Diffusion of a self-avoiding polymer

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We study the diffusion of a polymer where we take into account self-avoidance. We introduce a reptation model in which the diffusion of stored length is infinitely rapid. For this model, we find that the diffusion coefficient scales with the length of the polymer as $N^{2\nu-2}$, where ν is the self-avoiding walk exponent for N ranging over almost two orders of magnitude. This result is used to argue that for physical polymers the diffusion coefficient is proportional to $N^{2\nu-3}$ when self-avoidance is significant.

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I. INTRODUCTION

Reptation as a means of describing the dynamics of polymer is well established [1,2]. However, in the usual approach the self-avoidance character of the polymer is not taken into account. The argument used to justify this approximation is that in many cases screening occurs. In a polymer melt, the other polymers screen the self-interaction so that even the radius of gyration exponent is found to take the value $\nu = 1/2$, as for a noninteracting polymer. In another situation, that of a single polymer in a good solvent, hydrodynamic interactions are important. Hydrodynamic interactions describe the effect that a moving polymer drags along its surrounding solute. In this article, we consider a single polymer diffusing through a gel. For a rigid structure neither of the two mechanisms described above is active and hence the self-avoidance may be important. A gel is a random medium, and this may influence the dynamics through entropic trapping [3]. Here we consider the diffusion through a periodic array of obstacles so that entropic trapping is not important.

To be sure, the effect of self-avoidance on the diffusion of a polymer has been considered before. In his seminal article in which the concept of reptation was introduced, de Gennes suggested that self-avoidance might change the diffusion exponent [1]. Later a specific proposal to this supposition was made by Lerman and Frisch [4]. The critical issue is whether the renewal time is affected by the self-interaction. Kremer and Binder suggested that the Rouse time becomes larger [5] and scales with the length of the polymer as $N^{1+2\nu}$. As a consequence, the renewal time would scale as $N^{2+2\nu}$ and the diffusion exponent would then have the value of the noninteracting polymer.

As yet the issue of whether self-avoidance changes the

diffusion exponent is unresolved. Experiments are usually interpreted assuming that the diffusion exponent is 2, and deviations are ascribed to corrections to scaling (see, e.g., [6]). As mentioned above, there are many effects that are important in an experiment so that the influence of self-avoidance on the diffusion is hard to resolve. We are not aware of a simulation study in which the diffusion exponent of a self-avoiding polymer was systematically investigated. Most of the current studies are concerned with fairly short polymers, up to about $N = 100$ [5]. Recently Barkema et al. [7] studied the diffusion coefficient for a noninteracting polymer model and found that there are very large corrections to scaling. For $N = 100$, this correction is larger than 20%. Because of these corrections to scaling, very long polymers have to be simulated in order to obtain a reliable estimate of the diffusion exponent. We present here a model with which we have obtained reliable values of the diffusion coefficients for polymers of lengths ranging from $N = 50$ to $N = 3000$. We find that for a reptating polymer in a regular medium, self-avoidance substantially changes the diffusion exponent.

II. FAST EXTRON MODEL

We study a simplified model of reptation, which combines the two basic ingredients of reptation. In the reptation model, the shape of the polymer can change only due to the motion of the end groups. In addition, the polymer is assumed to be not completely elongated, and it contains some stored length. This stored length diffuses along the polymer. When an excess of stored length arrives at an end group, the polymer can grow. In the reverse situation when there is a shortage of stored length, the polymer shrinks. We consider here a simple model that contains these two ingredients in a pure form (Fig. 1). The polymer moves on a square lattice, and it is assumed to consist of beads of polymer that we will call reptons. These reptons can hop into neighboring cells following the path of the polymer. These internal hops
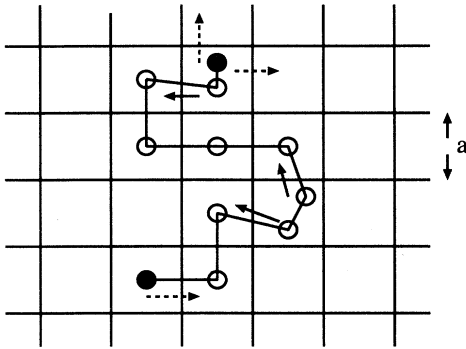
FIG. 1. The model of Rubinstein [8] as modified by Duke [9]. The circles denote subunits of the polymer, called reptons. The lines represent the segments of the polymer, which determine the shape of the polymer. The possible moves of the reptons are indicated by arrows. Internal moves can take place only in those cells in which there are more than one repton, or equivalently, when there are extra reptons (extrons) in a cell. The end points (solid circles) can make the moves indicated by the dashed arrows. For this specific distribution of extrons, the lower end point can only move back and shorten the chain as there is no extron in this cell. The upper end point has one extron, and the only external moves it can make is to grow. Whether an end group is allowed to grow or shrink is determined by the presence or absence of an extron in the cell. Due to the self-avoidance, the polymer is allowed to grow only in two directions in this specific configuration. In the extron equilibrium model, the chain is fully character-ized by the total number of reptons N (in this figure $N = 11$), the length of the chain L (here $L = 8$), and the shape of the polymer. The number of extrons is $M = N - L - 1 = 2$.

can only take place if there are at least two reptons in a given cell. The excess of reptons in a cell we call extrons (extra reptons). The end group can shrink if there is no extron in the end cell. Conversely, the polymer can grow if there is at least one extron in the last cell. The rules are made clear in Fig. 1. The growing of new segments can take place only into empty cells, thus incorporating self-avoidance in the model. This model is the zero field case of a self-avoiding version of a model introduced by Rubinstein [8] and modified by Duke [9]. We denote it as the (self-avoiding) repton model [(SA)RM].

For reasons that will be made clear below, we will actually simulate a different version, in which the ex-trons move very rapidly compared to the end groups. This model, which we studied before for the non-self-avoiding case [10], we call the self-avoiding fast extron model (SAFEM). In the SARM, for any configuration, each end group can either grow or shrink, depending on the extron distribution. In the SAFEM, the extrons dif-fuse very rapidly, and after each move of the end groups they instantaneously attain the equilibrium distribution, which has a constant extron density. In the SAFEM, the dynamics of the extrons need not be treated explicitly. The dynamics are carried entirely by the end groups and the extrons affect the dynamics only through probabili-

ties according to which end group may grow or shrink.

We consider a model of N reptons. For a specific poly-mer configuration with length L there are $M = N - L - 1$ extrons. Considering the model in which an arbitrary number of extrons is allowed in each cell, the extrons obey Bose statistics. The probability Θ of finding at least one extron in the last cell is a simple exercise in equilibrium statistical physics. The number of distinct ways to put M bosons into $L + 1$ cells is identical to the number of ways in which L separations can be inserted into a line containing $L + M + 1 = N$ beads. This number is

$$Z_{LM}^{(B)} = \binom{N-1}{L}. \tag{1}$$

The probability of finding no extrons in a specific cell is $Z_{(L-1)M}^{(B)}/Z_{LM}^{(B)}$ and therefore

$$\Theta \equiv p(n_L > 0) = 1 - \frac{\binom{N-2}{L-1}}{\binom{N-1}{L}} = \frac{M}{N-1}, \tag{2}$$

where L denotes the last cell occupied by the polymer. As there is no external field, the probability Θ is identical for all the cells. The rates with which the polymer shrinks out of a given configuration is

$$W_s = W(1 - \Theta), \tag{3}$$

where W is the number of shrinks per unit time for a fully stretched polymer. This rate is identical for both ends of the polymer. The growth rate is

$$W_g = W\Theta, \tag{4}$$

for each of the allowed direction. The total growth rate is $nW\Theta$, where n is the number of unoccupied neighbor-ing cells of the two ends. In equilibrium the shrink rate equals the growth rate

$$\langle n \rangle = \frac{1 - \langle \Theta \rangle}{\langle \Theta \rangle}, \tag{5}$$

where the angular brackets denote the equilibrium av-erage. As fluctuations in the length, and hence Θ are small, these fluctuations can be ignored. In the Monte Carlo simulations the possible moves are enumerated, and one of the moves is selected with relative weights pro-portional to the rates mentioned. The dynamics of the model studied here are ergodic, which means that start-ing from any configuration and waiting long enough, any state is reached with the proper weight. To see this, note that any configuration has a set of legitimate moves to-wards a configuration of length zero, i.e., all the reptons in one cell. This is an important feature not shared by all methods; for instance, the so-called "slithering snake" algorithm is not ergodic [11]. The boson model studied here can easily be extended by slightly changing the rules. If one allows only one extron in each cell, Fermi statistics are obeyed and the probability of finding one extron in a specific cell is found to be
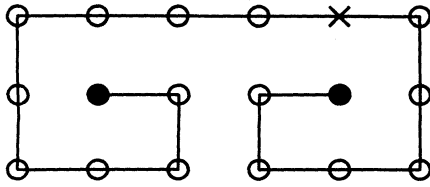
FIG. 2. A configuration that may have a renewal time that is substantially larger than average. The empty circles now denote cells with many extrons, and the only cell without extrons is the cell marked by the cross. In order for the polymer to come out of a configuration such as this, two subsequent shrinks have to occur, which is unlikely due to the large number of extrons. The simulation results suggest that configurations such as these are rare and not important for the diffusion of the polymer. For extrons obeying Fermi statistics, two subsequent shrinks are impossible and the polymer is stuck in this configuration.

$$\Theta_{\text{Fermi}} = \frac{M}{L+1} \qquad (M \leq L+1). \qquad (6)$$

The self-avoiding repton model with Fermi statistics will have somewhat different properties, for instance, it is nonergodic (see Fig. 2). As far as the main research question of this paper is concerned, the value of the diffusion exponent for the self-avoiding repton model, the extron statistic is expected to be unimportant. All our simulations are for the Bose model.

III. EQUILIBRIUM PROPERTIES

The models introduced, the SARM and SAFEM have the same equilibrium distribution, in which all configurations are equally likely. However, in the SAFEM, the extron distribution is not an interesting quantity as it is always in a (homogeneous) equilibrium. A special feature of these models over other self-avoiding walk models is that the length fluctuates. We now establish the probability distribution for finding a polymer with length L. The number of self-avoiding walk (SAW) configurations with length L is asymptotically [12,13]

$$Z_L^{(S)} = K c^L L^{\gamma-1}, \qquad (7)$$

where K is a constant, $\gamma = 43/32$ in two dimensions, and $c = 2.638\,15 \cdots$ for a two-dimensional square lattice. The number of distinct partitions of M bosons distributed over $L+1$ sites is $Z_{LM}^{(B)}$, so the total number of configurations of length L is

$$Z_L = Z_L^{(S)} Z_{LM}^{(B)}. \qquad (8)$$

For large number of reptons $N = L + M + 1$ this is a Gaussian distribution. The average length is

$$\langle L \rangle = \frac{c}{1+c} N \equiv lN. \qquad (9)$$
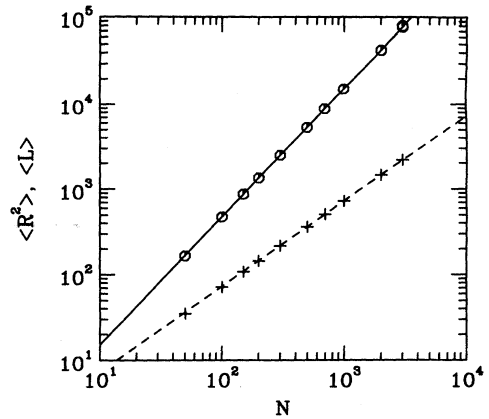
This average length is observed in simulations and it

FIG. 3. The average end-to-end distance $\langle R^2 \rangle$ as a function of the number of reptons N in the two-dimensional fast extron model (circles). The solid line is a $N^{3/2}$ line, which is based on the known value of the self-avoiding walk exponent $\nu = 3/4$. The pluses are the average length of the polymer, which coincides with the dashed line which is the prediction of Eq. (9), $L = 0.725\,13N$.

serves as a check on the simulation method (Fig. 3). Note that the length does not depend on the exponent γ. Fluctuations in the length are

$$\left\langle L^2 - \langle L \rangle^2 \right\rangle = \frac{c}{(1+c)^2} N, \qquad (10)$$

so these are indeed small for long polymers. However, length fluctuations can give rise to corrections to scaling. Throughout this paper we will be interested only in the behavior of long polymers and we will ignore finite size corrections to the scaling behavior. For fermions we find

$$Z_M^{(F)} = \binom{L+1}{M}, \qquad (11)$$

and as a consequence

$$\left\langle L^{(F)} \right\rangle = \frac{1}{2} \left[1 + \left(\frac{c}{1+c} \right)^{1/2} \right] N. \qquad (12)$$

The mean end-to-end distance R is defined as $R^2 = \langle \vec{R}^2 \rangle$, where $\vec{R}$ is the end-to-end vector. For an unbranched polymer R is proportional to the radius of gyration [2]. It is well known that $R \propto L^\nu$ with ν the SAW exponent. In two dimensions $\nu = 3/4$, whereas in three dimensions $\nu = 0.586$ [12–14]. This exponent is reproduced in the simulations of the SAFEM, see Fig. 3. The present simulation scheme is not the most efficient algorithm for finding the self-avoiding walk exponents, more efficient algorithms exist [14].

IV. DYNAMIC PROPERTIES

The scaling behavior of the diffusion coefficient was first established by de Gennes [1]. We use here the line

of thought expressed by Barkema, Marko, and Widom [7]. The diffusion constant is given by

$$D = \lim_{t \to \infty} \frac{\langle [\Delta R(t)]^2 \rangle}{2dt}, \tag{13}$$

where d is the dimension and ΔR is the displacement of the center-of-mass after time t. For a noninteracting polymer there will be no dynamic correlations after all the segments of the polymer have been renewed. So the diffusion coefficient is given by

$$D = \frac{R^2}{2dt_R}, \tag{14}$$

where R is the average end-to-end distance and t_R is the renewal time. To find the renewal time, we consider the curvilinear displacement. For the repton model (RM), the curvilinear displacement ΔC is increased by an amount $1/N$ each time a repton jumps to the right, whereas it is decreased by an amount $1/N$ each time a repton jumps to the left. Left and right are defined with respect to the repton index, one end, say $i = 1$ corresponding to the left and the other end, $i = N$ corresponding to the right. In order to really replace one segment, N reptons have to hop in the same direction, hence the factors $1/N$. In the absence of an external field, subsequent jumps are uncorrelated on the average and the time dependence of the curvilinear displacement follows a random walk so

$$\left\langle (\Delta C)^2 \right\rangle = 2D_c t, \tag{15}$$

with D_c the curvilinear diffusion coefficient. This curvilinear diffusion coefficient is given by the number of jumps per unit time times the square curvilinear displacement per jump, which is $1/N^2$. For bosons, the number of jumps per unit time is $l(1 - l)NW$ for large polymers [15,16] so

$$D_c = \frac{l(1 - l)}{N}W. \tag{16}$$

In order for the polymer to completely renew itself, the curvilinear mean square displacement has to be L^2, and the renewal time becomes

$$t_R = \frac{l^2 N^2}{2D_c} = \frac{l}{2(1 - l)}\frac{N^3}{W}. \tag{17}$$

Hence the renewal time scales as N^3, as is well known [1,2].

For the FEM a different power law is obtained. In the FEM only the two end reptons move. In equilibrium the growth rate equals the shrink rate Eq. (3) and we find that the curvilinear diffusion coefficient is

$$D_c = \frac{4W(1 - \Theta)}{4}, \tag{18}$$

where the numerator is the rate of moves of the end groups and the denominator expresses that after one move the center-of-mass coordinate along the polymer is

shifted over half a segment. As on the average $\Theta = 1 - l$,

$$D_c = lW. \tag{19}$$

For the FEM we find the renewal time

$$t_R = \frac{l}{2}\frac{N^2}{W}. \tag{20}$$

Here we notice an important difference between the RM and the FEM: the renewal time depends on a different power of N.

For a noninteracting polymer, the average end-to-end distance is $R = aL^{1/2}$ and the diffusion coefficient is

$$D = \frac{a^2 L}{2t_R} = (1 - l)\frac{Wa^2}{dN^2} \tag{21}$$

for the repton model. In one dimension $D = Wa^2/3N^2$, which was first found by Van Leeuwen and Kooiman [15], and confirmed in computer simulations of Barkema et al. [7]. For the fast extron model

$$D = \frac{Wa^2}{N}, \tag{22}$$

which is identical to our previous results [10]. Both expressions have the form

$$D = C\frac{Wa^2}{N^\mu}, \tag{23}$$

for some constant C and diffusion scaling exponent μ.

So far in the section we have discussed the noninteracting polymer. The interacting case has been studied to some extent before. Lerman and Frisch [4] proposed to use Eq. (14) with t_R having the scaling exponent 3, as in Eq. (17). This results in

$$D = \frac{R^2}{2dt_R} \propto N^{2\nu - 3}, \tag{24}$$

so $\mu = 3 - 2\nu$. This argument was put into question by Kremer and Binder [5] who argued that the Rouse time t_s, and consequently also the renewal time scales as $t_R \propto N^{2\nu + 2}$, resulting in $\mu = 2$, i.e., the noninteracting exponent. As yet the issue has not been resolved. There is little hope that a simple theoretical argument can resolve the issue. As is illustrated in Fig. 2, one can easily find configurations that have renewal times substantially larger than average. The question is whether such configurations are important.

V. SIMULATION RESULTS

We performed simulation on the SAFEM. The use of the SAFEM enables us to obtain the values for the diffusion exponent accurately. For the RM, the renewal time scales as N^3, Eq. (17). However, during one time unit N reptons hop so that the amount of computational effort required for one polymer renewal scales as N^4. Hence, the largest systems studied for the repton model has
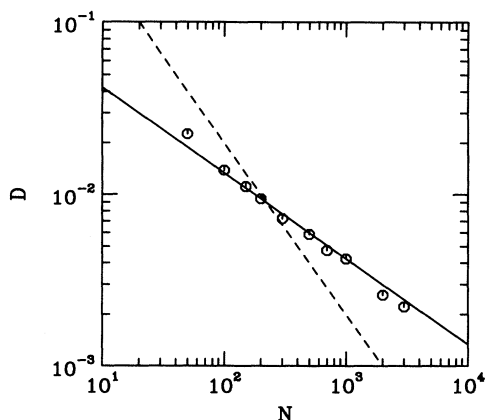
FIG. 4. The dimensionless diffusion coefficient D as a function of the number of reptons N in the two-dimensional SAFEM. In all the figures, dimensionless units are used in which $W = a = 1$. The solid line is a $N^{-1/2}$ curve and the dashed line is the N^{-1} curve. It is clear that $D \propto N^{2\nu-2}$ gives a good prediction. The errors in the diffusion coefficients are of the order of 5%, which is about the size of the plotting symbols.

FIG. 6. The dimensionless diffusion coefficient D as a function of the number of reptons N in the three-dimensional SAFEM. The solid line is a $N^{2\nu-2}$ curve with $\nu = 0.586$ and the dashed line is a N^{-1} curve. The simulation results suggest that the solid line provides a better fit.

$N = 400$, and seems unlikely that substantially larger systems can be studied. $N = 400$ seems to be too small to resolve issues concerning scaling behavior. This is even more so as it is known that there are large corrections to scaling in the diffusion coefficient of the repton model [7].

The case is much better for the SAFEM. As only the end points move, the amount of work required for a single renewal scales as N^2 [see Eq. (20)]. We have gone up to $N = 3000$ on a simple workstation for the two-dimensional simulations. In three dimensions, the system size studied was limited by the effort required to keep track of the self-avoidance.

In Fig. 4 we present our data for the diffusion coefficient. It demonstrates clearly that

$$D \propto N^{2\nu-2} = N^{-1/2} \tag{25}$$

in two dimensions. Deviations we ascribe to $1/N$ corrections to scaling, see Fig. 5. For three dimensions (3D) the simulation data do not provide as strong evidence, but as is shown in Fig. 6 there is some evidence that the diffusion exponent $\mu = 2\nu - 2$ also in three dimensions. A least squares fit assuming $D \propto N^{-\mu}$ produces $\mu_{3D} = 0.83 \pm 0.06$. However, finite size corrections cannot be ruled out entirely as explanation of the deviations from a N^{-1} behavior.
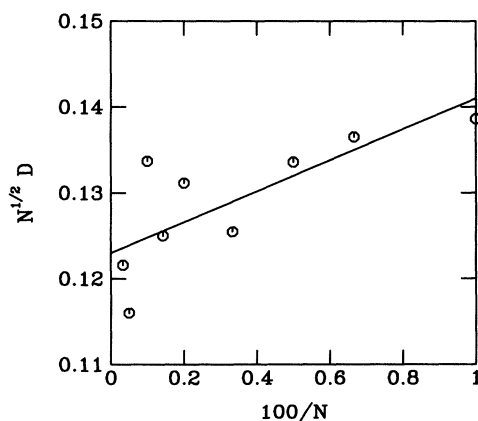

FIG. 5. The dimensionless diffusion coefficient times the square root of the number of reptons as a function of the inverse of the number of reptons. The solid line is a least square fit. Based on this figure, we expect that deviations from the scaling law $D \propto N^{2\nu-2}$ are due to finite size corrections to scaling. However, other behaviors such as, for instance, logarithmic corrections cannot be ruled out.
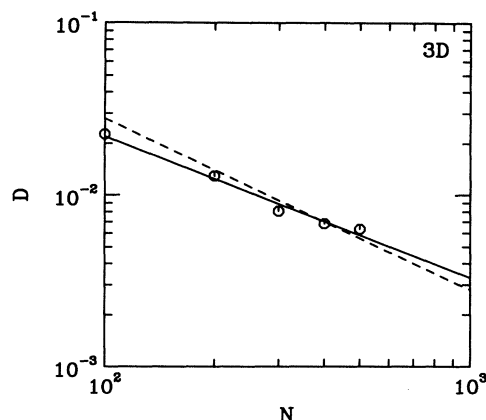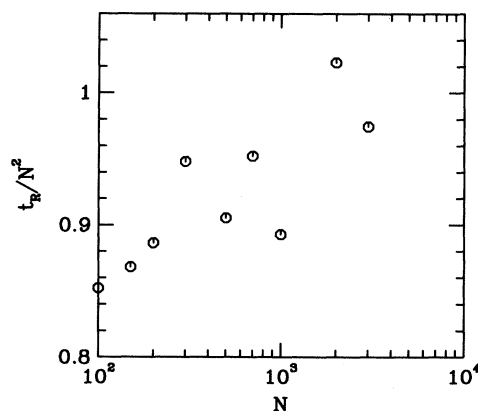

FIG. 7. Simulation results for the renewal time $t_R = \langle R^2 \rangle /2dD$ as a function of the number of reptons for the two-dimensional SAFEM. The noninteracting fast extron model has $t_R = l/2N^2W = 0.3626/N^2W$ (using the SAFEM length). We conclude that self-avoidance increases the renewal time, yet the renewal time remains proportional to N^2.
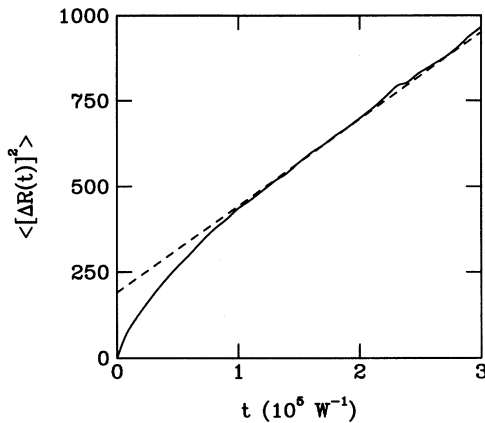
FIG. 8. The mean square displacement as a function of time for the two-dimensional SAFEM with $N = 200$ reptons (solid). The dashed line is a straight line indicating the long time behavior. The renewal time for this polymer is $t_R = 3.5 \times 10^4 \ W^{-1}$. Clearly the diffusion coefficient has converged to its long time value after $t \simeq 10^5 \ W^{-1}$, which corresponds to about three renewal times.

The result presented was for the fast extron model. This may be a good model for polymers in which the end groups are special and determine the time scale of the dynamics. This will be the case for only a limited class of polymers, so the question arises to what extent the results transfer to the repton model, which is more physical. As pointed out above, it is very difficult to answer this question by a direct simulation of the repton model as the amount of work needed is large by a factor N^2. Yet we believe that there are good reasons to believe that for a physical polymer $D \propto N^{2\nu-3}$. The main uncertainty is in the scaling behavior of the renewal time. The influence of the self-avoidance on the renewal time is only in the prefactor of Eq. (20), which is found

to increase by about a factor of 3 (Fig. 7). This result suggests that while configurations may be trapped for some time, the renewal time, being proportional to N^2, is so large that the polymer has enough time to find the "pockets" in phase space. The mean square displacement as a function of time (Fig. 8) appears to converge rapidly to its asymptotic value, suggesting that there are no important correlations after a few renewal times. For the repton model, the renewal time should be even less affected as the renewal time is larger and a larger fraction of phase space is sampled, making the "holes" more important. Assuming that the reptation model correctly describes polymer dynamics, $\mu = 3 - 2\nu$ then also is the scaling of a physical polymer diffusing through a periodic array of rigid obstacles.

Usually experiments are interpreted by comparing the measured diffusion coefficient with a N^{-2} power law, and deviations are ascribed to corrections to scaling. The results presented in this paper put this interpretation into question. As mentioned in the Introduction, the validity of the model for physical situations is unclear. Yet there are experiments that suggest that $\mu < 2$. The experiments of Arvanitidou and Hoagland for polystyrenesulfonate in agarose [6] can be interpreted as evidence for a mobility exponent ranging from 1.73 to 1.9 depending on which of their data points are used in a fit. This at least is compatible with the finding of this paper, $\mu = 1.828$.

ACKNOWLEDGMENTS

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