and the value of σ experimentally measured depends on many physical and chemical parameters. In particular, the simple relation $\mu = 2 - 2\sigma$ assumes reptation dynamics and it is not obvious how this combines with the slower dynamics attributed to the existence of bottle necks in a random medium. Nevertheless, we may wonder to what extent the presence of impurities in solution of wormlike micelles could favour the apparition of a distribution of the form of equation (5) and therefrom a Levy flight.

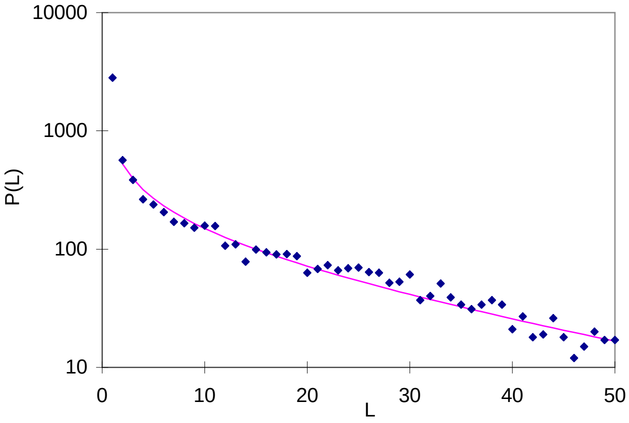

Fig. 6. Semi-log plot of the chain length distribution at $\rho = 0.495$.

Below ρ_{cross}, the living polymers does not follow a simple scaling behaviour for the dependence of $\langle R_e^2 \rangle$ with $\langle L \rangle$ (Fig. 4) as observed with dead polymers [40,41]. When the type of MWD remains the same, the mean value $\langle R_e^2 \rangle$ and $\langle L \rangle$ have the same qualitative dependence, $\langle R_e^2 \rangle \sim \langle L \rangle^{2\nu}$, as the mean value at fixed contour length $R_e^2(L) \sim L^{2\nu}$ [27]. Hence the change of the MWD form from equations (4) to (5) can be responsible of this effect.

The comparison of the present work with previous numerical works on dead polymer is not straightforward. Instead of Gaussian chains [32,34], self avoiding walk (SAW) chains are used with an excluded volume interaction between monomers of the same type than between monomers and obstacles. Only one study with dead polymers modelised as SAW's in a porous medium at various obstacles density has been made until now [37–39]. The authors see clearly a reduction of the effective scaling exponent relating R_e^2 to L from $\nu = 0.68$ to $\nu = 0.59$ that they suggest to be due to the collapse of the chain to the pore size. For their system ν remains always above 1/2 and ρ was limited to 0.3 so that they may never reached the limit $\rho\langle L\rangle \to \infty$.

The value of $\nu \sim 0.5$ observed at high value of ρ in this simulation implies, and this is not surprising, that the obstacles screen the excluded volume interaction between monomers of the same chain. Even if the concentration in monomers present is counted as the fraction ϕ_{eff} of monomers on available sites ($\phi_{\text{eff}} = 0.25/(1-\rho)$) with a maximal value of $\phi_{\text{eff}} = 0.74$ in the present simulation), previous simulation have never shown [27], although $\langle L\rangle$ was greater, an exponent ν of 0.5 for a system with $\phi < 0.8$ in absence of obstacles.

Conclusion

The present simulation gives a short insight of the living polymers behavior in random media. The dependence of $\langle R_e^2\rangle$ on ρ is the same as for dead polymers in the limit $\rho\langle L\rangle \to \infty$ although the mean contour length $\langle L\rangle$ also varies with ρ. The most important effect of the presence of obstacle is the modification of the molecular weight distribution shape so that it enables theoretically the presence of a Levy flight.

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