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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these media is polydisperse, and the pore size distribution is measured by using capillary and imbibition methods.[2-4] The relation between the parameters such as capillarity and tortuosity which are used to characterize the porous media and the local details at the same length scales of a polymer chain is not known. In order to understand the underlying physics in these problems, it is necessary to study the properties of the polymer in well-characterized porous media. Since this is not yet feasible in real experiments so far, we have used computer simulations to study a model problem. The simplest system of polymers in random media consists of a single flexible polymer chain in a medium where a certain number of obstacles are randomly distributed. The Monte Carlo simulation of this model and scaling analysis of the results form the subject of this paper.

The additional motivation for the present work is that the familiar reptation dynamics[16,17] assumed for the diffusional behavior of a single chain in a polymer melt was originally[21] proposed by considering the simple system addressed in this paper. While certain properties of polymer solutions appear to be adequately described by the reptation model, the differences between the predictions of the reptation idea and the experimental results are quite significant.[10-13] There have been many efforts to reconcile these differences,[10,17,22-26] and some difficult computer simulations[27,28] indicate that the chain dynamics in a dense system can be different from reptation. While it is quite interesting to continue along this direction to understand the disparity between the experiments and the reptation idea, it is also desirable to return to the cradle of the reptation idea and scrutinize the chain behavior. The latter is attempted here.

Recently Baumgartner and Muthukumar[29] carried out a Monte Carlo simulation in which a given volume was divided into a large number of equivolume cells. A known fraction of these cells were randomly occupied by the obstacles (which are solid cubes) using the site percolation algorithm.[30] The obstacles were frozen in their positions. Taking the cells unoccupied by the obstacles to constitute a continuum (as long as the density of the empty cells is above the percolation threshold[30]), a Gaussian chain was introduced in the continuum. New chain configurations were created by using the kink-jump technique[27] subject to the constraint that the chain segments cannot occupy the cells of the obstacles. Both the equilibrium and dynamic properties of the chain were followed by averaging over the chain configurations and the configurations of the random medium for different chain lengths and densities of obstacles. In these simulations the authors[29] did not observe the reptation dynamics. Instead they found new dynamical laws where chain diffusion is slower than even reptation. For example, while the chain diffusion coefficient D should depend on chain length N according to $D \sim N^{-2}$ if reptation is valid, the observed apparent N dependence is $D \sim N^{-3}$.

In this paper, we generalize the computer simulations of ref 29 to a self-avoiding walk chain. Once again, we report below that the diffusion of the chain is slower than even reptation. Such a slow dynamics emerges from the presence of randomly distributed bottlenecks. The chain is forced to squeeze through narrow channels to occupy regions of the random medium which are entropically favorable. The entropic barrier arising from the presence of such bottlenecks slows down the dynamics significantly. The effect of entropic barriers on the diffusion of the chain has been studied by considering a well-defined system (see the preceding paper[31]), and the results can be adequately explained by scaling analysis. We apply the same method here and conclude that the chain diffusion in random media is controlled predominantly by the entropic barriers present in the system.

The model and the simulation technique are outlined in section II. The results and discussions are presented in sections III and IV, respectively.

II. Model and Simulation Technique

Consider a large cube of linear dimension L. A simple cubic lattice of lattice spacing a is constructed out of this cube so that $L = 300a$. The randomness of the medium is introduced by occupying each of the 300^3 cells with probability $1 - p$ $(0 < p < 1)$ according to the random site percolation algorithm.[30] The occupied cells constitute the solid particles, and the unoccupied cells represent the fluid phase which is taken to be a continuum. Thus p is the porosity and $(1 - p)$ is the volume fraction of the solid phase. For $p \geq 0.3117$ ($=p_c$, where p_c is the site percolation threshold) the fluid phase is continuous. The infinite size of the porous medium of reality is approximated by imposing periodic boundary condition[29] on the surfaces of the original cube of volume L^3.

The polymer chain is introduced in the fluid phase and is modeled as the "pearl-necklace" chain[27] of N hard spheres of diameter h which are jointed together by $N - 1$ rigid links of length l. The chain configurations are generated by using the conventional kink-jump technique:[27] a chain configuration is changed locally by trying rotations of two successive links around the axis joining their end spheres, by an angle ϕ chosen randomly from the interval $(-\Delta\phi, \Delta\phi)$. The parameter $\Delta\phi$ is chosen arbitrarily. If an end sphere of the chain is chosen, the terminal link is rotated to a near position by specifying two randomly chosen angles (ϕ, θ) in three dimensions, with $\cos\theta$ being equally distributed in the interval $-1 < \cos\theta < 1$. We rejected all rotations which lead to an overlap with any other sphere of the chain (self-excluded volume) or with the solid particles constituting the random medium. When such a rejection takes place, we follow the procedure of the dynamical Monte Carlo method[27] by retaining the old configuration and counting it as the new configuration.

In this procedure, the corners of cubic cells of the solid phase are allowed to be cut by the links although the hard-sphere beads are fully excluded by these cubes. Therefore, some of the cells constituting the solid phase actually exist only as polyhedra. Only in the limit of $l/a \to 0$, the polyhedra become cubes. On the other hand, if $l/a \ll 1$, chains of very large N must be simulated in order to work in the regime of $Nl/a \gg 1$ studied here. Since we expect the underlying physics to be unaltered whether the solid phase is made up of cubes or polyhedra, we have tolerated the overlap of the links with some corners of the cubes of the solid phase.

We have studied two cases of the polymer chain, viz., $h/l = 0.9$ and 0.5. In the case of $h/l = 0.9$, the chain is fully self-avoiding where both the intersections of the links of the chain and the overlap of spheres are forbidden. In the case of $h/l = 0.5$, the self intersections of the links are allowed but the spheres do not overlap. This is an intermediate case between the situation of $h/l = 0.9$ and the freely jointed random walk (RW) chain studied in ref 29.

The average quantities such as mean-square radius of gyration at equilibrium, the time-dependent mean square displacement of the center of mass of the chain, etc. are obtained for both cases by averaging over the various polymer configurations and different realizations of the porous medium at a given p. Simulations have been performed for $10 \leq N \leq 80$ and various porosities $0.5 \leq$

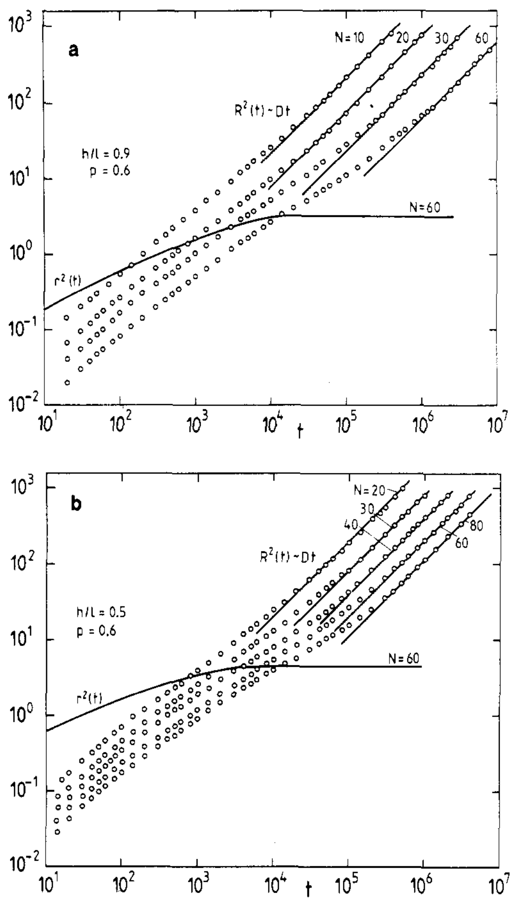

Figure 1. log–log plot of the mean-square displacement of the center of mass $R^2(t)$ and that of one bead relative to the center of mass $r^2(t)$, respectively, versus time t for various chain lengths and p = 0.6. h/l = 0.9 and 0.5 in a and b, respectively.

$p \leq 1$. The averaging over the porous medium has been carried out by using typically 10 realizations of the porous medium for each p.

We give below the results for the two cases (h/l = 0.9 and 0.5) studied here and merely quote the results for the random walk chain (h/l = 0) from ref 29.

III. Results

We have determined the mean-square radius of gyration $\langle S^2\rangle$

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

where $\mathbf{r}_i$ is the position vector of the ith bead connecting two successive links and the angular brackets indicate the averaging over all possible chain configurations as well as different realizations of the porous medium at a given value of p. We find that $\langle S^2\rangle$ is proportional to $N^{1.2\pm0.06}$ for both cases of h/l = 0.9 and 0.5 in the ranges of N and p studied here ($10 \leq N \leq 80$ and $0.5 \leq p \leq 1$). This result is to be contrasted with the shrinkage of a RW chain (h = 0) reported in ref 29.

We have monitored the displacements of the center of mass of the chain and a typical segment of the chain as functions 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, $R^2(t)$

$$R^2(t) = \langle[\mathbf{R}_{\rm cm}(0) - \mathbf{R}_{\rm cm}(t)]^2\rangle \tag{2}$$

where $\mathbf{R}_{\rm cm}(t)$ is the position vector of the center of mass of the chain at t, is plotted against the Monte Carlo time t in parts a and b of Figure 1 for h/l = 0.9 and 0.5, respectively. These graphs correspond to the case of p = 0.6 for various N values. The plots of the mean-square displacement of the $(N/2)$th segment with respect to the center of mass of the chain, $r^2(t)$

$$r^2(t) = \langle[\mathbf{r}_i(0) - \mathbf{R}_{\rm cm}(0) - \mathbf{r}_i(t) + \mathbf{R}_{\rm cm}(t)]^2\rangle \tag{3}$$

where $\mathbf{r}_i(t)$ is the position vector of ith bead at time t, are also included in parts a and b of Figure 1. We have a family of graphs similar to that of Figure 1 as p is changed, analogous to the series of graphs given in Figure 4 of ref 29. Since the qualitative features are still the same, we have presented the figures for the typical case of p = 0.6 only.

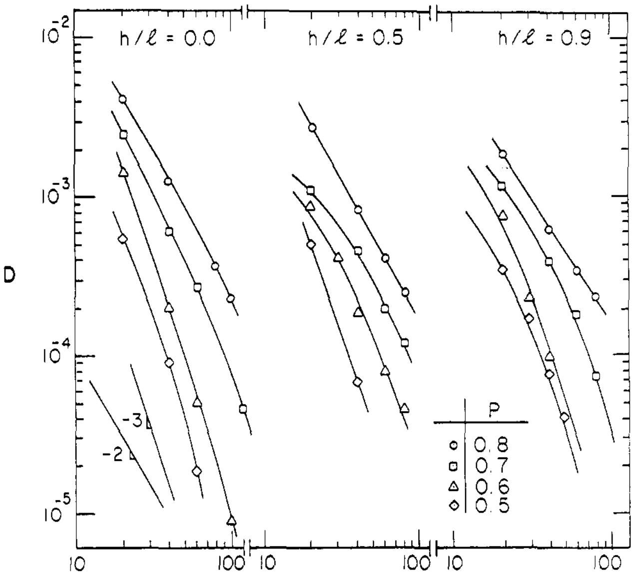

Figure 2. log–log plot of D versus N for different values of p and for the three cases of h/l. The slopes of −2 and −3 are shown for guidance.

For both values of h/l, there are three distinct regimes for the time evolution of the mean-square displacement of the center of mass of the chain, as in the cases of RW of ref 29 and the bottleneck problem studied in the preceding paper.[31] In the early and late time regimes, there is classical diffusion, $R^2(t) \sim t$. The duration of the intermediate crossover regime is longer as the chain length is increased and p is decreased. The mean-square displacement of a monomer $r^2(t)$ shows an approximate Rouse behavior[16,17] of $t^{1/2}$ for short times and smoothly crosses over to time independence.

The diffusion coefficients D_0 and D in the early and late regimes of classical diffusion are obtained as the intercepts of the lines shown in the figures. The raw data of D are presented in Table I for different values of p and N corresponding to all the cases of h/l. The error bars on the data of Table I are within 10%. The data of ref 29 are also included for convenience.[32] The diffusion coefficients D_0 in the short time regime for all values of p are the same for a given N and equal to D for p = 1 within the 10% error bar mentioned above. From the data of Table I for p = 1, we find that $D_0 \sim N^{-1\pm0.1}$, in accordance with the Rouse law. The values of D from Table I are plotted against N for different values of p in Figure 2 as a double logarithmic plot for h/l = 0.0, 0.5, and 0.9. It is clear from Figure 2 that the reptation law, $D \sim N^{-2}$, is not supported by our simulation data. Since D appears to obey an apparent law, $D \sim N^{-3}$, and we expect the local partitioning of the chain to play a dominant role, the ratio D/D_0 as determined from the intercepts is plotted against N in

Table I
The Raw Data of 10^3D for Different Values of N, p, and h/l[a]

		N								
p	*h*/*l*	10	20	30	40	50	60	80	100	120
1.0 ($D = D_0$)	0.0		8.85		4.17			2.08		
	0.5		6.02		3.01		1.94			
	0.9	9.58	4.12	2.67	2.01	1.59	1.30	0.926	0.74	
0.8	0.0		4.17		1.29			0.37	0.23	
	0.5		2.78		0.83		0.42	0.25		
	0.9		1.88		0.63		0.34	0.23		
0.7	0.0		2.55		0.60		0.27			0.046
	0.5		1.11		0.46		0.20	0.12		
	0.9		1.15		0.39		0.18	0.073		
0.6	0.0		1.44		0.20		0.051		0.009	
	0.5		0.88	0.42	0.19		0.083	0.046		
	0.9	2.08	0.78	0.23	0.099					
0.5	0.0		0.56		0.093		0.019			
	0.5		0.32		0.069					
	0.9	1.04	0.35	0.17	0.078	0.042				

[a] All entries have an error of <10%. The diffusion coefficient D_0 in the early time regime is the same as D for $p = 1$ and is independent of p.

Figure 3 as a semilog plot. Parts a and b of Figure 3 correspond to the cases of $h/l = 0.9$ and 0.5, respectively. The data of ref 29 obtained for the random walk cahin are presented in Figure 3c.

IV. Discussions

The porous medium created by the random site percolation is very rich in details. In general the space available to the polymer chain differs in length scale from location to location. In its time evolution, the chain is moving from one confining domain of certain size to another of different size. Thus the diffusion of the chain is controlled by the entropic barrier set up by the squeezing of the chain from a domain to another through bottlenecks. This effect must be averaged over all possible sizes of the domains and sizes and lengths of the bottlenecks. Since it is very difficult to calculate these length scales, we assume that there exist an average domain size, C_1, and an average size, C, for the bottleneck and both sizes decreasing as p is decreased.

With these assumptions, the problem of chain diffusion in our porous medium then reduces to that of the well-defined bottleneck problem discussed in the preceding paper.[31] We now apply the scaling results derived there to understand the data of parts a–c of Figure 3. When the bottleneck is not large enough to contain the chain fully, the scaling analysis shows that (see eq 13 and 14 of ref 31)

$$\frac{D}{D_0} = \exp\left\{-N\left[f\left(\frac{1}{C}\right)^{1/\nu} + \left(\frac{1-f}{z} - 1\right)\left(\frac{1}{C_1}\right)^{1/\nu}\right]\right\} \tag{4}$$

where f is the fraction of monomers inside the bottleneck and z is the average number of domains per gate available for the remainder of the chain. ν is the usual exponent relating the radius of gyration of the chain and N. f is a crossover function with limits

$$f = \begin{cases} 1 & \zeta \leq 1 \\ N^{-1}C^{(1/\nu-1)} & \zeta \gg 1 \end{cases} \tag{5}$$

Here, $\zeta \sim R^2_\perp R_\parallel / C^2\lambda$, with $R_\perp$ ($R_\parallel$) being the component of the radius of gyration of the chain in a plane perpendicular (parallel) to the axis of the bottleneck and λ being the length of the bottleneck (capillary).

If p is small enough (higher density of obstacles), then when a chain is squeezed from a domain into a capillary, there are many of the obstacles to effectively confine the chain so that the factor f is in the limit of unity. For such values of p so that $f \sim 1$, we expect an exponential decay of D with N from eq 4, i.e., a linear plot of ln (D/D_0) against N. However, at higher values of p, i.e., lower volume fraction of the obstacles, f deviates from unity and becomes N-dependent. For such higher values of p we expect a deviation from straight lines in the plots of ln (D/D_0) versus N. According to eq 5, the deviation is more for larger N at a given value of p. These are the features that are exhibited in the graphs of parts a–c of Figure 3 for all the three cases of self-avoiding walks with $h/l = 0.9$ and 0.5 and the random walk chain.

In an attempt to check the relevance of the scaling form of eq 5, we have redrawn the data of Figure 3 for all the three cases as plots of N^{-1} ln (D/D_0) against N^{-1} in Figure 4. For large values of N, f is expected to scale as N^{-1} (see eq 5) so that the curves of Figure 4 are consistent with these predictions of eq 4 and 5. Thus the simple scaling results of section IV of ref 31 based on local partitioning effects are found to be consistent with all available simulation data for the three different models of the chain reported here.

V. Conclusions

Motivated by the necessity to study a well-defined model to understand polymer dynamics in porous media and the desire to verify the presence of reptation dynamics in its original context, we have undertaken a series of Monte Carlo simulations. In these simulations, a polymer chain is introduced into a system, with a fraction $(1 - p)$ of which being already occupied by randomly distributed immobile cubic obstacles (using site percolation algorithm). The time evolution of the chain configurations and the center of mass of the chain were followed employing the dynamical Monte Carlo method which uses the kink–jump technique.

The results for the case of a Gaussian chain were already reported in ref 29. These results show that for long times and $p > p_c$ (= 0.3117), the diffusion coefficient D of the center of mass of the chain obeys an apparent power law

$$D \sim N^{-2.9\pm0.3} \tag{6}$$

where N is the chain length. This demonstrates that the chain diffusion is slower than even reptation according to which D should be proportional to N^{-2} only. In this paper, we have studied two cases of a self-avoiding chain in the same random medium as above. In one case ($h/l = 0.9$) the chain is fully self-avoiding where both the beads and the links are not allowed to intersect. The second case ($h/l = 0.5$) is an intermediate situation between the first case and the random walk chain considered in ref 29, where the

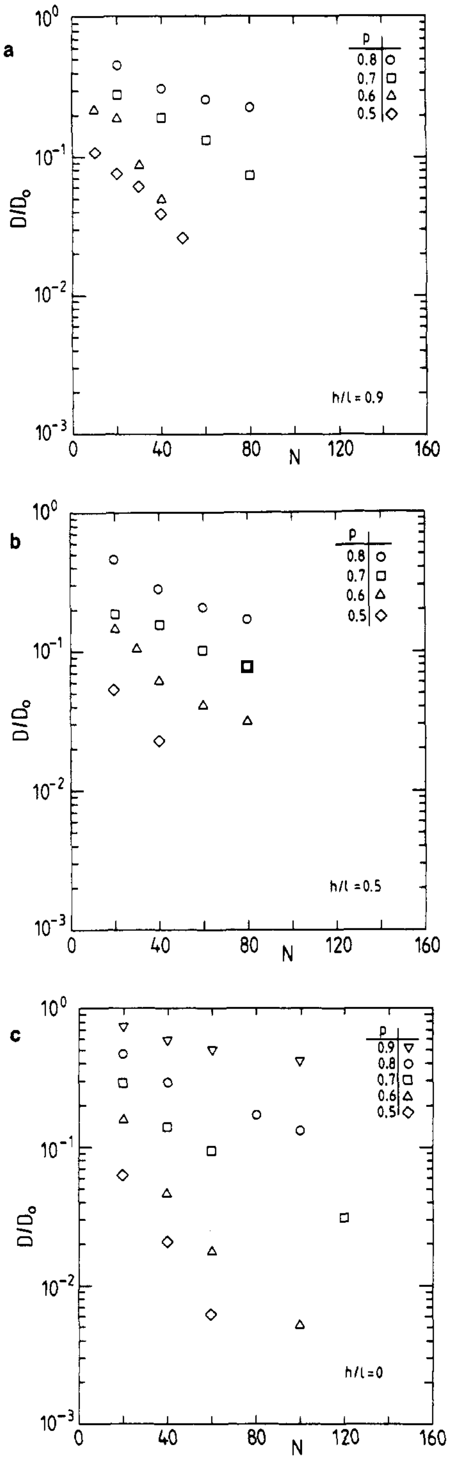

Figure 3. Semilog plot of D/D_0 versus N for different values of p. h/l = 0.9, 0.5, and 0.0 in a, b, and c, respectively.

links are allowed to intersect but the beads are self-avoiding. In both cases studied here the chain diffusion is slower than reptation analogous to that of a random walk chain as shown in Figure 2.

The slow dynamics of the chain (cf. eq 6) observed in the random medium considered in our simulations is due to the presence of bottlenecks in the trajectory of the chain. These bottlenecks squeeze the chain and consequently reduce the entropy of the chain, thus setting up entropic barriers in random locations. In an effort to understand the influence of such entropic barriers on chain diffusion we have studied a well-defined model bottleneck problem as described in the preceding paper.[31] The observed results can be satisfactorily explained by scaling analyses. We

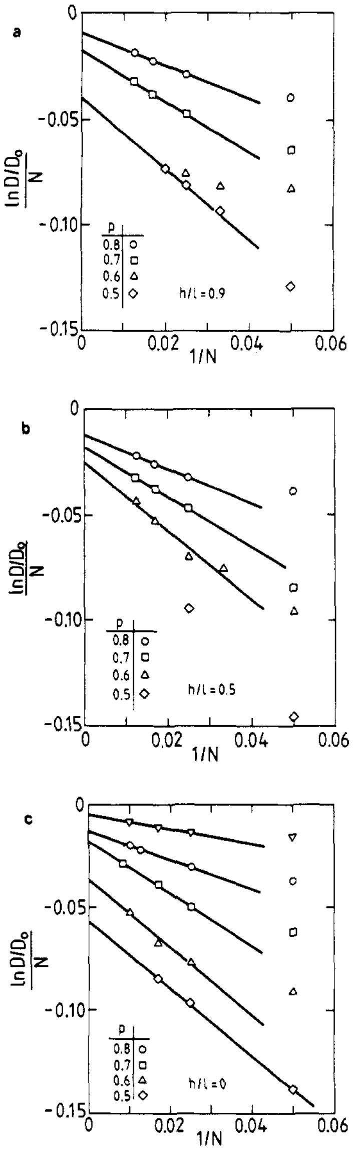

Figure 4. Plot of N^{-1} ln (D/D_0) versus N^{-1} for different values of p. h/l = 0.9, 0.5, and 0.0 in a, b, and c, respectively.

have applied the same scaling results here to explain the observed dynamics of the chain (both self-avoiding and Gaussian) in random media.

The scaling analyses predict that if p is small enough (higher density of obstacles), D/D_0 decays exponentially with N, where D_0 is the Rouse diffusion coefficient. However, as p is increased deviations from this exponential law should occur, with the deviation being stronger for larger N at a given value of p. Also, plots of N^{-1} ln (D/D_0) versus N^{-1} should be linear for large values of N and deviations should occur for shorter chains at all values of p. The data reported in Figures 3 and 4 are consistent with these predictions demonstrating that the chain diffusion in random media is controlled by entropic barriers present in the system. The agreements reported here between the scaling forms and the simulation data are only qualitative. A quantitative comparison is not feasible due to the lack of knowledge regarding the prefactors of all the scaling results.

It must be pointed out that a chain trapped in a random medium described here should obey the reptation dynamics if it is infinitely long so that the only available degree of freedom for the chain motion is through the chain ends. Therefore, it can be argued that reptation is not observed in our simulations due to the finite chain length. *But the* *remarkable result is that the entropic barriers arising from the bottlenecks of the system force the chain diffusion to be slower than even reptation.* Of course, one might wonder about the crossover from such an entropically activated dynamics regime (with an apparent power law, $D \sim N^{-x}$, $x > 2$) for chains of moderate length to the reptation regime ($D \sim N^{-2}$) for infinitely long chains. Again, questions like what the crossover N and the various amplitudes are and whether this crossover is of any physical interest to a particular experimental situation are very interesting. Simulations for longer chains are in progress in an attempt to answer some of these questions. It is hoped that this simulation study would stimulate tests of the validity of the scaling form presented here for realistic experimental systems.

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Scaling Properties of Branched Polyesters

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ABSTRACT: The growth of branched polymer structures up to the gel point has been examined in a polyester system at two different branch agent concentrations. Several independent measurements of the size and molecular weight of these polymers were made using elastic light scattering, quasi-elastic light scattering, intrinsic viscosity $[\eta]$, and size-exclusion chromatography with low-angle light scattering detection. In all cases, scaling relationships between these various properties were displayed for the whole range of molecular weights examined. The weight-average molecular weight scaled as $(p_c - p)^{-\gamma}$, where p is the extent of reaction and p_c is the extent of reaction at the gel point. The exponent γ was found to be 1.8 ± 0.3. Scaling exponents from the radius-M_w and $[\eta]$-M_w relationships were evaluated for unfractionated samples. Using these exponents, another critical exponent of gelation, τ, and the exponent relating size to molecular weight for a branched polymer in a good solvent, ν^B, could be evaluated. These were compared with values for the same exponents obtained through size-exclusion chromatography of the polymers. The critical exponent τ was obtained from this fractionation experiment through the shape of the observed distribution function and from the scaling relation between the molecular weight M_{max}, corresponding to the fraction making the largest contribution to light scattering in this separation, and M_w for each sample. Good agreement was observed between these two separate measures of τ and the one from the unfractionated samples, as well as ν^B from both fractionated and unfractionated samples. The measured values were $\tau = 2.29 \pm 0.03$ and $\nu^B = 0.48 \pm 0.02$. The distribution functions for polymers were described by a single universal distribution function. The critical exponents for gelation were compared to percolation and Flory–Stockmayer predictions and were found to favor the percolation results, but the agreement with percolation for the exponent τ was marginal.

Introduction

Gelation is one of the most interesting and important phase transitions in polymer science and has been the subject of considerable theoretical and experimental study for the past half century. The first theoretical treatment was the mean-field theory developed by Flory[1] and Stockmayer[2] in the early 1940s, which elucidated many key features of the sol–gel transition. Although the mean-field theory did not predict experimental results quantitatively, for a number of years further developments were limited to applying corrections to this classical approach. In the mid-1970s, de Gennes[3] and Stauffer[4] proposed that the

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