

Reptation, Entropic Trapping, Percolation, and Rouse Dynamics of Polymers in "Random" Environments

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We study the dynamics of polymers in 2D periodic arrays of obstacles where a fraction $(1 - c)$ of the obstacles have been removed. As expected, we find Rouse and reptation dynamics for $c \rightarrow 0$ and $c \rightarrow 1$, respectively. However, we also find that the diffusion coefficient D decreases when we start removing obstacles due to entropic trapping of the polymer within "pores." These pores begin to form large clusters when $c \approx 0.80$, and D increases when c is decreased further. Our results clarify the nature of the different regimes for a simple random environment and predict that $D(c)$ can be a nonmonotonic function of c .

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Muthukumar and Baumgartner [1–3] have shown that polymer chains can be entropically trapped in "random" environments. Under these conditions, the diffusion coefficient D was found to decrease very quickly with molecular size M , in agreement with a model which predicts that diffusion is then governed by narrow passages which reduce the entropy of the molecules when they move between the larger open areas or "pores" of the system. This new phenomenon was observed in computer simulations of the dynamics of non-self-avoiding [1] as well as self-avoiding [2] chains in random environments composed of monomer-size obstacles (placed randomly in space at a concentration below the percolation threshold), and for environments composed of large empty boxes connected by narrow channels [3]. Hoagland and co-workers [4,5] and Maver, Slater, and Drown [6] observed a new regime of gel electrophoresis where the mobility of long polyelectrolytes decreases quickly with M ; both groups interpreted these results, which cannot be explained by standard models, as an indication that polyelectrolytes such as DNA can become entropically trapped in the larger pores of the sieving gel. Rotstein and Lodge reported that for linear polystyrenes diffusing in poly(vinyl methyl ether) gels, D scales roughly as $1/M^{2.7}$, which is consistent with the predictions of entropic trapping [7].

However, the concept of a random environment is ill defined and the conditions for which entropic trapping dominates are currently unknown. Also, the transition from entropic trapping to Rouse or reptation dynamics is ill understood. Moreover, we also note that it is uncertain whether the simulation conditions used by Muthukumar and Baumgartner can be used to infer the dynamics of polymer chains in real gels (this was also noted in [7]); for instance, their distributions of block obstacles do not support their own weight. A more realistic gel would be more like the structures formed by cluster-cluster aggregation, or similar diffusion limited aggregation algorithms.

In this paper, we study the dynamics of polymer chains in imperfect periodic arrays of obstacles. Our basic goal

is to find the minimum degree of randomness required to observe entropic trapping. We thus begin with a periodic array of obstacles from which we remove obstacles at random. This system possesses two main advantages: first, the degree of randomness is directly controlled by the concentration of obstacles, and, second, the low and high concentration limits should automatically yield the Rouse and reptation dynamics, respectively. We find that entropic trapping begins essentially as soon as we create pores; this means that very little disorder can lead to nonreptative behavior. Our results differ from those of Muthukumar and Baumgartner because the large pores that we create by removing a few obstacles are very far from one another; as a result, D is found to actually decrease when the concentration of obstacles is first reduced. This is a remarkable but somewhat counterintuitive result of entropic trapping *in isolated pores*. Finally, we find that entropic trapping essentially ceases once the obstacles stop forming a percolating cluster that limits the long-range diffusion of the polymers.

We chose to study a two-dimensional (2D) system for three main reasons: (i) 3D systems would require substantially more CPU time; (ii) it is somewhat easier to visualize and quantify the dynamics in 2D in order to estimate of the degree of localization of the polymers; and (iii) the excluded volume effect is more pronounced in 2D, which enables a better estimate of its impact on the power law exponents. The four-site bond-fluctuation algorithm [8] was used since it yields the proper 2D Rouse dynamics for free self-avoiding chains. The obstacles are represented by single squares, like the monomers themselves, and the rules which take into account the excluded volume effects are identical for monomer-monomer and monomer-obstacle interactions. The obstacles form a periodic lattice with lattice parameter $q \geq 4$. The results presented in this Letter were obtained for $q = 4$. A fraction $(1 - c)$ of the obstacles is removed randomly from a 840×840 system, and periodic boundary conditions are applied. The initial polymer conformation is genera-

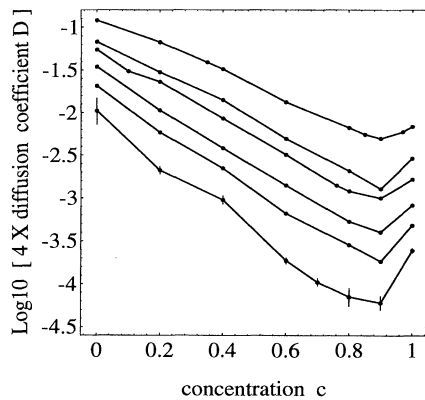


FIG. 1. Semilogarithmic plot of $4D$ vs obstacle concentration c for polymer molecules of length (from top to bottom) $M = 5, 8, 10, 15, 20,$ and 30 , respectively. For clarity, the error bars are included only for the $M = 30$ case, for which they are the largest.

ted as a random chain of M monomers and $M - 1$ links of length 2, and each simulation is preceded by a long warm-up period. For $c = 1$, the $q = 4$ lattice of obstacles corresponds to a chain moving in a tight tube (the dynamics is then qualitatively like the one suggested by the repton model [9]) and reptation behavior is found for molecules as small as $M = 5$. The simulations were carried out on three IBM as well as two SUN workstations. The slope of the $\langle r^2(t) \rangle$ vs t plot was used to obtain $4D(M, c)$, where $r(t)$ is the displacement of the center of mass of the polymer at time t ; the relaxation time $\tau(M, c)$ was obtained from the slope of the linear (long-time) part of the $\ln[C(t)]$ vs t plot, where $C(t)$ is the autocorrelation function of the chain end-to-end vector.

Figure 1 shows how D varies with c for polymer molecules of size $M = 5, 8, 10, 15, 20,$ and 30 . We notice a clear drop in the diffusion coefficient $D(M, c)$ as c decreases from 1.0 to about 0.9, followed by a marked increase as c decreases further. This nonmonotonic behavior is quite surprising since it implies that, initially, decreasing the number of obstacles actually hinders the polymer's ability to diffuse through the system. As far as we know, this peculiarity of entropic trapping has previously never been reported. This effect increases with size M .

We also observe that the radius of gyration R_g reaches a shallow minimum around $c = 0.80$ (R_g decreases by a few percent; results not shown); we attribute this to the fact that the pores are not large enough for 2D self-excluded polymer chains to collapse entirely within them. The scaling law is consistent with $R_g \propto M^\nu$, with $\nu = 0.75$, for all concentrations.

The relaxation time τ was also found to be a non-monotonic function of c . An example is given in Fig. 2 where we plotted $C(t)$ vs t for $c = 1.0$ and $c = 0.90$ with $M = 30$. We clearly see that short-time relaxation

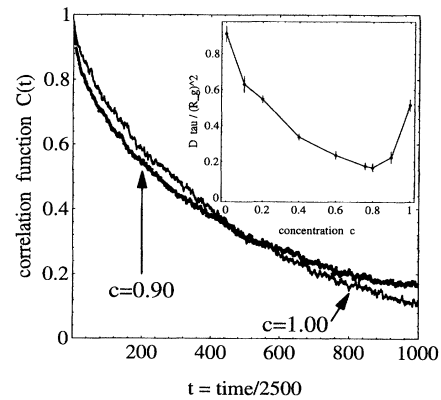


FIG. 2. Autocorrelation function $C(t) = \langle \mathbf{h}(t) \cdot \mathbf{h}(0) \rangle / \langle h^2 \rangle$ of the end-to-end vector \mathbf{h} vs time t for a polymer molecule of size $M = 30$ and two different concentrations c . The inset shows the ratio $D_{\min} / (R_g)^2$ vs concentration c for $M = 10$, where τ is the terminal relaxation time of $C(t)$.

is faster for $c = 0.90$, but that long-time relaxation is slowed by the disorder present in this more dilute system. This effect disappears for $c < 0.8$. The crossover is found here at time $t \approx 500 \times 2500$. Using the value $D(M = 30, c = 0.9) \approx 15 \times 10^{-6}$, this corresponds to a mean drift of about $(D\tau)^{1/2} = 4.3$ lattice units, while $R_g \approx 11.7$ for this polymer and the minimum pore size created by a single missing obstacle is about $a = 3$ units in radius (hence the polymer is not entirely trapped inside the pore). Therefore, we conclude that for $c = 0.90$ the polymer relaxes faster on length scales smaller than the pore size a , but that partial trapping by the pore greatly slows down the relaxation over length scales comparable to R_g , presumably because the interaction between the pore and the molecule does not allow the latter to rotate very easily. The inset shows how the ratio $D_{\min} / (R_g)^2$ varies with c for a $M = 10$ molecule. We find a decrease by a factor of 5.4 at around $c = 0.8$; the polymer then migrates over a distance much smaller than its own dimensions during the relaxation process, an indication that it is strongly localized.

Entropic trapping has been traditionally studied in terms of the dependence of the diffusion coefficient $D(M, c)$ upon molecular size M . Figure 3 shows how the exponent α , implicitly defined by $D \propto M^{-\alpha}$, varies with c (the inset shows, as an example, our data for $c = 0.90$). We observe that $\alpha \approx 1.89$ for $c = 1$ and $\alpha \approx 1.04$ for $c = 0$, consistent with the well-known reptation and Rouse limits, respectively. However, we also observe that $\alpha > 2$ when $0.90 > c > 0.40$ (this is characteristic of entropic trapping [1-5]), with a maximum value of 2.44 at $c = 0.80$.

Thus the first three figures show the existence of a broad intermediate regime, between the Rouse and reptation limits, where D is lower and more molecular size dependent than expected. Moreover, this regime is char-

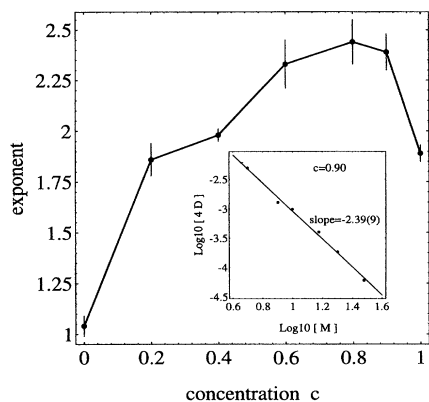


FIG. 3. Exponent α vs concentration c . The exponent was obtained from a regression analysis of the diffusion coefficients, on a log-log plot of $4D$ vs M , using the form $D \propto M^{-\alpha}$ (the inset shows an example for $c = 0.90$). The error bars correspond to a 90% confidence level.

acterized by a relaxation process which is fast over a length scale fixed by the typical pore size, but has a slow component for longer length scales. Curiously, our results also indicate that the intermediate regime disappears when c decreases below about 40%, almost irrespective of the size M of the diffusing molecule. Figures 1 and 3 suggest that this intermediate regime exists even for c very close to unity.

In order to investigate the nature of this intermediate regime, we computed the number of times the four middle monomers of a $M = 10$ polymer chain visited each site in a reduced (96×96) lattice. Figures 4(a)–4(e) display our results in the form of density plots. The sites are shaded such that the most visited ones are darker; moreover, the sites are grouped such that the monomers actually spend 25% of their time on each of the four distinctly grey shaded areas. Five different cases are shown. When $c = 0.90$, the polymer spends 25% of its time in or around the few pores that have been created: Those empty sites, which cover less than 2% of the total surface, thus act like deep, isolated “entropic” traps. Note that the molecule must reptate between each trap since the gel concentration is unity in these regions. For $c = 0.80$, the number of pores is larger, but these pores are still isolated and trapping is still very strong. For a more dilute system ($c = 0.60$), many pores are connected by wide passages that begin to form a percolating path through the system. At $c = 0.40$, the lattice of obstacles is dilute and the obstacles stop forming percolating clusters that can hinder long-range diffusion. Finally, when the concentration is small ($c = 0.10$), the obstacles play only a minor role (the pores percolate through the system) and one recovers Rouse dynamics with little entropic effects. These results are in agreement with the quantitative results presented before and explain why entropic trapping disappears for the same

concentration (40%) for all molecular sizes: This critical concentration represents the percolation threshold of the underlying lattice of obstacles for this geometry [10].

Our simulation results indicate that the diffusion coefficient of a flexible macromolecule is not necessarily a monotonically decreasing function of the density of the medium. This new prediction is directly related to the entropic properties of flexible polymers in random environments, and to the nature of the randomness (and the percolation limit) of this environment. Saxton has reported that, in some fractally random systems, the diffusion constant of spherical particles can be independent of the size of the particle [11]. It is not inconceivable that there exist other types of random environments where the diffusion coefficient might become a nonmonotonically decreasing function of the molecular size of the polymer. There have been a few reports where the electrophoretic mobility of polyelectrolytes shows such behavior [12,13].

The diffusion properties of macromolecules are influenced by the precise architecture of the environment and of the molecule itself. This means that one must be careful when analyzing experimental data since nontrivial results, such as those presented here, can occur. The system we studied could be tested using the “2D arrays of posts” of Volkmuth and Austin [14].

Our results also indicate that very little randomness is required to kill reptation. In fact, we already have very strong entropic trapping for $c = 0.97$ (results not shown). At this time, we are studying the stability of reptation vs the degree of randomness in our system. It appears that reptation is an intrinsically unstable process in a dense, random frozen environment; i.e., the chains become easily trapped within large pores and this dominates the long-term diffusion of their center of mass. The situation for very large molecules, which can span the distance between two large pores, should be most interesting since it is uncertain as to whether these molecules will reptate or will become trapped (or pinned) by many pores simultaneously.

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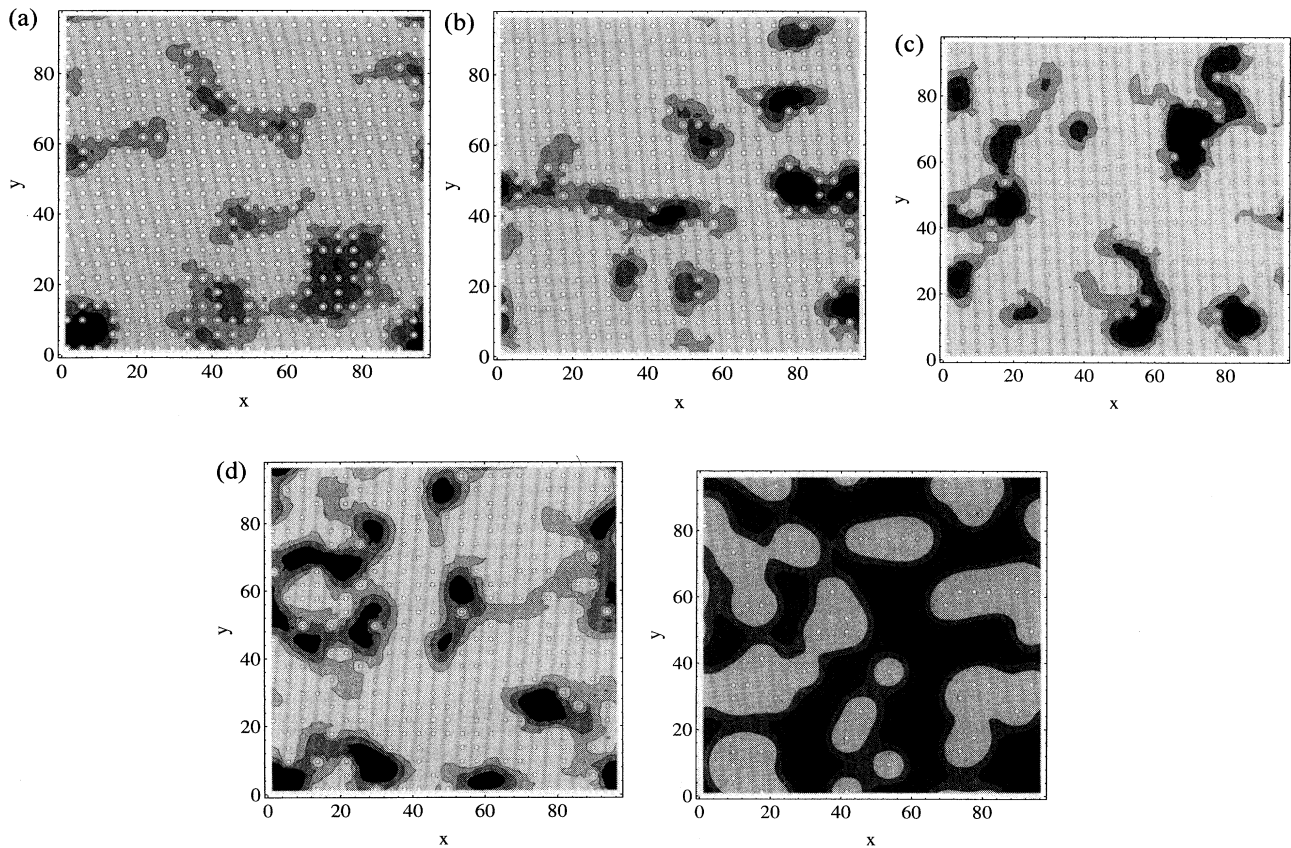


FIG. 4. Density plots showing the number of times the (four) middle monomers of a $M = 10$ polymer molecule visited the different sites within a 96×96 lattice (with periodic boundary conditions). The darker lattice sites have been visited more often. The small white squares are centered at the location of the obstacles. The monomers visited each of the four grey shaped regions for an equal period of time. In the following, we give the fraction (in %) of the total surface area covered by each of the four regions (from light grey to black) as a measure of the degree of localization of the polymer; for a trapping-free case (e.g., when $c = 0$), these fractions would be 25:25:25:25. (a) $c = 0.90$; areas=71:19:8:2. (b) $c = 0.80$; areas=73:16:7:4. (c) $c = 0.60$; areas=68:18:9:5. (d) $c = 0.40$; areas=56:21:14:9. (e) $c = 0.10$; areas=40:23:20:17.

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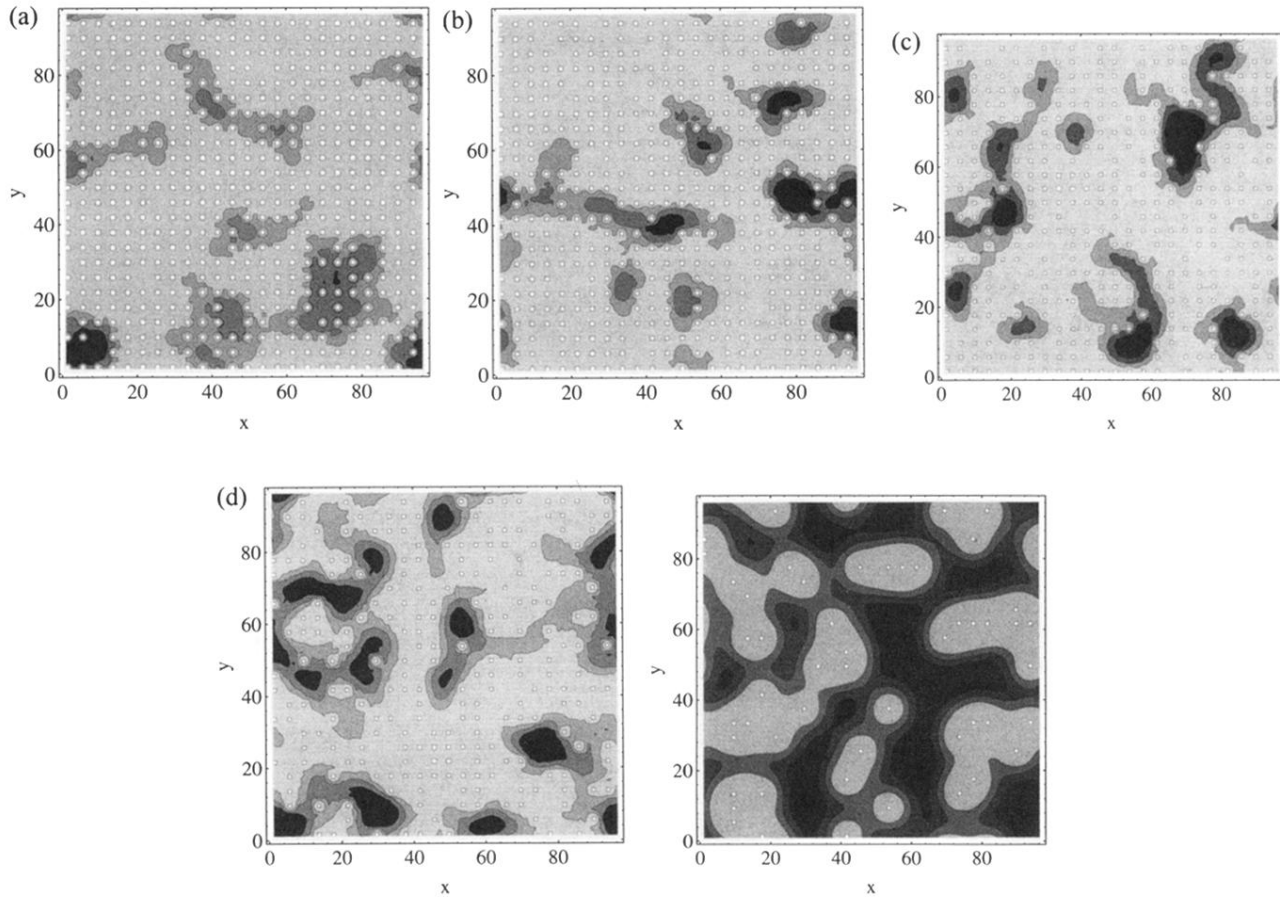


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