

## Diffusion of a polymer chain in porous media

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Using an off-lattice Monte Carlo bead-spring model of a chain in a random environment, we study chain conformations and dynamic scaling of diffusivity and relaxation times with chain length  $N$  and density of the host matrix  $C_{\text{obs}}$ . Our simulational results show that with growing  $C_{\text{obs}}$  the mean size (gyration radius) of the polymer,  $R_g^2$ , initially slightly decreases and then rapidly increases as the macromolecule exceeds the size of the average entropic wells and stretches through bottlenecks into neighboring wells. The chain dynamics changes from a Rouse-like one into a reptational one as the permeability of the matrix decreases. Although at variance with some previous treatments [M. Muthukumar, *J. Chem. Phys.* **90**, 4594 (1989)], these findings agree well with a recent analytic approach (S. V. Panyukov, *Zh. Éksp. Teor. Fiz.* **103**, 1287 (1993) [*Sov. Phys. JETP* **76**, 631 (1993)]) to chain conformations in random media. We also suggest a simple scaling analysis, based on a ‘‘blob’’ representation of the polymer chain, whereby the blob size is governed by the size of the cavities in the host matrix and yields a faithful description of our computer experiments.

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### I. INTRODUCTION

The statistical properties of polymer chains in a quenched random medium or under geometry constraints [3] have been the subject of intensive investigation during the last decades, both theoretically [1–12] and experimentally [13–21] because diffusion is of great relevance for a number of phenomena, such as chromatography, membrane separation, ultrafiltration, biology, sedimentation, oil recovery, etc.

Due to difficulties and uncertainties in the experimental characterization of the porous media [17], and the inevitability of approximations in the analytical treatment of the problem [1,2], however, the nature of the chain movement in a random medium is still far from being well understood, and theoretical predictions, pertaining even static conformational properties of such chains, are controversial [1,2]. Thus, on the ground of replica calculations within a variational approach one predicts three regimes [1] in which the scaling of the gyration radius  $R_g^2$  with the number of repeatable units of the chain with excluded volume interactions,  $N$ , goes as  $R_g^2 \propto N^{6/5}$  for low-,  $R_g^2 \propto N$  for medium, and  $R_g^2 \propto C_{\text{obs}}^{2/3} N^{2/3}$  for high density of obstacles,  $C_{\text{obs}}$ , so that the porous medium generally shrinks the size of the coil [24–26]. On the contrary, a regular expansion in a small parameter [2] predicts a Gaussian statistics for chains, shorter than the localization length of the medium whereas sufficiently long chains are typically distributed over several *entropic* potential wells so that  $R_g^2 \propto N^{6/5}$ , that can be interpreted as a self-avoiding random walk, each step of which is equal to the average distance  $L$  between neighboring wells,  $L \propto C_{\text{obs}}^{1/3}$ . Chains of medium length,  $N < L$ , are expected to stretch out into a string,  $R_g^2 \propto N^2$ .

The scaling dependence of the diffusion coefficient,  $D_N$ , on  $N$  and  $C_{\text{obs}}$  poses a number of questions too. While the original scaling predictions, based on reptation dynamics [27,40],  $D_N \propto N^{-2}$ , have been verified by Guillot, Leger, and Rondelez [15] and Lumpkin [12], significant discrepancies between the reptation idea and other experimental measurements have been reported [18–21]. Attempts to interpret ex-

isting data in terms of alternative models, e.g., the so called ‘‘hydrodynamics scaling model’’ [21] are unable to describe observations [22] either [23].

Computer simulations, one might believe, which, in principle, are statistically exact within the framework of the respective model, and are free from undesirable side effects of laboratory experiments, could prove important in resolving much of the controversy. However, simulational results also differ, mainly because different models of the host matrix (the porous medium) are used. Thus it has been suggested that the chain dynamics in a dense system can be different from reptational ones [28–31], with  $D_N \propto N^{-3}$  for a Gaussian chain [30] and  $\ln(D_N) \propto -N$  for such ones with excluded volume interactions.

In the present investigation, we use, as a host matrix, an equilibrated dense solution of identical polymer chains which is frozen in different configurations, and let a single chain (or a small number of chains) move through these realizations of a random medium, Sec. II. As will be shown below, Sec. III, the computational results agree well with a recent treatment of the conformational properties of a chain in a random environment [2]. We also suggest a simple scaling description of our results in Sec. IV, so that data for various chain lengths and different density of the medium collapse on a single functional relationship. As is emphasized in Sec. V, it appears, that a representation of the polymer chain as a sequence of ‘‘blobs,’’ with size equal to the mean size of the cavities in the host matrix, provides a basis for a possible scaling analysis and a good description of computational results, at least for the range of chain lengths and obstacle densities, feasible in contemporary computer experiments.

### II. THE MODEL

An off-lattice bead-spring model of a polymer chain [32], placed in a random medium of obstacles is studied by a Monte Carlo simulation technique. This model of a coarse-grained macromolecule has been successfully used recently

for studies of polymer solutions at  $\theta$  conditions [33,34], in constrained geometries (capillaries, slits) [35,36], or at adsorbing surfaces [37,38], and is known to reproduce faithfully the expected Rouse behavior of a polymer system with excluded volume interactions. In our Monte Carlo simulation we use a standard Metropolis algorithm whereby an attempted move of a randomly selected particle in a random direction is accepted with probability, equal to

$$P = \begin{cases} \exp[-(E_{\text{new}} - E_{\text{old}})/k_B T], & \text{for } E_{\text{new}} > E_{\text{old}} \\ 1, & \text{otherwise} \end{cases} \quad (1)$$

where  $E_{\text{new}}$  and  $E_{\text{old}}$  are the energies of the new and old system configurations, calculated with the following interaction model potentials.

The so called FENE (finite extensible nonlinear elastic) potential is used for the bonded interaction between neighboring beads along the chain,

$$U(r) = \begin{cases} -kR^2 \ln[1 - (r/R)^2], & \text{for } -R < r - l_0 < R \\ \infty, & \text{otherwise} \end{cases} \quad (2)$$

where  $r$  is the distance between two successive beads,  $l_0 = 0.7$  is the unperturbed bond length,  $R = 0.3$  and  $k = 20$  (in our units of energy  $k_B T = 1.0$ ) are the elastic constant of the FENE potential which behaves as a harmonic potential for  $r - l_0 \ll R$ .

The nonbonded interaction is described by a Morse potential,

$$U(r) = U_M [\exp(-2ar) - 2\exp(-ar)], \quad \text{for } 0 < r - r_{\min} < \infty \quad (3)$$

where  $r_{\min} = 0.8$ ,  $U_M = 0.1$ , and the large value of  $a = 24$  makes interactions vanish at distances larger than unity, so that an efficient *link-cell* algorithm [32] for short-range interactions can be implemented. The total volume is thereby divided into hypothetical cells of size unity so that a particle in a particular cell may interact only with other particles in the adjacent cells (26 such cells in three dimensions). The radius of the beads and the interactions, Eqs. (2) and (3), have been chosen such that the chains may not intersect themselves or each other in the course of their movement within the box.

The porous medium consists of an initially relaxed and then frozen network of polymer chains of length  $N = 16$  and the monomers have the same size as those of the diffusing chain. The concentration of the network  $C$  is varied and the behavior of diffusing chains of various length  $N$  is studied in the good solvent regime,  $k_B T = 1.0$ , since, from previous studies of the model, it is known that the  $\theta$  temperature  $k_B T_\theta = 0.62$  [33].

Several types of mean-square displacements [32] are calculated as functions of time, measured in Monte Carlo steps (MCS) per monomer (bead), whereby 1 MCS is the time needed for all monomers to perform an attempted move  $\Delta x, \Delta y, \Delta z \leq \pm 0.5$  in a random direction.

$$\begin{aligned} g_1(t) &= \langle [r_{N/2}(t) - r_{N/2}(0)]^2 \rangle, \\ g_2(t) &= \langle [r_{N/2}(t) - r_{CM}(t) - r_{N/2}(0) + r_{CM}(0)]^2 \rangle, \\ g_3(t) &= \langle [r_{CM}(t) - r_{CM}(0)]^2 \rangle, \end{aligned} \quad (4)$$

where  $r_{CM}, r_{N/2}$  are the radius vectors of the center of mass and of the middle inner monomer of a polymer chain. With  $g_3(t)$  from Eq. (4) the diffusion constant  $D_N$ , defined as

$$6D_N = \lim_{t \rightarrow \infty} [g_3(t)/t] \quad (5)$$

and several relaxation times  $\tau_1, \tau_2, \tau_3$ , defined as [39]

$$g_1(\tau_1) = \langle R_g^2 \rangle, g_2(\tau_2) = \frac{2}{3} \langle R_g^2 \rangle, g_3(\tau_3) = g_2(\tau_3) \quad (6)$$

are calculated.

The simulations that have been performed use a volume of  $32^3$  and in the highest concentration regime they contain up to 49 152 fixed monomers in 3072 chains of length  $N = 16$  which form the porous media. The single diffusing chain immersed into this host matrix has been chosen with lengths of 8, 16, 32, and 64 monomers. For longer chains even at intermediate obstacle densities it was found that the chains practically do not move. To estimate the diffusion constant within an error of less than 10% we performed up to  $10^8$  MCS for the diffusing chain in the highest concentration regimes, and averaged the results of about 100 independent runs in two or three different random media.

### III. MAIN RESULTS

#### A. Static properties of the diffusing chain

In Fig. 1 we plot the variation of  $R_g^2$  with an increasing system density  $C$  and, for comparison, also give the respective change for a system of moving medium (dynamic host matrix) of equal density. Evidently, one observes an initial weak decline and then a growth of the gyration radius with increasing density of the obstacles. This is one of our central results, and it does not confirm earlier predictions [1], but is in agreement with a more recent result [2]. From Fig. 1 it is also seen that this increase of  $R_g^2$  sets in at a lower density of the porous medium when the diffusing chain is longer. We believe that this crossover effect sets in when a long chain is not able to fit into the cavities which play the role of entropic ‘‘traps’’ in the host matrix.

If one defines an effective Flory exponent,  $\nu_{\text{eff}}$ , from the scaling relation  $R_g^2 \propto N^{2\nu_{\text{eff}}}$ , it is then evident from Fig. 2 that in contrast to the case of a polymer solution with no obstacles, where the screening of excluded volume interactions with increasing concentration renders all chains to behave like Gaussian,  $\nu_{\text{eff}} \rightarrow 0.5$ , in the porous medium  $\nu_{\text{eff}}$  grows as the free volume of the medium decreases. Of course, since we deal generally with rather short chains, one could reformulate this result in terms of a growing *persistent* length of the chains as the host matrix becomes denser, rather than in terms of  $\nu_{\text{eff}}$ . One may thus conclude that in the high density regime of obstacles and long chain lengths the conformation of the chain is governed predominantly by the density fluctuations of the porous environment. The chain follows the distribution of the cavities and channels, formed in the polymer network, and one observes an effective renormalization of the Kuhn length of the chain, which becomes equal to the average distance between the cavities. This leads to the observed increase of the gyration radius of the chains.

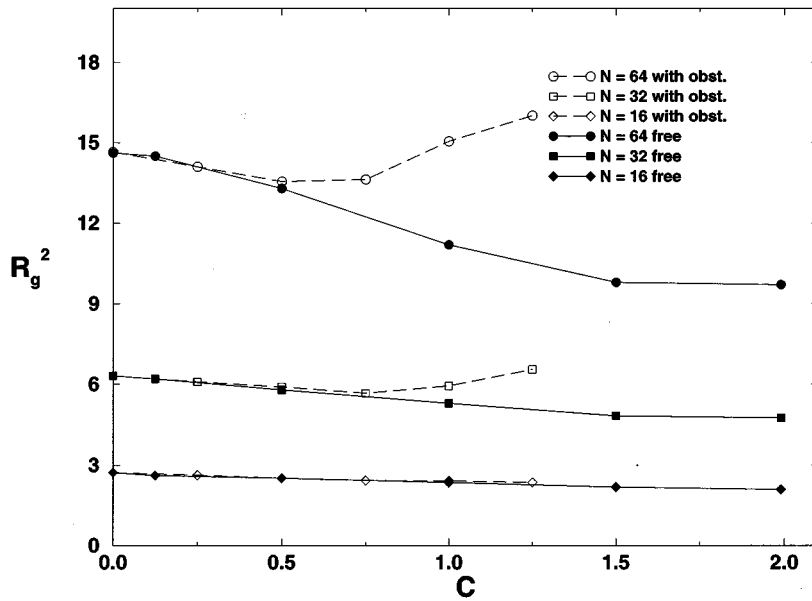


FIG. 1. Mean-square gyration radius  $R_g^2$  vs total density  $C$  of the system for three different chain lengths (given as a parameter) in the case of equilibrated polymer solution (no fixed obstacles) (full symbols), and for a frozen host matrix (empty symbols) at equivalent total density.

Eventually we should also like to point out that not only the overall dimensions of chains vary, but also the bond length  $\langle l^2 \rangle$  itself—Fig. 3. Evidently the decrease of  $l$  does not exceed 3% but one should bear in mind that as far as each monomer in a coarse-grained model accounts for several chemical bonds, a compression also occurs at the length scale of a few bonds.

### B. Dynamic properties of the diffusing chain

Typical dynamic properties like the scaling of diffusion coefficient  $D_N$  with  $N$ , Fig. 4, and of relaxation times, e.g.,  $\tau_1$ , Eq. (6)—Fig. 5—were found to change systematically from typical Rouse-like behavior ( $D_N \propto N^{-1}$ ,  $\tau \propto N^{2\nu+1}$ ) to reptational behavior [40],  $\Phi_N \propto N^{-2}$ ,  $\tau \propto N^3$  as the free volume of the porous medium decreases. Because of the very slow dynamics of the chain among the obstacles some other characteristic times as  $\tau_3$  could not be determined ( $\tau_3 \approx 3.7\tau_1$  [32,33]) within the time interval of the simula-

tion. Thus we believe that we find a clear evidence that with growing density of the medium the reptational character of transport through the obstacles becomes progressively dominating. Indeed, as the porous medium becomes denser, one should expect the chains to move along existing channels by means of a reptational mechanism, as is demonstrated for  $D_N$  and  $\tau_1$  here. We were not able to study the very high concentration regimes or longer chains, where we find that the diffusing chain is blocked by the obstacles and practically does not move.

## IV. CROSSOVER SCALING OF A POLYMER IN A QUENCHED MEDIUM: THEORETICAL PREDICTIONS AND SIMULATIONS

### A. Crossover scaling for statics properties

To study the crossover scaling for the gyration radius  $R_g$  and the end-to-end distance  $R$  of a polymer chain in a

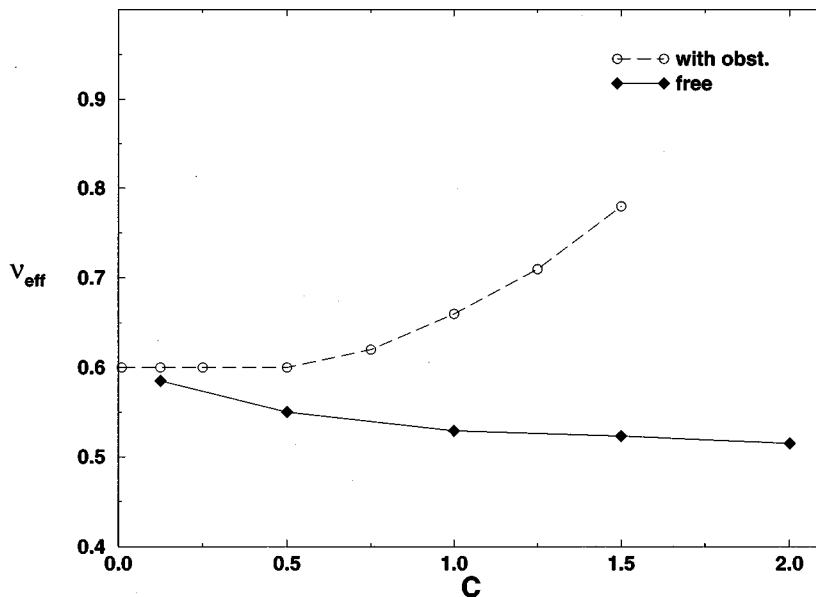


FIG. 2. Variation of the effective Flory exponent  $\nu_{\text{eff}}$  with total density in a polymer solution (full symbols), and in a porous medium (empty symbols) at equivalent density of the obstacles.

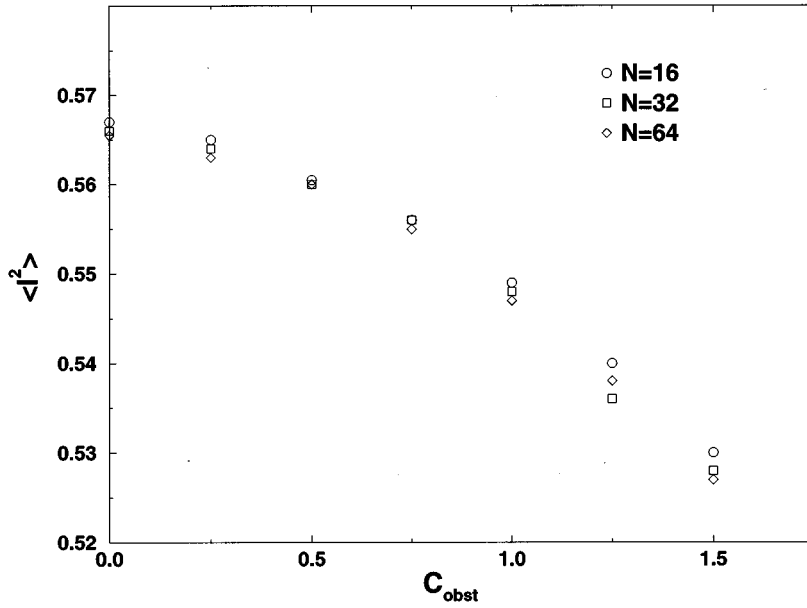


FIG. 3. Averaged squared bond length  $\langle l^2 \rangle$  vs host matrix density for three different chain lengths.

quenched random medium, we follow the work of Paul *et al.* [41] about a polymer solution. In the case of diffusion of a single chain, placed in a random medium of frozen polymer chains, one must distinguish between the statistical parameters of the diffusing chain and those of the surrounding immobile chains, while in the case of a polymer solution [41] they are identical.

The characteristic size of the pores is the correlation length of the frozen polymer solution of obstacles  $\xi_{\text{obs}}$ , and it depends on the volume fraction of the obstacles  $C_{\text{obs}} = Cl^3$  as

$$\xi_{\text{obs}} \propto C_{\text{obs}}^{-\nu/(3\nu-1)}, \quad (7)$$

where  $\nu = 0.588$  is the Flory critical exponent.

In the dilute limit the chain does not feel geometric constraints and  $\langle R_g \rangle_0$  scales as

$$\langle R_g^2 \rangle_0 \propto N^{2\nu} \quad (8)$$

with  $N$  the length of the diffusing chain in monomer units.

At high obstacle concentrations (small  $\xi_{\text{obs}}$ ) or for a large enough chain, when  $\langle R_g^2 \rangle \gg \xi_{\text{obs}}^2$  we see (cf. Fig. 2) that the mobile polymer chain behaves more like a stretched string, as  $C_{\text{obs}}$  is raised, which can be expressed as

$$\langle R_g^2 \rangle \propto C_{\text{obs}}^x N^{2\nu_{\text{cross}}} \quad (9)$$

with some exponent  $x$  which is still to be determined. Here  $\nu_{\text{cross}}$  is the limiting value of the effective Flory exponent for a diffusing chain at high obstacle concentrations.

The crossover occurs at obstacle density  $C_{\text{obs}}^*$  when the size of the polymer becomes equal to the sizes of the pores,  $\langle R_g^2 \rangle = \xi_{\text{obs}}^2$ . At this regime from Eqs. (7) and (8) it follows:

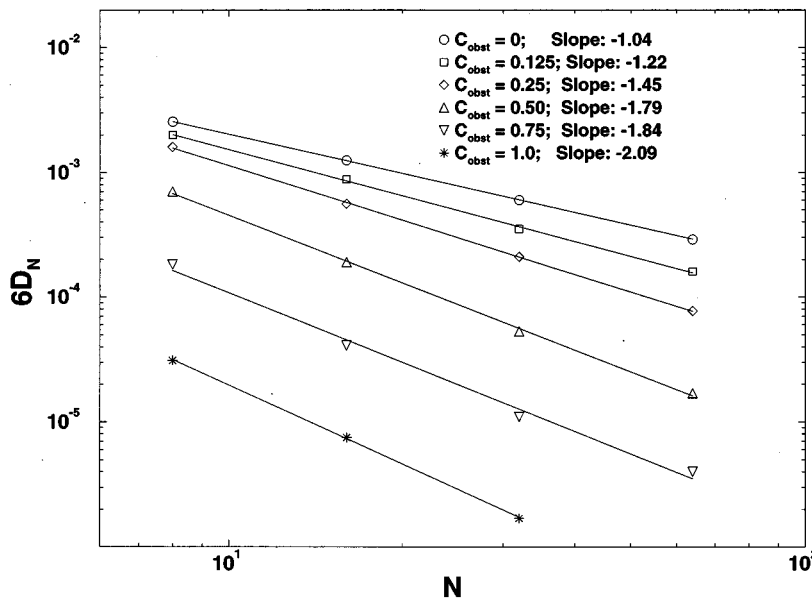


FIG. 4. Log-log plot of diffusion coefficient  $D_N$  vs chain length  $N$  at different density of the obstacles. The change of the slopes from  $\approx -1$  at  $C_{\text{obs}}=0$  to  $\approx -2$  in a porous system with vanishing free volume is given in the legend.

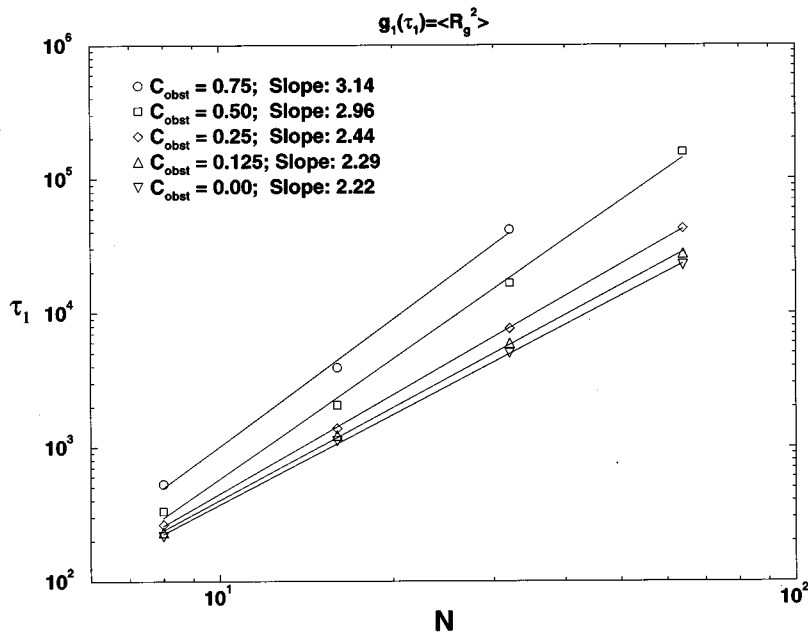


FIG. 5. Scaling of relaxation time  $\tau_1$ , Eq. (6), with chain length  $N$  at several obstacle densities. The limiting slope values 2.22 and 2.96 are close to 2.18 and 3, characteristic for Rouse- and reptational behavior, respectively.

$$C_{\text{obs}}^* \propto N^{-(3\nu-1)}. \quad (10)$$

The exponent  $x$  in Eq. (9) has to be determined from the condition of a smooth matching between Eqs. (8) and (9) at  $C_{\text{obs}} = C_{\text{obs}}^*$  which yields

$$x = 2 \frac{\nu - \nu_{\text{cross}}}{1 - 3\nu}. \quad (11)$$

When substituted in Eq. (9) and using Eq. (7)

$$\langle R_g^2 \rangle \propto C_{\text{obs}}^{-(2\nu-2\nu_{\text{cross}})/(3\nu-1)} N^{2\nu_{\text{cross}}} \propto \xi_{\text{obs}}^{2-2\nu_{\text{cross}}/\nu} N^{2\nu_{\text{cross}}}. \quad (12)$$

Using as a new variable

$$\zeta = \langle R_g \rangle_0 / \xi_{\text{obs}} = N^\nu C_{\text{obs}}^{\nu/(3\nu-1)},$$

the relative change of the gyration radius with the concentration of obstacles in the system can be expressed as a crossover scaling function  $f_{\text{gyr}}(\zeta)$  of the parameter  $\zeta$ , which behaves at the limiting cases as

$$\frac{\langle R_g^2 \rangle}{\langle R_g^2 \rangle_0} = f_{\text{gyr}}(N^\nu C_{\text{obs}}^{\nu/(3\nu-1)}) = \begin{cases} \text{const}, & \zeta < 1 \\ \zeta^{-[2-2(\nu_{\text{cross}}/\nu)]}, & \zeta > 1. \end{cases} \quad (13)$$

The main difference in our result in comparison to the case of a polymer solution is the different power of  $\zeta$  for large  $\zeta > 1$ . In the case of a polymer solution, where  $\nu_{\text{cross}} = 0.5$ , this exponent is equal to  $-(2-1/\nu) \approx -1/3$ , thus determining a decreasing scaling function  $f_{\text{gyr}}(\zeta)$  for  $\zeta > 1$ , while in the case of a porous medium we obtain an exponent equal to  $-(2-2\nu_{\text{cross}}/\nu) > 0$  for  $\nu_{\text{cross}} > \nu$  since the conformations of the chain in the host matrix are not Gaussian. Hence, we should expect an increasing power-law behavior of  $f_{\text{gyr}}(\zeta)$  for  $\zeta > 1$ . Within the range of lengths of chains which do really diffuse through the medium we measure at high obstacle density  $\nu_{\text{cross}} = 0.7-0.78$ , (Fig. 2) and the

power of  $\zeta$  in Eq. (13) is about 0.37–0.64. However, when we plot the scaling function,  $f_{\text{gyr}}$  expressed as  $\langle R_g^2 \rangle / N^{2\nu} \langle l^2 \rangle$  vs  $N(Cl^3)^{1/(3\nu-1)}$ , in contrast to [41] we do not obtain any reasonable scaling for large  $\zeta > 1$  [Fig. 6(a)].

We observe a good scaling only if we plot  $\langle R_g^2 \rangle / N^{2\nu} \langle l^2 \rangle$  vs  $N(Cl^3)^{2/(3\nu-1)}$  [Fig. 6(b), region I,II] and the slope of  $f_{\text{gyr}}$  in a log-log plot at  $N(Cl^3)^{2/(3\nu-1)} > 1$  in region II equals 0.6, as indicated by the solid line, that corresponds to  $\nu_{\text{cross}} = 0.78$  in Eq. (13). This result can be explained by renormalization of the polymer length  $N$ , taking into account the growing persistent length of the chains as the host matrix becomes denser, as has already been mentioned above. The sufficiently long chain follows the distribution of cavities, formed in the polymer network, so that neighboring cavities are separated from each other by narrow channels (bottle-necks). The average number of monomers  $g$  of the chain per cavity of characteristic size  $\xi_{\text{obs}}$  is

$$g \propto \xi_{\text{obs}}^{1/\nu} \propto C_{\text{obs}}^{-1/(3\nu-1)}. \quad (14)$$

If we neglect the fraction of monomers, situated in bottle-necks, the number of globules (or, the number of occupied cavities)  $N_g$  per chain will be

$$N_g = N/g \propto N C_{\text{obs}}^{1/(3\nu-1)} \quad (15)$$

and, consequently,

$$N_g C_{\text{obs}}^{1/(3\nu-1)} \propto N C_{\text{obs}}^{2/(3\nu-1)}. \quad (16)$$

This means that we obtain a good scaling of  $f_{\text{gyr}}$ , as a function of  $N_g (Cl^3)^{1/(3\nu-1)} = N(Cl^3)^{2/(3\nu-1)}$ , rather than of  $N(Cl^3)^{1/(3\nu-1)}$ .

Consequently, Eq. (13) becomes valid if for  $\zeta > 1$  the polymer length  $N$  is replaced by the renormalized length  $N_g$ . As far as for  $\zeta < 1$  the crossover function  $f_{\text{gyr}}(\zeta)$  is a constant, independent of  $\zeta$ , we may formally replace  $N$  with  $N_g$  in  $\zeta$  even for  $\zeta < 1$ , thus obtaining the same crossover

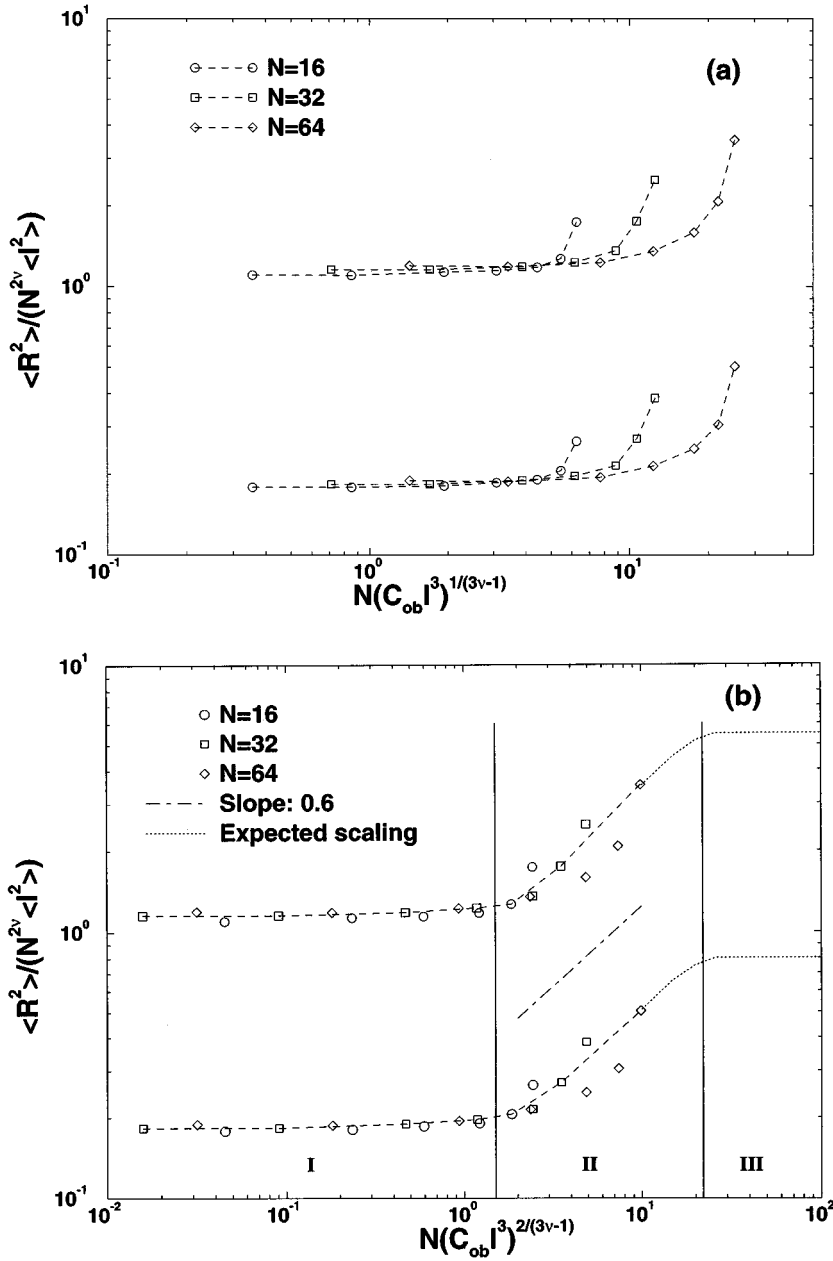


FIG. 6. (a) Log-log plot of the scaling function  $f_{\text{gyr}}$  vs the scaling variable  $NC_{\text{obst}}^{1/(3\nu-1)}$ . The upper curves give the data for the mean-square end-to-end distance  $R^2$ , while the lower ones show the results for  $R_g^2$ . (b) The same vs the scaling variable  $NC_{\text{obst}}^{2/(3\nu-1)}$ . Region I—free chains, II—crossover, and III—renormalized free chains. The slope 0.6 corresponds to  $\nu_{\text{cross}}=0.78$ .

function, but of a modified argument  $\zeta_m = N^\nu C_{\text{obs}}^{2\nu/(3\nu-1)}$  [note that  $\zeta_m$  dependence on density  $C_{\text{obs}}$  is here *squared*, in contrast to Eq. (13)].

Our main conclusion is that the crossover scaling function  $f_{\text{gyr}}$ , derived for polymer solutions, can be applied to the case of a polymer in porous media when the scaling variable  $\zeta$  is replaced by  $\zeta_m$  due to the renormalization of the Kuhn length of the chain. This renormalized Kuhn length should reflect thus the properties of the porous medium rather than characterize those of the unperturbed polymer chain itself. When the free volume of the porous medium is small we use an exponent  $\nu_{\text{cross}}$  rather than the Gaussian exponent of 0.5. Moreover, for very long chains,  $N \rightarrow \infty$ , we expect  $\nu_{\text{cross}} \rightarrow \nu$ , i.e., in the asymptotic limit  $\zeta \gg 1$  the chain should behave as a self-avoiding random walk (the cavities in the porous medium, already occupied by parts of the chain, remain inaccessible for the rest of the chain) with a step length determined by the properties of the medium [Fig. 6(b), re-

gion III]. An indication for this expected behavior is suggested by Fig. 1, where for  $N=64$  and  $C > 1$  the gyration radius  $R_g$  appears to saturate with obstacle density  $C$ . The same considerations are also valid for the mean-square end-to-end distance  $\langle R^2 \rangle$ , which is proportional to  $\langle R_g^2 \rangle$  with a factor of 6, and is depicted in Fig. 6 too.

### B. Crossover scaling for the diffusion coefficient $D_N$

In a similar way we analyze the crossover scaling of the diffusion coefficient too. In the dilute limit we observe Rouse behavior of  $D_N$

$$D_N^0 \propto N^{-1}. \quad (17)$$

At high obstacle concentrations we find reptational diffusive behavior (cf. Fig. 4) which could be expressed as

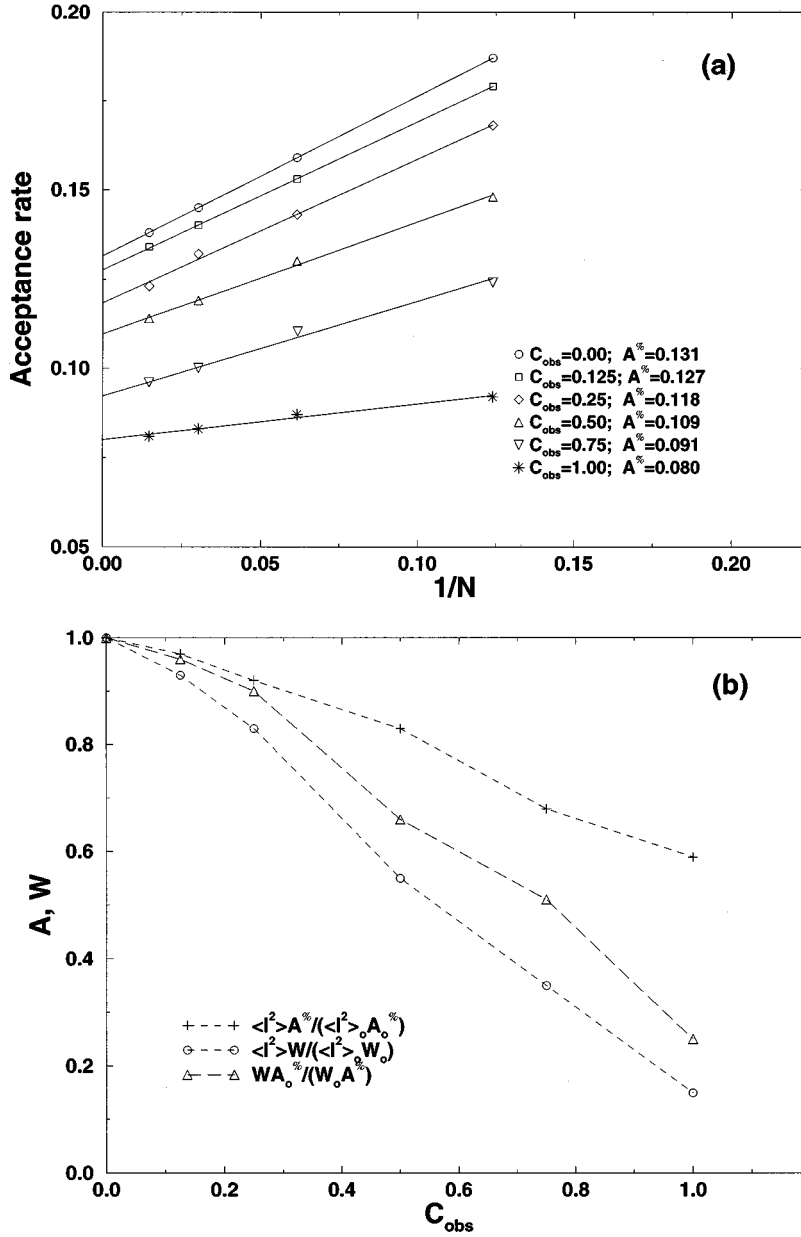


FIG. 7. (a) Extrapolation of the acceptance rate  $A(N)$  vs  $N^{-1}$  for obstacle densities ranging from 0 to 1.0. (b) Acceptance rate  $\langle l^2 \rangle A^{\infty} / \langle l^2 \rangle_0 A_0^{\infty}$  and mobility  $\langle l^2 \rangle W / \langle l^2 \rangle_0 W_0$  vs density  $C_{\text{obs}}$  and the ratio  $(W/W_0)/(A/A_0)$  vs density.

$$D_N \propto N^{-2} C_{\text{obs}}^z. \quad (18)$$

The smooth matching of these two equations at the crossover regime yields the same  $z$  as for a polymer solution [41]:

$$z = -1/(3\nu - 1) \quad (19)$$

and

$$D_N \propto N^{-2} C_{\text{obs}}^{-1/(3\nu-1)}. \quad (20)$$

Hence the relative (dimensionless) diffusion coefficient  $D_N/D_N^0$  becomes a scaling function  $f_D(\zeta)$  of the ratio of two characteristic lengths  $\zeta = (R_g/\xi_{\text{obs}})$

$$f_D(\zeta) = f_D(N C_{\text{obs}}^{1/(3\nu-1)}). \quad (21)$$

However, the density dependence of  $D_N$  is not trivial. Following Paul *et al.* [41] we introduce, in our analysis, the effective monomer reorientation rate  $W$  which accounts for

the density dependence of monomeric friction and is calculated from  $g_1(t)$  defined with Eq. (4) as suggested in [41]. Its introduction is needed in order to allow for the effect of chain ends movements which are much faster than those of the inner monomers and affect the scaling of time. As a matter of fact, one needs a measure of how the elementary movements of the monomers, which contribute essentially to diffusion, change with varying density of the medium. This is evident from Fig. 7(a) where the acceptance rate of the attempted moves  $A$  (that is, the percentage of successful jumps over the total number of attempted moves per monomer) is shown to scale as  $N^{-1}$  in consequence of the higher mobility of monomers near the chain ends. Since  $A$  is averaged over all monomers of the chain, the behavior shown in Fig. 7(a) is observed. The extrapolated ( $N \rightarrow \infty$ ) acceptance rate  $A$ , plotted as  $\langle l^2 \rangle A^{\infty} / \langle l^2 \rangle_0 A_0^{\infty}$  and mobility  $\langle l^2 \rangle W / \langle l^2 \rangle_0 W_0$ , where the subscript 0 denotes extrapolation to  $C_{\text{obs}} = 0$ , shows [Fig. 7(b)] similar behavior, as in the case of a solution [41,39].

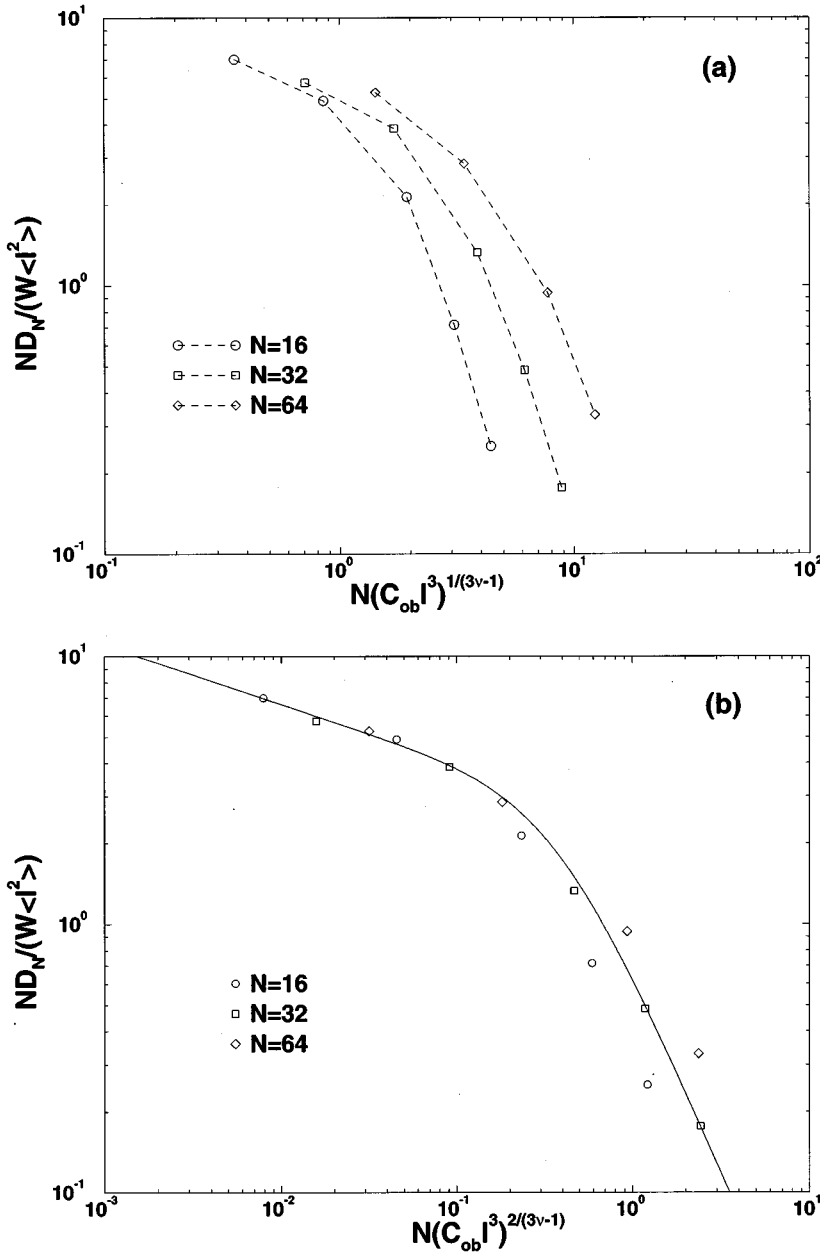


FIG. 8. (a) Scaling plot of  $ND/W\langle l^2 \rangle$  vs  $N(Cl^3)^{1/3\nu-1}$  for the chain lengths as indicated in the figure. (b) The same vs  $N(Cl^3)^{2/3\nu-1}$ .

There is a difference, however, between  $A$  and  $W$ , the latter decaying much faster with increasing density than  $A$ . Since  $A$  refers to *all* attempted moves, including highly correlated ones like forward and backward jumps, which contribute nothing to the chains movement, one sees from Fig. 7(b) that for  $C_{\text{obs}}=0.5$  only about 50% of the moves contribute to diffusion as compared to  $C_{\text{obs}}=0$ . Therefore we plot in a log-log scale the normalized diffusion coefficient  $ND_N/W\langle l^2 \rangle$  vs  $N(Cl^3)^{1/(3\nu-1)}$ —Fig. 8(a)—and vs  $N(Cl^3)^{2/(3\nu-1)}$ —Fig. 8(b). Again we find poor scaling for  $N(Cl^3)^{1/(3\nu-1)}$  as scaling variable [Fig. 8(a)], and much better scaling for  $N(Cl^3)^{2/(3\nu-1)}$  [Fig. 8(b)]. This suggests that the renormalization effects, discussed above, play an important role for the dynamics too, and we must use  $\zeta_m = N_g(Cl^3)^{1/(3\nu-1)} = N(Cl^3)^{2/(3\nu-1)}$  from Eq. (16) as an argument for the scaling function. With this rescaled variable we do see all three curves in Fig. 8(a) collapse on a single master curve in Fig. 8(b) which qualitatively resembles that for a polymer solution [41].

## V. DISCUSSION

In the present investigation we examine the variation of static and dynamic properties of isolated polymer chains diffusing in a quenched environment of randomly distributed polymer chains with increasing density of the medium. Since we focus our studies on chain lengths for which a detectable displacement of the chain center of mass is still possible, our findings deviate from some previous analytic predictions [1] and support others [2], based on a different treatment.

Thus clear evidence for a change from Rouse-like to reptational dynamics with decreasing free volume of the porous medium is produced which proves that our coarse-grained polymer chains are still long enough so as to perform reptational movement between adjacent potential wells.

The static host matrix, in which our species move, is observed to lead to progressive stretching of the chains as the cavities of the medium decrease in size with growing density. Assuming that such cavities are filled with monomers



and may be considered as a sequence of generalized "blobs," each of a size determined by the density of the host matrix, we suggest a simple scaling interpretation which provides a consistent description of the size of the chain and of its diffusion coefficient in the whole interval of density and chain lengths examined.

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