low, an S-shaped isotherm can be observed, and the adsorbed amount in the plateau region is high. Clearly, the surface acts as a condensation nucleus. Reducing the length of the A block or increasing the solvent quality raises the cmc and diminishes the S-shape of the isotherm. Competition between adsorption and micellization is observed only for weakly adsorbing A blocks in a very poor solvent. If the lyophilic block adsorbs on a lyophilic surface, a bilayer can be formed on the surface.

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Effects of Entropic Barriers on Polymer Dynamics

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ABSTRACT: Dynamic and static properties of a self-avoiding polymer chain in an infinite periodic array of cubic cavities separated by short bottlenecks have been investigated by Monte Carlo simulations and analyzed by scaling arguments. At the locations of the bottlenecks, entropic barriers are set up due to the reduction of the number of possible chain configurations in these positions. Consequently the chain diffusion coefficient D is smaller than the Rouse diffusion coefficient D_0. The scaling analysis of the effect of entropic barriers shows that D/D_0 decays exponentially with chain length N if the cross section of the bottleneck C is large and that it is independent of N for small C but is now a function of C, according to $N^{-1} \ln (D/D_0) = A - sN^{-1}$ where s depends inversely on C and A depends inversely on the size of the cavity and is negative. The simulation results are in agreement with the scaling analysis demonstrating that the chain diffusion in this problem is dominantly controlled by the entropic barriers.

I. Introduction

Diffusion of polymer chains in random media controls a wide variety of phenomena such as exclusion chromatography, membrane separations, ultrafiltration, viscoelasticity of polymer solutions, etc. In view of this, extensive literature exists on the experimental results on porous media, membranes, and polymer solutions dealing with these phenomena.[1-10]

The fundamental issue in these problems is the transport of a polymer chain from a region of larger volume where the chain entropy is higher to another region of smaller volume where the chain entropy is lower. Thus the polymer chain moves across an entropic barrier. Since the experimental situations are typically very complex and many factors contribute to the observed phenomena, it is desirable to perform computer simulations on a well-characterized model system in order to understand the effects of entropic barriers on polymer dynamics. Such an effort is the main focus here.

In this paper we study the effects of entropic barriers on chain diffusion by following Monte Carlo simulations of the escape of a self-avoiding chain from a well-characterized cubic cavity through the gates (bottlenecks or capillaries) at the centers of the walls of the cavity (cf. Figure 1). We have actually considered an infinite three-dimensional periodic array of such cavities with each cavity containing six bottlenecks. By changing the chain length N and the size C of the bottlenecks we have monitored the chain diffusion coefficient D and its dependence on N and C.

Whenever the chain transports from a region of large volume to another region of small volume, the monomer concentration is partitioned[11-14] between these two regions due to the differences in chain entropy in different confining spaces. The diffusion coefficient of the chain is determined by the partition coefficient which is the ratio of the monomer concentration in the capillary to that in the cavity. The partition coefficient was first calculated by Casassa[11] for Gaussian chains. This calculation was later generalized by Daoud and de Gennes[12,13] and Brochard and de Gennes[14] using scaling arguments for good solutions. These scaling predictions have been verified by Guillot et al.[7] by an experimental investigation of diffusion of large flexible chains through model membranes.

Since the length of the bottlenecks is very short in the model considered here, the scaling arguments[12-14] of de Gennes and co-workers must be accordingly modified. The consideration of small length of bottlenecks in the present study is motivated by the presence of bottlenecks in the

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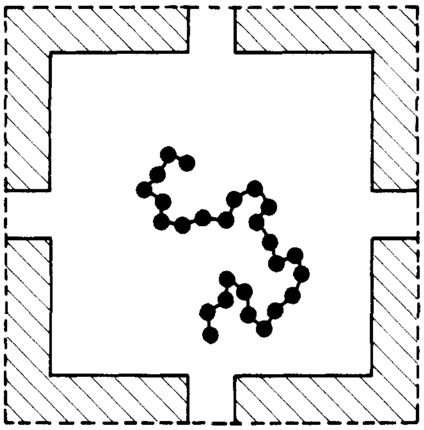

Figure 1. Two-dimensional sketch of one cavity with four capillaries and a "pearl-necklace" chain. The variables C, h, l, λ, and L are defined in the text.

random medium problem[15] (see the following paper[16] also). These bottlenecks squeeze ("pinch") the chain at random locations. Modifying the scaling arguments of de Gennes and co-workers for this pinching effect, we have derived scaling laws for the chain diffusion from a cavity with bottlenecks.

We find that the observed dependencies of the chain diffusion coefficient on chain length and the size of the capillary can be adequately described by our scaling arguments. Thus the chain diffusion in a periodic array of cavities that are connected by short capillaries is predominantly determined by the entropic barriers set up by different numbers of chain configurations in different locations.

The model and the simulation technique are described in section II. The results are presented in section III. The scaling arguments and the discussion of the results are contained in section IV.

II. Model and Simulation Technique

Consider a cubic cavity of side dimension L, into which a polymer chain will later be introduced. The cavity is covered by impenetrable walls of thickness λ. Each of the six surrounding walls contains a hole at the center of the wall to provide a possible flux of the polymer to the outside of the cavity. Each hole has the form of a capillary with cross section. The length of the capillary is λ, and the side of the square cross section is C (Figure 1). We then make an infinite three-dimensional periodic array of such cubic cavities in the x, y, and z directions, as a model for the porous medium.

A polymer chain is introduced into the central cavity. The model for the polymer molecule is the "pearl-necklace" chain.[17,18] This consists of N hard spheres of diameter h which are freely jointed together by $N - 1$ rigid links of length l. Ensembles of configurations have been generated by the conventional kink–jump technique, i.e., by attempting to rotate a randomly chosen sphere with its two links around the axis joining the first nearest neighbors of the sphere through a random angle. If an end sphere is chosen, the terminal link is rotated to a random new direction. We rejected all rotations which lead to an overlap with any other sphere of the chain (self-excluded volume) or with the surrounding solid (walls of cavities or of capillaries). When such a rejection takes place the old configuration is retained and counted as the new one. We call this procedure the "dynamical" Monte Carlo method.

Simulations have been performed for this model with $L/a = 3$, $\lambda/a = 0.06$, $h/a = 0.27$, and $l/a = 0.3$ for different values of N and three different sizes of the capillary, viz., $C/a = 1.2$, 1.6, and 2.0. Here a is the basic linear spacing unit to set the scale. It should be noted that, since $h/l > (3/4)^{1/2}$, the self-excluded volume condition prevents[18] also chain intersections during any attempted rotation of the links. Since the principal objective is to study the effect of bottlenecks, we have chosen a small value of λ. Also notice that there are only three independent length parameters, viz., L, λ, and h.

Table I
Ratio of the Root-Mean-Square Radius of Gyration to the Side of the Cubic Cavity, $(6\langle S^2\rangle)^{1/2}/3^{1/2}L$, for Various N and C/h[a]

N	C/h 4.4	5.9	7.4	∞
20	0.35	0.35	0.36	0.37
30	0.43	0.45	0.46	0.48
40	0.50	0.53	0.55	0.57
50	0.59			
60		0.71	0.72	
80		0.86	0.88	0.89
100		0.99	1.0	1.01

[a] All entries have an error bar of less than 10%.

III. Results

For the values of the sizes of the cavity and the bead studied here, the fraction ϕ of the cavity space occupied by the polymer is given by

$$\phi = \frac{4}{3}\pi\left(\frac{h}{2L}\right)^3 N = 3.82 \times 10^{-4}N \qquad (1)$$

Since the chains of N values only up to 100 are considered in this paper, the polymer volume fraction is low as given by eq 1.

The equilibrium size of a polymer chain is characterized by the mean-square radius of gyration of the chain $\langle S^2\rangle$

$$\langle S^2\rangle = \frac{l^2}{N^2}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\langle(\mathbf{r}_i - \mathbf{r}_j)^2\rangle \qquad (2)$$

where r_i is the position vector of the ith bead and the angular brackets indicate the averaging over all possible chain configurations. The chain configurations involving several cavities being simultaneously occupied are also included in the averaging. We have determined $\langle S^2\rangle$ using the Monte Carlo method described above. The raw data for the ratio $(6\langle S^2\rangle)^{1/2}/3^{1/2}L$ for various N and capillary sizes (C/h) are presented in Table I, in order to obtain the relative average end-to-end distance of the chain with respect to the linear dimension of the cavity. The data for a chain in an infinite continuum are also included in Table I corresponding to $C/h \to \infty$. All entries have an error of less than 10%. From these data we obtain

$$\langle S^2\rangle^{1/2} = (0.13 \pm 0.01)N^{0.6\pm0.03} \qquad (3)$$

for all values of the capillary sizes and chain lengths. Therefore the chain obeys the self-avoiding walk statistics, and there are no significant screening effects due to the low polymer concentration in the cases reported here.

We have also monitored the displacement of the center of mass of the chain as a function of time by using the dynamical Monte Carlo method described above. The time-dependent mean-square displacement of the center of mass of the chain $R^2(t)$

$$R^2(t) \equiv \langle[\mathbf{R}_{\mathrm{CM}}(0) - \mathbf{R}_{\mathrm{CM}}(t)]^2\rangle \qquad (4)$$

is plotted against the Monte Carlo time t in parts a–c of Figure 2 for various capillary sizes and chain lengths. These figures also contain the plots of the mean-square

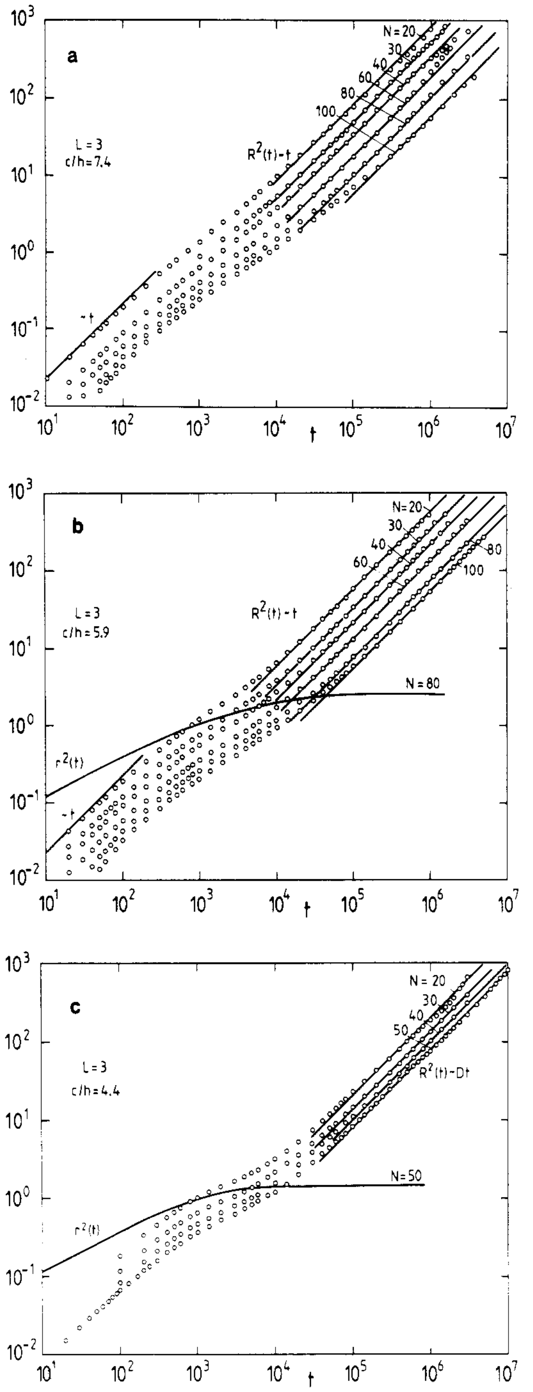

Figure 2. log–log plot of the mean-square displacement $R^2(t)$ and $r^2(t)$ of the center of mass and one bead relative to the center of mass, respectively, versus time t for various chain lengths N for three capillary sizes C/h: (a) 7.4, (b) 5.9, and (c) 4.4.

displacement of the $(N/2)$th segment with respect to the center of mass of the chain $r^2(t)$

$$r^2(t) \equiv \langle [\mathbf{r}_i(0) - \mathbf{R}_{\mathrm{CM}}(0) - \mathbf{r}_i(t) + \mathbf{R}_{\mathrm{CM}}(t)]^2 \rangle \tag{5}$$

where $\mathbf{r}_i(t)$ is the position vector of ith segment at time t.

It is clear from these figures that there are three distinct regimes for the time evolution of $R^2(t)$. In the early and late time regimes, the diffusion law, $R^2(t) \sim Dt$, is observed and the diffusion coefficients

$$D = {}^1\!/_6 \frac{\mathrm{d}}{\mathrm{d}t} R^2(t) \tag{6}$$

are obtained as the intercepts of the plots in parts a–c of Figure 2. D_0 and D, which denote the diffusion coefficients in the early and late time regimes, respectively, are given in Table II for different values of N and C/h. It is to be noted that the value of the diffusion coefficient in the early time regime is the same as that of a single chain in infinite space without any geometrical constraints due to the low concentration of the polymer in the cavity (cf. eq 1). See also ref 16. It follows from Table II and $l = 0.3$ that D_0 obeys the Rouse law

Table II
Monte Carlo Estimates of the Diffusion Coefficient $6Dl^2 \times 10^4$ of the Center of Mass of the Chain for Various N and C/h[a]

		C/h		
N	$6D_0l^2 \times 10^4$	7.4	5.9	4.4
20	23	8.5	5.7	2.0
30	15	5.1	3.4	1.4
40	11	3.4	2.1	1.0
50	8.6			0.8
60	7.0	1.9	1.3	
80	5.0	1.0	0.75	
100	4.0	0.7	0.53	

[a] D_0 is the Monte Carlo estimate of the Rouse diffusion coefficient observed in the early time regime. All entries have an error of less then 10%. D_0 reported here is indistinguishable from the Rouse diffusion coefficient estimated[16] from the Monte Carlo simulation of a single chain in an infinite continuum.

$$D_0 = (8.5 \pm 1.0) \times 10^{-2} N^{-1\pm0.1} \tag{7}$$

where the numerical prefactor is of course not significant in such Monte Carlo simulations.

In the intermediate time regime, the chain probes the "gates" of the cavities and appears to undergo anomalous diffusion. The duration of the intermediate crossover region depends on N and C/h. The larger the chain length and smaller the size of the bottleneck, the longer the crossover region.

We now proceed to understand the dependence of D on N and C/h reported in Table II by using scaling arguments.

IV. Discussion

The problem of equilibrium partition of a polymer chain between an infinitely large volume of solution and a cavity of given geometry is of long standing interest. By calculating the change in conformational entropy associated with the transfer of a Gaussian chain from the outside to the cavity, Casassa[11] showed that the partition coefficient K decays exponentially with $\langle S^2 \rangle / C^2$ where C is the characteristic size of the cavity. Using scaling arguments,[12–14] this result was generalized by Daoud and de Gennes to the partitioning of a chain in good solvents into a capillary or slit from the bulk solution. These scaling results can be summarized, for the partitioning of a chain between two cavities of characteristic sizes C_1 and C_2 as

$$K = \rho_2/\rho_1 \sim \exp(-\Delta F/k_{\mathrm{B}}T) \tag{8}$$

$$\Delta F/k_{\mathrm{B}}T \equiv F_2 - F_1 \tag{9}$$

$$F_i \approx N(1/C_i)^{1/\nu} \tag{10}$$

Here F_i is the scaling form for the free energy per chain of confinement in the ith cavity, measured from the reference state of $C_i = \infty$. ρ_i is the polymer concentration per unit volume of the ith cavity. N is the chain length, and l is the Kuhn step length. ν is the usual exponent relating the radius of gyration of the chain and N, $\langle S^2 \rangle \sim N^{2\nu}$. The scaling form given by eq 10 is valid only if the cavities are large enough to contain the whole chain. Furthermore, Guillot et al.[7] have shown that D/D_0 is proportional to the partition coefficient K so that

$$\frac{D}{D_0} = \exp(-\Delta F/k_BT) \tag{11}$$

where D_0 is now the diffusion coefficient of a single chain in the free solution without any geometrical constraints. In the work of Guillot et al.[7] D_0 is actually close to the Zimm diffusion coefficient.

For the particular system investigated above by using the Monte Carlo simulation, $C_1 = L$ and $C_2 = C$ with the important difference that the length λ of the parallelepiped capillary is very short. Since the length of the bottleneck λ is not enough to fully confine the chain inside the capillary, especially for the case of small values of C, eq 9 should be modified by introducing the appropriate weight factors. Therefore the free energy change associated with the partial confinement of a chain per each bottleneck is written from eq 9 as

$$\Delta F/k_BT = fF_2 + \left[\frac{(1-f)}{z} - 1\right]F_1 \tag{12}$$

where f is the fraction of monomers in the second cavity and z is the average number of cavities which contain the $(1-f)N$ unconfined segments per bottleneck. Note that $z = 1$ if $f = 0$. The asymmetry in the prefactors of F_1 and F_2 in eq 12 arises from the possibility that the chain can reside simultaneously in several cells and bottlenecks and the number of cells need not be equal to the number of bottlenecks. Since we are interested in only the scaling forms, we do not attempt at details of the numerical factors.

Substituting eq 10 and 12 into eq 11, we get

$$\frac{D}{D_0} = \exp\left\{-N\left[f\left(\frac{1}{C}\right)^{1/\nu} + \left(\frac{1-f}{z} - 1\right)\left(\frac{1}{C_1}\right)^{1/\nu}\right]\right\} \tag{13}$$

If C and λ are sufficiently large, the capillary (bottleneck) is large enough to confine the chain completely so that f is unity. As C and λ are decreased, f decreases.

For small values of λ at a given value of C, a scaling form of f can readily be obtained. Consider a chain of N segments fully confined in a long capillary of cross section C. The familiar scaling argument is that we assume the chain to consist of g blobs each of size C. The number m of segments in each blob scales with C according to $C \sim m^{\nu}$. The total length R_c of the capillary required to fully confine the chain at a given C is $R_c \sim gC$. Since g is N/m, R_c is proportional to $NC^{1-1/\nu}$. Now f is the ratio of the length of the capillary actually available for the chain confinement to the total length of the capillary necessary to fully confine the chain at a given value of C. Therefore, $f \sim 1/R_c \sim N^{-1}C^{1/\nu-1}$.

Thus, the asymptotic limits of the crossover function f are given by

$$f = \begin{cases} 1 & \zeta \leq 1 \\ N^{-1}C^{1/\nu-1} & \zeta \gg 1 \end{cases} \tag{14}$$

Here, $\zeta \sim R_{\perp}^2 R_{\parallel}/C^2\lambda$, with $R_{\perp}$ and $R_{\parallel}$, respectively, being the components of the radius of gyration of the chain in a plane perpendicular and parallel to the axis of the capillary. In view of this crossover, we can rewrite eq 13 as

$$D/D_0 = \exp[-N\Delta F(N,C,C_1)] \tag{15}$$

where ΔF is, in general, dependent on N.

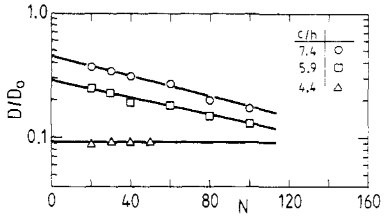

Figure 3. Semilog plot of D/D_0 versus N for different values of C/h.

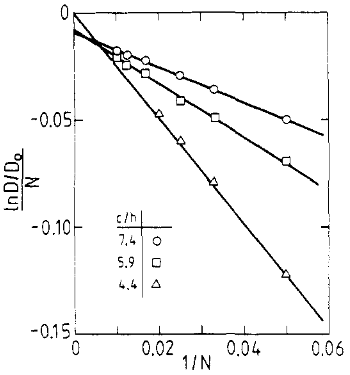

Figure 4. Plot of $N^{-1} \ln (D/D_0)$ versus N^{-1} for different values of C/h.

Equations 13 and 15 reduce to the exponential decay of K with N obtained by Casassa and Daoud and de Gennes for the partitioning of a chain from the bulk ($C_1 = \infty$) to a capillary of sufficient length to fully accomodate the chain ($f = 1$). However, we expect a deviation from this exponential law for the system studied here due to the presence of the factor f which depends on N according to eq 14. The values of D/D_0 given in Table II are presented in Figure 3, as a semilog plot against N. For large values of C ($f \rightarrow 1$), the exponential decay of D/D_0 with N is observed as expected. However, for small $C/h = 4.4$, we observe an N independence for D/D_0 with a substantial deviation from the exponential law. This is in conformity with eq 13 and 14. For such small values of C, the first term of the square bracket of eq 13 dominates over the second term and is proportional to N^{-1} so that $N\Delta F(N,C,C_1)$ is independent of N. Since D_0 is proportional to N^{-1}, the chain diffusion for $C/h = 4.4$ appears to obey the Rouse law. However, this apparent Rouse diffusion should be distinguished from the genuine Rouse behavior observed in the absence of bottlenecks.

In order to check the scaling form of eq 14, we rewrite eq 13–15 as

$$N^{-1} \ln (D/D_0) = A - sN^{-1} \tag{16}$$

where s is proportional to $C^{-1}(1 - z^{-1}(C/C_1)^{1/\nu})$ and A is proportional to $(1/C_1)^{1/\nu}$ and is negative. Thus a plot of $N^{-1} \ln (D/D_0)$ versus N^{-1} should be linear with a slope proportional to $C^{-1}(1 - z^{-1}(C/C_1)^{1/\nu})$. The data of Table II are replotted in Figure 4 according to eq 16, and we observe the linear law in accordance with the scaling prediction of eq 13 and 14. Furthermore, we observe that the slopes of these lines increase with decreasing C, in agreement with the predictions.

V. Conclusions

Using Monte Carlo simulations, we have studied the mean square radius of gyration and the diffusion coefficient of a self-avoiding chain in an infinite periodic array of cubic cavities which are connected by short bottlenecks. We observe the self-avoiding walk statistics of the radius of gyration since the cavities are taken to be large enough to maintain a dilute concentration for the polymer.

For times shorter than the time (τ_C) taken by the chain to travel a distance comparable to the size of the cavity, the diffusion coefficient of the chain is the same as that of the Rouse model (D_0) corresponding to the situation where there are no obstacles. For times longer than τ_c but shorter than another characteristic time τ'_C, the motion of the center of mass of the chain deviates from the diffusion law and is slower due to the explorations of the bottlenecks by the chain. For times longer than τ'_C, the diffusion law is observed once again with diffusion coefficient D which is smaller than D_0.

The slow diffusion observed in the presence of bottlenecks is due to the squeezing of the chain through the bottlenecks. Such squeezing reduces the entropy of the chain so that the chain faces entropic barriers at the locations of the bottlenecks. Whenever a chain is transported from a region of high entropy to another region of low entropy, the diffusion coefficient is determined by the partition coefficient. We have calculated D/D_0 by modifying the scaling method of Daoud and de Gennes to account for the presence of short bottlenecks in our problem instead of long capillaries.

Our scaling analysis of the effect of bottlenecks shows that D/D_0 decays exponentially with chain length N if the cross section of the short bottleneck C is sufficiently large. However, if C is reduced, there is a crossover from this exponential law to D/D_0 independent of N but exponentially small depending on the value of C. Thus, if we plot $N^{-1} \ln (D/D_0)$ versus N^{-1} according to eq 16, we should get a straight line with the slopes changing from small at large C to large at small C. These predictions are in agreement with the observed data of the simulations. Therefore, we conclude that the slow diffusion of the chain in the model considered here can be attributed mainly to the entropic barriers arising from the changes in the chain configurations in different locations of the system.

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Diffusion of a Polymer Chain in Random Media

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ABSTRACT: Dynamic properties of a self-avoiding walk chain, which performs Brownian motion between randomly distributed impenetrable fixed obstacles, have been investigated by Monte Carlo simulations. Analogous to the case of a random walk chain in random media, the chain dynamics is found to be slower than even reptation demonstrated by a stronger inverse dependence of the chain diffusion coefficient on chain length. This phenomenon is attributed to the slowing down of the chain due to the presence of bottlenecks in the random medium. The bottlenecks squeeze the chain and reduce the chain entropy setting up entropic barriers at random locations. A scaling analysis is adopted to account for the effects of such entropic barriers on chain diffusion. The simulation data are consistent with the predictions of the scaling arguments demonstrating that chain diffusion in random media is controlled by the entropic barriers of the media.

I. Introduction

Diffusion of polymer chains in random media controls many phenomena[1-4] such as viscoelasticity of polymer solutions, exclusion chromatography, membrane separations, ultrafiltration, etc. Extensive experiments[5-13] have been carried out on transport of polymers into pieces of porous glass, nuclepore filters, membranes, polymer solutions, etc. in the context of these phenomena. Typically, the experimental situations are very rich and complex as demonstrated by these investigations and mean field theories[14-17] have been proposed with simplifying assumptions and conditions. While certain dynamical properties such as diffusion coefficients of a labelled chain appear to be adequately described by such theories, the disparity between the experimental data on the viscoelastic properties and theoretical predictions continues to be present.[10,11,17]

The realistic porous media, where the diffusion of polymer chains have been investigated experimentally, are very complicated[9,18-20] in nature. The size of the pores in

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