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The diffusion coefficient of a polymer in an array of obstacles is a non-monotonic function of the degree of disorder in the medium

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Abstract

Using Monte Carlo simulations, we have found that there is a surprising non-monotonic dependence of a polymer's diffusion coefficient upon the degree of disorder of the surrounding environment. Starting with a two-dimensional periodic lattice of obstacles, we randomly displace obstacles to create a quenched gel system with a tunable degree of disorder. Very small displacements increase the diffusion coefficient of polymers since they increase the width of the tube through which the polymer chains reptate. As we displace the obstacles further, however, entropic trapping is observed and the diffusion coefficient of the polymer decreases dramatically. This is a striking example of the delicate balance between entropic and frictional effects for a polymer diffusing in a dense system.

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Entropic trapping (ET) of polymer chains in random gels or porous systems is a concept that was originally proposed by Muthukumar and Baumgartner in a seminal 1987 paper [1]. In ET, the spatial dependence of a chain's conformational entropy (or free energy) is equivalent to an external potential that tends to trap the chain in those regions of the gel where its entropy is maximized. Dense gel regions lower the conformational entropy of the chain, and are thus avoided. Empty regions, on the other hand, maximize the entropy and act as potential wells that trap the chain for extended periods of time. Long-time diffusion is thus limited by the time it takes to jump between large pores separated by dense regions (the latter then act as potential barriers). Evidence for ET has been reported, for example, in the case of DNA gel electrophoresis [2–4]. The concept of ET has also been used to create novel microfluidic devices [5,6]. Recently it has been suggested that ET might also be involved in binding in some biological systems [7].

We previously demonstrated that ET sometimes leads to surprising and counter-intuitive effects. Using the bond-fluctuation Monte Carlo algorithm [8,9], we examined a polymer chain diffusing in a two-dimensional array of periodically distributed obstacles. The dependence of the diffusion coefficient $D(C)$ on the fraction $1 - C$ of obstacles removed from the array was non-monotonic. The limiting cases were fully consistent with the Rouse ($C = 0$) and reptation ($C = 1$) models. As $1 - C$ increases (more obstacles are removed), one intuitively expects a monotonic increase of $D(C)$ since the removal of obstacles should obviously make it easier for the chain to diffuse. However, it was not the case for this model system. Starting with a perfectly periodic lattice of obstacles, removing a small percentage of the obstacles actually caused a considerable decrease in the diffusion coefficient [8,9]. This is due to entropic trapping in the voids left after obstacles are removed. These local entropic traps acted as potential wells, reducing the diffusion coefficient of polymers. The strongest trapping occurred when only $1 - C = 10\%$ of the obstacles were removed [9]. As more obstacles were removed, the traps became stronger, but also got larger, reducing the distance between traps. Eventually the traps

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all joined and they were no longer isolated: A percolating pathway was created and the diffusion coefficient rapidly increased towards the value $D(0)$ expected for a free chain.

This interesting non-monotonic transition between the reptation and Rouse limits is the non-trivial result of ET. However, one of the weaknesses of the previous study was that removing obstacles simultaneously increased both the degree of disorder in the array of obstacles and the free volume available to the chain. We now report a study of a similar system where we keep the number of obstacles constant and increase the amount of disorder by randomly moving the obstacles in the vicinity of their initial position. Due to the nature of the model we have a small decrease in the free volume available due to the creation of lakes (empty sites completely surrounded by obstacles), as well as channels which are too narrow (only one site wide) to allow a monomer to pass through. However, the change in the free volume is always less than seven percent. Thus, this model reduces the effect of changes in the obstacle density (concentration of the gel) and allows us a new look at the transition from a periodic distribution of obstacles (where polymer reptation is known to occur [10]) to a totally random distribution of obstacles (where ET is expected to dominate dynamics [11]).

The model used in our simulations is based on the two-dimensional Bond-Fluctuation Monte Carlo algorithm [12] (see Fig. 1) on a square lattice (whose mesh size is $a = 1$). This is the same model as used in previous simulation of entropic trapping done in our group, and has been described in detail in previous papers on this topic [9].

A polymer chain consists of N monomers (represented as one square plaquette on the lattice) which are linked by bonds which can vary between $2a$ and $\sqrt{13}a$ in length (this yields 36 possible bond vectors linking adjacent monomers). This, combined with the fact that two monomers cannot occupy the same site on the lattice or touch one another, prevents bond crossing. A move consists of attempting to move a random monomer one site in the $\pm x$, or $\pm y$ direction. Monomer moves are accepted as long as the new bond lengths remain in the range $[2a, \sqrt{13}a]$ and there is no monomer or obstacle blocking the way. One Monte Carlo Step (MCS) consists of N such moves. The polymer is only added after the system of obstacles is properly prepared, so as to ensure that its presence does not affect the final obstacle layout.

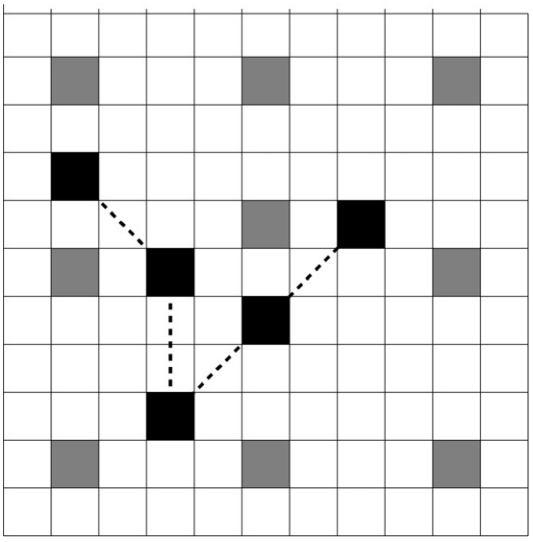

Fig. 1. A simple schematic representation of our simulation model. The grey boxes represent obstacles while the black boxes are monomers. The dotted lines show the bonds between adjacent monomers. The obstacles initially form a periodic array (here with a periodicity of 4). In this example, only the central obstacle was moved from its initial position in order to add some disorder in the system.

Our obstacles are also represented as square plaquettes on the lattice that cannot overlap or touch one another. First, the obstacles are placed periodically to form a regular array with a simple square symmetry of periodicity $\lambda \geqslant 4a$. We make the lattice large enough (at least 5000 sites by 5000 sites, with periodic boundary conditions) that finite size effects are negligible.

We then add a tunable degree of randomness to the system by allowing each obstacle to move in the harmonic potential

$$U(r_i) = \frac{1}{2}K(\vec{r}_i - \vec{r}_{oi})^2 \tag{1}$$

about its initial position $\vec{r}_{oi}$, where K is the spring constant that controls the amount of disorder in the system. When $K \to \infty$, the obstacles do not move from their initial location and therefore remain periodic in space. The other extreme is when $K \to 0$: In this limit, the position of the obstacles take on a totally random (or disordered) distribution. Values of K between these two extremes will result in an intermediate amount of disorder in our obstacle distribution.

We displace the obstacles using monomer-like random moves that we accept, if there is no other obstacle blocking the move, with a probability given by a standard Metropolis test: $P = \exp\{-(\frac{U(\vec{r}_{\text{new}}) - U(\vec{r}_{\text{current}})}{k_{\text{B}}T})\}$, where k_{B} is Boltzmann's constant and T is the temperature. The obstacles are prepared (or warmed up) for a total of 250 attempted moves per obstacle. The equilibrium distribution (neglecting volume exclusion) of the obstacles about their initial positions $\vec{r}_{oi}$ is given by the Boltzmann distribution

$$\rho(r) \sim \exp\left(-\frac{Kr^2}{2k_{\text{B}}T}\right), \tag{2}$$

where $r^2 \equiv (\vec{r}_i - \vec{r}_{oi})^2$. Due to the finite number of attempted moves and volume exclusion effects between obstacles, our data does not fit this distribution perfectly, although it is very close (the $K = 0$ case is obviously special). Once we have completed this warm-up period, we quench the obstacles in place for the rest of the simulation. An approximate value (neglecting volume exclusion and the finite warm up time) for the root mean square obstacle displacement can easily be found by evaluating the simple Boltzmann sum

$$r_{\text{rms}} = \left\langle r^2 \right\rangle^{1/2} \approx \sqrt{\frac{\sum_{ij} r_{ij}^2 \exp\left(-\frac{Kr_{ij}^2}{2k_{\text{B}}T}\right)}{\sum_{ij} \exp\left(-\frac{Kr_{ij}^2}{2k_{\text{B}}T}\right)}}. \tag{3}$$

The difference between the values found using Eq. (3) and our simulations are tabulated in Table 1.