

# Sequence dependence of polymer dynamics in quenched disordered media: Weak attraction facilitates transport

Sung-Joo E. Lee

*Biophysics Graduate Group, University of California, Berkeley, California 94720  
and Physical Bioscience Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

Arup K. Chakraborty

*Department of Chemical Engineering and Department of Chemistry, University of California, Berkeley, California 94720 and Materials Science and Physical Bioscience Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720*

(Received 8 July 2002; accepted 17 September 2002)

We study the dynamics of polymers in a random disordered medium of fixed obstacles using kinetic Monte Carlo methods. The polymers can have monomers which have attractive (A-type), repulsive (R-type) or neutral (H-type) interactions with the fixed obstacles that comprise the disordered medium. Several classes of homopolymers and heteropolymers with diverse sequences have been studied. Our most noteworthy result is that, above a threshold temperature, polymer bearing monomers that are attracted to the disordered medium translocate faster through the medium than those bearing neutral or repulsive monomers. We discuss how a delicate balance between energetic and entropic factors leads to this counterintuitive outcome. By examining heteropolymers with different sequences, we also find that the dependence of mobility on average composition is stronger than that on higher order correlations characterizing the sequence distribution. Connections between our results and experiments with synthetic and biological systems are noted. © 2002 American Institute of Physics. [DOI: 10.1063/1.1519838]

## I. INTRODUCTION

Diffusion of polymers through random disordered media is of practical interest for applications including enhanced oil recovery, drug delivery, gel electrophoresis and exclusion chromatography, and DNA sorting. The behavior of a single polymer chain in a disordered medium has also served as a model system to study fundamental aspects of the importance and effects of chain entropy.<sup>1</sup> Most studies of polymers in disordered media, beginning with the pioneering studies by de Gennes, Muthukumar, Baumgartner, and Edwards, focus on homopolymers in a random medium composed of a set of fixed obstacles.<sup>1-3</sup> These studies have revealed that dynamics of polymers in random disordered media can be classified into three different regimes. When the radius of gyration of the polymer  $S$  is much smaller than the average pore size  $m$ , the polymer does not feel the strong topological constraints imposed by the randomly placed obstacles. Here the Rouse model<sup>4</sup> is appropriate, and  $D \sim N^{-1}$ , where  $D$  is the diffusion constant and  $N$  is the chain length. In the opposite extreme, when  $S \gg m$ , due to the strong topological constraints chain motion along its contour becomes the most facile mode. In this regime de Gennes' reptation model<sup>4,5</sup> predicts  $D \sim N^{-2}$ . In an intermediate regime, where pore sizes are comparable to chain size,<sup>1</sup> entropic traps slow down the dynamics even more strongly than reptation. Void spaces in the medium that are comparable to unperturbed chain dimensions serve as traps where the chain resides for long periods of time.<sup>6</sup> While these results originated in theoretical and simulation studies, similar results were obtained by gel electrophoresis experiments of DNA.<sup>7</sup> Recently, the impor-

tance of entropy in directing polymers (DNA) from confined spaces to larger voids has been demonstrated using fluorescence microscopy.<sup>8</sup>

Heteropolymers, or copolymers, are macromolecules with more than one kind of monomer. Heteropolymer sequences may vary from highly regular repeats (e.g., block copolymers) to completely random arrangements, as in random heteropolymers. Many biologically important macromolecules are also heteropolymers. While DNA and protein sequences are usually aperiodic, certain glycosaminoglycans are mainly composed of two repeating monomer units.<sup>9</sup> Heteropolymers have been studied in many contexts in the preceding decade. The phase behavior of molten block copolymers<sup>10</sup> and random heteropolymers<sup>11</sup> has been studied using theory, computer simulation, and experiments. Heteropolymers with random or disordered sequences have been used as model systems to study the physics of protein folding.<sup>12</sup> Field theories<sup>13</sup> and computer simulations<sup>14</sup> have also been employed to study the principles of pattern recognition between heteropolymers and surfaces bearing binding sites. The thermodynamic behavior of heteropolymers in a three-dimensional disordered medium where in the sites that comprise the medium interact differently with the two kinds of segments that constitute the heteropolymer has been elucidated using replica field theory<sup>15</sup> and computer simulations.<sup>16</sup> Scaling arguments regarding the dynamics of heteropolymers in random media have also been presented.<sup>17</sup>

In this paper we employ Monte Carlo simulations to investigate the dynamics of several heteropolymers and homopolymers in random media. Specifically, we consider two-letter heteropolymers in a random medium comprised of sites that interact differently with the two kinds of het-

eropolymer segments. Our most striking result is that chains containing segments that exhibit attractive interactions with sites that comprise the medium translocate faster through the medium than when chain segment interactions with the medium are purely repulsive. We argue that this is because attractive segment-site interactions can facilitate transport of molecules through entropic bottlenecks. Such a phenomenon is observed in the facilitated transportation of cargo molecules through nuclear pore complexes (NPCs) on the nuclear envelope.<sup>18</sup> This principle is used to interpret our results for the dependence of chain motion on heteropolymer sequence. The dynamics of random, blocky, and perfectly alternating sequences are studied.

This paper is organized as follows: The model and Monte Carlo simulation method is described in Sec. II. The main results are presented and discussed in Sec. III. In Sec. IV, we offer brief concluding remarks.

## II. MODEL AND METHOD

Our simulations employ kinetic Monte Carlo techniques of a single freely jointed polymer chain<sup>19</sup> in a box with periodic boundary conditions. The simulation box is partitioned into cells of size  $a \times a \times a$ , where  $a$  is an arbitrary unit of length. Each cell is either void or occupied by a fixed spherical obstacle (disordered particle) of diameter  $R_D = a$  with a probability,  $\rho$ . Therefore,  $\rho$  is the fraction of occupied cells, and the site-site density fluctuations in the medium exhibit short-range correlations only. An off-lattice freely jointed polymer chain of  $N$  spherical beads (segments) and  $N-1$  rigid bonds is equilibrated in the simulation box after creating a realization of the disordered medium. The bond length between beads of the chain is  $l/a = 0.6$ . The diameter of each bead  $R_B = l/a\sqrt{3}/4$  which is just large enough to prohibit chain crossing. Excluded volume interactions are enforced between all particles in the system. Interactions of the chain segments with sites that comprise the medium are further augmented in ways that depend upon the type of chain segment. We use three kinds of beads, *A*-type, *H*-type, and *R*-type all of same size but exhibiting different interactions with the medium. The segment-site interactions that correspond to these three types of chain segments are shown in Fig. 1. The potentials that describe each type of bead-disordered site interaction are

$$U_{H,A,R}^{\text{BD}} = \infty \quad \text{when } r_{ij} \leq \sigma,$$

$$U_H^{\text{BD}} = 0 \quad \text{when } r_{ij} \geq \sigma,$$

$$U_R^{\text{BD}} = -U_A^{\text{BD}} = \max \left[ \epsilon, 4\epsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right) \right]$$

when  $\sigma < r_{ij} < 2\sigma$ ,

$$U_{A,R}^{\text{BD}} = 0 \quad \text{when } r_{ij} \geq 2\sigma,$$

where  $r_{ij} (= |r_i - r_j|)$  is the separation between the  $i$ th bead and  $j$ th site in the medium.  $\epsilon = 1k_B T_{\text{ref}}$ , where  $k_B$  is the Boltzmann constant and  $T_{\text{ref}}$  is a reference temperature. Interaction lengths are controlled by  $\sigma$  where  $\sigma/a = (R_B + R_D)/2$ . While *H*-type beads interact as a hard sphere,

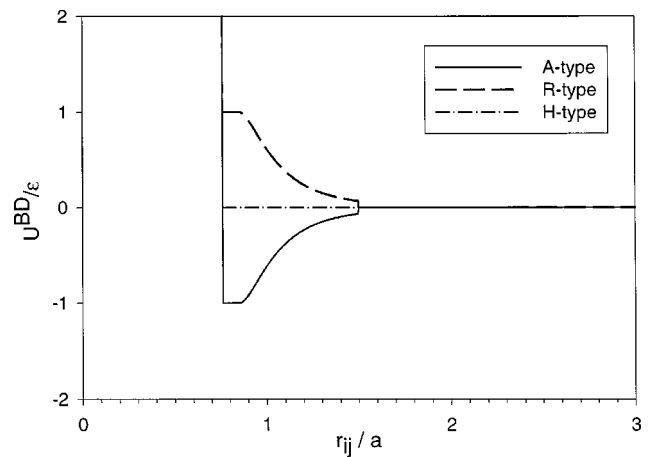


FIG. 1. Potentials that describe the three types of interactions between polymer segments and sites that comprise the disordered medium.

*A*-type beads exhibit attractive interactions and *R*-type beads exhibit repulsive interactions beyond the excluded volume constraints. All bead-bead (intrachain) interactions are of the excluded volume type only. This is done for convenience in order to focus attention on the effects of disparate interactions between the chain segments and the sites that comprise the medium.

The kink-jump algorithm<sup>19</sup> is used to evolve chain conformation and location. At a given Monte Carlo step (MCS), one of the  $N$  beads is chosen. If this bead is one of the end beads, the bond connecting it to its neighbor is rotated to a new position in a spherical motion through randomly chosen azimuthal and polar angles. Otherwise, the bead is rotated by a random angle in a circular motion by rotating the bonds formed with the two neighboring beads. The axis of this rotation coincides with a straight line connecting the two neighbors of the rotated bead. Each attempted move is accepted according to the Metropolis criterion with probability  $\min(1, \exp(-\Delta U/k_B T_{\text{ref}}))$ , where  $\Delta U$  is energy difference between the new and old chain. The energy  $U$  is defined as

$$U = \sum_{i=1}^N \sum_j U_{ij}^{\text{BD}} + \sum_{i=1}^{N-1} \sum_{k=i+1}^N U_{ik}^{\text{BB}},$$

where  $U_{ij}^{\text{BD}}$  is energy between bead  $i$  and disorder  $j$  and  $U_{ik}^{\text{BB}}$  is energy between the beads  $i$  and  $k$ .  $N$  is the chain length.

Each MCS consists of  $N$  attempted moves. Quantities such as the long time mean square displacement are calculated by averaging over different realizations of the disordered medium and initial chain configurations. Typically, quenched averages were computed using 60 or more realizations of the disordered site distribution for each value of  $\rho$ . Monte Carlo simulations of heteropolymer chain dynamics in each realization of the disordered site distribution were started with a different seed configuration of the chain.

## III. RESULTS AND DISCUSSION

### A. Effect of type of segment-site interactions on chain dynamics

We calculated the mean square displacement of the center of mass of the chain,  $R^2(t)$ ,

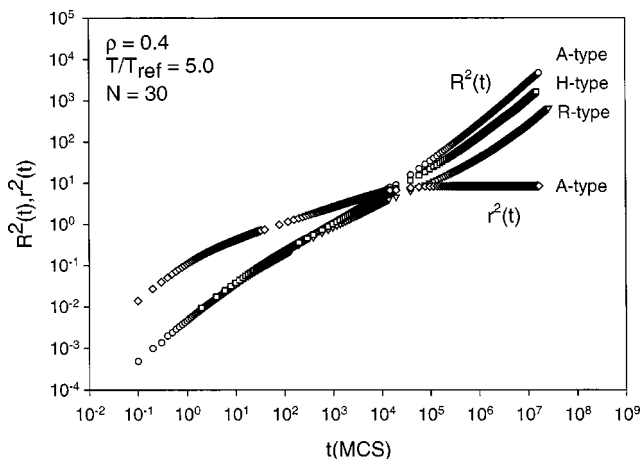


FIG. 2. Plots of mean square displacements of center-of-mass  $R^2(t)$  and the mean square displacement of the  $(N/2)$ th segment around the center-of-mass  $r^2(t)$  as a function of time in units of Monte Carlo steps (MCS) for three types of homopolymers (A,H,R-type).  $r^2(t)$  of the H,R-type are not plotted since it is very similar to that for an A-type homopolymer.

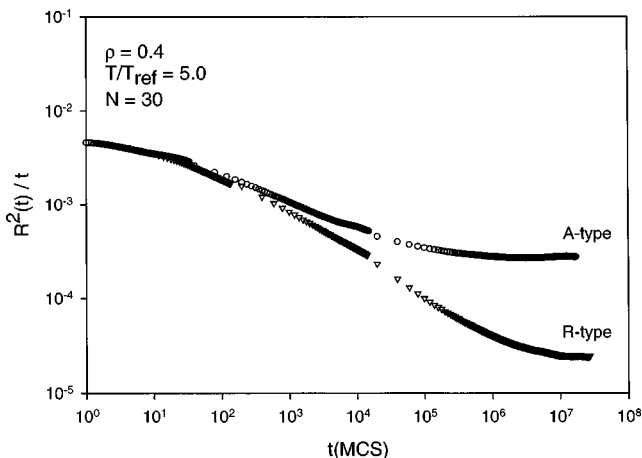


FIG. 3. Plots of  $R^2(t)/t$  as a function of simulation time ( $t$ ). Diffusion coefficient is estimated from the long time asymptotic limit.

$$R^2(t) = \langle [R_{cm}(t) - R_{cm}(0)]^2 \rangle$$

and  $r^2(t)$ , the mean square displacement of the  $(N/2)$ th bead around the center-of-mass,

$$r^2(t) = \langle [R_{cm}(t) - R_{N/2}(t) - R_{cm}(0) + R_{N/2}(0)]^2 \rangle.$$

These quantities are plotted as a function of the number of MCS (or time) in Fig. 2 for  $N=30$ ,  $\rho=0.4$ , and  $T/T_{ref}=5.0$ . The behaviors of three homopolymers (A-type, H-type, R-type) are compared. As shown in Fig. 2, the simulation time far exceeds the equilibration time,  $\tau_N$ , which is determined by the condition,  $r^2(t) \sim t^0$ .

The self-diffusion coefficient of the center-of-mass is defined by

$$D \equiv \lim_{t \rightarrow \infty} \frac{1}{6} \frac{R^2(t)}{t},$$

and is estimated by the long time limit of  $R^2(t)/t$ . In Fig. 3, the variation of this quantity with  $t$  is illustrated for A and R-type homopolymers. Figure 3 makes it clear that our simulations are sufficiently long for  $R^2(t)/t$  to reach an asymptotic constant value. Thus, we can extract a value for the diffusion coefficient for chains with different sequences.

We will focus attention on the three homopolymers. Surprisingly, Figs. 2 and 3 show that the A-type homopolymer diffuses faster than H-type and R-type homopolymers. We find this to be true for values of  $\rho \leq 0.5$ . Simulations for conditions where more than half the sites are occupied by obstacles ( $\rho > 0.5$ ) are computationally prohibitive since  $\rho$  is close to the percolation threshold.

The result that chains containing segments that have attractive interactions with the medium move through the system faster than those that exhibit repulsive interactions is counterintuitive. We naively expected that attractive interactions would slow down chain mobility in the medium. Further insight into this issue is obtained by the simulation results shown in Fig. 4. The ratio of the diffusion coefficient for homopolymers with attractive segments ( $D_A$ ) to that of a

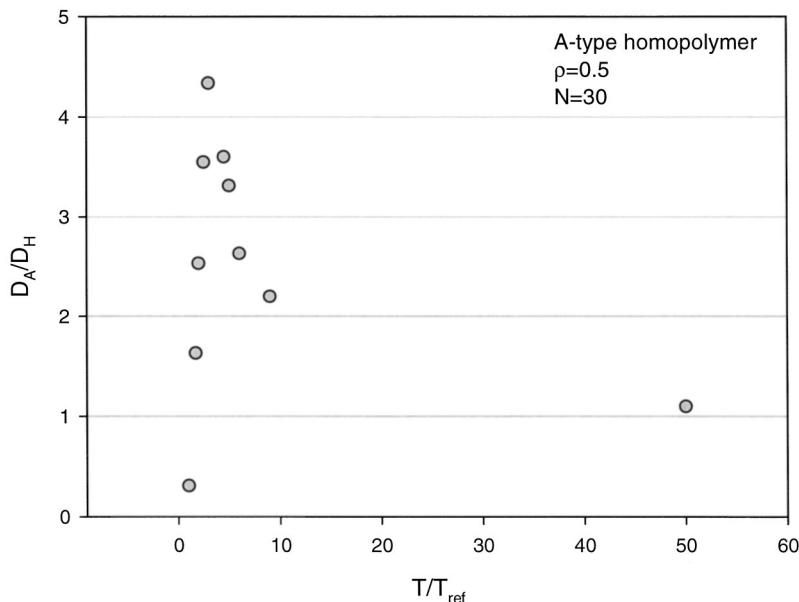


FIG. 4. Dependence of the diffusion coefficient of the A-type homopolymer ( $D_A$ ) for constant  $N$  and  $\rho$  as a function of temperature. The ratio  $D_A/D_H$  ( $D_H$  is the diffusion coefficient for H-type homopolymer) is plotted.

purely hard sphere system ( $D_H$ ) is shown as a function of temperature for constant  $N$  and  $\rho$ . The variation is nonmonotonic. At low temperatures bead-disorder attraction dominates and the chain is strongly bound to the quenched distribution of sites that comprise the medium. Thus, the value of the diffusion coefficient for an attractive chain is smaller than the diffusion coefficient of chains that have segments that exhibit hard sphere interactions with the sites that comprise the medium. Above a threshold value of the temperature,  $D_A/D_H > 1$  with its asymptotic limit being  $D_A/D_H = 1$ . The latter limit is due to the fact that as  $T \rightarrow \infty$  the attractive interactions are small compared to the thermal energy, hence the hard sphere limit is realized where the entropic contribution to the free energy dominates. The results shown in Figs. 2 and 3 correspond to an intermediate temperature where  $D_A/D_H > 1$ , and the chain with attractive segments is more mobile than those with  $H$  and  $R$ -type segments. We note in passing that recent molecular dynamics simulations concerning experiments with sticky colloidal spheres exhibit the same nonmonotonic dependence of diffusion coefficient on temperature, where at an intermediate temperature sticky colloidal spheres are more mobile than hard spheres.<sup>20</sup> What is the physical reason that underlies the result that, at intermediate temperatures, chains with attractive segments are more mobile than chains with  $H$  or  $R$ -type segments?

Previous studies<sup>3,21</sup> have clearly demonstrated that polymer chains with hard-sphere interactions with sites that comprise a random medium spend a large fraction of time in void spaces that are commensurate with unperturbed chain dimensions. This is because these void spaces serve as entropic traps (*vide supra*). Translocation from one such void space to another requires that the chain pass through a narrow opening which, in turn, corresponds to a more constrained conformation, resulting in lower configurational entropy. This is illustrated in Fig. 5. Once the chain is in such a constrained circumstance (II), motion to another void space (III) is facilitated by the entropic advantage of passing to a void space. This idea of entropy giving chains a “shove” as they pass to large void spaces has recently been demonstrated experimentally.<sup>8</sup> The free energy barrier for transport from one void space to another is thus primarily associated with the entropy loss in going from a large void space (I) to a more constrained environment (II). As sketched in Fig. 5, attractive interactions between segments and sites that comprise the medium can attenuate this free energy barrier. An appropriate metaphor is that threading a needle is easier if the eye of the needle is decorated with attractive moieties. Modification of the free energy landscape due to attractive bead-disorder interaction in the void spaces ( $F_I^A - F_I^H$ ) is smaller in magnitude in comparison to that of the narrow channel ( $F_{II}^A - F_{II}^H$ ). Therefore the free energy barrier from I to II is smaller for  $A$ -type than in  $H$ -type homopolymers. This is due to the fact that the chain has minimal contact with surrounding disorders in void spaces I and III, whereas in II it adopts an elongated conformation that is subject to plentiful contact with disordered sites. Evidence of such correlation between elongated chain conformation and energetic interaction with disordered sites will be discussed later in the

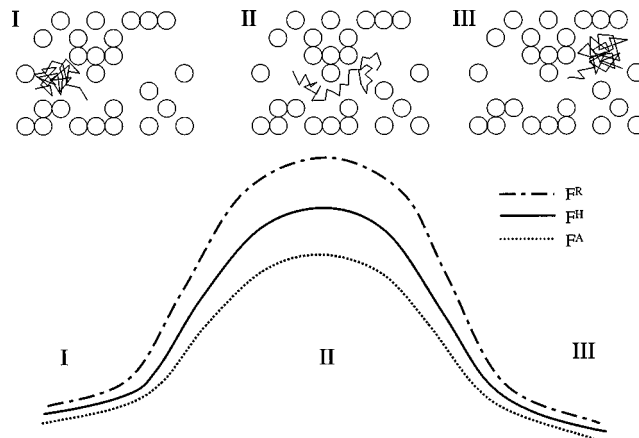


FIG. 5. Two-dimensional cartoon of a polymer chain translocating between neighboring void spaces. For clarity, only the bonds of the chain are shown. In situations where the chain resides in void spaces as in I and III, the chain increases configurational entropy, and therefore lowers its free energy. In order to translocate through the narrow channel connecting void spaces, the chain is subject to an elongated conformation as shown in II, which is entropically unfavorable. In such elongated conformations, interactions with the disordered sites (circles) comprising the medium are more pronounced. Attractive and repulsive interactions ( $A$ -type and  $R$ -type) with the disordered site can modify the free energy profile, which is sketched below.

paper. However facilitation of chain transport due to attractive interactions with disorder sites cannot be true at low temperatures. For chains with attractive segments, the barrier to simply move away from adjacent disordered sites can become significant due to strong attractive interactions. This provides an explanation for the results shown in Fig. 4.

Figure 6 provides further support for the arguments presented above. Here we show examples of trajectories for the chain center-of-mass in a particular realization of the random medium for  $A$ -type and  $H$ -type homopolymers. For clarity, the sites that comprise the medium are not shown. Both trajectories correspond to the same total simulation time. Notice, however, that the scales on the axes that measure the spatial extent of the trajectories are different. In this particular trajectory the  $H$ -type homopolymer travels three void spaces going back and forth via narrow interconnecting channels. During the same time interval the  $A$ -type homopolymer traverses a larger volume spending less time in each void space and quickly moving through several void spaces via narrow channels. Our explanation for this is the attenuation of the entropic trapping effect due to attractive interactions between  $A$ -type segments and the medium.

Arguments for facilitated transport due to attenuation of entropic traps by attractive interactions are further buttressed by the simulation results shown in Fig. 7. In Fig. 7, normalized distribution functions for the mean square radius of gyration  $\langle S^2 \rangle$  are compared for different types of chains with  $N=32$ ,  $T/T_{\text{ref}}=3.0$ ,  $\rho=0.45$ , and  $\rho=0.0$ . The mean square radius of gyration is defined as

$$\langle S^2 \rangle = \frac{l^2}{N^2} \sum_{i=1}^{N-1} \sum_{j=i+1}^N \langle [r_i - r_j]^2 \rangle.$$

The average corresponds to both average over chain conformations and the quenched average over many realizations of

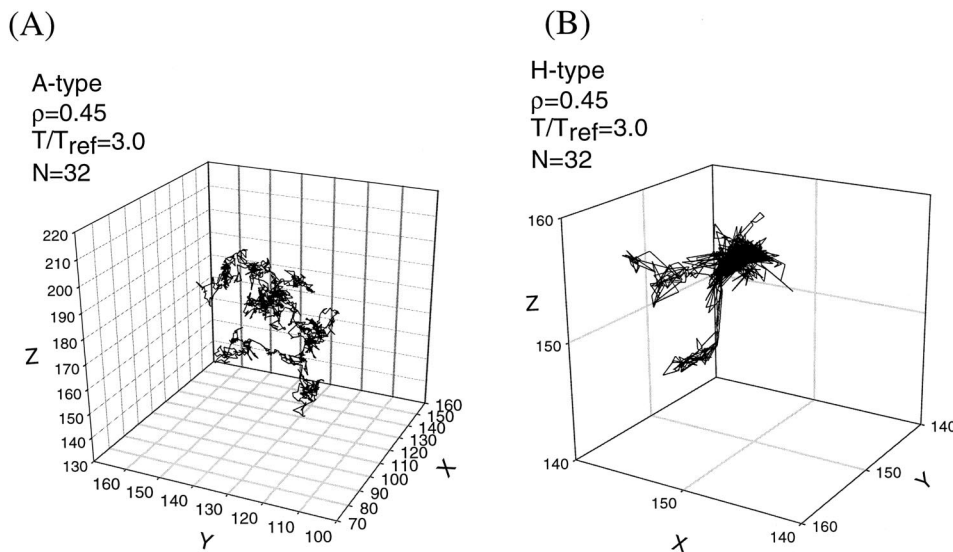


FIG. 6. Trajectory of the center-of-mass of (A) A-type and (B) H-type homopolymer. For clarity, the disordered sites are not shown. Note the difference in length scales in both three-dimensional plots. Both trajectories correspond to the same total number of Monte Carlo steps.

the disordered distribution of sites comprising the medium. Figure 7 demonstrates that the distribution of  $\langle S^2 \rangle$  is widest for the A-type homopolymer. This suggests that the A-type homopolymer spends a longer fraction of time in an extended form traveling through narrow channels than the H-type homopolymer, which stays in void spaces in more or less unperturbed conformations for a longer fraction of time. The same trend is seen by comparing the results for H-type and R-type homopolymers. Note that at  $T/T_{ref}=3.0$ ,  $\langle S^2 \rangle$  of the  $N=32$  homopolymer in the absence of disorder ( $\rho=0$ ) is larger than H-type and R-type homopolymers, but smaller than the A-type homopolymer at  $\rho=0.45$  (at  $\rho=0$ , the distinction between A-type, H-type and R-type become meaningless). The presence of the quenched disorder shrinks the size of the homopolymers that have purely repulsive interactions with the sites comprising the disorder. For temperatures below a threshold ( $T/T_{ref} \sim 4.5$  in our simulations), attractive interactions lead to a larger size for A-type homopolymers that exhibit attractive interactions along with short range re-

pulsions with the disorder. Above this threshold temperature,  $\langle S^2 \rangle$  for the  $N=32$  homopolymer at  $\rho=0$  becomes smaller than the A-type homopolymer at  $\rho=0.45$ .

Consider the covariance and correlation of the chain energy ( $U$ ) and  $S^2$ . Covariance and correlation are defined as

$$\text{covariance}(x,y) = \langle (x - \langle x \rangle)(y - \langle y \rangle) \rangle,$$

$$\text{correlation}(x,y) = \frac{\text{covariance}(x,y)}{\sigma_x \sigma_y},$$

$$-1 \leq \text{correlation}(x,y) \leq 1,$$

where  $\sigma_x$  and  $\sigma_y$  are standard deviations of the variables  $x$  and  $y$ . Correlation ( $U, S^2$ ) for the A-type homopolymer (for  $\rho=0.45$ ,  $T/T_{ref}=3.0$ , and  $N=30$ ) is  $-0.16$ . Negative correlation indicates that when the chain conformation is elongated, chain energy is lower. Correlation ( $U, S^2$ ) = 0.25 for R-type homopolymer under the same conditions. This indicates that there is a strong energetic penalty when the chain is in elongated shape. In order to travel through narrow channels the chain must adopt an elongated shape. For R-type chains, these entropically unfavorable situations are also associated with energy penalties.

The arguments we have made to explain facilitation of chain mobility due to attractive segment-site interactions do not hold if the medium is not comprised of sites that are distributed in a fashion such that void spaces comparable to chain size are present. Facilitation of chain transport due to attractive interactions should not be a strong effect in an ordered medium where the density of the sites that comprise the medium is homogeneous in space. We set up an ordered medium such that, in the  $xy$  plane, even lattice sites in the simulation box are occupied by fixed spheres. Such a plane is repeated in the  $z$  direction. This represents an array of fixed rods in the  $z$  direction. Although the difference is small, our simulation data (not shown) suggest that diffusion is consistently faster in H-type homopolymer than in A-type homopolymer at  $N=10-50$ ,  $\rho=0.5$ ,  $T/T_{ref}=3.0$ .

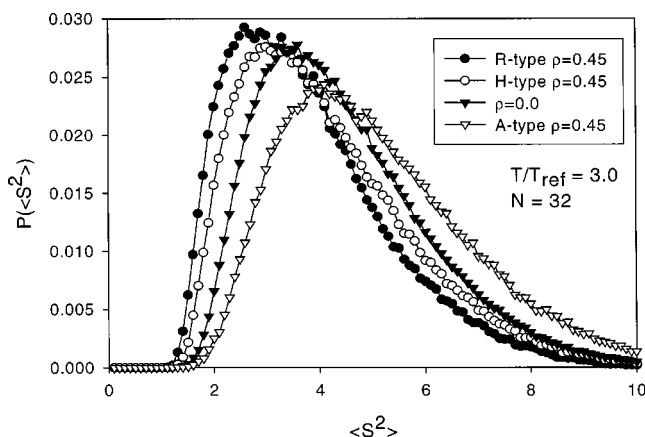


FIG. 7. Normalized distribution functions for the mean square radius of gyration  $\langle S^2 \rangle$  are compared for different types of chains with  $N=32$ ,  $T/T_{ref}=3.0$ , and  $\rho=0.45$ . For comparison  $\langle S^2 \rangle$  for an  $N=32$  athermal homopolymer in the absence of sites comprising the disorder is also shown.

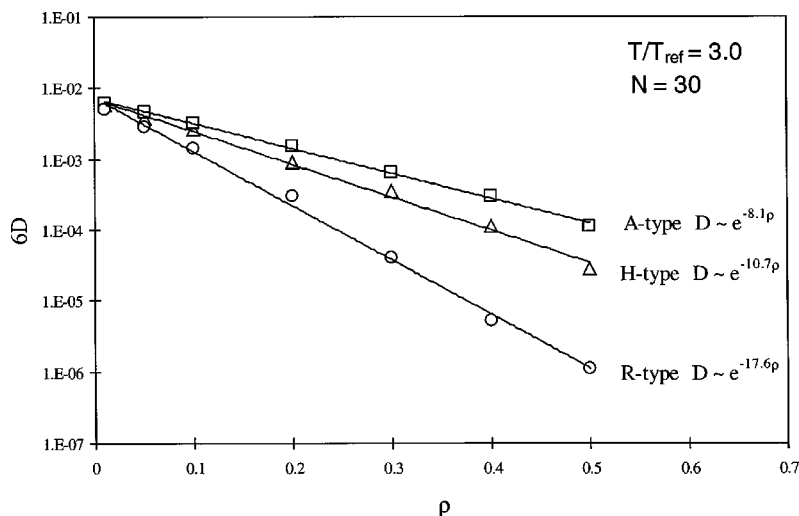


FIG. 8. Diffusion coefficients of A, H, and R-type homopolymers as a function of disorder strength  $\rho$  at constant  $N$  and  $T$ .

To probe how porosity of the disordered medium influences dynamics of A, H, and R-type homopolymers, we have carried out simulations over a range of disorder strengths. As  $\rho$  increases, the average size of the void space becomes smaller, and in a given volume there are a larger number of narrow channels connecting them. Since facilitated diffusion of A-type chains should depend on the number of narrow channels, the higher  $\rho$  is, the more dramatic the facilitation should be. This is demonstrated to be true in Fig. 8. As  $\rho$  increases, the differences among the diffusion coefficients of A, H, R-type homopolymers ( $D_A$ ,  $D_H$ , and  $D_R$ ) becomes more prominent at  $T/T_{\text{ref}}=3.0$ , a temperature where A-type diffuses faster than H-type homopolymer. Figure 8 also shows that the diffusion coefficient is a very strong function of the disorder strength.

### B. Dependence of chain dynamics on heteropolymer sequence

Keeping the average composition constant, we probed the effects of sequence on the diffusion of an AR heteropolymer in random media. Figure 9 shows a comparison of the dynamics of an AR diblock copolymer with an AR random heteropolymer, both of symmetric composition. The differences in the diffusion coefficients are not as dramatic as the difference between the three homopolymers, but the random heteropolymer is more mobile than the diblock copolymer. To further quantify this trend, four groups of 30-mer copolymer chains [Fig. 10(A)], differing in the length of each block of A and R-type beads were tested and compared in a random medium corresponding to  $\rho=0.5$ . All chains have 15 A-type beads and 15 R-type beads. We observe that the shorter blocks of A and R-type beads are, the larger the value of the diffusion coefficient [Fig. 10(B)]. Perhaps this is because, upon course graining the sequence on scales shorter than  $m$  ( $1 < m < N$ ), the AR heteropolymer roughly approximates a H-type homopolymer, but with an attenuated repulsive interaction with the disorder. Chains with longer blocks of R-type segments diffuse slower because, once the end of the chain enters the narrow channel, it takes a bigger fluctuation to drag a long block of R beads through. Exponential slowdown of random heteropolymer dynamics suggested by Cule and

Hwa<sup>17</sup> is not observed in our simulations because the chains we simulate are not long enough to be in the regime corresponding to reptation.

Animations constructed from our simulations (see animations in EPAPS material,<sup>23</sup>) demonstrate that when the chain translocates from one void space to the other, typically the chain end first enters the narrow channel and then the rest of the chain follows. Similar observations have been made by Muthukumar<sup>22</sup> in his studies of a polymer chain coming out of a hole. This suggests that, keeping the composition constant, changing sequence at the end of the chain will influence the dynamics of the chain in random media. However, this only affects dynamics on short time scales as illustrated by the dependence of  $R^2(t)$  on time for  $R_8A_{16}R_8$  and  $A_8R_{16}A_8$  triblock copolymers (Fig. 11). Both triblock copolymers have the same composition. At short times, the A-bead tail (or head) of  $A_8R_{16}A_8$  quickly samples its environment and enters the narrow channel, resulting in a higher  $R^2(t)$  than  $R_8A_{16}R_8$ . At longer times,  $A_8R_{16}A_8$  is slower than  $R_8A_{16}R_8$  because despite having the advantage of entering the narrow channel earlier, it is disadvantaged on long

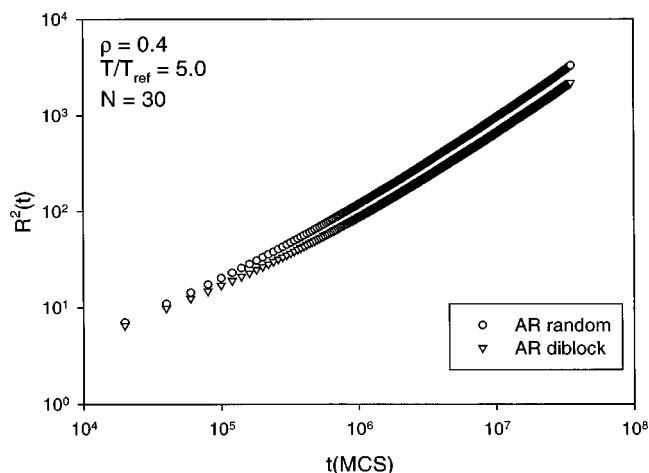


FIG. 9. Mean square displacements of center-of-mass  $R^2(t)$  as a function of time in units of Monte Carlo steps (MCS) at constant  $\rho$ ,  $T$ ,  $N$ . Both are diblock and the random heteropolymer consist of  $N/2$  A-type and  $N/2$  R-type monomers.

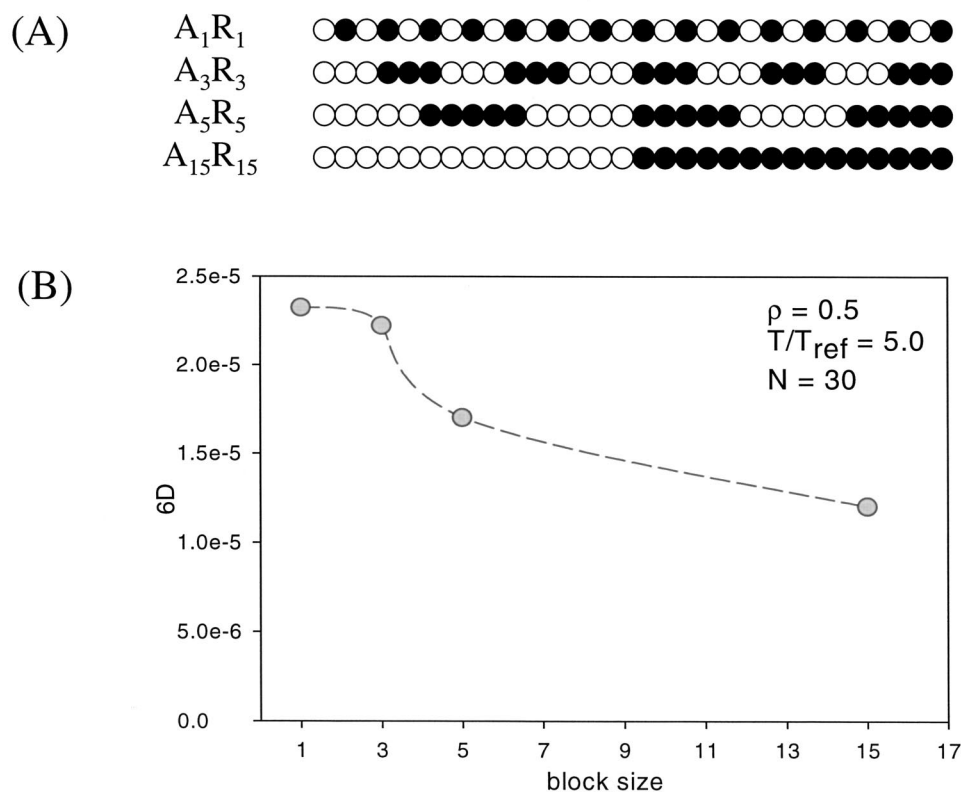


FIG. 10. (A) Sequences of four  $N = 30$  AR heteropolymers with different block lengths. (B) Diffusion coefficient as a function of block length for polymer sequences shown in (A).

times because it has a longer stretch of  $R$  that requires a bigger fluctuation to drag itself through the channel.

#### IV. CONCLUDING REMARKS

Using kinetic Monte Carlo simulations, we have studied how polymer sequence influences the dynamics of polymers in quenched disordered media. Counter to our intuition, we find that, above a threshold temperature, polymers bearing monomers that are attracted to sites comprising the medium are more mobile than those which exhibit repulsive or neutral interactions. We clarify that this surprising effect origi-

nates from the fact that attractive interactions alleviate the entropic barrier of entering a narrow pore connecting neighboring void spaces in the disordered medium. We argue and show that this effect is strictly due to the presence of void spaces and bottlenecks that arise from the disordered distribution of sites comprising the medium. We also study the dependence of mobility on sequences of different heteropolymers. Our results are relevant to a number of problems in biophysics and bioengineering including gel column separations, transportation of DNA, and facilitated transport through the nuclear pore complex.

#### ACKNOWLEDGMENTS

Fruitful discussions with S. Qi, Y. Hori, and Professor M. Muthukumar and critical review of the manuscript by S. Raychaudhuri and J. Liu are gratefully acknowledged. This research is supported by the U.S. DOE (Basic Energy Sciences).

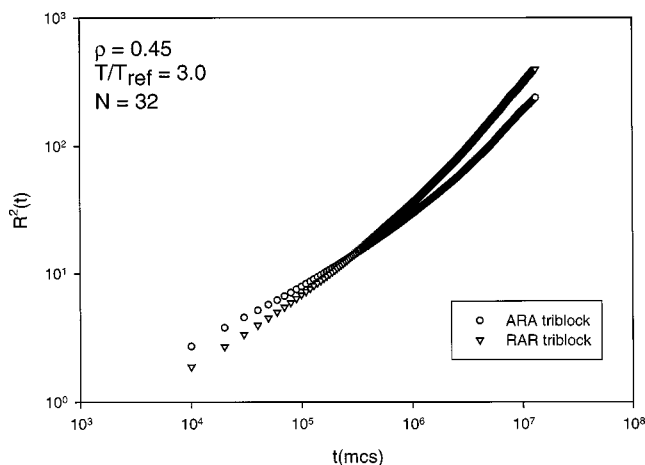


FIG. 11. Mean square displacements of center-of-mass  $R^2(t)$  as a function of time in units of Monte Carlo steps (MCS) at constant  $\rho$ ,  $T$ ,  $N$ . Both ARA and RAR triblock copolymer chains have identical composition, but differ in what type of segment is at the ends of the chain.

- <sup>1</sup>M. Muthukumar, *J. Non-Cryst. Solids* **131**, 654 (1991).
- <sup>2</sup>P. G. de Gennes, *J. Chem. Phys.* **55**, 572 (1971); M. Muthukumar and A. Baumgartner, *Macromolecules* **22**, 1937 (1989).
- <sup>3</sup>A. Baumgartner and M. Muthukumar, *J. Chem. Phys.* **87**, 3082 (1987); S. F. Edwards and M. Muthukumar, *ibid.* **89**, 2435 (1988).
- <sup>4</sup>M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1986).
- <sup>5</sup>P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- <sup>6</sup>M. Muthukumar and A. Baumgartner, *Macromolecules* **22**, 1937 (1989).
- <sup>7</sup>J. Rousseau, G. Drouin, and G. W. Slater, *Phys. Rev. Lett.* **79**, 1945 (1997).
- <sup>8</sup>S. W. P. Turner, M. Cabodi, and H. G. Craighead, *Phys. Rev. Lett.* **88**, 128103 (2002).

- <sup>9</sup>R. E. Hileman, J. R. Fromm, J. M. Weiler, and R. J. Linhardt, *BioEssays* **20**, 156 (1998).
- <sup>10</sup>F. S. Bates and G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **41**, 525 (1990).
- <sup>11</sup>C. D. Sfatos and E. I. Shakhnovich, *Phys. Rep.* **288**, 77 (1997); A. K. Chakraborty, *ibid.* **342**, 1 (2001).
- <sup>12</sup>L. Mirny and E. Shakhnovich, *Annu. Rev. Biophys. Biomol. Struct.* **30**, 361 (2001); J. D. Bryngelson and P. G. Wolynes, *Proc. Natl. Acad. Sci. U.S.A.* **84**, 7524 (1987); H. S. Chan and K. A. Dill, *Phys. Today* **46**, 24 (1993).
- <sup>13</sup>S. Srebnik, A. K. Chakraborty, and E. I. Shakhnovich, *Phys. Rev. Lett.* **77**, 3157 (1996).
- <sup>14</sup>A. J. Golumbfskie, V. S. Pande, and A. K. Chakraborty, *Proc. Natl. Acad. Sci. U.S.A.* **96**, 11707 (1999); A. K. Chakraborty and A. J. Golumbfskie, *Annu. Rev. Phys. Chem.* **52**, 537 (2001).
- <sup>15</sup>A. K. Chakraborty and E. I. Shakhnovich, *J. Chem. Phys.* **103**, 10751 (1995).
- <sup>16</sup>D. Bratko, A. K. Chakraborty, and E. I. Shakhnovich, *Phys. Rev. Lett.* **76**, 1844 (1996); *J. Chem. Phys.* **106**, 1264 (1997).
- <sup>17</sup>D. Cule and T. Hwa, *Phys. Rev. Lett.* **80**, 3145 (1998).
- <sup>18</sup>K. Ribbeck and D. Grollich, *EMBO J.* **20**, 1320 (2001).
- <sup>19</sup>K. Binder and D. W. Heermann, *Monte Carlo Methods in Statistical Physics: An Introduction*, 2nd ed. (Springer-Verlag, Berlin, 1992).
- <sup>20</sup>K. N. Pham, A. M. Puertas, J. Bergenholtz, S. U. Egelhaaf, A. Moussaid, P. N. Pusey, A. B. Schofield, M. E. Cates, M. Fuchs, and W. C. Poon, *Science* **296**, 104 (2002).
- <sup>21</sup>M. E. Cates and R. C. Ball, *J. Phys. (France)* **49**, 2009 (1988).
- <sup>22</sup>M. Muthukumar, *Phys. Rev. Lett.* **86**, 3188 (2001).
- <sup>23</sup>See EPAPS Document No. E-JCPSA6-502247 for animations constructed from simulations. A direct link to this document may be found in the online article's HTML reference section. The document may also be reached via the EPAPS homepage (<http://www.aip.org/pubservs/epaps.html>) or from <ftp.aip.org> in the directory/epaps/. See the EPAPS homepage for more information.